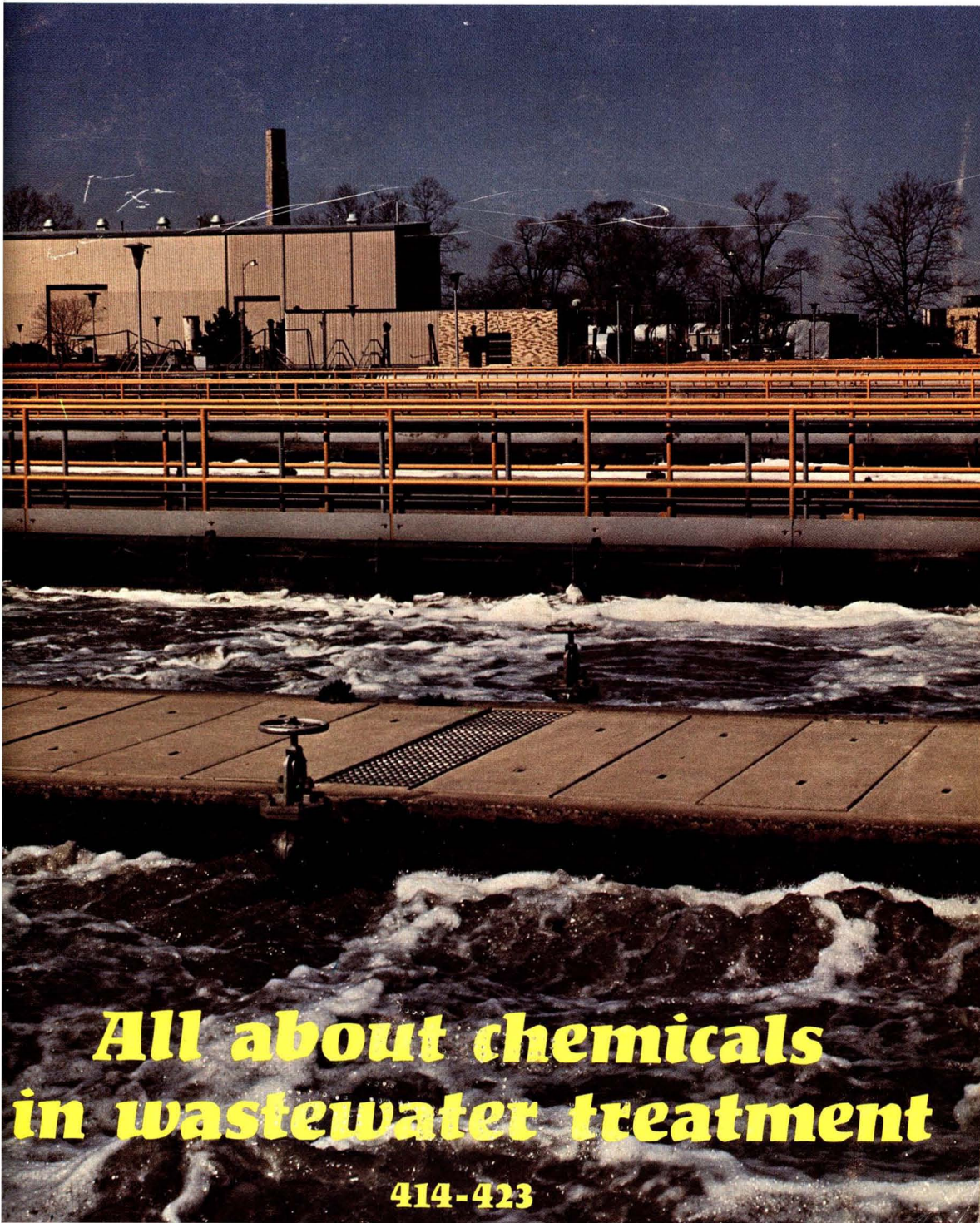


Environmental

Science & Technology

MAY 1974



**All about chemicals
in wastewater treatment**

414-423

A black and white photograph of a man in a dark suit, white shirt, and patterned tie. He is crouching on a rocky bank next to a rushing stream. His right hand is resting on his knee, and his left hand is extended outwards towards the water. The background shows the turbulent flow of the stream over rocks.

**Weigh the economy of our
heavy metal pollution control system
against existing standards.**

**There's a clean stream
in the balance.**

The outstanding efficiency, economy and ease of use of our Sodium Borohydride Pollution Control System has already made it the natural choice of a number of mercury processing plants, chlor-alkali plants and a major tetraethyl lead manufacturer. In addition to the removal of mercury and lead, our commercially tested system removes and recovers valuable heavy metals including: certain precious metals such as platinum, palladium, gold and silver; cadmium; copper; cobalt; and nickel. You can rely on Sodium Borohydride to remove up to 99.5% or more of the discharged heavy metal from your plant effluent, leaving it substantially cleaner and well within established standards. And the value of the metal recovered often offsets and in some cases turns a profit on the system investment. In the case of silver, there's real economic leverage.

1 lb. of Sodium Borohydride will recover 22 lbs. of pure reusable silver. That's 1.4¢ of Sodium Borohydride for every dollar of silver recovered. Add this to the facts that our system requires a minimal capital investment, is space-efficient, and can be operated by existing staff working only a few hours per week. It should really tip the balance for a clean stream.

Ventron's Sodium Borohydride System: It's worth considering.

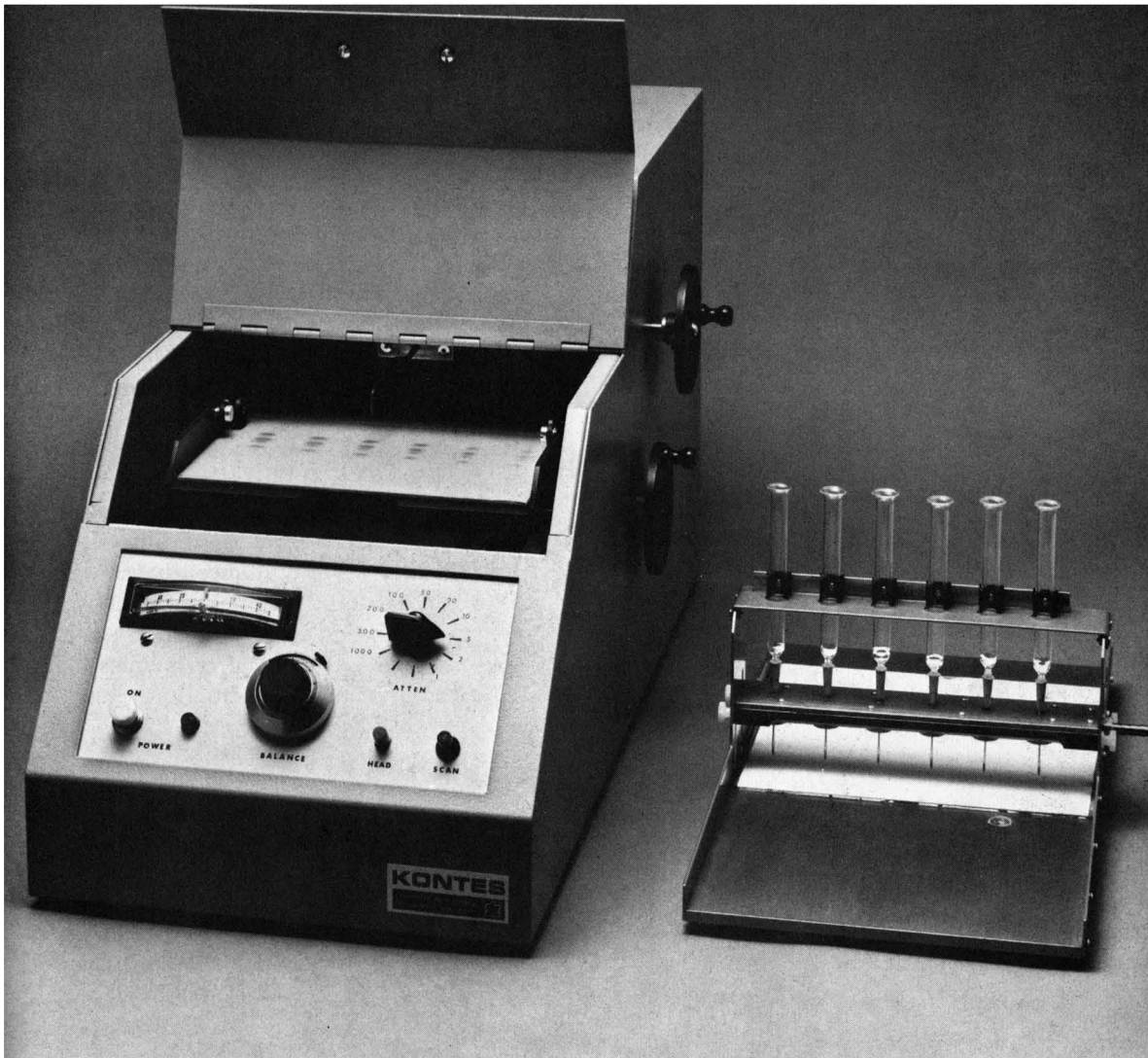
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**"Determination of Reflectance of Pesticide Spots on Thin-Layer Chromatograms Using Fiber Optics", Morton Beroza, K. R. Hill, Karl H. Norris, ANALYTICAL CHEMISTRY, September 1968, U.S. Patent 3,562,539. Other patents pending.

***"An automatic spotter for quantitative thin layer and paper chromatographic analysis by optical scanning." Melvin E. Getz, Journal of the AOAC, Volume 54, No. 4, 1971. Patent Pending.

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(Ammonia, Nitrate, Nitrite, Ortho-Phosphate)

No. of Water Samples Per Day	Commercial Laboratory	Technician Manually	Technician and AutoAnalyzer
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40	7.00	1.48	.45
60	7.00	1.48	.30

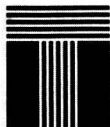
These cost figures are based on national averages. The AutoAnalyzer II comparison is based on being used normally—no “special” conditions.

For a copy of our nutrients in water cost-per-test kit, just circle the reader service number below.

Or, perhaps you'd like to see the complete Technicon AutoAnalyzer II cost-per-test presentation. It's a 14-minute film and it's very revealing! Just write to Technicon Industrial Systems, Tarrytown, New York 10591 on your letterhead. Our local representative will call you and set up a meeting.



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CIRCLE 16 ON READER SERVICE CARD

Environmental Science & Technology

Volume 8, Number 5, May 1974

ESTHAG 8 (5) 385-482 (1974)
ISSN 0013-936X

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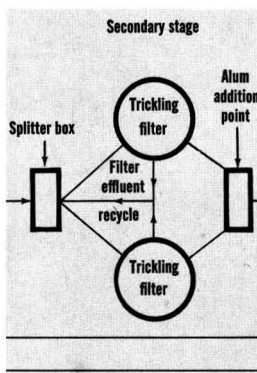
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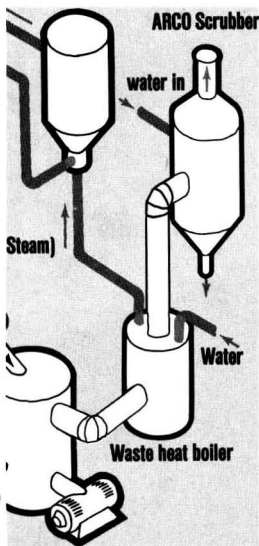
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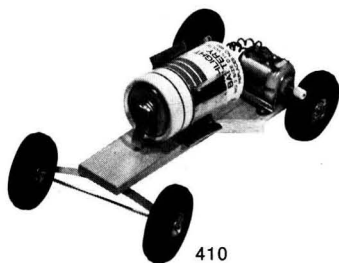
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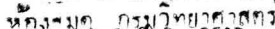
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CURRENT RESEARCH

History of metal pollution in the Southern California coastal zone 425

K. W. Bruland, Kathie Bertine, Minoru Koide, and E. D. Goldberg

The fluxes caused by human populations of heavy metals into the sediments along the coast of southern California were determined. The contributions of the different transporting agencies; winds, sewer outfalls, storm runoff and river runoff, could not be evaluated.

Reactivity of SO₂ with supported metal oxide-alumina sorbents 432

R. F. Vogel, B. R. Mitchell, and F. E. Massoth

Alumina-supported metal oxides were tested for SO₂ removal at 343°C from a mixture of gases. Alkali and alkaline earth were superior, with copper and strontium being especially reactive. A kinetic treatment was developed and rates of sorption were calculated.

Characterization of aerosols in California by X-ray-induced X-ray fluorescence analysis 436

R. D. Giauque, L. Y. Goda, and N. E. Brown

The elemental composition of aerosols collected on impactor film and filter media was determined by X-ray fluorescence. Diurnal patterns were found and elemental distribution was correlated with particle size distribution.

Fuel gasification. Prediction of sulfur species distribution using free energy minimization 441

S. J. Stinnett, D. P. Harrison, and R. W. Pike

Thermodynamic free energy minimization was applied to fossil fuel gasification processes. Particular attention was given to sulfur compounds, so requirements for desulfurization methods could be defined.

Theoretical model for relating indoor pollutant concentrations to those outside 444

F. H. Shair and K. L. Heitner

When the time between changes in outdoor pollutant concentrations is long compared to indoor concentration changes, the indoor/outdoor levels can be related by a simple expression. Good agreement between theory and experiment is found in the case of ozone levels in buildings in smoggy regions.

NOTES

Experimental verification of the linear combination model for relating indoor-outdoor pollutant concentrations 452

C. H. Hales, A. M. Rollinson, and F. H. Shair

The model for relating indoor-outdoor pollutant levels was investigated by comparing model predictions with indoor pollutant concentrations as a function of time in areas of a large laboratory office building.

Petroleum-derived and indigenous hydrocarbons in recent sediments of Lake Zug, Switzerland 454

Walter Giger, Martin Reinhard, Christian Schaffner, and Werner Stumm

An analysis of recent sediments in Lake Zug found high levels of fossil fuel hydrocarbons near the densely populated northern shore, while presumably indigenous hydrocarbons from aquatic organisms predominate in the middle of the lake.

Operational limits of vibrating orifice aerosol generator 456

J. B. Wedding and J. J. Stukel

It was found that the reported frequency range for monodisperse aerosol generation is not applicable for all aperture diameters. Results are given for the frequency range for which monodisperse aerosols are generated with varying aperture sizes.

Approximations to discrepancies between visual and instrument opacity readings for submicron particulate material 458

C. D. Wolbach

A mathematical formula for approximating the magnitude of discrepancies between instrument and visual opacity readings is derived. Values for these discrepancies are plotted and a specific case is calculated.

Mercury-organic matter associations in estuarine sediments and interstitial water 459

S. E. Lindberg and R. C. Harriss

Core samples from the Florida Everglades and Mobile Bay revealed associations between sediment mercury and sediment organic matter and between dissolved interstitial mercury and dissolved organic carbon.

Selenium in North American paper pulps 462

L. W. Anderson and L. Acs

Spectrophotometric and fluorometric methods were used to examine 22 samples of paper pulp from different regions of the United States and Canada for selenium content. Concentrations in all samples averaged less than 0.04 ppm.

Feasibility of automatic isokinetic stack sampler 464

S. H. Dworetzky

A technique is suggested for the isokinetic sampling of emissions from stack sources. Two capacitance manometers with a common pliable element are used to compare the stack and probe flows.

This issue contains no papers for which there is supplementary material in microform.

Credits: 397, The White House; 399, BP photograph; 404 (center), DOD; 405, EPA; 408, B. F. Goodrich; 409 (left), USDA; 409 (lower right), U.S. Forest Service; 410, Gerald M. Quinn; 423, Allied Chemical Corp.

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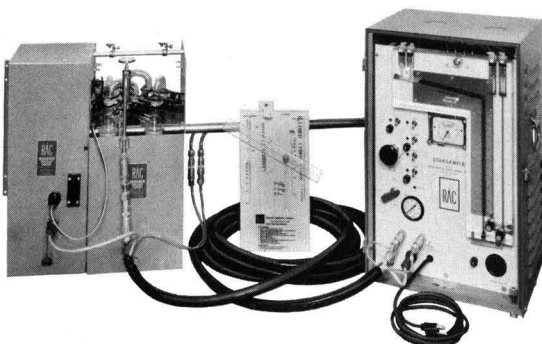
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is No. 1

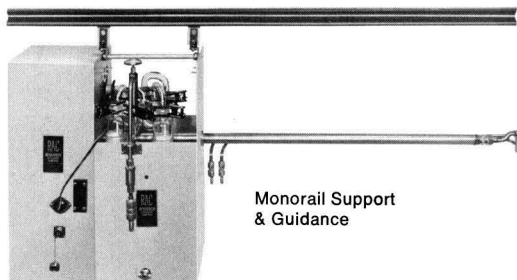
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- ★ most imitated design of its type

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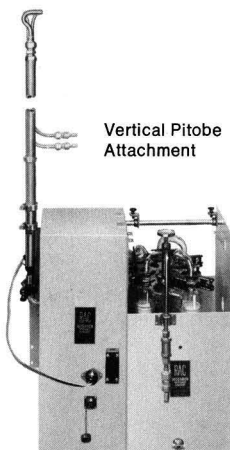
RAC's depth of expertise assures top-quality products that are as rugged and reliable in performance as they are precise in manufacture. Perhaps this is the reason why the RAC Staksamplr train system is the most widely copied design of its kind.



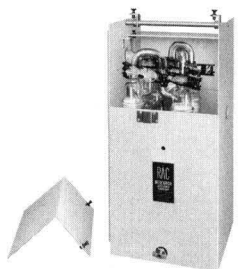
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And now . . . a new lightweight sample case for the No. 1 stack sampling system

Featuring aluminum construction, RAC's all-new sample collecting case is a dual-module design that includes a detachable, interchangeable module for the impinger sampling train. This design permits a series of isokinetic samples to be taken, in sequence, by using several impinger modules. Each impinger module is furnished with two snap-on aluminum cover plates that convert it into a convenient, lightweight, protective carrying case for the glass sampling train.

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The new sample case can be easily adapted to existing RAC Staksamplr systems to enhance their operating capabilities and versatility.

Write for BULLETIN 2343-R1 for full details.

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AMERICAN CHEMICAL SOCIETY
1155 16th Street, N.W.
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For author's guide and editorial policy, see June 1973 issue, page 517, or write Katherine I. Biggs, Manuscript Reviewing Office, *ES&T*

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

The present administration called for an environmental decade for the 70's; environmental watchers attest to that. But its recent lack of action indicates that no real cleanup is possible. And despite the fact that Congress legislated deadlines for air and water cleanup, it and the rest of us now simply are finding them unachievable.

To be sure, many arguments have surfaced on both sides of the cleanup necessity. A real one is that the time frame for cleanup was contingent with the funding specified in the legislation. Proponents here point out that with the impoundment of funds in the water case, how can the deadlines be achieved in the specified time?

Much of the existing air legislation was geared for a clean society by mid-decade or shortly thereafter. Why a new push, a new start has not been made for the upcoming bicentennial anniversary of this nation is not clear. The cleanup intent becomes muddled by other issues, mainly the energy issue, which is tied obviously to economic considerations.

As an ardent environmental cleanup watcher, we reflect that it took the late President Kennedy to commit this nation to a space program and the late President Johnson to call for a Great Society. Where is the present administration's call and what is its commitment?

Congress did its job, or so it thinks. The administration did its job, or so it thinks. And the public, we submit, has done its job, or so it thinks. But the idealistic calls for a clean society, an environmental ethic that a former EPA administrator used to talk about seems blowing in the wind.

Make no mistake. Industries in this country are taking cleanup steps. But everyone these days seems to be stalking the EPA more and more. Perhaps it's only reasonable considering that 56 pages of precise requirements in the air legislation and 88 pages of provision after provision in the water law are subject to different interpretations. Each of the laws has created mountains of paperwork and strengthened the federal bureaucracy even more. Stretching out the cleanup deadlines is simply the way the cleanup ball game is being played this season.



LETTERS

Sager interview

Dear Sir: I am writing to congratulate your office, with the absolute approval of the head of this department, on your cover of the December 1973 issue. The refreshing change as far as covers of this day and age are concerned was indeed a strong incentive to see inside the journal. Once again we were pleasantly surprised to read that it was a photograph of Dr. Martha C. Sager, the chairman of the Effluent Standards and Water Quality Information Advisory Committee.

We would graciously congratulate Dr. Sager too as there are so many of the mature ladies even in Rhodesia fulfilling key positions with little or no recognition. We do not wish in any way to usurp men's positions but I am sure you will agree that every human being is encouraged by a little appreciation. It was most satisfying to see that, in spite of Hollywood and the many others, the true value of experience and womanhood is commended and promoted. Our sincere congratulations.

Mrs. Rosaleen Kerr
Government Analyst's Laboratory
Salisbury, Rhodesia

Small particles

Dear Sir: I read with great interest your editorial "Who's Afraid of Small Particles?" (*ES&T*, Dec. 1973, p 1085). Your editorial is most timely and I concur with your statements.

At Purdue University, I am directing the Industrial Source Sampling Phase of an NSF-funded Research Project in which we are working with a number of industrial collaborators. One of the prime objectives of the project is to characterize the flow of particulates into the atmosphere via stack gas streams. Particle size distribution of these particulates and subsequent analyses for trace metals, particle morphology, etc., have been and are being carried out. At the present time we have some very interesting results from stack gas streams from power plants, zinc smelters, and the Northwest Indiana steel mill operation.

Robert B. Jacko
Purdue University
West Lafayette, Ind. 47907

Small particles instrumentation

Dear Sir: The editorial (*ES&T*, Dec.

1973, p 1085) indicates in two places, that there is no commercial equipment available to measure small particles—"less than 3 microns."

Bausch & Lomb has manufactured and sold in the commercial and military markets for at least eight years, an aerosol counter which covers the size range of 0.3 micrometer to greater than 10 micrometers. There are at least four other companies which manufacture and sell similar type equipment.

I refer to your own publication, (*ES&T*, Oct. 1967, p 801-4) showing test results of existing equipment or prototypes which resulted in commercially available equipment.

Editorials can be and usually are useful means for stirring up the status quo. However, their impact is reduced or nullified if the editor shows his ignorance of the subject by including statements which are not true. Your editorial did not fall on deaf ears in this case, but its impact on my current activities is probably nil.

Douglas D. Doonan
Bausch & Lomb
Rochester, N.Y. 14625

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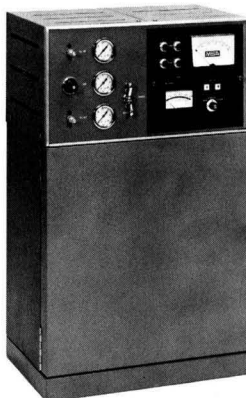
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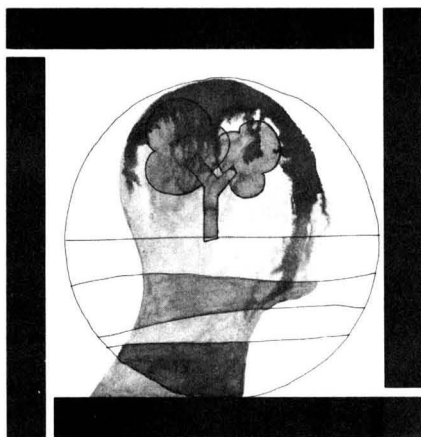
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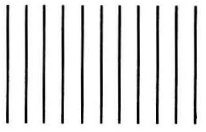
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Calgon water report

Spring, 1974

Two P/C Sewage Plants to Use Calgon Carbon

Calgon will supply 2.5 million pounds of Filtrasorb® 300 granular activated carbon for use in physical/chemical sewage treatment plants being constructed at West Fitchburg, Massachusetts and Rocky River, Ohio.

The 15-mgd Fitchburg plant, designed by the consulting firm of Camp Dresser & McKee, will treat wastewaters from two paper manufacturers and domestic wastes from a portion of the city, a regional vocational school, and in the future, the town of Westminster.

The 10-mgd Rocky River plant was designed by the consulting firm of Willard F. Schade and Associates and is being constructed by Spohn Corporation, both Cleveland-based firms. It will serve the communities of Rocky River, Fairview, Westlake and Bay Village and is designed to remove 90 percent of suspended solids, dissolved organics and phosphorus.

Criteria for Decision

According to Robert E. Schade, the
(continued on page 3)

International Water Conference Oct. 29-31

The 35th annual International Water Conference of the Engineers' Society of Western Pennsylvania will be held October 29-31 in Pittsburgh.

Purpose of the conference, according to 1974 General Chairman R. G. Knight of Duquesne Light Company is the advancement of new developments in the treatment, use and reuse of water for industrial and engineering purposes and the dissemination of related information. R. N. Baum, marketing coordinator in Calgon's Water Management Division, is program chairman.

Detailed information on the conference is available from W. M. Porter, Secretary, Engineers' Society of Western Pennsylvania, William Penn Hotel, Pittsburgh, Pa. 15230.



Calgon's new plant in Bayport assures the efficiencies of bulk blending and handling of cooling water treatment chemicals to large-volume users in the Gulf Coast area. Tank trucks deliver chemicals in bulk to plant storage tanks from which chemicals are directly fed into cooling water systems. Bulk service eliminates warehousing, in-plant materials handling and equipment needed to prepare solutions of dry chemicals, thus reducing cooling water treatment costs.

Low Chromate Cuts Corrosion and Fouling

A large Eastern organic chemical plant went on-stream five years ago using a non-chromate corrosion inhibitor in an effort to comply with expected regulations concerning chromate discharge. The plant has multi-metal heat exchanger equipment with water on both the shell and tube side. There are both vertical and horizontal coolers with exit water temperatures as high as 130°F. With the non-chromate treatment, corrosion rates averaged 8-10 mpy on carbon steel, and iron fouling of critical exchangers resulted in unscheduled outages.

The Calgon representative recommended that a low chromate-zinc product, Calgon Hagatreat 168, be used to supplement the organic phosphonate treatment. The level of 2 ppm chromate recommended deviated considerably from historic use of chromate inhibitors. Constant monitoring of corrosion rates resulted in a decision to feed 2-3 ppm chromate and 30 ppm of Calgon CL-77.

This low level of chromate presented no problem in the plant discharge. The

(continued on page 4)

Cat-Floc T Is Newest Cationic Liquid Polymer

Calgon broadened its line of liquid cationic polyelectrolytes for use in potable water clarification with the introduction in 1973 of Cat-Floc® T.

Cat-Floc T is the third cationic polymer accepted by the Environmental Protection Agency for treatment of potable water. Others are Cat-Floc B and Cat-Floc, the first synthetic, cationic, organic polyelectrolyte accepted for use in treatment of potable water.

Acceptance was granted in 1967.

Raw water characteristics and mixing capability at treatment plants are key considerations in choosing the proper Cat-Floc product. The following can be used as a general rule of thumb:

Cat-Floc—primary coagulant in high solids or high turbidity waters; sufficient in-plant rapid mixing required.

Cat-Floc B—with alum in high solids or high turbidity waters; good mixing required.

Cat-Floc T—as a primary coagulant or in conjunction with alum in very low solids or low turbidity waters.

Water Pollution, Odor Control Papers Available

Magazine article reprints and preprints of presentations before technical societies on the above subjects are available at no charge. Please address requests to Calgon Water Report, Public Relations Department, Calgon Corporation, P. O. Box 1346, Pittsburgh, Pa. 15230.

Water

"Carbon Adsorption—Case Studies at Several Textile Plants" by M. M. Stark and J. L. Rizzo; Midwinter Conference on Textile Wastewater and Air Pollution Control, January 1974.

"Carbon Adsorption Knocks Down BOD₅ to 62 Lbs./Day Limit"; CHEMICAL PROCESSING, January 1974 (reprint 27-10).

"Inroads to Activated Carbon Treatment"; ENVIRONMENTAL SCIENCE & TECHNOLOGY, January 1974 (reprint 27-11).

"Industrial Wastewater Treatment by Granular Activated Carbon" by D. G. Hager; AMERICAN DYESTUFF REPORTER, November 1973 (reprint 27-12).

"Chemical Treatment for Municipal Wastewater" by F. E. Bernardin, Jr. and Robert Kusnirak; 46th Annual Conference of the Water Pollution Control Federation, October 2, 1973.

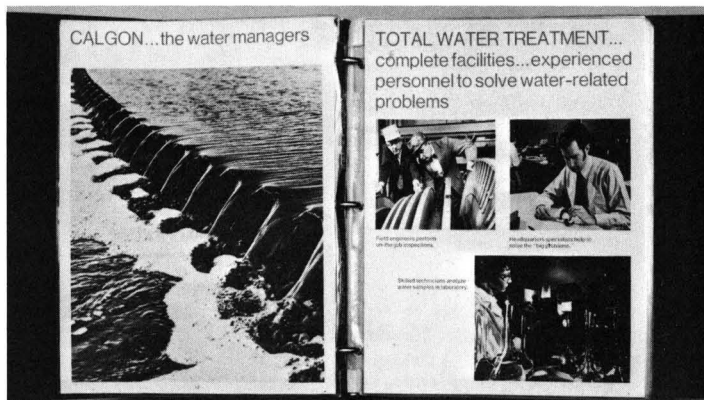
"Experience with Granular Activated Carbon in Treatment of Textile Industry Wastewaters" by D. G. Hager, J. L. Rizzo and R. H. Zanitsch; EPA Technology Transfer Seminar, September 1973.

"Granular Carbon Handles Concentrated Waste" by V. A. Brunotts, R. T. Lynch and G. R. Van Stone; CHEMICAL ENGINEERING PROGRESS, August 1973 (reprint 20-53).

"Carbon Adsorption: An Approach to Industrial Wastewater Treatment" by D. J. Killmeyer; PROFESSIONAL ENGINEER magazine, August 1973 (reprint 27-9).

"Carbon Towers" by F. F. Mendicino; 60th Annual American Electroplaters Society Technical Conference, June 1973.

"Granular Activated Carbon Reactivation System Design and Operating Conditions" by W. G. Schuliger and J. M. MacCrum; AIChE Detroit Meeting, June 1973.



"Adsorption—A Unit Process for Textile Wastes" by J. M. MacCrum and G. R. Van Stone; MODERN TEXTILES, June 1973 (reprint 27-8).

"Polymers Can Help" by R. A. LoSasso; WATER AND WASTES ENGINEERING, June 1973 (reprint 12-68).

"P-C Treatment Gets Industrial Trial"; ENVIRONMENTAL SCIENCE & TECHNOLOGY, March 1973 (reprint 20-54).

"Gaging and Sampling Industrial Wastewaters" by J. G. Rabosky and D. L. Koraido; CHEMICAL ENGINEERING, January 8, 1973 (reprint 9-47).

Odor

"Activated Carbon Methods for Controlling Stationary Source Air Pollutants" by W. D. Lovett and F. T. Cunniff; 66th Annual Meeting of the AIChE, November 1973.

"New Developments in Ambient Odor Control by Adsorption" by R. S. Joyce, J. R. Lutchko, R. K. Sinha and J. E. Urbanic; New York Academy of Sciences Conference on Odors: Evaluation, Utilization and Control, October 1973.

"The Use of Activated Carbon to Control Gasoline Marketing Loss Emissions" by R. A. Fusco and R. L. Poltorak; National Petroleum Refiners Association Annual Meeting, September 1973.

"Odor Control Methods Using Granular Activated Carbon" by W. D. Faulkner, W. G. Schuliger and J. E. Urbanic; 74th National Meeting of the AIChE, March 1973.

"Foundry Odor Control with Activated Carbon" by R. L. Poltorak; MODERN CASTING, August 1973.

Presentation Outlines Total Water Treatment*

Drawing from what is probably the world's most extensive library of customer case histories, Calgon's Water Management Division has prepared a concise, desk-top presentation that takes you into operating plants, inside process equipment, and into the laboratory to let you see where, why and how serious water-related problems begin.

Relying heavily on color photographs, supporting graphics and an easy-to-follow problem-solution format, the presentation illustrates and explains the causes, economic hazards and control of corrosion, scale, deposit fouling and microbiological growth.

To schedule a presentation, write W. J. Reese, Water Management Division, Calgon Corporation, P. O. Box 1346, Pittsburgh, Pa. 15230.

*A service mark of Calgon Corporation.

Cooling Coil Assures Safety in Sampling

The Chemonitor® Sample Cooler is an efficient counterflow heat exchanger designed for cooling high-temperature, high-pressure fluid samples, such as boiler water, steam, feedwater, hot chemical solutions, etc., for tests at atmospheric pressures and temperatures. The pressure rating on the coil is 5000 psi at 800° F. Rugged, coil-within-a-shell construction provides trouble-free service.

The Chemonitor Cooling Coil also enables users to comply with regulations of the Occupational Health and Safety Act which require minimization of hazards associated with processing of hot, flashing liquid samples. (Bulletin B-5-027c)

Survey Shows Carbon Effective On Most Organics

A study of wastewater samples from 68 different manufacturing operations has shown carbon adsorption to be almost universally applicable as a viable wastewater treatment method for dissolved organics removal. The results of the study were announced by Donald G. Hager, director of marketing for Calgon Adsorption Systems, in a speech presented at the 4th Joint Chemical Engineering Conference held in Vancouver, British Columbia.

222 Samples Examined

Laboratory feasibility tests conducted on 222 wastewater samples included determinations of pH, suspended solids, total organic carbon (TOC) and carbon adsorption applicability. Selective removals of color and phenol were evaluated on 42 and 13 samples, respectively.

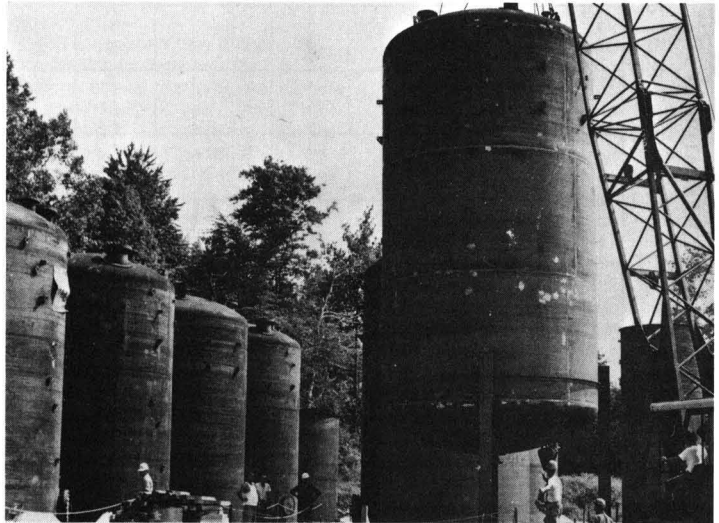
Of the samples evaluated, 100 contained between 100 and 1000 mg/1 TOC, and 86 others contained between 1000 and 10,000 mg/1 TOC. In 72 percent of the samples, TOC was reduced 85 percent or better. Color and phenol removals were 98 percent and 92 percent, respectively, in more than 90 percent of the samples.

Combined Treatments Required

Hager said, "In view of the generally high levels of TOC in the untreated wastewater, it is likely that a combination of treatment processes will be required to meet high TOC reduction objectives at the lowest possible cost. The high selectivity of granular carbon for color and phenol suggests the likelihood of using adsorption as a pretreatment to biological systems to remove toxic and refractive substances. Treatment of industrial wastewaters for selective removal of specific substances prior to discharge to municipal systems appears to be technically and economically opportune." he said.

Samples used in the survey were categorized by Standard Industrial Classification (SIC) and included wastewater effluents from food, paper, chemical, textile, plastic, rubber, pharmaceutical, petroleum, and metals industries.

The paper, "Industrial Wastewater Treatment by Granular Activated Carbon," is available in preprint form.



The last of eight carbon columns is lowered into place at the physical/chemical treatment plant being constructed at Rocky River, Ohio. Each column will contain 92,500 pounds of Filtrasorb granular activated carbon.

P/C Sewage Plants to Use Filtrasorb

(continued from page 1)

decision to employ physical/chemical treatment at Rocky River was based on the following:

The system could be placed within the available space eliminating the need to condemn adjacent residential property which would have been required to accommodate an activated sludge system.

The entire secondary system could be completely housed and would be more aesthetically acceptable in terms of building design and absence of odors.

Construction costs were less than the cost of an activated sludge plant.

Estimated operating costs were only slightly higher than the cost of biological treatment but at a higher effluent quality.

System Advantage

A unique advantage of the system is that although the sewage will contain approximately 4.5 tons of suspended solids, 3.7 tons of biochemical oxygen demanding materials (BOD), 6.5 tons of chemical oxygen demanding materials (COD), and 500 pounds of phosphorus daily, no secondary sludge will be produced. This will eliminate the need for secondary sludge handling equipment and treatment chemicals and will reduce annual operating costs by about \$30,000 based on 10 mgd.

The carbon system will consist of eight columns, each containing approximately 92,500 pounds of Calgon's Filtrasorb 300 carbon, a carbon handling system and a

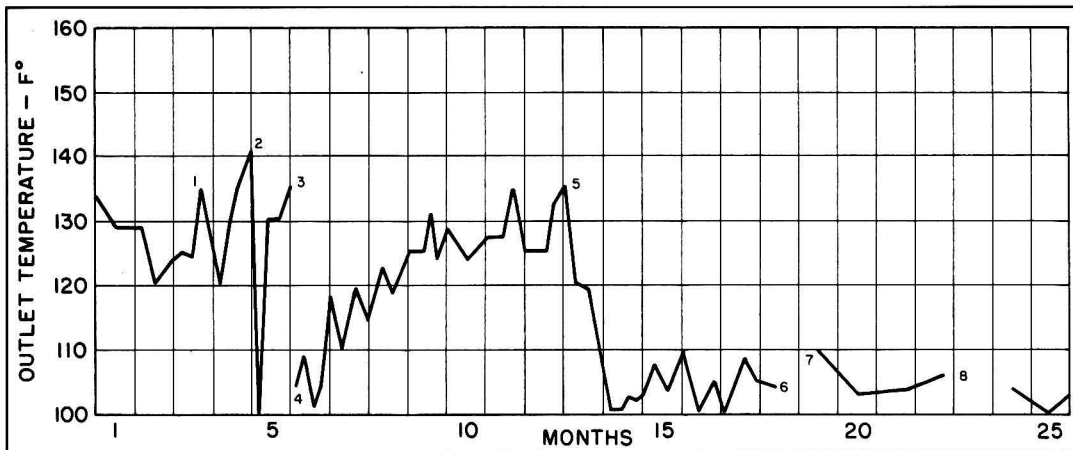
500 pounds per hour reactivation furnace. The furnace will be equipped with both an afterburner and scrubber to eliminate discharge of volatilized organics and particulates

West Fitchburg Plant

At West Fitchburg, BOD and COD will be reduced by 90 to 95 percent, insuring compliance with discharge regulations which specify that dissolved oxygen be maintained at not less than 5 mg/1 during at least 16 hours of any 24-hour period, nor less than 3 mg/1 at any time.

The carbon portion of the physical/chemical treatment system consists of 12 downflow columns, each containing 150,000 pounds of granular carbon (8x30 U.S. Standard Sieve size). Ten columns will operate in parallel at a flow rate of 1000 gallons per minute each, while the carbon in the remaining two columns is being backwashed and reactivated. Carbon will be reactivated on-site in a six-hearth furnace with a daily capacity of 28,000 pounds. The furnace will be equipped with a scrubber to remove particulates from the exhaust.

According to Camp Dresser & McKee Vice President Dr. Richard L. Woodward, pilot studies demonstrated that physical/chemical treatment will produce a better quality effluent than activated sludge primarily because of more effective removal of BOD, COD and color. Also, the plant will be less prone to upsets caused by variable industrial operations, Woodward said.



Silt Control Treatment Cools Heat Exchanger

Successful use of Calgon CL-65 Silt Control Treatment, a high molecular weight, polymer-based liquid, is dramatically illustrated in the above graph which is an actual plot of heat exchanger water outlet temperatures measured over a 25-month period at a major Gulf Coast refinery. Initially, temperatures ranged between 135° F and 120° F. Mechanical

cleaning (1) proved to be relatively ineffective, and temperatures climbed to 140° F in less than two months. Acid cleaning (2) reduced temperatures drastically, but before the system was shut down less than one month later (3), temperatures had climbed back to 135° F. Following startup (4), outlet temperatures rose steadily for the next seven

months, again averaging about 135° F. At this point (5), treatment of the cooling water with CL-65 was initiated, and temperatures dropped to the 100° F range. In the year that followed, temperatures remained below 110° F. Numbers 6, 7 and 8 are points of plant shut-downs and startups for routine maintenance activities.

Water Treatment Papers and Articles

Magazine article reprints and preprints of presentations before technical societies on the above subject are available at no charge. Please address requests to Calgon Water Report, Public Relations Department, Calgon Corporation, P. O. Box 1346, Pittsburgh, Pa. 15230.

"A Comparative Study of Chelating Agents: Their Ability to Prevent Deposits in Industrial Boilers" by J. L. Walker and J. R. Stephens; INTERNATIONAL WATER CONFERENCE OF ENGINEERS' SOCIETY of WESTERN PENNSYLVANIA, October 31, 1973 (reprint 10-69).

"Municipal Water Treatment with Polyelectrolytes" by J. P. Kleber; PUBLIC WORKS, October 1973 (reprint 12-73).

"Predicting Chelate Performance in Boilers" by J. R. Stephens and Jerry Walker; INDUSTRIAL WATER ENGINEERING, July/August 1973 (reprint 10-68).

"Identify and Control Microbiological Organisms in Cooling Water Systems" by A. L. Smith and R. A. Muia; POWER magazine, July 1973 (reprint 9-49).

"Detection and Measurement of Microorganisms in Drinking Water" by A. E. Sylvia; JOURNAL OF THE NEW

Calgon Can Assist In Fuel Cost Review

With fuel shortages growing and costs rising, ways to reduce the consumption of fuel used for steam generation should be reviewed.

Calgon's Hall Laboratories has updated its nomographs which make possible the calculation of the cost of fuel savings resulting from reducing boiler blowdown and installing a flash tank.

If you are interested in reviewing your own situation, please call your nearest Calgon representative.

ENGLAND WATER WORKS ASSOCIATION, June 1973 (reprint 20-56).

"The Weirs Water Treatment Plant, Laconia Water Works, Laconia, New Hampshire" by R. A. Morin; JOURNAL OF THE NEW ENGLAND WATER WORKS ASSOCIATION, June 1973 (reprint 20-57).

"Colloid Destabilization with Cationic Polyelectrolytes as Affected by Velocity Gradients" by J. J. Morrow and E. G. Rausch; AWWA National Conference, May 1973.

"Industrial Water Pretreatment" by F. H. Seels; CHEMICAL ENGINEERING, February 26, 1973 (reprint 9-48).

Cooling Water 'Bugs' Are Topic of Paper

Identification and control of microorganisms in cooling water systems is the subject of a comprehensive paper by A. L. Smith and R. A. Muia of Calgon's research and development group. The paper was published by POWER magazine and is now available from Calgon. Please request reprint 9-49.

Low Chromate Cuts Corrosion and Fouling

(continued from page 1)

treatment has been used for better than 3 years, and the results have been outstanding.

Corrosion rates are now consistently below 0.4 mpy on mild steel and less than 0.1 mpy on admiralty coupons. There has been no evidence of localized pitting on any coupons since addition of the chromate-zinc inhibitor. Iron fouling is no longer a problem, and unscheduled outages have ceased.



SUBSIDIARY OF MERCK & CO., INC.
PITTSBURGH, PA. 15230

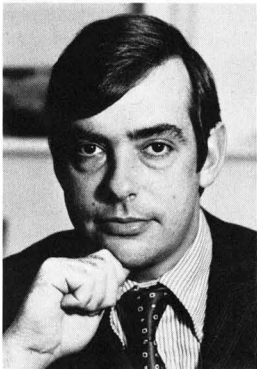
CIRCLE 2 ON READER SERVICE CARD

CURRENTS

WASHINGTON

The achievement of clean air in the U.S. could suffer as much as a 13-year setback if the administration's proposed changes in the Clean Air Act are enacted. As sent to Congress by EPA Administrator Russell Train, the proposals would delay the implementation of automobile antipollution standards for two years, or until 1977. In addition, they would postpone for up to 10 years clean air deadlines for some cities. The package also authorizes the EPA to order electric utilities to shift from oil- to coal-burning furnaces. Train told newsmen the retreat is necessary to "balance" the nation's environment and energy needs. He made it clear, however, that he was not happy with all the proposals.

The administration apparently sees the U.S. importing great amounts of oil by 1980 after all—despite Project Independence. Richard Fairbanks, the President's special assistant for domestic affairs, told an *ES&T* editor



Administration's Fairbanks

at the National Conference on Coastal Zone Management in Charleston, S.C., that rather than independence, as such, the administration seeks to build a new position of strength from which a new import relationship with oil-producing nations could be formed. He said the development of our full energy potential—through offshore drilling, the Alaskan pipeline, coal and shale development—would mean that future oil embargoes by foreign producers would not impose as serious a threat as the recent embargo.

The Tennessee Valley Authority is continuing its campaign for tall stacks instead of chemical scrubbers in dealing with SO₂ emissions. TVA chairman A. J. Wagner has released a report claiming the tall stacks are "superior." He said "this country's knowledge of scrubbers has not yet progressed to the point where TVA can have any degree of assurance that it is not buying a billion-dollar pig in a poke." He claims the tall stacks and other equipment would cost about \$100 million to install and about \$17 million annually to operate compared to a billion dollars to install and about \$225 million annually to operate for the scrubbers. The TVA would need U.S., EPA, and state permission to scrap scrubber technology.

The first-ever grants to assist states in developing coastal zone management programs have gone to Rhode Island, Maine, and Oregon. Almost \$635,000 was awarded by the National Oceanic and Atmospheric Administration under the Coastal Zone Management Act of 1972. The money is to encourage effective management, beneficial use, protection, and development along the nation's sea coast and Great Lakes shores. About \$155,000 went to Rhode Island, \$230,000 to Maine, and \$250,000 to Oregon. The individual states are contributing a matching share of the coastal zone management funds, which by law must amount to one third of the total program cost. Although the law was passed two years ago, the program was not funded until recently.

The Office of Technology Assessment has launched a major study on home units for generating solar energy electricity. Sen. Edward Kennedy (D-Mass.) who chairs the Technology Assessment Board, said in an announcement of the study that solar power promises homeowners throughout the nation the electricity they need for appliances, heating, and cooling. He added that the units probably would even allow people to recharge their electric cars at night for use the next day. Advocates feel that solar on-site generation of electricity could be a reality in the 1980s. The study will look at the technical factors, costs, and the impact on energy supplies, the environment, transportation, and housing patterns.

The Public Interest Campaign (PIC, Washington, D.C.) is suing the National Academy of Sciences (NAS) and its Committee on Motor Vehicle Emissions (CMVE). PIC alleges that its suit stems from frustrated efforts to obtain information on CMVE's activities. PIC charges violation of the Freedom of Information and Federal Advisory Committee Acts which require that meetings be open, and that papers, agendas, drafts, and like documents be open to public inspection and reproduction. The NAS/CMVE maintained that access to NAS archives "by scholars" is not permitted until after 50 years from the date of the requested material.

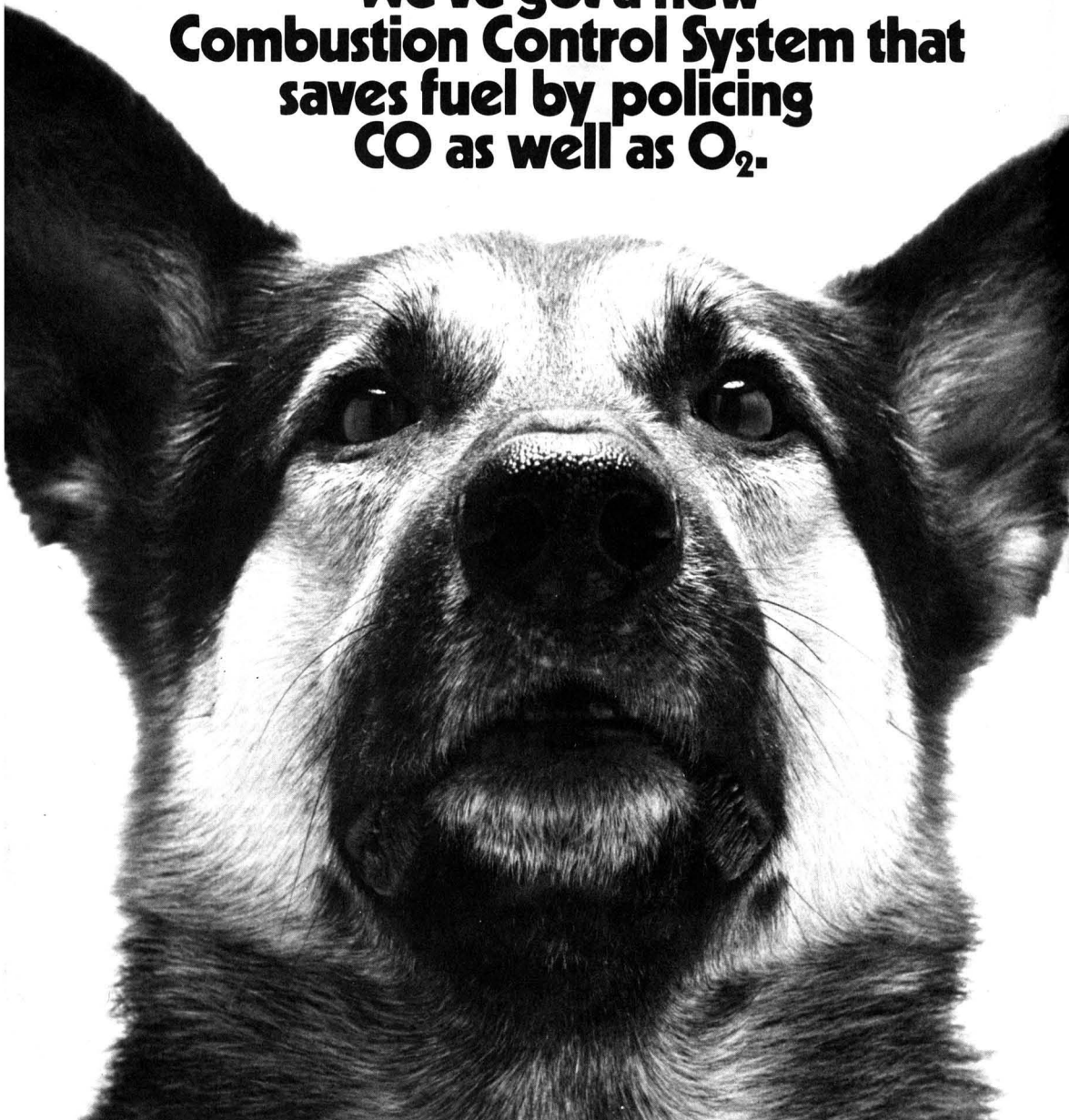
STATES

Illinois' environmental protection program for fiscal 1975 was outlined recently by its governor, Dan Walker. Some goals and objectives of the program include the establishment and implementation of a new wastewater discharge permit system that will put industries on a schedule to comply with clean water standards in time to meet federal deadlines in 1977 and 1983; development of guidelines to reduce the cost of preparing environmental impact statements for projects using public funds; and conducting a systematic search for unknown public water supplies. Simultaneously, the governor announced his fiscal '75 budget requests, with emphasis on energy needs.

Oregon has created a citizen's task force on subsurface sewage, chaired by state senator Mike Thorne. The purpose of the task force is to review and monitor the Department of Environmental Quality's new subsurface rules and regulations; seek acceptable alternatives to their application; recommend appropriate variances due to regional climate, soil, and groundwater differences; and suggest new rules or other changes for future revisions. Members of the group hold varied professions—professor, county commissioner, city manager, and lawyer. One of the first undertakings of the group will be the study of the septic tank regulation.

As many as 8 million Mississippi chickens will be destroyed as a result of dieldrin contamination. The

We've got a new Combustion Control System that saves fuel by policing CO as well as O₂.



Intertech designed it to extract every possible BTU out of today's scarce fuel supplies. And it does this so well that the system can readily save its own purchase price.

The monitoring of carbon monoxide in flue gas, as well as excess oxygen, provides much more sophisticated control of air/fuel ratios than possible before.

First, you eliminate the deviations from optimum air/fuel ratio inherent in control systems based on O₂ only. Second, where you're using high-sulfur fuels, corrosion from sulfur trioxide can be minimized through better control of excess O₂. The Inter-

tech System, in fact, consistently and precisely balances combustion of fuel at the optimum point. That is, the lowest level of excess O₂ in flue gas that does not produce any measurable amount of CO.

Two very advanced Intertech analyzing instruments form the heart of the system:

Uras 2T for CO. A highly stable, sensitive and accurate solid-state infrared gas analyzer.

Magnos 5T for O₂. Makes use of the paramagnetic behavior of oxygen. Rugged. Accurate. Solid-state.

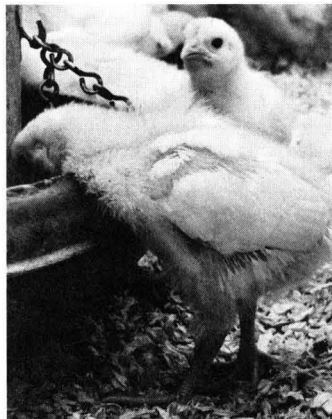
But the added Intertech ingredient is Total System Capability. We fur-

nish all necessary compatible components—analyzers, probes, filters, adsorbers, indicators, controllers, etc. To this, we add the know-how to design it all into an automatic, virtually maintenance-free system, "tailor-made" to your facility.

Write or call for a paper describing recent combustion tests with the Intertech System. Intertech, Dept. C.C., 19 Roszel Road, Princeton, New Jersey 08540. Phone: (609) 452-8600.

INTERTECH 
A Subsidiary of Ethyl Corporation/Instrument Division

CURRENTS



Dieldrin contaminates chickens

chemical, used in some batches of food crops, was detected in the broilers at levels beyond 0.3 ppm, the maximal level set by the Government. The decision to kill came after major poultry producers pleaded with EPA officials to raise the danger level of dieldrin, known to cause cancer in laboratory animals and suspected to be carcinogenic to man. Prospective losses can be millions of dollars, representing about 7% of the total number of chickens in production in the U.S. It is hoped by Mississippi officials that Congress will approve indemnities that could average about \$1 per chicken destroyed.

Air quality in the vicinity of five Indiana coal-fired power plants will be investigated by a team from Purdue University, under sponsorship of six electric utilities and the state's department of commerce. A sampling system consisting of four mobile monitoring stations will be located in a fixed pattern, systematically rotating around each of the five power stations. The monitors will be moved on a weekly basis from one station to the next for a period of one year. Ambient SO₂, suspended particles, wind speed and direction, and vertical atmospheric temperature profile will be measured. The overall study will encompass 2½ years, and will cost \$273,184.

An activated sludge system is going to be used in New Orleans (La.) in its Sewerage and Water Board's \$26 million East Bank treatment plant expansion. The system OASES (Air

Products and Chemicals, Inc.) will use high-purity oxygen, generated on-site from two 70 tons/day cryogenic oxygen generators to sustain and enhance the microbiological life needed to increase the capacity for secondary wastewater treatment. The present plant operates as a primary treatment facility for the city. The expansion, targeted for start-up in June 1976, will allow a high level of secondary treatment at flows up to 122-mgd, with 85% reduction in BOD₅ and suspended solids.

Carson City's (Nev.) sewage sludge will be disposed by incineration instead of digestion. The changeover will involve the installation of a multiple hearth sludge incinerator, centrifuge, sludge thickener, chemical feed and ash slurry equipment, and modification of the two digesters at the existing sewage treatment plant. The \$0.5 million project, awarded to Nichols Engineering & Research Corp., will increase the capacity of the secondary treatment facility from 1.50 to 3.75-mgd by mid 1974. The new system will be able to process up to 400 lb/hr of dry solids (1600 lb of wet cake) and will comply with Nevada's air pollution code by venting fumes from the thickener to the incinerator to be burned.

MONITORING

Direct measurement of lead, copper, cadmium, and other heavy metals in air, water, petrochemicals, and many aqueous solutions, without sample pretreatment or preparation, has been developed by Environmental Sciences Association (ESA). Certain other metals and halides can be easily determined after normal preparative chemistry. Lead, cadmium, and copper can be read out digitally; others on an analog strip recorder, in 20 sec to 3 min. The instrument is non-destructive, will function on micro samples, and has an inherent accuracy of ±2% at the 10-ng level, according to ESA.

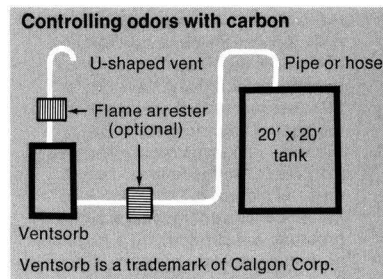
Accurate synoptic measurement and mapping of heated effluents can be accomplished by airborne infrared scanning, according to Daedalus Enterprises, Inc. (Ann Arbor, Mich.). From infrared scanning and digital data processing, a map, dramatically revealing thermal distribution and

flow patterns for a cooling pond was made by Daedalus for Commonwealth Edison and for Sargent & Lundy Engineers, both of Chicago. The same technique works to measure thermal discharges or seepages into rivers and lakes. Data can be displayed as easily read color mosaics and isothermal contour maps for engineering purposes.

TECHNOLOGY

Wastewater treatment by an optimized system package for jet aeration will cost a fraction of pure oxygen system's price and use 25% less power in a scheme developed by the Penberthy Division of Houdaille Industries, Inc. Deep-submerged jets, in clusters or along manifolds, entrain compressed air and waste liquor in homogeneous mixtures, and shoot them back into the treatment tank's depths. This technique provides necessary motive mixing force and oxygenation. High transfer velocity at nozzle discharge and low-pressure shearing between fine bubbles and mixed liquor provide high oxygen transfer efficiency. The system is more economical to install than a pure oxygen system, according to Penberthy.

Granular activated carbon could control many industrial odors, and at the same time save 75–97% of energy, according to Calgon Corp. In a paint bake oven, for example, concentrating odor-causing chemicals on activated carbon and then incinerating everything can offer up to 97% energy use reduction. In plastics, styrene vapor can be adsorbed on activated carbon, and then desorbed with 95% styrene recovery. Food processing, carpet dyeing, foundry operations, sewage treatment, and rendering



CURRENTS

may all benefit pollution- and energy-wise. In many cases, the activated carbon is regenerable.

Providing raw oil shale feed to a retorting facility initially will probably be underground room-and-pillar mining. The mine would be large enough to allow high-capacity open-pit-type equipment underground. T. Kauppila and E. Carnahan of the Cleveland-Cliffs Iron Co. (Rifle, Colo.) told the American Chemical Society (ACS). About 150,000 tpd will be required to supply a 100,000 bbl/day retort system, double the productive rate of any underground mine in the world today. Spent shale will be transported and compacted in proper surface disposal areas, and as much as 50% may ultimately be backfilled into mined-out areas underground.

Control of SO_x emissions from non-power generating sources is becoming increasingly important. Konrad Semrau of Stanford Research Institute (Menlo Park, Calif.) reported to the ACS. Besides various smelters, iron ore sintering and pelletizing plants, coke plants, oil refineries, sulfuric acid plants, and Claus plants, coal gasification and liquefaction facilities will be significant. SO_x treatment is different from that needed for combustion sources, and in some cases, will be closely related to process technology, whose changes may reduce SO_x or increase off-gases, thus improving control and recovery economy.

INDUSTRY

Consolidated Edison Co. (New York, N.Y.) said that use of coal at its Ravenswood and Arthur Kill plants could result in 4–5% cut in electric bills with no environmental degradation. On a year-round basis, coal at present prices could reduce fuel costs—automatically passed on to the customer—by as much as \$100 million, ConEd's chairman Charles Luce said. In answer, Robert Low, administrator of New York City's EPA, estimated fuel savings at 3% of the cost of electric generation, and termed it "an investment which New Yorkers might feel appropriate to make in clean air." Low also said that Luce was addressing a sulfur problem, but overlooking a more important particulate problem, which is the major concern with coal.



Bethlehem Steel's Ritterhoff

C. William Ritterhoff, a vice-president of Bethlehem Steel Corp., defended three bills seeking to amend certain Pennsylvania environmental quality legislation. Ritterhoff, v-p for production, steel operations, said that ambient air standards, the same set by the federal government to protect public health and welfare, would still be required under the bills. He said that these standards should not be confused with emission standards which put limits on stack discharges regardless of whether such standards are needed to protect health. Ritterhoff maintained that the bills seek to substitute "reasoned limits for arbitrary ones" and obviate great costs and waste of fuel and energy when federal standards are already being met.

Union Electric Co. (UEC, St. Louis, Mo.) plans to build a solid waste utilization system capable of handling essentially all of metropolitan St. Louis' solid waste. UEC will set up and run five to seven collection centers capable of handling 2.5–3 million tons/year of refuse. The refuse will

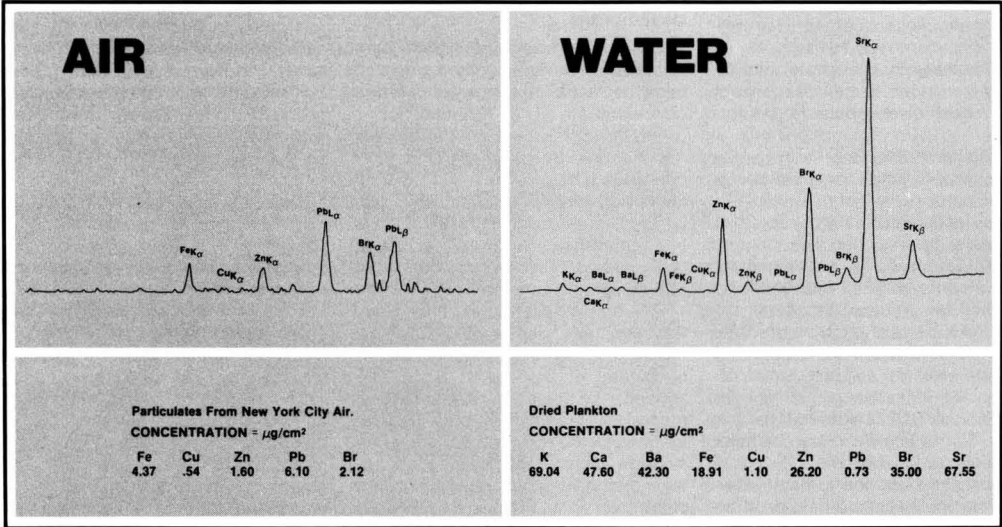
be shipped in closed containers to UEC's Meramec and Labadie power plants. Combustible wastes will be burned with coal to generate electricity; noncombustibles will be sold for recycling. According to UEC, such a large commitment hinges upon realistic environmental rules for refuse-burning boilers, and an assured refuse supply for enough time to justify the capital investment involved.

Sales of instrumentation for air pollution analysis will continue to expand so that government agencies and industry may comply with current and future laws, according to Frost & Sullivan (F&S, New York City). According to F&S, the energy crisis will temporarily retard this expansion, since air pollution rules for power and heating may be delayed and relaxed, and the economy may stumble over the next few years. Still, the cumulative 1973–85 market will total \$645 million in the view of F&S in its 209-page report on the subject.

Olson Laboratories, Inc. (OLI) is seeking information on vapor recovery systems which can control gasoline vapor emissions. Such emissions occur when a tanker truck refuels a gas station's underground storage tanks, when these tanks are vented, or when motor vehicles receive gas. The systems OLI seeks may be developed or prototyped. OLI's president, R. L. Gibney, said OLI will work up a field evaluation program for the American Petroleum Institute for which selected equipment will be judged on the basis of vapor recovery effectiveness.

John McGoldrick, director of communication for American Can Co., said that the Oregon and Vermont "bottle bills," mandating a refund on beer and soft drink containers, met with "less than overwhelming success." McGoldrick pointed out that these containers in Oregon and other states never comprised more than 20% of roadside litter, and that Oregonians are paying \$10 million/year more for beverages than they did before the bill became law. According to McGoldrick, the impact of a "bottle law" on processing and distribution could be disastrous; the real answer lies in resource recovery and solid waste management, and not in simplistic, hurried response.

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CIRCLE 5 ON READER SERVICE CARD

OUTLOOK

Determining environmental standards

Webster's Third New International Dictionary defines "standard" in many different ways. As far as the environment is concerned, the following definitions may be used:

- something that is established by authority, custom, or general consent as a model or example to be followed

- definite level or degree of quality that is proper and adequate for a specific purpose.

These definitions were the focus of discussion at the National Conference on Standards for Environmental Improvement (NCSEI). Sponsored by the American National Standards Institute (ANSI) and cosponsored by the American Society for Testing and Materials (ASTM) and the American Society of Mechanical Engineers (ASME), the NCSEI was held at Arlington, Va. in late February. Perhaps the major issues were:

- whatever gaps there may be between standards established, or to be established by authority, and standards which various industries feel might be better established by custom or general consent

- what constitutes degrees of quality proper and adequate for the specific purpose of effecting environmental improvement.

How the federal authority first establishes standards was explained in the keynote speech by EPA administrator Russell E. Train. "Contrary to some opinion," Train said, EPA, in fashioning environmental standards, does not "pluck them out of a cloud or pull them out of a hat." Nor do these standards "spring forth in full bloom from someone's imagination," but are "the end product of a very comprehensive process and a lot of hard work."

Train said that the criterion of an environmental standard is protection of human health and welfare. Such a standard must be based on soundest scientific and technical information, meet all requirements of laws under which they are issued, and be legally enforceable. However, when risks are balanced against benefits, the standard "must contain a margin

of safety on the side of public health and welfare."

Uniform tests

The EPA administrator continued, "An environmental standard ought to be a norm of tolerance indicating a concentration of a pollutant for a given duration of time." He pointed out that the standard should specify the test method to be used, and include adjustments to bring other recognized and feasible test methods into equivalency with the specified test method. The same would hold true for sampling methods.

This may be easier said than done. For example, James R. McNesby, manager for air quality at the National Bureau of Standards (NBS), described the disparity of measurements for cadmium (Cd) in fly ash, as done by 90 testing laboratories on a given sample. Methods used ran the gamut of accepted, modern physiochemical techniques. Results ranged between 1.0 and 6.0 μg Cd per gram of fly ash.

"Life would be far simpler," McNesby said, "if all measuring instruments produced a response proportional to the concentration of pollutant, oblivious to the presence of other pollutants. Single point calibration of the instrument with the Stan-

dard Reference Material [SRM, containing an accurately known pollutant concentration in air or water] would guarantee everyone's ability to measure pollutant concentration accurately." McNesby feels that it would be "nicer" if instrument response to pollutant concentration were linear, with effects of interference removed, so that calibration would not necessitate a multitude of calibration points.

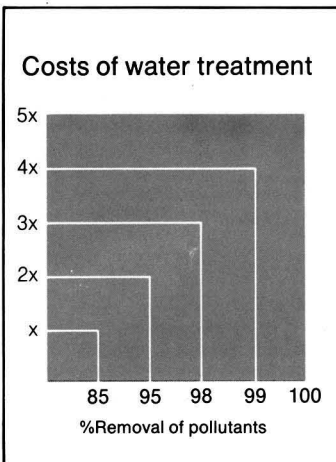
Over the past few years, NBS has been engaged in developing SRM's on which to base such instruments. The SRM's would be officially certified according to the rigorous specifications of NBS, and serve as reference materials against which calibrating materials can be standardized. Typical SRM's are shown.

The pioneering work that NBS is accomplishing will certainly help to determine quantitatively whether given environmental standards are being met by a certain facility at a given time. What is less certain, or at least, less agreed upon, is just what those standards should be, and how they could best be arrived at and then met. Hopefully, the NCSEI would be a major step in bridging this "agreement gap."

Industry views

Some industry representatives expressed a view that some industries, in concert with highly regarded standard-oriented organizations, such as ANSI and ASTM, were able to work realistic standards, based on criteria acceptable to the industries and these societies, that the industries could adopt. The acceptance and adoption of these standards would enable the industries to improve the environment, particularly with respect to water and air quality, with the minimal "pain." These industry representatives largely felt that many local, state, and federal government bodies also recognized these standards as part of generally accepted technological practice, as far as environmental protection and improvement were concerned.

For that reason, the industry representatives, from a cross section of



Perhaps standards societies, such as ANSI, ASTM, and ASME, can be the vehicles which government and industry can use to reach agreement

companies, appeared to take EPA a little bit to task. The feeling was that EPA, in-house and with the aid of contractors not fully familiar with industries to be affected by forthcoming standards and regulations, arrived at standards sometimes arbitrary

because the standards often were evolved in an unhealthy atmosphere. This atmosphere was one of crisis which was predictable, but arose because competent pleadings were ignored (much as today's energy crisis came about). Also involved

particularly with regard to water quality, as increasingly improved technologies are required, and finally "zero discharge" is sought. Ling took the example of a certain stretch of river to be cleaned up efficiently to a point where it may serve many purposes, including recreation and aquatic life support (perhaps not for a species as delicate as trout). Ling took 85% clean as a figure of merit.

Therefore, Ling asks, "How clean is clean?" We must determine this not with arbitrary criteria, as we are doing now, but on the basis of scientifically determining what is needed to maintain a harmonious and balance coexistence between man and his environment, in Ling's view.

Another question troubling much of industry is investment in technology to meet ever more rigid standards in equally rigid time frames. Most feared is the prospect of being forced to buy and install technology whose useful life is limited, or which would require extensive modification as air, water, and other standards become ever tighter. Moreover, these standards are formulated and promulgated, in many industries' broader view, without industry having sufficient opportunity to participate in their development (*ES&T*, April 1974, page 314).

Getting it all together

Whatever previous attitudes may have been in certain quarters, industry now recognizes the need for environmental improvement, and wants to take a strong lead in bringing it about. Industry is asking, however, for a greater opportunity to take a larger part in the process of environmental standard development, perhaps with the able assistance of organizations such as ANSI and ASTM, which are old hands at standard establishment and updating. Industry also welcomes the chance to devise and apply technology for environmental improvement, as it is doing now, and feels that it could do an even better job if undue technological and economic strain could be minimized. JJ

Fossil fuel standard reference materials

SRM no.	SRM	Concentration
1621, 2, 3	S in resid, fuel oil	0.27, 1.0, 2.1%
1624	S in distillate fuel oil	0.21%
1630	Hg in coal	0.13 ppm
592, 3, 4, 5, 6, 7, 8, 9	Hydrocarbon blends	...

Source: NBS

Gaseous standard reference materials

SRM no.	SRM	Concentration, ppm
1610, 11, 12, 13	CH ₄ in air	1-1000 ppm
1601, 2, 3	CO ₂ in N ₂	308, 346, 384 ppm
1625, 6, 7	SO ₂ permeation tube	Ambient

Source: NBS

and considerably at variance with the "realistic" or "acceptable" ones developed by the industries, and at least provisionally recognized by ANSI and ASTM through practice, experience, and educated consensus.

Some problems involved in recent standard formulation were set forth by Robert A. Baker, Sr., executive vice-president of Public Service Electric and Gas Co. (Newark, N.J.). Baker said that environmental regulatory standards reflect public concern on what is needed to protect health and welfare. However, Baker explained that in the setting of standards, politics and emotions have been important factors. Also, standards have been developed in the abstract, and their formulation and enforcement have been, and are subject to a multiplicity of levels and to conflicting authorities.

William R. Smith, manager of environmental control for Kaiser Aluminum and Chemical Corp., pointed out that standards problems may have

been distortion of facts, since environmentalists, government and industry people, and some members of the public may each have had their own axes to grind. Finally, there was a feeling of mistrust, because of which each group of interested parties refused to believe in the reports, positions, and data of other groups.

Rigidity

Perhaps all of these factors, and more, individually and combined, led to development of environmental standards which many industry people feel represent reaction rather than action, and are far more rigid than they really need be. This reaction mechanism may also be behind attempts at solutions to environmental problems in what Joseph T. Ling, director of environmental engineering and pollution control for 3M Co., fears are being worked on in a piecemeal way, with separate and unrelated pieces of pollution control laws.

Ling had much to say concerning future compliance with standards,

Water, Air groups talk money

Water Pollution Control Federation and Air Pollution Control Association members fear that lack of funds will undermine water and air programs

Money was the unavoidable topic of discussion at the back-to-back Water Pollution Control Federation (WPCF) and Air Pollution Control Association (APCA) legislative seminars held recently in Washington, D.C. Members were pretty well agreed that the lack of it—because of underfunding, impoundments, and the Environmental Protection Agency's "slowness" in administering what funds are available—means standards set in the air and water laws simply cannot be met.

tions when we have to. It would be the worst kind of profligacy to abandon the environment at this point in favor of energy considerations."

The Council on Environmental Quality's John Busterud offered yet another disquieting possibility concerning funding. He said there is likely to be increased competition for money at the federal level because of the new energy research and development program that calls for more than \$10 billion over a 5-year period. "While on the one hand I see

There also is likely to be an adverse effect upon waters because of increased burning of coal and high sulfur oil. This would result from the generation of extra amounts of sulfur dioxide, and in turn harmful sulfates, which could affect water supplies at considerable distances from where the fuels are burned, Busterud said.

The energy crisis and related problems also figured importantly in the APCA Government Affairs Seminar. This meeting's principal speaker, Sen. J. A. McClure (R-Idaho), mem-



Frederick Clarke
Cost will be staggering

In keynoting the WPCF session, Frederick Clarke, executive director of the National Commission on Water Quality, held that the cost in meeting the 1983 clean water discharge goal will be staggering. He pointed out that the "needs" survey indicated the states and EPA would require \$60 billion just to achieve secondary sewage treatment for all municipalities, but that a figure twice this amount would be more realistic. (The costs of sewer constructions, excessive infiltration problems, and combined sewer overflows were not considered in the study.) As for attaining best practicable treatment by 1977, Clarke said there is "no realistic hope" the nation will meet this requirement.

A new dimension—energy considerations—has been added to the pollution/money problem, Clarke went on to say. He said statesmanship is needed to put these three facets of the same problem in balance. "They can exist together, but we must be willing to hit the brakes in all direc-



John Busterud
Sees competition for funds

some signs of a letup in allocation restrictions on water quality financing, I do feel that this competition between environmental funding and energy funding could have some impact upon some of your programs," he told the group.

Energy cost impact

Water pollution abatement programs also are likely to feel the impact of considerably higher rates for electric power, Busterud said. He noted the cost for power needs to operate sewage treatment plants and to manufacture pipe and other equipment will increase greatly.

A slightly different cost problem could intensify water quality problems if a weak strip mining bill is enacted. Busterud said that measures now before Congress do not have adequate provisions for preventing degradation of landscapes, acid runoff, and other adverse environmental effects. If these matters are treated at all it will be under programs already existing, he speculated.



Sen. James McClure
Critical of bureaucracy

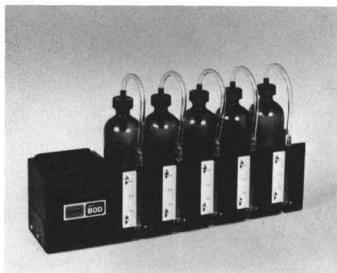
ber of the Interior Committee and the Public Works subcommittee on environmental pollution, said the time has come for Congress to take another look at the Clean Air Act. He was especially critical of the EPA bureaucracy, and of CEQ which he said is "usually negative" in its treatment of environmental impact statements.

In pointing out that a draft environmental impact statement must go both to the EPA and the CEQ after first receiving internal approval by the agency at the operating level, McClure said the whole process could take 90 days or even longer. "Sometimes after all this rigamarole, the statement is returned by CEQ without comment," he said. When CEQ rules negatively, a series of review and adjustments becomes necessary in order to comply with the objections. McClure complained, "While the draft goes through this baroque process, planning is delayed and the cost escalates geometrically."

In answer to such charges, EPA

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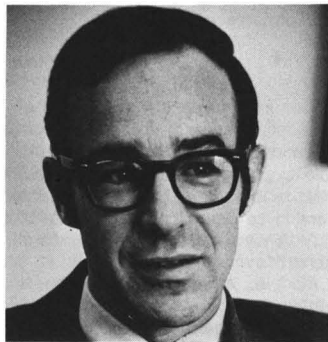
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CIRCLE 26 ON READER SERVICE CARD

deputy administrator, John Quarles, Jr., told a joint meeting of the two groups, "These problems are largely behind us for the Clean Air Act... and most of the delays are behind us in implementation of the Water Law." Although state agencies and local governmental units face substantial burdens under these laws, the EPA is moving to simplify the work that remains to be done, Quarles said. "The amount of paperwork can be reduced, and we are attempting to give state and local governments more time to respond to EPA requests."

Quarles went on to point out that the EPA's regional administrators have been given substantial discretion in interpreting the agency's regulations. He speculated it might be possible to simplify procedures further by accepting state certification of municipalities' compliance with certain regulations rather than having the EPA duplicate such work. The



John Quarles
Problems behind us

EPA is trying hard to be flexible and realistic in administering these statutes, he said. "Give us your thoughts; I will listen eagerly to your suggestions about how to administer our environmental laws so that we will create the least burden for those who are affected by them—and the greatest benefit for the air and water."

Founded in 1928 as a technical membership organization, WPCF serves the needs of the field. It has more than 25,000 members in the U.S. and other countries who design, construct, operate, and manage water pollution control collection and treatment facilities.

The APCA has a membership of almost 7000. It is a nonprofit technical and educational organization dedicated to advancing the art and science of air pollution control. Organized in 1907, it is divided into 18 geographical sections throughout the U.S. and Canada; members also reside in 40 other countries throughout the world.

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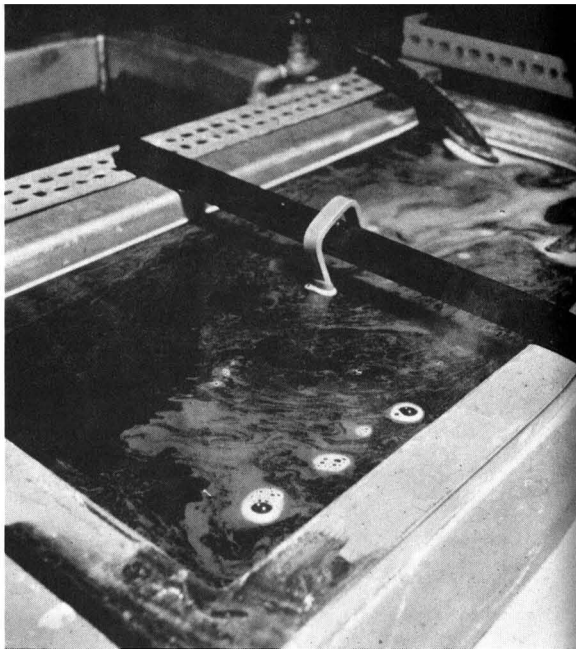
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CIRCLE 10 ON READER SERVICE CARD

The electroplaters are polishing up

Ultimately, they may not only reduce toxic effluents, but also optimize recovery of valuable metal resources



Typical nickel-plating bath

In the past, waste disposal at electroplating and other metal finishing plants and shops could be accomplished by dumping into a sewer or stream. Effluents could contain one or more of a variety of metal ions, although zinc, hexavalent chromium, copper, and nickel were among those materials more frequently encountered. Additional pollutants included suspended solids (SS) and cyanide.

The toxicity of these effluent components motivated many state and local authorities, as well as many electroplaters, to commence action to limit sharply the amounts of noxious or objectionable materials which could be discharged. This effort was prompted not only by a sense of civic responsibility, but also by a search for ways to realize considerable savings.

The standards hassle

More recently, this industry came under the purview of the federal EPA which is setting up effluent guidelines and standards step by step. A first set of proposed standards is based on best practicable control technology currently available (BPCTCA). A second set of new source performance standards (NSPS) is based on the best available demonstrated control technology (BADCT). Both appeared in the *Federal Register* (*Fed. Regist.*) on October 5, 1973. These standards covered copper, nickel, hexavalent

chromium, total chromium, oxidizable cyanide, total cyanide, and SS. After a comment period, standards were to be promulgated February 15, 1974. They were signed off on March 20, 1974.

At the American Electroplaters' Society Pollution Abatement Seminar (AES/PAS), held at Reston, Va., in March, one complaint was that the industry had only six working days to comment on the proposed EPA standards. Another complaint concerned the manner in which the proposed standards were generated.

The evolution of what became the proposed standards was the result of a contract which EPA awarded to Battelle Memorial Institute pursuant to the new water laws. The contract was performed with standard formulation based on the following:

- technical and economic feasibility of removing metals from water, whether or not the metals are toxic
- feasibility of limiting the amount of wastewater constituents discharged into streams, with the idea that if numbers for these limits cannot be established, then uniform standards do not exist
- achievement of no discharge (ND) by 1983, predicated on forecasts of best available technology economically achievable (BATEA) up to and through that time
- surveys on the industry not of a statistical nature, but rather with a view to listing limitations (as, in Battelle's view, these limitations "should

be"), based on present and future technology.

Many of the industry people at the seminar took exception to the manner in which Battelle came up with its standards numbers. Opinions included:

- Too few shops were examined (53 out of a total of about 20,000 in the industry).
- Effluent sampling methods largely involved taking occasional "grab" samples whose validity could be open to question, particularly from chemical, statistical, and confidence level viewpoints.
- The 53 shops chosen were selected out of an underlying desire to find the most exemplary shops and base figures on data somewhat biased in favor of these exemplary shops.

Industry position

At an evening panel session, Richard Crain of Industrial Filter and Pump Mfg. Co. (Chicago), an equipment supplying company which could benefit from new environmental regulations, said that suppliers are joining electroplaters and metal finishers in a fight against the proposed effluent standards. For one reason, these companies, Crain said, have neither the equipment nor supplies platers and finishers would need to comply with the standards. Moreover, he said that if the proposed standards are indeed promulgated and enforced, someone will file suit, and no

supplier would want to be involved.

James Rogers of Raytheon, Inc. (Lexington, Mass.) called the EPA proposed standards "distressing, impractical, and unenforceable," and warned that "they won't work." As presently constituted, he said, these standards could cost the industry \$2-3 billion/yr; treatment costs in the industry exceed estimates by a factor of 2 to 5; and treatment level "can't come close to EPA expectations."

Rogers said that practical effluent standards should be three times those proposed, that suppliers and consultants do not know how to comply with the proposed standards, and that platers and finishers, faced with a prospect of standards numbers changing virtually overnight, will not put in wastewater systems.

Federal criticism, too

Rumbles about the proposed guidelines came not only from the industry, but from the U.S. Department of Commerce (DOC). According to one viewpoint, DOC flatly opposed promulgation of ND for 1983 because technical and economic feasibility have not been demonstrated; energy consumption may be very high in relation to achievable environmental benefit; and problems and costs of land disposal of dried waste have not been seriously analyzed. Also, DOC objected to the units EPA used in setting standards (effluent/m² of plated area, and total metals), and suggested units of concentration and dissolved metals instead. Moreover, DOC feels that many of the limitations proposed, even for as early as 1977, are unrealistically low, and might not be achievable.

DOC was rather parsimonious in its praise for the economic analysis of the proposed effluent guidelines, saying that the data base was inadequate; that the economic survey violated the most fundamental principles of statistical methodology; and that any statement or finding based

Standards, daily values, over 30-day period

	EPA proposal mg/m ²	Battelle study, mg/m ²
Copper	40	16
Nickel	40	40
Hexavalent chromium	4	4.4
Total chromium	40	24
Zinc	40	24
Oxidizable cyanide	4	3.2
Total cyanide	40	N.A.
Suspended solids	1200	1020

N.A. = figure not available. Source: Fed. Regist. and AES/PAS.

upon the survey, done under EPA contract, cannot be accepted as being credible. DOC further charged that the analysis using the data was itself faulty, and that conclusions derived from it are unacceptable as an assessment of the probable impact of the guidelines on the electroplating industry.

Destruction vs. recovery

In any case, electroplaters' and metal finishers' discharges, especially those deemed incompatible with the environment, are coming under increasing controls. The approaches to discharge reduction and elimination would generally involve destruction of wastes, waste recovery and reuse, or a combination of both. Water and energy conservation would also come into play. Where feasible and economical, however, recovery would probably be desired.

Where recovery is not practical, destruction is employed. Cyanide would be transformed into cyanates and then, ideally, further changed into carbon dioxide and nitrogen. Hexavalent chromium is reduced to trivalent chromium. Metals, such as chromium, nickel, copper, and others, are insolubilized, preferably not in gelatinous hydroxide forms, and

then dewatered to sludges of 20-50% solids. If metal reclamation from the sludges is not practical, the sludges would go to approved landfills. Unfortunately, some districts may forbid use of such sludges in landfills, and then sludge storage and disposal could become a problem.

Recovery presents problems in concentrating ions in the effluent and separating mutually interfering materials, as well as other difficulties. Yet, recovery may eventually be the "way to go," to make a good thing out of pollution control, and to conserve and recycle increasingly scarce metal resources. Evaporative (evap), counterflow (CF), reverse osmosis (RO), and ion exchange (IX) methods, and others, may all be vehicles for recovery of metal values.

Rockwell-International Corp. (Troy, Mich.) installed a chromium evap/CF recovery system, with seven CF's, developed by the Pfaudler Co., at a Rockwell plant in Canada. Estimated annual savings from recovered chromium were \$61,380, less \$9301 for operating costs. However, because chemical, labor, and operation/maintenance costs for a destruction scheme were not incurred, total savings were estimated at \$82,152.

Warsaw Plating, Inc. (WPI, Warsaw, Ind.), a large job shop, started cleaning its effluent in 1962. In 1964, Pfaudler installed a continuous chromium recovery system for WPI, and in 1966, nickel recovery. WPI is putting in an evap/RO/IX zinc recovery system which will cut out water use from 800 to 300 gpm of water, and the chromium recovery enabled WPI to cut chromic acid purchases from 14,000 lb/yr to 2500 lb/yr.

RO may come into increasing use, and perhaps materially turn pollution control from a cost to a saving. Dean Spatz, president of Osmonics, Inc. (Minneapolis, Minn.), estimates that savings realized by installation of his company's RO recovery system can pay back the system's capital cost in less than one year, with faster payback if the recovered metal is of higher value. Another Minneapolis firm, North Star Research and Development Institute, may shortly announce an RO system with 99.7% removal that could work even with seawater and, in any case, strongly advance reclamation potential.

In the long run, recovery would be the desired course, and new technology hopefully will be developed to make it practical and economical, even for small shops. The incentive is not only pollution control and conservation, but also a reduction in dependence upon certain raw material suppliers.

JJ

Some typical systems currently available

Company	City	Operating principle	Material	Aim
ABCOR	Cambridge, Mass.	RO	Nickel, copper zinc	Recovery
ECO-TEC	Toronto, Ont., Canada	CF/IX	Chromium	Recovery
North Star R&D	Minneapolis, Minn.	RO	Various	Recovery
Osmonics	Minneapolis, Minn.	RO	Various	Recovery
PCI Ozone	Stamford, Conn.	OZ ^a	Cyanide	Destruction
Pfaudler	Rochester, N.Y.	Evap, CF, RO, IX	Chromium, copper, nickel, zinc, others	Recovery
Sethco	Freeport, N.Y.	INS ^b	Acid/alkali, chromium cyanide	Destruction

^a OZ = ozonation. ^b INS = insolubilization. Source: AES/PAS company exhibits.

Events force toxic substances issue

Recent cases involving dieldrin and PVC dramatize need for coherent toxic substances legislation

There are nine toxic substances, according to the waterway effluent standards proposed by the U.S. Environmental Protection Agency. Actually, the list is much longer, but present provisions for defining them are limited to those provided for under the Federal Water Pollution Control Act (FWPCA). Although a bill dealing with toxic substances in a more comprehensive way is in the offing, as yet the Senate and House have been unable to agree on its contents.

There are other laws that deal with chemicals that are toxic, of course, such as the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), as amended in 1972, and the Air Pollution Control Act and its amendments. But these laws, too, are concerned with toxic substances only in indirect ways. Lacking a bona fide toxic substances law, the EPA has had to rely upon the water quality provisions.

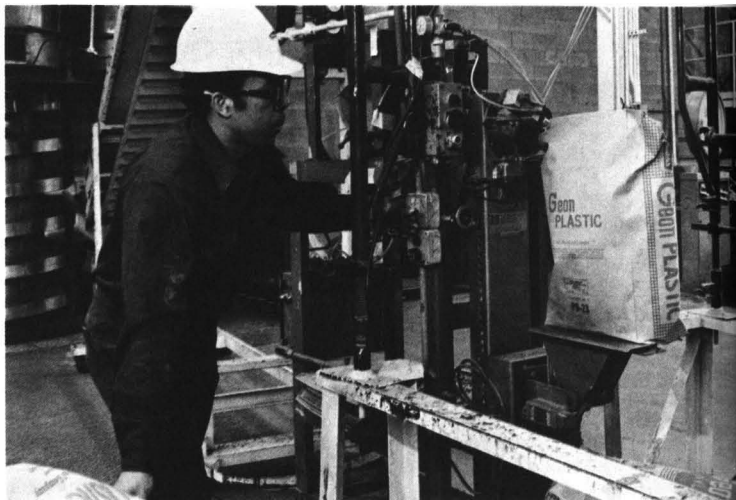
Under this mandate, the EPA, in December 1973, proposed effluent standards for aldrin, dieldrin, benzidine, cadmium, cyanide, endrin, DDT (DDD, DDE), mercury, PCB's, and toxaphene. The standards are based upon water quality criteria proposed in October 1973, and are designed to protect against short-term and long-term toxic damage to man, animals, and other organisms. The EPA says final standards will be promulgated in June of this year.

In addition, the agency has published a list of pollutants from which it may identify toxic substances in the future. According to the Sept. 7, 1973, *Federal Register* (Vol. 38, No. 173), the EPA plans to examine arsenic, selenium, chromium, lead asbestos, selenium, zinc, chlordane, lindane, acridine, hydroquinone, ortho-chlorophenol, beta-naphthol, alpha-naphthol, beryllium, nickel, antimony, heptachlor, camphor, methyl parathion, parathion, di-*n*-butyl phthalate. The agency also will examine other pollutants, including chlorinated hydrocarbons, organophosphates, metals (heavy), and materials listed as occupational carcinogens by the Department of Labor in the May 3, 1973, *Federal Register* (Vol. 38, No. 10929).

Four criteria

In choosing pollutants for its initial list, the EPA set up four criteria. The

first one concerns the actual or potential damage that a water discharge of these materials may create. Specifically, it seeks to determine whether bioaccumulations, carcinogenic, mutagenic, and teratogenic effects, and high acute toxicity, are produced.



The second criterion seeks to determine the nature and extent of toxic effects associated with the pollutant, the extent to which discharges of the pollutant have been identified, and the production, distribution, and use pattern of the pollutant. It requires documented evidence showing that discharges of the compound, or a subsequent combined form of the compound, result in damage to important organisms.

The third criterion concerns the setting of effluent standards for pollutants on the list. The fourth criterion concerns the overall environmental effect of the control measures available, including the possible effect upon groundwater and other environmental media. The use of substitute products is suggested where available.

The inadequacy of the water quality act by itself to deal with the total problem of toxic substances was underscored recently with the realization that polyvinyl chloride, which is not strictly speaking a waterway threat, nevertheless has serious toxic properties. So far some 12 cases of

angiosarcoma, a rare liver cancer, have been found among PVC workers in Kentucky, New York, Texas, West Virginia, and Great Britain. While this plastic product—used for a variety of purposes including wrapping foods—is thought to be inert in its solid state, the low levels of vinyl

chloride gas that may escape from PVC are not. Medical researchers feel PVC's are greatly understudied.

New compounds yearly

Scientists at an American Cancer Society's science writers' seminar in St. Augustine, Fla., recently estimated that some 10,000 new chemical compounds are introduced into the environment each year. Besides the problem of keeping tabs on all these chemicals, such substances as PVC seem to have a delayed effect in the harm they do to individuals. Scientists say the PVC-induced cancers observed today had their origin 15–35 years ago. Also, it has been said that thousands of men and women have died of cancers caused by asbestos following work-related exposures between 1930 and 1950.

The advantages of knowing the toxic properties of a chemical in advance was shown recently when the EPA moved to have several million broiler chickens destroyed because of contamination by the pesticide, dieldrin. It was found that the dieldrin levels in the chickens, appar-



where field surveys verify the existence of infections that could cause significant damage to dry pea crops. Other restrictions are being imposed to ensure that the DDT is properly used, and that record-keeping and monitoring are undertaken. Under a similar program last year, less than half the total dry pea acreage was treated.

Contacts are encountered almost daily

Data are beginning to show long-term harm can arise for workers who spend years around polyvinyl chloride products. Less well understood are the possible effects to the consumer whose total exposure is considerably less. Another undecided question is just when do pesticide and insecticide chemicals warrant use. In many cases they increase crop and timber yields, but also harm birds and other animals



ently confined to the state of Mississippi, were as high as 10 times the permitted level. Although the economic loss was staggering, a serious health threat to humans was avoided.

In yet another toxic substance matter, EPA administrator Russell E. Train reversed an earlier ruling on DDT and will allow its use in two "trial" instances this summer. But the decision-making had the benefit of a DDT data base, which is at least partly the result of prior listing of it under the water quality law. Train said the agency was well aware of DDT's toxic properties, but that insects in both of these cases present a more serious threat to the environment. Right or wrong, at least an educated decision was possible.

The first of these rulings allows limited use of DDT to control an expected pea leaf weevil infestation in Washington and Idaho. The second involves the use of DDT against the tussock moth in Oregon, Idaho, and Washington. The use of DDT, in both cases, carries certain restrictions.

As for pea leaf weevil use, the chemical will be permitted only

Administrator hopeful

Train said, in making the tussock moth use decision, that the permission "is not a directive from EPA that DDT be used this summer against the tussock moth." He said it's hoped that no actual emergency will arise, that the egg hatch will not produce such large numbers of the insect. The Forest Service will determine whether an actual emergency exists. In its caterpillar stage, the moth eats the needles of the Douglas and other fir trees—thus defoliating and killing them.

What a Toxic Substances Control Act could do, if passed by Congress, is to ensure the study of, and immediate and strict control of, those chemicals that may kill or injure the unsuspecting citizen. It also could unify into one coherent bill, provisions presently contained in other federal legislation.

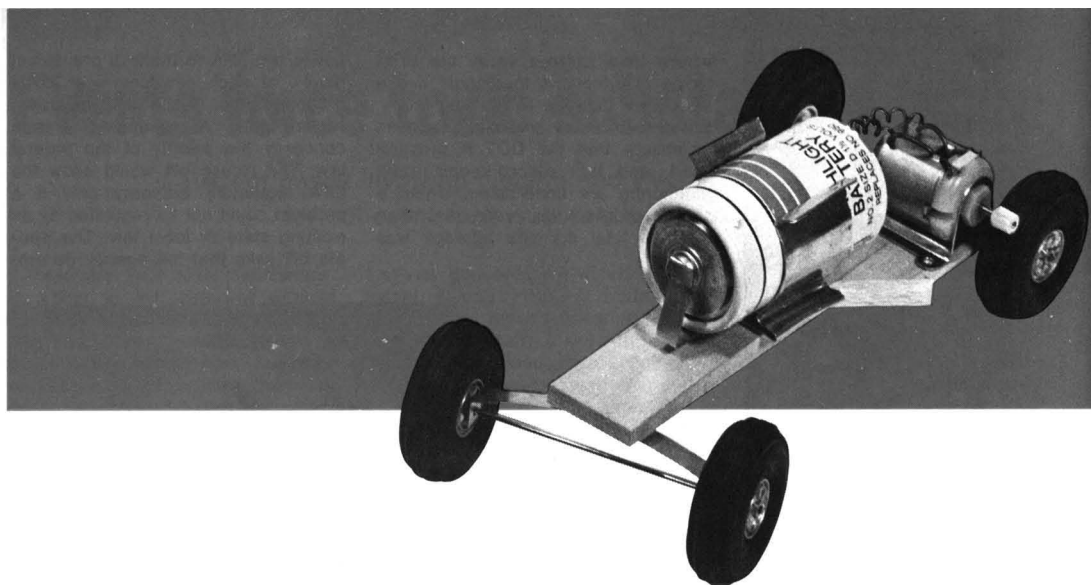
As for the present status of legislation, both houses passed toxic substance bills last session, but the bills died when crucial differences could not be worked out. The Senate bill, the stronger of the two, would em-

power the EPA to make a premarket review of each new chemical to be produced; the House bill would not require this. A second difference concerns the priority of the federal law. The House bill would allow the EPA regulatory authority only if a problem could not be regulated by an existing state or local law. The Senate bill asks that the agency be em-

powered to act according to whichever federal bill would deal most effectively with the problem.

The growing concern over environmental poisonings from toxic chemicals is by no means restricted to the United States, although the problem is most severe in industrialized countries. The Society of Toxicology, (SOT), which met in Washington in March, was asked to provide data upon which toxicological decisions could be reached worldwide. Frank C. Lu, chief of food additives for the World Health Organization (WHO), Geneva, Switzerland, requested information especially in cases where manufacturers' research facilities are too small to provide toxicological data.

This worldwide interest is essential, but such groups as WHO lack legal mandates to enforce toxic substances policy. This realization makes the efforts, undertaken in individual countries such as the United States, loom large indeed. What we do will affect the health and safety of millions of people here, and perhaps millions of others worldwide. WSF



Switching on electric vehicles

All shade-tree mechanics wish at some point that they could just sit and relax on the weekend instead of hassling with their cars. Their time-consuming chores include getting in line for gasoline; changing the oil; cleaning and gapping spark plugs and points; changing the condenser; adjusting the carburetor; and checking the distributor cap, muffler, and fuel line. Though annoying, they put up with these tasks rather than give up the luxury of car transportation. The electric cars, with none of the above-designated tribulations, should come as a welcome relief.

However, results of a recent national consumer survey show that only 20% of the public is aware that electric cars exist. Others are uninformed about the availability of additional electric-powered vehicles, such as fork-lift trucks, delivery vans, buses, golfcarts, lawn mowers, garden tractors, and miniature submarines.

Design parameters

Speakers and exhibitors at the recent "Third International Electric Vehicle Symposium and Exposition" (Washington, D.C.) extensively discussed the makeup of the electric vehicles. Basically, the electrical system for converting potential energy to propulsion is comprised of five subsystems:

- energy source
- traction motor
- motor controls
- vehicle controls
- differential/gearing.

The **energy source** is usually a set of lead-acid batteries. Their cost is relatively low (about \$200 in Sebring-Vanguard's Citicar) with reasonable power capabilities (about 28 mph maximum speed for the Citicar). Their energy storage capability is limited, however, requiring frequent recharging (12 hr at 110 V, every 50 mi). Research and development efforts are also focusing on several other types. There are problems related to each, most commonly high-temperature requirements.

In electric vehicle design, battery location is the prime consideration. Most manufacturers, like Ford and General Electric, mount the batteries under the passengers. Although this arrangement increases wind resistance because of the high roofs, it does increase crashworthiness compared to behind- or beside-passenger battery locations.

Another energy source undergoing considerable testing is the fuel cell, a method of converting a hydrocarbon fuel directly into electricity by chemical means. It has a major advantage over the battery in its logistics of refueling. It does, however, cost more, requires fuel, and must cope with the transport of reagents and products.

The **traction motor and vehicle controls** are usually mechanical contactors, although some manufacturers prefer the solid state devices or circuits. Motor configurations come in two major classes—the dc commutator and the brushless type. The former uses the standard series dc traction motor and can be controlled

by contactor or solid state systems. The latter uses only solid state controls and is smaller and lighter than the other. The brushless type is still under development and is expected to be easier to maintain than the dc type which requires changing brushes (twice yearly in the Citicar). Much debugging is still needed.

Gearing is primarily dependent on the motor speed and conditions of normal utilization. For most electric vehicles, gear changes are not necessary, although low speed efficiency is improved by introducing one or more gear changes.

The **bodies** of the electric vehicles are either modified ICE (internal combustion engine) bodies or complete redesigns. The first approach was used, for example, by Ford's Cortina and GM's Electrovaire; the second by Sebring-Vanguard's Citicar. Citicar uses aluminum structural members and a body made from lightweight "Cycolac" ABS plastic (Borg-Warner Chemicals). This plastic is highly impact-resistant, noncorrosive, and does not chip.

Those options

The **heater/defroster** system for a typical four-passenger vehicle generally has a capacity of 6-9 kW. In the electric vehicle, the system would circulate the air from the passenger compartment through the motor and controller to pick up heat, and back through heating and defrosting ducts into the passenger compartment. This method cannot supply the total energy needed and requires assis-

Though ideal as stop-go, short-distance and nonpolluting runabouts, they are lagging in the ICE race

tance from other means. Development efforts on the supplemental systems range from radiant heat panels, in-seat heating coils, and fossil fuel-burning heater to exotic devices (catalytic heaters or lithium hydride systems).

Air conditioning in the electric vehicles can be achieved by the use of an electrically driven compressor powered by traction batteries, or possibly by a fossil fuel-burning air conditioner.

Power brakes/steering are being considered for electric vehicles with modified ICE bodies which can be three or four times heavier than "plastic" bodies. Basically, the mode of operation is similar to that in conventional vehicles.

Experimentation has shown that the vacuum needed to drive the booster diaphragm for the power brakes could be created by a small electric pump and a vacuum accumulator and that secondary braking systems (regenerative or dynamic) could also be incorporated. Testing also demonstrated that the hydraulic pump used for the power steering

could be driven by an electric motor. Increased power consumption for these additional electrical gadgets would be minimal.

What is available

An international listing of currently available units by electrical product category can be obtained from Electric Vehicle News (Westport, Conn.). Of chief interest to most people, at least to the commuter set, are the electric bikes, cars, and buses.

Corbin Gentry Inc. (Somerville, Conn.), one of the bike makers, will be selling their city bikes this year, at about \$1395. They quote a 3-hr charge time every 20-25 mi. Weighing 370 lb, these bikes can travel at 32 mph maximal speed and are said to cost the rider 5¢/25 mi.

Cars making their debut this year will include Electric Fuel Propulsion's (Ferndale, Mich.) four-passenger car, and Sebring-Vanguard's (Sebring, Fla.) two-passenger Citicar. Figures were available for the latter at the exhibition, listing the price at \$2068. Weighing 1100 lb, the car can accelerate up to 28 mph and requires a 12-hr recharge every 50 mi. It is said to cost the driver 1.5¢/mi for electricity and battery depreciation.

Buses will be marketed by at least two companies—Batronic Truck Corp. (Boyertown, Pa.), and Electrobus (Studio City, Calif.)—by mid-year. Transit authorities in Long Beach (Calif.) and other cities have already placed their orders based on encouraging feasibility studies.

One such study was carried out in Honolulu. A team of workers from the University drove a self-propelled electric bus over everyday routes and noted the power and energy requirements. With a curb weight of 20,000 lb, seating capacity of 49 passengers

and containing 4375 lb of lead-acid traction batteries, the bus was capable of making one round trip, up to 12.1 mi with one battery charge, if air-conditioning was not used. With air-conditioning, the maximal distance traveled before recharge was 6.2 mi.

The experiment was based on assumptions that total power output of the batteries was 175-260 kW and that the total usable energy (60% of stored) was 31-36 kWh. Ideally, the establishment of on-route recharge stations will increase the driving range.

Pros and cons

Electric vehicles are attractive because they are relatively noiseless, nonpolluting, and, according to J. W. Simpson (president, Westinghouse Power Systems, Co.), nationally can save up to 1.5 billion barrels of oil per year. They are viewed as a long-term alternative to gasoline and diesel engines, since they can call upon a number of energy resources—hydroelectric, solar, tidal, wind power, geothermal steam, nuclear, and magnetohydrodynamics.

Advocates of electric vehicles do not foresee any significant effects the wide-scale use of such vehicles would have on projected energy needs. They feel that if as many as 1 million electric cars were on the road in 1972, their combined total demand for electricity would have been only 2% of the reserve capacity of the U.S. electric utilities.

In addition, the vehicles would be recharging mostly during nighttime hours when demand for electricity is at its lowest. Even if more power plants were constructed to accommodate the power needs of the vehicles, pollution from these stationary sources would still be less than ICE emissions.

Of course, there is still a large competition gap between the conventional and electric vehicles—speed and distance for openers. For most people who dig accessible and convenient freeways, these are prime requirements.

Other unsolved concerns include: the heavy weight of the lead-acid batteries found in most electric vehicles, the inherent danger of acid spillage resulting from bad accidents, battery life, energy savings over gasoline-driven types vs. limitations.

There is also the drudgery of recharging and the prime inadequacy of the total watt hours of energy per pound deliverable by the batteries. A look at one major manufacturer's research data would point out that ICE can generate some 5900 Wh/lb whereas a set of 12 lead-acid batteries can produce only 150 Wh. Hopefully, intense R&D will provide cost-effective answers. LCG

Electrochemical power sources

System	Expected performance		Development status	Principal problems
	Wh/lb	W/lb		
Lead-acid	15	20-30	Commercially available	Low energy density
HIGH TEMPERATURE				
Sodium-sulfur	80-100	80-100	**	Selection of appropriate materials of construction
Lithium-sulfur/sulfides	>100	>>100	*	
Lithium-chlorine	50	>100	**	
AMBIENT TEMPERATURE				
Iron-air	40-50	10-20	***	Cathode corrosion, limited power density
Zinc-air	40-50	10-20	***	
Nickel-zinc	20-25	>100	**	Prevention of dendrites
Nickel-iron	20-25	50+?	***	Maintenance requirements
Zinc-chlorine	60-80	100?	**	Complexity, hazards
Zinc-bromine	20	40-50	**	Low energy density

* Energy density and power density refer to anticipated maximum values at, respectively, very low and very high discharge rates. *** batteries tested; ** cells tested, some batteries; * cells tested.
Source: Arthur D. Little, Inc.

MHFs solve a sludge disposal dilemma

Envirotech's multiple hearth furnaces have been ordered for more than half of all units specified for municipal systems last year

For many years disposal of municipal sewage sludge has been regarded as more of a nuisance than a problem. Today, wastewater treatment planners are having to deal with the reality of ultimate sludge disposal. Due to the higher treatment standards coming into effect under the new water law, P.L. 92-500, the problem will grow in proportion to the added sludge volumes from new plants. While some people regard sludge as still a largely unsolved problem, there is a growing confidence in and commitment to incineration processes as the best available sludge disposal systems.

In everyday practice, consulting engineers are designing and specifying modern multiple hearth furnace systems at a record pace. In calendar year 1973 alone, there were 30 incineration projects bid with a total value of \$52-75 million. The rapid growth in the acceptance of sludge incineration by some practicing engineers, while others still regard it as inadequate technology, indicates that there is a great deal of misunderstanding about the advanced state of the art and practical application of multiple hearth systems.

Several examples of recent incineration installations and projects under design by Envirotech's BSP Division (Brisbane, Calif.) will help to dispel the uncertainty surrounding incineration. These examples reinforce the fact that this sludge processing system will meet requirements of the future and is available today.

Systems approach

The many advantages of a total systems approach to sludge handling are evident in the facilities being designed for Granite City, Ill. The heart of the system is a third generation multiple hearth furnace (MHF) operated in an energy-conserving mode by recovering waste heat for sludge heat treatment.

R. C. Haller, vice-president of the consulting engineering firm of M. W. Inc. (Indianapolis, Ind.), says that the closed loop energy conservation system begins with gravity thickening



M. W. Inc.'s Haller
Closing the energy loop

of the combined primary and waste-activated sludge. The thickened sludge is then thermally conditioned in one of two 6000-gph BSP Heat Treatment Systems. The effects of thermal conditioning at 250 psig and 380°F allow the sludge to be mechanically dewatered without chemicals to approximately 30% solids prior to incineration. The sludge at 30% solids is autocombustible, needing no other fuel for complete burning.

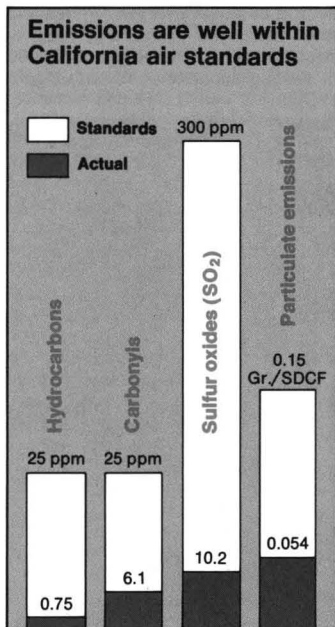
The Granite City plant, a 23-mgd secondary treatment facility is scheduled to go on stream in late 1975. At design, an estimated 11,000 lb/hr of dewatered sludge will be reduced to 1000 lb/hr of inert ash via an 18-ft diameter, seven-hearth BSP multiple hearth furnace. Except during start-up and standby operation, no auxiliary combustion fuel will be required. Exhaust gases from the furnace will pass through a waste heat recovery heat exchange/boiler wherein ample steam will be produced for operating the sludge thermal conditioning systems. Finally, the exhaust gases will be cleaned and cooled via an ARCO/Envirotech scrubber.

Any air pollutants?

A new 35-mgd regional wastewater treatment plant in Palo Alto, Calif., has two multiple hearth furnaces to oxidize the combined primary, secondary sludge. Ronald Doty of the City of Palo Alto, says that the Envirotech furnaces have been operating since December 1972, well within the tight regulations of the Bay Area Air Pollution Control District (BAAPCD).

John Jenks of the consulting and design engineering firm of Jenks Adanson (Palo Alto) says, "These furnaces are equipped with impingement scrubbers and a hybrid afterburner in the top hearth. When the system was nearing final steps, in 1972, new and more stringent standards were adopted by the BAAPCD. Design modifications were made to accommodate the new standards."

In Contra Costa County, Calif., the



consulting engineering firm of Brown & Caldwell was engaged by local authorities for the design of an advanced wastewater treatment system to meet water quality standards as well as recapturing waste heat from a furnace to provide steam for heat and power elsewhere in the wastewater plant. Again two multiple hearth furnaces are included in the design for co-combustion of organic sludge and calcination of lime sludge.

Bill Loftin of Livermore says that when the above application was first made in June 1971 to obtain a permit to construct the facility from the BAAPCD, the permit was denied. "The Board was forced to take this action since the plant would be located in the Livermore Valley, already designated a critical air area for oxidants, and therefore no new sources of any air emissions could be built," he says.

Following this denial, the application was resubmitted along with statements on the overall favorable impact of a water reclamation plant and the relatively insignificant emissions to result from the furnaces. Recognizing the importance of the project, the BAAPCD Board voted to amend their regulations to allow construction of "insignificant sources," endorsing the insignificance of the furnace emissions by granting the permit for construction.

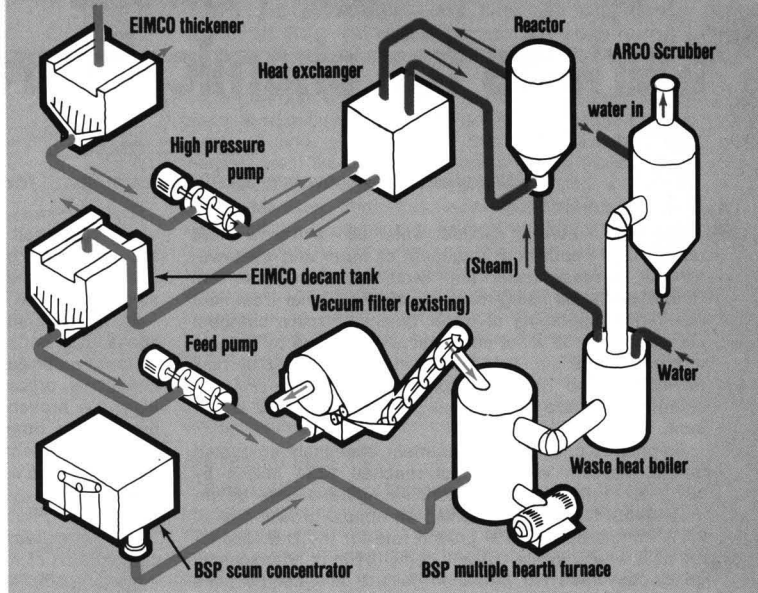
In comparison to other emission sources in the valley, the furnaces under the worst conditions would be only a tiny fraction of those due to automobiles and about equal to the minimum emissions from alternate systems of trucks hauling the sludge 10 miles to the border of the valley. After all this, approval of the project was unfortunately delayed because of limited federal funding. The plant will be under construction within the next year, as soon as federal funding is received.

What to do with the ash

Sometimes incineration is not regarded as an end to the sludge problem. Some say the problem has only been reduced; you still have the ash to dispose of. Unlike biological sludge, however, the ash is sterile and harmless. Liquid sludge disposal practices reveal that in many cases sludge drying beds or sludge piles are carelessly tended, with little regard for the potentially dangerous pathogens which may be present. Cases of possible groundwater contamination were common with few disposal sites being maintained to the degree required for solid waste sanitary landfill sites, for example.

On the contrary, sludge ash is free of bacterial contamination and re-

Closed energy loop, sludge handling systems incorporates heat treatment, incineration, and heat recovery



duced 90% in volume from the original wet sludge. It also is potentially beneficial to the environment. It is useful as a soil conditioner, and in Japan it is marketed as quasifertilizer for its phosphate content.

The energy factor

Now that the energy crisis is everywhere apparent, there has been concern that sludge incineration may be draining away precious energy resources and that limited fuel availability may make furnaces white elephants.

Make no mistake, multiple hearth furnace systems can be designed to be self-sustaining if the sludge cake is dried to 30-35% solids. Once this condition is reached, the sludge becomes a fuel resource in itself. The resulting heat can be recovered for processes such as heat treatment, or space heating.

Other sludge handling and disposal systems, designed with a closed loop energy cycle to convert fuel, are being designed for the Chesapeake-Elizabeth wastewater treatment plant (Va.) and the Western Branch plant (Prince Georges County, Md.).

Some auxiliary fuel is needed for start-up and standby operation. A wide variety of fuels may be used including digester gas, natural gas, heating oil, or at the Virginia plant site, one of five under the Hampton Roads Sanitation District, No. 6 fuel oil. Fuels with high sulfur contents can be used without creating an SO₂ emissions problem. The high efficien-

cy ARCO wet scrubbing systems have been shown to remove up to 90% of SO₂ created in the combustion cycle, according to test results of Envirotech's BSP Division. In some cases, the fuel value of the sludge may be supplemented by mixing in waste and heavy grade oils or even pulverized coal.

A recent report from the EPA detailed the electrical energy demands of all the unit processes in a wastewater treatment. Analyses of flow-sheets in such systems reaffirm that energy demands of incineration are a minor contributor to total plant usage of electricity. For example, in a 100-mgd activated sludge plant, which would conveniently serve a population of 1 million, MHF incineration accounted for only 4% of the total requirement of electricity. If digestion is used with the activated sludge plant, the requirement drops to 2.4% of the total electricity requirement.

Incineration has several other clean advantages over other methods of sludge disposal:

- The sludge problem is handled on site without having to transport potentially dangerous material to outlying and usually reluctant rural communities.
- The pollution resulting from truck or barge operation is eliminated.
- The energy demands of pumping are avoided.
- Only small areas of urban land are required in contrast to large drying beds.

FEATURE

Markets for chemicals grow and grow

Andrew C. Gross

Cleveland State University and Predicasts, Inc., Cleveland, Ohio 44106

During the current decade, water use will grow more rapidly than population; treatment of water and wastewater will increase faster than water use, and chemical treatment will be rising more rapidly than other treatment types. The upgrading of water quality to more stringent standards can be most economically achieved by the use of more chemicals. This trend will be reinforced by new technology and favorable comparisons in the price of chemicals relative to the costs of land, labor, and equipment.

Shipments of all water treatment chemicals amounted to \$166 million in 1960, but reached \$384 million by 1970. By 1980, the corresponding figure should be almost \$950 million, representing an annual growth rate of 9.4% compared to a 7% growth rate for the U.S. economy as a whole. While currently only 0.1 lb of chemicals is being consumed per thousand gallons of water use, the figure should double in 10 years.

Growth patterns among specific chemicals will vary; the most significant trend will be that of upgrading. For example, polyelectrolytes will grow more rapidly than inorganic coagulants, membranes faster than other filter media, and ion exchange resins faster than lime. Oxygen will be more widely utilized than air. As a general rule, sales of chemicals for wastewater treatment should grow much more rapidly than those for water treatment, though the latter market will remain more substantial (Table 1).

The water treatment chemical industry is highly fragmented and quite diversified. Large chemical companies supply most of the bulk materials; six specialty firms pro-

vide almost half of the formulations. The markets of the two types of organizations often overlap. Only a handful of publicly owned firms derive more than 25% of their sales from water treatment chemicals.

It is customary when looking at water pollution to speak of a series of dual categories—industrial vs. municipal, water vs. wastewater treatment, equipment vs. chemicals, organics vs. inorganics. In this feature, chemicals are broken down by type of treatment or market; but, unless otherwise stated, figures refer to the total market for such chemicals. The statistics are best estimates, with $\pm 5\%$ deviation likely even by 1975.

In the business

The water/wastewater treatment chemical industry is a combination of many small, medium, and large firms; the majority come from the chemical industry, but there is representation from the machinery, petroleum, and other industries. Four categories can be discerned, based on size of firm, "market reach," and product line.

The first group comprises the giants of the chemical industry, with sales in the \$1 billion and above range: Du Pont, Monsanto, Dow, Union Carbide, and others. Such firms are primarily active in the sale of bulk, rather than specialty chemicals, though some do pursue the more specialized segments of the market. For example, Celanese entered the field of internal water treatment compounds by acquiring Stein, Hall & Co. More usually, however, the giants try to move a specialty chemical into bulk status.

In the second category, there are firms with sales in the \$0.7-7.0-million range. These groups of medium and small chemical manufacturers are both bulk and specialty chemical firms—Diamond Shamrock, International Mineral & Chemical, and Stauffer Chemical, on the one hand, and Betz, Nalco and Mogul on the other. As a general rule, these firms show a higher rate of return on sales than do the giants of the first group. Attention to their customers' problems did develop strong loyalty on the part of such firms' clients.

The third group consists of manufacturers from other industries. In the case of machinery, equipment, and oil companies, entry into the chemical field represented a natural diversification. Examples are Crane, Keene, Petrolite, and Culligan International. Others, like Ecological Science Corp., a consulting firm, pursue the path of backward integration.

The fourth category consists of very small companies, which usually feature a narrow product line and operate on a regional basis. They tend to specialize around a group of related products, such as boiler feed chemicals. Examples of such firms, from the East and Midwest, are Hungerford & Terry, Purification Sciences, CWC Industries, Creative Chemical, Deady Chemical, and Vulcan Laboratories.

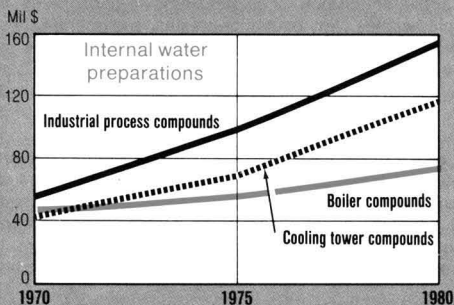
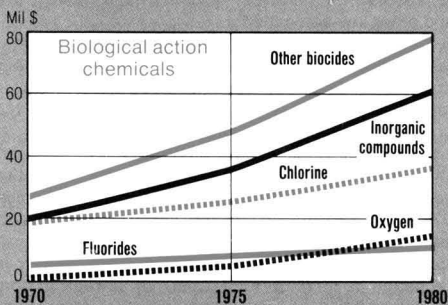
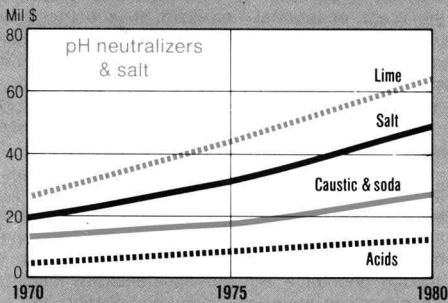
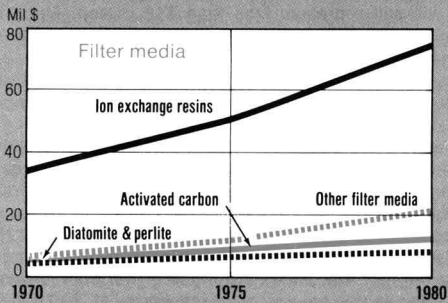
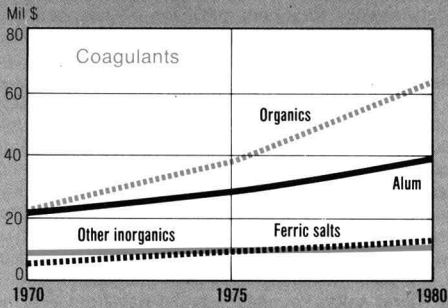
However, size alone is no assurance of a high rate of return on sales. As already noted, the best performance records tend to belong to the medium-sized firms, rather than the very large or very small ones. The middle-size chemical firm is large enough to operate with a systems approach and yet small enough to have carved out se-

TABLE 1
Water and wastewater treatment chemicals

Item	1970	1980	Annual % change, 1970-80
MILLION POUNDS			
Coagulants	1326	2085	4.6
Filter media	556	926	5.2
pH neutralizers and salt	5950	11925	7.2
Biologicals	993	4427	16.2
Internal preparations	484	870	6.1
Total volume	9309	20233	8.1
Cents per pound	4.1	4.7	1.4
MILLION DOLLARS			
Coagulants	56.7	126.0	7.6
Filter media	48.0	115.9	9.2
pH neutralizers and salt	64.6	152.8	9.0
Biologicals	71.9	200.4	10.8
Internal preparations	143.0	348.0	9.3
Total value	384.2	943.1	9.4
Industrial and municipal water consumption (Tgal)	95.6	146	4.3
Lb/M gal	97	139	3.6
Gross national product (bil \$)	974	1900	6.9
Antipollution chemical sales/000\$ GNP	0.39	0.50	2.5

Source, Predicasts, Inc.

Water and wastewater treatment chemical sales



lected segments of the total market as its "pockets of profitability." Working frequently with a well-trained research and sales staff, these firms are able to stay abreast of the latest technology and pay close attention to client problems beyond the mere sale and delivery of products.

Mergers and acquisitions in this field have been taking place at about the same rate as in other sectors of the chemical and petrochemical industries. Examples of mergers from the previous decades include the purchase of Calgon by Merck, Wyandotte becoming a part of BASF, Madison Chemical fused into Chemtrust Industries, and the acquisition of several small firms by Stauffer Chemical. As for entry and exit, both tend to occur, often at the same time. Slick Corp., an airline in the West, chose to abandon that field and stress its chemical manufacturing via its Drew division, only to be bought by U.S. Filter in 1972. At about the same time, KDI Corp. abandoned the water/wastewater treatment chemical area. CWC Industries of Cleveland has been active in the sale of specialty goods, while Allyn Chemical of the same city chose to quit the antipollution chemical field.

The "Big Six Pack"

Betz Laboratories, (Trevose, Pa.) is one of the leading manufacturers of water and wastewater treatment chemicals. Along with Nalco, it plays a key role in the supply of internal or formulated water treatment compounds for industrial users and to a lesser extent for municipal markets. Sales have grown five-fold since 1960, now exceeding the \$50-million mark. The product line ranges from biocides to polyelectrolytes and from coagulant aids to cooling system chemicals, but the firm recently diversified into the pollution control equipment field. The firm is more than one third family owned.

Chemed (Cincinnati, Ohio) is still almost 90% owned by W. R. Grace & Co., but the decision to sell shares to the public and to show operations separate from the parent firm represent a step away from the idea of wholly owned subsidiaries. Several plants are operated in the U.S., the U.K., and Canada. The product line is a wide-ranging one, but again there has been diversification into medical and consumer products. Antipollution chemicals and services grew from 10% of sales in 1966 to over 20% at the start of this decade. Starting in 1970, total annual sales exceeded \$100 million.

Mogul (Chagrin Falls, Ohio) is a fast-growing firm and a major force in the antipollution chemical field. Though operating several divisions (hospital, life science, educational, veterinary, and water treatment), over a third of its \$40 million sales come from the water pollution control segment. Mogul pays close attention to customer problems, including maintenance and compliance with regulations. The company recently won a coveted award by the Sales and Marketing Executives group. It held merger talks with F. M. Scherer, a pharmaceutical firm with a complementary product line, but it now appears that the proposed merger is called off.

Merck (Rahway, N.J.) has become an important factor in the water treatment chemical field by its acquisition of Calgon in 1968, followed by the purchase of Havens International (a water reclamation systems firm), Baltimore Aircoil (cooling equipment), and Technique & Distribution (a European marketer of water conditioning equipment). The parent firm is best known for its drug line. Calgon makes a variety of detergents and specialty chemicals besides those intended for clarification of water and wastewater. In the latter line, products include ion exchange resins, activated carbon, softening compounds, and specialized polymers. Sales of the parent firm hover in the \$1-billion range.

Nalco Chemical (Chicago) is one of the leading and oldest manufacturers of specialty chemicals for water

and wastewater treatment. Sales have been growing in excess of 20% per year during the past five years and now stand at the \$200-million mark. Foreign operations, strong research efforts, and aggressive marketing contribute to this growth, along with the systems approach of dealing with the totality of client problems. Nalco has developed a strong loyalty among its clients. Among recent developments are a line of organic coagulants and improved ion exchange resins.

United States Filter (New York) has been active in the pollution control field for some time. With its acquisition of Slick and hence the Drew Chemical division of that firm, it has solidified its position in that area even more. Sales of \$123 million in 1972 had the following distribution: water pollution control and chemical systems 32%, air pollution 31%, and energy, nuclear engineering, and other activities 37%. Drew is a manufacturer of a wide variety of chemicals for wastewater treatment, boiler feed, and cooling tower operations. It is also a major supplier of biocides, defoamers, and other chemicals to the paper and paint industries.

Coagulants

These chemicals promote the process whereby suspended solids and colloidal materials in the water or wastewater are agglomerated by chemical means into masses sufficiently large to settle. Basically, they neutralize the charge on particles, allowing them to come together. Currently, municipalities use more coagulants than industry and more coagulants are consumed for water clarification than wastewater treatment. However (Table 2), industrial use should grow faster than municipal use and sewage treatment should increase faster than that of water clarification.

Because of changing technology, prices, and market requirements, the types of coagulants used are also changing. While alum, ferric salts, and other inorganics should double approximately in dollar volume during the current decade, organic coagulants should increase three-fold.

In 1970, about 800 million pounds of alum was used in water pollution control; four fifths of this went for water and one fifth for wastewater treatment. Alum usage in sewage flocculation is small; ferric salts are preferred, since they are cheaper and the flocs formed are heavier and settle better. But as alum is a low cost material and its use can be enhanced by the addition of polyelectrolytes, about 1250 million pounds will be used by 1980. Alum is produced by numerous firms, including Allied Chemical, American Cyanamid, Du Pont, Essex, Monsanto, Olin, and Stauffer.

Ferric salts, along with lime, are the leading coagulants for wastewater treatment and sludge flocculation. Use of iron salts for clarification of supply water is negligible since they add hardness and impart undesirable

taste and color. Ferric salts are used in both primary and secondary sewage treatment and have experienced good growth rates so far. In the long run, however, they will meet increasing competition from coagulants which generate less sludge per pound of solids removed. Usage in water pollution control applications should rise from about 130 million pounds in 1970 to 225 million pounds by 1980, corresponding to the rise in dollar terms. Major producers are Allied Chemical, Chem-Met, Conservation Chemical, Dow Chemical, Pennwalt, South California Chemical, and Steel Chemical. Most sales are that of ferric chloride and are in bulk.

A wide range of other inorganic coagulants is employed, but their rate of growth will be slower than that of alum or ferric salts. Poundage should rise from 350 million in 1970 to about 500 million by 1980, but the latter figure will still represent less than \$12 million. Much of the poundage in this category consists of clays—bentonite and kaolin—which assist in wastewater oil removal.

Organic polymers are used in water and wastewater treatment as coagulating aids and increasingly as coagulants. They improve performance and lower costs in water clarification, sewage treatment, dewatering sludges, and other industrial water pollution control areas. They are nontoxic, biodegradable, small in volume, easily incinerated, and effective under varied pH and temperature conditions. Volume should almost triple by 1980 from the 1970 mark of 45 million pounds. This will occur despite the fact that prices are much higher than for inorganic coagulants; natural organics come at \$0.10–0.50 and synthetics at \$0.40–2.50/lb. Major markets currently lie in the areas of internal treatment of industrial water and municipal wastewater, but municipal clarification and industrial sewage treatment should develop into equally important markets. Among key producers are American Cyanamid, Dow, Hercules, Merck-Calgon, Nalco, National Starch, Reichhold, Rohm & Haas, United States Filter, and Vistron.

Chemical filter materials

Filter media are being used increasingly to supplement the work of mechanical filters. Their total market should go from almost \$50 million in 1970 to \$115 million by 1980, though poundage will grow more slowly because the more expensive materials—activated carbon, ion exchange resins, membranes—will increase faster than sand and other low-value media.

Activated carbon, in both powder and granular form, is used as a filter material because it has high adsorbent capacity and because its surface attracts a variety of chemicals. Utilized in the collection of such organic materials as phenols, solvents, and pesticides, it has the ability to remove objectionable taste, color, odor, and some harmful biological matter. Consumption more than doubled in the last decade and should do so again during the 1970's, to 125 million pounds by 1980. Application has been mostly in tertiary treatment of wastewater and in supply water clarification so far, but there is now increased usage in secondary treatment of sewage in competition with biological processes. On the other hand, since activated carbon does not remove phosphates or inorganic wastes, ion exchange resins and membranes, as well as oxygen treatment, will become competitive alternatives. The largest producer is Westvaco, followed by several firms, such as American Norit, Atlas Chemical, Calgon, Barnebey-Cheney, National Carbon, Pittsburgh Chemical, and Witco.

Ion exchange resins have been used for many years for water-softening purposes, but the newer members of this family are being utilized in treating industrial sour waters, brackish waters, acid mine drainage, and secondary sewage effluents. A decade ago, supply water treatment represented the only end-use market, but now other

TABLE 2
Coagulants by end market (%)

Item	1970	1980
WATER CLARIFICATION		
Municipal	31	25
Industrial	32	33
Total	63	58
WASTEWATER TREATMENT		
Municipal	29	30
Industrial	8	12
Total	37	42
ALL WATER TREATMENT		
Municipal	60	55
Industrial	40	45
Total	100	100

Source, Predicasts, Inc.

applications account for almost one fourth of the poundage. Total amount used in water and wastewater treatment by 1980 should be about 110 million pounds, compared to about 45 million in 1970. Ion exchange processes will encounter increasing competition from reverse osmosis and other membrane processes. Ion exchange resins are produced by Diamond Shamrock, Dow, Rohm & Haas, and Sybron.

Diatomite and expanded perlite are used for fine particle filtration by industries where applications (as in food processing) must meet stringent clarity and biological requirements. These materials have other uses, including oil and beverage filtration, paint and explosive manufacturing, plastic filling and insulation. Consumption of the two materials for water and, to a much lesser extent, wastewater treatment amounted to 150 million pounds in 1970 and should reach 275 million pounds by 1980. About three fourths of the current volume is diatomite, but perlite is growing more rapidly. Growth prospects are due to rising consumer spending for beverages, food, drugs, cosmetics, and recreation. Major diatomite producers are Johns-Manville, General Refractories, Eagle-Picher, and 10 other producers. Expanded perlite is offered by over 80 companies.

Other chemical filter materials are sand, coal, zeolites, and membranes. While volume shipped is large—about 300 million pounds in 1970, to rise to 420 million by 1980—the value of shipments is low and, except for membranes, growth prospects are not good. There is a wide variety of membrane materials, including vinyl, polyethylene, cellulose acetate, and nylon. Membrane processes are used to separate or purify liquid phase solutions. Among the better known current processes are reverse osmosis, dialysis, and ultrafiltration. While volume treatment of wastewaters is in the early stages of development, pollution regulations should spur secondary and tertiary wastewater treatment. There is a trend to hollow fibers, because of their high surface area-to-weight ratio and because they are self-supporting. Producers include Du Pont, Monsanto, Abcor, Amicon, and Eastman Chemical. Dialysis membranes are made by Ionics, AMF, Dow, and Ionac Chemical.

Other major chemicals

pH neutralizers and salt are used in water and wastewater treatment to provide a balance of ions necessary for the desired chemical and biological processes to take place. Such chemicals adjust pH, metal, and nutrient levels. These are low cost materials and their volume consumed is huge—6 billion pounds in 1970 and a projected 12 billion pounds by 1980. Generally, they will grow in proportion to the amount of water and sewage treated.

About 3.4 billion pounds of lime was consumed in 1970 for purifying water, two thirds for water and one third for wastewater treatment. Since lime is very cheap compared to other neutralizers and coagulants, consumption will rise to about 6.7 billion pounds by 1980. In water treatment, lime has an advantage over alum in acidic, but not in alkaline waters. Lime usage in wastewater treatment is growing more rapidly than in water treatment; by 1985, the two end uses should be about equal in size. Lime can be utilized in forming sludge, neutralizing acid mine drainage, and phosphate removal. Lime is produced by about 200 companies, including U.S. Gypsum, National Gypsum, and major steel producers.

Caustic soda and soda ash are strong bases used for increasing pH in order to improve alum and ferric chloride coagulation. Soda ash is used in conjunction with lime for precipitating calcium, while caustic soda is used with ferrous salts in sewage treatment to get good flocculation, as well as for regenerating anionic exchange resins. Thus, usage is tied to the extent to which other chemicals—coagulants, resins, lime—are utilized.

Growth is seen from 600 million pounds in 1970 to over 1100 million pounds by 1980.

Sulfuric acid and other acids are also used for controlling pH balance, again frequently in an assisting role to other chemicals. In addition, acids are employed for removing barium ions from industrial wastes and for regenerating cationic exchange resins. Sulfuric acid is preferred, because other acids are more expensive. Acid consumption should just about double during the decade from the 300-million-pound figure in 1970.

Salt is used in water treatment for the regeneration of sodium zeolites and ion exchange resins, but usage rate will be slower than for resins due to improved application techniques. Consumption in water pollution control applications should rise from near 1700 million pounds in 1970 to 3500 million pounds by 1980.

Biological action chemicals are currently employed in water treatment as disinfectants in municipal and as biocides in industrial water supply. Current consumption for wastewater treatment is very small, but a rapid growth can be expected for such chemicals in this area. Rising capital and land costs will make aeration, lagooning, trickling filters, and other processes somewhat less attractive; new standards and processes will favor the use of oxygen instead of air for altering the biological characteristics of wastewater. Total consumption should go from near 1 billion pounds in 1970 to over 4 billion by 1980, with oxygen accounting for over one half of the 1980 figure.

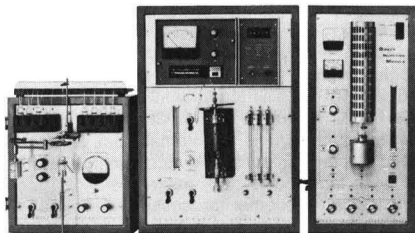
Chlorine is still the most widely used biocidal agent today in water treatment. Aside from its well-known disinfectant role in water supply, it is being used increasingly for controlling bacteria count in activated sludge and for secondary sewage effluent. Chlorine does have some disadvantages vis-a-vis more expensive biocides. Total usage in water and wastewater treatment should be 1.4 billion pounds in 1980 (about double the 1970 figure) which is still only 3% of the total chlorine production in the U.S. Manufacturers are major chemical firms, from Allied to Wyandotte.

Calcium hypochlorite, sodium hypochlorite, and other inorganic chlorine compounds have shown a faster growth rate than chlorine, mostly because these compounds are more stable and more persistent. They are also easier and safer to handle and they can reduce capital costs. Applications range from water supply to boat sewage treatment. Hypochlorous acid may compete with activated carbon in tertiary treatment. In the presence of ultraviolet light it can be effective in removing organic matter from sewage. Inorganic chlorine compounds should almost triple their 1970 figure of 100 million pounds used in water pollution control by the end of the decade. Major producers are Olin, Pennwalt, and PPG, but there are numerous smaller manufacturers.

Organic chlorine compounds, other halogens and their compounds, quaternary ammonia compounds, toxic salts, and other strong oxidizing agents constitute our next class of biocides. There are varied applications, one of which is the use of organic chlorine compounds for controlling microorganisms in industrial water treatment. Ozone is currently used in the sterilization of water and the oxidation of cyanides and phenols in industrial wastes. Total demand in water and wastewater treatment for this miscellaneous group of biocides should be about 150 million pounds in 1980, more than twice the 1970 figure.

There is evidence that oxygen is becoming a major wastewater treatment chemical. Aeration with oxygen can greatly improve secondary treatment processes. In several cases, capital and operating costs have been halved by going from using air to utilizing oxygen in the aeration system. From negligible usage in 1970, oxygen should rise to a 2.5-billion-pound consumption figure by

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CIRCLE 11 ON READER SERVICE CARD

1980, but forecasts of 24 billion pounds by 1985 seem optimistic. Key producers are the Linde Division of Union Carbide (half of total sales now), Air Reduction, Air Products and Chemicals, Chemetron, and others.

Fluorides are used almost exclusively in water treatment to affect drinking water supplies in order to make teeth more resistant to decay. Almost 60% of the U.S. population is affected. Use in wastewater treatment is minimal. Growth is envisioned at 110 million pounds by 1980, compared to 70 million pounds in 1970.

Internal water preparations are specially formulated chemicals (containing several chemical compounds) which are used for affecting industrial water supplies. By contributing to a higher quality of water intake, their use indirectly affects the quality of effluent. The design of an optimum formula or package for a specific facility is a complex art which most industrial users do not possess. Thus, suppliers offer survey of user requirements, formulation of compounds, delivery, and continuing assistance. The "Big Specialty Six" control about half of this market. Several trends, including the move toward nuclear power production, should boost sales of such preparations from under 500 million pounds in 1970 to nearly 900 million pounds by 1980, with dollar volume showing an even healthier growth.

Boiler compounds are chemical preparations added to boiler feed for scale or corrosion control, and the inhibition of caustic embrittlement and carryover of moisture. Chemicals utilized range from phosphates to polyelectrolytes, and volatile amines to tannins. Demand should rise from 140 to over 180 million pounds in this decade.

Cooling tower compounds are special preparations for preventing fouling by microorganisms and for inhibiting chemical or biological attacks on wood. Control agents include organic chlorine compounds, chlorinated phenols, copper salts, ammonium compounds, and mercurials in a variety of preparations. Increased electric power generation, trend to nuclear energy, and concern with thermal pollution will lead to doubling of consumption between 1970 and 1980, with a total of almost 300 million pounds used by the latter date.

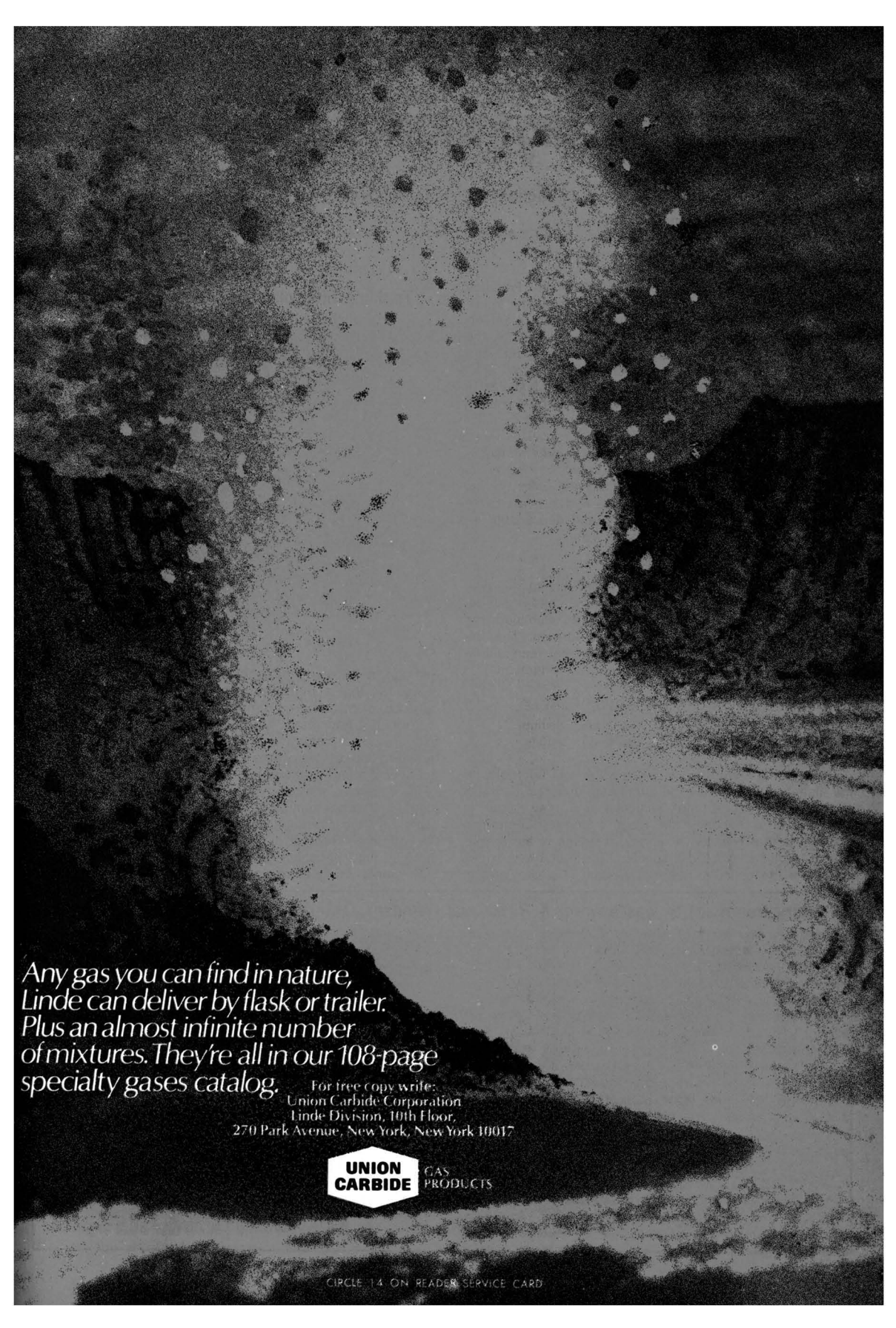
Industrial process compounds are tailor-made preparations employed in the process industries. Ingredients include a variety of inhibitors (against corrosion, scale, mildew), demineralizers, deemulsifiers, and pH control chemicals. Sales of these items are growing more rapidly than production in the industries using them. The 1970 figure of 200 million pounds consumed should double by 1980.

Projection

Inflationary forces in the economy are becoming more dominant. Gross national product is now projected to exceed \$2150 billion by 1980. Correspondingly, the prices of antipollution chemicals are expected to rise. Thus, the dollar figures cited may have to be raised by 7-8% for 1975 and about 15% for 1980. Nevertheless, the growth in sales of water and wastewater treatment chemicals will exceed the growth rate of the economy. Despite the competitive situation, numerous companies in this field should prosper.



Andrew C. Gross is an associate professor at Cleveland State University, teaching marketing, industrial relations, and international business courses. A professional engineer with extensive experience in industry and government, he is also consultant to Predicasts, Inc., and the Science Council of Canada.



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CIRCLE 14 ON READER SERVICE CARD

FEATURE

In-plant usage works and works

Richard W. Ockershausen

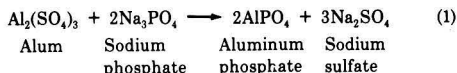
Allied Chemical Corp., Morristown, N.J. 07960

Meeting the objectives of the 1972 Water Pollution Control Act has required the study of wastewater nutrients and the methods for upgrading treatment plant effluents. In the process of modernizing and increasing the capacity of wastewater treatment plants, consulting engineers and cities have found that chemical storage tanks and feeders can be rapidly and economically installed in existing plants. This is being done routinely where interim treatment is required as well as for permanent installations.

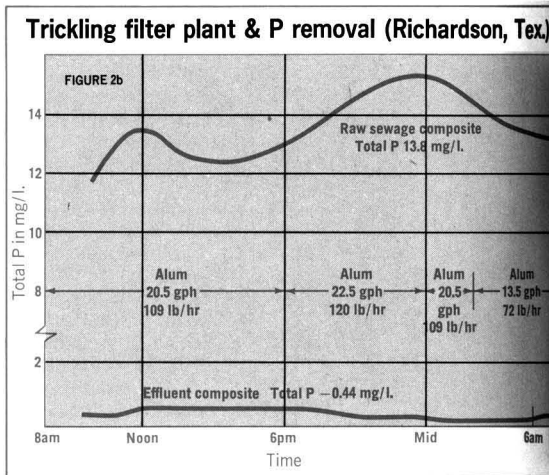
Certain concentrations of carbon, nitrogen, phosphorus, potassium, silicon, and other elements are essential in the support of microorganisms, fish, and other marine life. When an overabundance of these nutrients are present, excessive algae growths result, and degradation of the water begins as the microorganisms die.

Reducing P, SS, BOD

Phosphorus is the nutrient most amenable to removal. It can be precipitated by the addition of salts of aluminum, iron, or calcium. With aluminum, an aluminum hydroxy phosphate or other complex is formed. The following equation represents the reaction between aluminum sulfate (alum) and soluble phosphorus compounds:



Other components in the wastewater will compete for the aluminum ion. While the aluminum ion's reaction with phosphorus is considered selective and may occur in fractions of a second, the most important competing reaction is that with the alkalinity, resulting in the formation of insoluble hydrolysis species. The metal hydroxides coagulate the colloidal material present in wastewater in



addition to the aluminum phosphate precipitate. Ideally, it is desired that a maximum amount of the aluminum ion be used for phosphorus removal, and a minimum quantity to form the floc mass. In practice, there is little control over this, and treatment is primarily meeting the coagulant demand of the waste by adding alum in sufficient quantity to affect high clarity.

In Sweden, where over 300 wastewater treatment plants are using alum for phosphorus reduction, the operators vary the chemical dose in relation to the clarity of the effluent. Generally, when high clarity is obtained, there is high phosphorus removal. Experience in the 70 U.S. plants using alum confirms this. All too frequently,

Primary treatment of waste water & P removal (Windsor, Ontario)

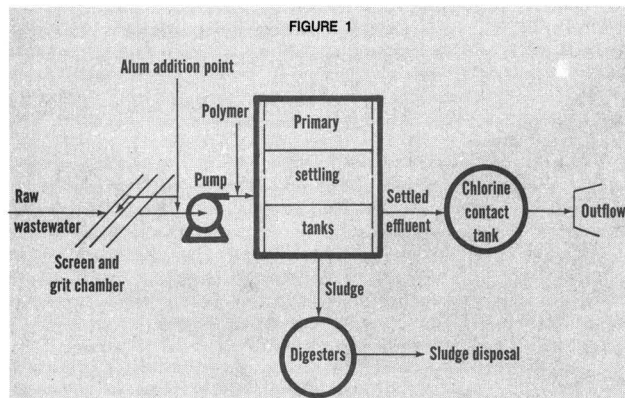


TABLE 1

	Raw	Final	% Reduction
Flow, mgd	22.0	22.0	—
SS, mg/l.	187	30	84
BOD, mg/l.	108	42	61
Phosphorus			
Total P, mg/l.	7.8	1.0	86.5
Total Ortho, mg/l.	4.5	0.4	91.1
Dissolved Ortho, mg/l.	3.1	0.14	95.4
Alum Dose: 90 mg/l.			
Polymer Dose: 0.4 mg/l.			

the coagulant demand bears only a partial relationship to the phosphorus concentration in the raw wastewater.

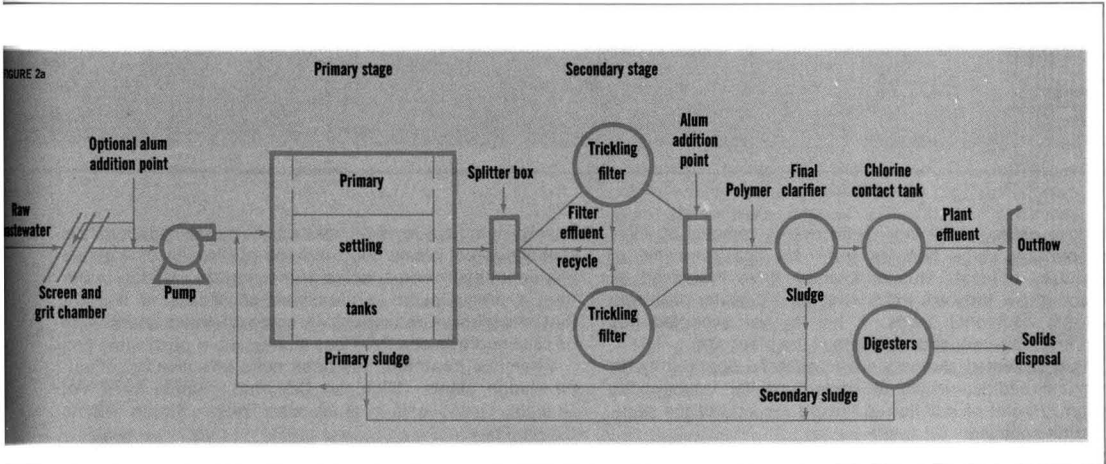
The soluble phosphorus ion (SP), rather than the total phosphorus (TP), is the form which exerts a chemical demand. Theoretically, 0.87 mg/l. of aluminum ion (Al) will precipitate 1.00 mg/l. of SP; 0.87 mg of Al equates to 9.6 mg of alum. For example, if the wastewater contains 6 mg/l. of SP, the minimum alum dose to precipitate this would be 58 mg/l. Insoluble forms of phosphorus will be mechanically removed in the floc mass. The total alum requirement is determined by laboratory floc tests.

Two chemical methods are suggested for minimizing over-treatment with the coagulant. One method is the use

improve the reductions of SS and BOD without further major plant construction. Where plants are hydraulically overloaded or have inadequate sludge digestion capacity, there is no alternative but to expand these facilities to accept higher flows and greater solids loads. Chemical facilities can be designed into such expansions.

In-plant uses

Approximately 2800 plants, 20% of the total plants in the U.S., provide minimum primary treatment. While waiting for secondary treatment equipment, these plants can be equipped inexpensively for chemical treatment. Chemical treatment will approximately double the plants' solids and BOD reduction and decrease P to low levels. In pri-



of acid to reduce the high alkalinity and buffered pH often found in wastewater. While alum precipitates phosphorus at conventional pH values, numerous researchers have confirmed that maximum phosphorus reduction occurs in the pH range of 5.7-6.3. The use of an acid salt such as alum reduces the pH toward the optimum. A pH between 6 and 7 can be accomplished with a two-chemical feed system, acid and alum, or by use of excess metal salt. The second method is to use a polyelectrolyte just after the alum addition. Polymers do not react with phosphorus, but they do knit together the fine precipitates and the colloidal material into a floc which settles well.

Without chemical treatment, phosphorus reduction in a plant is poor. It may vary from 10-30% of TP and usually very little SP is removed. With chemical treatment, 90% and higher reductions are obtained and effluent concentrations of 0.5-1.0 mg/l. are commonplace. Levels less than 0.5 mg/l. will be sought in some areas. Filtration of the plant effluents is expected to yield 0.1-0.2 mg/l. of phosphorus.

Some wastewater treatment plants will be required to improve suspended solids (SS) and biochemical oxygen demand (BOD) reductions. In river waters, treated for potable purposes, chemical coagulation for turbidity reduction is the usual practice. The same technology is used in wastewater treatment. The addition of metal salts to wastewater performs the dual function of reducing P and SS simultaneously. Treatment for one results in improvement of the other. Along with the reduction in SS, some of which are organic materials, a reduction in BOD will be obtained. Soluble BOD-producing compounds are not reduced by chemical coagulation, however.

In many treatment plants, the simple addition of chemical storage and feeding devices will enable the plant to

primary plants, alum addition to the raw wastewater is usually at the intake side of the pump, the grit chamber, or just before the bar screens. All these points allow rapid mixing (Figure 1). At the Windsor (Ontario) 22-mgd primary plant, SS of 187 mg/l. are reduced to 30 mg/l. (84%), BOD of 108 mg/l. to 42 mg/l. (61%), and total P of 7.8 mg/l. to 1.0 mg/l. (86%). The alum dose is 90 mg/l., equal to 8.1 mg/l. of Al.

In trickling filter plants (Figure 2), P reduction and upgrading of plants can be accomplished by chemical addition at the outlet of the trickling filters, in the primary stage, or by splitting the chemical dose between these stages.

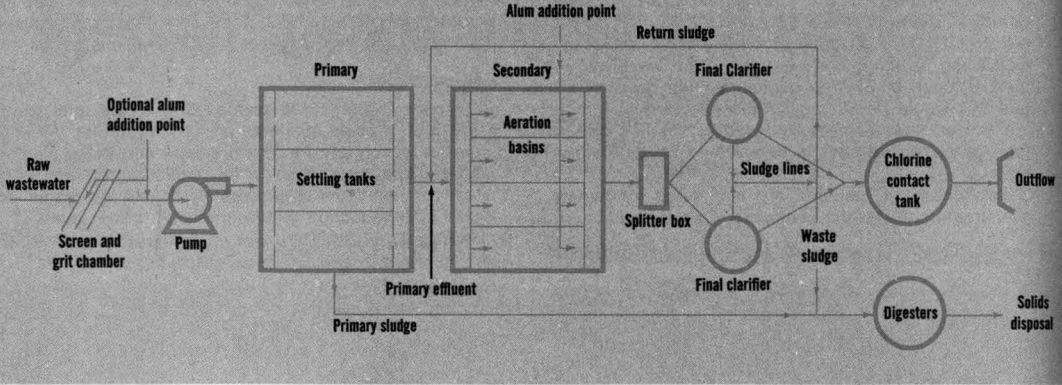
In Alexandria (Va.), an 18-mgd trickling filter plant operating at 20-mgd is achieving 84% SS and 85% BOD reduction by chemical treatment. Alum (110 mg/l.) and 0.4 mg/l. polymer are added before the primary settlers. The plant has reduced its BOD load to the Potomac River by 50%. Two trickling filter plants at Occoquan-Woodbridge (Va.) are obtaining reductions of 88% BOD, 93% SS, and 87% of P. Alum addition is before the primary clarifiers.

At a Melbourne (Fla.) wastewater treatment plant which uses high-rate trickling filters, the raw waste flow is between 1.5 and 2.0 mgd. Secondary effluent and secondary sludge (0.5 mgd) are recycled to the primary stage. This flow is treated with approximately 80-100 mg/l. of alum plus a coagulant aid added in the line transferring secondary sludge to the primary. SS and BOD reductions have averaged well over 90%, resulting in the lifting of the ban on sewer connections.

At another Florida plant in Palmetto, a design flow of 1.5 mgd treats approximately 0.8-0.9 mgd by trickling filters. Prior to chemical treatment, SS were 30-40 mg/l. in the final effluent for an average reduction of 83%. By the addition of 45 mg/l. of alum after the trickling filters, final

Primary and secondary activated sludge treatment and P removal

FIGURE 3



SS have averaged 11 mg/l. with overall removal of 93%. The primary stage benefits from the heavy recycle of secondary effluent. Sludge volumes have increased as expected, but they are experiencing no digester problems with the additional solids. A benefit not expected has been the sharp reduction in odors at the plant site.

In an activated sludge plant (Figure 3), opportunity for chemical addition exists at several points. Usually, the preferred point of addition is toward the end of the aeration tank because:

- The primary clarifiers and the aeration tank tend to equalize variations in the solids content, pH, and other properties of the raw wastewater
- The condensed forms of P are converted to the more easily precipitated ortho forms
- The plant's capacity to remove some P is utilized and this saves chemicals
- The tendency to mix the chemical too violently and reduce floc size is minimized
- Advantage is taken of the ability of the aluminum hydroxide in the recycled sludge to reduce P.

One of the best reasons for treating in the aeration stage is the economic benefit obtained from the chemical floc being recycled in the activated sludge. In several plants where chemical addition has been stopped for a period, the secondary units have continued to reduce P for the next few days before returning to their normal, rel-

atively inefficient level of removal. The mechanism of this removal is not clear, but it may be absorption of P by the aluminum hydroxide species in the recycled sludge rather than a precipitation as aluminum phosphate. It is clear that phosphorus reductions in some of these plants can be obtained with one third less alum.

Chemical treatment has been quite effective in activated sludge plants (Michigan City, Ind.; Sandusky, Ohio; Guelph, Ont.), and contact stabilization plants (Punta Gorda, Fla.).

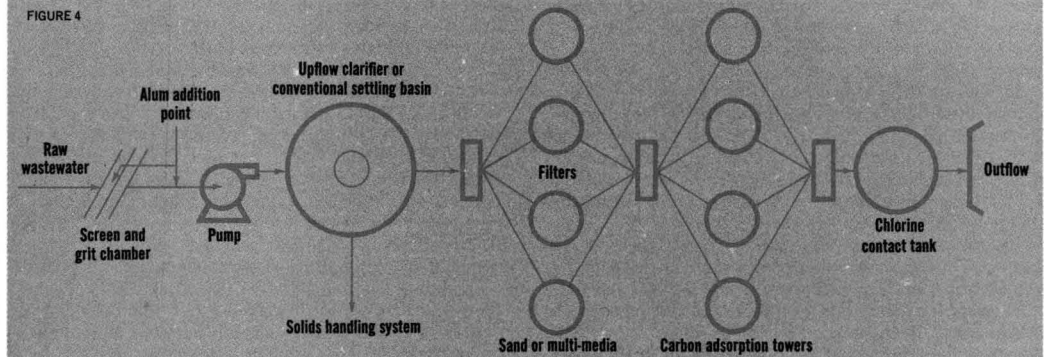
The 1-mgd Punta Gorda facility includes sand filtration of the effluent from the biological stage. Alum is added in the splitter box prior to surface aeration. Month-long activated sludge pilot plant studies at Buffalo (N.Y.), with 60–80 mg/l. of alum added to the end of aeration, consistently produced the desired 0.5 mg/l. P in composite samples of the effluent.

Physical-chemical treatment is another method (*ES&T*, Jan. 1974, p 14; March 1973, p 200) which can be used for upgrading an existing plant or for an entirely new facility. Chemical precipitants remove solids and P as in primary treatment. Filtration of the settled chemically treated wastewater delivers highly clarified water to a series of activated carbon columns. The carbon adsorbs soluble organic material and some trace metals. Regeneration of spent carbon is possible in large plants.

For plants too small to be equipped properly, regional

Physical chemical treatment & P removal

FIGURE 4



City	BOD—mg/l.		SS—mg/l.		Total P mg/l.
	No chem.	With chem.	No chem.	With chem.	
MICHIGAN CITY (IND.)					
Raw	172	172	144	144	10.7
Final eff.	13	9	19	7	0.79
% Reduction	92	95	87	95	92.6
SANDUSKY (OHIO)					
Raw	160	160	188	384	4.4
Final eff.	9	2	24	15	0.9
% Reduction	94	98	87	96	80
GUELPH (ONTARIO)					
Raw	182	182	179	179	6.1
Final eff.	26	14	38	22	0.78
% Reduction	86	92	79	88	87
PUNTA GORDA (FLA.) (contact stabilization)					
Raw	108		161		11.8
Final eff. (after sand filtration)	0.9		3		0.15
% Reduction	99		98		99
CHEMICAL DOSES (mg/l.)					
	Michigan City Alum 60, Polymer 0.3		Guelph Alum 100, 4 Act. Silica		
	Sandusky Alum 50		Punta Gorda Alum 45		

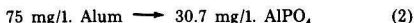
regeneration plants may be built to process the carbon. Following adsorption, disinfection of the effluent with chlorine is standard procedure. Physical-chemical plants (Figure 4) require less space than biological systems. They are also less susceptible to upsets from heavy metals and other toxic materials.

Generating solids

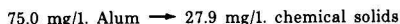
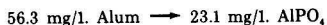
The quantity and volume of solids produced from wastewater treatment plants are a prime concern of plant management. Chemical treatment's purpose is to precipitate phosphate and coagulate and settle additional SS from the wastewater.

Chemical treatment inevitably results in more solids than conventional processes; to do otherwise it would fail in its function. The important question is, "How much sludge is generated?" From the phosphorus precipitation (Equation 1) and the well-known hydrolysis equation, the amount of chemical solids can be calculated from a typical activated sludge plant treating with 75 mg/l. of alum.

Assuming all of the alum is used to precipitate phosphorus, the following solids are generated:



If an activated sludge plant utilizes the aluminum values efficiently, and if it is assumed that three quarters of the alum precipitates aluminum phosphate and one quarter of the alum application forms aluminum hydroxide, the following chemical solids are produced:



To the chemical solids must be added the additional SS captured and settled with the floc. In an activated sludge plant the additional SS removed above normal treatment may be 5–15 mg/l.

There are insufficient data on the volume of sludge produced; some reporting more concentrated sludge resulted, others indicating 25–50% more volume was produced. A few trickling filter plants have reported higher volumes. A 300-mgd activated sludge plant is pumping 8.5% solids sludge, after concentration, to its digesters. Others are reporting from 3.5–7% solids, with or without concentration prior to digestion. In general, where the plants have adequate digester capacity, good gas pro-

duction and digester operation are resulting and sludge is being handled by conventional techniques.

Evaluating the costs

To arrange its financing, a city must know the capital and operating costs involved in upgrading its wastewater treatment. Consulting engineers are best qualified to study each system and to estimate the appropriate costs. Kumar and Clesceri (*Water and Sewage Works*, March 1973) estimate capital costs for 1-mgd, 10-mgd, and 100-mgd plants—\$48,900, \$126,000, and \$367,000. The costs can be reduced where advantage can be taken of existing buildings, heating, and laboratories. In southern climates, storage tanks can be outside, eliminating housing and heating costs.

Operating costs include the cost of chemicals, labor, power, maintenance, extra sludge dewatering or hauling or disposal, testing, and supervision. The vast majority of plants will be treating with 50–150 mg/l. of alum. At an alum approximate cost of 2.75¢/lb, the chemical cost will range from about \$11.50–\$34.50 per million gallons or 1.15–3.45¢ per 1000 gal (ptg). On the basis of a per capita use of 100 gal per day, the annual per capita chemical cost will range from \$0.43–1.29, with an average of about \$0.86/yr.

Using the average annual per capita chemical cost of \$0.86 and including amortization of capital costs and operating and maintenance labor, additional sludge disposal costs, maintenance of equipment, supervision, power, and insurance, it is estimated that the total costs of P reduction and additional BOD and SS removal for 1-mgd, 10-mgd, and 100-mgd plants are 7.58¢, 4.28¢, and 3.42¢ ptg. These sums are equivalent to \$2.77, \$1.56, and \$1.25 in terms of cost/person/yr.

Kumar and Clesceri assume a 10-mgd activated sludge plant has a capital cost of \$4.5 million. The inclusion of facilities for P reduction adds \$125,000 or less than 3% to the capital costs. With conventional operating costs estimated at 18.5¢ ptg, the chemical treatment and associated costs add 4.27¢ ptg or 23%.

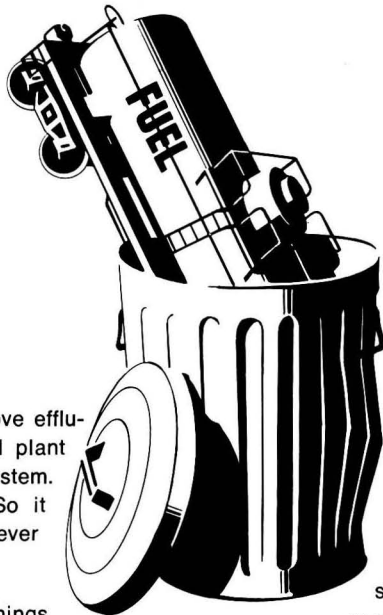
Chemical treatment at the municipal wastewater treatment plant removes phosphorus from all sources. These include human, food, and industrial wastes, detergents, storm water, and others. In addition, alum treatment provides benefits in SS and BOD reductions which often approach tertiary treatment performance. Color, bacteria, virus, and trace metal reductions can be additional benefits from successful chemical treatment.

Most plants require only the simple addition of a storage tank and a feeding device to accommodate liquid alum treatment. The costs of these facilities are less than 3% of total capital costs for a modern activated sludge plant. The total costs per capita per year are estimated at \$1.25–2.27 depending on the size of the plant. These are small costs in view of the upgrading of effluents possible with chemical treatment.



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CURRENT RESEARCH

History of Metal Pollution in Southern California Coastal Zone

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■ The anthropogenic fluxes of Pb, Cr, Cd, Zn, Cu, Ag, V, and Mo into the sediments of the San Pedro, Santa Monica, or Santa Barbara Basins, off the coast of Southern California are determined. At the present time it is not possible to evaluate the contributions from different transporting agencies—the winds, sewer outfalls, storm runoff, and river runoff.

Human populations, concentrated in coastal regions, can mobilize materials to the marine environment in amounts similar to, or even exceeding, those introduced through weathering processes. Records of the anthropogenic and of the natural fluxes of elements may be found in coastal sediments which accumulate rapidly enough so that annual strata can be distinguished through radiometric dating techniques and in some cases varving. Natural fluxes of elements can be determined in the older parts (i.e., a century ago) of the sedimentary column. The addition of anthropogenic fluxes to the natural ones are reflected in the composition of recently accumulated phases.

Inner basin sediments off the coast of California near Los Angeles are especially attractive for such studies. Their rates of sedimentation, of the order of millimeters per year, can be determined by Pb-210 and Th-232/Th-232 geochronologies and in some cases by annual varves (Koide et al., 1973). The strata below the upper centimeter or so are anaerobic, and the sediments are not disturbed by bioturbation. The organic carbon levels in the Southern California deposits are of the order of several percent by weight and their clay size fractions (less than 2 μ) are approximately one third of the sample. Such phases can effectively scavenge heavy metals from seawater.

Initial work in our laboratory was carried out by assaying lead levels in these sediments—present-day fluxes appear to be up to seven times greater in lead levels than those of a century ago (Chow et al., 1973). Source of the lead is lead alkyls used as antiknock additives to gasoline, and lead isotopic compositions in the modern sediments differ from those in the older deposits. Recent sediments have isotopic ratios similar to those of lead additives to gasoline in the Los Angeles area; the isotopic makeup of the older lead in the deposits resembles that of the weathering basin.

Use of the sedimentary record to reveal metal fluxes to the environment depends upon the rapid removal of the metal from the water following its entry. Such appears to

be the case for lead. The aim of this investigation is to ascertain what other elements, besides lead, are being mobilized to coastal waters and subsequently to the sediments in amounts similar to those involved in the weathering cycle.

Methods

Samples. Sediments were taken from three inner basins off the coast of California—San Pedro (33° 30' N; 118° 19'

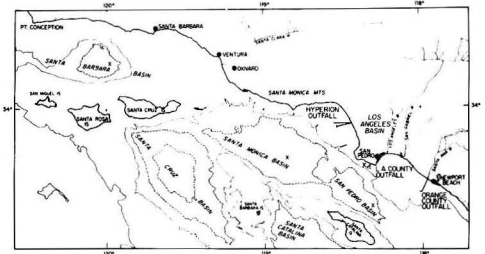


Figure 1. Inner basin region off the coast of southern California; X, coring site

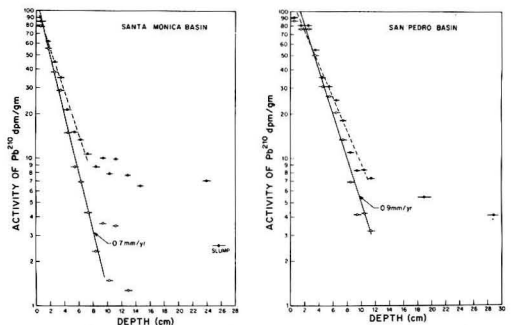


Figure 2. Pb-210 activities as a function of depth

Filled circles and dashed lines refer to the total Pb-210 in the sediment. Unfilled circles and heavy lines refer to unsupported Pb-210 activities—i.e., Ra-226 supported Pb-210 has been subtracted from the total Pb-210. Sedimentation rates are based upon unsupported Pb-210 activities. In San Pedro Basin plot, the upper two points fall off the curve. This reflects dilution of Pb-210 by the higher salt contents and to a lesser extent the higher organic matter and CaCO₃ levels. In a previous paper (Koide et al., 1973), the same phenomenon was observed in the Santa Barbara Basin deposits. We attributed it to a possible diffusion of lead in the sedimentary column. This rationale is no longer required. Normalizing the Pb-210 activities to aluminum concentrations removes these surface discrepancies. Santa Monica Basin deposits are least affected by such dilutions in their surface strata

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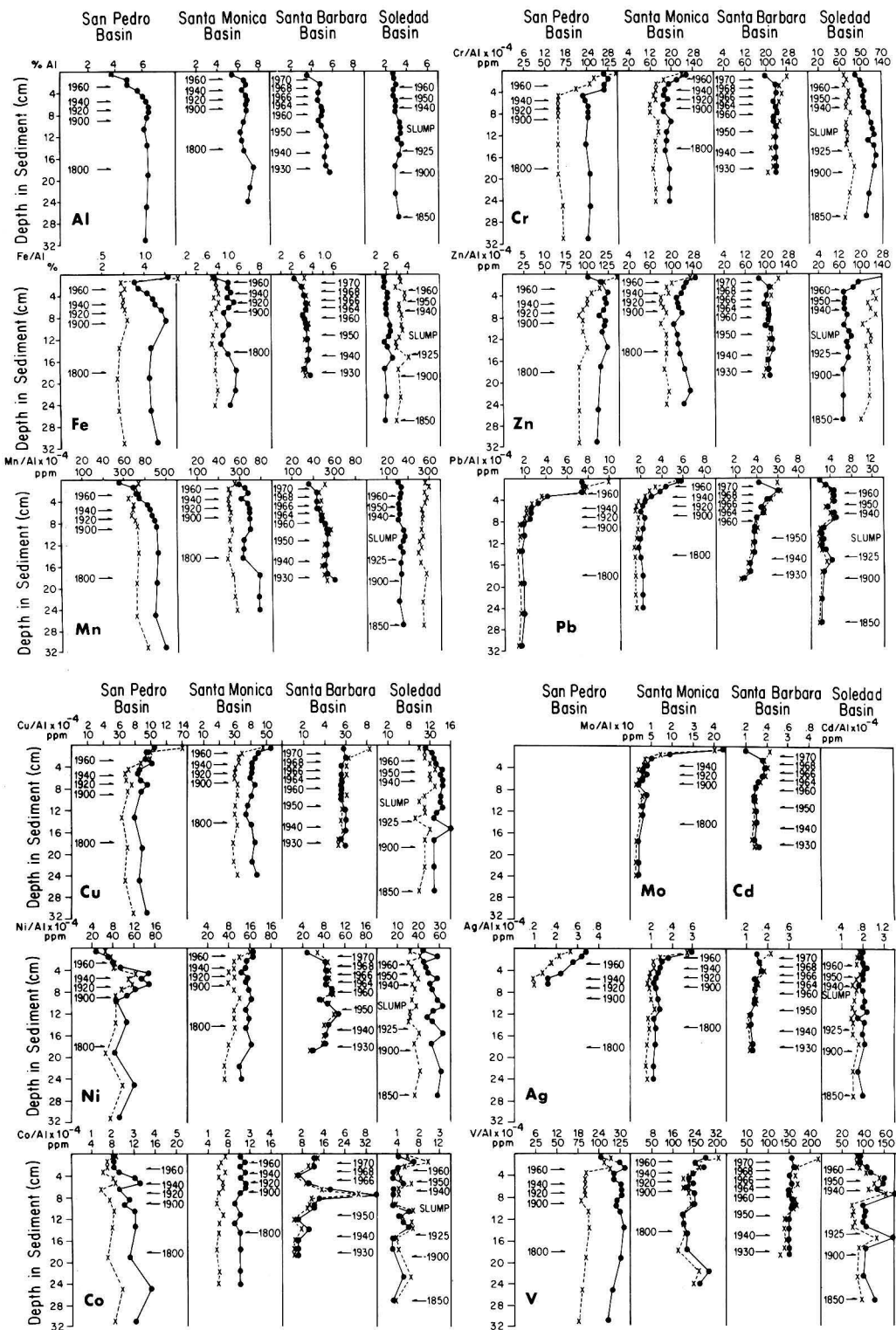


Figure 3. Distribution of heavy metals in the California and Baja California Basins as a function of depth or time

Dates were obtained by Pb-210 and Th-228/Th-232 geochronologies. Filled circles and heavy curves refer to absolute concentrations in the sediments. Dashed lines and X's refer to the ratios of the species concentration to that of aluminum

W; 890 meters); Santa Monica (33° 45' N; 118° 52' W; 930 meters); and Santa Barbara (34° 14' N; 120° 1.5' W; 575 meters); off Baja California—Soledad Basin (25° 14' N; 112° 41' W; 520 meters); from an area near the Whites Point waste outfall (33° 42' N; 118° 22' W; 75 meters). Locations are shown in Figure 1. Samples were recovered with hydraulically slowed box corers which retain the uppermost strata of the deposit in contact with the overlying waters.

Dating Techniques. The Pb-210 and Th-228/Th-232 geochronologies were carried out by previously described techniques (Koide et al., 1973) and the ages so derived are probably accurate to within a year or two for the recently deposited phases and to within a decade for ages extending back a century or so. In this previous work, the Santa Barbara and Soledad Basins were accumulating at an average rate of 0.4 and 0.27 cm/year, or 90 and 40 mg of solids/cm²/year based on a density of 2.6 g/cm³ (Emery, 1960) for the solids, respectively, over the last century. Pb-210 curves for the San Pedro and Santa Monica Basins (Figure 2) are corrected for the Ra-226 supported Pb-210 (Koide et al., manuscript in preparation) which extend the applicable time range of the Pb-210 method to 150 years. The average sedimentation rates over this time period for the San Pedro and Santa Monica cores are 0.9 and 0.7 mm/year, respectively (28 and 24 mg of solids/cm²/year).

The San Pedro and Santa Monica Basins are accumulating too slowly for the utilization of the Th-228/Th-232 technique in obtaining sedimentation rates. In both cases, however, the value of the activity ratio of these two isotopes was greater than one in the upper cm and indicated that the upper portions of the deposit were recovered in the coring operation.

In the three California basin cores, the sedimentation rates in the upper few centimeters can be as much as a factor of two higher than those further down in the deposit as a consequence of their higher water contents (i.e., lack of compaction). This is evident in the varve thicknesses found by Koide et al. (1973) in the Santa Barbara Basin, where those closer to the surface were greater than those further down, in the Th-228/Th-232 rates as com-

pared to the Pb-210 values and in the high water content of the surface strata (Table I).

The Whites Point core, taken about 2 km away from a large domestic waste outfall, had uniform activities of Pb-210 (24 dpm/g) throughout its length of 26 cm. The concentrations of Pb (Chow et al., 1973) and other heavy metals are also relatively constant in concentration over the core length. One or more of the following concepts may explain these results: a very rapid accumulation rate such that the accumulation of recent ages only are observed, extensive mixing in the deposit site, or slumping.

Elemental Analyses. Elemental analyses were carried out by atomic absorption spectrophotometry upon the total sample. A deuterium background corrector was used when the wave lengths were under 3000 Å. The sediments were put into solution after ashing at 400°C for 1 hr using successive treatments with HCl, HF, HNO₃, and HClO₄. For the cadmium determination the sediments were not subjected to the ashing step inasmuch as cadmium volatilization was observed. Such volatilizations were not found for any of the other elements assayed. The precisions for the analyses are: Fe, 7%; Al, 10%; Mn, 5%; Cr, 6%; Cu, 5%; Zn, 8%; Ni, 5%; Co, 10%; V, 10%; Pb, 10%; Ag, 10%; Cd, 20%; and Mo, 20%.

Table I. Water Contents as Determined by Weight Loss at 110°C, and Salt-Free Sedimentary Components in Basin Sediments

Depth, cm, or deposition period (years)	Weight loss at 110°C, %	% sediment on salt-free basis ^a	Wt % Al	Wt % Al corrected to salt-free basis
San Pedro Basin				
0-1	82.1	14.9	3.7	4.5
1-2	80.6	16.5	4.8	5.7
2-3	77.7	19.5	4.8	5.5
3-4	75.1	22.2	5.8	6.5
4-5	73.2	24.1	6.0	6.6
6-7	69.6	27.9	6.3	6.9
7-8	68.2	29.3
8-9	66.7	30.9	6.2	6.7
9-10	64.7	33.0
10-11	65.1	32.5	6.0	6.5
13-14	62.9	34.8	6.2	6.6
18-20	57.9	40.0	6.3	6.6
24-26	61.2	36.6	6.2	6.6
30-32	59.5	38.3	6.1	6.4
Santa Barbara Basin				
1970-71	88	9.2	3.5	4.7
1968-70	84	13	4.8	5.9
1966-68	84	13	4.6	5.7
1964-66	85	12	4.6	5.8
1962-64	84	13	4.9	6.1
1960-62	82	15	5.0	6.0
1958-60	83	14	4.9	6.0
1956-58	81	16	4.6	5.4
1954-56	80	17	4.9	5.7
1945-50	76	21	5.3	6.0
1940-45	78	20	5.4	6.2
1935-40	76	22	5.2	5.8
1930-35	72	25	5.3	5.9
1926-30	70	27	5.7	6.2

^a Calculated on the basis of a salinity of 35‰ in the interstitial water.

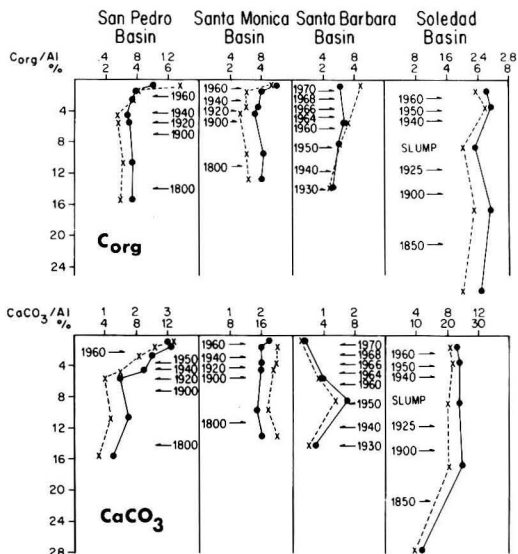


Figure 3 (contd.).

Fractional Extraction. Insight into the associations of heavy metals with various components of the sediments can be obtained by chemical leaching experiments. The technique prescribed by Presley et al. (1972) has been used. Three categories of sedimentary phases have been defined: First, a fraction extractable by 25% acetic acid in a solution of hydroxylamine hydrochloride. Such a treatment will remove these species in acid-soluble phases like carbonates and some sulfides and those associated with reducible materials such as organic matter or themselves reducible to a soluble form. In addition, surface sorbed materials, displaceable by hydrogen ions will be found in this fraction. A second sedimentary phase has been defined as a fraction extractable with 30% hydrogen peroxide. This treatment results in an oxidation of a substantial part of the organic matter and of other oxidizable phases with the consequential solution of some species. The third phase is as a resistant residue.

Results

The concentrations of 13 elements in the four marine basin sediments are plotted in Figure 3 both as absolute concentrations and as the metal/aluminum ratios. Aluminum is assumed to have a uniform flux to the sediments over the past century from crustal rock sources. Consequently, changes in the water, salt, CaCO₃, or organic matter content, especially in the upper layers can be compensated for through normalization of the metal concen-

trations to that of aluminum. The justification for this may be seen in Table I in which the aluminum content in the salt-free sediments of the San Pedro and Santa Barbara Basin deposits appears to be relatively uniform with depth. In both cases, there is an evident increase after the first few centimeters, perhaps attributable to organic matter, a correction we have not made. Two major elements, aluminum and iron, and three minor elements, cobalt, nickel, and manganese, in these basin deposits do not appear to be significantly influenced by the activities of man, if at all (see following sections)—ratios of the four to aluminum are constant with depth (or time of deposition) (Figure 3).

From Figure 3, the heavy metals, Pb, Cr, Cd, Zn, Cu, Ag, V, and Mo, appear to be accumulating at higher rates in the San Pedro and Santa Monica and less distinctly in the Santa Barbara present-day deposits than a century ago. This change can be attributed to the mobilization of these metals by the activities of man. On the other hand, the sediments in the Soledad Basin, off the coast of Baja California, show no concentration changes in these metals as a function of depth. This site, similarly anaerobic, is used as a baseline depositional area, not measurably affected by human activity. (There is an enhanced zinc content in the upper levels of the Soledad Basin sediments. This material was recovered in a galvanized box—the only core of those analyzed that was taken in this way. We suspect the upper portions of the core may have been contaminated during the removal processes, even though care

Table II. Fluxes of Heavy Metals into Sediments of California Coastal Basins

Element	Flux	Fluxes in $\mu\text{g}/\text{cm}^2/\text{yr}$					Santa Catalina rainfall (Lazrus, 1970), $\mu\text{g}/\text{cm}^2/\text{yr}$
		San Pedro	Santa Monica	Santa Barbara	Soledad	Av	
Pb	Anthropogenic	1.7	0.9	2.1		1.6	
	Natural	0.26	0.24	1.0	0.23	0.5	
	Rainfall						1.3
Cr	Anthropogenic	3.1	2.6	2.9		2.9	
	Natural	2.8	2.1	10.7	4.6	5.2	
Zn	Anthropogenic	1.9	2.1	2.2		2.1	
	Natural	3.1	2.8	9.7	2.8	5.2	
	Rainfall						4.6
Cu	Anthropogenic	1.4	1.1	1.4		1.3	
	Natural	1.2	1.0	2.6	1.4	1.6	
	Rainfall						0.5
Ag	Anthropogenic	0.09	0.09	0.10		0.09	
	Natural	0.05	0.03	0.11	0.08	0.06	
V	Anthropogenic	1.5	2.6	7.8		4.0	
	Natural	3.5	3.4	13.6	4.6	6.8	
Cd	Anthropogenic			0.07		0.07	
	Natural			0.14		0.14	
Mo	Anthropogenic		0.8			0.8	
	Natural		0.08			0.08	
Ni	Natural	1.6	1.3	4.1	2.3	2.3	
	Rainfall						0.24
Co	Natural	0.33	0.26	1.0	0.17	0.53	
Mn	Natural	13.	8.	24.	7.	15.	
	Rainfall						0.36
Fe	Natural	1260.	1200.	3060.	840.	1800.	
Al	Natural	1740.	1630.	4860.	1280.	2700.	

Table III. Composition of Suspended Particulates and of 1970-71 Sediments Deposited in Santa Barbara Basin

	Particulates		Santa Barbara basin sediments 1970-71
	October 1971	July 1972	
Mn/Al $\times 10^{-4}$	63	46	51
Fe/Al	0.64	0.58	0.63
Ni/Al $\times 10^{-4}$	4.5	7.3	6.9
Cr/Al $\times 10^{-4}$	22	34	28
Zn/Al $\times 10^{-4}$	107	40	25
Co/Al $\times 10^{-4}$	1.5	2.3	3.4
V/Al $\times 10^{-4}$	16	27	44
Cu/Al $\times 10^{-4}$	13	9.6	8.3
Pb/Al $\times 10^{-4}$	16	12	6
Dpm/g Pb-210/% Al	10	10	14

was taken to remove the outer portions in contact with the zinc coating.)

Anthropogenic fluxes may be calculated by subtracting the baseline flux, measured 50 or more years ago, from the total flux of the element measured in 1970 (Table II). The natural fluxes for the Santa Barbara basin are substantially higher for all metals than for the San Pedro, the

Santa Monica, or the Soledad deposits, reflecting its higher sedimentation rate. As a consequence, the impacts of man are less evident in the metal concentrations in the Santa Barbara deposits. With the exception of vanadium, the anthropogenic fluxes for the different basins are similar for each element. Perhaps, the natural oil seeps in the Santa Barbara basin are introducing vanadium and possibly nickel-containing porphyrins.

The heavy metals in these sediments can result from particulate transport from rivers or atmosphere and waste outfalls, scavenging from the water column by suspended particulates, or from being sorbed by the sedimented solids at the water/deposit interface. To gain some insights into these processes, we have analyzed suspended particulates collected at 100-meter water depth over a period of a month during October 1971 and again in July 1972 in the Santa Barbara Basin by Andrew Soutar of the Scripps Institution of Oceanography. We have compared our results, normalized to aluminum, with those from the Santa Barbara sediments accumulated during 1970-71 (Table III).

It is quite striking that for each species at least one of the suspended particulate values is always within a factor of two of the sedimentary value. Usually, the agreement of both particulate analyses for a given element with the sedimentary value is much closer. These results suggest that either the uptake processes are within the water column and perhaps primarily in the upper levels or the results reflect particulate transport from outside the basin.

The disposition of elements between the acid-reducible,

Table IV. Distribution of Heavy Metals Between Various Sedimentary Phases

Element	Phase	San Pedro		Santa Monica		Santa Barbara		Soledad		Whites Point	
		%	Ppm	%	Ppm	%	Ppm	%	Ppm	%	Ppm
Pb	Reducible	51	4.5	58	6.4	59	5.9	78	5.5	83	357
	Oxidizable	<5	<0.1	<5	<0.1	<5	<0.1	<5	<0.1	4	17
	Resistant	49	4.4	42	4.6	41	4.1	22	1.5	13	56
Cr	Reducible	8	8	11	10	8	9	19	22	49	358
	Oxidizable	9	9	11	10	8	9	42	49	37	270
	Resistant	83	84	78	71	83	97	40	47	14	102
Cu	Reducible	4	2	4	2	6	2	11	4	31	190
	Oxidizable	4	2	5	2	3	1	17	6	49	300
	Resistant	93	41	91	37	91	26	72	24	20	120
Zn	Reducible	14	16	15	17	17	16	18	13	85	1530
	Oxidizable	9	11	14	10	10	11	18	13	8	144
	Resistant	77	90	71	88	73	80	64	46	7	126
V	Reducible	13	16	23	32	28	42	32	36	20	34
	Oxidizable	9	11	9	13	5	7	28	32	10	17
	Resistant	78	97	68	95	68	103	40	46	70	118
Ag	Reducible	40	0.6	42	0.5	43	0.6	49	1.0	70	14
	Oxidizable	<13	<0.2	<10	<0.1	<14	<0.1	<15	<0.3	9	2
	Resistant	47	0.8	50	0.6	43	0.6	36	0.7	20	4
Ni	Reducible	20	11	23	13	25	9	27	15	39	33
	Oxidizable	15	8	16	9	15	6	48	27	26	22
	Resistant	65	35	61	36	59	22	25	14	25	29
Co	Reducible	3	0.4	5	0.5	3	0.2	<4	<0.2	17	2.4
	Oxidizable	5	0.6	4	0.4	5	0.3	<10	<0.4	20	2.8
	Resistant	91	11.	91	9.1	91	55	86	3.4	63	8.8
Mn	Reducible	7	32	10	35	13	35	7	12	11	42
	Oxidizable	4	18	4	14	4	11	11	19	15	58
	Resistant	89	407	86	301	83	223	82	139	74	286

Table V. Trace Metal Concentrations in Air and Their Environmental Fluxes

Metal	Aerosol concentrations in ng/m ³			$\mu\text{g}/\text{cm}^2/\text{yr}$			
	(1) Wraymires, England (Peirson et al., 1973)	(2) San Francisco (John et al., 1973)	Reasonable value from (1) and (2)	Washout fluxes		Sedimentary basin fluxes	
				Calculated	Santa Catalina (Lazrus, 1970)	Anthropogenic	Natural
Pb	112		100	2	1.3	1.6	0.50
Cr	3.1	8.2	5	0.1		2.9	5.2
Zn	103.	136	100	2	4.6	2.1	5.2
Cu	34.	50	50	1	0.5	1.3	1.6
Ni	7		7	0.14	0.24	0.0	2.3
Mn	14	17	15	0.3	0.36	0.0	15
Co	0.4	1.0	0.7	0.014		0.0	0.53
V	10	5.4	7	0.14		4.0	6.8
Al	335	863	600	12		0.0	2700
Fe	297	1670	1000	20		0.0	1800
Cd			20 ^a	0.4		0.07	0.14
Ag			2 ^a	0.04		0.09	0.06
Mo			10 ^a	0.2		0.8	0.08

^a Robertson, D., personal communication (1972).

oxidizable, and resistant categories for the California and Soledad Basins is given in Table IV along with that for the Whites Point deposit near the Los Angeles County outfall. The former sediments are from the lower portions of the cores and do not contain any measurable contributions of elements from man's activities. Most of the heavy metals (Pb, Cu, Cr, Zn, Ag, Ni, and Co) in the Whites Point sediments are more readily mobilized by reduction or oxidation than in the California and Soledad Basin sediments. In the latter the heavy metals appear to be associated with the minerals resistant to chemical attack. Manganese, a metal whose concentration in the sediments is not seriously affected by man's activities, shows similar distributions in the Whites Point and Basin sediments, a not unexpected result. Such is also the case with vanadium, a result somewhat difficult to interpret. A simple explanation would involve the resistant nature of the vanadium species introduced anthropogenically.

Both lead and silver have high concentrations in the reducible phases in the California and Soledad basin sediments in comparison with the other metals. A common feature to accommodate this finding might be their occurrence in seawater as anionic species. If this be the case, they might be sorbed to different phases than those heavy metals existing primarily as cations in seawater.

Discussion

In addition to identifying those elements whose fluxes to the sediments as a result of man's activities are significant in comparison with the natural mobilization rates, the transport paths from the continents to the sediments for the individual elements are of interest. These include the atmosphere, waste outfalls, and river and storm runoff.

Atmosphere. The elemental fluxes in the sediments are similar to those in atmospheric precipitation (Table II) collected during a six-month period in 1966 and 1967 on Santa Catalina Island (Lazrus et al., 1970). The precipitation samples were filtered through a 5- μ membrane filter prior to analysis. On the basis of comparisons with other analyses conducted throughout the United States, the authors concluded that rainfall near industrial areas contained anthropogenic fluxes of lead, zinc, copper, iron,

and manganese. Nickel appeared to be introduced solely from natural crustal rock particles. Their results are not inconsistent with the findings of this investigation. Whereas lead, zinc, and copper are markedly enriched in the more recently deposited sediments, iron, nickel, and manganese levels are uniform with depth. The first three elements are now being introduced by man at rates nearly equal to or exceeding the natural ones. On the other hand, iron, nickel, and manganese must have natural sedimentation rates much greater than the atmospheric fluxes generated by man. For example, the anthropogenic rainfall flux of manganese is 0.36 $\mu\text{g}/\text{cm}^2/\text{year}$ compared with sedimentary fluxes ranging between 8 and 24 $\mu\text{g}/\text{cm}^2/\text{year}$. Unfortunately there is no comparable rainfall data for iron. The natural nickel fluxes to the sediments exceed those generated via rainfall as a result of man's activities by an order of magnitude.

An assessment of atmospheric fallout for all of the elements can be approached in another way. There have been some recent measurements (Table V) of aerosol contents in the atmosphere of San Francisco Bay (John et al., 1973) and in England (Peirson et al., 1973). There is a marked correspondence between the English and California trace metal concentrations in air. This suggests the possibility of a worldwide dust burden in the air of the northern hemisphere that combines both anthropogenic and natural entries.

Combining the English and California data (Table V) and assuming 40 rainfalls per year which sweep out this standing crop of heavy metals from an atmospheric height of 5000 meters, one can calculate an annual washout flux (Goldberg, 1971). Such fluxes do compare reasonably well with those reported by Lazrus (1970), generally within a factor of two. As a first approximation, the flux values for those elements not measured by Lazrus are probably valid as an atmospheric flux to the sediment basins.

The calculated fluxes for Cr and V are an order of magnitude less than the sedimentary anthropogenic flux. The calculated flux of chromium of 0.1 $\mu\text{g}/\text{cm}^2/\text{year}$ is an order of magnitude less than the calculated anthropogenic fluxes for the San Pedro, Santa Monica, and Santa Barbara Basins (range of 2.6-3.1 $\mu\text{g}/\text{cm}^2/\text{year}$) and the natural fluxes for these basins and for Soledad (range 2.1-10.7

Table VI. Heavy Metals in Waste Water Particulates (SCCWRP, 1973) and Sediments

Metal	Waste water particulates, mg/kg dry wt				Sediments, mg/kg dry wt		(2)/(1) × 100	% Contribution from waste water particulates required to balance anthropogenic increases in sediments
	(1), Whites Point	Hyperion	Orange County	Av	(2), Whites Point	Av ^a		
Zn	4,100	2300	2330	2900	1800	113	44	1.6
Cu	1,120	1500	1850	1500	590	38	53	1.9
Pb	570	320	920	600	430	10	75	6.0
Cd	65	108	245	140				0.6
Cr	1,700	1440	1330	1500	730	103	43	4.5
Ag	32	130	40	70	20	1.4	63	3.6
Ni	220	520	220	320	84	50	38	
Co	8	4		6	14	9	175	
Fe	20,000	5400	7000	11,000	51,000	43,000	255	
Mn	150	108	120	125	276	360	184	

^a Average for the Santa Barbara, Santa Monica, and San Pedro Basins.

μg/cm²/year). On the basis of these data, it appears that the primary anthropogenic mobilization of chromium is through river, storm, or sewer waters and not through the atmosphere. This is not in accord with the conclusions of Winchester and Nifong (1971) on the fluxes of trace elements to Lake Michigan from pollution aerosol fallout. They found major atmospheric input of chromium to the lake as compared to lesser stream inputs.

The marked similarity in the anthropogenic sedimentary fluxes and in the rainfall fluxes for several elements would suggest the possibility of an atmospheric transport of these metals to the Southern California coastal areas and to the area of the Soledad Basin. Confirmation of this idea might be found in the measurement of the anthropogenic metal fluxes in the basins seaward of these inner ones. If the flux values are the same, atmospheric transport would be reasonable. If the flux values are higher in the near-coastal basins, then contributions from sewers, rivers, and storm runoff would provide an explanation.

Sewer Outfalls. The elemental concentrations of particulates in waste waters from the Los Angeles County, Los Angeles City, and Orange County outfalls are given in Table VI. For comparison, the composition of the Whites Point sediments, taken somewhat over a kilometer from the Los Angeles County outfall is tabulated. There is a remarkable consistency in the composition of the particulates from these three outfalls, reflecting uniform social and industrial patterns of this area. It appears as if about 50% of the sediment a kilometer from the Whites Point outfall is contributed by the sewer outfall and the remainder by other sources, both natural and anthropogenic.

The sewer discharges have their least effect upon iron, cobalt, and manganese. For these elements the natural concentrations appear to be several times those associated with the waste materials.

For those elements considerably enriched in the waste water particulates (Zn, Cu, Pb, Cr, and Ag), amounts ranging from 0.6-6.0% are required to balance the average sediment increases found in 1970 (Table VI). The higher organic matter in the upper levels of the basin cores (Figure 2) suggests that some portion of the wastes may be reaching these basins.

Table VII. Fluxes of Materials to Southern California Coastal Region in Units of Metric Tons/Year/12,000 Km²

Element	Flux of anthropogenic components to sediments	Waste waters (SCCWRP, 1973)	Storm water plus dry weather flow (SCCWRP, 1973)	Washout fluxes
Pb	190	213	90	156
Cr	350	649	25	12
Zn	250	1680	101	550
Cu	160	567	18	60
Ag	11	15	1	5
V	480	17
Cd	8	54	1	48
Mo	100	24

A complementary way of assessing the relative contributions of elements to these basin areas is to compare the fluxes of elements to the California coastal regions from waste waters and storm waters plus dry weather flow and washout with the fluxes of anthropogenic components to the sediments integrated over 12,000 km² (Table VII). On the basis of these data, a substantial fraction of the anthropogenic Pb, Zn, Cu, and Cd could originate in washout and/or the outfall wastes. Ag and Cr probably originate principally from the waste. Unfortunately, there are no data for Mo in the waste particulates. However, they probably contribute to the anthropogenic components since the atmospheric flux is unable to account for the increase. A refinement of this type of thinking will come about when flux data are available for the outer basins. In case of atmospheric transport, the fluxes for a given element would be expected to be similar. For waste water entries one would expect a smaller flux for the outer basins.

Acknowledgment

The authors are indebted to Andrew Soutar and Eric

Gamble of the Scripps Institution of Oceanography who provided the box-core materials.

Literature Cited

Chow, T. J., Bruland, K. W., Bertine, K. K., Soutar, A., Koide, M., Goldberg, E. D., "Lead Pollution: Records in Southern California Coastal Sediments," *Science*, **181**, 551-2 (1973).
Emery, K. O., "The Sea off Southern California," 366 pp, Wiley, 1960.
Goldberg, E. D., "Atmospheric dust, the sedimentary cycle and man. Comments on earth sciences," *Geophys.* **1**, 117-32 (1971).
John, W., Kaifer, R., Rahn, R., Wesolowski, J. J., "Trace element concentrations in aerosols from the San Francisco Bay Area," *Atmos. Environ.*, **7**, 107-18 (1973).
Koide, M., Bruland, K. W., Goldberg, E. D., "Th-228/Th-232 and Pb-210 geochronologies in marine and lake sediments," *Geochim. Cosmochim. Acta*, **37**, 1171-87 (1973).
Lazrus, A. L., Lorange, E., Lodge, J. P., Jr., "Lead and other

metal ions in United States precipitation," *Environ. Sci. Technol.*, **4**, 55-8 (1970).
Peirson, D. H., Cawse, P. A., Salmon, L., Cambray, R. S., "Trace elements in the atmosphere environment," *Nature*, **241**, 252-6 (1973).
Presley, B. J., Kolodny, Y., Nissenbaum, A., Kaplan, I. R., "Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia—1. Trace element distribution in interstitial water and sediment," *Geochim. Cosmochim. Acta*, **36**, 1073-90 (1972).
SCCWRP, "The Ecology of the Southern California Bight: Implications for Water Quality Management," Southern California Coastal Water Research Project, 1973.
Winchester, J. W., Nifong, Gordon D., "Water pollution in Lake Michigan by trace elements from pollution aerosol fallout," *Water, Air, Soil Pollut.*, **1**, 50-64 (1971).

Received August 27, 1973. Accepted November 18, 1973. Work supported by a grant from the U.S. Atomic Energy Commission, Division of Biology and Medicine, AT(04-3)-34, Project 84.

Reactivity of SO₂ with Supported Metal Oxide-Alumina Sorbents

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■ A number of impregnated metal oxides supported on alumina was evaluated for removal of SO₂ at 343°C from a mixture containing O₂, N₂, H₂O, and SO₂. A fixed-bed, flow reactor was used with the effluent monitored for SO₂ removal by infrared analysis. A kinetic treatment of the system was developed and rates of SO₂ sorption were calculated. A 5% SO₂ breakthrough point was chosen for practical rating of the various sorbents. The relative capacities of the sorbents were in general agreement with those of bulk oxides in that the alkali and alkaline earth metals were superior in reactivity. Compared to the Bureau of Mines coprecipitated, alkalinized alumina, the Na-impregnated alumina sorbent had a much higher rate for SO₂ sorption. Supported Cu and Sr proved to be especially reactive. The presence of water vapor affected the capacity of several sorbents.

Recent legislation against air pollution has forced many industries critically to review the quality of their stack gas emissions. Major sources of sulfur dioxide emissions are from power plants and sulfuric acid plants. The petroleum industry, although a relatively minor contributor, is not without its own sources of SO₂ pollution, of which the most prevalent are Claus sulfur units and fluid cracking regenerators. One of the methods for SO₂ removal from stack gases receiving much attention is sorption or reaction with solid sorbents, notably oxides. A successful sorbent must have a high capacity and rapid removal rate for SO₂ in low concentrations, as well as being regenerable. Theoretical examination of potential candidate materials for reaction with SO₂ has centered mainly on oxides capable of forming stable sulfites or sulfates. On the basis of SO₂ reactivity alone, the oxides of the alkali metals are best, followed by Ag, Hg, and then the transition metals (Welty, 1971). A comprehensive theoretical study of sulfite-sulfate formation and decomposition has suggested

that the most promising oxides are: Al, Bi, Ce, Co, Cr, Cu, Fe, Ni, Sn, Ti, V, U, Zn, and Zr (Lowell et al., 1971). These studies have not considered mixed oxides, or supported oxides, both of which could increase the choice of potential candidate materials. Although these evaluations can eliminate some candidates from consideration, reaction rates of promising ones cannot be predicted.

The Bureau of Mines was the first to demonstrate the potential of solid oxide for SO₂ removal. Extensive work was done on an alkalinized alumina sorbent (Bienstock et al., 1964). Other studies included a wide range of unsupported solid oxides (Bienstock et al., 1961). Besides the alkalinized alumina, bulk oxides of Mn, Co, and Cu were found to be active.

Dispersing active metals and metal oxides on high area supports to considerably increase their available surface area over the bulk forms has been long recognized in the application of catalysts in the oil industry. A properly supported active sorbent for SO₂ removal by either simple adsorption or chemical reaction should exhibit an enhanced reactivity over the bulk material, although total capacity per volume of sorbent plus support may or may not improve depending upon active solid utilization. Recently, processes employing CuO supported on alumina have been reported (McCrea et al., 1970) (*Oil and Gas Journal*, 1971).

In the present paper we report on a screening program for SO₂ removal from a simulated stack gas employing a wide range of metal oxides supported on alumina.

Experimental

Potential sorbents were prepared by impregnating Filtrol Grade 86 alumina with metal nitrates. An alkalinized alumina (BM), supplied by courtesy of the U.S. Bureau of Mines, was chosen as the standard for a comparison of sorbent capacities. The BM standard contained 31% Na and 2% K by chemical analysis. All experimental sorbents contained about 30% of the metal equivalents found in the standard. This enabled high atomic weight elements to be evaluated on the same basis of theoretical capacity since

reasonable metal levels could be prepared. All sorbents were calcined in air at 538°C for 10 hr prior to use and sieved to 10–20 mesh. Bulk densities ranged from 0.60 g/cc for the alumina to 0.93 g/cc for the 41% Pb sorbent. Most were about 0.7 g/cc. The bulk voidage, E , was required for kinetic measurements, and a value of 0.38 cc/cc sorbent was assumed (Haughey and Beveridge, 1966).

Two gas blends were examined: 4.7% SO₂, 6% O₂, and 89.3% N₂; and 4.7% SO₂, 6% O₂, 2% H₂O, and 87.3% N₂. This level of SO₂ was chosen to provide sufficient accuracy for the kinetic data analyses. Although the SO₂ concentration is higher than normally encountered in flue gas applications, Russell et al. (1970) concluded that reaction rates are first order in SO₂. The effects of CO₂ and NO_x, components in normal flue gases, were not determined because of interference with the ir analysis.

Four identical Pyrex glass reactors, 35 cm long by 3.2 cm i.d., were employed to facilitate screening of sorbents. Uniform heating was achieved by tube furnaces containing multiple heating elements manually controlled by variacs. Thermowells provided means of measuring sorbent bed temperatures. Gas flow, measured with standard flow rotameters, was downflow through the reactors. Reactors were charged with 25 grams of sorbent, the excess volume being filled with quartz. Sorbents were pretreated with hydrogen overnight at 482°C to remove any residual nitrates remaining from the impregnation step. This was necessary because nitrogen oxides were liberated upon treatment with SO₂, interfering with the ir analysis. Reactors were maintained at 343°C during sorption. Flow rates were 600 cc/min.

A Perkin-Elmer model 137B infrared spectrophotometer, equipped with attached strip chart recorder, was used to monitor SO₂ concentrations. The total effluent gas flow from the reactor was passed through a 4-cm long Pyrex ir cell containing sodium chloride windows. Water vapor was removed from the effluent gas by a tube containing Drierite placed immediately before the gas cell. The instrument was maintained at the wavelength of maximum absorption for SO₂ which was 7.3 μ. The lower limit of detection was about 0.05% SO₂. Sorbents were tested until at least 50% breakthrough of SO₂ was observed in the exit gas. The time required to reach the 5% and 50% breakthrough points was used to calculate efficiency and capacity of sorbents.

Treatment of Data

Two important parameters of sorbents for removing an active component from a gas stream are the loading capacity and the sorption (reaction) rate. For the alkalinized alumina sorbent, Russell et al. (1970) found that the sorption rate of SO₂ could be fairly well described by the concentration of the reacting SO₂ and the fraction of sorbent remaining unreacted, viz.

$$\frac{dm}{dt} = k_r C E \left(1 - \frac{m}{m_\infty}\right) \quad (1)$$

where t = reaction time, min
 m = loading capacity at time t , mol/cc sorbent
 m_∞ = maximum capacity, mol/cc sorbent
 k_r = reaction rate constant, min⁻¹
 C = gas reactant concentration, mol/cc
 E = void volume of sorbent, cc/cc sorbent

To evaluate the desired parameters from fixed-bed experiments, a mathematical treatment developed by Chu and Houser (1964) was used. This model assumes plug flow through the sorbent bed. The equation expressing the concentration of the active reactant at the outlet to the bed is given by:

$$\ln\left(\frac{C_o}{C_e} - 1\right) = \frac{k_r L C_o E}{u m_\infty} + \ln\left[\exp\frac{k_r L}{u} - 1\right] - \frac{k_r C_o E t}{m_\infty} \quad (2)$$

where C_o = reactant concentration at reactor inlet, mol/cc
 C_e = reactant concentration at reaction outlet, mol/cc
 L = sorbent bed length, cm
 u = interstitial gas velocity through bed, cm/min

Under practical experimental conditions, $\exp(k_r L/u) \gg 1$, and $C_o E/m_\infty \ll 1$; thus, Equation 2 reduces to:

$$\log\left(\frac{C_o}{C_e} - 1\right) = \frac{k_r E V}{2.3 F} - \left(\frac{k_r C_o E}{2.3 m_\infty}\right) t \quad (3)$$

where V is the sorbent volume, cc, and F the total gas flow rate, cc/min. Since Equation 3 is linear in t , k_r may be computed from the slope, s , of a plot of the left-hand side (LHS) vs. t ; viz.,

$$k_r = 2.3 s m_\infty / C_o E \quad (4)$$

Furthermore, when the exit concentration becomes one half of the inlet value at time $t_{1/2}$, the LHS of Equation 3 becomes zero, from which m_∞ may be calculated according to the equality,

$$m_\infty = C_o F t_{1/2} / V \quad (5)$$

Although Equation 5 has been derived from the basic kinetic Equation 1 with certain simplifying assumptions, it should be appreciated that Equation 5 is a simple material balance statement applicable for any kinetics in which the breakthrough curve is symmetrical about the time point, $t_{1/2}$.

Although sorbents should normally be evaluated for both capacity and rate of sorption for design purposes, a single criterion combining both is probably as useful for screening studies. In this case, an arbitrary breakthrough time is measured—e.g., 5% of inlet concentration at reactor outlet. Then “useful sorption capacity” can be determined by using the approximate material balance,

$$m_b \approx C_o F t_b / V \quad (6)$$

where m_b and t_b are the respective loading and time at breakthrough. In this way many sorbents can be readily ranked in preliminary screening tests.

To expedite calculation of rate constants a two-point method was adopted in place of plotting the data according to Equation 3. This involved combining Equations 3–6, taking the experimental points at:

$$t_b, C_e/C_o = 0.05$$

$$t_{1/2}, C_e/C_o = 0.50$$

to yield the following expression,

$$k_r = A \left(\frac{m_\infty}{m_\infty - m_b}\right) \quad (7)$$

where

$$A = \frac{2.3 F}{V E} \log 19$$

The value for k_r for each run was then calculated from the experimental conditions and the calculated values of m_∞ and m_b , obtained from Equations 5 and 6, respectively.

Results and Discussion

X-ray patterns of several spent materials revealed the presence of bulk sulfate salts. Thus, SO₂ removal is not simply a surface sorption process but actually involves a

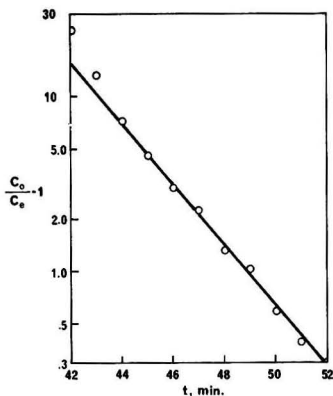
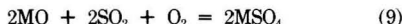


Figure 1. SO₂ breakthrough curve vs. time

chemical reaction of SO₂ with the metal oxide to form sulfur oxide salts. The process taking place may be represented by the following chemical reactions:



or



where M is a divalent metal. These reactions are representative of the overall process since the actual mechanism is probably more complex than that indicated by Equation 8 or 9. In this paper, sulfate or sulfite formation will be referred to as a sorption process.

A brief examination of the reasonableness of the adopted rate equation was made in some preliminary runs using an SO₂/N₂ blend. An example of the data fit obtained with Equation 3 is illustrated in Figure 1 using the 12.8% Cu sorbent. The good conformance to the predicted straight line shows that the assumption of first order in fraction of unreacted sorbent is reasonable. There is a deviation of the data from the straight line at earlier times, as was also reported by Russell et al. (1970) using the same basic model. Despite this, Equation 7 was used to calculate rate constants for convenience in treating large amounts of data where relative sorbent rankings were desired.

To check the assumption of first order in SO₂ concentration, several runs were made at lower concentrations by dilution with extra nitrogen. The data of Table I for three different sorbents show little effect of SO₂ level on the rate constant as calculated by Equation 7. The error inherent in the rate constant is considerably higher than that in the capacity determinations, since the difference in 5% and maximum capacities is involved in Equation 7.

A large number of supported metal oxides were evaluated for SO₂ sorption using a blend of SO₂-N₂-O₂-H₂O and the results are shown in Table II. The sorbents are listed in order of decreasing capacities at the 5% breakthrough level. In general, the maximum capacities do not deviate from this order with the exception of the BM sorbent. The slope of the breakthrough curve is dependent upon the rate of sorption. Thus, if the rate is low, the breakthrough point will be considerably lower than the maximum capacity except in those cases where the maximum capacity is very low. As a result, the breakthrough point becomes a direct indication of the material's usefulness in a process of this nature. Rate constants were calculated from Equation 7 and are presented in column four. The last two columns in Table II present a measure

of the efficiency of the materials based upon the percent of metal reacted. An alumina blank was run to establish background adsorption and its contribution to the 5% breakthrough of these sorbents was negligible.

The Bureau of Mines alkalinized alumina had the greatest maximum capacity of 20.3 grams SO₂/100 cc sorbent with 69% of the metal reacted. However, its useful capacity was only 7.9 grams SO₂/100 cc sorbent due to the very low rate of SO₂ sorption with this material. In fact, its rate constant of 200 min⁻¹ was the lowest observed. The highest useful capacity was obtained with a sodium-impregnated sample. This sorbent had the highest rate of sorption and at the 5% breakthrough point more metal was used than for any other material evaluated. As mentioned earlier, all sorbents, with the exception of the BM, were made with identical metal equivalents to provide a direct comparison of all results. The BM material actually contains 3.4 times as much sodium as the experimental sample yet its useful capacity is approximately 10% less. These differences in capacities of the two sodium sorbents might be attributed to differences in their methods of preparation. The BM sorbent is prepared by coprecipitation of sodium carbonate and aluminum sulfate (Bienstock et al., 1961) while the experimental sorbent was prepared by sodium nitrate impregnation on an alumina support. With coprecipitation, at least some portion of the active component may be buried within the support ma-

Table I. Effect of SO₂ Partial Pressure on Reaction Rate

Alumina-supported sorbent	Loading, grams SO ₂ /100 cc			
	SO ₂ , Vol %	5% capacity	Max. capacity	Rate constant, k _r , min ⁻¹
9.2% Na	2.6	5.36	10.00	770
	0.9	4.99	9.52	930
BM	2.6	0.86	1.24	400
	0.9	0.97	1.43	370
12.8% Cu	4.7	1.71	2.16	600
	0.9	1.68	2.05	740

Run Conditions: SO₂/N₂ blend, 600 cc/min.
^a Calculated according to Equation 7.

Table II. SO₂ Removal from SO₂-N₂-O₂-H₂O Simulated Flue Gas

Alumina-supported sorbent	Loading, grams SO ₂ /100 cc sorbent		Rate constant, k _r , min ⁻¹	% metal reacted	
	5% capacity	Maximum capacity		5% capacity	Maximum capacity
9.2% Na	8.69	9.94	1130	89	102
BM	7.94	20.3	200	27	69
17.6% Sr	6.59	8.58	620	67	87
12.8% Cu	5.29	6.85	550	62	79
8.0% Ca	4.19	5.23	650	47	59
7.0% Cr	4.01	4.82	770	46	55
27.4% Ba	2.44	3.16	600	26	34
41.4% Pb	1.81	2.72	510	15	23
22.4% Cd	1.27	1.74	560	13	18
5.5% Mn	0.98	1.38	430	11	16
4.8% Mg	0.81	1.08	520	9	12
7.5% Fe	0.72	1.21	330	8	13
6.0% Sc	0.65	0.96	400	7	11
11.8% Co	0.50	0.65	600	5	7
11.8% Ni	0.49	0.69	430	6	8
13.0% Zn	0.28	0.47	360	3	5
16.5% Sb	0	0	—	0	0
4.1% V	0	0	—	0	0
Al ₂ O ₃	0	0.38	—	—	—

^a Calculated according to Equation 7.

terial, resulting in reduced surface concentration of the metal and a possible loss in activity. This problem is not present when impregnation is used to deposit active metal components. Of course, in both cases, metal surface area may be reduced by formation of large crystallites during calcination.

As can be seen in Table II, large differences in percent metal reacted were obtained for the various sorbents. Thermodynamic limitations cannot account for these differences as equilibrium strongly favors sulfate or sulfite formation under the reaction conditions employed (Lowell et al., 1971), at least for those sorbents which exhibited some SO₂ sorption. Likewise, different intrinsic metal reactivities seem unlikely to account for the differences since variation in the rate constants is not large between the various sorbents. A possible explanation may lie in diffusional limitations caused by product inhibition over varying metal oxide crystallite sizes. Presumably, high capacities imply high dispersion of the metal oxide over the support and vice versa.

These materials were also evaluated in a dry atmosphere to determine the importance of using realistic conditions for this type of study. A comparison of the sorbents useful capacities with and without water is shown in Figure 2 in which the effect of water is clearly evident. The capacity of the BM material was appreciably increased by the presence of water vapor as had been shown by the Bureau of Mines work (Bienstock, et al. 1961). In addition Na(=K), Ca, Sr, Ba, Cu, Cd, and Cr-impregnated samples all had greater capacities in the presence of water. Only Fe, Co, and Ni metals showed lower capacities. Additional studies were not pursued and an explanation for the observed effect of water cannot be offered. However, it is certainly evident that water plays an important role in the process of SO₂ removal.

Two supported metal sorbents; namely, copper and strontium, which had high SO₂ capacities but were theoretically capable of removing more SO₂ (last column, Table II) were promoted with various metal additives in an attempt to improve their useful capacity. The results are given in Table III. The calculated capacities presented in column four are based upon total metal content. At 5% breakthrough, 62% of the copper had reacted. With chromium and sodium addition, the percent metal reacted increased to 80% and 73%, respectively. Zirconium had essentially no effect upon the capacity and the remaining metal additives decreased its capacity. The strontium sorbent was not promoted by any of these additions but instead was deactivated in varying degrees. It appears that addition of an inherently active sorbent as promoter had a

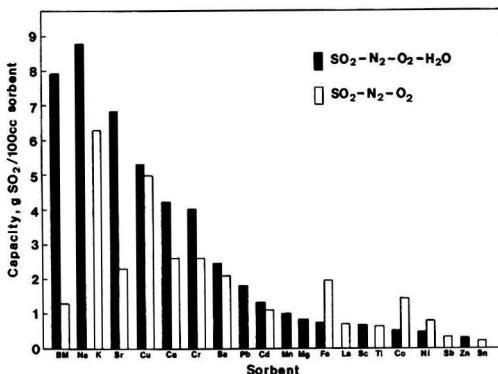


Figure 2. Capacity at 5% breakthrough

Table III. Effect of Promoters on Cu and Sr Sorbents

Metal promoter	% metal reacted		Metal promoter	% metal reacted	
	5% capacity	Max capacity		5% capacity	Max capacity
	12.8% Cu			17.6% Sr	
None	62	79	None	67	87
1% Cr	80	98	5% Zr	32	48
1% Na	73	90	1% Cr	30	34
3% Zr	62	74	1% Na	29	35
1% V	43	60	1% Fe	27	34
1% Mn	40	86	1% K	24	30
1% K	29	36	1% Mn	24	28
1% Fe	23	101	1% V	24	27

positive synergistic effect for the Cu sorbent but not for the Sr whereas, addition of less active promoters had a negative effect in both cases.

Conclusions

The results of this study are summarized in the following listing:

Group	Metal Oxide on Al ₂ O ₃	Reactivity to SO ₂
IA	Na (=K)	Good
IIA	Sr > Ca > Ba > Mg	Good to poor
IIIA	Sc	Poor
IVA	Ti	Poor
VA	V	Poor
VIA	Cr	Good
VIIA	Mn	Poor
VIII	Fe = Co = Ni	Poor
IB	Cu	Good
IIB	Cd > Zn	Poor
IIIB	Al	Poor
IVB	Pb > Sn	Fair to poor
VB	Sb	Poor

These are in general agreement with the theoretical predictions mentioned earlier for bulk oxides in that the alkali metal and alkaline earth metals were superior in reactivity. However, two exceptions were observed, notably the especially good reactivity of Cu, and of Sr in the alkaline earth series. The supported Mn and Co sorbents were not as active as the Cu, contrary to the results reported for the bulk oxides (Bienstock et al., 1961).

Overall, capacities and rates of reaction for SO₂ removal with the more active supported metal oxides compared favorably to the Bureau of Mines alkalinized alumina sorbent.

Acknowledgment

The authors are grateful to James Adamson for experimental assistance and to Gulf Research & Development Co. for permission to publish this work.

Nomenclature

- C = gas reactant concentration, mol/cc
- C_o = reactant concentration at reactor inlet, mol/cc
- C_e = reactant concentration at reactor outlet, mol/cc
- E = void volume of sorbent, cc/cc sorbent
- F = total gas flow rate, cc/min
- k_r = first-order rate constant, min⁻¹
- L = sorbent bed length, cm
- m = loading capacity at time t, mol/cc sorbent
- m_∞ = maximum capacity, mol/cc sorbent
- m_b = loading capacity at breakthrough, mol/cc sorbent
- s = slope of Equation 3, min⁻¹
- t = reaction time, min
- t_b = reaction time at breakthrough, min
- u = interstitial gas velocity through bed, cm/min
- V = sorbent volume, cc

Literature Cited

- Bienstock, D., Field, J., Myers, J., *Amer. Soc. Test. Mater.*, p 353, July 1964.
- Bienstock, D., Field, J., Myers, J., "Process Development in Removing Sulfur Dioxide from Hot Flue Gases, 1. Bench-Scale Experimentation," *Bur. Mines Rep. Invest.*, 5735, 1961.
- Chu, H., Houser, F., *J. Catal.*, 3, 668 (1964).
- Haughey, D., Beveridge, G., *Chem. Eng. Sci.*, 21, 905 (1966).
- Lowell, P., Schwitzgebel, K., Parsons, T., Sladek, K., *Ind. Eng. Chem. Process Res. Develop.*, 10, 384 (1971).

- McCrea, D. H., Fornez, A. J., Myers, J. G., *J. Air Pollut. Contr. Ass.*, 20, 12, 819 (1970).
- Oil Gas J.*, p 105, September 20, 1971.
- Russell, J., Town, J., Kelly, H., "Mathematical Evaluation of SO₂ Sorption-Regeneration Reactions with Alkalinized Alumina," *Bur. Mines Rep. Invest.*, 7415, 1970.
- Welty, A., Jr., *Hydrocarbon Process.*, p 104, October 1971.

Received for review January 16, 1973. Accepted November 29, 1973.

Characterization of Aerosols in California by X-ray-Induced X-ray Fluorescence Analysis

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■ X-ray-induced X-ray fluorescence analysis was employed to determine elemental concentrations in aerosols collected on impactor films and filter media during Phase I of the "Characterization of Aerosols in California" study. Elemental diurnal patterns were established for aerosols collected over 2-hr periods. Elemental distributions were correlated with particle size distributions. Sensitivities routinely attainable within a 20-min counting interval corresponded to less than 10 ng/m³ of air for 12 of the 20 elements measured.

Elemental analyses of aerosols, coupled with meteorological and particle size distribution data, provide information which correlates the contribution of primary and secondary sources to the total airborne particulate matter (Gordon et al., 1971; Friedlander, 1973). From such data, evaluations of the contributions of anthropogenic sources may be made. Possible control strategies may then be established to reduce air pollution with considerable emphasis placed on the portions of the aerosols which can affect visibility and the human respiratory system. To determine what technique should be employed for the elemental analyses, following are five criteria that should be considered:

The technique should permit the analyses of a broad range of elements, with emphasis placed on certain elements.

High sensitivities must be attainable (ng/m³ level).

The procedure should be relatively rapid (minutes). This permits preliminary evaluations from which future studies may be prudently established.

The analyses must be quantitative and the costs should be small.

The technique should be nondestructive so that future measurements may be made.

A technique that satisfies these criteria is X-ray-induced X-ray fluorescence analysis.

Methods and Equipment

General Technique. Figure 1 illustrates the technique employed by us for X-ray fluorescence analysis. Exciting radiation provided by an X-ray tube impinges upon the

filter medium or impactor film containing the collected particulate matter. A fraction of the photons, if of sufficient energy, produces vacancies in the inner shells of atoms within the specimen, and in turn characteristic X-rays are emitted. These X-rays are detected by a semiconductor detector, sorted by their energies, and the elemental concentrations are determined from the intensities of the X-rays.

In addition to the photoelectric interactions, a portion of the exciting radiation is scattered either coherently or incoherently. For analyses of aerosols collected on typical filter media or impactor films, the intensity of the scattered X-rays is often quite large compared with that of the characteristic X-rays. To obtain high sensitivities, monochromatic exciting radiation is employed and is selected of an energy slightly greater than the *K* or *L* absorption edge energies of the elements to be analyzed, but of sufficient energy that the incoherently scattered radiation does not produce considerable overlapping background. With this procedure, high efficiencies are obtained for producing photoelectric interactions, and high X-ray peak intensities with respect to background are achieved. A molybdenum transmission X-ray tube (Jaklevic et al., 1972) produced the exciting radiation employed to obtain the data reported in this paper. High sensitivities for most of the elements in the periodic table may be obtained by employing an X-ray tube with secondary fluorescers (Goulding et al., 1973), or different characteristic X-ray tubes.

Equipment and Characteristics. For the experiments discussed in this paper, a guard-ring detector (Goulding et al., 1972) with pulsed-light feedback electronics and a 512-channel pulse-height analyzer were employed. The total resolution of the system, full width-half maximum, was 225 eV at 6.4 keV (FeK α X-ray energy). Excitation was provided by a molybdenum transmission X-ray tube with combined anode plus window thickness of 0.010 cm. The X-ray tube was operated at 42 kV and 300 μ A. The X-ray tube, specimen, and detector geometry are shown in Figure 1. The total area of the specimens used varied from 1-3 cm², depending upon the external tube collimation employed. Correction was made for system dead time resulting either through pile-up rejection or analyzer dead time using a gated clock that measured the total system live time.

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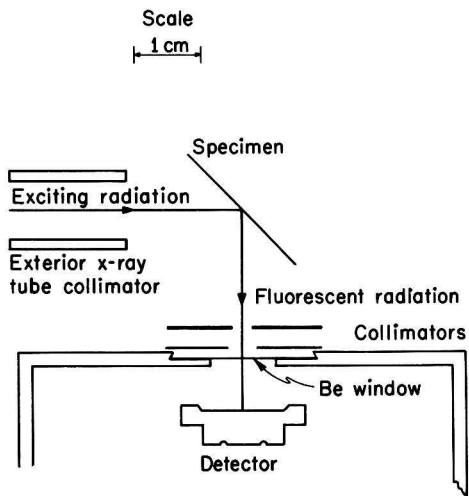


Figure 1. Schematic of X-ray fluorescence analysis technique

Calibration Method. Aerosols collected on filter media or impactor films can in general be considered as thin specimens. For most analyses of such specimens the concentration of an element is directly proportional to the intensity of its characteristic X-rays. However, if low energy X-rays (<4 keV) are employed for analyses, X-rays are not uniformly emitted (absorption effects) from within the individual larger particles (>1 μ). For the data reported in this paper, no corrections were necessary; hence, compensations for absorption effects will not be discussed.

Since the intensity of an X-ray line from an "infinitely" thin specimen is directly proportional to the concentration, $m_j(\mu\text{g}/\text{cm}^2)$ of the element, the relationship between intensities and elemental concentrations may be expressed as:

$$I = I_0 G K_j m_j \quad (1)$$

where I_0 is the exciting radiation intensity, G a geometry factor, and K_j ($\text{cm}^2/\mu\text{g}$) is a factor which relates the ability to excite and detect an X-ray from the element j . As previously reported (Giauque et al., 1973), the value of $I_0 G$ can be determined from a single element thin-film standard, and the relative values of K_j for characteristic X-rays from other elements are obtained by calculating the relative probability of fluorescence excitation and detection of X-ray lines as a function of Z . The thin-film standard is prepared by evaporation of the element onto a thin substrate. The standard is prepared thin enough that absorption effects are negligible (about 100 $\mu\text{g}/\text{cm}^2$). Calculated values of K_j for X-ray lines from eight elements have been reported to agree within several percent of measured values from evaporated thin-film standards (Giauque et al., 1973). In effect, standardization for exciting radiation intensity and total system geometry is made with the single-element thin-film standard, and factors converting counts/sec to $\mu\text{g}/\text{cm}^2$ for the other elements are calculated.

Analysis Program. X-ray spectra of the collected aerosol specimens are recorded on magnetic tape, and the analytical computations are made by a Control Data 6600 computer. Although our program has been established for the analyses of many types of specimens, much less than 50 K of core space would actually be required for the analyses of only aerosols. The analysis program is performed in three steps. First, the X-ray spectrum back-

ground due to the scattered exciting radiation is removed; second, the interferences due to overlapping X-ray lines are unfolded; and third, the concentrations of the elements in the original air sampled are calculated from the intensities of the appropriate X-ray lines employed for analysis.

The shape of the scattered exciting background is determined by employing a blank filter of mass similar to that of the filters used for the aerosol collections. The scattered X-ray background within various energy ranges to be employed for analysis is ratioed to the intensities of the incoherent plus coherent scattered exciting $\text{MoK}\alpha$ radiation. These scattered radiation background factors are employed for analyses. This procedure was possible since the typical aerosol loadings contributed only a few percent to the total mass of the filter plus collected aerosol. Also, the loadings were of average effective atomic number similar to that of the collection media.

Fixed sets of pulse-height analyzer channels corresponding to preselected energy ranges are employed for analyses. Although the spectrometer is stable over widely varying conditions, one of the more intense X-ray lines is used to compensate if a base-line shift occurs. To obtain high statistical accuracies, between 70% and 80% of the total peak areas are employed for analyses. The peak fractions used are established from elemental thin films. Corrections for overlapping X-ray lines are also determined from the elemental thin-films by establishing relationships between individual X-ray peak shapes and intensities. In effect, a series of simultaneous equations are established which compensate for overlapping X-ray lines occurring over the preselected energy ranges.

The concentrations of the individual elements present in the aerosol are then calculated from the individual X-ray line intensities using Equation 2.

$$\frac{\mu\text{g}(j)}{m^3} = \frac{C_j}{C_s} \times \frac{m_s}{V} \times \frac{1}{K_j} \quad (2)$$

where C_j and C_s are the characteristic X-ray count rates for element j and the thin-film standard, respectively; m_s is the mass ($\mu\text{g}/\text{cm}^2$) of the standard; V is the volume of air sampled, m^3 per cm^2 , of collection media; and K_j is defined by Equation 1.

Sampling. Sampling of aerosols was carried out during the summer of 1972 by the Air and Industrial Hygiene Laboratory of the California Department of Public Health as a part of the extensive aerosol characterization program sponsored by the California Air Resources Board. Several types of aerosol collection devices that used filter media and impactor films were employed. We limit the results reported in this paper to data obtained on some of the aerosols collected over 2-hr intervals for a period of 24 hr. Specifically, results obtained on total aerosols (<20 μ) or aerosols collected with a Lundgren four-stage impactor which provided particle size distributions of the elements are reported. Analyses were performed on particulate matter collected on stages 3, 4, and the after-filter of the Lundgren impactor. The respective 50% cut points for these stages were 1.5, 0.5, and <0.5 μ . Emphasis was placed on the analyses of particulate matter collected on stage 4 and the after-filter since these contain particles of the size range which affect visibility and are efficiently trapped in the human respiratory system.

Various collection media suitable for different types of instrumental analyses were employed during this study. These media were also used to evaluate bounce-off problems associated with the use of Lundgren impactors (Wesolowski et al., 1973). Either washed 0.8- μ GA-1 Gelman filters or silver membrane filters were employed for

Table I. Theoretical Limits of Detection

Media	Gelman filter	0.0006-cm Mylar
Mass, mg/cm ²	5.0	0.9
Air volume sampled, m ³ /cm ²	0.75	2.50
Area analyzed, cm ²	3	1
Element and spectral line		
SK α	—	160 ng/m ³
ClK α	—	80
KK α	110 ng/m ³	36
CaK α	50	15
TiK α	20	5
VK α	16	4
CrK α	13	3
MnK α	9	3
FeK α	10	2
NiK α	4	1
CuK α	6	1
ZnK α	4	2
GaK α	3	1
AsK α	4	1
SeK α	4	1
BrK α	5	2
RbK α	8	2
SrK α	9	3
HgL α	7	2
PbL α	7	2
PbL β	18	5

the total and after filters. Although dry or sticky Mylar or Teflon was used for the four impactor stages, only the dry Mylar impactor films were analyzed by X-ray fluorescence. Typical 2-hr collections corresponded to 0.75 m³/cm² for the total and after-filters, and to 2.50 m³/cm² for the impactor stages.

Results and Discussion

For most aerosol specimens, the concentrations or limits of detection of 20 elements were determined in 20 min or less. Table I lists the sensitivities attained for two types of collection media employed. The minimum detectable amount is defined as that quantity which gives a line intensity above background equal to three times the square root of the background for counting times not to exceed 1000 sec. The values listed in Table I include the background due to the Ca, Fe, Cu, and Zn impurities in the Gelman filters and the Zn impurity in the Mylar film.

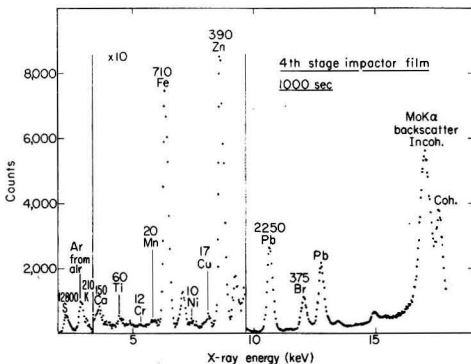


Figure 2. Spectrum of aerosol collected over a 2-hr interval on dry 0.0006-cm Mylar on the 4th stage of a Lundgren impactor

Figure 2 shows the spectrum and results obtained on an aerosol collected over a 2-hr interval on 0.0006-cm Mylar on the 4th stage of a Lundgren impactor. The results reported are in ng/cm². Since the volume of air sampled was 2.50 m³/cm² of impactor film, the concentrations of the elements in the original air (ng/m³) were two fifths of the values listed. Figures 3-9 illustrate a few of the diurnal patterns established during this study. When these

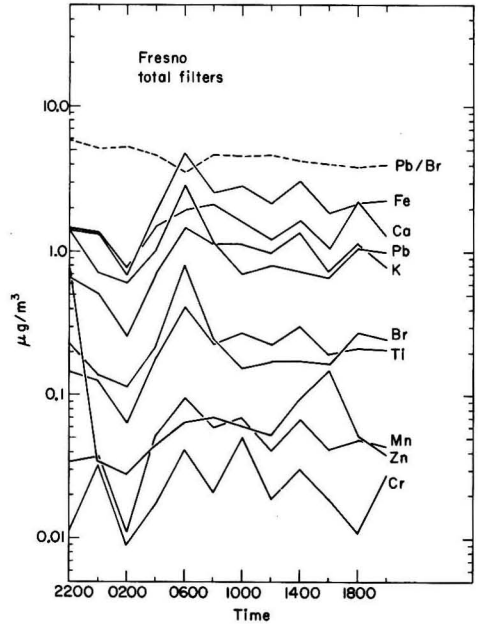


Figure 3. Diurnal patterns for elements collected on total filters at Fresno on 8/31-9/1 (1972)

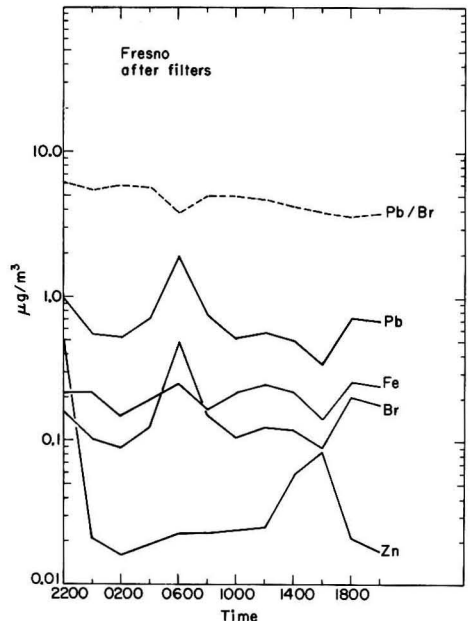


Figure 4. Diurnal patterns for elements collected on after filters at Fresno on 8/31-9/1 (1972)

data are united with meteorological, particle size distribution, and other chemical data, they provide considerable insight into the formation of aerosols. We will initially discuss possible interpretations from the X-ray data alone.

For the Fresno data, the diurnal patterns for K, Fe, Ti, and Mn are very similar for the total filter. These four el-

ements are most likely produced by a mechanical process, such as wind-blown soils (large particles), since their concentrations were an order of magnitude lower for the after-filter. The Ca was also present almost entirely in the large particles and is probably from a mixture of soil and cement particles. Approximately three fourths of the Pb and Br is present in the $<0.5\text{-}\mu$ range. (This is within the

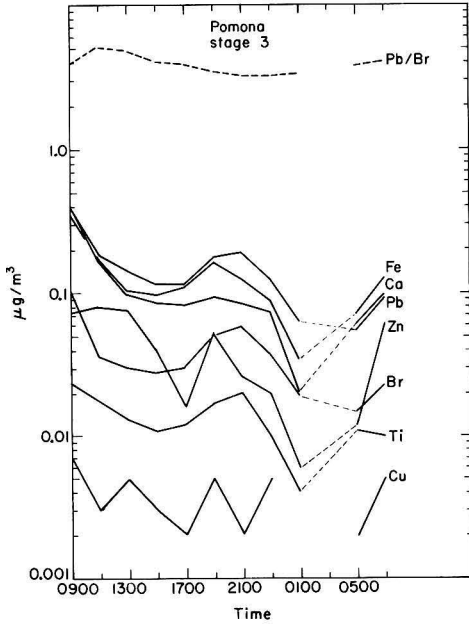


Figure 5. Diurnal patterns for elements collected on 3rd impactor stage at Pomona on 10/24-10/25 (1972)
One specimen was missing, hence the void in the data

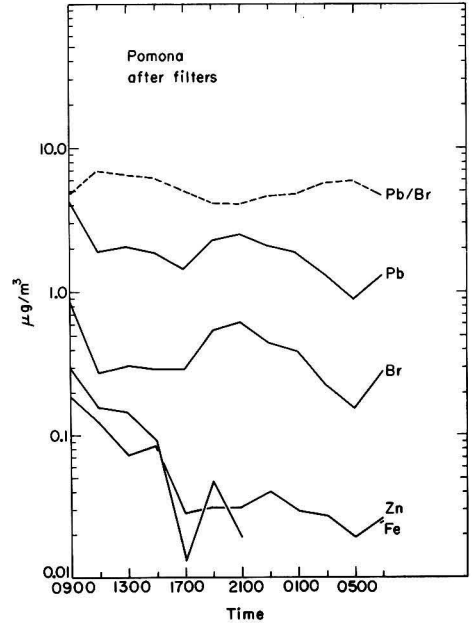


Figure 7. Diurnal patterns for elements collected on after filter at Pomona on 10/24-10/25 (1972)

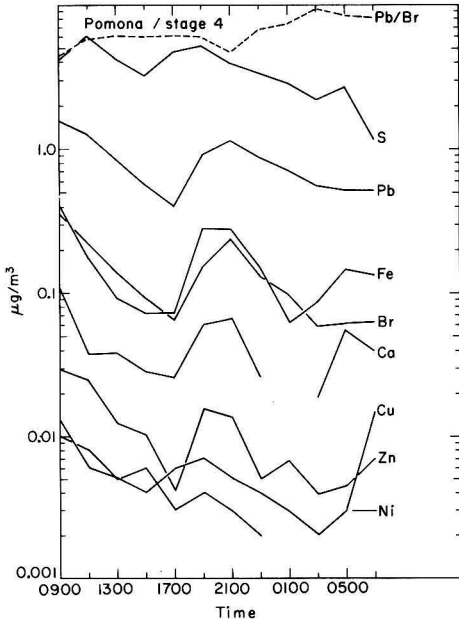


Figure 6. Diurnal patterns for elements collected on 4th impactor stage at Pomona on 10/24-10/25 (1972)

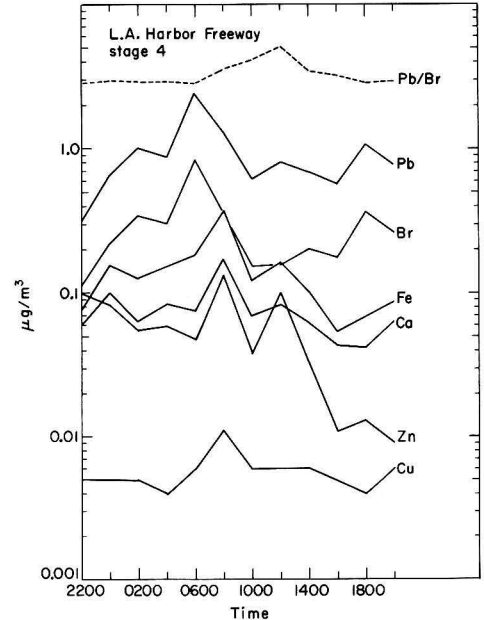


Figure 8. Diurnal patterns for elements collected on 4th impactor stage at Los Angeles Harbor Freeway on 9/19-9/20 (1972)

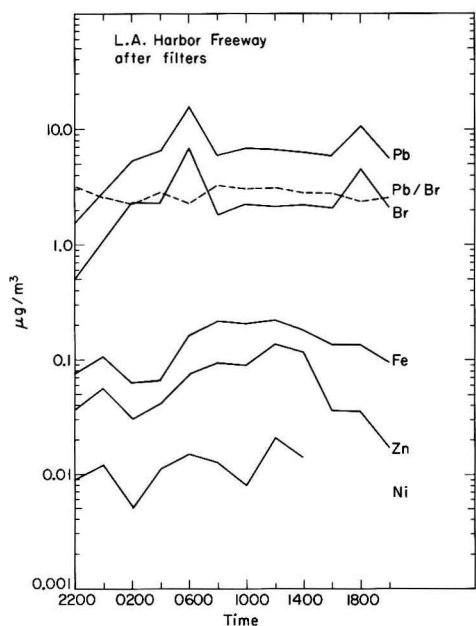


Figure 9. Diurnal patterns for elements collected on after filter at Los Angeles Harbor Freeway on 9/19-9/20 (1972)

size range of particles trapped with a high efficiency in the respiratory system, 0.05-1 μ .) The Pb and Br arise from auto emissions and the Pb/Br ratio indicates the Pb and Br are most likely from an aged aerosol. (The Pb/Br ratio from a fresh aerosol is less than 3.0.) Over half the Zn was present in the <0.5- μ range. The diurnal patterns established for Zn during this study usually did not correlate well with any of the other elements determined. Zinc is often thought to be associated with tire dust. During these studies, several episodes of high Zn concentrations, as is illustrated in the Fresno data at 2200, have occurred. The Zn in these cases was predominantly present in the small particle size range, <0.5- μ , and occurred during late evening or early morning hours. The Zn in these cases could be due to combustion sources, possibly from incineration of tires or tin cans. As shown in Figure 4, only one tenth of the total Fe was present in the small particles (<0.5- μ). The diurnal patterns for Fe and Pb were somewhat similar, indicating that possibly the Fe in the small particles had come from the same area as the auto emissions.

The Pomona data of 10/24-10/25, illustrated in Figures 5-7, are interesting inasmuch as three different particle size cuts, 1.5, 0.5, and <0.5 μ , were analyzed. The diurnal patterns for Pb and Br were similar for the three size cuts. However, the ratio of Pb present was 1:5:10 for the 3rd and 4th stages, and after-filter, respectively, again illustrating that Pb and Br were present in the small particles. For stage 3, the diurnal patterns for Fe, Ca, and Ti are also similar to those of Pb and Br, suggesting that possibly these elements in the 0.5-1.5- μ range originated from the same area. Very large amounts of S were detected in stage 4. The S values for stage 4 were typically 10-20 times larger than those for stage 3. Novakov has shown this S present as SO_4^{2-} (Hidy et al., 1973). The S was quite likely due to a secondary aerosol. Also, the Pb/Br ratio, which was over 7:1 between 0100 and 0700 for the 4th stage, indicates that in this particle size range the Pb

is from an aged aerosol. The concentration of Zn successively increased with decreasing particle size. Also, the diurnal patterns for Zn for the three particle size ranges were different. The Fe concentration was generally several times higher in the two larger particle size ranges than for those particles <0.5 μ .

The Los Angeles Harbor Freeway specimens collected on 9/19-9/20 were from the heaviest smog episode during the entire study. Figure 10 contains a plot of the data obtained from the particles collected on the total filter (silver membrane). Also included in this plot are the condensation nuclei count (CNC) and the wind direction determined by the Whitby Group (Hidy et al., 1973). The mobile laboratory was stationed approximately one block from the freeway, and the aerosols were collected from the direction of the freeway when the wind direction was above 180°. The two high Pb peaks episodes correspond to the heavy morning and evening traffic and to two of the broad CNC maxima. The wind direction shifted toward the freeway between 0700 and 0900, hence the episode peaked at the somewhat early hour of 0600. The high CNC between 1000 and 1600 is thought to be due possibly to a secondary aerosol. This is consistent with the fact that aged automotive emissions are detected during this period, as is evident by the increase in the Pb/Br ratio of somewhat larger particles, 0.5-1.5 μ , collected on the 4th stage of the Lundgren impactors. Also the diurnal patterns for Fe and Ca for this stage were very similar. The Fe and Ca may be due to the same source, possibly of sedimentary origination. The bulk of the Fe and Zn was present in the larger particles >0.5 μ . The diurnal patterns for these two elements were very similar for the total filter, suggesting that the majority of the Fe and Zn originate from the same area, and possibly from the same source.

During these studies aerosols were collected at San Jose on five separate days. On three of these days the Sr levels in the aerosols increased dramatically (the largest change being from <0.012-0.180 $\mu\text{g}/\text{m}^3$) between the hours of

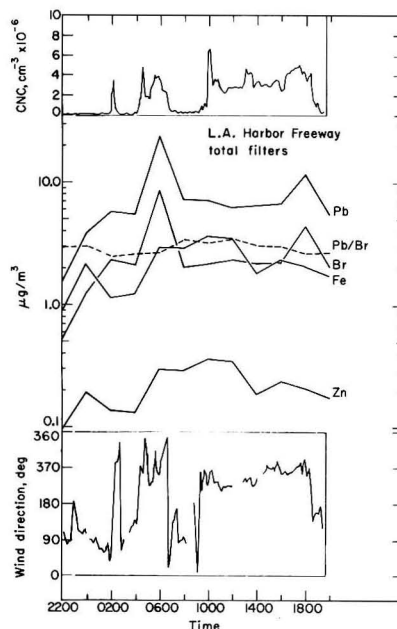


Figure 10. Diurnal patterns for elements collected on total filter (silver membrane) at Los Angeles Harbor Freeway on 9/19-9/20 (1972). Also included are CNC and wind direction data

0000 and 0400. Most of the Sr was in particles $<0.5 \mu$, indicating it came from an anthropogenic source. The Sr could possibly be attributed to the manufacture of fireworks or highway flares.

Although the data discussed in this report are only a fraction of the results obtained, they serve to illustrate some of the contributions X-ray fluorescence analysis can make in the study of aerosols. These data have been combined (Hidy et al., 1973) with a wealth of other chemical, physical, and meteorological data obtained by other experimenters during this study.

Acknowledgments

We are indebted to J. Wesolowski and A. Alcocer of the California Department of Public Health and to G. Hidy of the North American Rockwell Science Center for their support and cooperation in this work. The authors wish to express gratitude to F. Goulding and J. Jaklevic and other members of the Nuclear Chemistry Instrumentation Group for developing and supplying much of the equipment used. We also thank R. Garrett and D. Gok for their assistance. The authors are grateful to R. Pehl for his comments about the preparation of this paper and we thank J. Hollander for his encouragement.

Fuel Gasification

Prediction of Sulfur Species Distribution by Free Energy Minimization

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■ The principle of thermodynamic free energy minimization has been applied to fossil fuel gasification processes to predict the effect of operating variables on the composition of the equilibrium product gas. Particular attention has been paid to sulfur-containing species so that the requirements of potential desulfurization processes can be better defined. At conditions representative of current gasification technology, hydrogen sulfide, as expected, is the predominant sulfur species. Small, but significant amounts of carbonyl sulfide are also present at these conditions. Extension to gasification conditions likely to be encountered as technology progresses shows decreasing hydrogen sulfide concentration with carbonyl sulfide and/or diatomic sulfur concentrations increasing.

Calculation of chemical equilibria in complex gas-solid reacting systems is greatly facilitated by application of the principle of free energy minimization. This approach provides numerous advantages over the traditional equilibrium constant method, particularly when the number of species present is large. Practically speaking, the problem is changed from one of solving a set of nonlinear algebraic equations to one in which the minimum of the free energy function of the mixture is found. Further it is not

Literature Cited

- Friedlander, S. K., *Environ. Sci. Technol.*, **7**, 235-40 (1973).
Giauque, R. D., Goulding, F. S., Jaklevic, J. M., Pehl, R. H., *Anal. Chem.*, **45**, 671-81 (1973).
Gordon, G. E., Zoller, W. H., Gladney, E. S., Jones, A. G., *Proc. Amer. Nucl. Soc. Topical Meet.*, on Nucl. Meth. in Environ. Res., edited by J. R. Vogt et al., Univ. of Missouri, Columbia, Mo., 1971.
Goulding, F. S., Jaklevic, J. M., Jarrett, B. V., Landis, D. A., in "Advances in X-ray Analysis," Heinrich et al., Eds., Vol. 15, 470-82, Plenum Press, New York, N.Y., 1972.
Goulding, F. S., Jaklevic, J. M., Jarrett, B. V., Landis, D. A., Loo, B. Y., Menge, J. D., "An Automatic X-ray Fluorescence Analyzer for Air Particulate Filters," Lawrence Berkeley Laboratory, Berkeley, Calif., Rept. LBL-1743, 1973.
Hidy, G. M. et al., "Characterization of Aerosols in California," North American Rockwell Science Center, Thousand Oaks, Calif., Rept. SC524.191R, 1973.
Jaklevic, J. M., Giauque, R. D., Malone, D. F., Searles, W. L., in "Advances in X-ray Analysis," Heinrich et al., Eds., Vol. 15, 266-75, Plenum Press, New York, N.Y., 1972.
Wesolowski, J. J., Appel, B. R., Alcocer, A., "The Use of the Lundgren Impactor for Particle Size Measurements," Calif. Dept. of Public Health, Berkeley, Calif., Rept. AIHL 138, 1973.

Received for review July 9, 1973. Accepted November 30, 1973.
The X-ray fluorescence analysis work has been supported by both the U.S. Atomic Energy Commission and the California Air Resources Board.

necessary that the species composition of the reactant mixture be known—only the elemental composition of the mixture and those species present at equilibrium need be specified.

The thermodynamic basis of free energy minimization is well summarized (Van Zeggeren and Storey, 1970). Though the majority of past applications have been in the aerospace area, the need to predict equilibria in complex systems arises in many fields. The relationship between the equilibrium composition and the actual composition from a process which is governed by kinetic factors must be examined critically. However, for many high-temperature processes the kinetics are so rapid that the actual product composition and the equilibrium composition are quite close.

In this paper free energy minimization calculations are used to predict the distribution of sulfur species from fuel gasification processes. Limited published results (Robson et al., 1970) report the distribution of sulfur between H_2S and COS for specific gasification processes operating at fixed temperature and pressure. This paper reports the variation of sulfur species over a wide range of potential operating conditions.

The intelligent design of gas desulfurization reactors will require knowledge not only of the distribution of sulfur species but the reaction kinetics for each species as well. Thus these results should be useful in planning desulfurization kinetic experiments.

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Free Energy Minimization

The total free energy of a system composed of n gaseous species (assumed ideal) and $(q - n)$ pure condensed species having an activity coefficient of one is

$$F(\bar{x}) = \sum_{i=1}^n x_i [(F_T^\circ/RT)_i + \ln P + \ln x_i/\bar{x}] + \sum_{i=n+1}^q x_i (F_T^\circ/RT)_i \quad (1)$$

where x_i is the number of gram-moles of specie i and \bar{x} is the total gram-moles of gaseous species, $\bar{x} = \sum_{i=1}^n x_i$. In this equation the terms F_T°/RT represent the free energy function of the pure components while the logarithmic terms represent the free energy of mixing for ideal gases.

The problem thus becomes one of finding the proper combination of the gas and solid compositions, x_i 's, at fixed temperature and pressure such that $F(\bar{x})$ in Equation 1 is minimized. The system is further constrained since the number of gram-atoms, b_j , of each of the m elements in the system is specified—i.e.,

$$b_j = \sum_{i=1}^n a_{ij}x_i + \sum_{i=n+1}^q a_{ij}x_i \quad j = 1, 2, \dots, m \quad (2)$$

The coefficients a_{ij} represent the number of gram-atoms of the j th element in the i th species.

The computation procedure employs Newton's optimization method and satisfies constraints using Lagrange multipliers. Computer implementation of this mathematics also includes additional sophistication to ensure rapid convergence to the minimum free energy. One of these features is the procedure for temporarily eliminating trace species. With this and other features, machine time (IBM 360/65) for 42 species was less than 0.5 sec per case. Complete program details have been published (del Valle et al., 1967).

The following information is required as program input: (1) The free energy function F_T° for each of the n gaseous species and $(q - n)$ condensed species present in the equilibrium mixture. Such data are tabulated for large numbers of chemical species (McBride et al., 1963; Stull, 1965). As input to this program the tabulated data were fitted to a polynomial of the form:

$$\frac{F_T^\circ}{RT} = A_1(1 - \ln T) - \frac{A_2T}{2} - \frac{A_3T^2}{6} - \frac{A_4T^3}{12} - \frac{A_5T^4}{20} - \frac{A_6}{T} - A_7 \quad (3)$$

Thus the coefficients A_1 through A_7 are the actual input data.

(2) An initial estimate of the equilibrium composition of each of the gaseous and condensed species subject to the constraint imposed by Equation 2.

(3) The temperature and pressure of interest.

The number of species which may be considered is limited only by the availability of thermodynamic data and

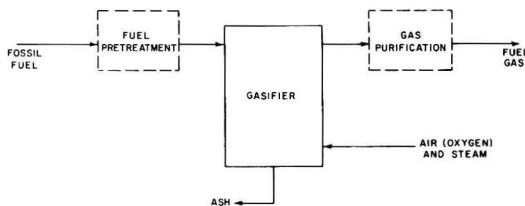


Figure 1. Schematic of partial oxidation process

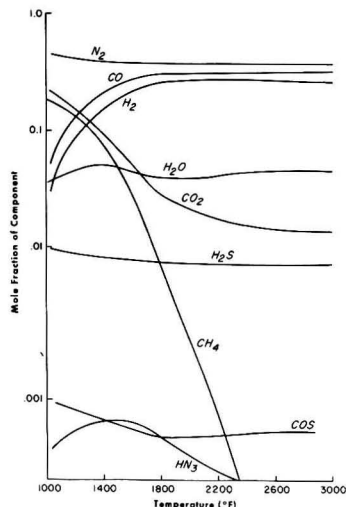


Figure 2. Effect of temperature: equilibrium gas composition

the storage capacity and execution time required on the computer. In the current study, as many as 42 species were considered in the early calculations. This number was gradually reduced by omitting those species whose equilibrium concentrations were less than 10^{-6} throughout the entire range of conditions.

Fossil Fuel Gasification

A large number of potential processes for fossil fuel gasification are under development (Robson et al., 1970). While each of these processes contains inherent differences, the initial partial oxidation step illustrated in Figure 1 is basically the same. This step determines the distribution of sulfur species in the product gas.

The primary operating variables in partial oxidation include: elemental composition of the fossil fuel, relative amount of air (or oxygen) and steam used, pressure, and temperature. In an operating system these variables are not all independent. For example, the temperature of the

Table I. Elemental Analysis of Fossil Fuels and Combined Feeds to Gasification Unit

Element	Fuel analysis, mass %		Gasifier feed analysis, at. %	
	Fuel I	Fuel II	Fuel I	Fuel II
Hydrogen	5.3	4.0	30.1	20.6
Carbon	68.5	75.2	15.8	17.4
Oxygen	8.5	0.0	18.6	19.8
Nitrogen	1.4	1.4	35.1	41.9
Sulfur	4.1	3.6	0.4	0.3
Ash	12.2	18.8	—	—

* Ash-free basis.

Table II. Chemical Species Considered as Possible Components of Equilibrium Mixture

C(S)	CHO(g)	C ₂ (g)	HO(g)	NO(g)	OS(g)
C(g)	CN(g)	C ₂ H ₂ (g)	HS(g)	NO ₂ (g)	O ₂ (g)
CH(g)	CO(g)	C ₂ H ₄ (g)	H ₂ (g)	NS(g)	SO ₂ (g)
CH ₂ (g)	CO ₂ (g)	C ₂ N ₂ (g)	H ₂ O(g)	N ₂ (g)	SO ₃ (g)
CH ₃ (g)	COS(g)	C ₂ (g)	H ₂ S(g)	N ₂ O(g)	S(g)
CH ₄ (g)	CS(g)	H(g)	H ₃ N(g)	H ₂ O ₂ (g)	S(s,1)
CHN(g)	CS ₂ (g)	HN(g)	N(g)	O(g)	S ₂ (g)

product gas is a function of the heating value of the fuel and the quantities of air and steam utilized. For the purposes of this computation, however, we have considered the variables to operate independently so that the effects of change in a single variable might be observed.

Results

Reference Cases. Two standard fuel compositions were considered in the current study. The ultimate analyses of both are summarized in the first two columns of Table I. Fuel I is typical of much of the high-sulfur coal found in the United States while fuel II is representative of a high-sulfur, low-temperature coal char. The potential importance of coal char for such uses as power generation has been discussed (Squires, 1970). The primary difference in elemental compositions results from the removal of hydrogen and oxygen during pyrolysis. While the sulfur content is lower than that for fuel I, fuel II is still considered to be high in sulfur.

Reference case gasification conditions were selected to be: temperature, 2300°F; pressure, 20 atm; oxidation mixture, columns 3 and 4 of Table I. Note that this mixture corresponds to 59% of the oxygen required for total combustion and a molar ratio of steam to air of 0.36. The 59% oxygen is the sum of the input from air and steam. These gasification conditions approximate the conditions expected in a third-generation coal gasification process (Robson et al., 1970).

As previously mentioned, as many as 42 chemical species were considered as possible components of the equilibrium mixture. These species are summarized in Table II.

The composition of major components in the equilibrium gas mixture for these reference cases is listed in Table III. As expected, the primary components are nitrogen, carbon monoxide, and hydrogen. Differences in hydrogen concentration between the two fuels are reflected in lower equilibrium concentrations of all hydrogen-containing species.

More than 99.5% of the total sulfur present appears as hydrogen sulfide plus carbonyl sulfide. However, the molar ratio of H₂S to COS drops from 28.9 to 16.5 when going from fuel I to fuel II. The sensitivity of sulfur distribution to available hydrogen is considered in more detail at a later point.

Effect of Temperature. In Figure 2 the variation in the mole fraction of the major components with temperature is shown when fuel I is gasified. At high temperatures, N₂, CO, and H₂ are the major components while H₂S and COS are the primary sulfur species. The fractions of CO₂

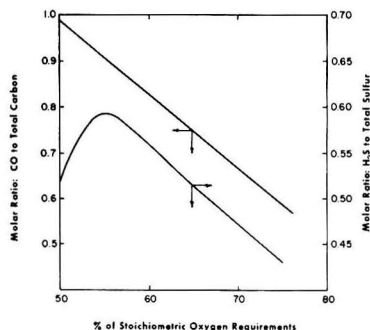


Figure 3. Effect of oxygen: decreasing CO and H₂S in product gas

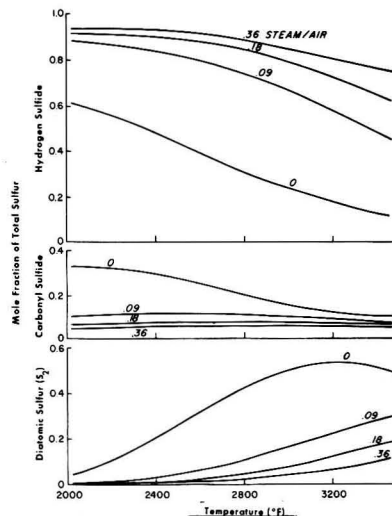


Figure 4. Effect of hydrogen: distribution of major sulfur species

and CH₄ are large at low temperature but decrease rapidly as the temperature is raised. Gasification conditions for this plot are identical to the reference case except that temperature becomes a variable. Similar results are obtained from fuel II except that the equilibrium concentration of all hydrogen containing species is lowered.

The distribution of sulfur species as a function of temperature is quite different for the two fuels. For fuel I H₂S comprises between 94% and 97% of the total sulfur present; for fuel II the fraction of sulfur present as H₂S varies from 72–95%. In all cases the sum of H₂S and COS sulfur account for more than 99.5% of the total sulfur.

Effect of Pressure. Pressure has very little effect upon the distribution of major components in the equilibrium gas over a range of 1–50 atm at temperatures from 1000–3500°F. For example, the equilibrium mole fraction of nitrogen changes by less than 1% while the fraction of H₂S changes by about 3%. Certain of the minor constituents do, however, exhibit considerable pressure dependence. At 2300°F, the mole fraction of methane increases by a factor of approximately 250 as the pressure is increased from 1–50 atm. However, the mole fraction of methane at the highest point is still less than 10⁻³.

Effect of Oxidation Mixture Composition. The composition of the oxidation mixture is important in determining equilibrium gas composition—particularly with respect to the sulfur species and carbon monoxide. This effect has already been encountered in Table II where the importance of fuel composition on the equilibrium gas product was illustrated.

Other than the composition of the fuel itself, the amounts of air (oxygen) and steam used during gasification are the primary mixture variables. As the amount of oxygen is raised toward 100% of stoichiometric, the amounts of CO and H₂S decrease as more CO₂ and SO₂ are formed. Figure 3 illustrates this situation for the gasification case of fuel II with varying quantities of oxygen and no steam added. This situation, it should be mentioned, is least conducive to hydrogen sulfide formation, as the only source of hydrogen is that initially present in the fuel.

The indicated increase in H₂S above 50% oxygen deserves explanation. When oxygen is extremely scarce (50% of stoichiometric), a significant amount of carbon com-

Table III. Equilibrium Composition of Reaction Mixture

Oxidation mixture: Analysis in Table I
Temperature: 2300°F
Pressure: 20 atm

Species	Fuel I, mol frac	Fuel II, mol frac
N ₂	0.3614	0.4339
CO	0.3080	0.3325
H ₂	0.2640	0.1620
H ₂ O	0.0412	0.0371
CO ₂	0.0177	0.0280
H ₂ S	0.0072	0.0061
COS	0.0002	0.0004
CH ₄	0.0002	0.0001
NH ₃	3×10^{-5}	2×10^{-5}

Composition at equilibrium of all other species was less than 10^{-4} .

bines directly with sulfur to form carbon disulfide. In fact, 17.5% of the total sulfur is present as CS₂ under these conditions. However, at 55% oxygen more carbon combines with oxygen and only 1.2% of the total sulfur appears as CS₂. This "liberated" sulfur initially forms H₂S corresponding to the H₂S peak at 55% oxygen. As the amount of oxygen is further increased, H₂S is gradually replaced by oxygen-sulfur species such as COS and SO₂.

Let us now inquire further into the effect of decreasing hydrogen on the distribution of sulfur species. An important function of the steam used in gasification is temperature control since the carbon-steam reaction is endothermic. Future gasification research will undoubtedly aim at higher exit gas temperature. Thus it is logical to assume that the amount of steam used in gasification will decrease in the future. Since steam is the primary source of hydrogen, this decrease will significantly reduce the pro-

portion of H₂S in the fuel gas with increasing amounts of COS and S₂(g). Figure 4 indicates the combined effect of hydrogen availability and temperature. All of the results are reported at a constant quantity of oxygen equal to 59% of stoichiometric. Thus, decreased steam is compensated by increased air to maintain the constant oxygen level.

In Figure 4, the fraction of the total sulfur contributed by the three major sulfur species is plotted as a function of temperature at four different steam/air ratios from zero to 0.36. Hydrogen sulfide, it will be noticed, decreases with increasing temperature and decreasing availability of hydrogen. The concentration of carbonyl sulfide is relatively independent of temperature except at the lowest hydrogen levels. S₂ increases rapidly with increasing temperature and with decreasing hydrogen. However, the S₂ concentration is quite small near the reference case temperature of 2300°F except at the lowest hydrogen levels.

Literature Cited

- del Valle, E. G., April G. C., Pike, R. W., Final Rept. CR-79677, National Aeronautics and Space Administration, 1967.
McBride, B. J., Hermel, S., Ebberes, J. G., Gordon, S., Rept. NASA-SP-3001, National Aeronautics and Space Administration, 1963.
Robson, F. L., Giramonti, A. J., Lewis, G. P. Gruber, G., Final Report CPA 22-69-114, National Air Pollution Control Administration, 1970.
Squires, A. M., *Science*, 169, 821 (1970).
Stull, D. R., JANAF Thermochemical Tables, Dow Chemical Co., 1965.
Van Zeggeren, F., Storey, S. H., "The Computation of Chemical Equilibria," Cambridge Press, London, 1970.

Received for review June 18, 1973. Accepted December 27, 1973. Support for the original development of the free energy minimization program was provided by the National Aeronautics and Space Administration (NASA Grant NGR 19-001-059). Application to fuel gasification conditions is supported by the Environmental Protection Agency (EPA Grant 802036) as part of a broader study of high-temperature gas desulfurization.

Theoretical Model for Relating Indoor Pollutant Concentrations to Those Outside

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■ A general ventilation model, which relates indoor pollutant concentrations to those outside, is discussed in detail. When the time interval associated with changes in the outdoor concentration is long compared to that required either to change the air within the building or to remove the pollutant by internal means, the indoor concentration of pollutant can be related to the outdoor concentration by means of a simple expression. In the case of indoor ozone associated with buildings located in photochemically smoggy regions, there is good agreement between theory and experiment. Theoretical considerations suggest that the indoor levels of ozone in many commercial buildings located in Los Angeles could be substantially reduced rather quickly and possibly with relatively little effort.

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Establishing clean indoor air can immediately improve the environment for certain groups, as well as significantly reduce the impact of air pollution upon the general population. One attractive feature about considering indoor air quality is that the decision to make improvements within a particular structure requires the involvement of relatively few persons, and need not wait for the development of the proper legislation and enforcement needed to improve the air quality outdoors. The work up to 1972 was reviewed by Benson et al. (1972). Wallick (1973) has stressed the importance of indoor air quality among other factors associated with the indoor environment experienced within American factories.

To provide a framework useful in understanding the dependence of indoor pollutant levels upon ventilation parameters, geometric factors, and outdoor pollutant levels, a dynamic theoretical model which allows rapid calculation of indoor pollutant levels is needed. Turk (1963),

Hunt et al. (1971), and Cote and Holcombe (1971) have used the well-mixed chemical reactor in their investigations. Sabersky et al. (1973) reported that the model of a well-mixed chemical reactor, involving an outdoor concentration which varied sinusoidally in time and a first-order heterogeneous decomposition step, gave qualitative agreement with data for indoor concentrations of ozone. However, there is a need to develop a dynamic model for reactive pollutants that permits rapid concise calculations useful in developing design guidelines. This work was aimed at the development of such a model.

Theoretical Development

General Aspects. We shall use the model of a well-mixed chemical reactor equation as a statement of mass balance for the airborne toxic substance. Concentration gradients throughout the system are neglected, and consequently the output concentration is equal to that throughout the system at any particular time. In our ventilation model for a structure of volume V , makeup air enters from the outside and passes through a filter at a rate q_0 , air is recirculated through another filter at a rate q_1 , and air infiltrates the structure (from the outside) at a rate q_2 . The indoor and outdoor concentrations of toxin at time t are C_i and C_o , respectively. The net rate at which toxin is added to the indoor air owing to internal sources, s , and internal sinks, R , is $s - R$. The filter, through which the makeup stream is passed, is characterized by a factor $F_0 = (C_{inlet} - C_{outlet})/C_{inlet}$, where C_{inlet} is the pollutant concentration in the air stream just prior to the filter, and C_{outlet} that in the air stream leaving the filter. The recirculated air passes through a filter characterized by F_1 .

For typical ventilation systems, the appropriate starting equation is

$$V \frac{dC_i}{dt} = q_0 C_o (1 - F_0) + q_1 C_i (1 - F_1) + q_2 C_o - (q_0 + q_1 + q_2) C_i + s - R \quad (1)$$

The first three terms on the right-hand side of Equation 1 represent the rate at which the toxin enters the structure via input streams; the fourth term represents the rate at which the toxin leaves the structure via output streams. Air exits the structure either through exfiltration or exhaust ducts. The sum of the rates of exfiltration plus exhaust is, of course, equal to the sum of the rates of infiltration plus makeup. A graphic description of the model is shown in Figure 1. Quite often both the makeup air and the recirculated air are passed through the same filter, in which case $F_0 = F_1 = F$. In general, the filter factors will be a function of pollutant, flow rate, and extent of use. The value of the filter factor and the rate at which it decreases with time must be determined a priori by experimental means. The infiltration rate should be determined a priori for any given operation of any given ventilation system. Generally, the source term will reflect emissions from equipment operated within the structure, and/or the product of chemical reactions. Usually the sink term will originate from either a homogeneous or a heterogeneous chemical reaction; it is likely that many cases of interest will involve either first-order or pseudo first-order kinetics as a result of the low concentrations (i.e., parts per million or less) at which most toxins are generally present. In the case of ozone, the main mechanism of decomposition indoors has been found to involve a first-order heterogeneous mechanism (Mueller et al., 1973; Sabersky et al., 1973); that is, $R = \sum_j k_j A_j C$ where k_j is the decomposition rate on the j th surface with area A_j .

For convenience we shall nondimensionalize Equation 1 to yield

$$\frac{d\theta_i}{d\tau} + \delta\theta_i = \epsilon\theta_o + \sigma \quad (2)$$

where $\theta_i = C_i/C_{ref}$, $\tau = q_0 t/V$, $\alpha = q_1/q_0$, $\beta = q_2/q_0$, $\gamma = \sum_j k_j A_j/q_0$, $\delta = 1 + \alpha F_1 + \beta + \gamma$, $\epsilon = 1 + \beta - F_0$, $\theta_o = C_o/C_{ref}$, and $\sigma = s/q_0 C_{ref}$. The reference concentration, C_{ref} , is any fixed concentration chosen for convenience.

The general solution to Equation 2 is simply

$$\theta_i = \epsilon e^{-\delta\tau} \int_0^\tau e^{\delta\tau} \theta_o d\tau + e^{-\delta\tau} \int_0^\tau e^{\delta\tau} \sigma d\tau + \theta_{i0} e^{-\delta\tau} \quad (3)$$

where $\theta_{i0} = C_{i0}/C_{ref}$ and C_{i0} is the indoor concentration at $t = 0$. Equation 3 relates the indoor concentration of pollutant to that outside. Although the outdoor concentration θ_o generally cannot be predicted accurately for any specific day, air monitoring stations can provide typical daily profiles of air contaminants for many regions throughout the nation. Although internal sources which vary in time can be treated, for convenience we shall take σ to be constant.

Nondimensional quantities are used throughout the presentation that follows in order to provide a more concise discussion than would otherwise be possible. It is also worthwhile to note that there are five separate time scales associated with this problem. First, there is a characteristic time, t_1 , associated with changes in the outdoor concentration. Next, there are four time scales associated with the quantity $\delta\tau$; these are V/q_0 , $V/q_1 F_1$, V/q_2 , and $V/\sum_j k_j A_j$, which represents the characteristic time to exchange the building air with makeup air, the characteristic time to remove the pollutant via the recirculation filter, the characteristic time to exchange the building air with infiltrated air, and the characteristic time to remove the pollutant via a first-order decomposition mechanism, respectively. When the value of t_1 is either small or the same order of magnitude of the inverse of the sum of the inverses of the latter four characteristic times, then the complete solution (Equation 3) should be used in

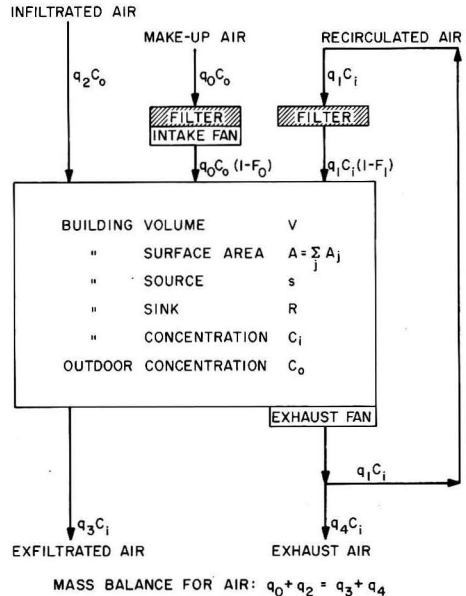


Figure 1. Schematic diagram of ventilation model. Generally, makeup air and recirculated air both pass through the same filter and intake fan system.

ventilation design calculations. However when t_1 is large compared to the inverse of the sum of the inverses of the other characteristic times, the last term in Equation 3 may be neglected, and when C_o can be represented by a straight line during t_1 , a useful approximate expression can be developed.

We shall now consider two specific cases; each case involves a different approximation to the time dependence of the outdoor concentration. The sinusoidal case is used to discuss briefly phase lags associated with the indoor concentrations as compared to those outside. The linear case is then analyzed in great detail because it provides an approximate expression which gives excellent agreement with data and provides a technique for very rapid calculation of indoor air quality for a variety of ventilation conditions and systems.

Sinusoidal Input. The outdoor concentration of a toxin may sometimes be approximated by a sinusoidal function. The typical daily increase of ozone in some photochemically smoggy areas appears roughly to follow a sine wave; in Pasadena the ozone concentration rises from zero at about 8:00 a.m. to some maximum value at about 1:00 p.m., and then decreases to zero at about 7:00 p.m. during a typical smoggy day. In this case $\theta_o = \sin \omega\tau$, C_{ref} is the maximum pollutant concentration outdoors, $\omega = 2\pi fV/q_0$, f is the frequency associated with the sinusoidal behavior of the outdoor concentration of pollutant. It should be noted that the representation of θ_o is valid only for values of $\omega\tau$ such that $\theta_o > 0$. Sometimes a better representation for θ_o is $\theta_o = 1 - \cos \omega\tau$ where C_{ref} is one half of the maximum pollutant concentration outside. In either case, the general aspects of the following discussion are the same. When $C_i = 0$ at $t = 0$ and for a constant source, the indoor concentration of pollutant is given by

$$\theta_i = \frac{\sigma}{\delta} + \left(\frac{\epsilon}{\delta^2 + \omega^2} \right) (\delta \sin \omega\tau - \omega \cos \omega\tau) + \left(\frac{\omega\epsilon}{\delta^2 + \omega^2} - \frac{\sigma}{\delta} \right) e^{-\delta\tau} \quad (4)$$

The first term on the right-hand side of Equation 4 represents the contribution due to internal sources, the second term indicates the possibility of phase lags developing between the indoor and outdoor concentrations, and the third term represents the usual transient part which, in the case of most ventilation systems, decays quite rapidly. In this case, $t_1 = (1/2)\pi/f$ and the other characteristic times are the same as those defined previously. Consequently, during most of the day the indoor concentration is given by the first two terms of Equation 4. It is of interest to note the behavior of Equation 4 in the two limiting cases $\delta \gg \omega$ and $\delta \ll \omega$.

When the outdoor concentration of pollutant changes slowly compared to the time either to change the air within the building or to remove the pollutant by internal means, $\delta \gg \omega$ and the phase lag is small since $\theta_i \sim \sin \omega\tau$; apparently this is generally the case with most commercial buildings.

When the outdoor concentration of pollutant changes rapidly compared to the time to either change the air within the building or to remove the pollutant by internal means, $\delta \ll \omega$ and the phase lag can approach $\pi/2$ radians or half the time period of the interval associated with the outdoor concentration. In this case $\theta_i \sim -\cos \omega\tau$ after t is such that $\omega\tau \gg \pi/2$ radians (i.e., $\theta_i > 0$). In general, the indoor concentration can lag the outdoor values up to $1/4$ of the period associated with the outdoor change.

Ramp Input. Many cases of practical interest involve an input function which does not warrant the use of a sophisticated interpolation procedure in order to predict the pol-

lutant concentration within a time interval defined by two successive data points. When such is the case it would appear that a linear interpolation between two successive data points would be appropriate. It should also be noted that a more sophisticated interpolation procedure does not appear justified in view of the more dominant uncertainties associated with other parameters such as building volume, decomposition rate, and surface area. When such is the case, we shall represent the outdoor concentration by the expression $C_o = C_{o0} + at$ where a is positive during periods of increasing outdoor concentration and negative during periods of decreasing concentration; the quantity C_{o0} represents the outdoor concentration at the beginning of the period and C_{o1} that at the end. The quantity t_1 represents the length of the time period. The value of C_{o1} associated with one time interval becomes the value of C_{o0} for the next. When the initial indoor concentration is C_{i0} and the internal source is constant, the indoor concentration of pollutant is given by

$$\theta_i = \frac{\epsilon\theta_{o0} + \sigma}{\delta} + \frac{b\epsilon}{\delta^2} (\delta\tau - 1) + \left[\theta_{i0} + \frac{\epsilon b}{\delta^2} - \left(\frac{\epsilon\theta_{o0} + \sigma}{\delta} \right) \right] e^{-\delta\tau} \quad (5)$$

where $\theta_{o0} = C_{o0}/C_{ref}$, $b = aV/C_{ref}q_0$, $a = (C_{o1} - C_{o0})/t_1$ and the rest of the terms are the same as those defined previously.

When there is a constant outdoor concentration of pollutant, a constant internal source, a single filter such that $F_0 = F_1$, and no sink, the steady state solution reduces to $\theta_i = (\epsilon + \sigma)/\delta = (1 + \beta - F + \sigma)/(1 + \alpha F + \beta)$ which is the same as that used by Cote and Holcombe (1971) in their discussion of indoor pollutant concentrations of particulate matter and carbon monoxide. When there is a constant outdoor concentration of pollutant, a constant internal source, a single filter such that $F_0 = 0$ but $F_1 > 0$, then Equation 5 reduces to that used by Turk (1963) in his investigations of models suitable for describing the transient concentration of odors within enclosures.

By solving Equation 5 for each of m time intervals of length t_1 , it can easily be shown that the indoor pollutant concentration after the m th time interval of length t_1 is equal to

$$C_{i(m)} = S + [AC_{o(m-1)} + BC_{o(m)}] + [A(C_{o(m-2)} - C_{o(m-1)}) + B(C_{o(m-1)} - C_{o(m)})]e^{-\delta\tau_1} + [A(C_{o(m-3)} - C_{o(m-2)}) + B(C_{o(m-2)} - C_{o(m-1)})]e^{-2\delta\tau_1} \dots + [A(C_{o(0)} - C_{o(1)}) + B(C_{o(1)} - C_{o(2)})]e^{-(m-1)\delta\tau_1} + [C_{i(0)} - S - AC_{o(0)} - BC_{o(1)}]e^{-m\delta\tau_1} \quad (6)$$

where $C_{i(m)}$ is the indoor pollutant concentration after the m th time interval of length t_1 , $C_{o(m)}$ is the outdoor pollutant concentration measured at the end of the m th time interval of length t_1 , $S = s/q_0\delta$, $A = \epsilon/2\tau_1$, $B = (\epsilon/\delta^2\tau_1)(\delta\tau_1 - 1)$, $\tau_1 = q_0t_1/V$, and the rest of the terms are the same as those defined previously.

In many cases of interest the time interval, t_1 , associated with the outdoor concentration is quite long compared to the time required either to change the air within the building or to remove the pollutant by internal means. In such cases, exponential terms in Equation 6 rapidly decay and can be neglected during most of interval, t_1 . During a typical smoggy day in Los Angeles, the outdoor concentrations of ozone may be approximated by a series of straight lines connecting the ozone concentration at each hour, whereas the average commercial air-conditioning system changes the air in a room five to six times per hour (Wohlers, 1971). Operating rooms are recommended to have

15 air changes per hour, and specialized rooms may have up to 20 air changes per hour (Wohlens, 1971). When the outdoor concentration can be approximated by a series of straight lines, and when exponential terms in Equation 6 can be neglected for most of the time, the indoor concentration at the end of the time interval can be calculated from the expression

$$C_{i1} = S + AC_{o0} + BC_{o1} \quad (7)$$

For convenience we shall drop the subscripted parentheses during the rest of the discussion; thus $C_{i(1)} = C_{i1}$, and so forth. Consequently, the indoor concentration consists of source term plus a linear combination of the outdoor concentrations at the beginning and end of the current linear segment time period. In the following discussion, Equation 7 is referred to as the linear-combination theory.

Presentation and Discussion of Results

The indoor concentrations of ozone, measured by a Dasibi Corp. Model 1003 monitor, were recorded in two connected rooms during each of five days in the summer of 1973. The rooms, 312 and 314 Dabney Hall of the Caltech campus, are a conference room and office, respectively; they have a combined volume of 7390 ft³, a combined surface area of 3600 ft², and are air conditioned by the same ventilation system. The makeup and recirculated air streams are passed through a glass fiber filter so that $F_0 = F_1 = F$, and for ozone $F \sim 0$. Duct measurements involving usual anemometry techniques were used to determine the value of q_0 and q_1 . Once the values of q_0 and q_1 were obtained, an exponential dilution test, similar to that described by Drivas et al. (1972) was conducted with a carbon monoxide tracer in order to determine the value of q_2 by difference. The outdoor concentrations of ozone (Huntzicker, 1973) were measured on the roof of the Keck Laboratory by a similar Dasibi monitor, located about 100 yards downwind of Dabney Hall.

When the air-conditioning system was adjusted to maximize the rate of makeup air, $q_0 = 680$ ft³/min, $q_1 = 770$ ft³/min, and $q_2 \sim 0$. On the other hand, when the air-conditioning system was adjusted to minimize the rate of makeup air, $q_0 = 148$ ft³/min, $q_1 = 1150$ ft³/min, and $q_2 = 289$ ft³/min. Fans placed within the room provided good mixing, and the mixing factor (Brief, 1960; Turk, 1963; Constance, 1970) was close to unity. It is especially important to note that increasing the recirculation rate of air significantly increased the infiltration rate. The increase in q_2 associated with an increase in q_1 is thought to be related to a decrease in the pressure difference between the inside and the outside of the building; in both cases, the building pressure was thought to be slightly above the outside static pressure. The infiltration rate should be

measured for any given ventilation system; however, when measurements are impractical, the rates of infiltration for some structures may be estimated by either of two general methods ("ASHRAE Handbook of Fundamentals," 1972). Mueller et al. (1973) found the ozone decay constant for an office to be 0.073 ft³/ft²-min, and that for a bedroom to be 0.122 ft³/ft² - min. In the calculations discussed below, we shall use a value of $k = 0.1$ ft³/ft² - min.

Nominal values of q_0 , q_1 , q_2 , k , A_b , and V were used in the following calculations in the comparison between theory and data. A better fit of the data could have been obtained by changing the value of one or more parameters, but that was thought not worthwhile.

Figures 2 and 3 show the data obtained with operation at the maximum rate of makeup air. The dashed lines represent the line segments connecting the outdoor concentrations of ozone measured each hour on the hour. The solid lines are the predicted indoor concentrations predicted by the linear-combination theory for $\alpha = 1.1$, $\beta = 0$, $\gamma = 0.53$, $\delta = 1.53$, $\epsilon = 1$, in this case and $\sigma = 0$; $C_{i1} = 0.077 C_{o1} + 0.58 C_{o0}$ which is in good agreement with the indoor data. The 1971 threshold limit value, TLV, of 0.1 ppm for ozone ("Documentation of the Threshold Limit Value," 1971) is indicated by the dotted line. As indicated, the linear-combination theory also predicts that filters with values of F greater than about 0.7 would have kept the indoor levels of ozone well below the TLV.

Figures 4 and 5 show the data obtained with operation at the maximum rate of makeup air but with the glass fiber filter replaced with a filter having a value of F between 0.1 and 0.2. In this case $\alpha = 1.1$, $\beta = 0$, $\gamma = 5.3$, $\delta = 2.6$, $\epsilon = 0.8$, $F \approx 0.2$, $\sigma = 0$; and $C_{i1} = 0.047 C_{o0} + 0.41 C_{o1}$ which is in agreement with the indoor data.

Figure 6 shows the data for the case of minimum makeup rate with the glass fiber filter in use. In this case $\alpha = 7.8$, $\beta = 2.0$, $\gamma = 2.4$, $\delta = 5.38$, $\epsilon = 2.9$, $F = 0$, and $\sigma = 0$; and $C_{i1} = 0.084 C_{o0} + 0.46 C_{o1}$ which is again in agreement with the indoor data.

Design of Ventilation Systems

As has been indicated above, by adjusting the makeup rate, the recirculation rate, and the filter factor, it may be possible to either design systems for new buildings or to modify existing ventilation systems in order to keep the ozone concentration from reaching 0.1 ppm.

For several cases of wide public interest, the "problem" of indoor air quality corresponds to economically treating the indoor air in such a manner to maintain $C_i/C_o \leq 0.2$. Since 1955, when the smog alert system was adopted in Los Angeles, about 85 first-stage smog alerts have been declared; and all but 3 or 4 have been due to the outdoor

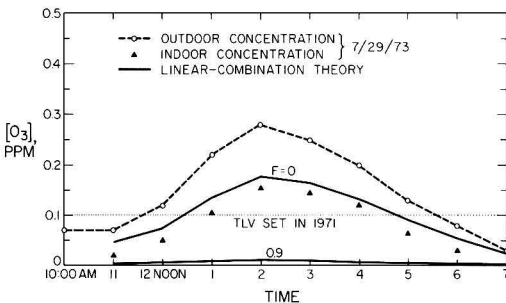


Figure 2. Indoor-outdoor concentrations of ozone for rooms 312 plus 314 of Dabney Hall. Theoretical curves for $F = 0$ and $F = 0.9$. Ventilation system operated at maximum makeup rate during 7/29/73. Filter factor ≈ 0 for ozone

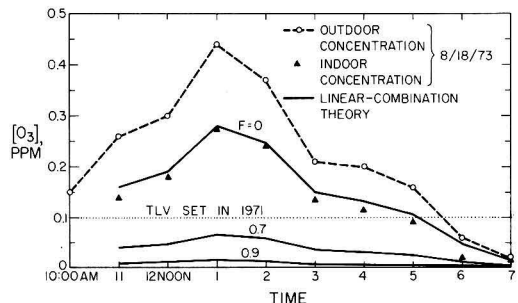


Figure 3. Indoor-outdoor concentrations of ozone for rooms 312 plus 314 of Dabney Hall. Theoretical curves for $F = 0$, $F = 0.7$, and $F = 0.9$. Ventilation system operated at maximum makeup rate during 8/18/73. Filter factor ≈ 0 for ozone

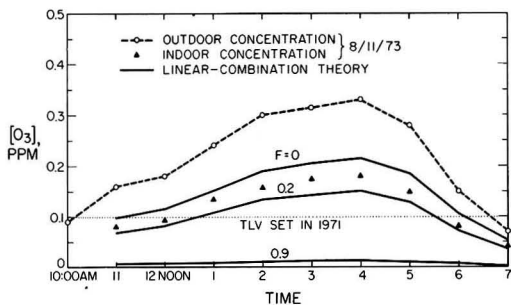


Figure 4. Indoor-outdoor concentrations of ozone for rooms 312 plus 314 of Dabney Hall. Theoretical curves for $F = 0$, $F = 0.2$, and $F = 0.9$. Ventilation system operated at maximum makeup rate during 8/11/73. Filter factor $\approx 0.1-0.2$ for ozone

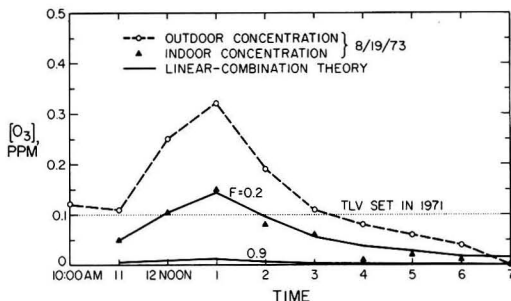


Figure 5. Indoor-outdoor concentrations of ozone for rooms 312 plus 314 of Dabney Hall. Theoretical curves for $F = 0$ and $F = 0.9$. Ventilation system operated at maximum makeup rate during 8/19/73. Filter factor $\approx 0.1-0.2$ for ozone

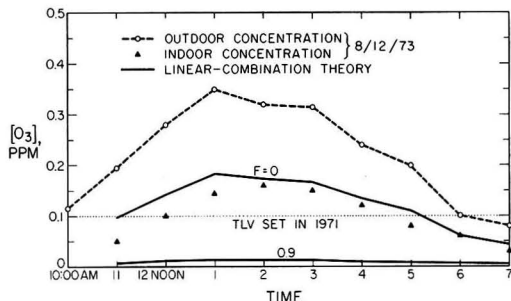


Figure 6. Indoor-outdoor concentrations of ozone for rooms 312 plus 314 of Dabney Hall. Theoretical curves for $F = 0$ and $F = 0.9$. Ventilation system operated at minimum makeup rate during 8/12/73. Filter factor ≈ 0 for ozone

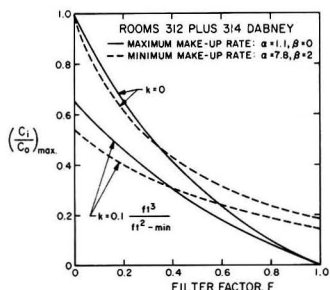


Figure 7. Predicted maximum value of ratio of indoor-outdoor concentrations of ozone as a function of the filter factor

level of ozone reaching 0.5 ppm. Consequently, ventilation systems which maintain $C_i/C_o \leq 0.2$ would have permitted $C_i > TLV$ for ozone only four or five days per year at the worst. In special cases, involving for example the elderly, the ill, and young school children, it may be desirable to maintain the indoor air quality such that $C_i/C_o \leq 0.1$; for such systems located in Los Angeles, the indoor concentrations of ozone during the last 18 years would seldom, if ever, have reached the threshold limit value (i.e., the value of C_o has never been observed to reach the second stage alert level of 1 ppm).

To demonstrate how the linear-combination theory can be used in designing ventilation systems, Equation 7 was used to construct the performance curves shown in Figure 7. For these calculations, the outdoor concentration of

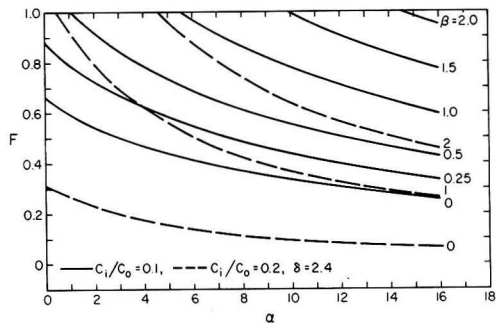


Figure 8. Predicted value of filter factor required to maintain values of indoor/outdoor concentration ratio of ozone for room 312 plus 314 of Dabney Hall. Values of the filter factor vs. recirculation rates of various infiltration rates

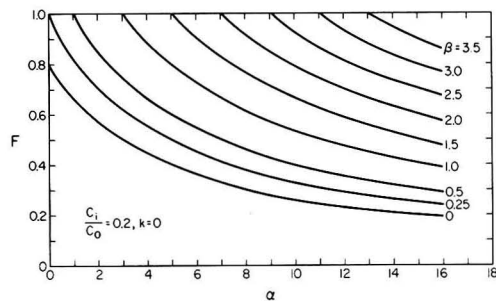


Figure 9. Values of filter factor required to maintain value of indoor/outdoor concentration ratio = 0.2. Sources and sinks neglected

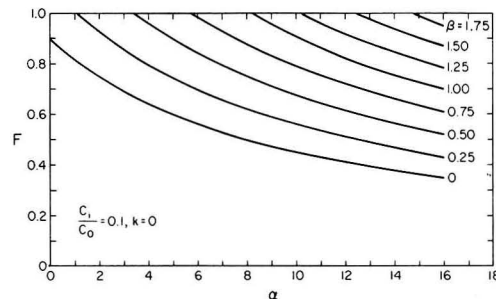


Figure 10. Values of filter factor required to maintain value of indoor/outdoor concentration ratio = 0.1. Sources and sinks neglected

pollutant was taken to be constant over the time period t_1 , and no internal sources were considered (i.e., $C_{00} = C_{01}$ and $\sigma = 0$). The values of α and β were those measured. The bottom two curves were those calculated for the actual system. With filters with $F < 0.4$, the indoor concentration of ozone would be lower with the maximum makeup rate as compared to that with the minimum makeup rate; this effect is due to the increased infiltration rate associated with the minimum makeup rate (i.e., maximum recirculation rate). In this particular case (C_i/C_o) < 0.2 for $F \approx 0.5$ for the maximum makeup rate, and F needs to be ~ 1.0 for the minimum makeup rate. To show the contribution of the heterogeneous decomposition term, the two upper curves, for which $k = 0$, are also presented.

The influence of the ventilation variables for the Dabney Hall rooms is clearly shown in Figure 8. Equation 7 was used to calculate the value of F needed to give $C_i/C_o = 0.1$ and $C_i/C_o = 0.2$, as a function of recirculation rate and infiltration rate. It should again be emphasized that for this case, and probably in general, the value of β will increase with increasing value of α , and should be measured. It is expected that the frequency and cost of either reactivating or replacing the filter to maintain the value of F greater than that indicated in Figure 8 will be important factors in determining the economic desirability of proposed changes in the design of ventilation systems.

If the heterogeneous decomposition is neglected then, for buildings without sources, a general set of curves can be drawn for various values of recirculation and infiltration rates. Values of F obtained from such curves will be somewhat higher than actually needed, and represent an upper bound required to produce the desired ratio of the indoor-outdoor concentrations. Figure 9 indicates the minimum value F , neglecting heterogeneous decomposition, required to establish $C_i/C_o = 0.2$ for various rates of recirculation and infiltration; Figure 10 is for $C_i/C_o = 0.1$.

To indicate typical values of the parameters used in Equation 7, several buildings (or portions thereof) on the Caltech campus were analyzed. The ventilation and geometric quantities are given in Table I. Each case involves a single ventilation system. The makeup rates for the Noyes Lab, and for the two systems in the Keith Spalding building are fixed. The other systems have makeup rates which change with changes in the outdoor temperature; to minimize the load on the air-conditioners, the makeup rates decrease with increasing outdoor temperature. Except in the case of Dabney Hall the surface areas " A_b " are those associated with floors, ceilings, and partition walls. For the room in Dabney Hall, the total surface area was actually measured; for all the other cases the surface area of furniture, books, and so forth was omitted and the " A_b " listings in Table I are minimum values of the surface area available for ozone decomposition. Except for the Dabney

Table I. Listing of Ventilation and Geometric Quantities

Case	Building	q_0 , cfm	q_1 , cfm	q_2 , cfm	s , cfm	V , ft ³	A_b , ft ²	A_b/V , ft ⁻¹	F_0	F_1	Remarks
1	Arms	34,000	0	0	0	475,200	169,100	0.36	0	0	Fixed q_0
2a	East Bridge	28,000	0	0	0	363,500	127,400	0.35	0	0	"
2b	West Bridge	33,000	0	0	0	379,000	140,000	0.37	0	0	"
3a	East Church	50,300	0	0	0	475,000	184,900	0.39	0	0	"
3b	West Church	41,200	0	0	0	384,000	142,000	0.37	0	0	"
4	Crellin	48,000	0	0	0	435,700	159,400	0.37	0	0	"
5a	Dabney Hall, 312 and 314	680	770	0	0	7,390	3,600	0.49	0	0	Max q_0
5b	Dabney Hall, 312 and 314	148	1,150	289	0	7,390	3,600	0.49	0	0	Min q_0
6a	Keith Spalding, basement and 1st floor	11,400	18,600	0	0	406,000	148,000	0.36	0	0	Fixed q_0
6b	Keith Spalding, 2nd, 3rd, and penthouse	6,500	31,700	0	0	376,000	155,000	0.41	0	0	"
7	Kellogg	7,000	0	0	0	218,000	74,800	0.34	0	0	"
8a	Lauritsen-Downs, subbasement	11,700	0	0	0	160,000	47,900	0.30	0	0	"
8b	Lauritsen-Downs, 1-4	8,500	0	0	0	775,000	252,500	0.33	0	0	"
9a	Millikan Library, 10 floors	53,500	0	0	0	673,000	214,000	0.32	0	0	Max q_0
9b	Millikan Library	11,270	42,230	0	0	673,000	214,000	0.23	0	0	Min q_0
11	Noyes Lab (west wing) 5 floors	49,350	94,600	0	0	1,120,000	308,000	0.26	0	0	Fixed q_0
12	Robinson	24,570	0	0	0	413,000	168,700	0.41	0	0	"
13	Sloan Lab	54,000	0	0	0	620,000	161,000	0.26	0	0	"
14a	Spalding, subbasement	19,400	0	0	0	127,500	41,600	0.33	0	0	"
14b	Spalding, basement	16,000	0	0	0	127,500	48,400	0.38	0	0	"
14c	Spalding 1-3 floors	90,000	0	0	0	473,000	161,500	0.34	0	0	Max q_0
14d	Spalding, 1-3 floors	50,000	40,000	0	0	473,000	161,500	0.34	0	0	Min q_0
15a	Steele Lab, 5 floors	90,000	0	0	0	533,000	254,000	0.48	0	0	Max q_0
15b	Steele Lab, 5 floors	18,000	72,000	0	0	533,000	254,000	0.48	0	0	Min q_0

^a In cases where not measured $q_2 = 0$ for purpose of calculation. In actual design calculations, the value of q_2 should be measured or properly estimated.

Hall experiments the infiltration rates were not measured, and were taken to be negligible for the purposes of calculation. The nondimensional parameters associated with Equation 7 are listed in Table II. For commercial size ventilation systems, values of several nondimensional parameters ranged as follows: $0 < \alpha < 5$, $0 < \gamma < 2.5$, $0 < \delta < 4$, $0 < A < 0.2$, $0.2 < B < 0.8$.

The challenge to improve indoor air quality can be translated to that of reducing the values of A and B under the constraints of overall safety, comfort and economics. For the cases discussed in Table II the relatively large values of recirculation rates, which can be obtained during hot smoggy days, suggests that the values of A and B can be easily lowered by inserting filters such that $F > 0$. This conclusion is in agreement with those based upon a previous preliminary investigation conducted by Bush and Segall (1970).

In Table III are listed the values of F needed to ensure that the indoor concentrations of ozone do not rise above 0.2 times the outdoor concentrations. It is important to note that, for all of the buildings we studied which had a recirculation stream, insert filters with $F \geq 0.5$ would ensure that all the indoor levels of ozone would not exceed the TLV of 0.1 ppm during more than four or five days a year. For the buildings which we studied which did not

have a recirculating stream, the corresponding values of F ranged upward to near 0.75; for buildings having negligible rates of infiltration, the maximum value of F required would be 0.8.

It should be noted that, except for the rooms in Dabney Hall, the calculations listed in the tables are for building averages. For any specific room of interest, the ventilation and geometric quantities for that room should be measured if accurate predictions are to be made using Equation 7.

It would appear that a substantial improvement in indoor air quality might be accomplished in the Los Angeles region without greatly sacrificing the other considerations involved in the design and operation of air-conditioning systems.

The example of indoor ozone, associated with buildings located in photochemically smoggy regions, was discussed in some detail. However, the linear-combination model may also be applied to other pollutants.

Summary and Conclusions

A dynamic model for relating indoor pollutant concentrations to those outside was developed and tested. There is good agreement between theory and experiment.

In certain instances the outdoor concentration changes

Table II. Indoor Air Quality Table of Nondimensional Parameters

Case	Building	α	β	γ	δ	ϵ	τ_1	S	A	B	$A + B$
1	Arms	0	0	0.49	1.49	1.0	4.30	0	0.104	0.57	0.67
2a	East Bridge	0	0	0.45	1.45	1.0	4.63	0	0.10	0.58	0.68
2b	West Bridge	0	0	0.42	1.42	1.0	5.22	0	0.094	0.61	0.70
3a	East Church	0	0	0.36	1.36	1.0	6.35	0	0.084	0.65	0.74
3b	West Church	0	0	0.34	1.34	1.0	6.45	0	0.086	0.66	0.74
4	Crellin	0	0	0.33	1.33	1.0	6.62	0	0.085	0.67	0.75
5a	Dabney Hall, 312 and 314	1.1	0	0.53	1.53	1.0	5.52	0	0.077	0.58	0.66
5b	Dabney Hall, 312 and 314	7.8	2	2.43	5.38	2.9	1.20	0	0.084	0.46	0.54
6a	Keith Spalding, basement and 1st floor	1.6	0	1.30	2.30	1.0	1.7	0	0.11	0.32	0.43
6b	Keith Spalding, 2nd, 3rd, and penthouse	4.9	0	2.40	3.40	1.0	1.0	0	0.21	0.21	0.30
7	Kellogg	0	0	1.07	2.07	1.0	1.93	0	0.12	0.36	0.48
8a	Lauritsen-Downs, subbasement	0	0	0.41	1.41	1.0	4.38	0	0.11	0.60	0.71
8b	Lauritsen-Downs, 1-4	0	0	2.96	3.96	1.0	0.65	0	0.097	0.15	0.25
9a	Millikan Library, 10 floors	0	0	0.40	1.40	1.0	4.8	0	0.11	0.63	0.74
9b	Millikan Library, 10 floors	3.7	0	1.90	2.90	1.0	1.0	0	0.12	0.23	0.35
10	Mudd	0	0	0.72	1.72	1.0	3.17	0	0.11	0.47	0.58
11	Noyes Lab, (west wing) 5 floors	1.9	0	0.62	1.62	1.0	2.6	0	0.15	0.48	0.63
12	Robinson	0	0	0.68	1.68	1.0	3.56	0	0.099	0.49	0.59
13	Sloan Lab	0	0	0.29	1.29	1.0	5.22	0	0.12	0.66	0.78
14a	Spalding, subbasement	0	0	0.26	1.26	1.0	7.55	0	0.084	0.71	0.80
14b	Spalding, basement	0	0	0.24	1.24	1.0	9.17	0	0.07	0.74	0.81
14c	Spalding 1-3 floors	0	0	0.32	1.32	1.0	6.35	0	0.091	0.67	0.76
14d	Spalding, 1-3 floors	4	0	1.62	2.62	1.0	1.27	0	0.115	0.27	0.38
15a	Steele Lab, 5 floors	0	0	0.28	1.28	1.0	10.1	0	0.060	0.72	0.78
15b	Steele Lab, 5 floors	4.0	0	1.40	2.40	1.0	2.0	0	0.087	0.33	0.42

$$\alpha = a_1/a_0, \beta = a_2/a_0, \gamma = \sum_i A_i/a_0, \delta = 1 + \alpha f_1 + \beta + \gamma, \epsilon = 1 + \beta - f_0, \tau_1 = a_0 t_1/V$$

$$S = s/a_0, A = \epsilon/\delta \tau_1, B = A(\delta \tau_1 - 1)$$

$$C_{ii} = S + AC_{00} + BC_{01}$$

Table III. Filter Factor Required to Establish $(C_i/C_o) = 0.2$ Assuming Building Is Well Mixed

Case	Building	F for $C_i/C_o = 0.2$
1	Arms	0.70
2a	East Bridge	0.71
2b	West Bridge	0.72
3a	East Church	0.73
3b	West Church	0.73
4	Crellin	0.73
5a	Dabney	0.57
5b	Dabney	0.12
6a	Keith Spalding	0.41
6b	Keith Spalding	0.16
7	Kellogg	0.59
8a	Lauritsen-Downs	0.72
8b	Lauritsen-Downs	0.21
9a	Millikan Library	0.72
9b	Millikan Library	0.24
10	Mudd	0.66
11	Noyes Lab	0.49
12	Robinson	0.66
13	Sloan Lab	0.74
14a	Spalding	0.74
14b	Spalding	0.75
14c	Spalding	0.74
14d	Spalding	0.26
15a	Steele Lab	0.74
15b	Steele Lab	0.29

$$F = (0.8 - 0.2\gamma)/(1 + 0.2\alpha)$$

rather slowly and can be adequately approximated by a straight line within a time interval which is long compared to the time required either to remove the air within the structure or to remove the pollutant by internal means. This is true for ozone pollution associated with buildings located in photochemically smoggy areas such as the Los Angeles region. In such cases the indoor pollutant concentration at the end of any given time interval is equal to the sum of three terms; the first term represents the contribution due to internal sources, and the other two terms represent a linear combination of the outdoor concentrations at the beginning and end of the time interval. Nondimensional coefficients involve the makeup rate, recirculation rate, infiltration rate, filter efficiencies, and first-order chemical reaction terms.

Based upon an analysis of several buildings on the Caltech campus, it appears that for air-conditioned buildings it would be rather easy to reduce the indoor ozone levels to 0.2 of those outside. If this were done, the indoor levels of ozone would exceed the threshold limit value of 0.1 ppm probably no more than four or five days a year, whereas the outdoor concentrations and current indoor concentrations typically exceed this value over 200 days each year.

Acknowledgment

Thanks are due to Leverett Davis, Jr., George Gavalas, Joe Spiegel, Mike Segall, Gordon Peterson, Peter Drivas, Robert Derham, and Judy Speights for their assistance and/or advice during parts of this work. The present study is a part of a continuing program which is being carried out under the joint direction of Rolf H. Sabersky and Fredrick H. Shair, one of the authors.

References

- "ASHRAE Handbook of Fundamentals," Published by The American Society of Heating, Refrigeration and Air-Conditioning Engineers, Inc., 345 East 47th St., New York, N.Y. 10017 (1972).
- Benson, F. B., Henderson, J. J., Caldwell, D. W., "Indoor-Outdoor Air Pollution Relationships: A Literature Review," Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, N.C. 27709 (1972).
- Brief, R. S., *Air Eng.*, 2, 39 (1960).
- Bush, A. F., Segall, M., "Reduction of Smog Effects in California Institute of Technology Buildings," ASHRAE Semiannual Meeting (January 1970).
- Constance, J. D., *Power*, 114, 56 (February 1970).
- Cote, W. A., Holcombe, J. K., "The Influence of Air Conditioning Systems on Indoor Pollutant Levels," Proceedings of Second Conference on Natural Gas Research and Technology, IGT/AGA, J. W. White, Ed., Information Services IGT, 3424 S. State St., Chicago, Ill. 60616 (March 1971).
- "Documentation of the Threshold Limit Values for Substances in Workroom Air," Published by the American Conference of Governmental Industrial Hygienists, 3rd ed. P.O. Box 1937, Cincinnati, Ohio 45201 (1971).
- Drivas, P. J., Simmonds, P. G., Shair, F. H., *Environ. Sci. Technol.*, 6, 609 (1972).
- Hunt, C. M., Cadoff, B. C., Powell, F. J., "Indoor Air Pollution Status Report," NBS Rept. 10591, U.S. Dept. of Commerce, NBS, Washington, D.C. 20234 (April 19, 1971).
- Huntzicker, J. J., *Calif. Inst. Tech.*, 1201 E. Calif., Pasadena, Calif. 91109 (1973).
- Kalika, P. W., Holcombe, J. K., Cote, W. A., *ASHRAE J.*, 12, 44 (1970).
- Mueller, F. X., Loeb, L., Mapes, W. H., *Environ. Sci. Technol.*, 7, 342 (1973).
- "Profile of Air Pollution Control," County of Los Angeles Air Pollut. Contr. Distr., 434 South San Pedro Street, Los Angeles, Calif. 90013 (1971).
- Sabersky, R. H., Sinema, D. A., Shair, F. H., *Environ. Sci. Technol.*, 7, 347 (1973).
- Segall, M., *Calif. Inst. Tech.*, 1201 E. Calif., Pasadena, Calif. 91109 (1973).
- Turk, A., *ASHRAE J.*, 5, 55 (1963).
- Wallick, F., "The American Worker: An Endangered Species," Ballantine Books, Inc., New York, N.Y. (1973).
- Wohlers, H. C., Suffet, I. H., Blakemore, W. S., Kenep, D., Coriell, L. L., McGarrity, G. J., *Am. Ind. Hyg. Ass. J.*, 32, 831 (1971).
- Yocom, J. E., Clink, W. L., Cote, W. A., *J. Air Pollut. Contr. Ass.*, 21, 251 (1971).

Received for review October 12, 1973. Accepted December 19, 1973. This work was supported in part through the Caltech's President's Venture Fund.

Experimental Verification of Linear Combination Model for Relating Indoor-Outdoor Pollutant Concentrations

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■ The linear combination model appears to provide an "upper bound" in relating indoor concentration of ozone to those outside. Tests conducted with a rather large office laboratory indicated that the model is in excellent agreement with ozone concentrations in hallways. The model is in good agreement with ozone concentrations in rooms; however, ozone concentrations vary somewhat from room to room depending on the local ventilation and geometric parameters.

A ventilation model, which relates the indoor concentration of a pollutant to that outside, has been proposed recently by Shair and Heitner (1974). Where valid, the model yields a simple expression which permits rapid concise calculations useful for developing design guidelines. This model is based upon approximating the air flow throughout a building by means of a well-mixed chemical reactor wherein constant sources and first-order reactions can occur and various input and output streams are present.

In the case of ozone, the main mechanism of decomposition indoors has been found to involve a first-order heterogeneous mechanism (Mueller et al. 1973; Sabersky et al. 1973). It is apparent from the above-mentioned references that an appropriate value of the decomposition constant for a building is about $0.1 \text{ ft}^3/\text{ft}^2\text{-min}$; this value of k was used in the calculations associated with this investigation. Preliminary experiments indicated that the model adequately predicts the indoor concentration of ozone for very small ventilation systems associated with buildings located in photochemically smoggy areas. If this model is found to provide an accurate description for large commercial buildings, then the improvement of the indoor air quality through the use of various filters can be adequately predicted; such predictions are important to make before the expenses associated with changes in large ventilation systems (such as those in schools, public libraries, or hospitals) are incurred. The purpose of this investigation was to compare the model predictions with indoor pollution concentrations measured as a function of time at various positions throughout a rather large laboratory-office building.

Characterization of Building

For convenience we decided to investigate the west wing of the Noyes Laboratory of Chemical Physics located on the Caltech campus. The west wing has a constant ventilation system which draws in 49,350 cfm of makeup air and has a recirculation rate of 94,600 cfm. All the windows are permanently sealed, and manometer measurements indicated that the building air pressure is about 0.005 in. of water higher than the outside static pressure; consequently the rate of infiltrated air was considered to be negligible. The west wing, comprised of a subbasement, base-

ment, first floor, second floor, and third floor, has a volume of 1,120,000 ft^3 and a total surface area of about 308,000 ft^2 . It should be noted that the surface area was obtained by using a string to measure the total length of the hull plus partitions as indicated on blueprints, and does not take into account such items as furniture, equipment, or books. During these tests the building was equipped only with treated cotton fabric filters which remove particulates but not gaseous pollutants such as ozone. This investigation focused upon ozone because it is a continuing and dominant pollutant associated with photochemical smog, and the filter technology currently exists (although not yet widely used) to maintain indoor concentrations below a desired level such as the threshold limit value of 0.1 ppm.

There are five fans associated with the ventilation sys-

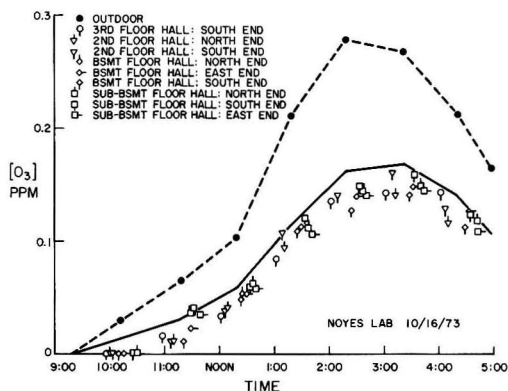


Figure 1. Concentration of ozone vs. time for hallways in Noyes Laboratory, October 16, 1973

Solid line represents prediction by linear-combination model

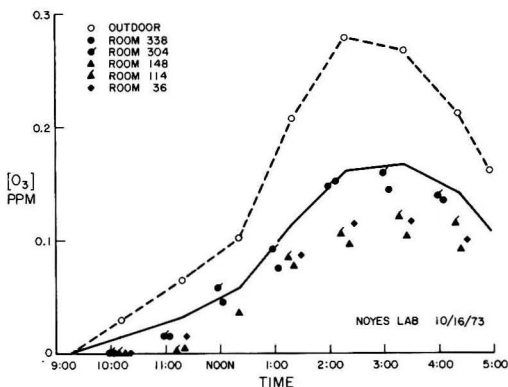


Figure 2. Concentration of ozone vs. time for various rooms in Noyes Laboratory, October 16, 1973

Solid line represents prediction by linear-combination model

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tem. One fan supplies the air used for the fume hoods. The makeup air, drawn in at ground level, is mixed with the recirculated air and then evenly distributed via three intake fans to the subbasement, basement plus first floor, and second plus third floors, respectively. Each room involved in this study has its own intake vent and its own exhaust vent. Except for the first floor, the hallways have separate ventilation inputs of 800 cfm, and participate in exchanging air with rooms via doorways. Following the notation in Shair and Heitner (1974), the ventilation and geometric quantities for the Noyes laboratory are $q_0 = 49,350$ cfm, $q_1 = 94,600$ cfm, $q_2 \approx 0$ cfm, $s \approx 0$ cfm, $V \approx 1,120,000$ ft³, $A_b \approx 308,000$ ft², and $F_0 = F_1 = 0$; the appropriate nondimensional parameters have values $\alpha = 1.9$, $\beta = 0$, $\gamma = 0.62$, $\delta = 1.62$, $t = 1$, $\tau_1 = 2.6$, $S = 0$, $A = 0.144$, and $B = 0.477$. It should be noted that the value of A_b was obtained from considering only the blueprints of the building. Consequently, the value of A_b is a "lower bound" since the surface area associated with items such as furniture, books, or equipment was not considered; correspondingly the values of A and B are thought to be "upper bounds."

Experimental Procedure

All measurements were taken with a Dasibi Corp. Model 1003 ozone monitor based upon ozone absorption of the 2537 Å line emitted from a mercury lamp. The ozone detector was transported throughout the building by a cart; two 12-V storage batteries and a converter (Abbott Transistor Laboratories, Inc., solid state converter model number PN24T-115-60) provided the portable power supply. The outdoor concentrations of ozone were obtained by placing the detector outside and a few feet upwind of the ventilation intake.

Presentation and Discussion of Results

Tests were conducted during several days. Typical results are shown in Figures 1 and 2. As indicated in Figure 1, the ozone concentration throughout the hallway system, except for the first floor hallway, is in excellent agreement with the values predicted from the linear combination model. The ozone concentrations associated with the first floor hallway fluctuated from values that were substantially lower to values just slightly lower than those predicted from the linear combination model; the fluctuations appear to be related to the frequent opening of the outside doors which occurs throughout the day. The first floor hallway is directly connected (via an open doorway), to the ventilation system associated with the east wing of the building. The east wing of the building is characterized with values of A and B which are much lower than those previously quoted for the east wing. When an outside door of the west wing is opened, it is thought that because of the pressure difference, air flows from the east wing into the first floor hallway and out the open door; this process is consistent with the observation that the ozone concentration between the east wing and the door would drop when the door was opened and would rise to values slightly below those predicted from the linear combination model when the door had been closed for more than 10 or 15 min.

As shown in Figure 2, the ozone concentrations associ-

ated with various rooms throughout the building individually followed the trend predicted from the model. The model did predict what appears to be an "upper bound." Although there was more variation from room to room than from hallway to hallway, the model does appear to be in good agreement with the data. A more detailed study of the individual rooms indicated that rooms with rugs, excess furniture, excess books, and/or papers had lower ozone levels than those with concrete floors and/or those rooms, with few books and papers present, that appeared to be neater.

Modifications of Filter Systems

When the Noyes Laboratory of Chemical Physics was designed, room was made available for about 95 additional filters to be located a few feet downstream of the particulate filters commonly used in commercial buildings. It should be noted that in this building, and in most commercial buildings, the recirculated air is mixed with the makeup air prior to passing through the above-mentioned particulate filters. Consequently the ozone filters, located downstream of the particulate filters, will be effective in removing ozone created from both internal and external sources; in the case of no internal source, ozone filters need only to take out about one half of the ozone per pass in order to maintain the indoor concentration of ozone at about 0.2 of that outside. However, in cases where there are no or "weak" internal sources, it may be more economical to provide filters which remove ozone from only the makeup air stream. That is, it may be more economical to filter out a portion of the ozone in the makeup air before the makeup and recirculated streams are combined, rather than first diluting the ozone in the makeup air with the recirculated air and then filtering the combined streams. If no internal sources are present, then about 70% of the ozone would have to be removed from the makeup air stream to maintain indoor concentrations less than 0.2 of those outside (i.e., $F_0 = 1 - 0.2(1 + \gamma) \approx 0.68$, and $F_1 = 0$). Currently there does not appear to be enough data concerning the values of filter factors as a function of exposure time, exposure levels, and exposure conditions to permit accurate economical calculations aimed at describing optimum placement, size, and type of filters to reduce the indoor levels to 0.2 of those outside.

Acknowledgment

Thanks are due to Mike Segall, Ken Heitner, Joe Spiegel, and Judy Speights for their assistance during parts of this work. The present study is a part of a continuing program which is being performed under the joint direction of Rolf Sabersky and Fred Shair, one of the authors. This study was also associated with the undergraduate laboratory in Chemical Engineering at Caltech.

Literature Cited

- Mueller, F. X., Loeb, L., Mapes, W. H., *Environ. Sci. Technol.*, 7, 342 (1973).
Sabersky, R. H., Sinema, D. A., Shair, F. H., *ibid.*, p 347.
Shair, F. H., Heitner, K. L., *ibid.*, 8, 444 (1974).

Received for review November 16, 1973. Accepted December 19, 1973. This study was partly supported through the Caltech President's Venture Fund.

Petroleum-Derived and Indigenous Hydrocarbons in Recent Sediments of Lake Zug, Switzerland

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■ Presented are hydrocarbon analyses of recent sediments from Lake Zug, Switzerland. The sediments near the densely populated northern shores of the lake contain large amounts of hydrocarbons, predominantly derived from fossil fuels; indigenous hydrocarbons, presumably derived from aquatic organisms, predominate in the middle part of the lake, adjacent to less densely populated areas.

The ubiquity of hydrocarbons in recent sediments and in living organisms is well established. Some of these compounds have biological origin, whereas others are derived from pollution by petroleum products (Blumer and Snyder, 1965; Blumer et al., 1972a,b,c; Han et al. 1968, 1969; Meinschein, 1969).

If petroleum products are spilled into rivers, lakes, or the sea, much of the higher boiling material is taken up by the sediments. There, biodegradation is retarded, especially below the water sediment interface (Blumer and Sass, 1972b). With repeated chronic pollution, hydrocarbons may therefore accumulate in the sediments. Some petroleum-derived hydrocarbons may show biological effects even at very low concentration levels.

To anticipate and assess the degradation of natural waterways, their sediments must be analyzed in detail, and a distinction must be made between indigenous and petroleum hydrocarbons.

Here we report an investigation by infrared spectroscopy and gas chromatography of sediment extracts from Lake Zug, Switzerland (Figure 1).

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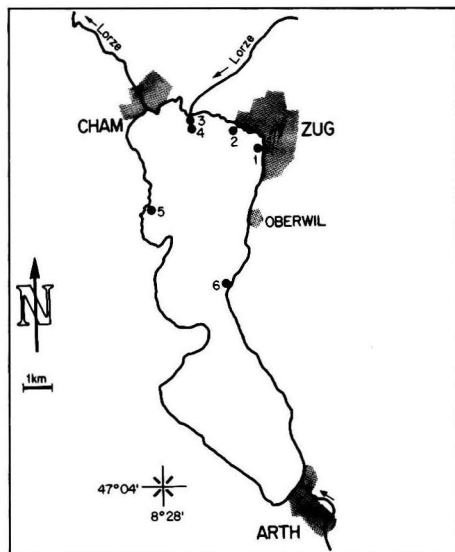


Figure 1. Lake Zug, locations of sampling stations

Experimental

Samples of the sediment surface were taken at six locations near the shores of Lake Zug (Figure 1) in water depths varying from 2–9 meters. Samples 1, 5, and 6 were taken by a diver, whereas at stations 2, 3, and 4 a grab sampler was used.

For infrared analyses, 50 grams of the wet sediment were shaken with 50 ml of CCl_4 for 20 min. The extracts were dried with Na_2SO_4 . The spectrum was recorded between 3500 and 2500 cm^{-1} in a Beckman-IR-8 spectrometer. After percolation through basic Al_2O_3 (Merck, activity I) the spectrum was measured again. The amounts of total extractables and of hydrocarbons were determined by measuring the C—H bands according to API Method 733-58 (1957).

For gas chromatography 50–200 grams of the wet sediment were shaken with 100 ml of pentane. The extracts were dried with Na_2SO_4 , percolated through basic Al_2O_3 (Merck, activity I) and concentrated at room temperature to 1 ml. Aliquots (1–2 μl .) of the solutions were injected into a Carlo Erba-GI gas chromatograph, equipped with a flame ionization detector and a glass capillary column (25m, OV-101, purchased from H. J. Jaeggi, Trogen AR, Switzerland). Helium was used as a carrier gas at a flow rate of 3 ml/min and the column temperature was programmed at 3°/min from 30–230°C.

Results and Discussion

The results of the infrared determinations (Table I) must be considered as only estimates, however the concentrations of hydrocarbons at stations 1, 2, 3, and 4 are significantly higher than at locations 5 and 6. The hydrocarbon concentrations at stations 1, 2, and 4 exceed the maximum concentration (320 $\mu\text{g/g}$ dry weight) determined by Unger (1971) in a similar study of Lake Constance. At stations 5 and 6 the hydrocarbon concentrations are in the same range as the lower values found in Lake Constance.

In the marine sediments of Buzzards Bay, Mass., the background of biochemically derived hydrocarbons lies close to 50–70 $\mu\text{g/g}$ dry sediment (Blumer and Sass, 1972c). The hydrocarbon concentrations in the sediments of the northern part of Lake Zug exceed this value, whereas stations 5 and 6 resemble the unpolluted marine sediments.

Table I. Organic Matter of Lake Zug Sediments Determined by Infrared Spectroscopy and Gas Chromatography

Station no. ^a	CCl_4 extractable, $\mu\text{g/g}$ dry wt	Hydrocarbons, $\mu\text{g/g}$ dry wt	$n\text{-C}_{17}\text{H}_{34}/\text{pristane}$	Pristane/phytane
1	2350	900	1.8	0.8
2	1590 ^b	610 ^b	1.0	1.0
3	570	240	2.8	1.0
4	2470	860	2.0	1.3
5	1010 ^b	140 ^b	c	c
6	300	50	c	c

^a Station numbers refer to Figure 1. ^b Average value of two independent determinations. ^c Not determinable.

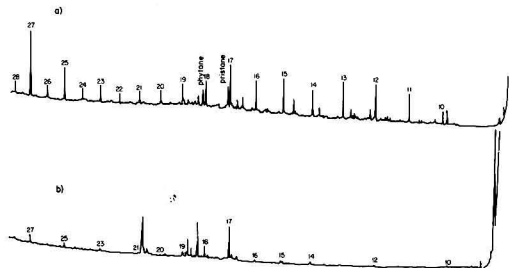


Figure 2. Gas chromatograms of sediment extracts
a. Station 4. b. Station 6. Numbers indicate carbon numbers of *n*-alkanes

The infrared determination of total extractable and hydrocarbon concentrations permits no clear distinction between indigenous and pollution-derived material. Still, it suggests that the sediments near the densely populated shores of the lake are contaminated with petroleum hydrocarbons.

For a better insight into the compositions of these hydrocarbons, the pentane extracts of the sediments were studied by gas chromatography. Stations 4 and 6 (Figure 2) are representative of the northern and middle part of the lake, respectively. Correspondingly, the gas chromatograms demonstrate a considerable difference in their hydrocarbon chemistry.

The main four features are described as follows:

The hydrocarbons at station 4 show a continuous distribution curve of *n*-alkanes in the range of carbon numbers $n = 10-24$; while at station 6 *n*-heptadecane dominates all other *n*-alkanes by a factor of at least 5. A smooth chain length distribution of the *n*-alkanes is typical for petroleum and petroleum products (Philippi, 1965; Zafiriou et al., 1972). The predominance of *n*-heptadecane in Figure 2b is attributed to hydrocarbons produced by algae and other photosynthetic organisms. It is very often the dominant compound in biogenic hydrocarbon mixtures (Han and Calvin, 1969; Youngblood et al. 1971). The *n*-C₁₇ alkane in Figure 2a is also more abundant than the adjacent straight chain alkanes, explained by a superposition of indigenous and polluting hydrocarbons.

The concentration of odd-numbered *n*-alkanes increases again in the range from *n*-C₂₃ to *n*-C₂₇. This feature is common for unpolluted recent sediments (Stevens, 1956; Han et al., 1968; Tissier and Oudin, 1973) and is often observed in terrestrial plants (Clark 1966). In station 4, material transported by the river Lorze may be the reason for the large increase toward *n*-C₂₇.

The isoprenoid hydrocarbons pristane (C₂₀) and phytane (C₂₁) are among the major constituents in station 4, whereas in station 6 they are absent or present only in trace amounts. These two compounds are also major constituents of many crude oils (Speers and Whitehead, 1969; Zafiriou et al., 1972).

The *n*-C₁₇/pristane ratio of the stations from the north-

ern shore varies between 2.8 and 1.0 (Table I). This may be attributed either to different sources or to different degrees of biodegradation of the fossil fuels (Blumer and Sass, 1972b). The pristane/phytane ratio, however, remains remarkably constant, close to unity. In unpolluted marine sediments, phytane is absent or present in a much lower amount than pristane (Blumer and Snyder, 1965).

The very distinct differences in the hydrocarbon compositions are best explained by the presence of fossil fuels in the northern part of Lag Zug. These pollution-derived hydrocarbons are superimposed over a background of indigenous compounds presumably derived from aquatic organisms and from land material transported by the river Lorze. The sediments near the less populated shores, however, seem to contain almost only indigenous hydrocarbons. It does not seem very likely that the contribution by recent metabolic activities changes so much throughout the lake.

To find the sources of those high hydrocarbon concentrations and to estimate the effects of these compounds on the surrounding biota, a more detailed study of sediment extracts and comparisons with possible sources is being pursued.

Acknowledgment

This study was supported in part by the Swiss Department of Commerce (Common Market Project COST 64b) and by the Canton of Zug. The authors would like to thank Max Blumer, Woods Hole Oceanographic Institution, Woods Hole, Mass., for very valuable discussions.

Literature Cited

- American Petroleum Institute, "Manual on Disposal of Refinery Wastes," Vol. IV, API Method I, 733-58, 1957.
- Blumer, M., Sass, J., *Mar. Pollut. Bull.*, **3**, 92-4 (1972a).
- Blumer, M., Sass, J., *Science*, **176**, 1120-2 (1972b).
- Blumer, M., Sass, J., Woods Hole Oceanographic Institution, Tech. Rept. No. 72-19, 1972c.
- Blumer, M., Snyder, W. D., *Science*, **150**, 1588-89 (1965).
- Clark, R. C., Jr., Woods Hole Oceanographic Institution, Tech. Rept. No. 66-34, 1966.
- Han, J., Calvin, M., *Proc. Nat. Acad. Sci. U.S.A.*, **64**, 436-43 (1969).
- Han, J., McCarthy, E. D., Van Hoesen, W., Calvin, M., Bradley, W. H., *ibid.*, **59**, 29-33 (1968).
- Meinschein, W. G., in "Organic Geochemistry," pp 330-56, ed. by G. Eglinton and M. T. J. Murphy, Springer Verlag, New York, N.Y., 1969.
- Philippi, G. T., *Geochim. Cosmochim. Acta*, **29**, 1021-49 (1965).
- Speers, G. C., Whitehead, E. V. in "Organic Geochemistry," pp 638-75, ed. by G. Eglinton and M. T. J. Murphy, Springer Verlag, New York, N.Y., 1969.
- Stevens, N. P., Bray, E. E., Evans, E. D., *Amer. Ass. Petrol. Geol. Bull.*, **40**, 975-83 (1956).
- Tissier, M., Oudin, J. L., *Prev. Cont. Oil Spills Joint Conf., Proc.*, pp 205-14, 1973.
- Unger, U., *Gas Wasserfach, Wasser Abwasser*, **112**, 256-61 (1971).
- Youngblood, W. W., Blumer, M., Guillard, R. L., Fiore, F., *Mar. Biol.*, **8**, 190-201 (1971).
- Zafiriou, O., Blumer, M., Myers, J., Woods Hole Oceanographic Institution, Tech. Rept. No. 72-55, 1972.

Received for review July 9, 1973. Accepted November 1, 1973.

Operational Limits of Vibrating Orifice Aerosol Generator

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■ The relationship between the aperture diameter and the operating frequency for monodisperse vibrating orifice aerosol generators is discussed. The previously reported range $3.5 \leq (\lambda/D_j) \leq 7.0$ for monodisperse aerosol generation is not applicable for all generator aperture diameters. Results are presented denoting the range of λ/D_j values for which monodisperse aerosols are generated with varying generator aperture sizes.

Aerosol generation work was conducted recently by Berglund and Liu (1973) using the vibrating orifice principle for liquid jet disintegration and the solvent evaporation technique. Basically, the device feeds liquid at a known rate through apertures held in place in a stainless steel cup by a Teflon O-ring. The cup is bonded to a piezoelectric transducer which, when excited by the correct ultrasonic frequency, f , causes the cylindrical liquid jet to become unstable and disintegrate into droplets that are injected into a turbulent jet of air to prevent coagulation. The device has great flexibility, if operated within certain limitations, in its ability to generate high-quality aerosols over a wide range of sizes by varying both the aperture size and the nonvolatile solute concentration in a volatile solvent for a particular aperture. The working of the device is described in full by Berglund and Liu (1973). In this note, the subject of the aforementioned limitations will be addressed.

Experiments using a prototype of the described aerosol generation system were carried out which verified the performance of the aerosol generator and the amazing monodisperse nature of the particles produced. By manually sizing several hundred particles using standard light microscopy techniques and utilizing standard statistical calculation methods, we found that the particle size relative standard deviation was ± 0.012 . Care, however, must be exercised in applying the working aerosol generator parameters to achieve these results. In particular, there exists a specific range of disturbance frequencies that cause the jet to break up into a controlled, quality aerosol. In the paragraphs that follow, these frequency bounds will be discussed.

Droplets cannot be made arbitrarily small by making disturbance wavelengths, λ , smaller and smaller by increasing the frequency modulation or by decreasing the velocity of the jet. The reason for this is that the liquid cylinder remains stable with respect to displacements from equilibrium for wavelengths less than πD_j . Thus, one established limitation not to be exceeded is the maximum frequency or minimum, λ , of

$$\lambda_{\min} = \pi D_j \quad (1)$$

where D_j is the jet diameter (which does not equal D_A , the aperture diameter). This result was predicted early by Rayleigh (1945) and later verified by Strom (1969) and Berglund (1972). On the other hand, an upper limit on λ , say λ_{\max} , or a general relation for λ which, when applied yields a range of λ in which only monodisperse aerosols are generated, has not been developed. This note will report on an operating range for λ in which the aerosol is monodisperse for various aperture diameters. It should be

noted that increasing the wavelength by decreasing the frequency or increasing the jet velocity can lead to operating difficulties because the range of the disturbance wavelength may be exceeded which causes the aerosol to become nonuniform with apparently little effect resulting from the mechanical disturbance.

Empirical results for disturbance wavelength aerosol generation such as those given by Schneider and Hendricks (1964) in terms of D_j are

$$3.5 \leq \frac{\lambda}{D_j} \leq 7.0 \quad (2)$$

helpful in establishing an approximate operating frequency range for generating monodisperse aerosols but the relation is not exact. The exact values must be determined experimentally as λ is a function of both aperture size and flow rate. The initial procedure to determine the exact operating range for λ is to apply Equation 1 and use the fact that Q (flow rate) and f are related to λ by the relationship

$$A_j \times \lambda = \frac{Q}{f} \quad (3)$$

and noting that the diameter calculated is not D_A (aperture diameter) but a larger value, D_j (jet diameter). Thus, by the time disturbance causes the jet to break up, the jet has spread out and the diameter is no longer D_A . (The disturbance acts only over an aperture thickness of 4 mils.) The diameter, D_j , then, is a diameter that can be used to compare results predicted by theory (Rayleigh, 1945) and is calculated utilizing the fact that the maximum frequency occurs at the minimum wavelength given by Equation 1 which was found to be agreeably identically

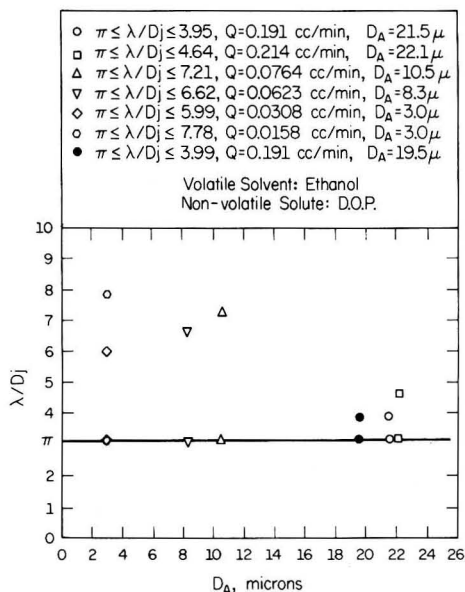
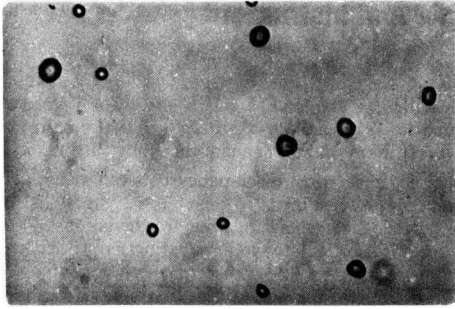
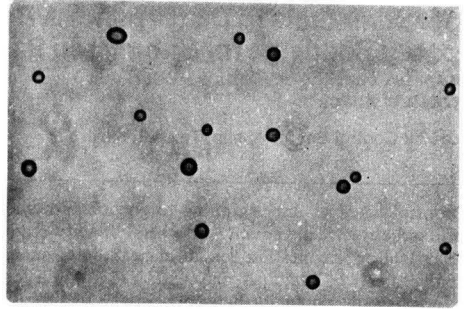


Figure 1. Variation of disturbance wavelength and jet diameter with orifice diameter

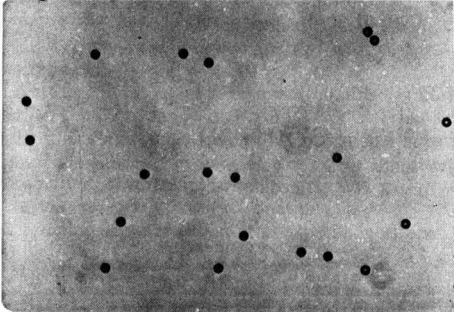
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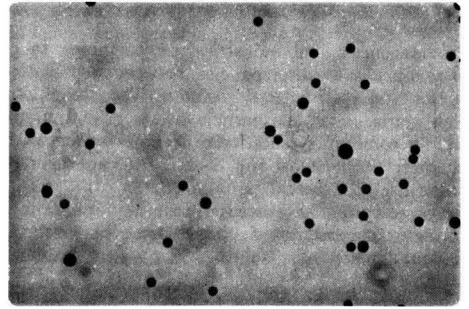
45 KHZ



70 KHZ



82 KHZ-103 K
(Monodisperse Range)



120 KHZ

Figure 2. Variation of particle size distribution with vibrating orifice frequency range

DOP dissolved in ethanol: $D_A = 21.5 \mu$, $Q = 0.191 \text{ cc/min}$, $D_j = 23.27 \mu$, monodisperse operating range $82 \text{ kHz} \leq f \leq 103 \text{ kHz}$ with particle diameter $= 8.45 \mu$. Particles collected on oilphobic glass slide

π . This same methodology was repeated for the upper limit on λ , λ_{\max} , using Equation 3 and the value just calculated for D_j . This procedure leads to a general relationship which includes all the operating parameters necessary to determine the disturbance wavelength which produces monodisperse aerosol when applied to a cylindrical liquid jet

$$\frac{Q}{f_{\max} \times A_j \times D_j} \leq \frac{\lambda}{D_j} \leq \frac{Q}{f_{\min} \times A_j \times D_j} \quad (4)$$

This result has been proved experimentally by applying the above procedure utilizing Equation 4 to various sized apertures and flow rates. Equation 4 has been left in expanded form for clarity purposes and for comparison with earlier published reports. The results are recorded graphically in Figure 1 to reveal the fact that λ/D_j is indeed variable and that any one empirical relation such as Equation 2 is not an exact expression. Equation 4 exactly gives λ uniquely for a range of aperture sizes and flow rates. It is seen in the plot that Equation 2 holds reasonably well for apertures in the $10\text{-}\mu$ size but that the operation envelope decreases to a small size range at the nominal aperture size of 20μ and increases at the smaller aperture size of 3μ . Thus, one is rather limited by the frequency one may apply and still have monodisperse aerosol.

An example illustrating aerosol quality applying Equa-

tion 2 is shown in Figure 2. It is seen that aerosols generated with λ/D_j values ranging between the empirical limits of 3.5-7.0 corresponding to an f range of 92-46 kHz results in poor aerosol quality (note photographs at 45 kHz and 70 kHz). Applying Equation 4 and the described procedure gives an optimum operating range of 103-82 kHz with D_j equal to 23.27μ for an aperture diameter of 21.5μ at a flow rate of 0.191 cc/min . As can be seen from Figure 2, this operating range results in a monodisperse aerosol. A sample at 120 kHz is included as an example of an excessive disturbance frequency and an aerosol of a polydisperse nature. It is felt that the information given in Figures 1 and 2 will be useful for those individuals attempting to generate monodisperse aerosol utilizing the disintegrated jet of liquid technique.

Literature Cited

- Berglund, R. N., PhD Thesis, University of Minnesota, 1972.
 Berglund, R. N., Liu, B. Y. H., *Environ. Sci. Technol.*, 7, 147 (1973).
 Rayleigh, J. W. S., "Theory of Sound," Vol. 2, p 131, Dover Publishing, New York, N.Y., 1945.
 Schneider, J. M., Hendricks, C. D., *Rev. Sci Instrum.*, 35, 1349 (1964).
 Strom, L., *ibid.*, 40, 778 (1969).

Received for review August 8, 1973. Accepted November 30, 1973.
 Work supported by the Environmental Protection Agency, Office of Air Programs, under Training Grant T900203.

Approximations to Discrepancies Between Visual and Instrument Opacity Readings for Submicron Particulate Material

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Control agencies are beginning to encounter numerous conflicts between instrument and visual opacity readings. Theoretical approximation to the magnitude of such discrepancies can be made. A mathematical formula for approximating discrepancies between visual and instrument opacity readings is derived. Some values for these discrepancies are plotted and a specific case is calculated.

State agencies and industries are beginning to come into conflict over discrepancies between visual opacity readings and instrumental readings. These conflicts invariably arise when the particle size is primarily submicron. By combining the efforts of earlier workers (Ensor and Pilat, 1970; Halow and Zeek, 1970), approximations to these discrepancies can be obtained.

Ensor and Pilat have derived a simple formula for calculating transmissivity of plumes from first principals. This equation is:

$$\ln (I/I_o)_i = -WD/k\rho \quad (1)$$

where W = mass concentration in g/m^3

D = plume diameter in meters

ρ = particle density in g/m^3

I_o = incident radiation intensity

I = transmitted radiation intensity

and k is a complex function of the particle radius, frequency distribution, refractive index of the material, and color of the material (white or black). Ensor and Pilat have calculated some curves for k .

On the other hand, Halow and Zeek have combined theoretical calculations for plume brightness and empirical observations of plume opacities to generate a curve relationship. The theoretical sky to plume brightness ratio is given by the formula:

$$\left(\frac{B_{ss}}{B_o}\right) = 10^7 \left(\frac{WD}{\rho}\right) \left(\frac{B_{ss}}{B_o}\right)_o \quad (2)$$

where W , D , and ρ are the same as given above but in units of pounds and feet. The term $(B_{ss}/B_o)_o$ is a different complex function of many of the same variables as k , B_{ss} is the function for plume brightness from scattered light, and B_o represents the background brightness of the sky.

When we determined a curve fit equation for Halow and Zeek's empirical curve relating $(B_{ss}/B_o)_o$ to opacity, the following relationship was obtained:

$$\ln [1 - (I/I_o)]_i = \left[0.9285 + 2.9 \times 10^{-4} \left(\frac{B_{ss}}{B_o}\right) \right] \ln \left(\frac{B_{ss}}{B_o}\right) \quad (3)$$

From Equation 1, instrument opacity readings will be:

$$[1 - (I/I_o)]_i = 1 - \exp(-WD/k\rho) \quad (4)$$

Thus

$$[1 - (I/I_o)]_v - [1 - (I/I_o)]_i = \text{opac (visual)} - \text{opac (instr)} \quad (5)$$

represents the theoretical discrepancy between visual and instrument opacity readings.

For a particle size geometric standard deviation (σ_g) of 2, the specific particulate volume/extinction coefficient ratio, k , in the region $0.1-1 \mu$ can be approximated by the hyperbolic curve function,

$$(\ln r_{gw} + 1.39)^2 = 2.07 (\ln k + 1.83) \quad (6)$$

while the concomitant plume to background brightness ratio $(B_{ss}/B_o)_o$ at 90° by Halow and Zeek can be approximated by

$$(\ln 2 r_{gw} + 0.69)^2 = -1.87 \left(\ln \left[\frac{B_{ss}}{B_o} \right] - 3.22 \right) \quad (7)$$

(These equations are for white particulate material with a refractive index of 1.5.) Solving for the dependent variables in terms of r_{gw} (geometric mass mean radius), we get:

$$k = 0.16 e^{-0.48 (\ln r_{gw} + 1.39)^2} \quad (8)$$

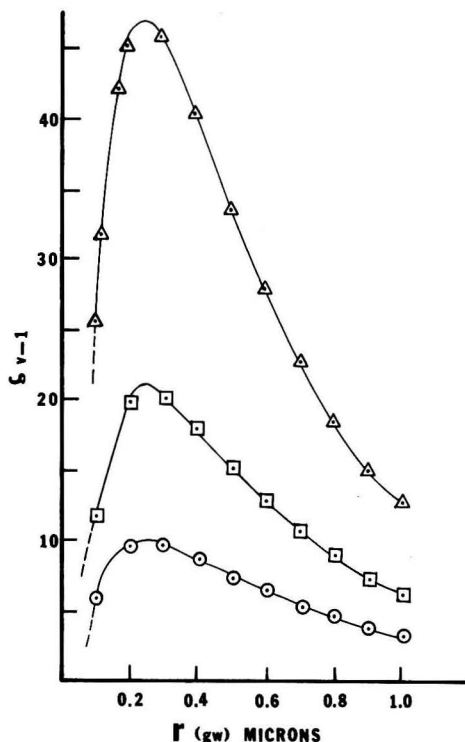


Figure 1. Discrepancies between instrument and visual opacity readings as a function of geometric weight mean particle size for various WD/ρ ratios

○ - 10^{-7} ft; ◻ - 2×10^{-7} ft; ◻ - 4×10^{-7} ft

Discrepancies are given in percent opacity of visual reading above instrument reading

and

$$\left(\frac{B_{ss}}{B_o}\right)_o = 25 e^{-0.53 (\ln 2 r_{gw} + 0.69)^2} \quad (9)$$

When we allow the prelog function in Equation 3 to approximate 0.94, substitute Equations 1, 3, 8, and 9 into Equation 5, and rearrange, the following difference function is obtained:

$$\delta_{v-i}(r_{gw}) = \left[2.5 \times 10^6 \left(\frac{WD}{\rho}\right) e^{-0.53 (\ln 2 r_{gw} + 0.69)^2} \right]^{0.94} + \left[e^{-6.25 \left(\frac{WD}{\rho}\right)'} e^{-0.48 (\ln r_{gw} + 1.39)^2} \right] - 1 \quad (10)$$

where δ_{v-i} represents the fraction difference between visual and instrumental readings. Equation 2 has been converted to read in fractions rather than percent; (WD/ρ) and $(WD/\rho)'$ are in units compatible with their respective parameters.

An example of the discrepancies obtained is plotted for various (WD/ρ) ratios in Figure 1. By varying the constants in Equations 8 and 9, δ functions for different refractive indices and viewing angles can be determined. Closer approximations could be obtained with computer solutions of the theoretical equations for k and $(B_{ss}/B_o)_o$ as functions r_{gw} . However, the experimental error in de-

termining the $(B_{ss}/B_o)_o$ to visual opacity relationship would probably negate the effort involved.

Experimental verification of this discrepancy was observed on a glass furnace stack. The observed parameters were:

$$\begin{aligned} \frac{WD}{\rho} &= 1.96 \times 10^{-7} \text{ ft} \\ r_{gw} &= 0.25 \mu \\ \sigma_g &= \sim 2 \\ [1 - (I/I_o)]_i &= 9 - 12\% \text{ (obsd)} \\ [1 - (I/I_o)]_v &= 35\% \pm 10\% \text{ (obsd)} \\ [1 - (I/I_o)]_v &= 30 - 33\% \text{ (predic)} \end{aligned}$$

The implications of this type of discrepancy will become quite serious in light of the increasing use of instruments vs. human observers for the determination of opacities. A detailed examination of the philosophies behind the use of opacity measurements is indicated.

Literature Cited

- Ensor, D. S., Pilat, M. J., "The Relationship Between the Visibility and Aerosol Properties of Smoke Stack Plumes," Second International Clean Air Congress of the IUAPPA, 1970.
Halow, John S., Zeek, Susan J., "Predicting Ringelmann Number and Optical Characteristics of Plumes," *J. Air Pollut. Contr. Ass.*, 23 (8), 676-84 (1973).

Received for review July 30, 1973. Accepted November 30, 1973.

Mercury-Organic Matter Associations in Estuarine Sediments and Interstitial Water

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■ Sediment from the Florida Everglades and Mobile Bay estuary reveal significant associations between sediment Hg and sediment organic matter and between dissolved interstitial Hg and dissolved organic carbon. The bulk of dissolved Hg and dissolved organic carbon exists in the <500 molecular weight fraction in Everglades pore water and in the >100,000 molecular weight fraction in Mobile Bay pore water. Mercury in sediments and interstitial water occurs at higher concentrations in the Everglades than in Mobile Bay, which receives anthropogenic mercury effluents. When normalized to organic content of the sediment or dissolved organic carbon concentration of the pore water, higher relative mercury concentrations occur in Mobile Bay. Interstitial dissolved mercury is enriched from 2.6 to 36 times over the associated surface water values, and in sulfide-rich pore waters far exceeds the thermodynamic solubility of HgS. Enrichment may be due to formation of organic and polysulfide complexes with mercury.

The quantitative importance and potential ecological effects of anthropogenic additions of mercury to natural aquatic environments have been well documented in the recent scientific literature (Harriss, 1971; Wallace et al., 1971). As a result of several cases of acute mercury contamination in Japan and Sweden, most large industrial sources have been identified and the discharge of mercury to natural waters reduced to negligible flux rates relative to natural sources. However, much of the mercury released prior to the implementation of pollution control

regulations has accumulated in the sediments of watersheds receiving discharges. For example, the combination of high reactivity with particulates (Cranston and Buckley, 1972) and physical conditions conducive to high sedimentation rates has trapped large quantities of mercury in near shore sediments.

The mobility and ultimate fate of mercury in the sedimentary environment are controlled to a large extent by its interstitial water chemistry. The present investigation is a study of sediment mercury and its interstitial water chemistry in an undisturbed estuarine environment, the western section of the Florida Everglades, and in an estuary known to receive industrially derived mercury effluents, Mobile Bay, Ala.

Materials and Methods

Sediment cores were obtained manually from near-shore marsh areas with a piston-fitted polycarbonate tube and immediately extruded into polyethylene Whirlpak bags kept near ambient temperature until squeezing (2-6 hr). Interstitial water was extracted using a nitrogen-operated, Teflon-lined squeezer similar to that described by Presley et al. (1967).

Salinity was determined in the field laboratory on freshly extracted pore water with a Goldberg refractometer (precision ± 0.5 ‰); 25 ml of pore water samples for dissolved Hg analysis were stored in Pyrex containers after acidification with HNO₃ to pH < 1 and addition of 6% KMnO₄; 5-ml samples for determination of dissolved organic carbon (DOC) were placed in glass ampules containing 100 mg of K₂S₂O₈ and 0.1 ml of H₃PO₄, and were then purged of inorganic CO₂ and sealed; sediment samples were kept at 0°C until laboratory analysis.

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Analysis for mercury was performed using the flameless atomic fluorescence technique developed by Muscat et al. (1972). The method consists of either wet digestion of an aqueous sample followed by reduction-aeration and detection of mercury vapor (Hg⁰) by atomic fluorescence, or dry combustion (800°C) of an oven-dried (60°C), homogenized, and pulverized sediment sample and similar detection of Hg⁰. Either technique afforded a limit of detection of 1 ng with an average analytical variation of ±3%.

DOC in the interstitial water was determined using the techniques of Menzel and Vaccaro (1964). The coefficient of variation was found to be ±4%. Sediment organic content, expressed as a percent of the total dry weight (60°C), was determined by weight loss at 550°C for 2 hr.

Total dissolved sulfide (ΣS²⁻) was determined using a modification of the silver-silver sulfide electrode technique of Berner (1963). The recent development of a sulfide antioxidant buffer (Orion, 1969) permits determination of total sulfide concentration down to 0.1 mg/l. Analytical precision was ±10%.

Molecular weight fractionations were performed using an Amicon model 50 stirred ultrafiltration cell with Amicon Diaflo ultrafiltration membranes. The technique is a form of membrane pressure dialysis based on the exclusion principle of gel column chromatography. Fractionation is accomplished by the selective permeability of the membranes to solutes of given molecular dimensions. Procedural details as well as limitations of the technique have been described elsewhere (Blatt et al., 1967). The ultrafilters used provided the following molecular weight ranges: <500; 500-50,000; 50,000-100,000; and >100,000. Boundaries of molecular weight exclusion for each membrane must be regarded only as relative ranges and are better characterized as Amicon cutoff limits. However, for purposes of discussion, they will be referred to as molecular weight ranges.

Results and Discussion

The interstitial water and sediment data collected during this study are summarized in Table I. For the Everglades samples no consistent trends in dissolved interstitial or total Hg concentrations with core depth are apparent. The large variability in dissolved Hg (cores 3E and 5E) suggests that distribution is influenced by a number of interacting factors in this environment. Parameters that may influence Hg distribution in these cores such as salinity, ΣS²⁻, DOC, and sediment organic content show similar variations. In contrast, the single core taken from Mobile Bay exhibits decreasing concentrations of total Hg and interstitial Hg with depth to apparent background levels near 20 cm. The observed gradients correlate with a recent (10-20 years) increment in the release of Hg-containing industrial effluents to this estuary.

To elucidate the geochemistry of Hg in these sediments, correlation and stepwise regression analyses were applied to the data. The concentration of Hg in the sediment is significantly related to the organic content of the sediment for the combined samples ($r = 0.80$). No significant change in the correlation coefficient is noted when the data are divided into more homogeneous groups such as Everglades samples, Everglades surface samples (0-10 cm), and Everglades subsurface samples (>10 cm). Similar correlations have been found in soils by Andersson (1967), in fresh water sediments by Kennedy et al. (1971), and in estuarine sediments by Bothner and Piper (1971).

For the Everglades samples the concentration of dissolved Hg in the pore water is significantly correlated with the concentration of DOC ($r = 0.55$). The correlation increases significantly when calculated for the Everglades surface samples ($r = 0.81$) but decreases to an insignificant level for the Everglades subsurface samples ($r = 0.46$). These results provide some insight into the pro-

Table I. Summary of Interstitial Water and Sediment Data

Core	Core depth, cm	Salinity, 0/00	ΣS ²⁻ , μg/ml	DOC, μg/ml	Sediment organic content, %	Dissolved, Hg, μg/l.	Hg in sediment ppm
1 E ^a	0-10	14.7	0.1	34	68.8	2.14	0.85
	10-20	19.7	1.4	—	69.0	—	0.72
	20-30	20.3	0.1	—	62.7	—	0.70
	30-40	20.8	0.1	30.5	56.1	—	1.62
2 E	0-10	20.8	0.1	32	46.3	1.85	0.73
	10-20	19.7	<0.1	29.9	71.5	1.44	1.33
	20-30	19.7	0.1	27.5	69.4	1.95	1.36
3 E	0-10	19.7	68	77	26.3	3.6	0.28
	10-20	19.7	140	—	27.2	2.98	0.22
	20-30	16.9	140	51	23.5	0.30	0.29
	30-40	16.9	22	54	14.8	1.77	0.24
	40-50	20.8	52	57	26.2	0.47	0.27
	50-60	22.0	22	62	19.3	1.40	0.35
	60-70	22.0	4.4	—	23.8	2.07	0.28
4 E	70-80	22.5	3.3	52	29.0	1.80	0.30
	0-10	16.4	<0.1	24.5	65.4	0.66	1.50
5 E	0-10	18.8	3.6	23.0	44.0	0.26	1.01
	10-20	18.8	.4	24.0	86.6	0.07	1.24
	20-30	19.3	<0.1	24.0	70.7	0.13	1.86
	30-40	18.8	<0.1	22.0	83.7	<0.03	0.76
6 E	0-10	19.7	24	31.5	28.8	0.57	0.76
	10-20	24.6	5.7	32	33.0	0.38	0.30
7 E	0-10	27.2	11.2	—	33.8	0.64	0.32
1 MB ^b	0-10	3.0	<0.1	9.2	19.3	1.04	0.50
	10-20	2.4	<0.1	9.5	21.8	0.64	0.23
	20-30	2.4	<0.1	8.8	19.6	0.36	0.22
	30-40	2.4	<0.1	8.8	4.6	0.25	0.22
2 MB	0-10	2.5	<0.1	6.0	10.2	1.07	0.22

^a Everglades, ^b Mobile Bay.

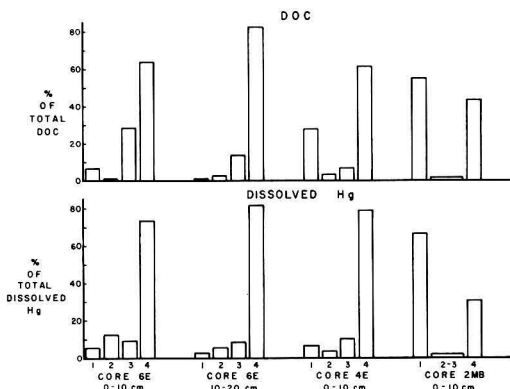


Figure 1. Pore water molecular weight distributions of dissolved Hg and dissolved organic carbon (DOC)

Total pore water and sediment data for these cores are presented in Table I (cores 6E and 4E are from the Everglades, core 2MB is from Mobile Bay). Molecular weight fractions are as follows: 1. >100,000; 2. 100,000-50,000; 3. 50,000-500; 4. <500

cesses that influence the distribution of Hg in recently deposited sediments of the Everglades. Andren and Harriss (1972) have discovered evidence for complexing between dissolved Hg and dissolved organic matter in surface waters of the Everglades. In the process of sedimentation, this complex enters the pore spaces between sediment particles. The decrease in correlation between dissolved interstitial Hg and DOC with increasing core depth suggests that early diagenesis reduces the integrity of the organo-Hg association.

Statistical analyses fail to reveal any significant relationships in the Mobile Bay core, other than the correlation between interstitial Hg and depth ($r = -0.98$). The observed distribution reflects the temporal variation in the release of Hg-containing effluents since the initial use of the Hg-cell chlor-alkali process by industries in this area. Pollution control regulations have recently (July 1970) forced these industries to substantially reduce their Hg loss.

It is interesting that in the Everglades, both dissolved interstitial and total sediment mercury for some samples occur at higher concentrations than those observed in Mobile Bay. Because of the statistical evidence that Hg is primarily associated with organic matter, it is more significant to compare the two environments after normalizing the pore water and sediment Hg concentrations to organic contents of the samples in question. These results can be summarized as follows: Everglades mean dissolved = 0.029 ± 0.022 ng Hg/mg DOC, Mobile Bay mean dissolved = 0.085 ± 0.061 ng Hg/mg DOC; Everglades mean total = 1.3 ± 0.7 ng Hg/mg sediment organic matter, Mobile Bay mean total = 2.3 ± 1.5 ng Hg/mg sediment organic matter. There is a significantly higher relative concentration of total and dissolved interstitial mercury per unit weight of organic matter in the Mobile Bay samples than in the Everglades samples.

The concentration of dissolved Hg in Everglades near-surface pore water (0-10 cm) represents enrichments of 2.6 to 36 times the average overlying water values measured by Andren and Harriss (1972). Dissolved sulfide should effectively precipitate Hg from solution (Krauskopf, 1956; Wallace et al., 1971); however, the calculated solubility of HgS under pH and ΣS^{2-} conditions measured in these cores is 10^{13} to 10^{31} times too small to account for the observed dissolved Hg concentrations. A possible ex-

planation is the formation of polysulfide complexes of relatively high solubility such as HgS_2H^- and $HgS(HS)_2^-$ (Schwarzenbach and Windmer, 1963; Barnes and Czarnske, 1967). Calculations show that formation of these complexes under conditions found to exist in the Everglades sediments could account for Hg concentration near the microgram per liter range (Lindberg, 1973).

A further mechanism of trace metal enrichment in interstitial water is the formation of soluble organometallic complexes (Presley et al., 1972). This is a possible explanation for the observed correlations between dissolved Hg and DOC in the pore water. The molecular weight distributions of organic carbon and associated Hg in pore waters from the Everglades and Mobile Bay are presented in Figure 1. The percent of the total dissolved Hg present in any one molecular weight fraction shows a strong correlation ($r = 0.94$) with the percent of the total DOC in that same fraction. This suggests a significant association between dissolved Hg and organic matter in all molecular weight ranges.

The molecular weight distribution of the organo-Hg complex is influenced by environmental and diagenetic factors. In pore water from Everglades surface sediments (Figure 1, 4E and 6E, 0-10 cm) the organic fraction less than 500 mol wt contains a large majority of the dissolved Hg (73.7-78.8%) and DOC (61.6-64.1%) while the fraction greater than 50,000 mol wt is relatively unimportant. With increasing depth in the core (from sample 6E 0-10 cm to 6E 10-20 cm), there is a general shift of Hg and DOC from higher to lower molecular weight ranges, suggesting that early diagenesis results in degradation of the organic matter. Dissolved organic matter with a molecular weight distribution similar to the Everglades pore water organic matter was described by Rashid and King (1969) as being terrestrially derived and composed primarily of natural fulvic acid compounds.

The greatest proportion of the pore water Hg (66.4%) and DOC (55.0%) exists in the >100,000 mol wt fraction for the Mobile Bay sample. Several hypotheses for the observed difference between the two environments include interaction between Hg and high molecular weight industrial and sewage effluents (Applequist et al., 1972; Rebhun and Manka, 1971) in Mobile Bay, as well as differences in the hydrology and characteristic microbial populations of the areas.

In studies of natural organic matter-trace metal interactions, the general conclusion has been that the lower molecular weight fractions are the most efficient in complexing ability due to their relatively greater total acidity (carboxyl plus phenolic hydroxyl groups) (Rashid, 1971). Table II was prepared by normalizing the absolute amount of Hg associated with selected molecular weight fractions to unit weight of dissolved organic carbon in that fraction. The results indicate a greater proportion of dissolved Hg complexed by the <500 mol wt organic fraction than by the >500 mol wt organic fraction or parent organ-

Table II. Mercury in Selected Molecular Weight Fractions Standardized to Unit Weight of Dissolved Organic Carbon

Sample	Salinity, 0/00	Ng Hg/mg C in molecular weight fraction		
		Parent fraction	>500	<500
6E ^a (10-20 cm)	24.6	11.8	11.7	11.8
6E (0-10 cm)	19.7	18.1	13.3	20.8
4E (0-10 cm)	16.4	27	14.9	34
2MB ^b (0-10 cm)	2.5	178	217	127

^a Everglades, ^b Mobile Bay.

ic fraction for the Everglades samples. The Mobile Bay sample did not follow this pattern.

The stability of the organo-Hg complex may be assessed by observing the Hg to dissolved organic carbon ratios for the parent fractions under different salinity regimes (Table II). If the complex is resistant to competition effects due to major cations, the ratio should remain constant. If, however, Hg has been replaced by other cations, a decrease in the ratio would be expected as salinity increases. Though only limited data is available, it seems apparent that increasing salinity has a negative effect on the Hg complexing capacity of the dissolved organic matter.

Acknowledgment

The authors thank J. Calder and M. Tripp for comments on the manuscript.

Literature Cited

Andersson, A. A., *Grundförbat.*, 28, 95-105 (1967).
Andren, A. W., Harriss, R. C., *Amer. Soc. Limnol. Oceanogr.*, 35th Meeting, Tallahassee, Fla., March 1972.
Appelquist, M. D., Katz, A., Turekian, K. K., *Environ. Sci. Technol.*, 6, 1123-4 (1972).
Barnes, H. L., Czamanske, G. K., in "Geochemistry of Hydrothermal Ore Deposits," pp 334-81. H. L. Barnes, Ed., Holt, Rinehart, and Winston, New York, N.Y., 1967.
Berner, R. A., *Geochim. Cosmochim. Acta*, 27, 563-75 (1963).

Blatt, W. F., Robinson, S. M., Ziplivian, E. M., Hudson, B. G., *Nature*, 216, 511-13 (1967).
Bothner, M. H., Piper, D. Z., in "Proceedings of the Workshop on Mercury in the Western Environment," D. R. Buhler, Ed., Oregon State University Press, Corvallis, Ore. (1971).
Cranston, R. E., Buckley, D. E., *Environ. Sci. Technol.*, 6, 274-8 (1972).
Harriss, R. C., *Biol. Conservation*, 3, 279-84 (1971).
Kennedy, E. J., Ruch, R. R., Shimp, N. F., III. *State Geol. Surv. Environ. Geol. Notes No. 44*, 1971.
Krauskopf, K. B., *Geochim. Cosmochim. Acta*, 9, 1-32 (1956).
Lindberg, S. E., M.S. Thesis, Florida State University, Tallahassee Fla., 1973.
Menzel, D. W., Vaccaro, R. F., *Limnol. Oceanogr.*, 9, 138-42 (1964).
Muscat, V. I., Vickers, T. J., Andren, A. W., *Anal. Chem.*, 44, 218-21 (1972).
Orion Research Inc., *Appl. Bull. No. 12*, Cambridge, Mass., 1969.
Presley, B. J., Brooks, R. R., Kappel, H. M., *J. Mar. Res.*, 25, 355-7 (1967).
Presley, B. J., Kolodnay, Y., Nissenbaum, A., Kaplan, I. R., *Geochim. Cosmochim. Acta*, 36, 1073-90 (1972).
Rashid, M. A., *Soil Sci.*, 111, 298-306 (1971).
Rashid, M. A., King, L. H., *Geochim. Cosmochim. Acta*, 33, 147-51 (1969).
Rebhun, N., Manka, J., *Environ. Sci. Technol.*, 5, 606-9 (1971).
Schwarzenbach, G., Windmer, M., *Helv. Chim. Acta*, 46, 2613-28, in Ger. (1963).
Wallace, R. A., Fulkerson, W., Shults, W. D., Lyon, W. S., Oak Ridge Nat. Lab. Rept. NSF-EP-1, Oak Ridge, Tenn., 1971.

Received for review July 5, 1973. Accepted December 14, 1973. This project has been financed in part with federal funds from the Environmental Protection Agency under Grant No. 801512.

Selenium in North American Paper Pulps

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■ In a collaborative study of four laboratories, 22 samples of paper pulp from different geographic regions of Canada and the United States were analyzed for their selenium content. The selenium concentration of all paper pulps analyzed averaged less than 0.04 ppm; none of the results exceeded 0.2 ppm. These results were obtained using the 3,3'-diaminobenzidine-spectrophotometric and the 2,3-diaminonaphthalene-fluorometric methods.

Various types of paper products have been analyzed for selenium content. Olson and Frost (1970) reported that the selenium concentration in these materials was generally less than 0.05 ppm. These values were about two orders of magnitude lower than those reported by others who in addition suggested that the high selenium content of papers is a major source of health and environmental concern (West and Cimerman, 1964; *Chem. Eng. News*, 1967; Johnson, 1970). In view of the disparity in selenium levels reported for paper products, a collaborative study was conducted to determine selenium contents of paper pulps originating from different geographic regions in North America. These pulps were obtained from various basic producers by the Selenium-Tellurium Development Association. Twenty-two samples were acquired and were analyzed independently by a collaborative effort of four laboratories (Table I).

Procedures

Extreme precautions were applied during handling and analyzing the samples to prevent contamination from at-

mospheric or other sources. All samples except Nos. 1, 2, 3, 5, and 16 were analyzed "as received." Moisture contents were determined on separate sample portions and results were corrected to dry basis (Table II). Samples No. 1, 2, 3, and 16 were air-dried for 24 hr at room temperature, ground in a Wiley mill using a 1.0-mm screen, then ground further in a ball mill for 24 hr. Sample No. 5 was dried by lyophilization, then ground as were the other four samples.

The samples were independently analyzed in the individual laboratories. Different analytical procedures were used, as shown in Table I.

Method A. Ten-gram samples were decomposed with nitric acid in the presence of ammonium vanadate as a catalyst. Selenium was collected by coprecipitation with arsenic, dissolved in nitric acid and determined spectrophotometrically with 3,3'-diaminobenzidine in a toluene extract (Luke, 1959).

Method B. Identical to Method A with the exception of substituting *o*-dichlorobenzene for toluene.

Method C. One- to five-gram sample portions were analyzed by the fluorometric 2,3-diaminonaphthalene method (Parker and Harvey, 1962; Watkinson, 1966).

Method D. One- to four-gram samples were analyzed by the fluorometric 2,3-diaminonaphthalene technique as described by Olson (1969).

For all methods, reagent blanks and selenium standards were carried with each set of three or four determinations.

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Extensive selenium recovery studies were performed by three of the laboratories, adding the equivalents of 0.01–0.10 μg selenium to pulp samples of 1–5 g-wt. Recoveries between 75 and 109% were reported, with the majority of values falling between 95 and 105%.

Discussion of Results

The materials were received in two groups. The Canadian pulp samples were analyzed in May 1971. Two of the participating laboratories used somewhat modified versions of the Luke (1959) procedure. The results obtained were very close to the lower limit of sensitivity for this approach. Samples from the United States were analyzed at the beginning of 1972 by the fluorometric diamionaphthalene method to provide adequate sensitivity for the low selenium level encountered.

All results are shown to one decimal place beyond the

lower limit of reliability to facilitate calculation of averages and standard deviations.

Three laboratories have analyzed repeatedly the NBS-SRM 1571 Orchard Leaves Standard. Results were in good agreement with the nominal, uncertified selenium value of 0.08 ± 0.01 ppm (Table II).

Moisture contents of the original samples varied between 5.3 and 80.2%. Multiple results on pulps of high moisture showed such heterogeneity that it was decided to dry and homogenize five of the samples (Nos. 1, 2, 3, 5, and 16). Precision improved considerably for homogenized pulps.

Acknowledgment

The authors gratefully acknowledge the valuable assistance of the following: The Pulp and Paper Research In-

Table I. Sample Description and Analytical Methods

Sample no.	Description	Method			
		Lab A	Lab B	Lab C	Lab D
I	Eastern groundwood (Canada)	C	B	—	A
II	Western groundwood (Canada)	C	B	—	A
III	Eastern kraft pulp (Canada)	C	B	—	A
IV	Western kraft pulp (Canada)	C	B	—	A
V	Eastern sulfite pulp (Canada)	C	B	—	A
1	Northern spruce-fir groundwood pulp (USA)	C	—	D	C
2	Northern bisulfite pulp (USA)	C	—	D	C
3	Southern hardwood kraft pulp (USA)	C	—	D	C
4	Southern newsprint pulp, 75% groundwood (USA)	C	—	—	C
5	Southern sulfite pulp (USA)	C	—	D	C
6	Western kraft pulp (USA)	C	—	—	C
7	Western hemlock sulfite pulp (USA)	C	—	—	C
8	Southern pine kraft pulp (USA)	C	—	—	C
9	Southern pine sulfite pulp (USA)	C	—	D	C
10	Midwestern natural softwood pulp (USA)	C	—	—	C
11	Midwestern hardwood pulp (USA) type 1	C	—	—	C
12	Midwestern hardwood pulp (USA) type 2	C	—	—	C
13	Midwestern softwood pulp (USA)	C	—	D	C
14	Midwestern pine softwood pulp (USA)	C	—	—	C
15	Midwestern softwood sulfite pulp (USA)	C	—	—	C
16	Midwestern hardwood pulp (USA) type 3	C	—	D	C
17	Midwestern softwood kraft pulp (USA)	C	—	D	C
SRM 1571	NBS orchard leaves	C	—	D	C

Table II. Analytical Results. Selenium in Ppm, on Dry Basis

Sample no.	Moisture, % ^a	Lab A		Lab B		Lab C		Lab D		All laboratories	
		n	Mean	n	Mean	n	Mean	n	Mean	Mean ^b	Std dev ^b
I	27.4	3	0.067	2	0.09	7	<0.10	<0.09	...
II	32.8	4	0.058	2	0.09	4	<0.10	<0.08	...
III	34.6	5	0.173	2	0.20	4	<0.10	<0.16	...
IV	31.6	6	0.107	2	0.14	6	<0.10	<0.12	...
V	7.5	3	0.043	2	<0.05	4	<0.10	<0.07	...
1	c	2	0.009	4	0.012	6	0.007 ^c	0.009	0.005
2	c	2	0.006	4	0.007	6	0.004	0.005	0.002
3	c	2	0.005	4	0.007	6	0.008	0.007	0.003
4	7.0	6	0.040	6	0.095	0.068	0.034
5	c	2	0.013	4	0.012	6	0.013	0.013	0.001
6	5.7	3	0.012	3	0.017	0.015	0.005
7	5.9	3	0.007	4	0.040	0.026	0.023
8	6.0	3	0.010	4	0.018	0.014	0.006
9	5.3	5	0.019	6	0.034	4	0.015	0.026	0.013
10	15.9	3	0.023	4	0.018	0.020	0.007
11	5.6	3	0.006	4	0.023	0.016	0.017
12	5.4	3	0.006	4	0.013	0.010	0.004
13	5.4	3	0.005	6	0.096	4	0.089	0.073	0.040
14	5.8	3	0.003	4	0.013	0.009	0.006
15	66.8	3	0.020	4	0.052	0.038	0.019
16	c	2	0.005	4	0.005	6	0.004	0.004	0.001
17	9.1	3	0.017	6	0.024	4	0.030	0.024	0.009
SRM 1571		3	0.077	6	0.087	4	0.080		

^a Average reported by all laboratories. ^b Calculated from all results. ^c Analysis on dry, homogenized samples.

stitute of Canada, Badger Paper Mills, Great Northern Paper Co., International Paper Co., Mosinee Paper Corp., and Rayonier Inc. for contributing pulp samples; The laboratories of American Smelting and Refining Company, Canadian Copper Refiners Ltd, Kennecott Copper Corp., and South Dakota State University for participating in the collaborative study; O. E. Olson for advice and technical contribution; and A. Szell and D. J. Henrie for performing some of the analyses.

Literature Cited

- Chem. Eng. News*, **45**, 12 (May 29, 1967).
 Johnson, H., *Environ. Sci. Technol.*, **4**, 850-3 (1970).
 Luke, C. L., *Anal. Chem.*, **31**, 572-4 (1959).
 Olson, O. E., *J. AOAC*, **52**, 627-34 (1969).
 Olson, O. E., Frost, D.V., *Environ. Sci. Technol.*, **4**, 686-7 (1970).
 Parker, C. A., Harvey, L.G., *Anal.*, **87**, 558-65 (1962).
 Watkinson, J. H., *Anal. Chem.*, **38**, 92-7 (1966).
 West, P. W., Cimerman, Ch., *ibid.*, **36**, 2013-16 (1964).

Received for review July 16, 1973. Accepted January 7, 1974.

Feasibility of Automatic Isokinetic Stack Sampler

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■ A technique is suggested for the isokinetic sampling of emissions from stack sources. Two capacitance manometers with a common pliable element are used to compare the stack and probe flows.

Smoke stack effluent must be sampled at the same rate as the stack flow (isokinetically) if errors are to be held within tolerable limits. This note suggests a novel technique for automatic isokinetic stack sampling through the use of an electrical pressure transducer. No technical skills would be required by the personnel involved in the measurement. Present techniques require the initial measurement of the stack velocity profile using a Pitot tube, which measurement is followed by the actual sampling. The Pitot tube technique, besides being extremely cumbersome, also involves the poor assumption that the velocity profile is stable.

The technique described here takes advantage of the pressure developed by a passing flow of gas, as described by Bernoulli's equation. An arrangement of two capacitors with a common pliable element is used as a pressure transducer to compare the probe and stack velocities. An electrical feedback circuit varies the probe flow motor, such that the pressure difference is zeroed, ensuring the equality of the flow rates. Monitoring the speed of the probe motor gives a continuous record of the stack velocity at the point being sampled.

A schematic representation of the device is shown in Figure 1. Here the lower portion of the probe forms two capacitors, A and B, and is electrically insulated from the remainder of the probe. Any difference between the flow velocities will result in a pressure difference as described by Bernoulli's equation. The pressure difference will displace the pliable membrane laterally, resulting in a difference between the capacitances of A and B. The resulting electrical signal is sent to the motor by means of an amplifier feedback circuit varying its speed until the stack and probe flows are equal, thereby equalizing the capacitances of A and B. From Bernoulli's equation the pressure difference Δp resulting from a velocity difference ΔV is

$$\Delta p = \frac{1}{2} \rho \Delta V^2 \quad (1)$$

where ρ is the density of the flowing medium. Assuming ρ to be the density of air and with the knowledge that laboratory devices can detect a pressure difference of $10^{-6} \tau$, we have

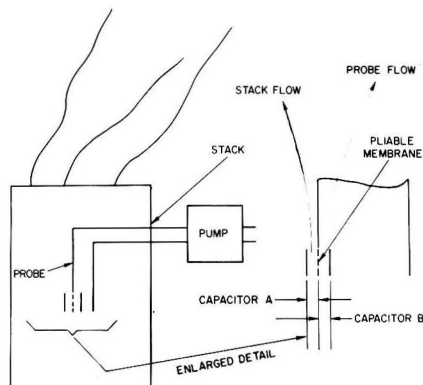


Figure 1. Schematic representation of the proposed isokinetic stack sampler

$$\begin{aligned} \Delta V^2 &= \frac{2\Delta p}{\rho} \\ &= 2 \times \frac{1.3 \times 10^{-9} \times 10^6 \text{ dyn/cm}^2}{1.3 \times 10^{-3} \text{ g/cm}^3} \\ &= 2 \text{ cm}^2/\text{sec}^2 \end{aligned} \quad (2)$$

Here atmospheric pressure is assumed to be 10^6 dyn/cm^2 and Δp is $10^{-6} \tau$ or $1.3 \times 10^{-9} \text{ atm}$. The density of air is taken to be $1.5 \times 10^{-6} \text{ g/cm}^3$. Considering the left side of Equation 2, we have

$$\Delta V^2 = 2V\Delta V \quad (3)$$

Then Equation 2 yields

$$\frac{\Delta V}{V} = \frac{1}{\sqrt{2}} \quad (4)$$

Since typical stack velocities are of the order of hundreds of centimeters per second, it appears that if the membrane can respond to pressure differences of $10^{-6} \tau$, then fractional measurements of approximately 10^{-4} may be obtainable. Since field measurements of 1-5% are quite adequate, it is obvious that considerable leeway is allowed for any problem which may be encountered in the development of this device. The possibility then exists that automatic isokinetic stack sampling may be effected with this device. The scheme presented here appears to be sufficiently promising to warrant serious development effort.

Received for review July 25, 1973. Accepted November 21, 1973.

INDUSTRY TRENDS

Public Service Electric & Gas Co. (Newark, N.J.) plans to locate a floating nuclear power plant 2.8 miles out in the Atlantic Ocean by 1980.

The Smelter Control Research Association, Inc. (New York, N.Y.) plans to do a pilot-plant investigation of the ammonia double alkali process for removal of SO₂ from copper reverberatory furnace gas.

Combustion Engineering, Inc. will build and install two 500 MW "Controlled Circulation" coal-fired steam generators at Commonwealth Edison's Will County Power Station (Joliet, Ill.); completion will be late 1977 to mid-1978.

ECOKEL (Ecodyne and M. W. Kellogg Corps.) will supply two natural draft hyperbolic concrete cross-flow cooling towers for two TVA 1221 MW nuclear units near Chattanooga, Tenn.

Phelps-Dodge will install high-flux, enhanced surface tubes for two Envirogenics Co. 2.25-mgpd desalination plants at St. Thomas, Virgin Islands.

Carus Chemical Co. received the rights to use Shell International's patented process, using a 1-3% potassium permanganate and 1% sodium hydroxide mixture to sweeten and deodorize petroleum fractions.

Grumman Corp. (Bethpage, N.Y.) will supply its Ozotherm (ozone/burning) wastewater treatment system for one of U.S. Steel's Great Lakes bulk carriers. The system will serve a 35-man crew.

Geraghty & Miller (Port Washington, N.Y.) will study alternative total water management methods to meet the Southwest Florida Water Management District's long-term water and ecosystem protection needs. Contract value is \$265,000.

Research-Cottrell, Inc. received a \$15 million contract to install two proprietary SO₂/wet fly ash removal systems for Arizona Public Service Co., near Joseph City, Ariz.

Betz Laboratories, Inc. has recently registered its Slimicide DE-508 biocide with the EPA. Slimicide DE-508 has low fish toxicity and detoxifies by natural hydrolysis or with a reducing agent, according to Betz Laboratories.

Environmental Data Corp. signed a 3-year agreement with Southern California Edison (SCE) for full warranty

and calibration services for stack gas monitors at SCE's Redondo Beach, Calif., plant.

Foote Mineral Co. (Graham, W.Va.) will invest \$6.9 million to expand its ferroalloys plant and install a 200-MW electric furnace with air pollution control equipment.

Dames & Moore (Los Angeles, Calif.) is performing environmental studies for Public Service Electric & Gas Company's Hope Creek Plant (Alloways Township, N.J.). The final report should be issued this month.

Dow Chemical Co. is to build a 150,000 ton/yr chlor-alkali plant on a deep-water bay 15 miles north of Salvador, Brazil.

Texas Instruments was awarded a \$1,257,421, 1-year contract by Con Edison (New York, N.Y.) to assess and evaluate fish habits near a proposed power plant on the Hudson River near Cornwall, N.Y.

Particle Data Laboratories, Inc. is expanding capabilities to include facilities for odor sampling, characterization, and analysis.

Research-Cottrell, Inc. has established its first European subsidiary, Research-Cottrell (Belgium), S.A., at Mons, Belgium, for sales, fabrication, and installation of pollution control products.

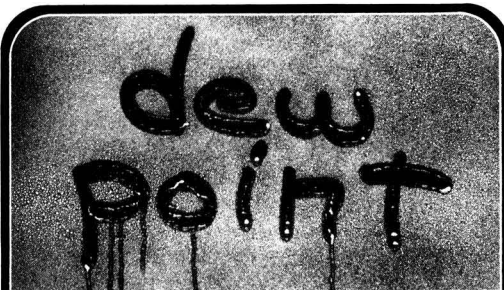
Airco Industrial Gases is now offering a full range of analytical services for a variety of users by providing custom-service laboratories with instruments and trained technicians.

National Airoil Burner, Inc. has formed NAO International, Inc. to market its patented combustion units and waste liquid and gas disposal equipment worldwide.

NRG, Inc. (Phoenix, Ariz.) hopes to supply pipeline-quality methane gas from a landfill to Arizona Public Service Co. If all goes well, 650,000 ft³/day could be available for over 3100 residential customers.

Peabody Galion Corp. received four water treatment contracts, worth a total of \$11 million, from Fall River and Everett, Mass.; Tampa, Fla.; and Hobart, N.Y.

The Beverage Industry Recycling Program (Phoenix, Ariz.) said that recycled aluminum can be melted for one tenth the energy needed for primary metal extraction.



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Sludge removal system

System of sludge removal offers clarifier or thickener capabilities at a low cost. It provides static underflow withdrawal. Isolated network sections are activated in sequential operation to give a sweeping collection action across the pond bottom. An adjustable programming unit automatically times the opening of pneumatically controlled valves. Barrett, Haentjens & Co. **102**

Cyanide meter

Device measures the cyanide level of industrial effluents, sewerage, and potable water directly down to 10 ppb. Results are read out on a large meter scale in ppm in three ranges: 0.01-0.1, 0.1-1.0, 1.0-10.0. The complete test can be performed in a matter of minutes. No operator skill is required to obtain accuracy equal to APHA standard procedure. Senso-rex **103**

BOD analyzer

Analyzer obtains BOD test results in a matter of minutes. It has a large sample capacity (1-4 liters), which is representative of actual wastes and permits readings of greater precision with no pretreatment of the sample required. It is easily calibrated from full scale of 10 ml of oxygen

to full scale of 100 ml of oxygen. Easy to use. Horizon Ecology Co. **104**

Reverse osmosis system

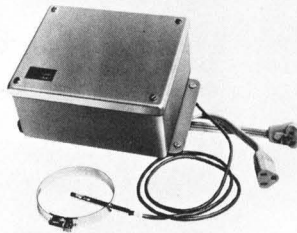
Reverse osmosis pollution control system recovers valuable metallic plating solution concentrates, and conserves rinse tank water. The compact unit pumps polluted rinse water in a closed-loop recovery operation under high pressure through a chamber containing a special hollow-fiber membrane permeator. The concentrated plating solution is returned and purified rinse water reused. Sethco Mfg. Co. **105**

Dust collector

Rock drill, fabric filter dust collector is self-contained unit that collects more than 99% of the dust from drilling operations and bags it in plastic bags for easy disposal. Twenty-four cloth bags trap fine dust as they move through the collector from the drill bit area. A shock wave of air periodically causes the dust cake to fall into a hopper. Dustex **106**

Heat recovery equipment

Heat economizer utilizes waste energy to increase temperature of boiler inlet water, thereby reducing the amount of fuel needed to produce steam. Virtually maintenance free, each device is custom-designed for the user. A boiler generating 50,000 pph of steam could save approximately 5000 barrels of oil per year, according to the manufacturer. Technotherm Corp. **107**



Air flow controller

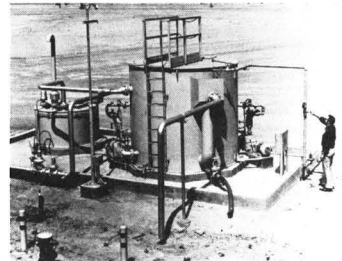
High-volume, constant flow controller is designed for high-volume air samplers in outdoor and occupational environments. Controls the flow rate and automatically corrects for filter loading, line voltage changes, temperature, and pressure. Unit easily attaches to all standard high-volume samplers. Flow can be controlled over range of 30-50 scfm with accuracy exceeding ± 1 scfm EPA specification. Sierra Instruments, Inc. **108**

Dewatering screen

High-capacity, adjustable, stationary dewatering screen is designed for the continuous clarification of industrial and municipal wastes. Special features include a simple manual adjustment for changing the slope of the dewatering deck, and an acceleration/fiber-orientation deck that accelerates the feed to optimum velocity while orienting the fibers. Kason Corp. **109**

Biodegradable foam

Pressure foam systems remove harmful/hazardous airborne particles in underground mining, stone crushing, cement manufacturing, preparation plants, and drilling and stack emissions. Foam is produced in closed system and can be ejected at high velocity from various nozzles directly into the dust-producing process. Therefore none of the particles become airborne. DeTer Company, Inc. **110**



Flotation unit

Flotation device for industrial wastewater treatment is capable of an extremely high percentage of oil and solids removal. It operates on principle of dissolving gas in a liquid under pressure, but without the use of a gas in a liquid under pressure, but without the use of a gas contacting tower. Either gas or air, injected on the suction side of the pumps through a premixing system to prevent gas locking, can be used. Pollution Control Engineering, Inc. **112**

Popper stopper

Stopper mechanically seals all pull tab cans, thus preventing waste of carbonated beverages and premature

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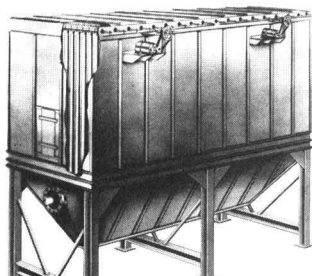
disposal of metal cans. The device is made of plastic and tough rubber. It is inserted in the opening of the can and twisted to keep unused portions of drinks fresh. It prevents both spills and contamination, and is reusable. ARTEC 113

SO₂ scrubber instrumentations

Instrumentation package provides operational and compliance data when installed on sulfur dioxide scrubbers. It includes two duct-mounted monitors, two recorders, and associated electronics. One monitor measures SO₂ levels at the scrubber inlet. At the outlet, a single instrument measures SO₂, NO, and opacity simultaneously and continuously. Environmental Data Corp. 114

Oil skimmers

Air-powered oil skimmers draw in spilled oil and pump it through a hose to a location where it can be recovered. Shaped much like the base of a lawnmower, the pump is devised so it can be operated by an air motor as well as an electric or gas motor—thus making it safer to use in the explosive atmosphere of an oil spill. They are relatively light and easy to maintain. Acme Pollution Control Co. 115



Dust filter

Intermittent-type dust filter for air pollution control features high filtering efficiency at low cost and minimal power requirements. Designed to be shipped shop-assembled, including bags, the device can be used for virtually all types of dust. Better than 99% filtering efficiency is achieved. Offered in range of sizes to accommodate from 1300 to 300,000 ft³ of air per minute. Joy Manufacturing Co. 116

Residential sewage plant

Aesthetically pleasing sewage plant is suitable for residential and commercial developments where design is a factor. A mansard roof can be added to precast concrete wall sections and components, which are

shipped directly to the plant site for quick assembly. Plants are odorless and remove 94%+ BOD. Models greater than 2 million gpd are available. Marolf 117

Wastewater aerator

Subsurface aerator system, constructed of high-density polyethylene, is designed to treat wastewater with a high salt content. The unit operates on the air lift pump principle. There are no moving parts in the basin, no air sprays, no damage to basin liners, no winter icing, and no electricity in the basin. One design uses no wetted metal parts. Kenics 118

Exhaust test system

Vehicle exhaust emission test system is designed to test automotive engines for Federal EPA 1975-76 standards. The system also can be utilized for hardware development and other analytical test procedures. It operates in conjunction with a constant volume exhaust gas sampler unit that fills three bags with a dilution of air sample and three other bags with an exhaust sample for testing. Air Monitoring, Inc. 119

Oil spill test tank

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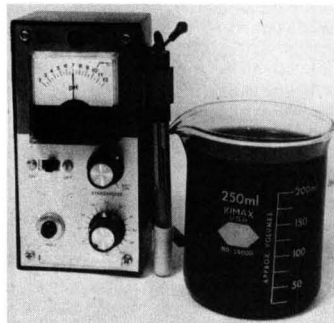
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pH meter

Portable pH meter allows pocket portability for field usage in measuring effluent discharges or stream environments. Low price allows individual usage by plant or field engineers to check control instrumentation, without need to rely on lab analysis. A 2-in meter readout provides a pH range of 2-12 accurate to ± 0.1 pH. Belnor Systems, Inc. 121

Machine noise enclosures

Line of modular and custom-dimension heavy duty machine enclosures substantially reduce in-plant noise and enhance safety. Fabricated of steel and lined with a highly effective acoustical absorbing material, the enclosures are now being sold to punch press, saw, and cutoff machinery operators. They can be designed to fit special equipment. Meet the OSHA requirements. Keene Corp. 122

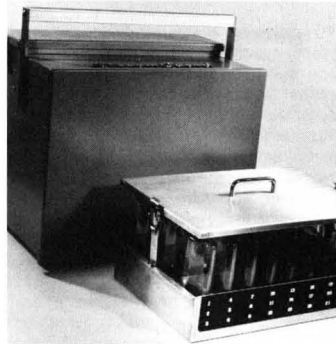
Trash-sorting computer

Minicomputer in electrical/mechanical system quickly and accurately sorts unadulterated trash into categories, immediately identifying waste for disposal or recycling. The unit receives many sensor inputs from a wide variety of trash items and makes classification decisions in $\frac{1}{10}$ sec. Trash and refuse are loaded onto a small wire mesh vibrating screen that shakes out objects by size. Computer Automation, Inc. 123

Field calibration kits

Contain samples with a known size and number of ppm certified to $\pm 5\%$ accuracy. The sample fluids, either oil or water, are together as a unit, which includes six 180-ml bottles of a selected calibration mixture,

two clean magnetic stirring bars, certification slip, certified number and size of ppm in five size ranges, and step-by-step procedures for calibration. High Accuracy Products Corp. 111



Liquid sampler attachment

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NEW LITERATURE

Separating cleaner. Literature announces Cleanbreak which cleans, separates, and produces nonpolluting, nontoxic discharge water from oil water wastes. Chemical migrates to oil layer and prevents the formation of any emulsified interface. The separated water layer is then safe for disposal on land or at sea. Potential users include industrial plants, ocean vessels, and marine installations. Gamlen Chemical Co. **165**

Water test kits. Catalog 74 illustrates devices for water quality and pollution control such as dissolved oxygen testers. It also features accessories, reagents, analyzers, and other systems for environmental analysis and control. Ecologic Instrument Corp. **166**

Gas analyzer. Form 73D-621A describes portable model for measuring CO, CO₂, and O₂ in flue gases. Options can be included in model to measure SO₂ in the 0-3000 ppm range. Milton Roy Co. **167**

Flocculant aid. Bulletin contains applications for polyelectrolyte material used in treatment of petroleum refining and steel mill wastes, acid mine drainage, and sewage. Narvon Mining & Chemical **168**

Waste disposal. Brochure—How to Select the Right Waste Disposal System—tells of capabilities of wastewater treatment plant—thermal oxidation units, chemical and biological operations. Rollins Environmental Services **169**

Cooling water travelabs. Bulletin 718 lists services which provide on-site analysis and monitoring of industrial cooling water and solve problems involving corrosion, deposition and microbiological fouling. Betz Laboratories, Inc. **170**

SS analysis. Brochure describes liquid analysis meter for measuring turbidity, suspended solids, and sludge levels. Instrument can be directly installed in open channels, in tanks, or on pipes without requiring sampling pumps or lines. Biospherics Inc. **171**

Ultrafiltration system. Publication 436 covers uses for concentration, desalting, purification, or fractionation

of biologicals, colloids, and other macromolecular solutions. Amicon Corp. **172**

Centrifugal thickener. Bulletin describes device which mechanically dewateres liquid concentrates in wastewater processing, in the ranges of 100-300 gpm. Machine eliminates the need in most cases for thickening tanks, centrifuges, and vacuum filters. SWECO, Inc. **173**

Particulate monitor. Specification E66-45 details system for continuous measurement and indication of visible emissions in terms of percent opacity by responding only to the visible light spectrum. Bailey Meter Co. **174**

Precipitator efficiency. Reprint shows how a chemical system can help trap fly ash from low sulfur coal, so that utility boilers can meet state codes for particulate emissions. System can be installed without boiler shutdown. Apollo Chemical Corp. **175**

Aeration systems. Literature covers how deep submerged jets, either in clusters or along manifolds, entrain compressed air and waste liquor in homogeneous mixtures and shoot them back into the depths of the activated sludge treatment tank. Penberthy Houdaille Industries **176**

Program controllers. Bulletin 74-01-04 includes solid state systems for automatic testing and quality control of industrial processing, and for blending and mixing. FX Systems Corp. **177**

Asbestos dust. Article highlights use of agglomeration methods (pelletizing, extruding, briquetting) as an aid to environmental and health problems associated with fine, dusty wastes. Ferro-Tech Inc. **178**

Sulfur analyzer. Bulletin features instrument which uses gas chromatographic principles and a flame photo-

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metric detector to sample hydrogen sulfide and SO₂. Equipment is complemented by a permeation tube calibration system. Tracor Inc. **179**

Noise control. Booklet describes line of products for sound adsorption, vibration damping and noise attenuation. Soundcoat Co. **180**

Grease incineration. Brochure discusses method for processing municipal or industrial greases, scum, or oil by introducing these waste materials into the bottom of a furnace partially filled with water. Floatable wastes rise to the surface where they are ignited and burned on a "grate" of water. Nichols Engineering & Research Corp. **181**

Pumps. Catalog covers transfer, recirculation, metering, and agitating-type pumps for neutralizing both acid and alkaline waste solutions. It includes pressure and flow curves, horsepower requirements, and dimensional information. Serfilco Div., Service Filtration Corp. **182**

Oil analyzer. Bulletin 22 describes use of ir spectroscopy for the analysis of oil or hydrocarbons in waterways. Model enables the reading of concentration in ppm simultaneously as the CH stretching region is scanned. Perkin-Elmer Corp. **183**

Scrubbers. Six-page bulletin details line of Venturi type made of fiber reinforced polyester, designed to remove solid or liquid particulates in the 1-5 micron and submicron ranges from corrosive gas streams. Ceilcote Co. **184**

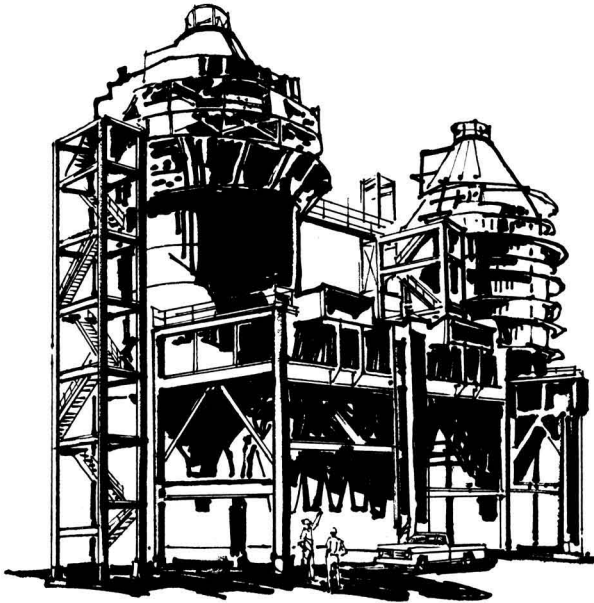
Fabric filters. Brochure covers line of industrial units for pollution or dust control and product recovery—SH tower, shaker-type; SJL, rotary-arm, low-pressure, reverse-jet filter; and others. It includes chart of applications, showing usual loads, particle sizes, and recommended filter. Air Purification Methods **185**

Heavy metals reduction. Literature, entitled "Inorganic Reductions with Sodium Borohydride Principals and Practices," narrates use of this reagent to remove and recover various heavy metals from plant effluents. Efficiency is claimed to be 99.5%. Ventron Corp. **186**

Phosphorus removal. Bulletin describes principles of process for removing phosphorus from activated sludge treatment plants, and contains pilot plant and full-scale results. Biospherics Inc. **187**

Pumps. Bulletin 410E covers series of horizontal, vertical, and flexible shaft split case models. It details engineering data specifications, perfor-

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mance charts, construction materials, and dimensions. Aurora Pump **188**

Transfer systems. Booklet details solid waste facilities of various capacities, including the costs of the facilities and comparison of present cost of operation with the facilities. Heil Co. **189**

Cooling water treatment. Bulletin 9025 describes approach for controlling bacteria, slime-forming organisms, scale, and corrosion. Dearborn Chemical Div., Chemed Corp. **190**

Energy services. Six-page brochure lists capabilities in energy conservation, fossil fuel and nuclear plant pollution control problems, intermittent emissions control systems, and environmental impact statement preparation. Science Applications, Inc. **191**

Coal. Report, "Illinois Minerals Note 53," reveals that 14% of more than 148 billion tons of coal compiling the total reserve of Illinois is lying in less than 150-ft deep seams. Illinois State Geological Survey **192**

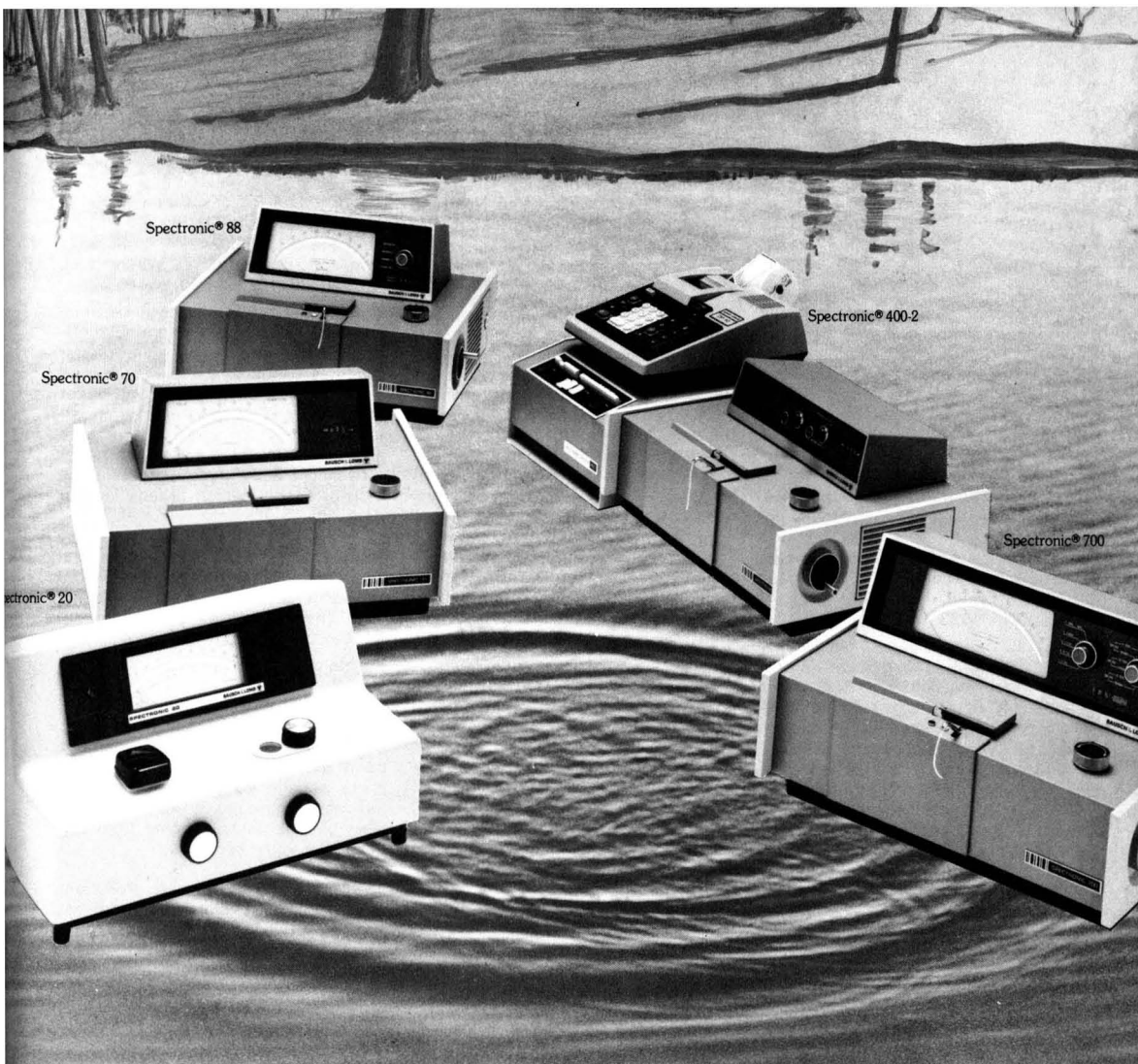
Air filtration. Brochure gives data showing that bags of Nomex aramid fiber have advantage over polyester bags in both nonacid and acid environments. Du Pont Co. **193**

Plastic valves. Bulletin CRT-700 provides resistance data of polyvinyl chloride, polypropylene, and chlorinated polyvinyl chloride to inorganic and organic chemicals. Hayward Manufacturing Co., Inc. **194**

Feeding system. Bulletin 500 explains how an exclusive atomizing design ensures positive dispersion of polyelectrolyte before being wetted in a cyclone wetting nozzle. System is suited to water clarification in paper and chemical processing, and for efficient separation of solids from water where standard coagulants are inefficient. Acrison Inc. **195**

RO evaluator. Brochure describes Osmotik pilot processor for testing efficiency of reverse osmosis or ultrafiltration processes. These processes are versatile in industrial pollution control, industrial processing, by-product recovery, and high-purity water recovery for reuse. Applications include pulp and paper and food processing industries. Universal Oil Products Co. **196**

Gas analyzers. Bulletin 373100 describes range of instruments using the chemiluminescent detection principle to measure ozone and nitrogen oxides from ppb to 1% concentration levels. McMillan Electronics Corp. **197**



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BOOKS

Solid Waste Management. D. Joseph Hagerty, Joseph L. Pavoni, John E. Heer, Jr. xiii + 302 pages. Van Nostrand Reinhold Co., 450 West 33rd St., New York, N.Y. 10001. 1973. \$16.95, hard cover.

Offers a many-sided look at the environment problems—and their possible solutions—that involve solid waste collection and disposal. Data are compiled to show how future systems for collection, disposal, and recovery will have to be designed and selected. The pros and cons of various systems now in use and specialized practices and facilities for transport and collection are discussed.

Power Lines and the Environment. Robert Goodland, Ed. 170 pages. Cary Arboretum, Box AB, Millbrook, N.Y. 12545. 1973. \$5.00, paper.

Contains proceedings of the colloquium "Biotic Management Along Power Transmission Rights of Way" held at the American Institute of Biological Sciences meeting, Amherst, Mass., in June 1973. Presents compilation exposés on how power lines affect the environment, dissects some aspects of the problem, and suggests how environmental degradation can be halted.

Solid Waste Recycling Projects: A National Directory. viii + 284 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1973. \$2.15, paper.

Purpose of the book is to identify and promote methods to recycle the valuable materials that we now throw away. It lists on a state-by-state basis citizen, municipal, and industrial recycling projects that serve as points of contact between individuals who wish to conserve resources and manufacturers who can reuse them as raw materials.

Chemistry of Water Supply, Treatment, and Distribution. Alan J. Rubin. viii + 446 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1974. \$22.50, hard cover.

Represents the most current research on the chemical aspects of producing and delivering potable water. Findings challenge and advance conventional treatment of water resources. The book begins with the criteria developed for new drinking water standards; examines raw water quality; investigates new analytical techniques; describes removal processes; and examines the quality of the finished water.

Environmental Control in Electronic Manufacturing. Philip W. Morrison, Ed. xiii + 474 pages. Van Nostrand Reinhold Co., 450 West 33rd St., New York, N.Y. 10001. 1973. \$23.95, hard cover.

Deals with the technical challenge of manufacturing products or precision devices where contaminants play a significant role. Outlines how and when to clean or purify the many facets of the manufacturing environment. The book begins by defining the basic elements of product manufacture, and their contaminants. It then discusses the role of microscopy and particle measurement systems in contamination.

The Salvage Industry: What It Is—How It Works. Arsen Darney, William E. Franklin. 32 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1973. \$0.30, paper.

This EPA-funded study evaluates potential markets for waste-derived materials. It is a summary report based on "Salvage Markets for Materials in Solid Wastes," by the same authors. It deals with how the salvage industry is structured, who buys its wares, and its trends and future developments. It specifically treats such salvageable commodities as paper, ferrous and nonferrous metals, glass, textiles, rubber, and plastics.

Environmental Planning: Law of Land & Resources. Arnold W. Reitze, Jr. x + 825 pages. North American International, P.O. Box 28278, Washington, D.C. 20005. 1974. \$19.95, hard cover.

The book deals extensively with the various aspects of land use planning. Treating both urban and nonurban areas, it considers such topics as wetlands, public lands, wild rivers, endangered wildlife, surface mining, power plant siting, ocean resources, and transportation. Stresses that all of mankind has a stake in the world that is considerably greater than the property to which we legally claim title.

Abyssal Environment and Ecology of the World Oceans. Robert J. Menzies, Robert Y. George, Gilbert T. Rowe. xxiii + 488 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1973. \$24.95.

Provides cohesive view of the paleogeography, ecology, adaptation, migration, and zonation of abyssal fauna in the Northwest Atlantic, Southeast Pacific, Arctic, and Ant-

arctic oceans. Unlike previous studies, which concentrate on fishes in the deep-water column, it emphasizes the benthic realm, including animal life in and on the sea floor. Presents data and conclusions pertinent to the regulation of oceanic pollution.

The National Buyer's Guide to Recycled Paper. Sally Dane. 208 pages. Environmental Educators, Inc., 1621 Connecticut Ave., N.W., Washington, D.C. 20009. 1973. \$4.00, paper.

Aimed at providing a link between potential customers and manufacturer/distributors of recycled paper products. Book is a mixture of hard facts about specific paper and paper products and a narrative that attempts to explain some of the more esoteric facts about paper and paper recycling. Sees main problem as lack of supply, which breeds lack of demand.

Responses of Fish to Environmental Changes. Walter Chavin, Ed. x + 459 pages. Charles C. Thomas, 301-27 East Lawrence Ave., Springfield, Ill. 62703. 1973. \$19.75, hard cover.

Intended for readers concerned with the biology, biochemistry, endocrinology, physiology, pathology, morphology, and behavior of fish, and the impact of the environment upon the fundamental processes in these aquatic vertebrates. The book includes contributions from scientists from various fields, ranging from the molecular to the behavioral.

The International Law of Pollution. James Barros, Douglas M. Johnston. xvii + 476 pages. Free Press, 866 Third Ave., New York, N.Y. 10022. 1974. \$14.95, hard cover.

Collection of research and teaching materials that deals specifically with the international law of pollution prevention and control. Using international agreements and judicial decisions, the book outlines evidence of transnational action taken to date. It also suggests the scope of future developments in the interdependent world community, based on the notion that purely national approaches are too limited.

Man, Materials, and Environment. National Academy of Sciences, National Academy of Engineering. xviii + 236 pages. MIT Press, 28 Carleton St., Cambridge, Mass. 02142. 1974. \$3.95, paper.

Book is concerned with the problem of enhancing our environment by taking a new look at the economic and technological processes needed to arrest, abate, and reverse the present trend of physical and social degradation. It seeks answers on reconciling the pressures of economic growth and the realities of resource limitations with our quest for the good life.

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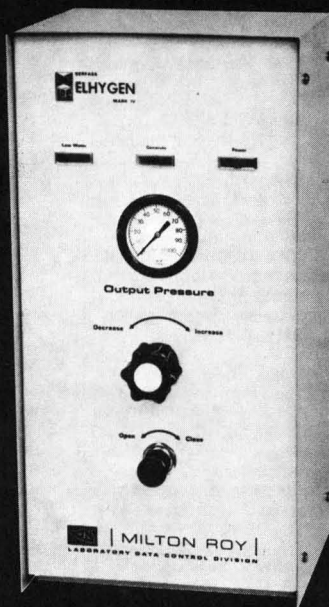
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MEETING GUIDE

May 23 Chicago, Ill.

June 12-16 Bermuda

National Association of Recycling Industries (formerly National Association of Secondary Material Industries). Midwestern and Eastern Division Meetings.

Write: NARI, 330 Madison Ave., New York, N.Y. 10017

May 28-30 San Diego, Calif.

Fine Particle Scrubber Symposium. EPA

Write: S. Calvert, APT, Inc., P.O. Box 71, Riverside, Calif. 92502

June 2-6 Pittsburgh, Pa.

Seventy-seventh National AIChE Meeting. American Institute of Chemical Engineers

Contact: Joel Henry, AIChE, 345 E. 47th St., New York, N.Y. 10017

June 4-6 Chicago, Ill.

1974 Noise Expo. Sound and Vibration

Contact: Sound and Vibration, 27101 E. Oviatt Rd., Bay Village, Ohio 44140

June 5-6 Pittsburgh, Pa.

Toxicity of Metals. Industrial Health Foundation

Write: IHF, 5231 Centre Ave., Pittsburgh, Pa. 15232

June 9-13 Denver, Colo.

Annual Meeting & Exhibition. Air Pollution Control Association

Write: APCA, 4400 5th Ave., Pittsburgh, Pa. 15213

June 9-14 Pacific Grove, Calif.

Geothermal Power. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

June 11-14 Washington, D.C.

Endangered Species Symposium. Wild Canid Survival and Research Center

Write: WCSRC, P.O. Box 16204, St. Louis, Mo. 63105

June 16-20 Boston, Mass.

Ninety-fourth Annual Conference of the American Water Works Association. Water and Wastewater Equipment Manufacturers Association

Write: WWEMA, 744 Broad St., Rm 3401, Newark, N.J. 07102

June 16-21 Chicago, Ill.

Inter/Micro-74. McCrone Research Institute

Write: McCrone Research Institute, 2820 S. Michigan Ave., Chicago, Ill. 60616

June 16-22 Boston, Mass.

Annual Conference. American Water Works Association

Theme is "Water Reuse-Resource of the Future." *Write:* David X. Manners Co., Inc., 237 East Rocks Rd., Norwalk, Conn. 06851

June 18-21 Austin, Tex.

Joint Automatic Control Conference. American Institute of Chemical Engineers

Contact: Joel Henry, AIChE, 345 E. 47th St., New York, N.Y. 10017

June 26-27 Washington, D.C.

ASTM Symposium on Automatic Sampling and Measurement for Water Pollution Assessments. American Society for Testing Materials

Contact: Jane B. Wheeler, ASTM, 1916 Race St., Philadelphia, Pa. 19103

June 26-28 Ithaca, New York

Water Quality Planning. American Society of Civil Engineers

Contact: Herbert Hands, ASCE, 345 E. 47th St., New York, N.Y. 10017

July 1-2 Golden, Colo.

Water Resources Problems Related to Mining. American Water Resources Association

Write: AWRA, 206 E. University Ave., Urbana, Ill. 61801

July 1-5 Hampton, N.H.

Environmental Sciences: Water. Gordon Research Conferences

Write: Alexander Cruickshank, GRC, University of Rhode Island, Kingston, R.I. 02881

July 7-12 Henniker, N.H.

Methanol as an Alternate Fuel. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 8-11 University Park, Pa.

Environmental Engineering Specialty Conference. American Society of Civil Engineers

Write: ASCE, 345 E. 47th St., New York, N.Y. 10017

July 8-12 Johnson, Vt.

Fourth American Society for Testing and Materials Committee D-22 Meeting. American Society for Testing and Materials

Theme is "The Concepts of Data Acquisition and Interpretation in Air Quality Monitoring." *Contact:* S. K. Kempner, Western Electric Co., 222 Broadway, New York, N.Y.

July 9-11 Houston, Tex.

1974 Summer Computer Simulation Conference. American Institute of Chemical Engineers and others

Write: Carl Malstrom, Publicity Chairman, Rhodes Engineering Research Center, Clemson, S.C. 29361

July 15-19 Montreal, Canada

Transportation Engineering Meeting. American Society of Civil Engineers

Write: ASCE, 345 E. 47th St., New York, N.Y. 10017

July 30-August 4 Seattle, Wash.

Intersociety Conference on Environmental Systems. American Society of Mechanical Engineers

Write: ASME, 345 E. 47th St., New York, N.Y. 10017

August 4-9 Rindge, N.H.

Engineering Coal Waste Disposal. Engineering Foundation

Conference on "Urban Runoff—Quantity and Quality" will be held at same location August 11-16. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 11-14 Syracuse, N.Y.

Annual Meeting. Soil Conservation Society of America

Theme is "Land Use-Persuasion or Regulation?." *Write:* SCSA, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021

August 18-21 Salt Lake City, Utah

Seventy-eighth National AIChE Meeting. American Institute of Chemical Engineers

Contact: Joel Henry, AIChE, 345 E. 47th St., New York, N.Y. 10017

August 21-23 Ft. Collins, Colo.

Annual Meeting. International Solar Energy Society, U.S. Section

Contact: S. Karaki, Dept. of Civil Engineering, Colorado State U., Ft. Collins, Colo. 80521

August 25-28 San Francisco, Calif.
National Conference on Control of Hazardous Material Spills. American Institute of Chemical Engineers and EPA

Contact: J. Henry, AIChE, 345 E. 47th St., New York, N.Y. 10017

August 26-30 Honolulu, Hawaii
Circum-Pacific Energy and Mineral Resources. American Association of Petroleum Geologists and others

Contact: Dolly Shivers, ASME, 345 E. Halbouty Bldg., 5111 Westheimer Rd., Houston, Tex. 77027

August 26-30 San Francisco, Calif.
Intersociety Energy Conversion Engineering Conference. American Society of Mechanical Engineers

Contact: Dolly Shivers, ASME, 345 E. 47th St., New York, N.Y. 10017

August 29-September 2 New York, N.Y.

Western Division Meeting. National Association of Recycling Industries

Other meetings held at various locations at different times. Write: NARI, 330 Madison Ave., New York, N.Y. 10017

September 8-12 Miami Beach, Fla.
Joint Power Generation Conference. American Society of Mechanical Engineers

Write: ASME, 345 E. 47th St., New York, N.Y. 10017

Courses

May 20-23 Los Angeles, Calif.
Acoustic Noise. West Coast University

Fee: \$220. Contact: West Coast U., 440 Shatto Pl., Los Angeles, Calif. 90020

May 21-22 Milwaukee, Wis.
Water Pollution—Law and Regulation. University of Wisconsin—Extension

Fee: \$100. Write: U. of Wisconsin, 600 W. Kilbourn Ave., Milwaukee, Wis. 53203

June 3-7 Lisle, Ill.
Stack Sampling Training. Chicago Scientific Inc. and others

Write: W. Wesolowski, CSI, 716 W. Irving Park Rd., Bensenville, Ill. 60106

June 3-7 University Park, Pa.
Industrial Noise and Engineering Control Seminar. Penn State University

Write: J. H. Stevens, Penn State U., J. Orvis Keller Bldg., University Park, Pa. 16802

June 3-7 Durham, N.H.
Fundamentals and Applications of Minicomputers. University of New Hampshire

Write: Audrey Savage, CIID-Kingsbury Hall, U. of New Hampshire, Durham, N.H. 03824

June 3-7 West Lafayette, Ind.
Machine Processing of Remotely Sensed Data. Purdue University

Contact: C. Jenks, Div. of Conferences and Continuation Services, Purdue U., West Lafayette, Ind. 47907

June 5-6 Chicago, Ill.
1974 Environmental Law. Government Institutes, Inc.

Write: Nancy McNerney, Government Institutes Inc., 4733 Bethesda Ave., N.W., Suite 303, Washington, D.C. 20014

June 6-7 New Orleans, La.
Effluent Variability from Wastewater Treatment Processes and Its Control. Tulane University and other

Fee: \$125. Write: A. J. Englande, Dept. of Environmental Health, Tulane Riverside Research Lab, Belle Chasse, La. 70037

June 11-14 Minneapolis, Minn.
Principles of Biohazard and Injury Control in Biomedical Laboratory. University of Minnesota, School of Public Health

Tuition free. Write: Dr. Vesley, U. of Minnesota, School of Public Health, 1158 Mayo, Minneapolis, Minn. 55455

June 17-21 Berkeley, Calif.
Energy—Resources, Conversion and Utilization. University of California Extension

Fee: \$300. Contact: U. of Calif. Extension, Continuing Education in Engineering, Berkeley, Calif. 94702

June 20-August 2 Houston, Tex.
Statistics in the Health Sciences. University of Texas

Write: U. of Texas, School of Public Health, P.O. Box 20186, Astrodome Station, Houston, Tex. 77025

June 24 Miami Beach, Fla.
Short Courses—ASME Boiler and Pressure Vessel Code. American Society of Mechanical Engineers

Contact: ASME, 345 E. 47th St., New York, N.Y. 10017

June 24-28 Ithaca, N.Y.
Industrial Wastewater Control. Cornell University

Contact: College of Engineering, Cornell U., Ithaca, N.Y. 14850

July 1-26 Boston, Mass.
Summer Institute on Air Pollution Management. Harvard School of Public Health

Aimed at increasing the understanding and teaching skills of faculty members in environmental science fields. Enrollment limited to thirty. Write: Dade Moeller, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115

July 8-26 Cambridge, Mass.
Nuclear Power Reactor Safety. Massachusetts Institute of Technology

Contact: Director, Summer Session Office, Rm E19-356, MIT, Cambridge, Mass. 02139

July 14-27 Fort Collins, Colo.
International School for Environmental Management. Westinghouse Electric Corp.

Write: J. H. Wright, Westinghouse Electric Corp., Westinghouse Bldg., Pittsburgh, Pa. 15222

July 15-19 Boston, Mass.
Evaluation and Control of Occupational Hazards. Harvard School of Public Health

Write: M. W. First, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115

July 15-19 Cleveland, Ohio
Industrial Noise Control Seminars. B&K Instruments, Inc.

Fee: \$200. Write: Bill Rhodes, Director of Communications, B&K Instruments, 5111 W. 164th St., Cleveland, Ohio 44142

Call for Papers

June 30 deadline
Seventh Mid-Atlantic Industrial Waste Conference. Drexel University

Conference will be held in Philadelphia on November 12-14. Emphasis on topics re air/water pollution control and solid waste disposal. Write: Dr. La Grega, Institute of Environmental Studies, Drexel U., Philadelphia, Pa. 19104

September 1 deadline
IFAC/75. International Federation of Automatic Control

Conference will be held August 24-30, 1975. Write: IFAC/75 Secretariat, 400 Stanwix St., Pittsburgh, Pa. 15222

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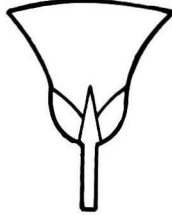
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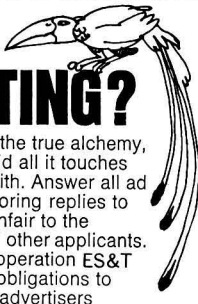
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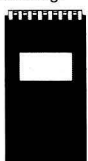
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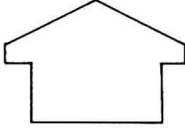


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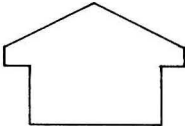
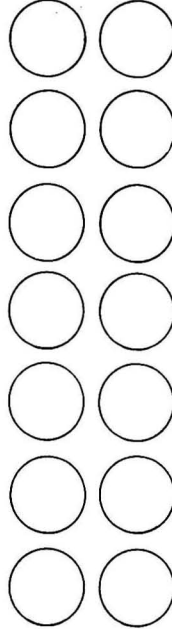


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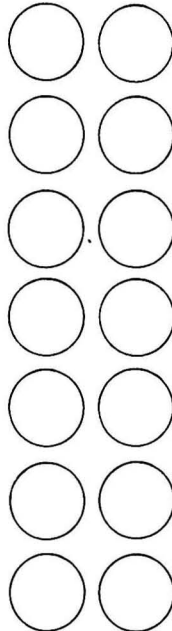
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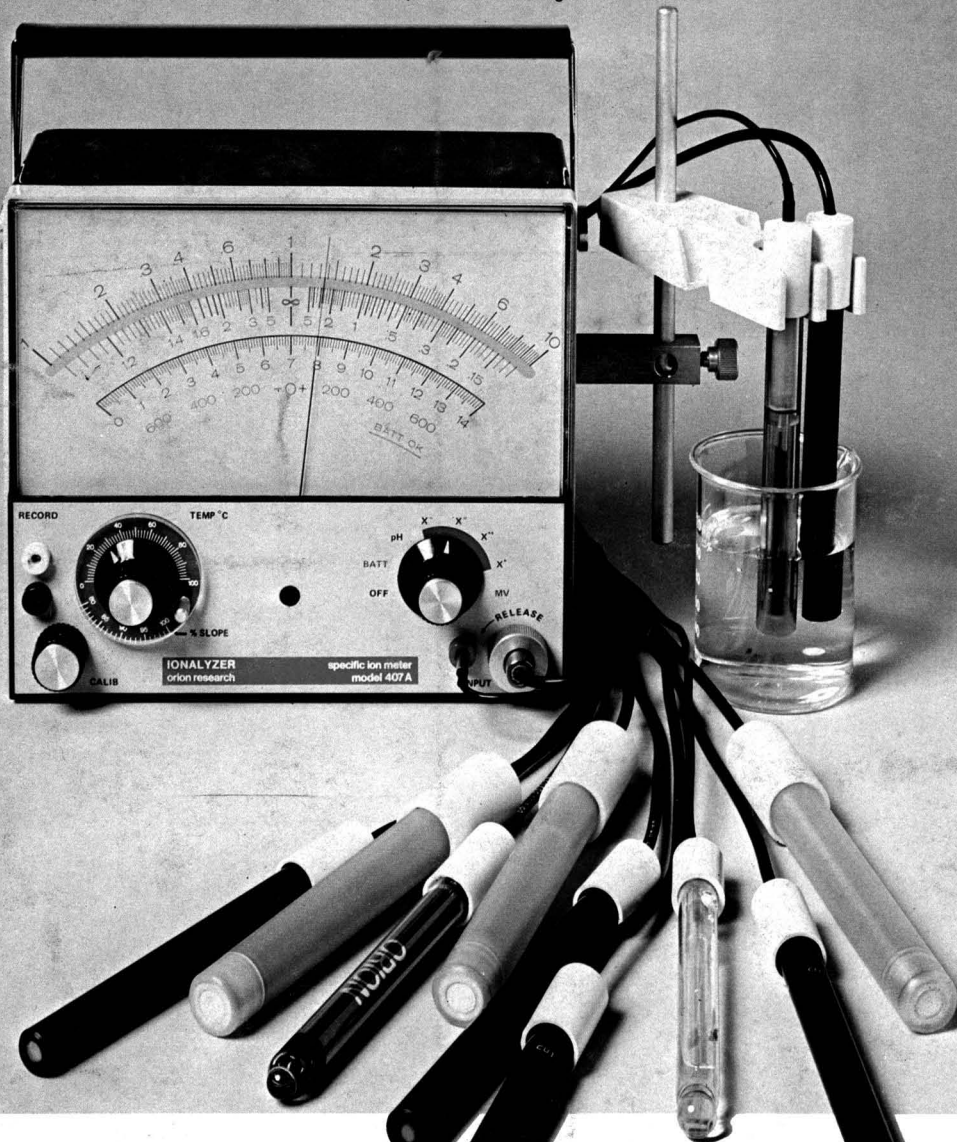
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