

SEPTEMBER 1978
ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T

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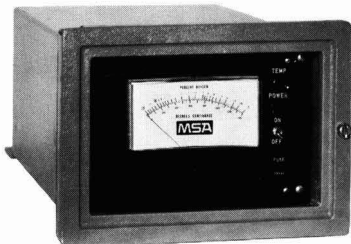
MSA INSTRUMENTS in the NEWS

COMBUSTION CONTROL • HEALTH & SAFETY • ENVIRONMENTAL • PROCESS

Accurate combustion control with MSA Oxygen Analyzer helps industry save scarce fuel.

Since its introduction in 1975, the Model 803 Oxygen Analyzer from MSA has received a warm welcome from combustion engineers across industry. Wherever fuel is burned for process heat, power generation or manufacturing, fine tuning of excess air in the combustion process pays big dividends. It used to be difficult to get reliable readings in the hot, dirty conditions in the stack. But the Model 803 O₂ Analyzer is changing all that.

Located right on the stack, the Model 803 gives you the shortest possible sampling line. It operates hot so that gases are kept above their dewpoint. That minimizes plugging problems and increases time on line without shutdown. The analyzer measures oxygen directly—not just an effect of



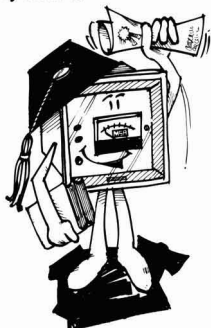
oxygen. So it produces a high-level signal. And its sensitivity holds through the full 0.1% to 21% O₂ range.

Many users have commented on the 803's speed of response when furnace operating conditions vary. Prompt corrective action saves them fuel and avoids pollution incidents.

MSA Oxygen Analyzer goes to "energy college."

The engineering department of a southern college conducts seminars to help industry improve their boiler operating efficiency. During the lecture portion, the Model 803 Oxygen Analyzer demonstrates the theory of excess air control; then the professor takes the group of boiler operators and superintendents to a nearby industrial plant to observe this combustion control theory in operation.

The class analyzes the combustion gases from the boiler with the Model 803 and correlates the analysis to Orsat tests. Conditions are deliberately varied, and effect on excess air and efficiency noted.



The fast response and trouble-free operation of the 803 verifies classroom data and confirms how simple it is to continuously maintain the correct excess air ratio.

Flue gas analysis goes portable.

The popular Model 803 is now also available as the 803-P Portable O₂ Analyzer. The 20-pound unit is complete in a single case with handle. It offers the same high levels of accuracy, measuring O₂ from 0.1% to 21%. The logarithmic scale provides highest accuracy at the lowest concentration levels.

While measuring flue gas excess oxygen is a major application, inert gas generators, heat-treating atmospheres and other combustion processes can all benefit from its use. You just plug it in at the test location, and within 20 minutes you're ready for accurate analysis of combustion oxygen level. Adjustments in ratios are recorded in seconds for fast correction of fuel/air imbalances.



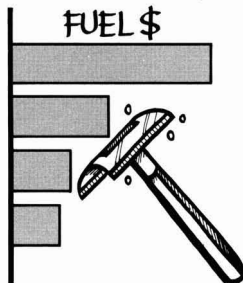
How can we help you?

MSA has experienced instrumentation engineers in your area who can review your needs and make specific proposals for your plant. They can also provide details on other MSA instruments for stack emission monitoring, health and safety analysis systems and air quality monitoring. Check the Yellow Pages for the nearest MSA

Multi-plant air analysis shows how to shave fuel costs.

In the dim, dark past when fuel was cheaper than controls, boiler operators didn't mind losing a little heat in the form of excess air. It was heated and then carried its Btu's right out the stack, but it didn't bother the burning rate or the operation.

Now, that "little heat" can add up to a loss of thousands of dollars every month. More and more industrial boiler operators are turning to oxygen monitoring and control as a cost-efficient way to reduce fuel consumption.



One multi-plant company studied the effect of increasing boiler efficiency from 1% to 5% for four classes of boilers. The figures showed, for example, that a 2% improvement for a 100,000-lb boiler would offer savings of \$3,000 per month when fuel was 26¢ a gallon. At that rate, the cost of controls could be paid off in a matter of months.

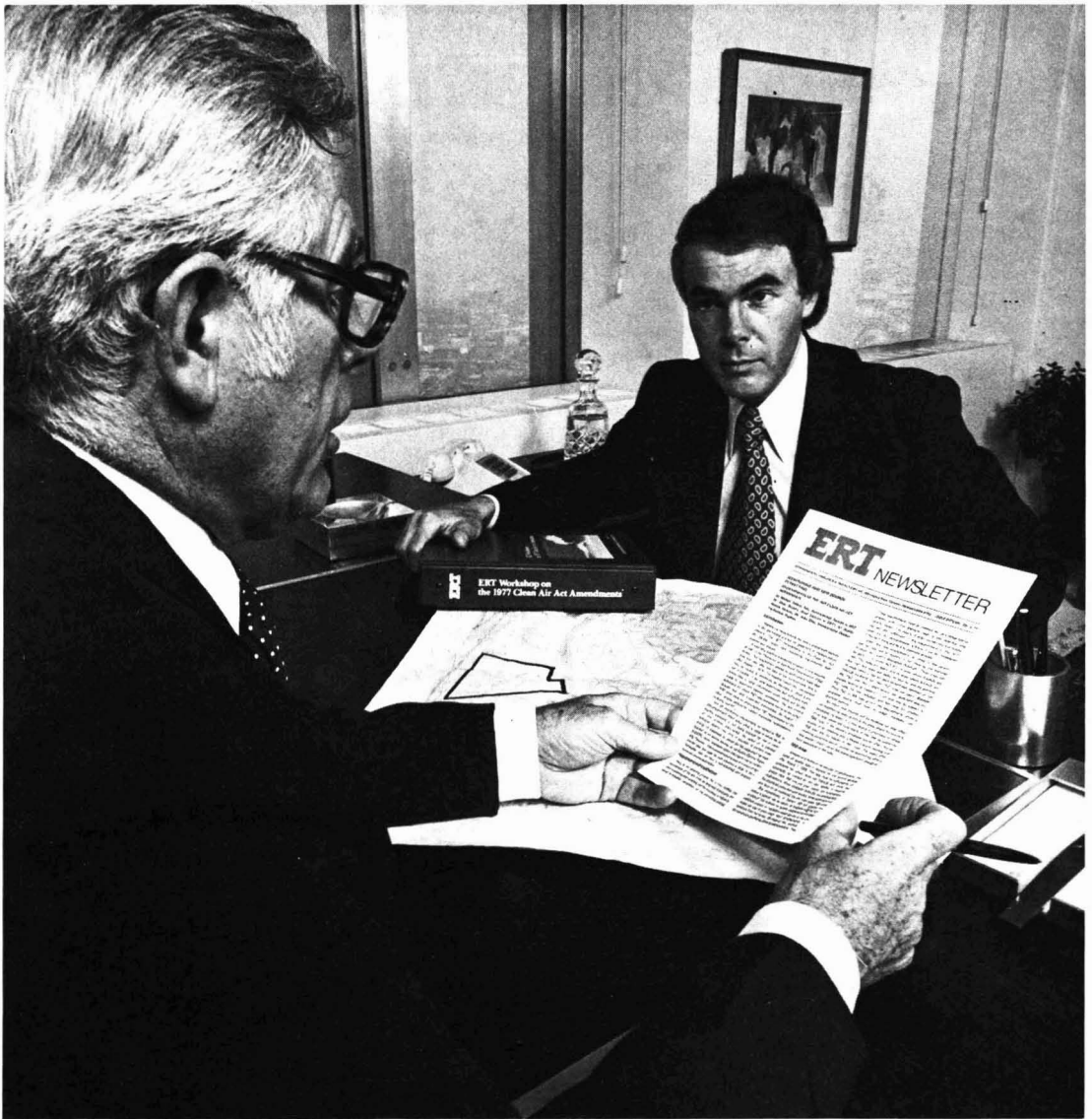
Today, saving fuel is not just a matter of economics—it can be the difference between operating or shutting down in cold weather.

As a bonus, efficient combustion processes are less likely to create air pollution problems from the stack.



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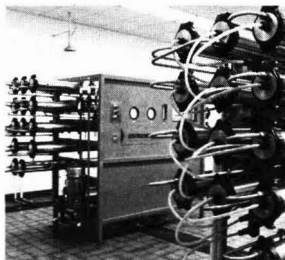
CIRCLE 6 ON READER SERVICE CARD

กองสมุด กรมวิทยาศาสตร์

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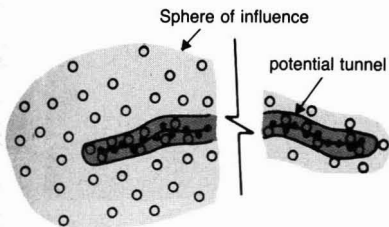
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Published monthly, with additional issue in October, by the American Chemical Society from 20th and Northampton Sts., Easton, Pa. 18042. Executive Offices: Editorial Headquarters, 1155 16th N.W., Washington, D.C. 20036. Advertising office: 25 Sylvan Road South, Westport, Conn. 06880. Second-class postage paid at Washington, D.C., and at additional mailing offices.

SUBSCRIPTION PRICES 1978: Members, 1 year \$13.00; 3 years \$33.00. Nonmember personal, 1 year \$20.00; 3 years \$48.00. Institutions, 1 year \$52.00. Foreign postage, \$5.00 per year. Air freight rates per year available on request. Single

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Credits: 999, ES&T's Julian Josephson; 1001, Camp, Dresser & McKee, Inc. (Boston, Mass.); 1002, 1003, 1012 (2 photos), ES&T's Julian Josephson.

Cover: Arend J. Vermeulen, Provinciale Waterstaat van Noord-Holland (Haarlem, The Netherlands)

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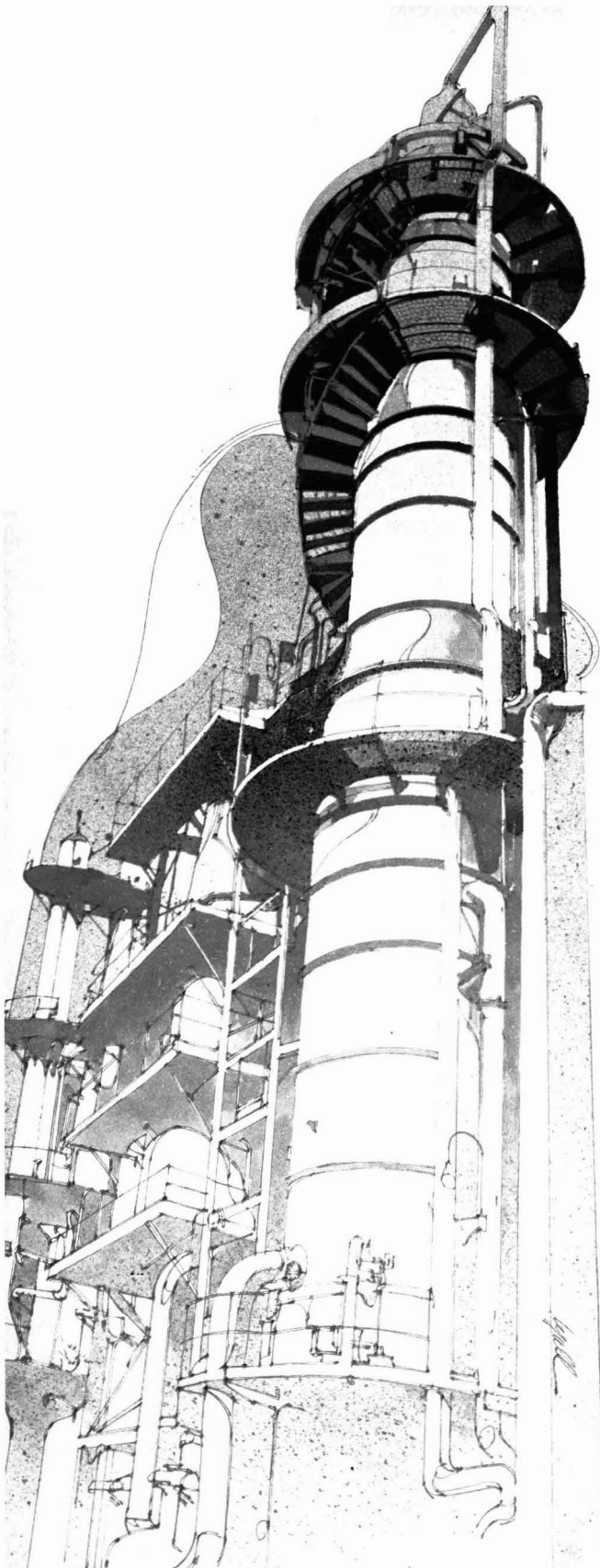
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Is the industry equal to the challenge?

The issue of trace organic contaminants in public water supplies presents a challenge to the waterworks industry; a challenge of greater scope and magnitude than any other of the past half century.

The Environmental Protection Agency has promulgated regulations to limit organic contaminants in public drinking waters, as detailed in the *Federal Register* of February 9, and subsequent supplemental notices. The regulations would require water utilities serving populations of 75 000 or more to employ granular-activated carbon systems for removal of such contaminants.

The logic of protecting the public from the potential hazards of known toxic and carcinogenic agents is eminently sound, the technology proven, and the responsibility of the waterworks industry clear. Yet, controversy and resistance surround the proposed regulations. Remarkably, much of the opposition emanates from the municipal waterworks industry and certain allied professional groups.

Opponents of the proposed regulations have advanced arguments challenging the need for such "drastic" measures, the effectiveness of the technology, and the associated costs. Other issues have been raised regarding a variety of possible "adverse side effects" of activated carbon systems. Some of the arguments represent real concerns on the part of those unfamiliar with the extensive history of successful use of activated carbon in water and wastewater treatment; others properly belong in the category of foot-dragging.

There is clear and substantial evidence that organic compounds of known toxic and/or carcinogenic character are ubiquitous to water supplies of metropolitan areas. Just as clear and substantial is the evidence that granular-activated carbon systems can be designed to remove such compounds effectively and reliably. Regarding adverse side effects, extensive experience with coal-based granular carbons in water

applications in both the U.S. and abroad has indicated no evidence of insoluble problems of "slug" release of adsorbed compounds, leaching of heavy metals or polynuclear aromatic compounds from the carbon beds, enhanced growth of pathogenic organisms in carbon beds, release of carbon fines to finished water, or air pollution caused by carbon regeneration. Such problems usually relate to inadequacy of design and/or operation rather than to any inherent deficiencies of granular carbon adsorption systems. The technical arguments against the proposed regulations thus appear directed more to diffusing the issue than to its resolution.

Estimates by the EPA place costs for carbon treatment of water supplies at between \$7-26 per year per family; the bases for these cost estimates are for the most part conservative and reasonably established. In view of the protection afforded the public, a measure that costs less per year than membership in a professional society can hardly be termed "drastic." Indeed, even in the unlikely event that the estimates err by a factor of two, the benefits still well merit the costs.

The effective challenge to the waterworks industry addresses its ability to implement innovative and advanced technology to ensure safe water supplies—a public trust. The industry must indeed be equal to the challenge.



Walter J. Weber, Jr.

Dr. Walter J. Weber, Jr. is Professor of Environmental and Water Resources Engineering and Chairman of the University Water Resources Program at the University of Michigan, Ann Arbor, Mich.

ES&T LETTERS

Process measurements

Dear Sir: I would like to call your attention to the omission of TRW's role in the implementation of the Process Measurements for Environmental Assessment Symposium (*ES&T*, May 1978, p 513). TRW was funded by EPA to run the symposium. Most of my coordinating activities for the implementation of the symposium were performed when I was employed by TRW; since January 1978, TRW has provided a subcontract to me at Systems, Science and Software (S-Cubed) to assure continuity in the implementation of the symposium. Through an EPA contract, TRW clearly was financially responsible for the symposium. In addition, many hours of TRW employees were spent in behalf of:

- informing the attendees of the symposium and the topics to be covered

- participating in the social activities planned, and
- performing the needed work of manning registration desks, providing visual aid support, and assuring things went well.

E. A. Burns
Systems, Science and Software
La Jolla, Calif. 92038

Toxin removal—correction

Dear Sir: In the feature article, "Target: Toxin Removal" (*ES&T*, May 1978, p 533), under the heading "Chemical oxidation", it was misstated that "Hydrogen peroxide and potassium permanganate would result in an oxidized by-product plus manganese dioxide". The corrected statement should read, "Hydrogen peroxide and potassium permanganate could also feasibly be used to oxidize toxins. The use of potassium permanganate would result in an oxidized by-product

plus manganese dioxide which is relatively insoluble in water."

Anthony V. Metzner
Ecodyne
Union, N.J. 07083

Power plant chlorination

Dear Sir: The figure in *ES&T*, July 1978, on page 781, shows "hot side" blowdown. This has been proscribed by 40 CFR 423 for all electric generating units constructed after 1974. The circulating cooling water system blowdown should be taken off between the cooling tower and makeup water injection. Hot side blowdown has the further disadvantage of wasting directly to blowdown some 10-50% of the excess chlorine passing the condenser. This chlorine should be used to maintain biological cleanliness in tower. As Zeitoun and Reynolds correctly pointed out, algae are the dominant problem in the tower; and it will

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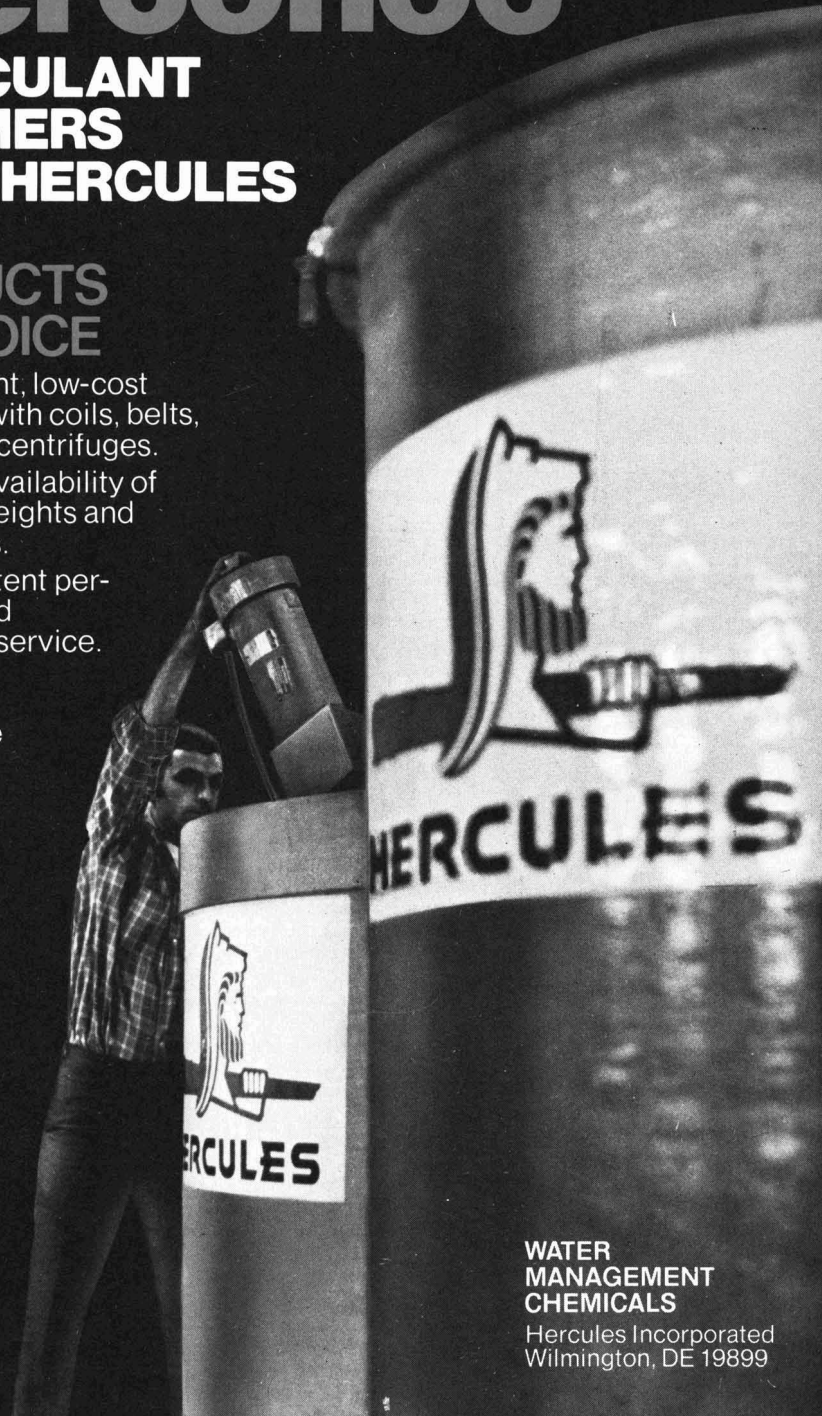
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sluff off and be carried to the condenser.

It is desirable, for the good of the biota of the receiving water, to minimize the chlorine in the blowdown. Regulations quite properly limit this discharge in both time and concentration. Cooling towers are aeration systems, and some of the residual chlorine is probably removed therein. I know of no quantitative test data showing how much of the residual chlorine in its various forms is removed by a cooling tower. I would appreciate any available data on these pages or by private communication.

Donald G. Frier, P.E.
Gilbert Commonwealth
Reading, Pa. 19603

Steel update—correction

Dear Sir: In the December 1977 issue, p 1225 of your magazine, there appeared reference to our study Environmental Steel Update with the price quoted as \$10 for the 250 page study. This information is incorrect.

The study sells for \$150 and there is a technical summary available for \$10.

Kare Hornschuch
Council on Economic Priorities
New York, N.Y. 10011

Research in water use

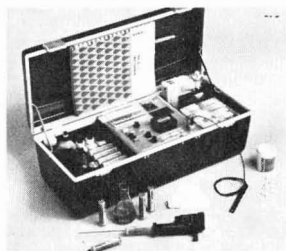
Dear Sir: In a guest editorial (*ES&T*, January 1978, p 5). Dr. Daniel A. Okun proposes that more efforts should be in addressing potable water quality standards rather than further research in water reuse. Dr. Okun's statement emphasizes how inadequate are our current water quality standards. Only some waters that meet current water quality standards are acceptable for use. Waters that meet these standards but are reclaimed from wastewaters are not acceptable for domestic use. And we know most domestic supplies are drawn from waters that contain wastewaters.

Indeed, further research on potable reuse of water will give the answers Dr. Okun looks for. He argues that a study of one waste will not give universal answers because all wastes are different. Aren't all water supplies? Studies on one water supply would then not answer universal questions either.

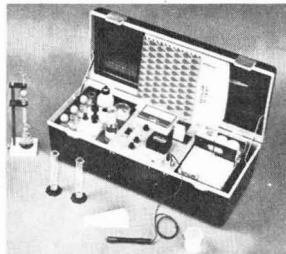
The quality of undesirable products and chemicals in wastewater is (or, at least it should be) greater than in a water supply. Therefore, these undesirable products should be easier to identify and it should be easier to demonstrate those processes that remove all of these undesirable products. A process that removes the undesirable

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products from reclaimed water, or at least reduces them to a lower level, demonstrates a process that can be used for drinking water supplies with assurance that such undesirable products will be removed or reduced to an acceptable level.

Water of a quality that meets our drinking water standards should be questionable to Dr. Okun and to all of us because the current drinking water standards are based on using the best available or desirable sources. Most sources presently available are contaminated to some degree, and larger rivers can be greatly contaminated as they contain greater amounts of sewage. Hence these best available or desirable sources do not provide the protection claimed by the current drinking water standards.

Why should we accept water quality standards based upon the source of the supply since the sources are the biggest unknown from a quality standpoint? Why should we not improve the water quality standards by developing such criteria as are necessary to ensure protection of the public health? The goal should be to develop one set of comprehensive water quality standards for drinking water regardless of source

of the water. This would do more to improve "the quality of waters now being consumed" than any other thing.

The development of such standards can be done by continuing and encouraging additional research on wastewater reclamation for potable reuse. When it is demonstrated that reclaimed water is suitable for potable reuse, then we will have adequate water quality standards suitable for use with any source.

Lloyd C. Fowler

Santa Clara Valley Water District
San Jose, Calif. 95118

Precipitator update

Dear Sir: The McGill Precipitator represents a new generation of electrostatic precipitators. It is fundamentally different from conventional EP's described in the report (*ES&T*, June 1978, p 657) in that there are no hanging discharge wires that require periodic maintenance. Also, because of the method used to create an electrical discharge corona, power consumption is considerably lower. This has been verified by more than fifty precipitators we have currently in operation throughout the U.S.

For special applications, we encourage pilot testing, using one of our Mobile Electrostatic Precipitators to determine the proper precipitator size and design considerations.

William R. Heifner
United McGill Corp.
Columbus, Ohio

Precipitator report

Dear Sir: To my knowledge no vendor of precipitator equipment other than Research-Cottrell subscribes to (1) the alkali/Na₂O ratio as a criterion for electrode fouling in hot side precipitators, or (2) that phosphorus pentoxide is responsible for corona quenching. Yet the article (*ES&T*, June 1978, p 657), "Keeping Fly Ash Out of the Stack", authored by Research-Cottrell employees presents these concepts as accepted facts.

Is there any independent published corroboration of these concepts or are you merely adding to the disheartening array of precipitator mythology that persistently afflicts customers and vendors alike?

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CIRCLE 4 ON READER SERVICE CARD

WIND ALARM.

A black and white photograph showing the silhouettes of several large cranes on the deck of a ship. The cranes are complex structures with long jibs and various pulleys. The background is a bright, overcast sky, and the water of the sea is visible at the bottom of the frame. The overall mood is industrial and somewhat somber due to the high contrast of the silhouettes.

It helps your
cranes keep their sea legs.

INTERNATIONAL

Minamata revisited? Perhaps, but this time in Thailand. A report in *Ambio* (Vol. VII, No. 3, 1978) cites mercury contamination of one species of fish in the vicinity of a Japanese caustic soda factory in Samut Prakarn Province; fish samples taken from other sites in Thailand had the lowest baseline mercury concentration in the world. Fish is an important source of protein in the Thai diet. Human hair samples showed signs of mercury accumulation in males, but not females living in the polluted area. As more industry moves into Thailand because of the country's lax environmental laws, bioaccumulation of industrial poisons becomes more of a threat.

WASHINGTON

EPA and TVA are conducting the largest U.S. air pollution study, known as the Tennessee Plume Study. The study is being funded to the tune of \$1.5 million by the EPA, and is the first major field experiment in the agency's Sulfur Transformation and Transport in the Environment (STATE) research program. TVA is furnishing the air quality scientists and equipment to conduct the study. Ten airplanes and helicopters will fly into the smoke plume of TVA's Cumberland Steam Plant, a coal-fired power plant northwest of Nashville, Tenn.; onboard monitoring equipment will track the pollutants for distances up to 200 mi. Weather balloons will be sent up to determine meteorological conditions during the experiments. Ground-level portable air sampling devices will also be used.

EPA on water issues: The agency is beginning the required reviews of variances and exemptions granted by states administering the Safe Drinking Water Act. Under initial review will be those actions taken by Ark., La., N. Mex., Okla., and

Tex. between June 24, 1977 and June 23, 1978. EPA administrator Douglas Costle, testifying before the House Subcommittee on Investigations and Review, defended continued federal funding for expensive advanced wastewater treatment (AWT) facilities, but acknowledged that EPA could do a better job in eliminating unnecessary AWT project proposals. EPA is considering amending its regulations, promulgated under the Clean Water Act, to strengthen its present policy on discouraging states from downgrading their water quality standards.



Rep. Rogers

In a letter to EPA administrator Douglas Costle, Rep. Paul Rogers (D, Fla.) urged an "expedient evaluation" of chemical flue-gas conditioning as a feasible and desirable pollution control device. Rogers, chairman of the House Subcommittee on Health and the Environment, cited several reasons for urging an immediate review of the technology; among these were: the technology has been proven effective for particulate emission reduction in a number of full-scale demonstrations; chemical gas conditioning does not require expensive capital outlays; and "gas conditioning may serve as an effective tool to reduce emissions in any interim period before a non-complying source is able to install the requisite equipment." EPA is scrutinizing this technology.

OSHA released its preliminary list of Category I, "confirmed" carcin-

ogens to encourage discussion of priorities for regulation under its proposed generic cancer policy. The tentative list contains 269 toxic chemicals, of which only 116 are produced annually in significant amounts; these latter 116 would be possible candidates for regulation. The list is based on NIOSH's preliminary review and categorization of some 2000 chemicals.

The Supreme Court overturned a district court's ruling that the Price-Anderson Act, which limits a utility's liability for damages resulting from a catastrophic nuclear reactor accident to \$560 million, violates the due process provisions of the Fifth Amendment. In an earlier ruling, the Supreme Court limited the role of lower federal courts in reviewing the actions of the Nuclear Regulatory Commission, which licenses nuclear power plant construction.

The formation of the American Council on Science and Health was announced in Washington, D.C. recently. Its executive director, Dr. Elizabeth M. Whelan, and Nobel Laureate Norman Borlaug, one of its founders, stated that the council will "combat the chemical phobia now rampant across the country." The group, funded by contributions from individuals, foundations and governmental agencies, will periodically issue position papers on issues concerning chemicals, the environment and human health. The first papers, to be issued late this fall, will focus on saccharin, the Delaney Clause, cancer in N.J., naturally-occurring carcinogens in food, and the relationship between diet and heart disease.

STATES

Blanketed by one of the heaviest smog layers in recent years, Los Angeles officials, in July, imposed mandatory antipollution measures on business and industry for the first time. Restrictions included a ban on the unloading of oil tankers,

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CIRCLE 14 ON READER SERVICE CARD

20% production reductions in smog-causing industries and the closing of business parking lots to non-carpool cars. Residents were asked to cut back voluntarily on home electrical usage and to avoid unnecessary driving. In a separate action, the Air Resources Board sued Gulf, Mobil and Powerine oil companies for "thousands of major smog law violations." ARB Chair-



Calif. ARB's Quinn

man Tom Quinn said the suit could force the companies to pay up to \$6 million in fines for selling gasoline diluted with excessive amounts of rapidly-evaporating hydrocarbons.

A Philadelphia-area polluter became the first person to be jailed under the Clean Water Act.

Manfred DeRewal was sentenced to six months in jail, placed on four and one-half years' probation and fined \$20 000 for pouring hazardous industrial chemical wastes into the Delaware River in March 1977. DeRewal, according to the EPA, has been cited for more than 100 state pollution violations over the past 13 years.

Maryland is the first state to require motor oil recycling.

Under the Maryland Used Oil Act, effective July 1, the state requires motorists who change their own motor oil to have it recycled. The used oil must be discarded at state-designated collection sites. Violators can be fined up to \$250 for the first offense and up to \$1000 or two months in jail for subsequent violations.

The world's first geothermal geopressured test well is being drilled in Brazoria County, Tex.

The well is being drilled by General Crude Oil Co. of Houston, Tex., under a \$6 million Dept. of Energy contract awarded last December.

Areawide 208 planning agencies, funded by the federal government

under the Federal Water Pollution Control Act, have been costly failures states Thomas D. Lustig in his Ph.D. thesis in water resource engineering at the Massachusetts Institute of Technology. Lustig states that the EPA has spent close to \$300 million to fund these agencies, and that little of a practical nature has evolved from their efforts. He claims that "the likelihood of their improving water quality is not great." A total of 176 agencies were designated under Section 208 of P.L. 92-500 and, according to Lustig, their most pervasive failure was their inability to develop plans that could or would be implemented. One cause was EPA's stress on the form of the 208 plan rather than on the solution to serious problems.

Colorado businesses seeking state income tax credits for pollution

control equipment have until the 20th of this month to apply to the state Dept. of Health for tax credit certification. To be eligible for this one-time tax credit, the air and water pollution control equipment must have been acquired or first used after Jan. 1, 1970. Residential sewage disposal systems and devices to control automotive emissions are not eligible for the tax credit. The tax credit will apply during 1979.

MONITORING

The EPA is proposing a new calibration method for measuring ozone in the atmosphere. The new method, based on ultraviolet photometry, would replace the 1% neutral buffered potassium iodine (NBKI) procedure. The proposal appeared in the *Federal Register* on June 22, p 26971.

Air pollutant concentrations as low as parts-per-billion are detectable

with the Trace Atmospheric Gas Analyzer (TAGA), developed by SCIEX Ltd. (Toronto, Canada), with help from the Canadian federal government. The technology is exclusively Canadian. Plans for a similar water monitoring system are in the works.

"Clear signs of recovery" are reported in the Great Lakes,

according to the International Joint Commission (Windsor, Ontario, Canada). Phosphorus, mercury, and DDT, for instance, have shown declines. But some industries perform

better than others, in cleanup, and the IJC warns against complacency.

TECHNOLOGY

About 2 billion bbl/d of oil could be made from coal by 1990

"with about half the effort devoted to landing a man on the moon," Charles Gullede, president of Dynalectron Corp. (McLean, Va.), said. He estimated costs of such capacity at \$20 billion for the plants, plus \$10 billion for the associated coal mines. However, Gullede forecast that these costs would be spread over 10 years, and represent less than 2% of the \$2 trillion gross national product. Dynalectron is providing technology—the H-Coal process—and engineering and procurement for a plant in Kentucky to convert 600 tpd of coal into 1800 bbl/d of oil.

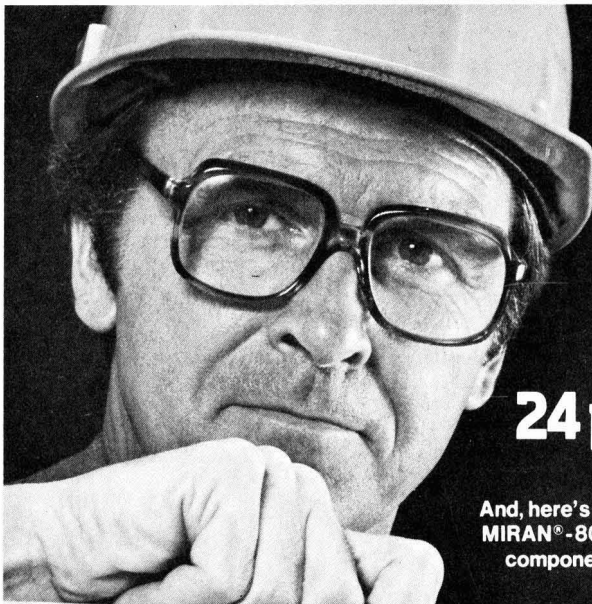
Combining petroleum refinery and olefin plant effluents

may be "synergistic," rather than "antagonistic," according to C-E Lummus (Bloomfield, N.J.). Lummus engineer Philip Chen said that the high salinity of olefin process effluents would be buffered by the dilution capacity of refinery effluents; the latter usually dominate flow volumes. Incidental streams of spent caustic or acid that the refinery generates can be handled by the neutralization system provided by the olefin plant, Chen said. The idea would be to treat the olefin plant effluents so that they become compatible with refinery effluents, and then treat them jointly at the end of the pipe.

The first large-scale solvent refined coal (SRC) plant

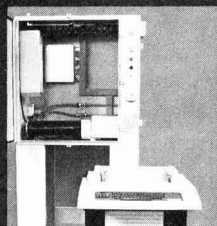
—to convert 6000 tpd of raw coal to clean coal—will be designed for DOE by The Southern Co. (Atlanta, Ga.). Southern president Alvin Vogtle predicted that such an SRC plant could be operational by 1983; preliminary design work is to be completed by mid-1979. The actual work will be done by Southern Company Services, Inc., Southern's engineering and special services subsidiary. Southern has gained experience through a 6-tpd pilot plant (*ES&T*, June 1974, p 510), and recently successfully burned SRC at Plant Mitchell (Albany, Ga.) under actual operating conditions.

Land treatment concepts may become an additional part of the al-



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8-HOUR TIME WEIGHTED AVERAGE (PPM)

	E	F	G	H	I	J
14		692	14			
15		704	10	.3	4.8	12
18		824	9	.2	3.2	17
45		758	12	.1	3.2	10
68		652	21	.1	3.3	11
74		640	23	.4	3.0	11
54		618	26	1.0	7.2	39
53		598	13	1.3	6.4	48
8		560	2	1.3	6.4	48
9		578	1	.1	2.0	42
10		584	1	.2	2.1	10
8		564	1	.1	1.9	9
29		840	16	.1	2.4	8
40		824	24	1.6	9.4	10
41		919	38	.2	4.6	22
68		1227	42	.4	4.8	18
62		1042	39	.2	2.4	34
58		983	24	2.1	2.8	58
44		1097	22	2.0	2.7	74
84		667	13	.3	2.4	58
44		643	11	.1	1.9	34
58		637	12	.3	12.8	13
18		658	12	.8	16.9	15
34		604	11	1.2	11.4	21
38					3.2	12

HIGHEST CONCENTRATION DURING SHIFT (PPM)

	E	F	G	H	I	J
24	11147	925 11147	32 15147	0.7 13122	9.4 15147	24 15147
32	9120	878 9120	18 9120	0.4 13124	8.6 15148	34 9120
49	9130	1222 9130	16 15150	0.2 8133	8.4 15150	22 9130
120	8135	1183 8135	28 15152	0.2 8135	8.4 15152	24 8135
138	8136	808 8136	41 15154	1.4 8136	6.8 15154	87 8136
162	8138	940 8138	58 13148	2.1 8138	12.4 14108	106 14108
83	8140	773 8140	65 12150	1.7 8140	14.2 14110	142 14110
96	8141	768 8141	22 15159	2.3 8140	12.4 14108	14 11101
17	12101	658 12101	4 12101	0.2 12101	3.8 8102	14 12101
20	12102	704 12102	2 12102	0.3 12102	3.6 8104	18 12102
22	12104	738 12104	1 12104	0.3 12104	3.6 8106	15 12104
15	12106	708 12106	2 12106	0.3 12106	3.5 8108	12 12106
47	8152	1043 8152	33 9139	3.2 8110	17.2 9139	62 8152
59	8154	1218 8154	42 9140	0.4 12108	11.1 8154	52 8154
84	8155	1441 8155	27 9142	1.2 8112	10.4 8155	32 8155
144	15132	2296 14150	78 15132	4.4 8114	7.2 14150	148 15132
128	15134	1848 15134	94 15134	3.8 8115	6.6 14152	162 15134
104	15135	1777 14153	76 14153	2.9 8117	8.4 14153	122 15135
154	15136	1975 15136	47 14155	2.8 8119	7.4 14155	104 15136
88	10158	810 10158	22 15138	0.7 12119	18.6 15138	32 10158
106	10159	744 15140	18 15140	0.6 12121	24.8 15140	28 10159
46	12117	788 12117	24 12117	0.2 12122	33.2 12117	34 11101
62	12119	1062 15143	19 12119	1.4 8126	18.4 12119	56 15143
72	12120	848 15145	17 15145	2.2 8128	7.8 12120	28 15145

NUMBER OF ALARMS DURING SHIFT

CIRCLE 22 ON READER SERVICE CARD

ready advanced wastewater treatment (awt) plant at South Lake Tahoe, Calif. Land treatment with secondary effluent in an existing flood irrigation system could cost much less than continued physical-chemical awt, according to Culp, Wesner, Culp (El Colorado, Calif.). Total costs could be reduced by 27%; local costs, by about 40%; and energy consumption by 50%, according to the firm. Energy required off-site to produce chemicals and materials could be cut by 80%. However, the consultant notes that political acceptance must be gained first.

Irradiation of mixtures of NO_x, hydrocarbons (HC), and diethylhydroxylamine (DEHA) was carried out in a large smog chamber at EPA (Research Triangle Park, N.C.). DEHA had been proposed as a smog control strategy. But when DEHA was consumed, increased ozone formation, rapid NO_x increases, increased HC consumption, increased PAN production and aerosols, and NO_x product profile changes resulted. EPA said that adding DEHA to an urban atmosphere "is much like adding fuel to the fire," because after DEHA is used up, smog could sharply increase. Moreover, DEHA is itself a smog former. Also, downwind rural conditions could become unacceptable.

Possibly 85% organic carbon recovery from eastern Devonian shales may be achieved with the HYTORT system developed by the Institute of Gas Technology (Chicago, Ill.). Options are to make synthetic nat-

ural gas or low-nitrogen synthetic crude oil. The eastern shales are estimated to contain a total of 423 billion bbl recoverable through above-ground hydrotorting. Over 99% of the sulfur would be recovered. Although 1000 acres would be disturbed at any given time, because of mining, reclamation would be a simple process, according to IGT. Acid mine drainage would be kept to an "acceptable minimum," and air emissions are not expected to be a problem.

INDUSTRY

OSHA should abandon the overall categorical approach to carcinogen control in the workplace, and, rather, develop standards for particular substances on an individual basis, two spokesmen for Tenneco Chemicals, Inc. (Saddle Brook, N.J.) suggested. However, they agreed that any materials posing a possible occupational carcinogenic risk should be regulated as soon as possible. The Tenneco spokesmen recommended that risks be assessed against benefits "since a 100% risk-free environment is not attainable." They also called for use of general criteria developed by the National Cancer Institute for assessing carcinogenic risk to humans.

Liquid methanol fuel production could be a major new industry in Canada, and create "tens of thousands of jobs," Environment Canada minister Len Marchand believes. He noted that methanol plants could use renewable forest resources in regions where economic development is most needed, and

use agwaste, coal, or garbage, as well. And the Electric Power Research Institute (Palo Alto, Calif.) also believes in methanol potential. EPRI is contributing part of \$2.5 million toward a 500-h, 6-mo demonstration of methanol in a power plant combustion turbine; about 2.7 gal of methanol will be used. Southern California Edison is also supporting the project.



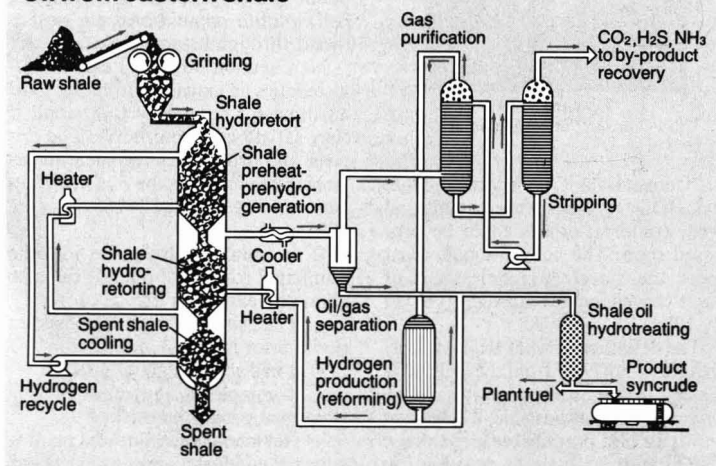
Camp Dresser & McKee's Banks

Water resources management must be considered in very broad terms, Harvey Banks, president of Camp Dresser & McKee's Water Resources Division observed. Effects on land, air, fish and wildlife, and local economy, of such management must be considered in any project planning and execution. Banks also said that present technology does not permit potable water reuse, as yet, but other applications, such as groundwater recharge with renovated water, should be considered. For other countries, however, he foresees that water reuse will be a "must." Banks noted that reuse was well demonstrated in Singapore, for example, and named Yemen as a nation in which reuse will be extremely necessary.

Innovative contribution by the chemical industry is threatened by the impact of waves of regulations, warns Gerald Laubach, president of Pfizer, Inc. If drug regulations made things tough, EPA, OSHA, NIOSH, and the Consumer Product Safety Commission have made things even tougher, Laubach said.

Optimism for small businesses in solar energy was expressed by the Solar Energy Industries Association (Washington, D.C.), in the wake of President Carter's signing of the Small Business Energy Loan Act of 1978. Small Business Administration loans of up to \$500 000 could be available with 90% federal guarantee.

Oil from eastern shale



Some rules were tightened; others were relaxed. But a desire for more clarity and equitability, as well as the will of Congress, were among EPA's reasons for

Modifying the NPDES

Those who follow water laws and regulations will recall that the Federal Water Pollution Control Act Amendments of 1972 provided for a National Water Quality Commission to recommend mid-course corrections in the national water clean-up program. The Commission's findings contributed to the writing of the Clean Water Act of 1977 (P.L. 95-217) which, in turn, provided for necessary changes in the National Pollutant Discharge Elimination System (NPDES). Addressing this subject at a meeting of the American Paper Institute (API) and National Forest Products Association (NFPA), held in Washington, D.C., in June, Leonard Miller, Director of the Permits Division of EPA's Office of Water Enforcement, said that the changes in the NPDES program, the keystone of the water pollution program, will have a direct effect on the 50 000-70 000 individual dischargers.

Stress on toxics

Miller noted that the new Act shifted the emphasis to toxic pollutants. He said that "best available technology" (BAT) for the 65 families of the toxic substances, as identified in the *Natural Resources Defense Council v. Train* Consent Decree must be met by July 1, 1984, rather than 1983. For pollutants subsequently designated as toxic, BAT will have to be met within three years of such pollutants' effluent limitation promulgation. Moreover, if toxic effluent standards are based on health considerations, as per section 307(a) of the 1977 Act, these standards must be met in one year, or, under certain conditions, up to three years.

In addition, the Act grants new authority to EPA to regulate toxic pol-

lutants at plant sites through the device of "best management practices" (BMP). This authority will allow the EPA, through its permits, to require, at a plant site, effective controls to prevent spillage and leakage of toxic pollutants into the nation's waters.

Three classes

The new Act also divides industrial pollutants into three classes for future treatment requirements: conventional, toxics, and non-conventional or "gray area" pollutants.



Leonard Miller
a shift in emphasis

"Conventional" pollutants include pH, BOD, total suspended solids and fecal coliform; others could be proposed soon. The conventionals must meet the statutory requirement of "best conventional technology" (BCT) by 1984.

The definition of what BCT actually requires is not clear from the legislative history. "The Senate saw it as BAT minus as little as possible. The House saw it as 'best practicable technology' [BPT] plus as little as possible. So

EPA works from both ends," Leonard Miller said.

Certain variances

"Gray area" pollutants are those that are neither toxic (the 65 families of pollutants in the Consent Decree, plus those that the Agency adds) nor conventional. Such pollutants are subject to BAT by 1984, or 3 years after effluent limitations are established, but not later than July 1, 1987. Unlike toxics are conventionals, however, gray area pollutants can be allowed variances from BAT on economic (301(c)) or environmental grounds (301(g)).

With an economic variance, a discharger may be under somewhat relaxed requirements which, nevertheless, must reflect maximum use of technology within the discharger's economic capabilities, Miller told the API/NFPA meeting. For environmental variances, relaxed requirements may neither interfere with public water supplies nor balanced fish/wildlife populations, nor pose a threat through bioaccumulation.

New section 301(i)(1) allows municipalities an extension from the 1977 deadline for secondary treatment, if they satisfy certain criteria. The criteria and procedures for such an extension are found in the *Federal Register*, volume 43, page 21266, May 16, 1978.

If an industry discharges into the municipal treatment plant it can also obtain an extension if:

- It can show its intention of such a tie-in, prior to July 1, 1977.
- It has acted in good faith.
- It completes any required pre-treatment program on schedule.
- The municipal treatment plant to which the industry discharges has an

extension, pursuant to 301(i)(1).

Industries that use innovative technology may also receive an extension from the deadline. In this case, production or control processes must result in greater reduction of effluent, or required effluent reduction must be achieved through an innovative system with potential for lower costs and industry-wide application.

Clarification of rules

The agency is taking steps to make the NPDES regulations more understandable. "NPDES regulations have been scattered all over Volume 40 of the Code of Federal Regulations," Jeffrey Miller, EPA's Deputy Assistant Administrator for Water Enforcement told *ES&T*. "Now, however, they will be consolidated, and updated to take into account the new law, as well as recent court interpretations of the Water Act," he said. While the NPDES "regulatory reform" project started in 1976, it gained impetus from the 1977 Act, and from the Carter Administration's call for such "reform." As Jeff Miller said, "We took a 'relook' at existing regulations and at the permit system, and found that substantial revisions were needed."

Beside the regulations needed to implement the changes in the law, amendments to the regulations were needed, so that permits for industries affected by "best available technology" for toxics would be reissued or



Jeffrey Miller

"substantial revisions were needed"

modified, once the effluent guidelines are promulgated. Such permits would contain a clause to reopen the permit, once a new guideline is promulgated. Regulations establishing this requirement, and general criteria under which EPA can veto State permits under the authority of 402(d)(2), have recently been promulgated.

Protection

Jeffrey Miller outlined certain other changes or clarifications in the NPDES regulations review. For instance, if a new source is working under a permit, and it is meeting new source standards, that source will have protection against guideline changes for 10 years, Jeff Miller said. This protection covers pollutants which the source is *already* discharging under new source performance standards.

However, there is no protection for additional pollutants not covered in new source performance standards, should effluent limitations for such a pollutant be promulgated.

There is also a certain protection against NPDES violations. If, for instance, a wastewater treatment (wwt) plant must be closed for necessary preventive maintenance, and there is no feasible alternative to a wwt by-pass (such as retention of wastes), the plant may temporarily by-pass the wwt system, and not incur a violation. This is at the discretion of the permitting authority, and is subject to controls to minimize the adverse effects of the by-pass.

All in one "book"

The foregoing represents some significant changes made to the NPDES program. There is a shift of emphasis to toxics. Certain changes were brought about by court decisions. In some cases, complicity is eased to a certain extent; in other cases, more stringent requirements are mandated.

However, there is also a sincere effort on the part of EPA to clarify and improve NPDES regulations in the light of past experiences, and to put them all in one easier to understand "book." Also, together with continuing efforts to meet national clean water goals, the aim is to mitigate onerous aspects, and to accentuate the equitability of the NPDES program. JJ

Levels of control required under 1977 Act^a

Pollutant	Name of required technology	Abbreviation	Statutory deadline	301(c) economic variance	301(g) environmental variance
Conventional	Best conventional pollutant control technology	BCT	July 1, 1984	No	No
Nonconventional, or "gray area"	Best available technology economically achievable	BAT	July 1, 1984, as appropriate ^b	Yes	Yes
Toxic	Best available technology economically achievable	BAT	July 1, 1984, as appropriate ^c	No	No
	Best management practices	BMP's	None	No	No
	Effluent standards (or prohibitions)		Up to 1 year after promulgation, as appropriate ^d	No	No

^a Applicable to existing sources. ^b July 1, 1984, or 3 years after limitations are established, whichever is later; but never later than July 1, 1987. ^c July 1, 1984, for those 129 toxic pollutants which appeared in 43 *Federal Register* 4108. For other pollutants which may be added to the toxics list, 3 years after limitations for such pollutants are established. ^d The effective date for an effluent standard for a toxic pollutant may be extended to 3 years after the standard is promulgated, if earlier compliance is technically infeasible.

Source: Presentation to API/NFPA meeting by EPA's Leonard Miller.

A zero discharge wastewater treatment system

PCA International, the world's largest portrait photographer and photofinishing operation, is also the cleanest

This year, PCA photographers will make color portraits of more than 7.5 million Americans—one out of every four children under six years of age in the U.S. All told, there are about 800 photographers in the company's 23 regions who ship 3000 rolls of film each week for processing to the laboratory and corporate headquarters in Matthews, N.C.

Last January, the company doubled the size of its operation with the construction of a new manufacturing complex costing \$6.5 million, including land, building and furnishings and its corporate headquarters and laboratory and technology complex on a 57-acre site. This plant operates round the clock, five days a week. On an average week the company processes 30 miles of film and 180 miles of 10-inch paper for prints, equivalent to a million 8×10 prints each week. PCA has facilities in the U.S., Japan, Canada, Sweden, Denmark and Holland. The film comes in by mail and, after processing, the portraits are returned by truck. Foreign film and portraits go by air freight.

In general, the PCA name is now known to the U.S. consumer because the company operates under retailers such as K-Mart and Woolco. PCA has working arrangements with 37 of the nation's 50 major discount chains and operates in 7200 discount stores. An average number of customers is 145 000 each week.

Customers are attracted by the offer of an 8×10 color portrait for 88 cents. Typically, one to three PCA photographers will be stationed in a store for 3–5 days. Three weeks later the PCA sales person presents the finished portraits to the customer and completes the sale.

PCA designed its own unique portrait camera, which permits photog-



raphers to photograph 180 subjects without changing the film. The design also permits the photographer to operate the camera while facing or standing next to the subject.

PCA has been a good corporate neighbor in Matthews, N.C. since its beginning in 1967. In its first 11 years the company reached an annual sales volume of \$123 million and a net profit of more than \$6 million.

An alert environmental watcher would immediately query the discharge of wastewater from such a large operation. Using a combination of new and available technology that the PCA engineers themselves developed, the company recycles 40 000 gallons of water each day. The technology includes reverse osmosis, countercurrent washers, electrolysis, ion exchange, and evaporation. In a year, the company recovers \$700 000 of silver and extracts enough ammonia to fertilize its many acres of lawns on the 57-acre company site. Before the completion of the zero discharge system, PCA spent

\$60 000/y on waste treatment. Today, the cost has been reduced to \$20 000, but there is no industrial discharge. However, sanitary wastes are sent to the local wastewater treatment plant, for which the company pays about \$10 000/y.

What makes PCA unique in this operation is that "proofs" have been eliminated. After the photographer has finished his job, the film is sent directly to the processing laboratory. There it goes through a series of steps starting with film development. After processing it goes to an editing department, where perhaps the most crucial step takes place—the selection of the poses that will be used to make up the portrait package.

This portrait package is produced on speculation. The customer must purchase the 8×10 portrait for 88 cents, but is offered the entire package of portraits for about \$34. A typical package consists of four color portrait charms, 10 wallet-size portraits, one 8×10 , two 5×7 s, and a 10×13 portrait. Because the selection is made from finished photographs, the customer can have the pictures the same day. PCA has found that the average sale is more than \$13 per customer.

Federal effluent guidelines

There are 3500–4000 photoprocessing laboratories nationwide, according to the National Association of Photographer Manufacturers. EPA proposed effluent guidelines for this industry in July 1977, which called for a discharge of no more than 4 gallons of wastewater per square foot of sensitized material processed. Bob Kinch of the EPA effluents guidelines staff said the agency surveyed 400 labs by telephone early last summer. Last August (1977) the agency tested the effluents from five labs. PCA was the

cleanest tested; it came out with a 0.129 gallon of wastewater per square foot of sensitized material processed. The guidelines for this industry, SIC category 7395, will be finalized in December 1979.

How PCA does it

Employees for the company number 1100 in Matthews, and total 4100 worldwide. There are 500 lab employees. Everyone in the operation from the production lines to the corporate offices is aware of and responsible for the quality control in the photofinishing operation.

Ed Schiller, director of product quality, explains that there are three areas responsible for the quality of the product. Schiller says that the Chemical Control and the Chemical R&D Departments are responsible for the full cycle of chemical needs within the laboratory and technology complex.

"This year PCA will begin to recycle 75% of its chemistry, 90% of its wash water, and have no industrial sewage discharge whatsoever," Schiller says. "We are four years ahead of the federal EPA schedule for BAT—best available technology." He explains that this includes the preparation, supply, recovery, and disposal of all chemistry used in the manufacturing of our products. "It is interesting to note that the wastewater treatment and controls were designed by our engineers by adapting off-the-shelf equipment."

The stepping stones that led to zero discharge, during a six-year period, are shown in the box material. PCA uses some 40 000 gallons of water a day.

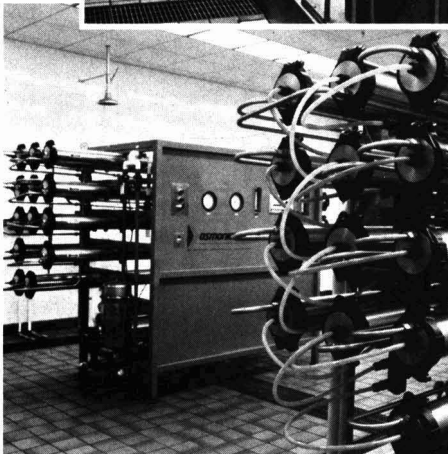
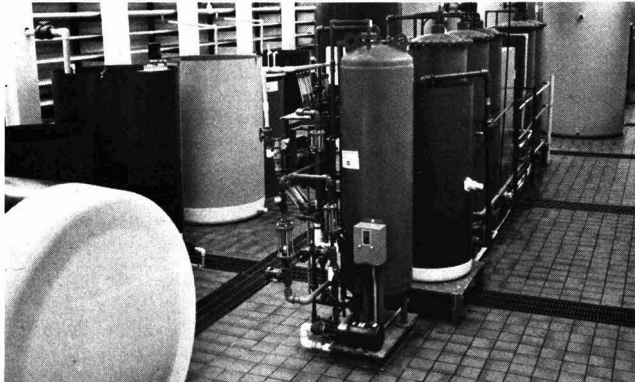
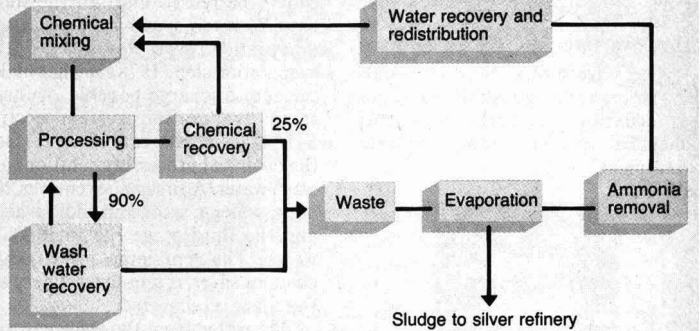
Some of the responsibilities of the color control department include:

- monitor and evaluate film and paper processing
- monitor and evaluate negative and film quality
- monitor and evaluate the photographic aspects of printing equipment
- render technical assistance for any product, equipment, or procedure effecting or effected by the product quality department
- maintain a constant and current knowledge of modern photographic technology.

The Product Evaluation Department is responsible for:

- monitoring the performance of production employees
- monitoring the quality of the product shipped to the customer
- monitoring the artistic and technical quality of the PCA photographer,
- providing the necessary statistics

PCA's zero discharge system



"Zero discharge" system. Designed by PCA technicians (top photo)

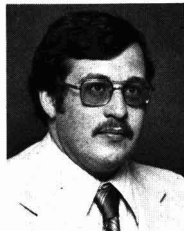
Silver recovery. \$700 000/y worth is recaptured by these electrolyzers (middle photo)

Reverse osmosis system. Handles film and paper waste (bottom photo)

to the laboratory management to ensure the efficient operation of the lab.

One, two, three, recycle

There are several steps that make the zero discharge possible and can be divided into three parts—chem mix, chemical recovery, and wastewater treatment.



PCA's Schiller
product quality is our business

Chem mix is the beginning and the end of the zero discharge cycle. Here, all the processing chemistry is prepared for use. Separate tanks are used for each solution, a practice which is not rigidly followed throughout this industry.

The preparation of the solution is controlled by computer panel. An operator selects the solution needed and pushes an "initiate" button on a control panel. A preset amount of water is added to the tank along with a measured package of chemicals. It is mixed, pumped into a storage tank, and metered to the processors.

Next is chemical recovery. Seven out of a total of 11 processing solutions are either partially or totally recycled. PCA reuses 90% of its process wash water. For example, in the regeneration of paper color developer—one of the steps that was added in 1977—the used developer solution is collected and unwanted by-products are removed by ion-exchange.

The processed developer is then pumped to chem mix, where it is analyzed and adjusted before reusing. The wash water is collected from both the film and paper lines and passed through reverse osmosis units. There are two RO units; one processes the wastewater from the print operation, the other processes that from the film operation. For the RO units the input is 32 gal/min. The RO units remove all the dissolved solids from 90% of the used wash water. The dissolved solids are concentrated into 10% of the original volume. The cleaned water is reused in the processors while the 10% containing all the pollutants is sent to waste treatment, the final step.

All excess water and chemistry is

collected at this point. Although the wastewater only contains 2% solids, it cannot be reused until all the solids have been removed by the process of evaporation. The addition of this evaporation step (1978) is what makes the zero discharge possible. A three-stage evaporation system costing \$416 000 will take care of wastes from the chemical processing solutions and wash water. A first stage removes 90% of the water, a second an additional 5% and the third stage the final 5% of water. The remaining paste, which contains silver, is sent to a refinery and the silver is recovered.

The water from the evaporators is condensed and collected; however, it contains ammonia. This water is put through an ion-exchange process in which the ammonia is removed. The clean water is then redistributed for reuse, thus completing the cycle.

Stepping stones to zero discharge, four years ahead of the BAT requirement

—recycle of an electrolytic recovery (from bleach fix), 1972

—recycle of ferricyanide bleach by ozone, 1972

—treatment of wastewater by ozone, 1972

—silver recovery from a wash water recycle of photographic processing wash waters, using reverse osmosis, 1975

—removal of heavy metals from photographic processing wastewater effluent, 1977

—recycle of prebath, 1978

—recycle final bath, 1978

—recycle of paper color developer, 1978

—water recovery for total recycle of water, using evaporators, 1978

—ion exchange to remove ammonia from evaporated water, 1978

Each year the company recovers 100% of all the silver used in its photo activity. This year silver value was \$600 000 and next year it will be in the neighborhood of \$700 000. Ninety percent of the silver is recovered from the bleach-fix and fixing solutions. It was important to reduce the iron EDTA in the bleach fix to the +2 state chemically before proceeding with the reduction of silver electrochemically. The silver removal process is then on the order of 2 hours, but would be three of four times longer (6–8 h) without the iron reduction being performed first.

Checking the solutions

On every 8-h shift there are 11 solutions that need to be analyzed—six for the film, and five for the paper—but each solution must be checked for from 3–6 components each, senior research associate Lou Daignault told



PCA's Daignault
checks on the analyses

ES&T. This check ensures that the chemical solutions are up to standards. Also, every three hours the wastewater from the processing operation is analyzed. Earlier, before installation of evaporators, PCA discharged 18 000 gpd of its wastewater into the local treatment plant—a 300 000 gpd activated sludge plant in Matthews.

"Chemical analyses are performed on all processing solutions, chemical recovery systems, and wastewater treatment systems," Daignault says. The test procedures include colorimetric and potentiometric titrations, UV and visible and AA spectroscopy. He elaborates that in the 3-h quality control check, analyses are reported on:

- pH
- specific gravity
- developing agent for specific organic compound
- bleaching agents
- biosulfate in the fixing solution
- sulfate
- silver for control
- bromide
- cadmium
- lead and iron in the wastewater.

Daignault says that there are four laboratory technicians spread over three shifts.

Smile

"Portraits for Today and Tomorrow" is the company slogan. Perhaps PCA has already processed a portrait of your child, and will be taking a 16 × 20 portrait of you and your mate soon. Two years ago there were about 25 quality department stores in the U.S. in which the PCA photographers operated. Today there are 130. In another year there will be more than 250 quality studios. So, when the photographer says smile remember that PCA may be processing your portrait for tomorrow. SSM

EPA's emission offset policy

One mechanism for allowing new industrial growth in nonattainment areas

Eight years ago, America heard the beat of the environmental drummer, picked up the cadence, and slowly proceeded to march itself into a corner bounded by nonattainment and no growth.

To wit: In 1970, the Clean Air Act Amendments were written and signed into law. Under this Act, EPA was charged with promulgating national ambient air quality standards (NAAQS) for several criteria pollutants.

Under the optimistic tempo that then existed, it was assumed that the states would meet the primary NAAQS by 1975, but no later than 1977. Perhaps because of this optimism, there was no clear-cut provision written into the Act for new industrial growth should the NAAQS not be attained.

By 1977, most areas of the country had still not attained the NAAQS for at least one pollutant. The implication could be drawn that no industrial growth could occur in these nonattainment areas.

However, there seemed to be a way out of this dilemma, and the solution appeared in the *Federal Register* of December 21, 1976, as an interpretative ruling on the preconstruction review requirements for new or modified stationary sources of air pollution. This ruling, one of the last things Russell Train did as EPA administrator, has since come to be known as the "emission offset policy," or simply the "offset policy."

Why the policy?

EPA's regulation implementing Section 110 of the 1970 act required that State Implementation Plans (SIPs) contain a regulation for preconstruction review of all new or modified air pollution sources, and permit disapproval of those sources which interfered with the attainment or maintenance of a NAAQS. Though not explicitly stated, the implication could be drawn that this section prohibited new growth in nonattainment areas. EPA, however, took a more liberal stance.

D. Kent Berry, director of EPA's Policy Analysis Staff, told *ES&T* that

to solve this conundrum, the agency's Region IX office in San Francisco conceived the offset policy. Simply stated, the policy says that a new source can locate in a nonattainment area if its emissions are more than offset by concurrent emission reductions from existing sources in that area. This policy, the agency believes, reflects congressional intent.

The policy, however, cannot be applied willy-nilly; certain stringent conditions must be met. These conditions are "designed to ensure that the new source's emissions will be controlled to the greatest degree possible; that more than equivalent offsetting emission reductions ('emission offsets') will be obtained from existing sources; and that there will be progress toward achievement of the NAAQS."

Incorporated into law

Congress thought so highly of this policy that it incorporated it, as Section 129, into the Clean Air Act of 1977, which was signed into law by President Carter in August last year. Certain changes were written into the law.

One major change concerned the size of sources, based on their emissions, subject to the policy. Congress changed the word "allowable" to "potential" emissions of 100 tons or more per year.

To achieve parallelism between its already published final Prevention of Significant Deterioration (PSD) regulations and its final amendments to the 1976 interpretative ruling (which, at press time, was to be published as a final ruling in the *Federal Register* in late August), EPA defines "potential" as that level of emissions generated by a source operating under design capacity *without* control equipment. "Allowable" refers to emissions after control. The effect of this one-word change is to net more sources under the offset policy.

However, in its final amended offset ruling, EPA not only defines potential emissions as uncontrolled emissions, it also sets up a two-tier system that exempts small sources from the policy. This two-tier system is also found in EPA's final PSD regulations.

Sources wishing to locate in a nonattainment area whose emissions, after meeting the applicable SIP emission limit or new source performance standard, are less than 50 tons/y, 1000 lb/day or 100 lb/h are exempt from the offset policy. New sources emitting more than these cut-off points are subject to the policy. EPA estimates a 40% increase in the number of sources now subject to the policy.

Congress did another major thing with the offset policy. It made it an

Target dates: past and future

July 1, 1975	Original attainment date for primary NAAQS
December 21, 1976	EPA's offset policy promulgated
August 7, 1977	1977 Clean Air Act enacted
March 3, 1978	Status of air quality control regions listed by EPA
May 19, 1978	EPA guidelines for SIP revisions published in 43 FR 21673
Fall, 1978	EPA guidelines on lowest achievable emission rate (LAER) published
January 1, 1979	State SIP revisions to be submitted to EPA
July 1, 1979	SIP revision must be approved by EPA by this date to avoid the no-growth sanction
December 31, 1982	New deadline for attaining primary NAAQS
December 31, 1987	Extended deadline for photochemical oxidants and/or carbon monoxide for areas unable to meet the 1982 deadline

interim measure, effective only until June 30, 1979. By this date, the EPA must approve or disapprove revised SIPs, which the states are required to submit to the agency by January 1, 1979.

These revised SIPs must contain a mechanism for "growth allowance" or an offset policy identical to or at least as stringent as the federal offset policy.

Should a SIP not be approved, the 1977 Clean Air Act states that "no major stationary source will be constructed or modified in any nonattainment area . . . if the emissions from such facility will contribute to concentrations of any pollutant for which a NAAQS is exceeded." In short: no new growth until EPA approves or promulgates a SIP revision.

The stringent conditions

EPA's amended final offset ruling, which also seeks further public comment on several issues, incorporates the public comments received on the 1976 ruling and the changes required by the 1977 Clean Air Act. While several things were changed in the amended ruling, the stringent requirements a new source must meet to receive a permit to build in a nonattainment area remain unchanged.

Requirements a new source must meet to build in a nonattainment area

- The new source must meet an emission limitation that specifies the lowest achievable emission rate (LAER) for that source.

- The applicant must certify that all the existing major sources it owns and operates in the same state are in compliance with the applicable emission limitations and standards, or are meeting the target dates of a compliance schedule.

- Emission reductions, greater than one-to-one, from existing sources in the area must be obtained to assure "reasonable progress toward attainment of the applicable NAAQS."

- These offsets must provide a "positive net air quality benefit in the nonattainment area."

LAER is defined in the amended final ruling as the most stringent emission limitation for that class or category of source contained in any SIP, unless the source can show that such limitations are not achievable; or the most stringent emission limitation

achieved in practice or which can reasonably be expected to occur in practice by that class or category of source. The more stringent of these two options must be applied.

EPA recognizes that the LAER provision may be technology forcing. It argues: "Congress intended to require new sources in nonattainment areas to apply the 'maximum feasible pollution control,' even if this involves 'technology-forcing.'" EPA, broadly interpreting this congressional intent, will allow the transfer of technology from one source type to another, if the transfer is feasible, for the purposes of determining LAER.

According to the agency, the "net air quality benefit" provision is "intended to ensure that the sources involved in an offset situation impact air quality in the same general area, but the net air quality benefit test should be made 'on balance' for the area affected by the new source." The final ruling does not clarify the term "on balance," but it does state that air quality improvement is not required at every location affected by the source.

Banking

Unlike the 1976 ruling, the amended final ruling contains a provision for banking offsets. That is, if the offsets achieved are considerably greater than the new source's emissions, a portion of this "excess" emission reductions can be "banked" by the source for use in future growth. But, after July 1, 1979, the states, if they choose to allow banking in their SIPs, become the bankers and decide how to allocate the banked emissions.

A subsidiary issue related to banking is credit taken for source shutdowns or curtailments that result from enforcement actions. In its final ruling, EPA will accept such credits for banking if the date of shutdown or curtailment occurred after passage of the 1977 Clean Air Act, or less than one year prior to the date the new source permit application is filed, whichever is earlier.

No interpollutant tradeoffs

EPA will not allow interpollutant tradeoffs. Thus, if a new source will emit hydrocarbons (HC), it will have to find offsets in existing sources that also emit HC. However, the sources need not be of the same type. For example, Sohio is seeking offsets in California to build a crude oil transshipment facility at the Port of Long Beach. The offsets are for HC, and Sohio is buying and/or cleaning up dry-cleaning establishments in that air quality control region.

Donald R. Holtz (Engineering-Science, Arcadia, Calif.), addressing a technical session at the June annual meeting of the Air Pollution Control Association (APCA), recommended that EPA allow interpollutant offsets, especially between HC and NO_x in an oxidant nonattainment area. EPA's Cheryl Wasserman (acting branch chief for Legislative and Policy Analysis) told the session that the agency had never considered interpollutant offsets, primarily because of the difficulty in assessing comparability between pollutants.



EPA's Wasserman

Holtz made other recommendations for the offset policy. Among these were that provisions should be made for:

- innovative technology
- unregulated emission sources
- fugitive particulate emissions
- carbon monoxide exclusion.

He felt strongly that small sources should fall under control regulations because their proliferation—their sheer numbers—could exacerbate attainment of the NAAQS in nonattainment areas.

Wasserman told the APCA session that her group at EPA is analyzing the technological, economic and social implications of the offset policy as part of a larger study on alternative methods of handling new source review provisions. Some of Holtz' recommendations are being assessed.

For this exercise in policy analysis, the EPA has contracted out for three regional studies—Houston/Galveston, Philadelphia and Chicago—and three industrial studies—petroleum refining/petrochemical, iron and steel and an industry screening study. These were to become part of a report to be submitted to Congress in October. None of the studies has been completed, but Wasserman told *ES&T* that an interim report would be released in late summer. The final October date, however, will probably slip.

Among the mechanisms Wasserman's group is looking at are incen-

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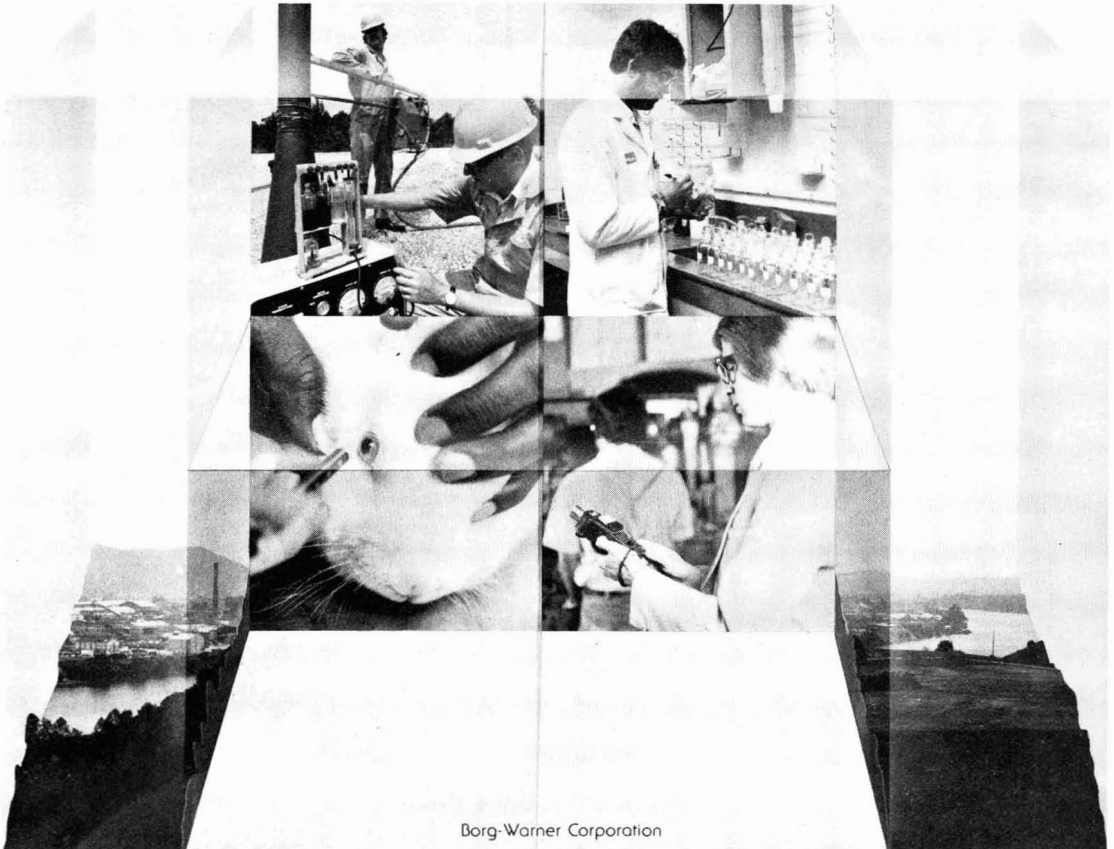
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tives, especially for innovative technology; emission fees; offset markets; marketable permits; and such institutional apparatus as clearinghouses for offsets.

To exempt or not

While the impacts of the offset policy are still being assessed, the EPA has proposed some conditions in its amended final ruling for which it is seeking further public comment. For example, in the final ruling EPA states that rural sources emitting volatile organic compounds will be subject to the offset policy if they locate in an oxidant nonattainment area. Exemptions will only be made for those sources locating in very remote rural areas, such as the Pittston Refinery at Eastport, Me. Further comments are being sought on this issue.

Sources that would emit pollutants for less than two years at one site are exempt from the offset policy. Such temporary sources would include pilot plants, portable facilities and emissions resulting from the construction phase of a new source. Resource recovery projects burning municipal solid waste would also be exempt.

These exempt sources would not have to meet the emission offset and positive net air quality benefit requirements of the offset policy, but they would have to comply with the LAER and other conditions of the ruling.

A thorny issue, still not decided at press time, and one which could delay the publication of the amended final ruling, was whether to exempt modified sources from the offset policy. The

issue is better known as the "bubble concept."

Under the promulgated PSD rules, a modification in an existing process unit is exempt from the PSD rules if the emissions resulting from the modification are accompanied by equal emission reductions elsewhere in the same plant. At press time, EPA did not plan to allow this type of exemption under the offset ruling because "it is much less appropriate to create this exemption in an area that needs to do everything possible to attain air quality standards, as opposed to a clean area where deterioration is the only concern." Further public comment would be sought, however.

A question of equity

Much consternation was expressed at the APCA meeting over the inequities of the offset policy. State air control officials and industrial representatives pointed out that the states that did the best job of cleaning up their air pollution now have the least opportunities for offsets, and are being penalized under EPA's policy.

Addressing this problem, Wasserman told *ES&T* that "We are concerned about the inequities, and we are trying to minimize them to the extent that we can. But inequities are inevitable given the inherent differences, from one region to another, in levels of economic activity, in air quality and in the meteorology."

EPA's Berry told *ES&T* that the problems of inequity should be eliminated once the SIPs are revised and approved. Then, most SIPs will be tightened up to RACT (reasonable

available control technology) levels, and only control of emissions beyond RACT levels will be acceptable for offsets.

Fervent activity

Despite the inequities, offsets have been sought and obtained. The three best known major cases are the Volkswagen Manufacturing Company of America's automobile assembly plant in New Stanton, Pa., the General Motor's truck assembly plant in Oklahoma City, Okla., and the Sohio oil-transfer facility at the Port of Long Beach.

In the first instance, Pennsylvania, desiring to locate new industry within its boundaries, obtained the offsets, revised its SIP to include provisions for reducing emissions from existing facilities, received EPA approval of the revised SIP, and issued permits for construction. In the latter case, Sohio is obtaining (and paying for) its own offsets, but with much difficulty. After several years, no construction permit has been sought by the company.

The most frequent offsets have been sought and obtained in EPA's Region IX, particularly in California. A list of all offset activity is being compiled under the direction of L. Douglas Carter. This compilation will be part of EPA's report to Congress to be submitted in the autumn.

As Carter's list will prove, the federal offset policy, for all its faults, has been tested and found workable. But, after July 1, 1979, the states have the choice of opting for a growth allowance policy rather than a case-by-case offset policy. LRE

Fuels and organic chemicals: renewable sources

*Identifying, and optimizing the use of such sources
comprised some of the topics discussed at the
CHEMRAWN Conference*

Sometimes one gets a feeling that he has come full circle 'round. Such a sense of *déjà vu* might be engendered when, for example, one hears about the use of wood as a prime source of energy and chemicals. Seems as though that happened before in this world!

At the CHEMRAWN conference, there was, however, a major shift in the

old way of thinking about wood, for instance. That shift involved rationalization and optimization of the use of wood, biomass in general, and other old or new non-petroleum sources of energy and organic chemicals, rather than older, rather haphazard approaches. Major enhancement of methods of using existing fossil re-

sources were discussed, as well.

This renewable source technology might not actually make great inroads into the chemical/energy economy until the 21st century. "But if that technology is to be in place by, say, the year 2005, the time to start working on it is now," said William Schneider, president of the National Research



Canada's Schneider
the importance of avoiding delays

Council Canada. He reminded the conference of the long lead times necessary to bring a new technology to fruition; that is why he warned that there should be no delay.

The biggest "battery"

Perhaps the biggest "battery" in the world is that which accumulates and stores solar energy through the photosynthesis process. It weights 800 billion tons, as represented by standing biomass, and is agumented by about 200 billion tpy, equivalent to an energy content of 3×10^{21} J. D. O. Hall, of Kings College, University of London (England), explained. Add to that some 900 billion tons of fossil fuel made through past photosynthesis.

"About 3 billion years ago, the development of blue-green algae solved the energy crisis by evolving the ability to split water, make storable hydrogen, and fix organic chemicals through enzymatic action. With a potential of about -700 mV, this ability, using photosynthesis, is the only way of using visible light directly," Hall noted. He reminded a press conference that photovoltaic cells can produce storable hydrogen in two stages, but that plants are a one-stage hydrogen producer/storer. "It seems time we learnt how plants do it," Hall observed.

"The problem is that biological systems die," Hall said. Thus, he cited efforts aimed at making synthetic systems that would not die. One step in this direction was development of an enzyme with an iron-sulfur protein catalyst, and similar enzymes that use manganese. These enzymes meet requirements of stability in oxygen, up to 70°C , and of durability "for ages."

The tough nut to crack is to arrive a a workable artificial photosynthetic energy/chemical resource production system which largely simulates that of nature. The photosynthetic principle is now known to work with ribulose diphosphate carboxylase, "the world's most plentiful enzyme," to assemble

plant sugars with water and carbon dioxide. These sugars would be the energy/chemical sources. But no one can do this artificially, as yet, Hall noted. Moreover, devising workable membranes for a man-made photosynthetic system is another big hurdle.

Driven to booze

If artificial photosynthesis as an economical chemical/energy source is far in the future, other efforts are under way now. Indeed, the government of Brazil is providing massive support to a project aimed at using ethanol as a major substitute for costly imported petroleum for fuel and chemical feedstock purposes, Walter Borzani of the University of São Paulo, explained.

A goal is that ethanol would furnish 10% of Brazil's liquid fuel by 1980, and 50% by 1990. Present production of 250 000 m^3/y would be raised to 4.5 million m^3/y by 1986. Management would be provided by the Sugar and Alcohol Institute, which was founded in 1933.

Sources of clean-burning ethanol could be sugar from cane, manioc (tapioca), sorghum, and Babassú coconuts. That coconut is presently used for oil in northern Brazil. Sorghum is the subject of expanded effort in the south-central Brazilian states of São Paulo and Minas Gerais.

Last year alone, Brazil invested



Attended by more than 750 people, many of them recognized experts in their respective fields, CHEMRAWN—Chemical Research Applied to World Needs—was held at Toronto, Canada, in July. CHEMRAWN was sponsored by the International Union of Pure and Applied Chemistry; cosponsored by The Chemical Institute of Canada and the American Chemical Society; and was the first conference of its kind. Its theme was: Future Sources of Organic Raw Materials.

Ethanol sources

Plant	Biomass productivity, t/ha	Ethanol productivity, L/t	Ethanol productivity, L/ha
Sugar cane	50	60	3250
Manioc	12	180	2160
Sorghum	35	35	2975
Babassú coconut	10	86	860

Source: CHEMRAWN paper authored by Walter Borzani, University of São Paulo, Brazil.

\$500 million in the program. Government experts there reckon that one ton of sugar can could yield 400 kg of sugar, or 65 L of 96% ethanol. One ton of manioc could yield 12 L of ethanol, but manioc could be produced up to 15 t/hectare (ha), and some 2.1 million ha of manioc are planted in Brazil.

Costs and jobs

To produce 20 000 m^3/y of ethanol, fixed investment could be \$17–56 million for sugar cane, or \$19 million for manioc. A 15-year payback is anticipated, with a 6.6%/y return. The Brazilian government would warrant ethanol purchase, but would not subsidize purchases of land for raising the necessary ethanol source-crops.

At present, Brazilians acknowledge that ethanol as a fuel and chemical feedstock is not competitive with petroleum or natural gas, but they expect rapidly rising oil prices to change that economic picture. Even so, they look for a foreign exchange saving of \$3.5 billion over 1977–1986, and the creation of 13 000 new jobs through the ethanol program.

Peat, pine, and birch

World wood reserves are about 350 billion m^3 , or 3 m^3/ha . Highly efficient forestry could raise this reserve to 8 m^3/ha . Vladimir P. Karlivan of the Institute of Wood Chemistry (IWC, Riga, Latvia, U.S.S.R.), told the conference. This added wood could be a very rich organic chemical source and, in fact, is to some extent today, he said.

Speaking through an interpreter, Karlivan explained that mechanochemical treatment of peat, wood, or agricultural waste (agwaste), together with a sulfuric acid catalyst, breaks down polysaccharides deeply and efficiently. The mechanochemical part consists of a screw conveyor hydrolyzer; the system is called "Riga hydrolysis method".

To carry investigations further, the IWC has a 1000-kg/h pilot plant

amenable to handling agwaste, peat, or wood. The wood is largely pine and birch. These raw materials can be broken down into furfural, for example. Alternatively, the wood's lignocellulose can be made into glucose solution (*ES&T*, September 1974, p 784, and November 1975, p 1011); thence into glucose, polyalcohols, lysine; or itaconic acid. Another chemical process "train" involves breakdown to levoglucosan from which polyurethanes, polyesters, and bioactive substances could be made.

A real sweetener

Also, among possible products from renewable wood resources are non-flammable resins and plastics which the IWC named "Rionol-2", "Ripor-2", and "Ripor-12", as well as birch wood-derived holocelluloses. But reaction temperature plays an important role in processing wood. At 160 °C, for instance, hemicelluloses and their derivatives would predominate as products. At 180 °C, one would look for more glucose production. At over 220 °C, one would expect no useful products.

For the future, these renewable raw materials are seen by IWC scientists as a source of substrates for single-cell protein manufacture. Also, a possible

product would be xylitol, a food-sweetening agent for those who should not consume sucrose.

Optimism and limits

Optimism that with an all-out research and development effort, renewable carbon fuel and feedstock sources would be available in "unlimited amounts" within 10 years, was expressed by S. J. Pirt of Queen Elizabeth College (University of London, England). The key would be accelerated use of anaerobic digestion, coupled with major advances in fermentation technology, and increased biomass production. An object is to make numerous wastes and other biomass materials, presently intractable to fermentation, suitable as substrates.

The realization of Pirt's optimism would certainly be a boon to mankind! But that realization would assume large increases in, and intensive culture of appropriate biomass substrate, be it wood, or agwaste.

If this biomass for food, fuel, fiber, or chemicals is to be cultured, however, there must be a very fine-tuned management of that mass with respect to climate, hydrology, topography, and soil, all of which are limiting factors. Moreover, cultural, political, and socioeconomic conditions can impose

additional productivity limits, Pieter Buringh of The Agricultural University (Wageningen, Holland), observed.

Buringh said that *technically*, the biosphere can produce enough for the world population, as well as wildlife, "for many future generations." But if (especially in poorer tropical countries)

- food production must be greatly enlarged by large-scale, mechanized commercial farming, as is presently done

- the chemical and energy industries plan to use more organic raw material sources from the biosphere, processes of land misuse and degradation, and ecological system disturbance might be markedly accelerated.

The results of such degradations might ultimately consist of even more biomass production limitations than those which exist today in, say, undisturbed nature. On the other hand, biomass production, under proper technical conditions, if achievable, could vastly increase the renewable resource base. That base might not fully justify Pirt's optimism, but it certainly would bring about a material reduction in the use of irreplaceable fossil resources. JJ

Advanced wastewater treatment Nature's way

Hyacinth retention ponds, added onto secondary treatment facilities, offer a simple, inexpensive solution to nitrogen and phosphorus removal

Question: How do you upgrade a secondary wastewater treatment facility to tertiary status efficiently yet inexpensively?

Answer: Plant water hyacinths!

That's correct, water hyacinths. Those pernicious weeds of voracious appetite and promiscuous reproducing habits, once the bane of water treatment engineers in the Sun Belt states, may turn out to be the simple and inexpensive answer to nitrogen and phosphorus removal.

The first large-scale field test of hyacinth's ability to remove nutrients from water efficiently enough to convert a secondary treatment facility to an advanced wastewater treatment plant is under way at Coral Springs,



Fla. Here Coral Ridge Properties has funded the construction of five experimental ponds and a sampling and analytical testing program.

The EPA is keeping a close watch on this project. The agency is evaluating the collected data, and will pub-

lish the results of the study at its completion, which is slated for May 31, 1979, after 13.5 months of operating experience.

Experimental design

The design of the five interconnected hyacinth ponds is based on research by Dr. Robert C. Wolverton of NASA's National Space Technology Center at Bay St. Louis, Miss., and by the wastewater engineering faculty of the University of Florida (Gainesville). The ponds receive the chlorinated secondary effluent from the activated sludge treatment plant of the Coral Springs Improvement District. This wastewater treatment plant receives only domestic wastes and operates at

95+% BOD and suspended solids removal efficiencies.

The ponds are designed to handle a flow of 100 000 gal/day, a quarter of the flow rate of the sewage treatment plant. This portion of the treatment plant's effluent is channeled through a 3-in. pipe to the ponds. The first pond is sized for a two-day retention period, and the remaining four ponds are each sized for one-day retention periods, for a maximum retention period of six days.

A biological alternative

By January 1, 1980, all Broward County wastewater treatment plants, including the Coral Springs Improvement District (CSID) plant, must meet the following advanced wastewater treatment standards: BOD, 5 mg/L; suspended solids, 5 mg/L; total nitrogen, 3 mg/L; and total phosphorus, 1 mg/L. Of these, the most difficult to meet are the standards for nitrogen and phosphorus.

The wastewater treatment facilities can meet the 1980 effluent standards by installing expensive chemical/mechanical processes, or they can seek less costly alternatives. Coral Ridge Properties, which is fully funding the experiment, convinced the CSID to seek the less costly biological alternative—nutrient removal by water hyacinths.

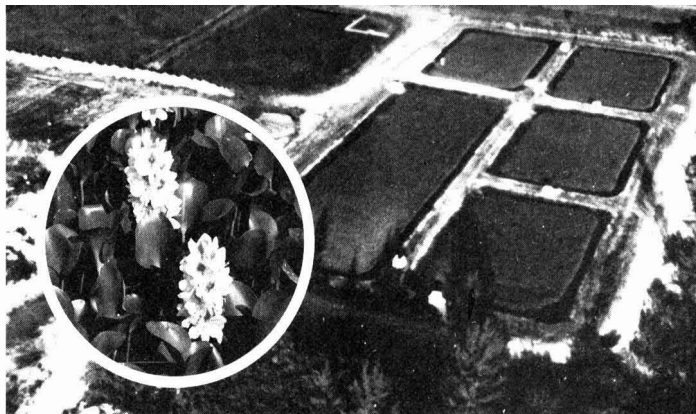
Why hyacinths? Because of their very high uptake rates, these plants incorporate nutrients into their biomass. Thus, as they grow and reproduce, they cleanse the water of contaminants.

To maintain maximum nutrient removal rates, however, the hyacinths have to be harvested periodically. The harvested plants can be dried, mixed with sludge and processed as fertilizer. Or, as Walt Disney Productions plans to do, the harvested hyacinths can be used to produce methane.

Some results

The hyacinths have performed admirably well. The plants were seeded on January 30, 1978; by mid-April, a little longer than was anticipated because of a freak February frost, the ponds were 100% covered by hyacinths. By the end of May, enough data had been collected and evaluated to indicate that the five-pond system could better than meet the tertiary nitrogen standard, but could not meet the phosphorus standard.

With a flow rate of 100 000 gal/day, and a six-day retention period, the mean nitrogen effluent level was 0.6 mg/L, down from influent levels of



Hyacinth ponds. *The plants completely cover these five retention ponds*

10–30 mg/L. The mean effluent phosphorus level, however, was 3.5 mg/L, down from influent levels of 5 mg/L.

On July 1, Dan Swett, Coral Ridge Properties' development research manager, reduced the flow rate to 75 000 gal/day to increase retention time in the hope that this measure would improve phosphorus removal. At press time, the data had not been completely evaluated. Although there was some indication that phosphorus removal had improved, there was no certainty that this improvement was significant.

Swett anticipates that an alum or ferric chloride precipitation step will probably have to be added to the hyacinth system to meet the tertiary phosphorus standard. But, he states that this precipitation step will, in the long run, be cheaper than increasing the retention time.

As fortune would have it, the hyacinth system has some added bonuses. For example, after chlorination at the sewage treatment plant, the ponds' influent total coliform and fecal coliform counts are about 256 and 124 organisms/100 mL, respectively. The ponds' effluent coliform counts are zero. And, after hyacinth treatment, chlorinated hydrocarbon concentrations are reduced 50%, from 0.01 mg/L to about 0.005 mg/L. Trace metals are also reduced to less than 0.001 mg/L.

And, the costs

Swett is now conducting experiments to ascertain the minimum retention time required to achieve the tertiary nitrogen standard of 3 mg/L. Once this minimum time is found, which in turn determines the maximum pond area needed, costs for the hyacinth system can be determined.

Data already accumulated indicate that, at a 100 000 gal/day flow rate, the retention time can probably be reduced, which means that the pond

size, currently totaling 1.25 acres, can be reduced. These reductions, of course, mean that costs decrease.

Even without these reductions, the costs to date have been surprisingly low. Total construction costs for this experimental set-up were \$65 000, probably higher than construction costs for ponds which would be an integral part of a normally operating treatment facility.

Operating and maintenance costs, according to Swett, have been insignificant, especially since harvesting has occurred less frequently than originally anticipated. At press time, August 1, the plants had not been harvested since May 27.

The largest sums, about \$75 000–80 000, are being spent for laboratory analyses. These analyses are being performed by an independent, EPA-certified laboratory, Spectrum Laboratories (Fort Lauderdale, Fla.). Some water samples, however, are being divided and analyzed by Spectrum and EPA laboratories.

In a recent internal memorandum, Swett wrote: "I rather expect that we'll be able to beat the capital cost of the conventional AWT system by at least \$3 per gallon of daily flow." Several communities find this cost reduction significant. San Diego, Calif., Lakeland, Fla., and Brandywine Valley, Pa., for example, are designing similar systems.

There are drawbacks to the hyacinth treatment system. One is the size of the community that can use such a system. As a community grows, there must be parallel growth in the wastewater treatment system, which for a botanical system means an increase in the acreage set aside for ponds.

But, for small communities, or as an interim measure for larger communities, hyacinths offer a simple, energy-saving, inexpensive yet efficient alternative to chemical/mechanical advanced wastewater treatment systems. LRE

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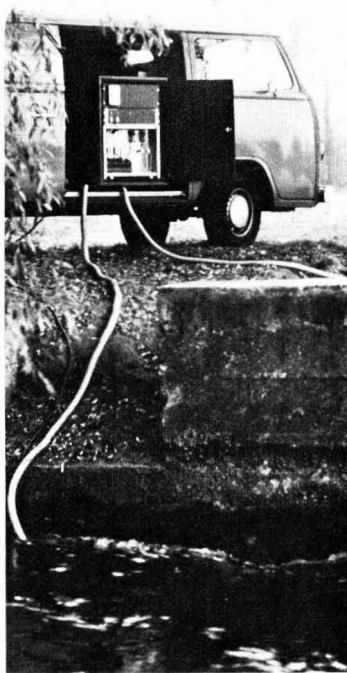
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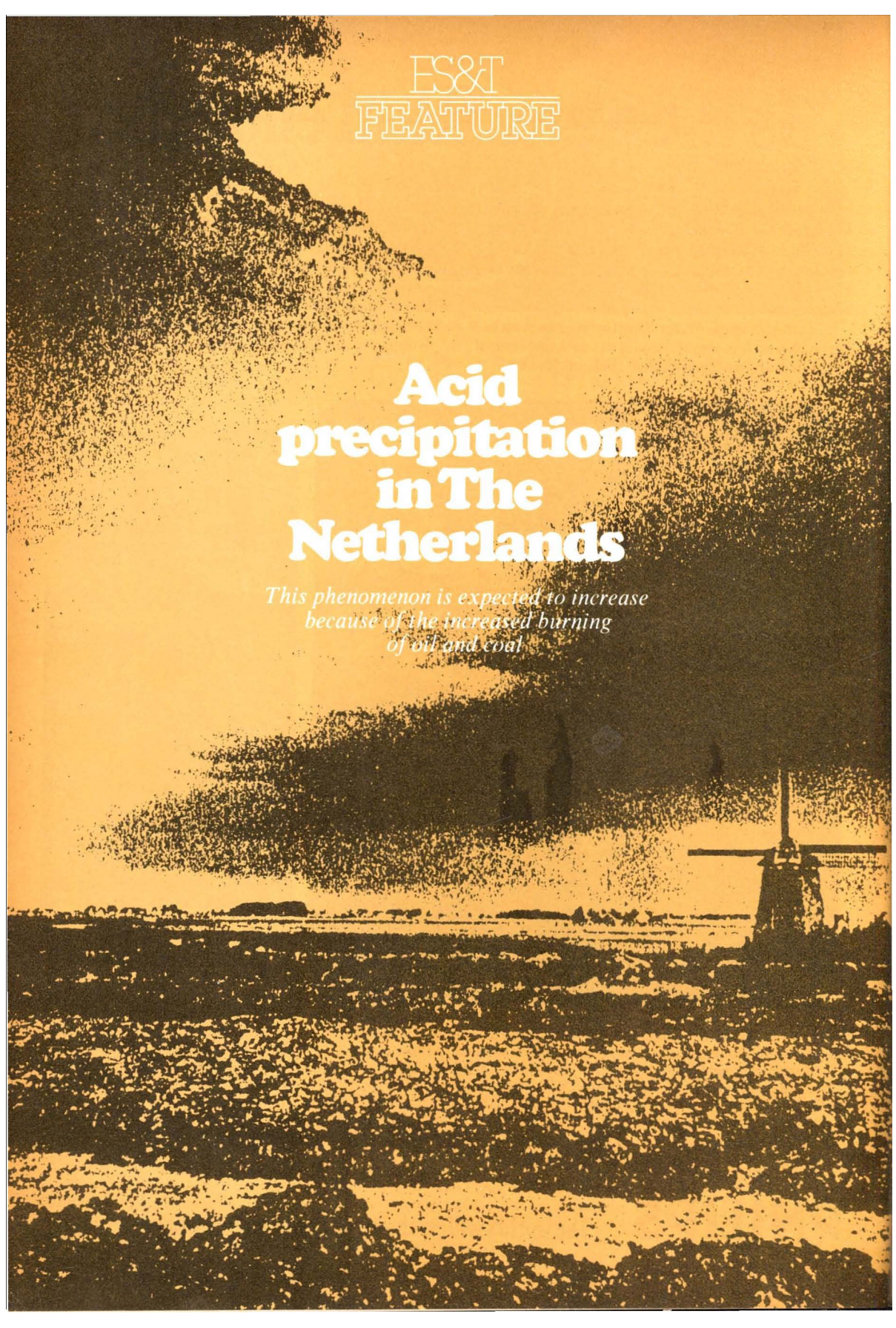
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ES&T
FEATURE

Acid precipitation in The Netherlands

*This phenomenon is expected to increase
because of the increased burning
of oil and coal*



Various tests of the chemical composition of precipitation indicate that acids are present in larger quantities than would occur naturally. This phenomenon is attributed to ever increasing sulfur dioxide (SO₂) and nitrogen oxides (NO_x = NO and NO₂) air pollution.

In Europe, the acidification of precipitation increased gradually in various countries. Because of this phenomenon and its possible environmental consequences, rainwater analyses were greatly enlarged. In 1952, at the initiative of Sweden, an extensive European monitoring network was installed; a few years later this network consisted of more than 150 measuring locations (IMI-network). In The Netherlands, the De Bilt, Witteveen and Den Helder stations are part of the network.

Around 1966, the highest acid precipitation measurements in the world (on a yearly basis) were made in The Netherlands. After 1967, the acid concentrations of rain decreased, simultaneously with a considerable reduction in SO₂ emissions.

As the coming years will again be characterized by a sharp rise in SO₂ emissions in The Netherlands, it is to be expected that the acidity of precipitation will increase as well, possibly up to values exceeding the 1967 figure at De Bilt when the pH was 3.78 on a yearly basis.

An attempt will be made here to indicate a relationship between the development of acid concentration in The Netherlands and total interior emissions of SO₂ and NO_x.

Some background

Rainwater, normally, is not acidic. In theory, its pH should lie near the neutral value 7. Carbon dioxide (CO₂) contained in the atmosphere will, to a certain extent, dissolve in rainwater to form carbonic acid, a very weak acid. The minimum pH of rainwater saturated with carbonic acid is about 5.5–5.6. In areas where the soil is calcareous and winds whip up bottom dust, the pH will reach values somewhat above 7.

By drawing up ion balances of rainwater samples preserved prior to 1930, one author has calculated that at that time (1930), pH values were around 7.5. In glacier ice from the Cascade Mountains, minimum pH values of about 5.6 were found, which

corresponded to the pH of water saturated with carbonic acid. Still other scientists, performing rainwater analyses from 1919–1929 in Geneva, N.Y., found relatively large quantities of bicarbonate. Since bicarbonate cannot exist in the presence of strong acids, the pH values of their samples must have been about 7. In The Netherlands, between 1932–1937, a scientist found pH values between 5 and 7, which he described as being "relatively low."

In the last few years, however, it appears that over large areas in the Western Hemisphere, pH values of single precipitations are fluctuating between 2–6. The averages, on a yearly basis, fall between pH 4–5 for large areas, and even below pH 4 in small areas. This translates to an acid content 10 to 10 000 times greater than is possible naturally.

From past data, it is clear that the acidification of precipitation is a phenomenon of the present day, particularly in densely populated and highly industrialized areas of the Western Hemisphere.

Rise of industry, decrease in pH

The gases SO₂ and NO_x are emitted into the air in large quantities. SO₂ is formed when fossil fuels are burned, and NO_x is formed during every combustion process in which high tem-

peratures arise. Sulfur dioxide and NO_x can be transformed in the atmosphere to sulfuric and nitric acids that are soluble in water (cloud water and raindrops). Consequently, in large areas in the Western Hemisphere, precipitation can be considered to be a dilute solution of an acid.

The considerable increase in the acidity of precipitation in the years after World War II coincided with enormous industrial expansion and the nearly exponentially rising consumption of energy in Western Europe. During a period of 15–20 years, the pH of precipitation declined at many measuring locations of the IMI network, on a yearly basis, from 6 to 4 pH units, which means an increase in acidity by at least a factor of 100.

In 1956, the center of acid precipitation in Europe was situated over the southeast of England, the northwest of France and Belgium, Luxemburg and The Netherlands; average pH values on a yearly basis ranged from 4.5–4.0. In 1961 and 1966, acidification further increased.

In The Netherlands, around 1966, measured pH values fell below 4 (on a yearly basis). In 1967, the year's average at De Bilt was 3.78, and regions with pH values between 4.5 and 4 are increasing in number. As The Netherlands is the most densely populated country in Europe, and is also highly industrialized, it is easily understood that with oil as the main fuel, acidification is so considerable.

In the U.S., particularly in the Northeast, an acidification pattern has developed that is comparable to the European experience. On the West Coast, one scientist found that in 1955–1956, the pH values ranged between 5.5–6.0, and for the northeastern part of the U.S., values were measured near 4.5. In the years 1972–1973, pH values on the West Coast were between 4.6–5.6 on a yearly basis, and in the northeastern part of America the highest degree of acidification was measured in the densely populated and industrialized areas.

Changing the fuel, lowering SO₂

In 1946 in The Netherlands, coal was the primary fuel burned; SO₂ emission amounted to roughly 200 000 tons/y. In 1956, the total SO₂ emission from burning coal and oil rose to about 400 000–500 000 tons. Owing to the expensive exploitation of pit coal, the growing energy needs in The Netherlands were being met by importing cheaper oil. However, because of the ever increasing consumption of oil with its higher sulfur content, SO₂ emissions rapidly increased.

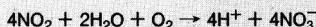
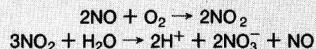
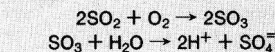
How the average annual pH values are calculated^a

- pH values are converted to H⁺ concentrations.
- The H⁺ concentrations are multiplied by the corresponding precipitation quantity.
- The total quantity of H⁺ ions is divided by the total precipitation quantity and the antilog is taken according to

$$\text{pH} = -\log \frac{\sum H_i \times \text{mm}_i}{\text{mm}_i}$$

^a By the IMI monitoring network.

The formation of acids in rainwater^a



^a The velocities with which these reactions take place depend on the degree and kind of pollution. The velocities can range from a few minutes to a couple of weeks or more.

Around 1967, SO₂ emissions reached a maximum value of 900–1000 × 10³ tons/y or, in other words, an emission pressure of about 31 tons/km². The consequences of the high-emission density were clearly perceptible. In many places in The Netherlands, especially under stagnating weather conditions, immission values of 500–2000 µg SO₂/m³ were measured frequently. The acid content of precipitation also increased considerably.

In 1967 it was easily foreseen that—assuming a constant rise in energy consumption, with oil as the main energy source—within a period of five years, the SO₂ emission density would increase to 60 tons/km² per year. In order to keep The Netherlands habitable, drastic measures were required immediately.

In 1968, the Dutch Clean Air Act was enacted. By means of this Act, the Dutch government, among other things, wanted to halt the increase in SO₂ emissions. The Act became effective on December 29, 1970. In anticipation of this, Dutch industries began to clean up their emissions; desulfurization installations were built;

the use of heavy fuel oil with a sulfur (S) content of over 2.5% was prohibited, and other types of oil with a lower S-content were imported; power stations switched over to oil having a S-content below 1.7, sometimes even below 1%.

Natural gas discovered

The graph of SO₂ emissions depicts decreasing SO₂ emissions after 1967–1968. However, the main reason for this absolute decrease is not the measures mandated by the Clean Air Act but, rather, the very lucky discovery of the largest coherent natural gas field in the world (a proven gas reserve of 2 100 billion m³). In 1967, this natural gas accounted for about 18% of The Netherlands energy consumption; in 1972, about 50%; and in 1976, 60%. In 1975, natural gas supplied 85% of the fuel needs of Dutch power stations.

From later calculations it became obvious that, if natural gas had not been discovered, measures taken in compliance with the Clean Air Act would have maintained SO₂ emissions at about 700 × 10³ tons/y from 1970 to the present.

In 1976, the Dutch Government issued a note stating that the government's policy for the coming years would aim at lowering and stabilizing the total SO₂ emission at about 500 000 tons/y. This is a Utopian scheme! As a consequence of the current exportation policy, natural gas for internal consumption will be endangered in the long term. Moreover, the build up of a strategic reserve (against oil boycotts) has proven to be very important.

Government policy for the years to come, therefore, aims at terminating the export contracts and reserving the natural gas for domestic heating only, until the year 2000. This means that power stations will have to reduce their natural gas consumption from 85% in 1975 to 13% in 1985, a loss they will have to make up with a proportionally

growing share of coal and mineral oil.

The discrepancy in the government's aims is clear. In spite of the measures taken to stimulate a further desulfurization of raw fuels and flue gases for the power stations alone, SO₂ emissions of 400 000–500 000 tons—equal to the total value aimed at by the Dutch Government—can be expected in 1985. By 1985, the SO₂ emissions from the power stations will be equal to 25–30% of the total interior SO₂ emissions, a total SO₂ emissions of 1200–1500 × 10³ tons can be expected, which is equal to a SO₂ emission density of 38–47 tons/km².

In view of the expected rise in energy consumption after 1985, the SO₂ emission density, when based on the most favorable situation of an average S-content for all fuels of about 1%, can still reach 70–80 tons/km² in the year 2000. This corresponds to an interior SO₂ emission of 2100–2700 × 10³ tons. This expectation is also based upon the assumption that until 2000, the share of nuclear energy in the Dutch energy production will not rise (in 1976, 1.65%; in 1985, max. 1.50%). Solar energy and wind energy are unlikely to play a major role in the total generation of energy in The Netherlands during the coming years.

Coal gasification

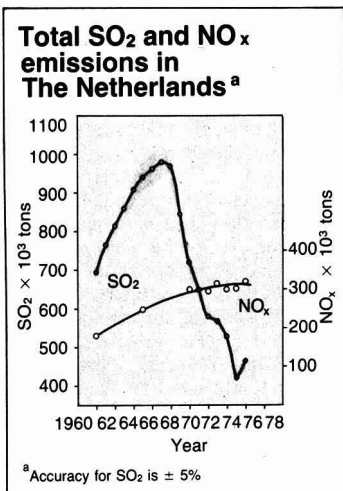
In order to combat air pollution by SO₂—caused by the reduction in natural gas consumption and the consequent increase in oil usage—and to counter the threatening shortage of oil and gas during the next decades, the general opinion in The Netherlands is that coal must be restored to a place of honor among the fuels; not the direct combustion of coal but its gasification to a useful fuel.

In The Netherlands, Shell is operating a coal gasification pilot plant that has achieved considerable success. During the process no—or hardly any—air pollution occurs. The sulfur contained in the coal is released as elementary sulfur, while the residues are transformed into a vitreous, pearl-like material suitable for several purposes in the construction industry.

At present, the cost of this gas, produced in The Netherlands, is approximately three times as high as that for natural gas. Only when applied on an extensive scale (probably not before 1986) will the price become competitive with those of the fuels in use today.

SO₂, NO_x emissions effects

Apart from SO₂, ever increasing quantities of NO_x are being emitted



SO₂ emission densities

	1968 ^a	1974 ^b
	Tons/km ²	
The Netherlands	31	12
Belgium, Luxemburg, U.K.	20–24	23–33 ^c
Western Germany	13	16
Denmark, France, Austria, Switzerland	3–6	3–14 ^d
Southern Sweden	2	3
Finland, Norway, Iceland, Northern Sweden	<1	<3

^a In Europe, the SO₂ emission density reached a maximum in The Netherlands. ^b Only The Netherlands showed a rapid decrease this year; all other countries showed an increase. ^c For Belgium. ^d For Denmark.

into the atmosphere. Contrary to the emission of SO₂, NO_x only shows an upward trend, although this growth seems to have decreased somewhat during recent years. One reason for this proportional decrease is known: the reduction in the number of old cars on the road and, for the coming years, the reduction of the total Dutch fleet of cars; the maximum will be about 4.6 millions cars in 1981.

In 1977, more than 40% of the total interior NO_x emission was caused by traffic. Nitrogen oxides are formed during combustion processes (at high temperatures) out of the nitrogen that forms part of the combustion air. With growing energy consumption, NO_x emissions in The Netherlands will rise, although probably not so rapidly as in past years. Statistical calculations show that the interior emission of NO_x has no great influence on the acidification of precipitation.

Since 1956, at the De Bilt, Den Helder and Witteveen monitoring stations, the pH of precipitation has been measured on a monthly basis, within the scope of the IMI-measuring program. From around 1950 until 1967, measurements showed a growing acidification of precipitation, followed, after 1967, by a rapid decrease.

The H⁺ concentrations were calculated from the pH values at these three locations. To collect representative samples, the measuring sites in The Netherlands are situated in areas not directly influenced by industrial activities.

Although there are increases and decreases in H⁺ concentrations from year to year, there are considerable fluctuations in H⁺-concentrations about a moving average. With regard to these fluctuations, in my opinion, the variations of the general weather pattern play an important part. For instance, it was clearly ascertained that pH values were constantly rising on days with rain or with weather patterns with a long, continued supply of air from northern (Arctic) directions (supply of unpolluted air); whereas, in case of a prolonged supply of air masses from southerly and easterly directions, because of the transport across vast land areas, this air is relatively loaded with SO₂ and NO_x (imported air pollution). In the latter situation, during rainfall, lower pH values were always found.

Modeling the effects

To indicate a relationship between the average acidity on a yearly basis, and the changes occurring in the total annual interior emissions of SO₂ and NO_x by means of a regression analysis,

the best estimators have been determined for the parameters β₁ in the following model

$$y = \beta_0 + \beta_1 \cdot x_1 + \beta_2 \cdot x_2 + \epsilon$$

in which y = the average acidity on a yearly basis in rainwater in µg/L, x₁ = the yearly emission of SO₂ in 1000 tons, x₂ = the yearly emission of NO_x in 1000 tons, and ε = a random variable indicating the variability of y round the basic relation β₀ + β₁ · x₁ + β₂ · x₂. It is assumed the ε is normally distributed with an average of 0, and a variance of σ².

For the 15–20 years for which figures are available, estimates b_i were found for parameters β_i as indicated. In this table the standard deviations s_i of these estimators are also given.

In view of the non-central position of the Den Helder measuring site, its relatively larger distance from emission sources than the other two sites, and the fact that eight out of ten times air passing over it is transported from the sea, it was assumed that the average acidity on a yearly basis measured in Den Helder is not related to the total interior yearly emission of SO₂ and NO_x. The model confirmed the assumption.

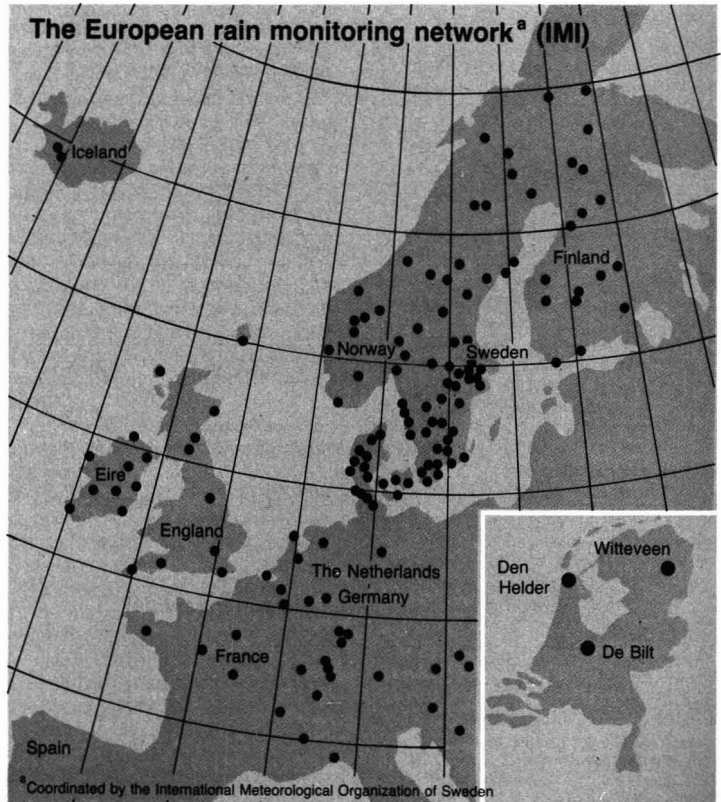
For the Witteveen and De Bilt

measuring sites, the model confirmed a relationship between the H⁺ concentration of precipitation, and SO₂- and NO_x emissions.

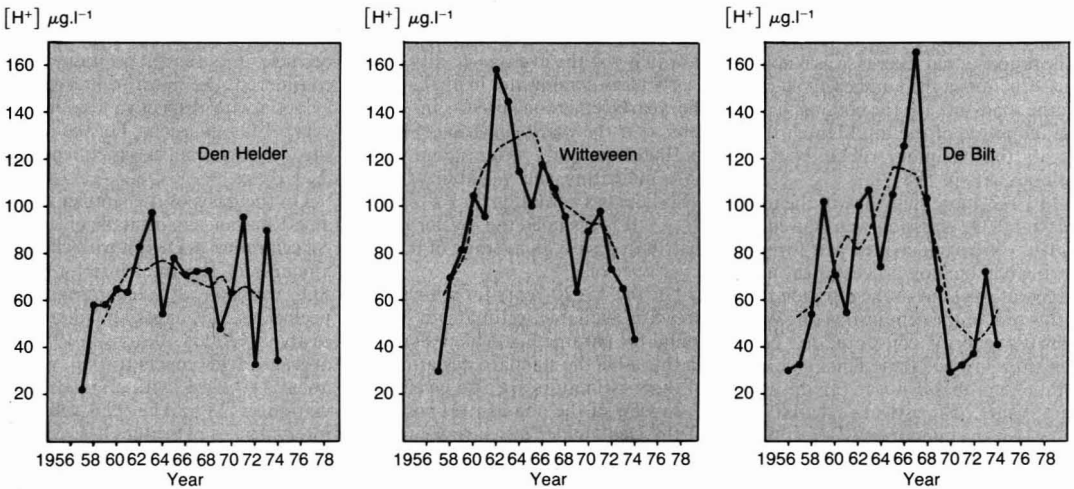
The De Bilt measuring location, because of its central position, can be considered the most representative location with respect to total interior yearly SO₂ emissions. For the De Bilt site, the model can be simplified to y = β₀ + β₁ · x₁ + ε.

On the basis of the simpler model, an estimation can be made of the acid concentration in De Bilt with changing amounts of the total interior yearly SO₂ emissions. If, according to expectations, this emission will amount to about 1300 × 10³ tons in 1985, the average acid concentration will be about 180 µg/L with a standard deviation of 23.6. The 99% reliability interval gives pH values between 3.60 and 3.96. At an expected emission of 2100–2700 × 10³ tons in 2000, on a yearly basis, pH values between 3.15 and 3.78 can be expected.

By using the model, a relationship between SO₂ and NO_x emissions and H⁺ concentration of precipitation was found for the Witteveen measuring site. Here the aspect of a decreasing acid concentration at an increasing NO_x emission is striking. It is assumed



The acid content of precipitation ^a



^a Annual weighted averages; acid expressed as H⁺ ions

Data from De Bilt, Den Helder and Witteveen . . .

Year	SO ₂ ^a	NO _x ^a	Acid content of precipitation, µg H ⁺ /L ^b		
			D.B.	D.H.	Witt.
1956			29.5		
1957			31.6	21.9	28.8
1958			53.7	57.5	69.2
1959			102.3	57.5	81.3
1960	694	182	69.3	64.6	104.7
1961	756	205	53.7	63.1	95.5
1962	816	215	100.0	83.2	158.5
1963	858	230	107.2	97.7	144.5
1964	908	240	74.1	53.7	114.8
1965	940	249	104.7	77.6	100.0
1966	960	260	125.9	70.8	117.5
1967	980	270	166.0	72.4	107.2
1968	970	280	102.3	72.4	95.5
1969	844	294	64.6	47.9	63.1
1970	723	294	28.8	63.1	89.1
1971	650	300	31.6	95.5	97.7
1972	580	301	37.2	32.4	72.7
1973	572	314	72.4	89.1	64.6
1974	530	301	40.7	33.9	42.7
1975	419	303	—	—	—
1976	463	315	68.0	—	16.7

. . . Best estimations for the parameters in the model ^c

Location	b ₀	b ₁	b ₂	s ₀ ^d	s ₁	s ₂
De Bilt	-68.6	0.194	-0.0187	71.6	0.0487	0.185
Witteveen	143.6	0.075	-0.398	57.6	0.0392	0.149
Den Helder	58.4	0.030	-0.0554	55.5	0.0377	0.144

^a Total interior emission × 10³ tons. ^b Annual average. ^c $y = \beta_0 + \beta_1 \cdot x_1 + \beta_2 \cdot x_2 + \epsilon$. ^d s = standard deviations.

that there is no causal relationship between NO_x and H⁺.

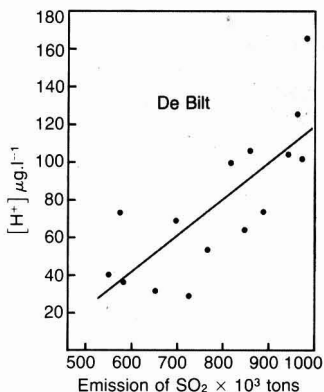
The deposition of acid—the quantity of acid that is deposited by precipitation on the soil per unit of time and per surface unit—depends on two factors, the acidity and the quantity of precipitation. The yearly acid deposition is found by multiplying the annual rainfall by the yearly average concentration of acid. The natural yearly acid deposition is about 1–3 mg H⁺/m². The measured values for De Bilt, Witteveen and Den Helder are much higher. For example, for De Bilt in 1985, the average acid deposition is estimated at 125–160 mg/m² for normal (800 mm) rainfall.

Consequences of acid rain

The ecological effects of acid precipitation for the most part are still unknown but, undoubtedly, they will be numerous. Some of the consequences, which can be quantified on the basis of extensive studies are: acidification of natural water sources and freshwater systems; leaching of the soil; damage to vegetation; and damage to materials (corrosion).

Because of the type of soil and the composition of surface waters in The Netherlands these ecosystems show a large buffering capacity to acid deposition, although ecological effects can still be demonstrated. For example, a survey on diatoms and macrophytes in some Dutch moorland pools shows that the biocenoses are seriously changed by human activities, especially by agriculture, recreation and acid precipitation. By inversion of the trophic pattern of the landscape, trophic gra-

Relationship between annual SO₂ emissions and average H⁺ concentrations^a



^aRegression line is $y = 74.9 + 0.195x$, where $y = \text{H}^+$ concentration and $x = \text{total annual SO}_2$ emission; $r = 0.72$

dients cannot be maintained and the biological differentiation within and between the pools seriously decreases. Most probably, in the future, only two types of moorland pools will survive: the hypertrophic type (enriched by run-off and drainage water) and the extremely acid type (acid precipitation).

From many investigations, it has already become obvious that the abundance of species of the epiphytic flora has considerably decreased. For example, around Bois-le-Duc (province of North Brabant), from 1900–1925 there were 117 known lichen species. In the seventies, of these 117 species only 47 were recovered.

A recent investigation of bryophyte vegetation (moss) on ash tree trunks in the Fazantenbos (near De Steeg, province of Gelderland), compared with other investigations during the past 25 years, clearly shows that before 1969 the acidophytes were strongly increasing and the neutrophytes and basophytes decreasing, whereas after 1969 the acidophytes decreased and the basophytes and neutrophytes increased.

The damage, caused by (imported) acid precipitation in Scandinavia, is widespread and increasing rapidly. A major part of the air pollution produced in Western Europe is transported in northeasterly directions toward Scandinavia. At an average wind velocity, distances of 1000 km and more can be covered in two to four days.

Because much of Scandinavia is underlain by highly resistant granitic rock with only a thin cover of uncon-

solidated glacial till and soil, the inland waters are characterized by low conductivities, low concentrations of major ions and extremely low buffering capacities.

For the above reasons, large areas of Scandinavia are quite vulnerable to pollutants deposited from the atmosphere. Acidification of freshwaters with the disappearance of fish populations, frogs and other water organisms has been particularly rapid over the last decades. In the Tovdal River catchment area in southern Norway, for instance, an area with 266 lakes, 48 lakes were without fish in 1950. In 1960, the number of fishless lakes increased to 75 and, in 1975, to 175!

Apart from the acidification of surface waters, leaching of the soil takes place, producing changes in vegetation. A situation comparable to that in Scandinavia is found in the area of the Adirondack Mountains in New York.

In summary

There is a pronounced relationship between SO₂ emissions and the acidification of precipitation in The Netherlands. However no such relationship can be demonstrated for NO_x emissions and acidification, probably because more than 40% of NO_x are emitted at a height of 30 cm above road level, and this part of NO_x will be absorbed by the direct surroundings. The remaining 60% (170 000 tons) will hardly play a role in acidification.

The coming years in The Netherlands will be characterized by a decreasing use of natural gas and an increasing use of oil with this consequence: an increasing emission of SO₂. Solar, wind and nuclear energy are unlikely to play a major role in the total generation of energy before 1985, and after 1985 their contribution will hardly be more than 5% unless, within a few years, the Dutch government begins building a number of nuclear plants.

An important alternative source of energy after 1985 is probably the gasification of coal. One expects that in The Netherlands, in 1985, the price of gas obtained by gasification of coal will be competitive with those of the fuels in use today.

Despite all measures to reduce SO₂ emissions in The Netherlands, the average S-content for all fuels will be at least 2% until 1985. Assuming that desulfurization methods will be further developed after 1985, for the year 2000 an average S-content for coal and oil of about 1% may be possible. Consequently, the SO₂ emission density can increase from about 12 tons/km² in

1975 to around 40 tons/km² in 1985, and about 60, possibly 75 tons/km² (depending on the composition of the fuel range) by 2000.

The consequences: around the year 1985, on a yearly basis, average pH values may be about 3.70, with a low extreme of 3.60; in the year 2000, average pH values may be 3.40, with a low extreme value of 3.15. This means that the acid concentration of about 40 μg/L (expressed as H⁺) in the year 1975 may increase to an average of 200 μg/L, with high extreme values of 250 μg/L in the year 1985, and 400 μg/L with high extreme values of 600 μg/L by about the year 2000. As a comparison, natural H⁺ concentration would be less than 10 μg/L.

Acid deposition may increase from an average of 140 mg/m² (expressed as H⁺) in the year 1985 (with high extreme values of 300 mg/m²) to an average of 370 mg/m² in the year 2000 (with high extreme values of 700 mg/m²). The natural background deposition would be about 1–3 mg/m² per year. The total effects of such an acidification of precipitation cannot be predicted at present.

Additional reading

Acid Precipitation, Proceedings of a Conference on Emerging Environmental Problems, held on May 19–20, 1975, at Rensselaerville, New York. EPA Report No. 902/9-75-001.

Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, U.S. Forest Service, General Technical Report NE-23.

vanDam, H., Kooyman-van Blokland, H., Man-made Changes in Some Dutch Moorland Pools, as Reflected by Historical and Recent Data about Diatoms and Macrophytes. *Int. Rev. Gesamten Hydrobiol.*, (in press).

Impact of Acid Precipitation on Forest and Freshwater Ecosystems in Norway. Summary report on the research results from the phase I (1972–1975) of the SNSF-project. Fagrapp FR6 (1976).

Reports on the problems of acid rain in Scandinavia are obtainable free of charge from: SNSF-project, NISK, 1432 Aas-NHL, Norway.



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WASTEWATER TREATMENT: THE ELECTRICAL CONNECTION

Normally, suspended solids carry a negative charge which must be addressed if unit operations are to be optimized

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Optimization of unit operations and a sequence of unit operations constitutes the staff of life for refinery engineers. Therefore, it is not unexpected that when new and restrictive wastewater treatment goals were imposed on the petroleum industry in the U.S., researchers with refinery background experience would bring a different perspective to bear on the problems of wastewater treatment. Using the refinery engineer's approach to achieve the best quality effluent in the most cost-effective manner has led to new perspectives in the understanding of the principles involved in, and the performance of, the basic water purification unit operations.

A significant improvement in wastewater purification using conventional unit operations is achieved when the overall treatment sequence is approached from the "systems optimization" point of view. All the individual unit operations are optimized, using for guidance an intrinsic property of solids in water, called zeta potential, which is defined later.

Systems optimization involves recognition that each unit operation in the end-of-pipe treatment sequence has a principal function. For example, obtaining maximum effluent purification involves maximum removal of soluble organics. The removal of soluble organics in the treatment sequence is by a biological process, the activated sludge process (ASP) being favored. Therefore, a systems optimization of a wastewater purification sequence

points to optimization of the ASP as the key element.

The ASP is generally used to achieve major reductions in suspended and colloidal material, as well as dissolved substances. When the refiner is almost wholly dependent on the ASP to achieve end-of-pipe treatment objectives, this operating mode may achieve the best overall reduction in contaminants.

Now, however, the refinery is confronted with very restrictive effluent limits on suspended solids, BOD, COD, ammonia, and some bioresistant materials, as well as variability limits for each parameter, as conditions for obtaining a National Pollution Discharge Elimination System (NPDES) permit. Under these conditions, the ASP becomes only one of a series of process steps required to meet the objectives.

When viewed in this context, the ASP can be optimized to achieve further control of process variability and increased removal of soluble contaminants: This is achieved by reversing the historic workhorse role of the ASP, and using the process only for the removal of essentially soluble contaminants.

Particle charges

Investigations into the optimization of each unit operation revealed that zeta potential (ZP) considerations provide a heretofore ignored basis of optimizing operation of essentially all unit operations used for purification of wastewaters. They include granular media filtration, dissolved air flotation (DAF), induced air flotation, clarification, and—surprisingly—the activated sludge process.

The suspended constituents of sewage and industrial wastewater, including microorganisms, dispersed oily colloids, inert suspended matter such as inorganic sulfides, silt, coke fines, and the like, have a negative electrical surface charge. The stability of colloidal and very slightly flocculated suspensions relates to the fact that the individual particles carry like electrical charges causing their mutual repulsion.

It is of utmost importance to recognize the impact of colloid scientists' work, when optimizing unit operations used in wastewater purification. Application of basic principles established by colloid scientists has led to a better understanding of fundamentals operative in wastewater processes, and yielded improved operating results. Fortunately, the principles can be utilized qualitatively, and are not limited to particles of colloid size.

The electric double layer

The electric double layer may be regarded as consisting of two regions:

- an inner region, which may include adsorbed ions
- a diffuse region in which ions are distributed according to electrical forces and thermal motion.

Stern proposed a model in which the boundary of the inner region (Stern layer) was located by a plane (the Stern plane) about a hydrated ion radius from the surface. Adsorbed ions attached to the surface by electrostatic or van der Waals' forces may be dehydrated in the direction of the surface. A certain amount of solvent will also be bound to the charged surface in addition to the adsorbed ions. The

shear plane, therefore, is probably located farther from the surface than the Stern plane. Ions with centers beyond the Stern plane are considered to be in the diffuse part of the double layer.

Electrokinetic potentials relate to the mobile part of the particle; therefore, the electrokinetic unit consists of the volume enclosed by the shear plane, which is rather inexactly known. The potential difference between the surface of shear and the solution is called the zeta potential (ZP).

DLVO theory

Unit operations used for wastewater purification essentially all involve solids in water. The DLVO theory quantifies particle stability in terms of energy changes when particles approach one another. The total energy is determined by summation of the attraction (London-van der Waals' forces) and repulsion (overlapping of electric double layers) energies in terms of interparticle distance. The general character of the resulting interaction energy-distance curve illustrates the very significant conclusions:

- attraction will predominate at small and large distances
- repulsion may predominate at intermediate distances, depending on the actual values of the two forces.

An important purpose of the chemicals used for destabilization is to reduce or eliminate the repulsion force at intermediate distances, so that attractive forces will predominate, and the particles will aggregate. This is a key consideration in optimizing physical separation operations. The reason is that the negative ZP of waterborne solids brings about natural repulsion by negative surface charges of granular filter media, such as sand and coal, and those of the gas-liquid interface of dissolved air and induced air flotation systems.

Colloid destabilization mechanisms

Destabilization of the waterborne suspended solids may involve four mechanisms:

- colloid entrapment or removal via the sweep floc mechanism
- reduction in surface charge by double-layer repression
- charge neutralization by adsorption
- bridging by polymers.

Colloid entrapment involves chemical treatment with comparatively massive amounts of primary coagulant. The amount of coagulant used is typically so great in relation to the amount of colloidal matter, that the nature of the colloidal material is not

relevant. The amount of primary coagulant used may be 5-40 times as much as is used for charge neutralization by adsorption. The rate at which the primary coagulants form hydrous metal oxide polymers is relatively slow, and depends chiefly upon water temperature and pH.

Coupled with the high concentration used, all negatively-charged colloidal material is initially exposed to charge neutralization by the transient cationic species. The polymer matrix is three-dimensional and voluminous, providing for entrapment of solids. As the polymer contracts, freeing solvent water molecules, and settles, the suspended solids remain enmeshed in the settling floc and appear to be swept from the water; hence, the description of the process as a "sweep floc" mechanism.

However, this destabilization mechanism can result in the generation of large amounts of wet alum (or iron) sludges, which are difficult and costly to dewater. Even though it is by far the most widely used mechanism for water clarification, it is not recommended, because of the sludge problem, and because the use of other mechanisms result in significantly lower operating and capital costs.

Double-layer repression

Reduction in surface charge by double-layer repression is caused by the presence of an indifferent electrolyte which, in refineries, is chiefly so-

Advantages of using the ASP only for soluble contaminant removal

- Sludge-settling characteristics of the activated sludge mass are excellent at very high sludge ages; for example, over 40 days.
- Process control is greatly simplified through operation at a greater than 40-day sludge age.
- Using a very high sludge age for process operation eliminates the need for many process control tests.
- Operating at a very high sludge age produces an exemplary effluent very low in total organic carbon and other contaminants.
- A very high sludge age provides a remarkably low cell yield.
- At a very high sludge age, the population dynamics of the sludge mass improve.
- Maximum ASP capacity for purification is achieved through operation at high sludge ages.

dium chloride from brackish water usage, or saltwater ballast. For double-layer repression of colloid surface charge in brackish waters, the sodium ions of the indifferent electrolyte, which surrounds the colloid particles in order to balance their negatively-charged surfaces electrically, have less tendency to diffuse away from the colloid surface as the salinity increases. Some salt concentration may eventually be reached so that the thickness of the double layer may be small enough that two colloids approach each other so closely that van der Waals' forces cause aggregation.

An important aspect of double-layer repression is that the quantity of colloidal charge itself is not significantly reduced, but just that extent to which it extends outward from the colloid surface. This relates to the nature of the destabilizing chemical (salt) and its mode of action; i.e., the sodium ions remain free in the solvent, and cause rapid dissipation of the charge, as the distance from the colloid surface increases.

For demineralized water, there are not many ions available; therefore, the charge on the particle surface is not reduced much by adsorbed ions in the Stern layer, or counter ions in the diffuse layers. As a result, the zeta potential is high, and extends for a considerable distance into the solvent; in other words, the double layer is thick.

Fresh water (not demineralized), on the other hand, comparatively may contain many salts. The presence of counter ions may lead to some adsorption and potential drop across the Stern layer. The concentration of counter ions in the diffuse layer is much greater than the demineralized water example, and causes the charge to dissipate more rapidly. The double layer is much thinner than in the case of demineralized water.

For brackish or saltwater, the comparatively high concentrations of sodium ions discourage their diffusion away from the particle surface. The counter ions occupying the Stern layer cause an apparent reduction in potential but are not strongly absorbed and, therefore, do not permanently alter the surface potential charge to the much lower charge of the Stern potential, and the charge actually measured, the zeta potential. The high electrolyte concentration causes any residual charge to dissipate rapidly; in other words, the double layer is very thin.

Charge neutralization and bridging

Charge neutralization by adsorption of the destabilizing chemical to the

colloid is a key mechanism for optimizing removal of waterborne solids from waters. The colloidal charge may not only be reduced to zero, but actually beyond zero; that is, reversed. Charge neutralization by adsorption infers that the colloid-water interface is changed, and thus, so are its physiochemical properties.

It does not require much extension of one's imagination to see how this destabilization mechanism can explain those cases in which optimal chemical dosages were found, and overdosing that resulted in a deterioration in, or failure of, direct filtration. This phenomenon is more typically experienced with very low molecular weight polyelectrolytes, or surfactant-type molecules with little bridging properties.

Bridging by organic and inorganic polymers describes the destabilization mechanism by which the molecules of the added chemical attach onto two or more particles, causing aggregation. There are two kinds of bridging. These comprise polyelectrolyte bridging between dissimilarly, and similarly charged materials. Bridging of negatively-charged colloids by high molecular weight cationic and anionic polyelectrolytes are examples of the first and second kinds, respectively.

Double-layer repression can improve solids removal by direct filtration, but this mechanism does not achieve the best results. Indeed, it can conceal the definition of optimal chemical pretreatment to achieve best filtration results, if the interference of this destabilization mechanism is not recognized. Refinery experience indicates that the colloidal aggregates destabilized by double-layer repression appear analogous to loose flocculation by the secondary minimum; the aggregates are readily redispersed by hydraulic forces, as if the net binding forces are very weak.

Polyelectrolytes

Polyelectrolytes used as water-treating chemicals are macromolecules having many charged groups. They may be classified as cationic, anionic, and nonionic, depending upon the residual charge on the polymer in solution.

In solution, the polyelectrolytes are dissociated into polyvalent macro-ions and a large number of small ions of opposite charge (counter ions). The macro-ion is highly charged, which is the cause for the characteristic properties of the polyelectrolytes. Most of the macro-ions are long, flexible chains. Their size and shape depend upon the macro-ion charge, and interaction with counter ions. With in-

creasing charge, the macro-ion extends; with decreasing charge, the macro-ion assumes a contracted random coil.

The source of the charge is illustrated by the polyacrylates, widely-used polymers. In distilled water, polyacrylic acid's carboxylic functional group is only slightly dissociated. The addition of sodium hydroxide (NaOH) reacts with the carboxylic acid groups, causing them to dissociate, leaving a charge on the macro-ion, and producing sodium counter ions.

In the case of polyelectrolytes, some counter ions at high concentrations screen the charged functional groups with an ionic cloud. Salinity, hydroxide, phenolics, and sulfides, are examples of the kinds of counter ions found to affect various cationics. Each wastewater application of cationics must address the contaminants present, if the most cost-effective polyelectrolyte is to be used.

Titration curves

A comparison of polyelectrolyte performance and determination of antagonisms and synergisms is conveniently and quantitatively determined by use of ZP titration curves. Because the stability of a suspension is determined by the balance between the short-range (van der Waals) attractive forces and the repulsive coulombic forces between the particles, the objective of ZP-cationic polyelectrolyte titration curves is to quantify the amount of polyelectrolyte needed to reduce the repulsive coulombic forces to levels that permit total destabilization by attractive forces.

Consider the refinery problem of the aggregation of coke fines in hydraulic decoking water, so they are readily removable. As shown in Figure 1, coke fines are originally stabilized by a negative ZP, but the negative charge is readily neutralized and reversed by cationic polyelectrolytes. One might think that too much cationic polyelectrolyte would simply restabilize the system as a positive colloid. However, the use of a cationic that has good bridging properties, in addition to charge neutralization, causes most of the solids to be enmeshed by the polymer.

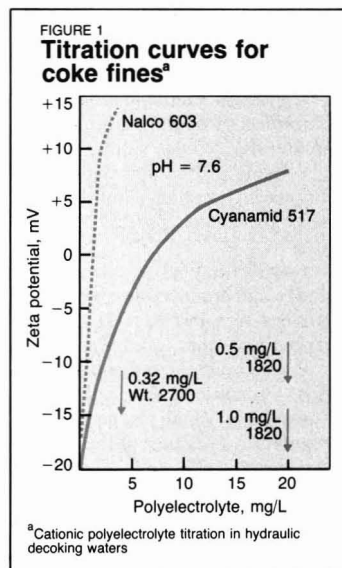
The larger size aggregates are more readily separable even though comparatively highly charged. Addition of a small amount of high molecular weight weakly anionic polyelectrolyte to the positively-charged cationic-treated coke particles will once again reverse the charge.

Rather than redispense the particles, however, the weakly anionic polymer efficiently "collects" the positively-charged particles into massive aggregates easy to separate. Once the high molecular weight weakly anionic polymer establishes bonds with the solids and forms aggregates, the aggregates are bound together with strong enough forces to resist redispersion by hydraulic forces in a clarifier, filter, or DAF unit.

Electrical models

Anionic polyelectrolytes are frequently used to flocculate negatively-charged colloidal systems. Even better appreciated is the capability of the activated sludge process to flocculate negatively-charged sewage, and industrial colloidal systems. An extreme case is the Contact Stabilization variation of the activated sludge process. Because the activated sludge mass and the anionic polyelectrolytes are both negatively charged, both of these destabilization examples seem to be counter to theory. However, a possible explanation for these extremely valuable properties lies in their electrical characteristics, and the environment in which they operate.

As discussed previously, ionizable groups of the polyelectrolyte are the source of an electric field. There are potential maxima in the region of the charged functional groups. There is a lesser potential field, outside the region of potential maxima, that might be described as a "potential tunnel." This is illustrated isometrically in Figure 2. When the polyelectrolyte is in the random coil conformation, as shown in Figure 3, there is an additional weak potential region (B) in the polyelec-



trolyte's sphere of influence. A fourth potential region is the solution in which there is no potential effect caused by the polyelectrolyte.

Each potential region has a different effect on counter ions. In the three potential regions within the polyelectrolyte's sphere of influence, counter ions can be considered as being bound to the polyelectrolyte. In the region of potential maxima, the bound counter ion may be localized at charged functional groups forming ion pairs. In the potential tunnel region, the bound counter ions are mobile, as they are in the weak potential region. Mobile counter ions establish an equilibrium, therefore, between the potential tunnel, weak potential field in the sphere of influence, and the solution.

An especially unique property of

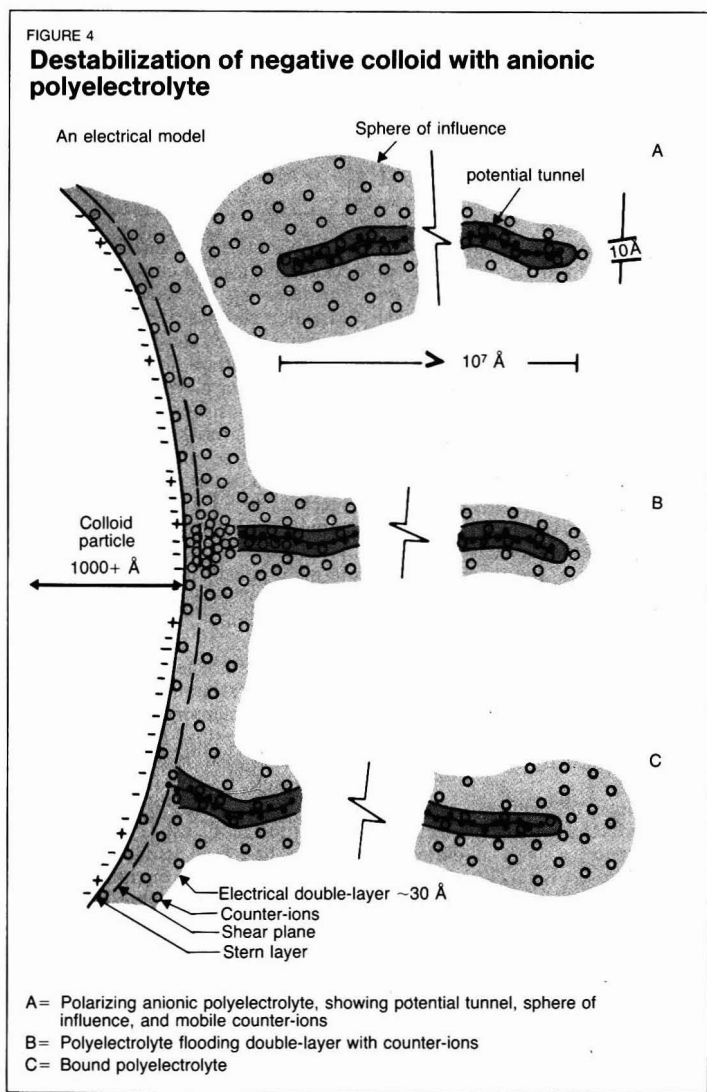
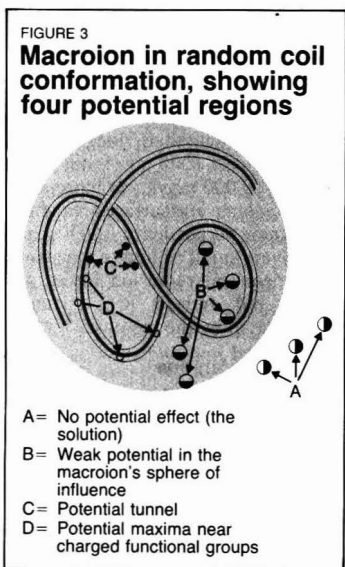
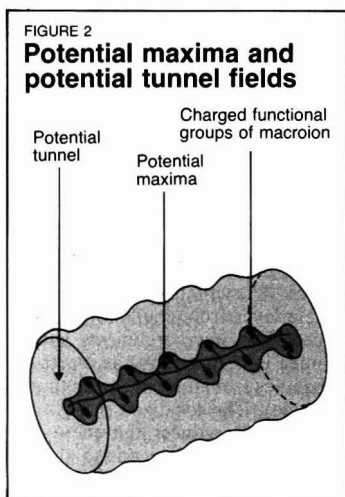
polyelectrolytes is that the bound counter ions in the potential tunnel area can move parallel to the polyelectrolyte molecule in the apparent volume occupied by the potential tunnel. Thus, counter ions can "flow" in the potential tunnel areas, analogous to water in a garden hose. Polyelectrolyte solutions, therefore, show an extremely large dielectric constant.

The dielectric constant, or polarizability of polyelectrolytes, is determined by the volume of polyelectrolyte in which counter ions are retained (not by the charge density of the polyelectrolyte), as long as a region of bound but mobile counter ions is formed. The dielectric increment depends on the geometry of the polyelectrolyte; extended polyelectrolytes give much larger dielectric increments than do

polyelectrolytes in the random coil conformation. Furthermore, the dielectric increment of polyelectrolytes in the extended (or helix) conformation increases rapidly with increasing length. Uniform and continuous distribution of charged groups, and the mobility of bound counter ions, are essential for large polarizability.

Polyelectrolyte destabilization

The means of negatively-charged polyelectrolytes to destabilize negatively-charged colloids is hypothesized to lie in the electrical properties of the polyelectrolyte. The proposed model in Figure 4 illustrates, approximately to scale, the colloid, its electrical double layer, the anionic polyelectrolyte, and its potential tunnel. Counter ions are cations in both cases.



Cations in the double layer are subject to at least two opposing electrical forces, one being the coulombic attraction to the colloid particle. They are also attracted to the solvent, to maintain an electrically balanced system.

When the sphere of influence of the anionic polyelectrolyte approaches the electrical double layer of the colloid, repulsion, caused by encountering like charges, might be expected. However, in this instance, apparently:

- The polarizing polyelectrolyte's electrical sphere of influence shields the counter ions in a localized area of the colloid double layer from the attractive, electrical solvent forces.

- The resulting electrical imbalance results in an increase in the negative coulombic potential in the localized area on the colloid.

- The increase in negative coulombic potential attracts the mobile counter ions from the potential tunnel region of the polyelectrolyte.

- The potential tunnel of the polyelectrolyte serves as a conduit for counter ions, which neutralize the surface charge in the localized area of the colloid surface.

- The charge neutralization achieved reduces the energy of repulsion at the localized site sufficiently so that the sum of the energy of repulsion and energy of attraction curves yields an interaction energy of attraction at the localized site.

- The positive interaction energy at the localized site permits attractive London-van der Waals' forces at the primary minimum between the polyelectrolyte and colloid to react.

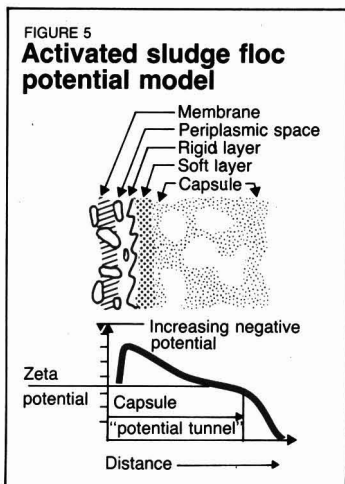
The key to this hypothetical model is the mechanism by which the anionic polyelectrolytes implement the initial shielding action of the colloid surface from the electrical solvent forces. This capability lies in the special properties of the polyelectrolyte. These include polarizability; bound, but mobile counter ions in the potential tunnel; the equilibria between counter ions in the potential tunnel, and spheres of influence established by coulombic forces.

This model also suggests why anionic polyelectrolytes do not effectively stabilize the very small colloid particles. The reason is that as the polyelectrolyte sphere of influence approaches the small colloid, the mass of the small colloid is so little that the repulsion forces predominate, and the particle moves away before the polarizing polyelectrolyte can shield the colloid from the solvent electrical forces. For these very small colloid particles, destabilization by the charge

neutralization, using cationic polyelectrolytes, is required.

"Bugging" a sludge system

The microorganisms constituting activated sludge also have a negative zeta potential. Glucuronic acid has been proposed as the source of the electrical charge (Figure 5).



The outermost surface of most bacteria is a slimy capsule varying in thickness up to 100 000+ Å. The capsule composition varies with species, and may consist of polymers of glucose or other sugars, amino and acid sugars, or polypeptides. Capsules generally consist of about 98% water. The function of the capsular layer is proposed as serving the microorganisms as an osmotic barrier; that is, a mechanism for guarding against too rapid an influx or efflux of water. It is proposed that the capsular layer performs an equally if not more important function of providing the potential tunnel region.

As previously stated, the zeta potential is the charge difference between the plane of shear and the solution. In the case of microorganisms, the shear plane is some small but indeterminate distance beyond the outer boundary of the capsule. It is hypothesized that the region beyond the shear plane is analogous to the diffuse layer of counter ions in the colloid double-layer model, whereas the capsule on the capsule side of the shear plane serves a function analogous to the potential tunnel region of polyelectrolytes. In other words, it provides for a region of bound but mobile counter ions.

The acidic polysaccharides in the outer layer of the soft layer are at least partially responsible for the negative, electric charge on the bacteria surface.

As in the polyelectrolyte example, mobile counter ions establish an equilibrium between the capsule layers (potential tunnel) and the solution, and the bound counter ions in the capsule layer can move parallel to the cell wall of the microorganism. The chief difference between the polyelectrolyte potential tunnel and the biological potential tunnel (capsule) is the comparatively large volume of the capsule—a desirable property.

Biological destabilization model

As for polyelectrolytes, the means for negatively-charged microorganisms to destabilize negatively-charged colloids also is hypothesized to be found in the electrical properties of the microorganisms. The model proposed for polyelectrolytes is analogous to the model for the biological system. Once again, cations are counter ions, in both cases. Dimensionally, the activated sludge floc and the capsule volume are larger than the comparative volumes occupied by the polyelectrolyte and its potential tunnel at the very low concentrations of polyelectrolyte used (frequently less than 1 mg/L).

As the diffuse counter ion layer of the double layers overlap, compared to polyelectrolytes, the massive size of the microorganisms floc more readily shields the counter ions in the colloid double layer from coulombic solvent forces. The microorganisms supply counter ions to satisfy the electrical imbalance from their potential tunnel (capsule). The localized increase in counter ions reduces the energy-of-repulsion curve analogous to anionic polyelectrolytes, and the particles flocculate into the biomass.

Once again, this model suggests why biopolymers (microorganisms) are more effective for destabilizing the very small colloids than anionic polyelectrolytes are. The polyelectrolytes are used in the range of 0.2–0.5 mg/L, whereas the activated sludge floc is usually at least 1000 mg/L, and may be up to 10 000 mg/L, or more. The massive volume and surface area of the biopolymer do not leave much space for the very small colloid to move into when electrical repulsion forces are encountered. Indeed, it is virtually encapsulated by the biomass.

Design consideration

Activated sludge has a bimodal floc size distribution. A good flocculating and settling sludge has a preponderance of large floc mass, compared to the fine particle fraction. The large floc mass is, in essence, a biopolymer analogous to a weakly anionic polyelectrolyte-type polymer. Thus, the

large floc mass is a biopolymer flocculant, and the fine particles represent the phase to be flocculated.

Qualitatively, when the ratio of the two phases overwhelmingly favors the biopolymer, as illustrated by the solid line in Figure 6, a good flocculating sludge results. When the fine particles predominate, their surface area overwhelms the capacity of the biopolymer for flocculation, and "arms and legs" (turbidity) are observed in the supernatant.

Inert and slowly biologically-oxidized colloids and suspended matter contribute to increasing the amount of fine particles in the sludge mass. Increasing sludge age increases their accumulation, thereby contributing to the deterioration in sludge flocculating properties. Removing colloids and suspended matter before ASP treatment results in an excellent activated sludge at very high sludge age.

ZP tells the story

There is another way of looking at the settling properties of activated sludge and the impact of the fine particle fraction on the settling properties that is much more enlightening in terms of understanding why solids are lost over an ASP final clarifier weir. That is to examine the zeta potential probability distribution of the activated sludge particles.

Zeta potentials are typically reported as averages, which are always misleading, particularly in the case of activated sludge. For example, the median ZP values of a good settling sludge could be -11 mV, and those of a poor settling sludge can be -12 mV (Figure 7).

This difference is not only difficult to measure but is really insignificant. What is significant is the slope of the distribution curve, and the ZP of the highest-charged particles.

If, for example, a ZP of -14 mV or more negative provides enough repulsive force that the fine particles will not flocculate, fully 8% of the solids in the poorly settling sludge mass resist flocculation and settling. On the other hand, essentially all the particles in the rapidly settling sludge are well below -14 mV ZP, and flocculate well. Limiting the accumulation of colloids in the activated sludge by effective phase removal in pretreatment facilities is a principal means of controlling the ZP probability distribution of activated sludge.

Additional reading

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FIGURE 6

Activated sludge bimodal floc size distribution

Fraction of particles

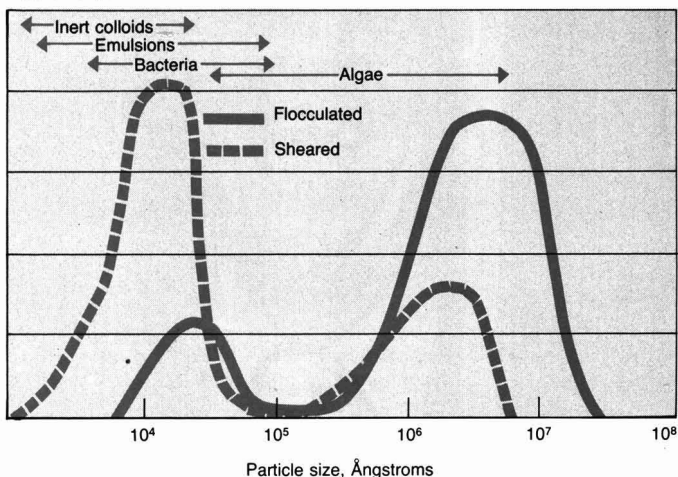
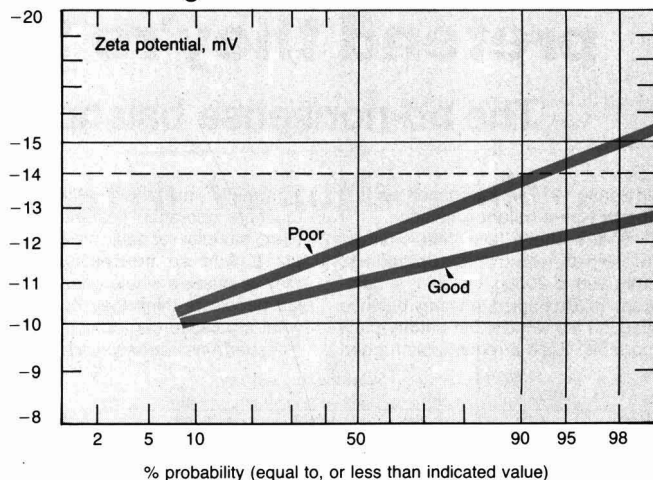


FIGURE 7

Probability curves for poor- and good-settling activated sludges



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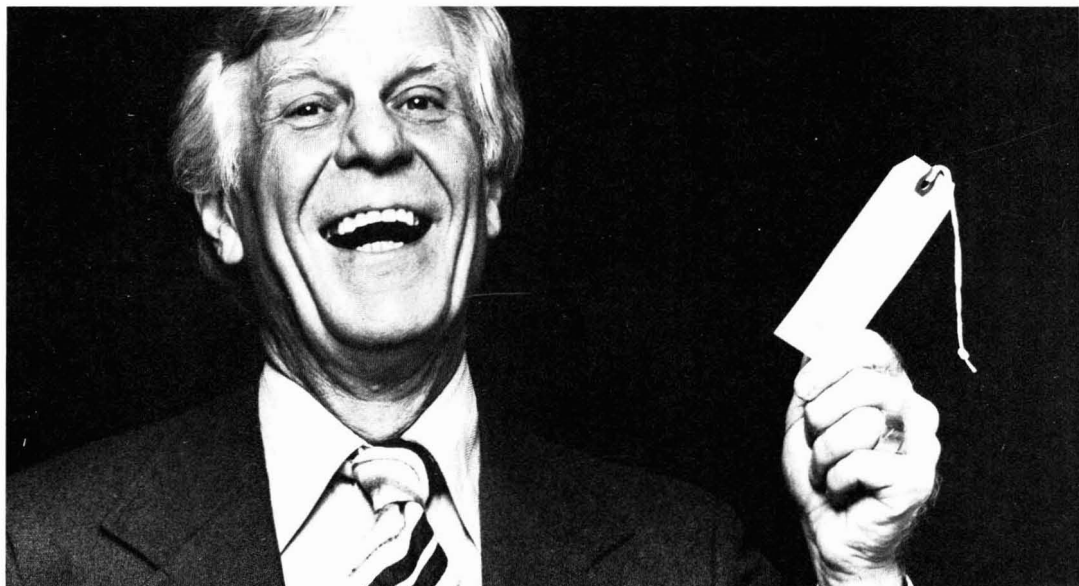
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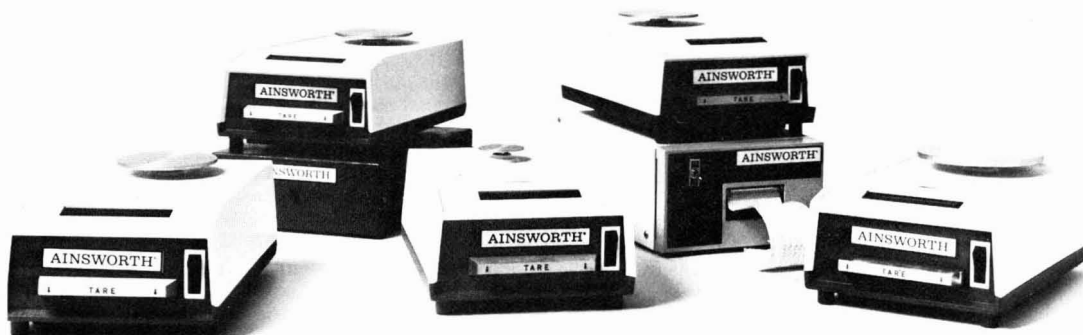
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Inactivation of Single Poliovirus Particles in Water by Hypobromite Ion, Molecular Bromine, Dibromamine, and Tribromamine

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■ The inactivating potentials of four common forms of oxidizing bromine in natural waters (dibromamine, NHBr_2 ; tribromamine, NBr_3 ; hypobromite ion, OBr^- ; and molecular bromine, Br_2) were examined in a dynamic flowing system of buffered water against single particles of poliovirus. Molecular bromine and NBr_3 gave linear \log_{10} survival kinetics. Hypobromite ion and NHBr_2 gave nonlinear kinetics even though the virus preparation contained >98% single particles. Aggregation of the virus therefore could not be the factor responsible for the nonlinear inactivation kinetics. All forms of free bromine, as well as NBr_3 , a common bromamine, appeared to inactivate poliovirus more rapidly than equimolar concentrations of HOCl . The initial rates for OBr^- , the linear rates for Br_2 , NBr_3 , and HOBr (taken from previously published data), and the initial rate for NHBr_2 at $10 \mu\text{M}$ were 3.85, 1.55, 0.15, 0.16, and 0.013 \log_{10}/s , respectively.

In previous publications (1-3) we have investigated the inactivating potential of hypobromous acid (HOBr) on uniformly dispersed single particle suspensions of viruses. These results demonstrated that when the virus preparation was in the monodispersed state, the rate of inactivation was very rapid and generally linear with time. In this paper we are concerned with the relative inactivating power of bromine in compounds other than HOBr . Although it will ultimately be necessary to make these comparisons with virus aggregated as it most likely is in polluted water (4), a start has been made with preparations of single virus particles to establish an uncomplicated basis for comparison. To this end, all the preparations of virus used in these experiments have been monitored by specially developed techniques for electron microscopy (5). The preparations of poliovirus used in these studies have <2% of their particles in an aggregated form, and the major part of the aggregated fraction is in the form of pairs of particles.

Although the most common chemical form of bromine is HOBr (6), we have examined other forms of bromine because bromine can also exist in water as Br_2 , OBr^- , NHBr_2 , and NBr_3 . Free bromine exists as Br_2 , HOBr , or OBr^- , depending on the pH and bromide concentration. Because ammonia is often present in natural water, NHBr_2 and NBr_3 are also found, depending on the concentration of bromine, ammonia, and pH (6). Previous work has shown that all of these compounds are effective bacteriocides (7), cystocides (8), and virucides (9), but little quantitative work has been done because

of the inability to control simultaneously the chemical composition and characterization of the virus suspension during disinfection under the wide range of pH, ammonia, bromine, and bromide concentrations required.

Materials and Methods

Virus. The preparation, purification, and plaquing of the Mahoney strain of poliovirus type I have been previously described (1). Monitoring of stock virus preparations for evidence of clumping was done by electron microscopy using the kinetic attachment (KA) method (5). All preparations were found to have >98% single particles when examinations were performed over the useful life of each virus preparation, approximately 4 months.

Reagents. Chlorine demand-free water was prepared from deionized, glass-distilled water chlorinated to about 5 mg/L for 4 days, and dechlorinated the day before the experiments with an ultraviolet lamp. This water, referred to as demand-free water, was used in the preparation of all solutions and reagents coming in contact with halogen solutions. It was stored protected from the atmosphere by 50% sulfuric acid scrubbers.

Hypobromite stock solutions, of approximately 8 mM concentration, were prepared by the reaction between hypochlorite and bromide (10) at pH 11.0, using equimolar amounts of NaOCl and KBr . Because of the slow decomposition of hypobromite (11), yielding bromate and bromide, stock solutions were used for a maximum of 1 month. To monitor decomposition, a differential titration procedure for hypobromite and bromate was devised. Excess sodium arsenite was added to two stock samples: one in acidic and the other in neutral media followed by an amperometric back titration of each, with bromate and iodine, respectively. Since bromate is determined only in the acid titration, while hypobromite is determined in both, bromate concentration is calculated by difference, indicating the magnitude of stock decomposition (12, 13).

Hypobromous acid, HOBr , was produced by adding the stock solution to pH 7 buffer (KH_2PO_4 - K_2HPO_4 , 0.01 M) just prior to the experiment. As in all experiments, including those involving acetate and NaOH buffers for other bromine species, the buffer was chlorinated to 3-5 mg/L for 4 days and dechlorinated with an ultraviolet lamp the day before the experiments.

Hypobromite, OBr^- , was also produced by adding stock solution to the buffer immediately before the experiments. One set of experiments was done at pH 10 (0.0001 M NaOH),

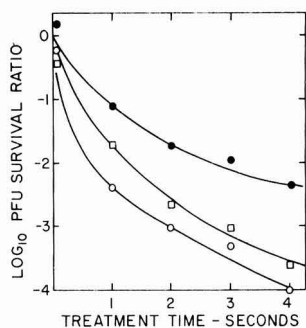


Figure 1. Kinetics of inactivation of poliovirus at 2 °C and pH 11 by hypobromite ion (OBr^-)

●—● 4.3 μM , □—□ 5.5 μM , ○—○ 9.6 μM OBr^-

and the other at pH 11 (0.001 M NaOH). Equilibrium calculations showed that at pH 11, the solution at 4 °C was 99% OBr^- and 1% HOBr , while at pH 10, it contained 91% OBr^- and 9% HOBr (14).

Molecular bromine, Br_2 , was produced by adding an OBr^-/Br^- mixture (pH 11) to a buffered pH 5 solution (0.05 M $\text{CH}_3\text{COONa}-\text{CH}_3\text{COOH}$). In each experiment the final bromide concentration was 5.0 μM , so that the final solution at 4 °C was composed of 89% Br_2 , 10% Br_3^- , and 1% HOBr (15). In addition, NaCl was added to the buffer to a final concentration of 0.3 M (except as noted below) to prevent viral aggregation (16).

Tribromamine, NBr_3 , was produced by simultaneously adding equal volumes of OBr^- and NH_4Cl solutions to pH 7 buffer ($\text{KH}_2\text{PO}_4-\text{K}_2\text{HPO}_4$, 0.01 M). The resulting solutions had an initial molar concentration ratio of $[\text{NH}_3]:[\text{Br}_2]$ of 1:3, so that the resulting solution existed entirely as tribromamine.

Dibromamine, NHBBr_2 , was also generated by simultaneous addition of equal volumes of OBr^- and NH_4Cl solutions to pH 7 phosphate buffer, 0.01 M. However, the initial molar concentration ratio $[\text{NH}_3]:[\text{Br}_2]$ was 3:1. Both the di- and tribromamine experiments were conducted within several minutes after preparing the solutions.

Bromine Analysis Procedures. Bromine concentrations were determined by the iodometric method (17). Immediately before and after each dynamic inactivation experiment, flow output samples were collected into 250-mL optical red flasks, which already contained 5 mL of 5% potassium iodide. Two milliliters of glacial acetic acid were then added, and the solution was titrated with sodium thiosulfate to an amperometric endpoint, using an applied potential of +200 mV vs. SCE applied to a rotating Pt electrode.

In addition to iodometry, ultraviolet absorption spectroscopy was used in the analysis of di- and tribromamine. Ultraviolet absorption spectra of samples from each experiment were taken on a Cary Model 14 spectrophotometer in 10-cm cells. Simultaneous Beer's law equations involving the molar absorptivities of di- and tribromamine at their absorbance maxima of 232 and 258 nm (6) were then solved, showing that each sample was essentially either all dibromamine or all tribromamine, with only minute traces of the other.

Disinfection Experiments. The procedure used for the disinfection experiments has been previously described (3). All experiments were done at 2–4 °C, using the fast flow apparatus previously described (3).

Results

Hypobromite Ion (OBr^-). Disinfection experiments on poliovirus with OBr^- were made at pH 10 and 11 at 2 °C at

concentrations of 2–12 μM (0.32–1.9 mg Br_2/L). Figure 1 shows kinetics of inactivation at pH 11 as the usual semilogarithmic or first-order plot. The inactivation rates were quite rapid initially, but there was a marked decrease in rate with time despite the fact that the virus sample entering the flowing stream of bromine solution was in a monodispersed state. The bottom two curves in Figure 1 (open squares and open circles) show OBr^- experiments performed in the usual manner. The top curve (filled circles) shows an OBr^- inactivation curve of a virus sample that was pretreated by centrifugation in a Beckman SW 50.1 rotor at 30 000 rpm for 25 min at 20 °C. This treatment removed all aggregates of size larger than pairs and left monodispersed virus in the top 3 mL of the tube. Thus, if any aggregates were present in the virus preparation that were not seen by electron microscopy, they would have been removed by the centrifugation. However, this OBr^- inactivation curve gave the same shape and concentration dependence as the nonprecentrifuged virus, indicating that virus aggregation played no part in causing the decrease in slope with time.

Table I shows the initial reaction rates at pH 11 for each of the three curves shown in Figure 1. These values were estimated by taking the first derivative of a polynomial fit to the points as a curve. Since all curves gave zero inactivation at zero time, the first derivative yielded an estimate of the slope of the curve at time zero, and hence an estimate of the initial rate of inactivation. These calculations were performed in this manner since there was no linear portion of the curve to use as a basis of comparison as there was with HOBr (7).

Figure 2 shows the kinetics of inactivation of poliovirus with OBr^- at pH 10. As at pH 11, all inactivation rates decreased

Table I. Calculated Values for Initial Rates of Inactivation of Poliovirus by Hypobromite (OBr^-) at pH 11 and 10

	pH 11		
Concentration of OBr^- (μM)	4.25	5.5	9.6
Initial rate ^a of inactivation (\log_{10}/s)	-1.28	-2.1	-3.85
	pH 10		
Concentration of OBr^- (μM)	2.0	6.0	12.0
Initial rate ^a of inactivation (\log_{10}/s)	-0.95	-1.9	-1.95

^a Calculated from the first derivative of the equation $y = ax^4 + bx^3 + cx^2 + dx$ at 0 time.

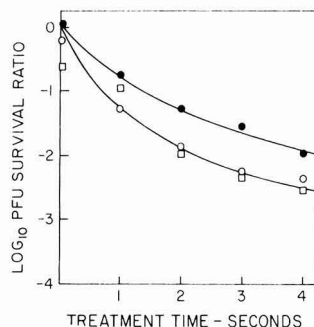


Figure 2. Kinetics of inactivation of poliovirus at 4 °C and pH 10 by OBr^-

●—● 2 μM , □—□ 6 μM , ○—○ 12 μM

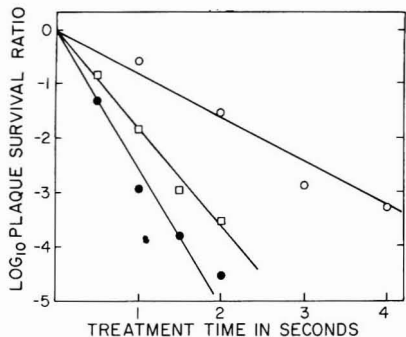


Figure 3. Kinetics of inactivation of poliovirus at 4 °C and pH 5 by Br_2 in presence of 0.3 M NaCl
 ○—○ 4.7 μM , □—□ 12.9 μM , ●—● 21.6 μM Br_2

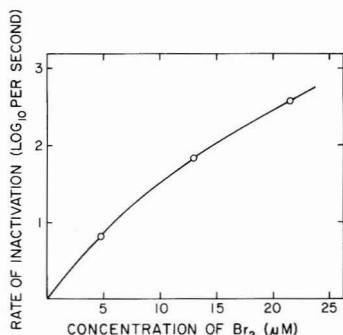


Figure 4. Dependence of inactivation rate for poliovirus on concentration of molecular bromine, Br_2

with time despite the use of nonaggregated virus; however, the rates of inactivation were less than at pH 11. Table I gives initial reaction rates at pH 10 which are in all cases less than $2.0 \log_{10}/\text{s}$.

Table I also demonstrates a saturation effect with respect to OBr^- at pH 10, similar to that observed with HOBr at pH 7 at 2 °C (1). Although the OBr^- concentration at pH 10 doubled from 6 to 12 μM , no increase was seen in the initial rate of inactivation. The pH 11 data do not show this effect since an increase of OBr^- from 5.5 to 9.6 μM (1.75-fold) yielded an increase of initial rate from -2.1 to $-3.85 \log_{10}/\text{s}$ (1.83-fold). This linear increase in rate at pH 11 was similar to that at pH 7 with HOBr at higher temperatures of 10 and 20 °C (1).

Molecular Bromine (Br_2). The inactivating power of Br_2 was tested at pH 5.0, under which conditions aggregation of the virus was massive (16). Therefore, to prevent aggregation of the virus, 0.3 M NaCl was added to the buffer solution as previously described (16). Figure 3 shows the kinetics of inactivation of poliovirus with Br_2 at concentrations of 4.7, 12.9, and 21.6 μM (0.75, 2.06, and 3.46 mg Br_2/L). The plots of these results were linear with time and showed no tendency to curve as did the OBr^- data. The reaction rates were -0.8 , -1.81 , and $-2.56 \log_{10}/\text{s}$, respectively, for the three concentrations of Br_2 tested. Although slower than the initial rates for OBr^- , they are approximately ten times greater than for HOBr (1). When the rate of inactivation was plotted against the bromine concentration (Figure 4), a generally linear increase in rate with increasing concentration was found.

To demonstrate the effect of aggregation on the inactivation of virus, a series of experiments was performed with Br_2 at pH

5 in the absence of added NaCl. Two such experiments at 12.9 and 19.7 μM (2.06 and 3.15 mg Br_2/L) are shown in Figure 5 (open triangles and squares) together with one experiment at 21.6 μM Br_2 (3.46 mg Br_2/L) in the presence of 0.3 M NaCl (open circles) for comparison. The virus sample was placed at pH 5 in acetate buffer 1 h before injection into the flowing stream to allow aggregation to occur. Under these conditions, the initial inactivation rate was similar to that of dispersed virus because of the presence of residual single particles, but the rate of inactivation decreased markedly with time due to the presence of viral aggregation. The data points were scattered to a much greater degree than those of the experiments without viral aggregation; this is a typical feature of aggregated virus.

Tribromamine (NBr_3). Kinetics of inactivation of poliovirus with NBr_3 at 4 °C are shown in Figure 6, and the relation between rate of inactivation and NBr_3 concentration is shown in Figure 7. At the lowest concentration tested, 3.2 μM NBr_3 (1.5 mg Br_2/L), there was a lag of several seconds in the kinetic curve before a linear phase of first-order inactivation was reached. Higher concentrations of NBr_3 gave strictly linear plots without the appearance of a shoulder, but there was a marked tendency toward saturation (Figure 7) above a concentration of 25 μM NBr_3 (12 mg Br_2/L). No further increase in reaction rate was observed at higher concentrations of Br_2 .

Dibromamine (NHBr_2). Dibromamine was the least effective compound of bromine tested. The rate of reaction was slow enough that a modification was necessary in the continuous flow apparatus to take samples at intervals of minutes

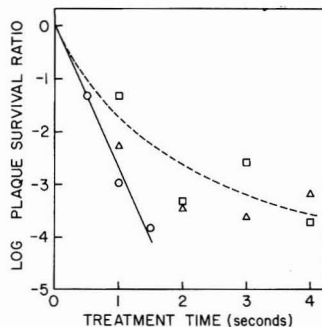


Figure 5. Kinetics of inactivation of poliovirus at 4 °C and pH 5 by Br_2
 △—△ 12.9 μM and □—□ 19.7 μM in absence of NaCl; ○—○ 21.6 μM Br_2 in presence of 0.3 M NaCl

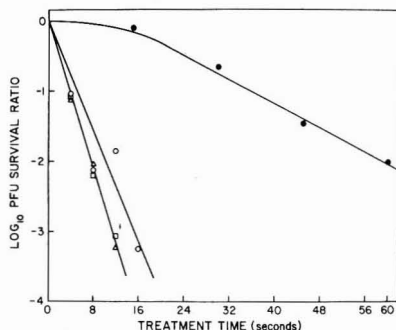


Figure 6. Kinetics of inactivation of poliovirus at 4 °C by NBr_3
 ●—● 3.2 μM , ○—○ 12 μM , □—□ 27 μM , △—△ 49 μM

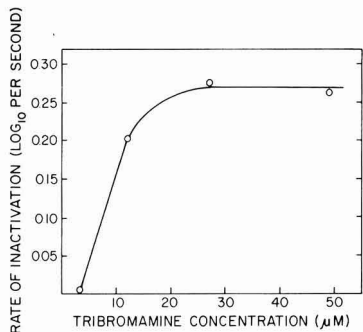


Figure 7. Dependence of inactivation rate for poliovirus on concentration of NBr_3

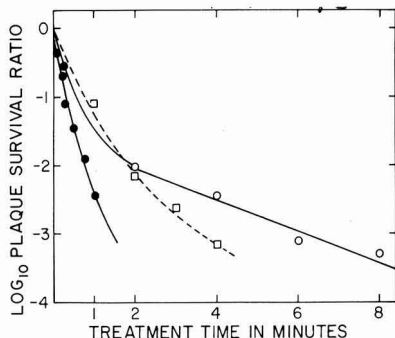


Figure 8. Kinetics of inactivation of poliovirus at 4 °C by dibromamine (NHOBr_2)
 ○—○ 2.9 μM , □—□ 13.8 μM , ●—● 39 μM . Data points at 39 μM represent two experiments, one with samples taken up to 15 s; second at times of 15–60 s

rather than seconds. The modification consisted of a flowing stream of 15 s length terminated by one sample port where a sample could be taken at this time point if desired. As soon as the virus-containing buffered bromine solution came to the end of the tube, approximately 60 mL (about 2 s in time) of solution was caught in a beaker and immediately placed in an ice bath to maintain the temperature at 2 °C. Samples were taken from this beaker at the appropriate intervals of time. The data from four experiments are plotted in Figure 8. At the highest concentration tested the results were essentially linear, while at the lower concentrations the results were very strongly curved in spite of the absence of any significant aggregation.

A graphical resume of all these data, including the results of earlier work (1) with HOBr at 2 and 10 °C, is shown in Figure 9. All of the data accumulated in this paper were obtained at 2–4 °C as indicated. Poliovirus inactivation rates for bromine at higher temperatures have not yet been determined except for HOBr as previously published (1).

Discussion

The four different compounds of bromine examined here for their destruction of the infectivity of poliovirus are very different in potency. In comparing these it is helpful to use molar concentrations; however, it is difficult to make an equally uniform statement of reaction rates. For those that produce a linear decline in log PFU with time (Br_2 , NBr_3 , and HOBr), rates can be expressed simply as the slope of the line, as \log_{10}/s . With OBr^- and NHOBr_2 , however, there is an ini-

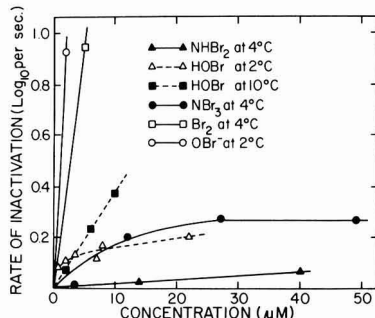


Figure 9. Rates of inactivation of poliovirus in relation to concentration of bromine reagent
 Data for HOBr at 2 and 10 °C taken from another work (1). OBr^- point at 2 °C taken from pH 11 data

tially rapid reaction whose rate decreases with time. For these, one may select the initial rate for comparison purposes, or one may choose to compare times required to reduce the starting titer of the virus to some selected value such as 10 or 1%, or 1/e as advocated by Morris (18). Of course, the latter procedure leads to very different potency ratios depending on the endpoint level selected, particularly when one of the agents compared produces a curve (on the logarithmic scale) and the other a straight line. We have elected to calculate the approximate slope at zero time by using a polynomial equation to estimate the initial rate of the OBr^- inactivation data because of its simplicity and applicability. Obviously, no system of calculations can yield an accurate initial rate at zero time in the absence of numerous data points at or near this time point, which are difficult to take in small fractions of the first second. Hence, there is no single number, ratio, or other statistic that can be devised to summarize the graphical data and give an overall statement of the relative potency of all five of the common bromine compounds in water.

Low temperatures (2–4 °C) were chosen for this work because at higher temperatures some of the reactions would have been too rapid to follow. The different pH values required for the different bromine compounds are well within the limits of stability of the poliovirus infectivity (19). Loss of titer, even at pH 11, is negligible in the short time required for these experiments.

The initial rate for OBr^- , the linear rates for Br_2 , NBr_3 , and HOBr (1), and the initial rate of NHOBr_2 , all at 10 μM concentration, are 3.85, 1.55, 0.15, 0.16, and 0.013 \log_{10}/s , respectively. There are no complete data for direct comparison with a similar set of chlorine compounds. Some points of comparison can be made; however, the state of virion aggregation has often been ignored in earlier experiments, and if data were taken on the time to reach a given decrement in virus titer the presence of aggregates may make reaction rates look low by comparison with data presented here. Generally speaking, it appears that bromine inactivates poliovirus faster than equimolar concentrations of either chlorine or iodine. Four publications of carefully controlled laboratory experiments have been chosen to illustrate this point. Weidenkopf (20) found that type 1 Mahoney poliovirus was inactivated at the rate of 1.23 \log_{10} units per minute when 5.5 μM (0.39 mg Cl_2/L) free chlorine (HOCl) was present at 0 °C, pH 6. Other concentrations in the range 1.43–23.6 μM were tested, and a graph of these values was plotted by us (1), which shows the same shape of curve as that for NBr_3 in this work. Although reaction rates increase with concentration, both bromine and chlorine appeared to lose efficiency with increased concentration. Figure 6 shows that at 3.2 μM NBr_3 (1.54 mg Br_2/L)

the virus was degraded 0.044 log₁₀/s or 2.64 log₁₀/min in the linear portion of the curve. This is about 5.3 times faster for similar μM concentrations than that given by Weidenkopf for chlorine. At 14 μM, where our data show NBr₃ reducing infectivity at 0.23 log₁₀/s, Weidenkopf found 1.8 log₁₀/min or 0.03 log₁₀/s. Here the ratio is 7.6 times faster for the same μM concentration of tribromamine.

Scarpino et al. (21) found that for 1 mg/L free chlorine (HOCl), which is 14 μM, there was a decrease in titer of 2 log₁₀ in 126 s, or 0.95 log₁₀/min, roughly 1/2 the rate of Weidenkopf even though the temperature was 5 °C higher.

Symons and Hoff (22), exposing poliovirus at pH 6, 5 °C to 1.5 mg Cl₂/L, obtained a curve, the initial slope of which we have calculated to be 0.21 log/s. This rate is nearly the same as our rate for HOBr and NBr₃. This high rate was not maintained, however. At 1 min it had declined to 0.033/log₁₀/s or 2 log₁₀/min.

Berg et al. (23), with 20 μM of elemental iodine (5.08 mg I₂/L) at pH 6 and 15 °C, obtained a two log₁₀ decrease in poliovirus titer in 58 min. A substantial lag period was observed before the reaction entered the linear semilog phase, but even in the linear phase the inactivation of the virus by iodine is less than 10% of the rate for bromine.

The experimental facts gathered here reveal a phenomenon heretofore obscured. When the inactivation rate decreases during the course of a disinfection experiment with purified virus, it is usually attributed to virion aggregation, assuming that genetic heterogeneity and depletion of the disinfecting agent are excluded. Here we have seen with two bromine compounds (Br₂ and NBr₃) and with HOBr (1), linear reaction rates extending three and four factors of 10 when aggregation is very low or absent. The same virus, however, shows a declining reaction rate when treated with two other bromine compounds (OBr⁻ and NHBr₂). This might be interpreted to mean that a small but significant amount of aggregation remains, and the two classes of bromine compounds respond to it in very different degrees. But it seems more likely that the influence of aggregation has been effectively removed, and different modes of action of these two groups of compounds on poliovirus are now clearly revealed. The next step must be to determine the nature of these reactions, and hence the manner of their difference.

Although no studies have been reported on the virucidal activity of OBr⁻, Taylor and Johnson (24) studied Br₂, HOBr, and NBr₃, and suggested that OBr⁻ should resemble OCl⁻ in activity. Preliminary experiments with OBr⁻ and poliovirus revealed rapid inactivation kinetics, and the results given herein have been reproduced several times. Thus, the activity appears to be consistently rapid. However, we have not yet been able to formulate a mechanism for the rapid activity of OBr⁻ compared to the much slower activity of OCl⁻ (24), and it will be necessary to study this phenomenon further before any definite mechanism can be revealed.

Acknowledgment

We acknowledge the assistance of David Hays and Guy Inman for bromine assays and preparation of buffers.

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Received for review July 28, 1977. Accepted March 21, 1978. Work supported in part by U.S. Environmental Protection Agency grant number R 804635010, and in part by contract number DAMD017-74-C-4013 with U.S. Army Medical Research and Development Command.

Mercury Emission in Hawaii: Aerometric Study of the Kalalua Eruption of 1977

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Mercury emission was followed before, during, and after the eruption of September 1977 at the Kalalua vents of the Kilauea East Rift (Island of Hawaii) and associated sites. A remote station in Honolulu, some 380 km to the NW, was also monitored. Ground-based measurements were supplemented with aerial samples at low altitudes over the vents and at higher altitudes between the islands. In proximity to the eruption sites, air mercury rose from typical preeruptive values of $1 \mu\text{g}\cdot\text{m}^{-3}$ or less to levels of $50\text{--}200 \mu\text{g}\cdot\text{m}^{-3}$ at the beginning of full scale activity. It also rose substantially at the Honolulu station. Aerial surveys revealed a rise in Hg from ground to 33 m and a decrease thereafter. Relatively high levels of Hg (about $1 \mu\text{g}\cdot\text{m}^{-3}$) were present at least to 2500 m altitude. Earlier aerometric data confirmed the facile dispersal of Hg from a volcanic source. A comparison of recently measured mercury values with published environmental health standards suggested that potentially hazardous air concentrations may exist in the Hawaii Volcanos National Park and the lower portions of the adjacent Puna District.

Geothermal activity has been established as a source of atmospheric mercury both at natural vents (1-5) and man-made wells (6-9). Aerometric studies have shown that although the atmospheres of nonthermal locations both in Iceland and Hawaii are appreciably lower in Hg than thermal sites, they nevertheless exceed markedly the normal "baseline" values, reported variously to be $0.001\text{--}0.03 \mu\text{g}\cdot\text{m}^{-3}$ (5, 10, 11). Continuous emission of mercury-laden gas can presumably account for high baseline values at some distance from source, as it does in the case of fallout collected on copper and gold foils; sample stations on the Islands of Maui and Oahu, respectively, 200 and 380 km NW of fumarolic sources on the Island of Hawaii recorded as much as one-tenth the mercury deposition found in close proximity to the fumaroles (12). Olafsson reported high air mercury levels during the massive Kirkafell eruption at Heimaey (Iceland) in 1973 (3), but there has been no direct aerometric study of mercury before, during,

and after a full scale eruption. The onset of such an eruption 20 km down the East Rift of Kilauea at Kalalua crater on 13 September 1977, afforded us the opportunity to follow mercury emission in a general area already under study and to obtain additional information about distribution and transport of the element.

Experimentation

Procedures for atmospheric sampling were similar to those described previously (2, 4). Air volumes of 100-280 L were passed through 10-cm Teflon tubes containing either 99.995% pure gold foil or Pyrex glass wool saturated with concentrated nitric acid. All trap materials were Hg free. Tubes were individually sealed while in clean air with parafilm until connected to portable battery operated pumps and resealed until returned for analysis.

Prior to analysis, acid with entrapped Hg-ions was eluted from glass wool traps with deionized water. Both gold foil and the inner surfaces of collecting tubes were each washed in a small volume of concentrated nitric acid, combined, and then diluted to a final volume of 100 cc with deionized water. The final concentration of acid in analytical samples of both types was approximately 0.1 N. The absence of residual Hg in glass fibers, on gold foil, and in sample tubes was confirmed by analysis.

Analyses were carried out using standard flameless atomic absorption with a sensitivity of $0.005 \mu\text{g}$. Data are presented as averages of duplicate samples or mean \pm standard error for 3-5 samples.

As a supplement to ground-based sampling on the Island of Hawaii, aerial operations were conducted on two occasions (Figure 1). In the first on 9 October, samples were collected at the open windows of a Cessna Model 305 and in the second on 15 October, from a Cessna Model 182. Sampling was conducted at air speeds of 36 and $48 \text{ m}\cdot\text{s}^{-1}$, respectively, on these occasions from elliptical flight patterns downward.

The first flight included collection over the actively fuming Kalalua vent site at 33 and 170 m above ground level when gas clouds exceeded 180 m altitude. During the second flight collections were made at 33 and 83 m when fume clouds had declined to approximately 10 m. During both operations, coordinated ground sampling was conducted with the cooperation of Hawaii Volcanos Observatory (U.S. Geological Survey).

During flight one, continuous 2-h samples were also collected in transit from Hawaii to Oahu. Sampling during flight two was divided between two altitudes on each limb of the round trip between Oahu and Hawaii and will be detailed below.

In addition to the aerial and ground-based sampling described above, measurements at the foot of the Manoa Valley, Honolulu, Oahu were started at the beginning of the eruption and continued thereafter. This site is of particular interest because it is 380 km NW of the eruption in an area generally considered to be dominated by the NE tradewinds.

Ground-based sampling data reported here were collected at temperatures of $17\text{--}26^\circ\text{C}$ during periods of generally clear to partially overcast conditions. Winds were light varied trades and sample collection was made downwind.

Results and Discussion

Aerometry. Open air Hg levels at specific fumarolic (site S) and magmatic (site F) sites (Figure 1) in Hawaii Volcanos

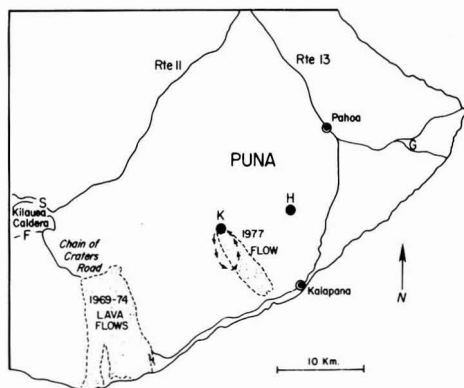


Figure 1. Sample collection sites in Puna District, Island of Hawaii. S, Halemaumau firepit and sulfur well areas of Kilauea, respectively; K, H, Kalalua Crater and Heiheiahulu spatter cones. Lava field formed between 13 September and 1 October: "1977 flow". G, location of University of Hawaii experimental well, HGP-A, shut down since May 1977. Aerial sampling site located in elliptical flight path at K

Table I. Mercury Aerometry at Ground Level Sites During Phases of Kalalua Eruption

Date	Time lapsed ^a (days)	Site	Hg $\mu\text{g}\cdot\text{m}^{-3}$
29–31 July	ca. -45	Preeruptive	
		HGP-A (inactive well), 20 km ENE (G) ^b	0.8 ± 0.2 ^c
		Sulfur well, 20 km WSW (S)	1.4 ± 0.3
12–13 Aug.	ca. -30	Heiheiahulua, 10 km E (down rift) (H)	7.9 ^d
		HGP-A (G)	0.5
		Sulfur well (S)	0.2
15 Sept.	+1.5	Halemaumau, 20 km WSW (F)	0.2
		Eruption begins at Kalalua Vents, 13 Sept.	
		HGP-A (G)	0.2
30 Sept.– 1 Oct.	+17/18	Sulfur well (S)	1.1 ± 0.4
		Kalalua, 1 km E of Vents (K)	>200.
		Manoa (Honolulu), 380 km NW	0.04 ± 0.01
		HGP-A (G)	4.9
		Sulfur well (S)	11.3
3 Oct.	+20	Halemaumau (F)	50.
		Kalalua, 300 m W of flow (L)	69. ± 18.
		Manoa	0.17 ± 0.06
		Fountaining ceases, 1 Oct.; fuming continues	
		Manoa	0.08
9 Oct.	+26	Kalalua (S. of Vents) (K)	1.88
		Kalalua (S. of Vents) (K)	1.94 ± 0.71
15 Oct.	+32	Fuming and tremors cease 10–12 Oct.; end	
		Kalalua (S. of Vents) (K)	1.21
		Manoa	0.06

^a Before (-) or after (+) beginning of eruption. ^b (Capital letter) designates map symbol (Figure 1). ^c Mean of three or more samples ± SE. ^d Average of duplicate samples.

National Park, based upon 34 samples taken during 1971–73, ranged from 0.7 to 40.7 $\mu\text{g}\cdot\text{m}^{-3}$ with a mean value of about 17.3 $\mu\text{g}\cdot\text{m}^{-3}$ (5). These, in combination with an additional 45 samples taken at the same sites in the period 1973–76, yield an overall figure of about 15 $\mu\text{g}\cdot\text{m}^{-3}$. The sulfur well (site S) and Halemaumau (site F), although major contributors to this overall average, were at the lower end of the range prior to and during the beginning phase of the Kalalua eruption (Table I). During this same period, air mercury at HGP-A (site F) reflected the general level produced by contamination from natural emission sites. Heiheiahulua (site H) yielded an anomalously high Hg level. This spatter cone has been a site of active gas emission with evidence of magmatic movement only during the past 18 months (13) and is only 10 km east of the Kalalua vents.

Before eruption the remote Honolulu station (Manoa) was at its normal baseline established since 1971. Incipient eruptive activity in the rift zone, however, was associated with the highest air mercury level yet recorded in Hawaii—over 200 $\mu\text{g}\cdot\text{m}^{-3}$ (even 1 km downwind of the vents).

Follow-up measurements taken 17–18 days after the start of the eruption yielded quite different data, suggesting involvement of about 20 km of the East Rift extending from the Kilauea caldera (30 km, if Heiheiahulua is included). Contamination by Kalalua could conceivably explain the air Hg level at the sulfur well (site S), but could not account for the 50 $\mu\text{g}\cdot\text{m}^{-3}$ output at site F, a comparable distance west of Kalalua. The two inactive sample areas nearby, site G to the East and Manoa far to the west, both yielded striking increases in Hg level. With cessation of fountaining, ground-based Hg levels fell rapidly, not only in proximity to the vents, but also at the remote Manoa station.

Although lava fountaining had ceased 8 days prior to the beginning of aerial measurements, the marked contrast in fume emission between the flights of 9 and 15 October (Figure 2) was paralleled by the peak mercury levels found on these respective dates (Figure 3). Our three-point sampling cannot define plume geometry; however, it is clear that the Hg level

rises from near-ground values to a maximum, perhaps at 33 m as shown here, and then declines. This pattern was evident on both occasions, differences in thermal activity not withstanding. These measurements show clearly that relatively large amounts of Hg can be transported into the lower atmosphere on ascending plumes. The upper limits of this process cannot be determined from these data alone.

Further insight into Hg transport, however, was obtained during interisland flights (Figure 4). Measurements on both dates and in both directions along the NW-SE flight line between Oahu and Hawaii show remarkably little variation even over a 1500-m variation in altitude. They fall into the same range as those found at the upper sample altitudes over the Kalalua vents.

The present study has been addressed primarily to the course of Hg emission and its dispersal, whereas earlier reports (2, 4, 12) devoted attention to the presence of elemental Hg and the ratio Hg⁰/Hg (oxidized). Thus, it was noted (12) that this ratio in fallout was higher at remote stations 200 or 380 km from source than in its immediate environs. The ratio on a number of occasions rose from proximal values of 0.2–0.5 to distant values of 1.8–5.2.

Upon calculating these ratios from the present data, the same trend toward Hg⁰ enrichment is seen and is evident in both the horizontal and the vertical distances sampled here (Table II). The observed Hg⁰/Hg (oxidized) ratios may reflect the fact that although many Hg compounds boil at temperatures of 300–500 °C (2), maintenance of a high vapor pressure is characteristic only of the element as temperatures fall into the nonthermal range. This may also account for the differences seen in Hg⁰/Hg (oxidized) between the two flights.

Hazard Potential. The present study has shown that increases of considerable magnitude in air Hg levels can occur during a full scale eruption, not only at sites of magmatic extrusion but along a considerable extent of associated rift zone. Dissemination takes place readily and relatively quickly to points up to nearly 400 km distant and in a direction normal to the prevailing NE trades. The transport process leads to



Figure 2. Vents of 1977 Kalalua eruption site in aerial view
 Top: intensive fuming on 9 October, 8 days after cessation of fountaining. Bottom: reduced activity on 15 October, 2–3 days after subsidence of tremors and technical end of eruption

relatively high Hg concentrations at medium altitudes, which are maintained even after cessation of the eruption, and also appears to generate even higher, if transient, concentrations at low altitudes. Accordingly, these findings are consistent with previous reports and speculations concerning remote transport of mercury (14, 15). They also support the previous conclusions (12) that the only significant mercury contamination at HGP-A (site G) originates elsewhere as a result of natural processes.

It is obvious that Kilauea and the East Rift Zone are responsible for high ambient air mercury levels in Hawaii Vol-

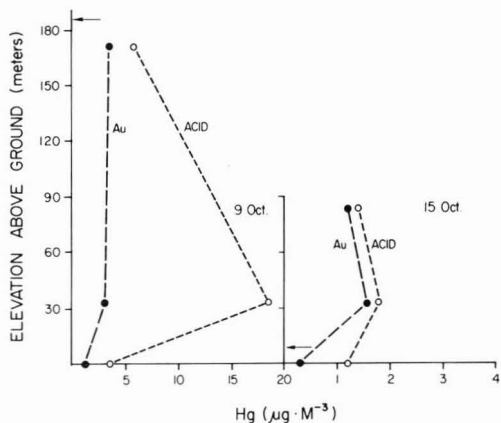


Figure 3. Vertical distribution of mercury at Kalalua vents on 9 and 15 October
 Solid circles: Hg⁰ amalgamated in gold. Open circles: total Hg trapped in nitric acid. Arrows: maximum altitude of smoke plume during aerial sampling operation

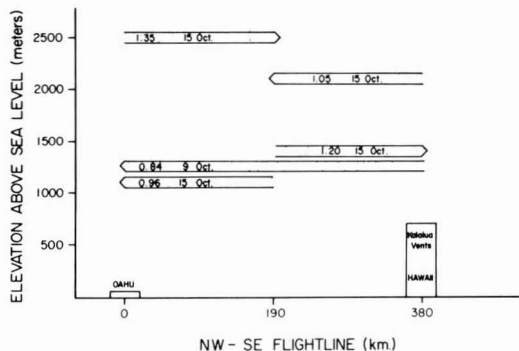


Figure 4. Interisland mercury levels on 9 and 15 October
 Distance covered by sampling (with duplicate pumps) given by length of arrow. Mean altitude of sample path above sea level indicated by position along ordinate. Bars representing Oahu and position of Kalalua vents are approximately to scale with arrows

Table II. Effects of Altitude on Ratio Hg⁰/Hg (Oxidized) in Emissions from Kalalua Vents

Date of flight	Elevation (m)	Hg ^{0 a} µg·m ⁻³	Hg (oxidized) ^b µg·m ⁻³	Ratio
9 Oct.	0	1.2	2.3	0.52
	33	3.0	15.5	0.19
	170	3.5	2.3	1.52
15 Oct.	0	0.3	0.9	0.33
	33	1.6	0.2	8.00
	83	1.2	0.2	6.00

^a Collected on gold. ^b Hg (oxidized) = Hg in acid - Hg⁰.

canos National Park and, at least, the lower section of the Puna District, Island of Hawaii. The 6-year combined average of approximately 15 µg·m⁻³ (at site S and F) alone demonstrates this.

Such averaging, however, included periods in which air mercury concentrations are greatly elevated (50–200 µg·m⁻³) in connection with intensified emission during eruptions. Although it would be premature to draw any conclusions as to the consequences for human population of exposure to these air mercury levels without clinical studies of the residents in this area, the hazard potential cannot be overlooked because police, fire, civil defense, and military personnel often work in proximity to heavy but odorless fumes. Smith (16) claims a close correlation between air, blood, and urinary Hg levels; thus, a 25 µg·m⁻³ air level of Hg corresponds to 2.5 µg·100 mL⁻¹ in blood and 100 µg·L⁻¹ in urine, and 100 µg·m⁻³ of Hg corresponds to 2 µg·100 mL⁻¹ in blood and 250 µg·L⁻¹ in urine.

The World Health Organization 1966 Survey (17) refers to a blood level of 3 µg·100 mL⁻¹ as "normal", but Gerstner and Huff (18) recommend 1 µg·100 mL⁻¹. The WHO Survey notes that 79% of their worldwide sample population excreted <0.5 µg·L⁻¹ of Hg in their urine, but the remaining 21% range widely, up to 221 µg·L⁻¹.

There are no legislated ambient air quality standards for mercury, and national occupational standards range from 1 to 100 µg·m⁻³ (18). It has been recently suggested, however, that the occupational threshold (for an 8-h working day) be placed between 10 and 100 µg·m⁻³ and that for general populations between 1 and 10 µg·m⁻³ (18).

Even the most conservative comparisons between these provisional environmental standards and the aerometric data presented above suggest the need for an in-depth study of the

impact of volcanic mercury emission on exposed human populations and other life forms as well.

Acknowledgment

The authors thank Gordon Eaton and his colleagues at the Hawaii Volcanos Observatory (USGS), Leonard Anderson, Daniel Dzurisin, John Lockwood, and Richard Moore for their cooperation; Richard Brill, Robert Stern, and I. Conday for assistance in the field; the Civil Air Patrol pilots Herbert Hardin and Philip Olson for their skillful assistance in carrying out aerial missions; and Gordon MacDonald for his critical reading of the manuscript.

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Received for review November 21, 1977. Accepted March 22, 1978. Work supported by Energy Research and Development Administration contract EY-76-C-03-1093 under the Geotoxicology Program of the Hawaii Geothermal Project, and by grants from the University of Hawaii's Environmental Center and Research and Training Revolving Fund.

Depletion of Selenium in Sulfur Emissions from Sulfur-Recovery Gas Plants

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■ Sampling 13 sulfur gas plants in west central Alberta indicated that the selenium content of stack gases was too low ($1.65 \pm 0.05 \mu\text{g}/\text{m}^3$) to have a toxic effect on livestock. Selenium emitted by the gas plants may be slightly beneficial to livestock near the gas plants, but overall the benefit is negligible. All the gas plants of Alberta together emit only about 70 kg of selenium per year. Examination of selenium mass balances in sulfur gas plants showed that selenium is depleted, relative to sulfur, in the stack and possibly further depleted in the plume. The selenium contents appeared to be reduced by factors of 5 and 50, respectively. The missing selenium is either retained in the main sulfur product or accumulated somewhere in the processing plant. There are indications that selenium is deposited inside the stacks of gas plants.

Selenium (Se) was discovered by Berzelius in 1817. The biochemical properties of this element and its compounds only gained attention in the 1930's, however, when selenium was identified as a potentially toxic substance for livestock and humans. Although high levels in the diet are toxic, selenium is an essential nutrient for humans and animals. In 1957, selenium was recognized as the essential component of a dietary factor that protected rats from severe necrotic degeneration of the liver (1).

The presence of selenium in the environment has taken on a new significance in the past few years. West (2) and Olson and Frost (3) found that various types of paper and tobacco contain significant amounts of selenium of physiological and toxic importance. The incineration of paper and smoking, therefore, may be an important source of environmental selenium. However, the importance of fuels as a possible source was overlooked until 1967 when selenium in the atmosphere was first quantified by Hashimoto and Winchester (4). They

reported that the average ratio of selenium to sulfur in samples collected in the greater Boston area was about 1×10^{-4} , with an apparent positive correlation between sulfur and selenium. Rubber, raw petroleum, coal, heavy petroleum, and petroleum were also analyzed by Hashimoto et al. (5) who claimed that fuel oils contained 0.5–1.1 $\mu\text{g}/\text{Se/g}$ and could therefore be an important source of selenium in the atmosphere. Recently, Andren and Klein (6) and Klein et al. (7) found that selenium is also discharged from coal-generated steam plants. By mass balance calculations, approximately 0.3% of the coal-derived selenium was incorporated in slag. Sixty-eight percent of the selenium was found on the fly-ash particles and the rest in the vapor phase. It was also indicated that 1.5–2.5 times as much selenium is mobilized by man through coal burning as by natural weathering.

Almost nothing is known about the occurrence of selenium in natural gas in Alberta. The objective of the present investigation was to attempt to account for the movement of selenium through several sulfur-recovery gas plants in Alberta and to determine whether the operation of sulfur-recovery gas plants alleviates or aggravates selenium deficiency problems in the west central Alberta livestock industry.

Experimental Procedures

A fluorometric method was adapted and modified for the analysis of selenium in the acid gases, stack gases, and plume samples obtained from 13 sulfur-recovery gas plants. Analyses were also carried out on stack construction materials. The published method of Levesque and Vendette (8) for determining selenium was modified to use H_2O_2 to oxidize the selenium compounds in the acid gases, stack gases, and filter collections of plume samples into selenite or selenate. Acid digestion was employed for the decomposition of the brick samples from the stack. In this way the selenium was uni-

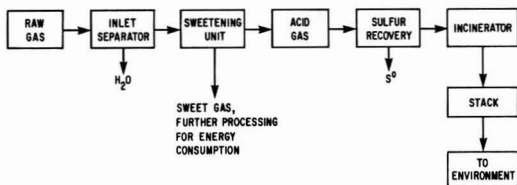


Figure 1. Simple block diagram indicating flow through sulfur-recovery gas plant

formly converted to selenite or selenate for fluorometric analysis.

Sulfur-Recovery Gas Plant Description. The purpose of a sulfur-recovery gas plant is to remove acid gases (H_2S and CO_2) from raw natural gas to make the gas suitable for transport and use as a fuel. A simple block diagram indicating flow through a sulfur-recovery gas plant is shown in Figure 1. Raw gas enters a gas plant through the inlet separator where condensate (natural gasoline) and produced water are separated from the gas stream. Acid gas is removed from the raw gas by absorption or other means in sweetening units. The acidic components (H_2S , CO_2 , H_2Se , etc.) are fed to the sulfur plant for the production of elemental sulfur. Unconverted acid gases (about 2–3% of the input) are incinerated and vented to the atmosphere through a stack (usually 30–130 m in height, depending on the size of the gas plant). These emissions commonly persist in the atmosphere in the form of a plume stretching many kilometers downwind from the stack.

Sample Preparation. A stream of the main inlet gas with a flow rate of 100 mL/min was passed through 0.1 N solution of NaOH containing 6% hydrogen peroxide to oxidize all volatile compounds of selenium and sulfur, largely H_2Se and H_2S , respectively. Dräger analysis was used constantly to determine the saturation point of collection by testing for unoxidized H_2S .

In the case of stack gases, the gas sample was drawn from the incinerator stack at a point about half way up the stack through a stainless steel probe for a period of 1.5 h. Again, a 0.1 N NaOH solution with 6% H_2O_2 was used to absorb the selenium dioxide and sulfur dioxide in a series of four impingers in an ice-water bath. A glass probe was also used for comparison. There was no difference in the measured selenium content of stack gases for a number of gas plants, from which it was concluded that the steel probe was satisfactory for collecting samples.

To check for the possible accumulation of selenium in the brick of an incinerator stack, samples of brick were collected from different heights of the stack. Each sample was divided into three layers, and each layer of brick was ground to pass 100 mesh sieves. The powdered sample (0.5 g) was digested in 5 mL of 70% HNO_3 and 2 mL of 60% HClO_4 in a Teflon bomb at 140 °C for 3.5 h. The resulting solution was diluted to 50 mL, and an aliquot of 20 mL was used for the selenium determination. In the case of the gas samples, the aqueous solution was heated to near dryness to remove residual hydrogen peroxide prior to analysis for selenium.

The plume from the incinerator stack was sampled using airborne equipment in a helicopter. A high-volume sampler (Hoskins) was used with power from a portable generator. The sample was equipped with two filters, the first a glass filter for particulates, and the second a cellulose filter impregnated with triethanolamine and potassium hydroxide for sulfur dioxide and volatile selenium. The plume was sampled with the helicopter stationed in the axis of the plume as indicated by ultraviolet-polaroid photography and an SO_2 monitor. Samples were taken at a point 0.5 km downwind from the stack. To obtain samples of sufficient size for selenium analyses, it was

necessary to collect for 20 min. Duplicate samples were collected. Because sample sizes were very small it was not possible to analyze the first and second filters separately. The data, then, are for the combined particulate and gaseous collections. To remove the selenium from the filters, they were washed exhaustively with 6% H_2O_2 in 0.1 N NaOH solutions.

Total Sulfur Determination as Sulfate. In all cases, total sulfur was determined to establish a reference base for reporting selenium. After oxidation of the sample by hydrogen peroxide in an alkaline solution, sulfur compounds were either measured gravimetrically as barium sulfate or estimated by the method of Johnson and Nishita (9). Standard solutions of sulfate were run to check the calculations for total sulfur. Total sulfur in the brickwork of the emission stack was measured by a Leco sulfur titrator.

Total Selenium Determination as Selenite. Total selenium was determined by the fluorescence method of Olson (10) as modified by Leveque and Vendette (8). In this method selenium forms a fluorescent compound with diamionaphthalene (DAN). Hydrochloric acid (0.1 N) is added, and the pH adjusted to 1.8 to assure the reduction of existing SeO_4^{2-} to SeO_3^{2-} , which form reacts with DAN. A stabilizer solution containing disodium EDTA is added to remove interfering ions. The fluorescence readings were taken using a fluorometer (Turner 110). The combination of filters (primary: 7–60, secondary: 58) resulted in the excitation of samples near 369 nm and the emission of a very narrow band of fluorescent light at 520 nm. Selenium concentration was determined by comparing results with those obtained using standards of known concentrations.

Spectra of DAN–Se Complex Fluorescence. The spectra of the DAN–Se complex shown in Figure 2 were recorded using a Turner 210 spectrofluorometer. There was no difference in the spectrum of this complex, whether isolated from the reaction mixture of the acid gas or from stack gas (Figure 2A, B), when compared to that of standards involving the reaction of DAN with known amounts of selenious acid containing 0.05 μg Se (Figure 2). While there was an extra fluorescent emission (at 470 nm) in the spectrum of stack gas extract, the extra emission was remote from that of the DAN–Se

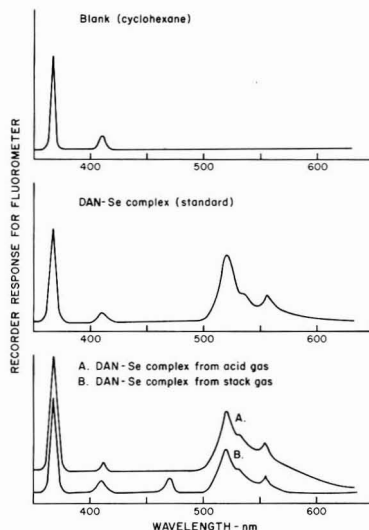


Figure 2. Spectra of fluorescent complexes of emitted selenium prepared by oxidizing sample with H_2O_2 to selenate (and some selenite), reducing total selenium to selenite with 0.1 N HCl and reacting with diamionaphthalene (DAN); fluorescence measured with Turner 210 spectrofluorometer

Table I. Depletion of Selenium Relative to Sulfur in Emissions^a from Sulfur-Recovery Gas Plants

Plant location	Selenium $\mu\text{g/g}$ of sulfur		Depletion factor
	Acid gas	Stack gas	
Windfall	1.00	0.29	3.4
Carstairs	1.70	0.23	7.4
Balzac	0.82	0.32	2.4
Burnt Timber	0.98	0.18	5.4
Simonette	0.42	0.05	7.8
Average	0.98 ± 0.21	0.21 ± 0.04	5.3 ± 1.0

^a Average of duplicate determinations.

Table II. Occurrence of Selenium Based on Se/S Ratio

Origin	Se/S ratio ($\times 10^{-6}$)
Lunar dust	443 ^a
Global ratio	
Igneous rock	167 ^b
Parent material of most soil	1000 ^b
Alberta origin	
Crude oil	6.26 ^c
Black soil	8.34
Grey-wooded soil	10.50
Alberta natural gases	
Acid gas	0.98
Stack gas	0.21
Stack plume	0.02

^a Data taken from Warner (17). ^b Rosenfeld and Beath (14). ^c Hitchon et al. (15).

complex with a very narrow band of fluorescent light at 520 nm.

Results and Discussion

Table I shows that selenium is depleted in the emissions of sulfur from sulfur-recovery gas plants by a factor of about five. Of the five emissions examined, all showed definite depletions ranging from 2.4 to 7.8. While there is some evidence that the depletion factor is inversely related to the absolute content of selenium in the stack gases, the data are too limited to firmly establish that possible relationship. Stack-gas depletion is not the only depletion associated with natural gas processing. Selenium in the sulfur of natural gas is strongly depleted when compared with the general relationship between selenium and sulfur in crystal rocks of the earth, by factors ranging from 200 to 1000 (Table II). So, also, it is depleted relative to sulfur when compared with selenium and sulfur in extraterrestrial minerals [e.g., in lunar soils (11)]. The depletion effect may well be related to factors of volatility, since the vapor pressures of sulfur and selenium are sharply different, and volatilities are undoubtedly important in geochemical processes as well as in the processing of natural gas.

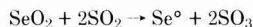
The results of the analysis of the brickwork of the disused emission stack of a sulfur gas processing plant tend to confirm the volatility factor, as shown in Table III. The stack was in service for many years, and the porous lining of the stack absorbed a substantial amount of sulfur. The point of principal interest in the present discussion is that the sulfur absorbed at the lower level was less depleted in selenium than was the sample from near the top of the stack. These data, along with those for the intermediate level, indicate that depletion of selenium in the sulfur takes place within the stack, presumably as a function of stack temperature. Thus, the temperature gradient within the stack appears to produce a corresponding gradient in selenium content in the stack gases.

Table III. Accumulation of Selenium in Brickwork of Incinerator Stack

Ht above ground, m	Selenium content ($\mu\text{g/g}$ brickwork)	Selenium, $\mu\text{g/g}$ sulfur
26		
Outside ^a	0.16	1.77
Middle	0.23	2.05
Inside	0.24	3.21
Overall	0.21	2.30
60		
Outside ^a	0.08	0.69
Middle	0.07	0.59
Inside	0.02	0.21
Overall	0.07	0.55

^a Brick samples were equally divided into three segments to represent the outside, middle, and inside sections of the stack, and a mixture of these three sections represents an overall sample. The inside of these three sections represents an overall sample. The inside section represents that part of the stack in contact with gas.

An important factor in dealing with emissions of selenium and sulfur is the chemical state of the emissions. Sulfur and selenium are incinerated in sulfur-recovery gas plants to SO_2 and SeO_2 . Both oxides are expected to oxidize further, and a good deal of study has been directed to the further oxidation and ultimate outfall of SO_2 . In general, sulfur dioxide is known to persist for at least tens of kilometers downwind from sulfur-recovery gas plants. SeO_2 is expected also to persist, but as the data in Figure 3 show, selenium has been more greatly depleted by the time it reaches the plume from the emission stack. This draws attention to the limited volatility of SeO_2 , and the possibility of SeO_2 being reduced by the SO_2 present in millionfold excess at high temperatures:



This reaction has been reported by Andren and Klein (6), Frost (12), and Zingaro and Cooper (13), and it is the basis for the commercial production of elemental selenium.

The picture that is emerging includes deposition of selenium within the stack, conversion of selenium oxide to selenium within the stack, the possible deposition of SeO_2 in the system near the stack, and, finally, the possibility of the oxidation of SeO_2 to SeO_3 with ultimate incorporation of selenium into the soil as Se^0 , SeO_3^{2-} , and SeO_4^{2-} . As noted above, selenium is clearly deposited preferentially within the stack, and the degree of deposition is likely a function of temperature and stack height. Even more, data for selenium in stack gases within the

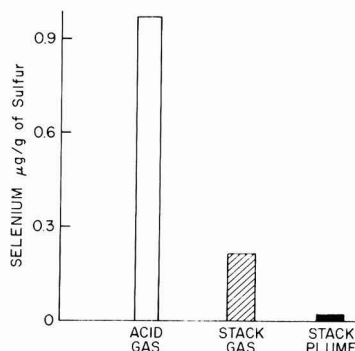


Figure 3. Selenium in acid gas, stack gas, and stack plume related to sulfur content, for five sulfur-recovery gas plants, showing marked depletion of selenium in sulfur effluents

Table IV. Selenium Content of Stack Gas from Selected Alberta Gas Plants

Location	Selenium content $\mu\text{g Se}/\text{m}^3$ ^a	Selenium content $\mu\text{g Se}/\text{g S}$ ^a
Crossfield	2.04	0.23
Olds	1.54	0.63
Kaybob	1.96	0.28
Nevis	2.70	0.38
Strachan	1.50	0.20
Carstairs	1.05	0.23
Wimborne	2.13	0.28
Wildcat Hill	1.38	0.23
Balzac, West stack	1.42	0.41
Balzac, East stack	1.26	0.32
Burnt Timber	1.34	0.18
Innisfail	1.56	0.27
Jumping Pound	1.21	0.17
Bonnie Glen	1.70	0.46
Average	1.65 \pm 0.05	0.30 \pm 0.01

^a Average of 2 tests.

stack indicate a loading far greater than that observed for the plume 0.5 km downwind. Thus, it is clear that the bulk of the selenium is deposited very close to the stack, i.e., well within 0.5 km of the stack. This is in keeping with the redox equation above in which sulfur dioxide is seen to reduce selenium dioxide, and also in keeping with the much lower volatility of the oxide of selenium. It is unlikely that H_2Se would persist from the original acid gas or would be formed in any reducing process involving SO_2 in the stack or plume.

The foregoing analysis and the data in Table II allow for an assessment of the environmental effect of emissions of selenium from sulfur-recovery gas plants. It is necessary to deal with both the question of toxicity and the question of selenium deficiency. The data of Table IV show that the total selenium content of stack gases (including H_2Se —if present, Se, SeO_2 , and SeO_3 —if present) ranges from 1 to $3 \mu\text{g Se}/\text{m}^3$. In terms of toxicity, the only relevant data are those specifically for H_2Se , where limiting concentrations were established at the $200\text{-}\mu\text{g Se}/\text{m}^3$ level by the American Conference of Government Industrial Hygienists. Since H_2Se is far more toxic than any of the other forms of selenium, the aggregated forms of selenium clearly present no problems of toxicity in stack emissions from sulfur-recovery gas plants of west central Alberta.

The next questions deal with the effect of the selenium outfall in the vicinity of the emitting plant. If the toxic effect in the stack gases is a hundredfold less than the proclaimed safe limit for humans, it may be concluded that the stack gases, after dilution by the ambient atmosphere air or at the ground level. There is not expected to be any problem of toxicity to livestock or other living things at the ground level unless some process of accumulation serves to concentrate the outfalling selenium in the local food chain. The region of west central Alberta is marked by soils that are deficient in selenium, and selenium collectors, such as the astragalus plants, are not common except in semiarid regions hundreds of kilometers away to the southeast. There is no indication of

abundant selenium in grains grown in the region of the sulfur-recovery gas plants.

Little alleviation of selenium deficiency problems is indicated by the data of this study. The outfall has two components: one, the direct outfall of selenium, as Se^0 , SeO_2 , and SeO_3 , and the other, the outfall of selenium as a trace element in the emitted sulfur. The total annual emission of selenium from all the sulfur-recovery gas plants in Alberta is very small, amounting to only about 70 kg assuming a Se/S ratio of 0.3×10^{-6} in stack gas from this study and 230×10^6 kg sulfur per year emitted in Alberta (16, 17). If based on Se/S of 0.02×10^{-6} in stack plumes, only 4.5 kg Se is emitted for the whole of Alberta. Clearly, this amount has an insignificant effect if spread out over the total airshed of Alberta. If restricted to the local region of the gas plants in west central Alberta, the output would increase the selenium in the soil by no more than 0.001% per year. If applied to the immediate area around a gas plant, the effect would still not exceed the 1% level and consequently would seem to offer no benefit and, concomitantly, present no problem of toxicity in the soil and vegetation.

As a trace element in the sulfur emissions, selenium offers no solution to the selenium deficiency problem of west central Alberta because the selenium level is depleted with respect to sulfur in the soil and crustal rocks. This depletion appears to be two-staged. In the first case, the selenium is depleted relative to sulfur on the occasion of the formation of the natural gas with its contaminants of hydrogen sulfide and hydrogen selenide. Secondly, the selenium is further depleted in the processing of the natural gas to remove these contaminants in the sulfur-recovery plants treating the natural gas.

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Received for review December 20, 1976. Accepted March 27, 1978. Work carried out as part of the program of UNISUL at the University of Calgary under a grant from the National Research Council of Canada.

Degradation of Aqueous Phenol Solution by Gamma Irradiation

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■ The gamma irradiation-induced degradation of oxygenated aqueous phenol solution was investigated with reference to the nature of the products employing a high-speed liquid chromatographic method. Hydroquinone, catechol, *p*-benzoquinone, *o,o'*-biphenol, 1,2,4-trihydroxybenzene, dihydroxyacetaldehyde, maleic acid, and carbon dioxide were isolated and identified as degradation products. The degradation of phenol was confirmed to be first order. The secondary degradation occurred near the stage of 60–70% phenol consumption, whereas the phenol conversion into carbon dioxide occurred at the stage when the primary degradation products are almost destroyed. The dose required for complete phenol conversion into carbon dioxide was over five times that demanded for complete phenol consumption. In addition to these results, the mechanism that accounts for aromatic ring-cleavage was inferred from the formation of dihydroxyacetaldehyde.

Ionizing radiation has the ability to oxidize or otherwise decompose or change the structure of organic compounds that resist ordinary biological treatment in wastewaters. The degradation of phenol in wastewater by ionizing radiation has been previously investigated by Touhill et al. and Sunada (1, 2). In these studies the spectrophotometric method was mainly employed in an investigation of the changes of phenol concentration in the degradation process. The phenol consumption would not imply complete phenol degradation because of the formation of secondary intermediate products by gamma irradiation.

The above-mentioned studies are mainly concerned with the removal of phenol. We can find some studies on radiolysis of the simple phenol–water system; action of hydroxyl and hydrogenperoxide radicals on phenol (3); clarification of primary process in pulse radiolysis of phenol (4); and estimation of rate constants corresponding to the reaction of solvated electron, hydrogen atom, and hydroxyl radical with phenol (5–8). However, phenol concentrations in these studies are greater than those in the ordinary treatment of wastewater, and gamma irradiations have not been carried out until phenol was completely destroyed. The identification of the ring-cleavage products formed from phenol and the formation mechanisms involved have not been elucidated.

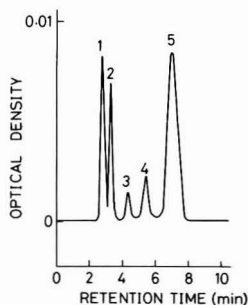


Figure 1. Liquid chromatogram of irradiated phenol solution. Initial phenol concentration: 100 ppm; total dose: 2×10^5 R. Peak 2 = *p*-benzoquinone, 3 = hydroquinone, 4 = catechol, 5 = phenol

We are interested in a complete phenol degradation of the phenol–water system by gamma irradiation. In order to make clear the complete phenol degradation, it is necessary to isolate and identify the degradation products. For this purpose, a high-speed liquid chromatograph was used in this study and has subsequently opened many possibilities for the identification of the degradation products.

Experimental

Materials. Phenol of specially prepared reagent grade (>99%) was used without further purification. *n*-Hexane of spectrograde was used as an eluent in a high-speed liquid chromatograph. All other reagents were of guaranteed reagent grade. The phenol was dissolved in triply distilled water.

Irradiation. The aqueous phenol solution was saturated with oxygen before irradiation. The irradiation was carried out with 200 Ci ^{60}Co gamma-rays at room temperature. The dose rate was 5.3×10^4 R/h, which was determined by Fricke dosimeter.

Analytical Methods. The isolation of some products formed in the aqueous solution was performed using a Du Pont Model 830 high-speed liquid chromatograph (HLC). Phenol, catechol, hydroquinone, and *p*-benzoquinone were effectively separated and determined under the reversed-phase chromatographic conditions. A sample of 10 or 50 μL of irradiated solution was directly introduced into the HLC. The conditions of the reversed-phase chromatography are: column: Permaphase ETH (Du Pont) 2.1 mm $\phi \times 1$ m; mobile phase: 0.01 M boric acid; column pressure: 60 kg/cm²; column temperature: RT; detector: UV photometer at 254 nm. For the analysis of products other than those described above, the irradiated solution was extracted three times with ether. By the use of a rotary evaporator, the residual aqueous layer was evaporated to dryness under reduced pressure. The residue was dissolved in ethanol, and 10 μL of this solution was introduced into the HLC. In this case, the chromatographic conditions are: column: Permaphase ETH; mobile phase: linear gradient from ethanol/*n*-hexane (5/95) to ethanol at 3%/min; column pressure: 40 kg/cm²; column temperature: RT; detector: UV photometer at 254 nm. To identify the degradation products, an ultraviolet (UV) spectrum of each product was taken on a Shimadzu Model UV-200 spectrophotometer to which a micro-flow cell was attached. In addition to UV spectra, infrared (IR) and mass (MS) spectra were supplementally taken on a Shimadzu Model IR-400 spectrophotometer and an Ulvac Model MSQ-500 mass spectrometer attaching a direct-inlet system, respectively.

As it is supposed that organic carbon in aqueous phenol solution decreases by the formation of carbon dioxide through irradiation, total organic carbon (TOC) in the solution was measured with an Oceanography International Model 0524 TOC analyzer.

Results and Discussion

Isolation and Identification of Products. The sample solution (100 ppm) irradiated to a dose of 2×10^5 R was analyzed according to reversed-phase chromatographic conditions mentioned above. The chromatogram is shown in Figure 1. The comparison of UV and MS spectra and the retention times of degradation products with those of authentic samples allowed identification of peaks 2, 3, and 4 as *p*-benzoquinone, hydroquinone, and catechol, respectively. Resorcinol, being an *m*-dihydroxy derivative, was not found in the irradiated

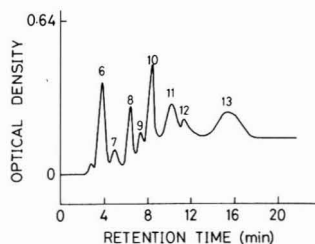


Figure 2. Liquid chromatogram of aqueous layer after ether extraction of irradiated phenol solution

solution. These results are similar to those obtained by Stein and Weiss (3). However, the ratio of hydroquinone/catechol in this study is distinct from that which they have reported as described later.

Since peak 1 was a mixture of polar compounds, the irradiated sample was extracted with ether to remove nonpolar compounds, and the residual aqueous layer was analyzed according to the method explained in the Experimental section. The chromatogram is shown in Figure 2. Eight peaks are detected. The spectral data of these peaks are shown in Table I. By comparison with the authentic samples, peaks 7, 8, 9, 10, and 12 could be identified as *o,o'*-biphenol, catechol, maleic acid, hydroquinone, and 1,2,4-trihydroxybenzene, respectively. For peaks 11 and 13, the following structural features were found from the measurement of IR, UV, and MS spectra and the retention times in HLC analysis.

Peak 11. The MS spectrum of this peak gives no fragments attributed to the benzene ring and resembles that of muconic acid. The compound might therefore be of a ring-cleavage type. The UV spectrum suggests that this compound is aliphatic acid or aldehyde. This information, however, was insufficient to identify this compound.

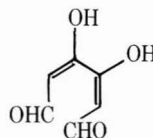
Peak 13. The aldehyde reaction with 2,4-dinitrophenylhydrazine reagent was positive. Thus, the obtained red-brown hydrazone showed a deep violet-blue color in alcoholic alkaline solution. The hydrazone has also a molecular weight of about 500, measured by gel permeation chromatography, which indicates the presence of at least two carbonyl groups. The infrared spectrum of peak 13 is shown at the left column in Table II. To identify the compound, this spectrum was compared with those of similar compounds, and β -hydroxymuconialdehyde (β -HMDA) was selected as the closest known compound among the investigated compounds (9). The retention time of peak 13 in ordinary phase chromatography is longer than that of β -HMDA, suggesting the presence of at

Table II. Infrared Spectra of Peak 13^a

Infrared spectra (frequencies, cm^{-1})	
peak 13	β -hydroxymuconialdehyde
3700–2900 s, vb	3600–2500 s, vb
2800 w	2800 w
	2715 w
1700 shoulder	1700 shoulder
1680–1540 s, vb	1680–1520 s, vb
1400 m	1430 m
	1360 m
1185 m	1185 m
1140 m	1140 s
1080 m	1085 m
	965 s
900 w	910 s
850 w	845 m
800 w	810 vw

^a s = strong, m = medium, vw = very weak, w = weak, vb = very broad.

least two hydroxyl groups. The UV spectrum also shows a striking pH dependence as well as β -HMDA, suggesting tautomeric change of keto and enol forms. However, the shift to a much higher wavelength is not great compared with those of α -hydroxymuconic semialdehyde (10), *p*-hydroxybenzaldehyde (11), etc. This difference is understood from the fact that the resonance in α -hydroxymuconic semialdehyde is across two intervening double bonds as opposed to one in the objective compound. These facts enable us to place OH on β position to an aldehyde group in the structure. From these results, peak 13 was tentatively identified:



Phenol Consumption. The degradation curves for the phenol solutions of 1000, 100, 50, and 10 ppm are shown in Figure 3. *G*(-PhOH) (i.e., the numbers of phenol molecule destroyed per 100 eV of radiation energy absorbed) determined in the low dose region is 3.0 for solutions over 50 ppm and 1.2 for 10 ppm solution. This phenomenon indicates that the recombination probability of radicals that are provided by irradiation becomes appreciable in low phenol concentration. Also, for the solutions over 50 ppm the numbers of phenol molecule destroyed per unit dose decrease as the residual phenol concentration decreases. On the other hand, the per-

Table I. Spectral Data on Chromatographic Peaks 6–13

Irradiated sample			standard		
peak no. (Figure 2)	retention time (min)	UV spectra max (nm)	compound	retention time (min)	UV spectra max (nm)
6	4.0	244			
7	4.5	210	<i>o,o'</i> -biphenol	4.4	210
		245			246
		285			285
8	6.2	215	catechol	6.2	217
		277			277
9	7.2	215	maleic acid	7.1	215
10	8.2	216	hydroquinone	8.1	217
		288			288
11	10.0	220			
12	11.2	213	1,2,4-trihydroxy benzene	11.2	215
		290			290
13	16.0	215			
		290			
		350			

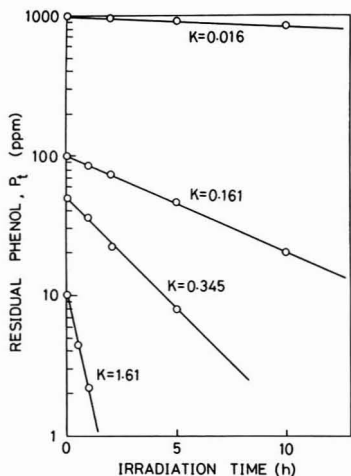


Figure 3. Plots of $\log P_t$ as a function of irradiation time
Dose rate: 5.3×10^4 R/h

centage of degradation increases as the initial phenol concentration decreases. For example, the irradiation with the dose of 10^5 rads destroys over 90 and 50% of phenol for 10 and 50 ppm solutions, respectively.

Figure 3 shows the relation between irradiation time and $\log P_t$, where P_t denotes the residual phenol concentration after t hours. This linear relationship indicates that the degradation of phenol is first order. Accordingly, the rate equation can be expressed:

$$\frac{d(P_0 - P_t)}{dt} = -K \cdot P_t \quad (1)$$

where P_0 and K denote the initial concentration of phenol and the rate constant, respectively. Both sides of Equation 1 can be integrated, giving

$$P_t = P_0 \exp(-K \cdot t) \quad (2)$$

On the other hand, the following Equation 3 is set up between the initial concentration and the rate constant, which is obtained through the slope of the straight line in Figure 3.

$$K \cdot P_0 = 16.1 \quad (3)$$

Substituting Equation 3 into 2, Equation 4 is yielded.

$$P_t = P_0 \exp\left(\frac{-16.1}{P_0} t\right) \quad (4)$$

The residual phenol concentration can be evaluated by fitting P_0 and t to Equation 4. The constant in Equation 4 is sub-

stantially dependent on dose rate. The equation would therefore be further generalized by taking this fact into consideration. The effect of dose rate was not examined in this study.

TOC Reduction. The concentrations of TOC and a few intermediates in irradiated solution against the irradiation dose are shown in Figure 4. The TOC concentration decreases with an increase in the irradiation dose. However, the rate of decrease in TOC concentration is slow in the lower dose region. The TOC concentration hardly decreases until over 95% of phenol is destroyed. Furthermore, the irradiation dose demanded for complete phenol conversion into carbon dioxide is over five times that required for destroying over 95% of phenol. These results indicate that the conversion reaction into carbon dioxide occurs not directly but through the process of conversion into lower molecular compounds.

The rate of decrease in TOC concentration comes to a maximum at a certain dose. As the degradation further proceeds, its rate becomes slow again because of a lowering of the organic matter concentration.

Dose Dependence on Yield of Products. Figure 5 shows the variation of product yields with the irradiation dose for the aqueous phenol solution of 100 ppm. Their yields of products decrease with the phenol consumption. The initial G -value for the formation of catechol, hydroquinone, and p -benzoquinone is 1.0, 0.67, and 0.26, respectively. The ratio of hydroquinone/catechol is 0.67 in this study, whereas the value is distinct from that obtained by Stein and Weiss (3), which is 1.5. On the other hand, the G -value for the formation of products other than those described above, namely, o,o' -biphenol, 1,2,4-trihydroxybenzene, maleic acid, and dihydroxyconicaldehyde, could not be determined because of difficulty in the determination of these products. However, it is considered that the gap between $G(-\text{PhOH})$ and 1.93, which is the sum of each G -value for catechol, hydroquinone, and p -benzoquinone, corresponds to the G -value of the products whose amounts could not be determined.

Each amount of these products comes to a maximum at a certain dose as shown in Figure 5. This maximum indicates that the primary degradation products are secondarily degraded. The catechol and hydroquinone show their maxima at the phenol degradation of 60–70%, whereas p -benzoquinone shows its maximum at the phenol consumption of 40%.

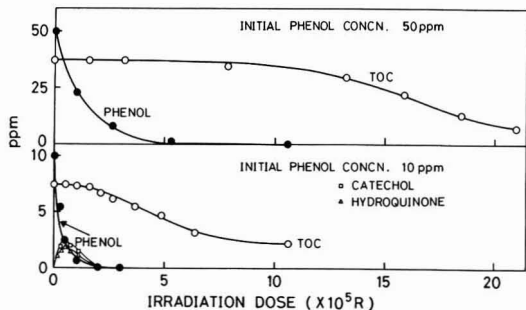


Figure 4. Variation of TOC with irradiation dose

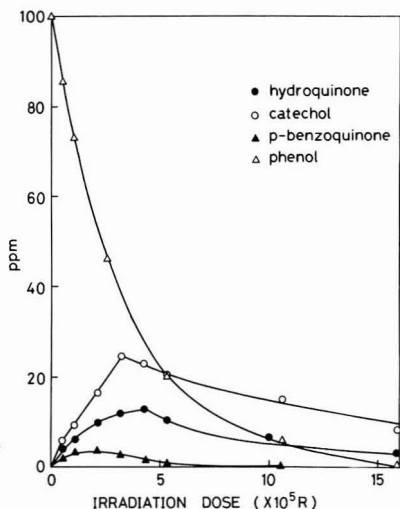


Figure 5. Relationship between yield of products and irradiation dose
Initial phenol concentration: 100 ppm

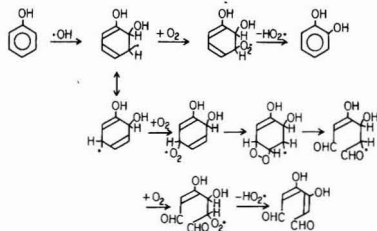


Figure 6. Formation of ring-cleavage product from phenol in aerated aqueous solution

Mechanism of Degradation. From the qualitative results of products, the mechanisms for the gamma irradiation-induced degradation of the aqueous phenol solution in the presence of oxygen are classified into three processes: (I) hydroxylation of benzene ring, (II) dimerization, (III) ring-cleavage reaction.

In radiolysis of oxygenated aqueous phenol solution, the formation of dihydroxybenzene has previously been reported by Stein and Weiss (3). In the present study, not only dihydroxybenzene but also 1,2,4-trihydroxybenzene was identified. The formation of these compounds suggests the hydroxylation of the benzene ring. The hydroxylation mechanism can be interpreted by the formation of the dihydroxycyclohexadienyl radical, which is produced by reaction of hydroxyl radicals with phenol (4). That is to say, this radical changes to a peroxide radical in the presence of oxygen, and from this unstable intermediate, dihydroxybenzene is produced. The formation of 1,2,4-trihydroxybenzene might occur as a result of further hydroxylation of dihydroxybenzene.

The production of *o,o'*-biphenol indicates that the dimerization process occurs. However, the amount of this product was very little in comparison with other products. Accordingly, the process of dimerization would not be significant compared with the other two processes in the degradation mechanism of oxygenated aqueous phenol solution.

From the formation of dihydroxymuconialdehyde and maleic acid, the ring-opening reaction occurs. From the fact that dihydroxymuconialdehyde is formed along with dihydroxybenzene at the low dose stage, the ring-cleavage mechanism of aqueous phenol in the presence of oxygen is proposed as shown in Figure 6. This mechanism requires dihydroxymuconialdehyde to be formed along with dihydroxybenzene in the system where hydroxyl radicals react with phenol in the presence of oxygen. The pulse radiolysis studies (4) of the phenol-water system have revealed that the initial product formed by the reaction of the hydroxyl radical with phenol is a dihydroxycyclohexadienyl radical. From this intermediate not only hydroxylated products but also the ring-cleavage product would be produced as shown in Figure 6. Similar

consideration has been made by Srinivasan (9) in explaining the action of ionizing radiation on oxygenated aqueous benzene solution.

On the other hand, the formation of maleic acid suggests that the process of conversion into a lower molecular compound occurs. Maleic acid is due to further degradation of a ring-cleavage product such as dihydroxymuconialdehyde. The low molecular products other than maleic acid could not be found in this study. Carbon dioxide was observed as a final product.

Conclusions

Both the phenol consumption and the formation of some products in the gamma irradiation-induced degradation of oxygenated aqueous phenol solution were followed by the use of a high-speed liquid chromatograph. As degradation products, hydroquinone, catechol, *p*-benzoquinone, 1,2,4-trihydroxybenzene, *o,o'*-biphenol, dihydroxymuconialdehyde, maleic acid, and carbon dioxide were isolated and identified.

The degradation of phenol was confirmed to be first order. The secondary degradation occurs near the stage of 60–70% phenol consumption, whereas the phenol conversion into carbon dioxide occurs at the stage when the primary degradation products are almost destroyed. The dose required for complete conversion into carbon dioxide is over five times that demanded for complete phenol consumption.

Hydroxyl radicals that are provided by irradiation and dissolved oxygen mainly participate in the phenol degradation processes. The main degradation processes are classified into three reactions: hydroxylation of the benzene ring, dimerization, and the ring-cleavage reaction. The mechanisms of hydroxylation and ring-cleavage reaction are deduced from the viewpoint of the formation of the dihydroxycyclohexadienyl radical by the reaction of the hydroxyl radical with phenol.

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Received for review August 15, 1977. Accepted March 28, 1978.

Continuous Method for Sampling Stack Gases for Total Carbon

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There is currently no generally applied method for testing industrial sources for organic emissions. The lack of a universal method is due in part to the scope of the analytic problem—any universal method must be capable of collecting and/or analyzing every organic compound which may be present in any source. Since any analytic technique will be based on a specific physicochemical property of the subject

compounds and since the "organic" class of compounds exhibits a wide range in such properties, a technique equally sensitive to all organics is difficult to find. Methods have thus been developed for specific rather than universal analytic applications. There is also a troublesome difference in the operating characteristics of the various processes that produce organic emissions. An integrated test method that works well

■ A continuous real-time method for sampling and analyzing stack gases for total oxidizable carbon (organic carbon as C₁ plus carbon monoxide) is described. The method, based on oxidation of the sample followed by CO₂ analysis, has been developed by the Bay Area Air Pollution Control District (BAAPCD) and is its preferred sampling method for total

carbon. Data taken under a wide range of lab and field conditions attest that its accuracy is superior to that of flame ionization detection, the best-known continuous sampling method. Continuous sampling methods have been found by the District to be generally superior to integrated sampling methods in reliability, labor requirements, and versatility.

at a smoothly operating power plant can be inadequate for a paint spray booth that starts up and shuts down unpredictably during the course of a test.

Several criteria are offered here for comparing the utility of various organics testing methods. An ideal method would:

- be sensitive to all organic compounds with a response proportional to carbon number
- yield both the total carbon concentration and a qualitative analysis by compound or class without prior knowledge of the composition of the stack gas
- be capable of including carbon monoxide in the total carbon analysis, when appropriate
- not be sensitive to methane, which is generally exempt from regulatory control
- require a minimum of time and labor in the field
- require a minimum of laboratory time
- incorporate continuous sampling and data production.

The last point is quite important in the view of BAAPCD personnel (1). Many industrial processes operate or emit organics erratically (paint or fiberglass spray booths, litho ovens, intermittent incinerators, etc.). Even if test personnel are aware of the frequent interruptions, obtaining a representative sample of the emissions during source operation is difficult with any integrated sampling method. If the test personnel are unaware of the process changes, completely irrelevant data could be generated by integrated sampling. Additionally, apparatus or technique problems such as leaks or poor probe location might affect test results but yet not be noticed with integrated methods until the laboratory analysis has been done.

Such pitfalls may be eliminated with continuous sampling. Peculiarities in the data output are immediately obvious, identification and correction of problems can be undertaken at once, and, if necessary, a portion of the recorded data can be ignored as unrepresentative. Continuous sampling also permits rapid accumulation of data on the effects of process changes (either experimentally controlled or random) on emissions, and it permits rapid checking for radial stratification in stacks.

Survey of Methods

A brief survey of methods used or proposed for organics emissions sampling, with comments on their limitations vis-a-vis the above criteria, follows.

Continuous Direct Analysis. FID. Flame ionization detection is a widely used tool in air monitoring with considerable utility in emissions sampling. However, the per carbon response of the FID varies significantly from compound to compound (2). Thus, without a separate qualitative analysis, the relation between the instrument output and the real total carbon concentration is always in doubt. Nevertheless, the FID is the most useful accepted method for continuous sampling, and the BAAPCD method has been evaluated against it.

NDIR. Nondispersive infrared analysis as applied to organics sampling is sensitive to functional groups. The sensitivity varies somewhat and thus, like the FID, the NDIR

cannot be absolutely calibrated for source-testing purposes. Also, interferences from water and carbon dioxide exist (2).

Semicontinuous Analysis. Chromatography/Oxidation/Reduction. At least one commercial instrument manufacturer has a prototype instrument package designed to perform total organic carbon analyses on a semicontinuous basis. An aliquot of sample is passed into a gas chromatograph column from which the CO, CO₂, water, and methane fractions elute quickly. Carrier gas (air) flow is then reversed to back-flush the organic gases through a catalytic oxidizer. The effluent is mixed with hydrogen and passed over a nickel catalyst to reduce the CO₂ (from oxidized organics) to methane which is then measured with a FID.

Little field data are available for this method (3). There is a high capital cost for the equipment, which may be difficult to justify for a method that only marginally meets the criterion of continuous analysis. (Cycle time per sample aliquot is over 10 min.)

Integrated Sampling. SCAQMD Method. The South Coast Air Quality Maintenance District has used a method called Total Combustion Analysis (4) in which an integrated sample is collected by drawing stack gases through a cold trap using an evacuated tank as a motive force. The tank contents (noncondensables) are later analyzed in a manner similar to that described above for the semicontinuous analyzer. The cold trap is heated to vaporize the condensed organic gases that are carried by a carrier gas through a catalytic oxidizer and an NDIR for CO₂ analysis and then into a collection vessel that may be sampled by GC for CO₂.

The SCAQMD has used this method successfully for several years. However, it has the disadvantages of being an integrated method and of yielding data only long after the sampling has been completed. Also, only one analysis per sample is possible, and a complex laboratory setup and procedure are required. Unless a large number of samples are to be taken on a continuing basis, the method may not be economical in many applications.

Absorptive Sampling. Absorptive methods have included the use of activated carbon beds for collection of organics and a method previously used by the BAAPCD in which three separate sampling trains are operated simultaneously. In one train, stack gas is pulled through beds of silica gel that are later stripped of absorbed organics with carbon disulfide and dimethylsulfoxide. In a second train, stack gas is pulled through impingers of 0.1 M NaOH to trap organic acids and phenols. In the third train, impingers of 3% sodium bisulfite solution trap carbonyls. All the dissolved organics are analyzed by chromatography. An evacuated tank sample is also taken for light hydrocarbons (C₁ to C₅) analysis by GC.

Difficulties with these absorptive methods (besides the inherent disadvantages of integrated methods) include poor absorption or desorption of some compounds, considerable field labor requirements, and extensive laboratory work.

BAAPCD Combustion Method. The BAAPCD's extensive favorable experience with continuous direct sampling (1) for other types of compounds (SO₂, NO_x, CO, O₂) and dissatisfaction with integrated organics methods led to development of a continuous method for total oxidizable carbon (TOC)

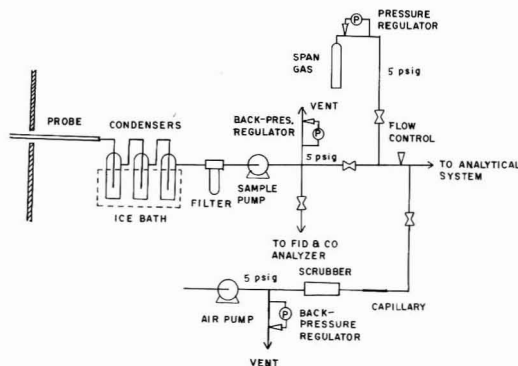


Figure 1. Schematic of sampling conditioning/zero air/span gas system

sampling to be used whenever a qualitative analysis of organic emissions is not necessary. The BAAPCD method compares favorably with the criteria presented earlier except that it includes methane in the total carbon analysis and cannot yield a qualitative analysis.

A continuous sample of stack gas, much larger than is needed for analysis, is dried to a 45 °F dewpoint and filtered of particulate material. A small portion is directed through a combustion tube capable of oxidizing all organic gases (including methane) to CO₂. This stream and a second stream of "uncombusted" sample are alternately passed through a nondispersive infrared (NDIR) analyzer sensitive to CO₂. The difference in the CO₂ concentrations of the two streams indicates the total oxidizable carbon (TOC) content of the stack gas. If necessary, a simultaneous measurement of the CO content of the gas with another NDIR allows the determination of the organic portion of the TOC by subtraction. (In some stack gases, notably incinerator outlets, the CO concentration may be much larger than the organic carbon concentration. In such cases, the organic portion of the TOC cannot be reliably calculated.)

The results of the method include methane, which must be separately measured if the nonmethane TOC concentration is desired. Methane analysis may be done in the laboratory by gas chromatography on an integrated tank sample or done in the field by FID on a sample stream that passes through activated carbon to remove all nonmethane organics.

When the CO₂ in the (untreated) stack gas exceeds 80% of the total of CO₂ plus TOC, the method is altered by preceding the combustion tube with a bed of soda/lime to scrub all the CO₂. Continuous analysis of the combustion tube effluent for CO₂ then yields the TOC.

Apparatus. The sample conditioning, zero air, and span gas system used in the BAAPCD sampling procedure is shown in Figure 1. The condensers are Greensburg-Smith impingers minus the impaction plate and lower half of the inlet stem. The filter is a tubular fibrous filter capable of 99.9+ retention

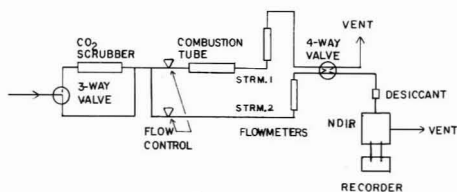


Figure 2. Schematic of analytic system

of 0.6 μ particles. The pumps are Teflon-lined diaphragm type. The span gas is carbon dioxide in nitrogen. The gas scrubber on the air line is a silica gel and activated carbon bed for removing organics followed by soda lime for removing CO₂. The capillary is used as a critical orifice to provide a constant air flow in case the sample gas requires dilution to provide sufficient oxygen for oxidation.

The analytic system is shown in Figure 2. The combustion tube is a 1/4-in. diameter quartz tube with a 16-mil platinum coil 36 in. long (uncoiled) operated at 21 V dc. For stack gases in which the CO₂ is less than 80% of the sum of CO₂ plus TOC, the scrubber is bypassed and equal flows are passed through streams 1 and 2. Switching the four-way valve alternately passes stream 1 or 2 through the NDIR. For higher CO₂ concentrations the sample passes through the soda-lime and then through stream 1 to the NDIR. The former method is then the "subtractive" technique, and the latter the "scrubbing" technique.

Besides the sample portion that is sent to the TOC analytic system, portions of the conditioned sample may be directed to an NDIR for CO analysis and to an evacuated tank or FID for a methane analysis.

The entire apparatus except the condensers is contained in a van. The condensers are placed immediately behind the probe at the sampling point, and 1/4-in. Teflon tubing is extended from the condensers to the van.

Experimental Procedures and Results

CO₂ Scrubbing Media. Use of the "scrubbing" technique requires a medium that will scrub the CO₂ from the sample gas while passing all or nearly all of the organic compounds. Generally, the basic media that will absorb CO₂ also strongly absorb alcohols and, to some extent, ketones. A considerable number of liquid, solid, and mixed phase basic media, shown in Table I, were tested for capacity to quantitatively absorb 3% CO₂ in air vs. capacity to remove 400 ppm of ethanol or methyl ethyl ketone. Of these candidate media, commercially

Table I. CO₂ Scrubbing Media

soda-lime ^a 12-mesh
soda-lime (50%), Ca(OH) ₂ (50%)
Na ₂ CO ₃ (50%), Ca(OH) ₂ (50%)
(NH ₄) ₂ CO ₃
(NH ₄) ₂ CO ₃ (50%), Ca(OH) ₂ (50%)
NH ₄ OH (1%), Ca(OH) ₂ (99%)
1% TEA on molecular sieve #
20% TEA on molecular sieve #
TEA (10%), CaO (90%)
TEA (10%), Ca(OH) ₂ (90%)
TEA (10%), Ca(OH) ₂ (85%), H ₂ O (5%)
Ca(OH) ₂ (5%), molec. sieve (95%)
Ca(OH) ₂ (10%), TEA (10%), NH ₄ OH (1%) on firebrick
Ca(OH) ₂ (10%), (NH ₄) ₂ CO ₃ (20%) on firebrick
CaO (50%), (NH ₄) ₂ CO ₃ (50%), H ₂ O (0.5%)
CaO (45%), (NH ₄) ₂ CO ₃ (45%), TEA (10%)
Ca(OH) ₂ (10%), H ₂ O (1%) on firebrick
Ca(OH) ₂ (50%), NH ₄ CO ₃ (50%), NH ₄ OH (1%)
Ca(OH) ₂ (89%), TEA (10%), NH ₄ OH (1%)
Ca(OH) ₂ (98%), TEA (1%), glycerine (1%)
Ca(OH) ₂ (89%), TEA (10%), H ₂ O (1%)
Ca(OH) ₂ (95%), glycerine (5%)
Ca(OH) ₂ (70%), glycerine (20%), H ₂ O (10%)

^a Both room temperature and heated soda-lime were tried.

available 12-mesh soda lime (mixture of NaOH and CaO) performed the best.

In Table II the concentrations of various test gases as measured by the scrubbing technique using soda lime are compared with the concentrations measured by the subtractive technique. There is also indicated the residence time in the soda lime bed (20 g) required to achieve 98% of the final concentration.

These experimental data suggest that with the exception of alcohols (for which no nonabsorbing basic media are known) a group of organic compounds commonly present in stack gases is less than 10% absorbed in soda-lime. The exact figure will, of course, vary according to the composition of the gas and the ratio of sample flow rate to weight of soda lime.

Organics Analysis. The test gases in Table III were analyzed by gas chromatography, FID (Beckman Model 400), and the BAAPCD subtractive technique. The FID was calibrated with a propane standard. For the nonoxygenated compounds, there was little deviation from the GC analyses by either the FID or BAAPCD method. Such deviation as existed may be attributable to experimental error. As expected, the BAAPCD method is much more efficient at detecting the oxygen-bearing compounds than the FID, which does not detect oxygen-bonded carbon.

These data suggest that the BAAPCD combustion method is an accurate analytical procedure for measuring total organic carbon under laboratory conditions and is superior to the FID if oxygenated organics are present. The question of the method's viability under field conditions is discussed in the next section.

Field Tests

Thirty-eight sets of FID and combustion method data obtained during source tests at 13 different locations were analyzed to compare the performances of the FID and the two combustion techniques under field conditions. Each data set (FID/combustor) was taken simultaneously, but there was no effort to choose sources or modify source testing procedures so as to facilitate comparison of the methods, i.e., the data offer a real "field" comparison. From the 38 sets available, data were selected (by criteria explained below) to make two general and distinct types of comparison:

- the ability of the FID vs. the abilities of the two combustion techniques (scrubbing and subtractive) to detect organic carbon; the point of comparison is between the ef-

Table III. Analysis of Test Gas by Three Methods

compound	GC	FID	BAAPCD	FID	BAAPCD	BAAPCD
				GC	GC	FID
aliphatics						
methane	...	130	128	0.98
propane	411	418	411	1.02	1.00	0.98
n-hexane	497	597	597	1.00	1.00	1.00
n-octane	402	398	...	0.99
n-octane	...	140	152	1.09
alkenes						
ethylene	420	423	406	1.01	0.97	0.96
i-butylene	411	418	392	1.02	0.95	0.94
1,3-butadiene	421	428	454	1.02	1.08	1.06
aromatics						
benzene	429	433	421	1.01	0.98	0.97
xylene	370	348	359	0.94	0.97	1.03
isopropylbenzene	384	380	373	0.99	0.97	0.98
average (all above)						1.00
oxygenates						
ethanol	386	270	396	0.70	1.03	1.47
butanol	384	244	311	0.64	0.81	1.27
MEK	(>385)	289	416	(<0.75)	(<1.08)	1.44
acetone	(>255)	178	301	(<0.70)	(<1.18)	1.69
Average (oxygenates)						1.47

ficiencies of the methods in analyzing field samples for organic carbon rather than between their performances as source test tools.

- the actual field performance of the FID/CO instrument combination compared with the performance of each combustion technique, under the circumstances in which it would normally be used, in generating the data required by the BAAPCD regulations.

Efficiency of Organic Carbon Detection. To determine the analytic capabilities of the combustion method and the FID, three questions were investigated: relative efficiencies of scrubbing technique and FID in detecting organic carbon; relative efficiencies of subtractive technique and FID in detecting organic carbon; and the relative loss of organic carbon in the scrubbing medium (soda-lime).

It was desired to use, as much as possible, only data that reflected the real analytic abilities of the techniques with minimum confounding of errors due to high CO or CO₂ background levels, erratic emissions, or other field problems. Accordingly, data were included only from cases in which the organic carbon represented at least 25% of the total combustor effluent. For cases whose results were widely outside the norm, the raw field data were reviewed, and some of the cases were deleted because of questionable testing procedure. Data from erratically operating sources were not used.

The data and statistics are shown in Table IV. Note that the hypothesis may be accepted with 99% confidence (Student *t*) that the subtractive technique yields higher average organic carbon results than the FID. In all cases, the subtractive technique yielded at least 90% of the FID value. If it is assumed that the FID analyses were low, the data affirm the laboratory test data which showed that the combustion method is overall more efficient than the FID at detecting organic carbon.

The average carbon loss in the scrubbing medium was 18(±10)% (90% confidence limits), or if two data points are rejected, 11(±5)%. This is a somewhat larger loss than in the laboratory tests (except for alcohols). However, the hypothesis

Table II. Holdup of Test Gases in Soda-Lime

compound	concentration		% loss	time ^a
	subtr	scrub		
methane	212	210	1	1
propane	411	397	3	1
n-octane	332	296	11	1 1/2
ethylene	406	396	2	2
i-butylene	392	359	8	1
1,3-butadiene	454	424	7	1
benzene	421	405	4	1
xylene	359	343	4	2
isopropylbenzene	373	345	8	
ethanol	396	0	100	(after 4 min)
butanol	311	0	100	(after 5 min)
acetone	280	269	4	5
MEK	416	351	16	8
average (excluding alcohols)			6	

^a Elution time through 20 g of soda lime relative to elution time for methane.

Table IV. Comparison of Efficiencies of Organic Carbon Detection

source and process	ratios of organic carbon analyses		
	scrub FID	subtr FID	subtr-scrub subtr
fiberglass sprayer		0.97	
luminescent paint sprayer			0.08
can coating sprayer		0.99	
can coating sprayer	0.97		
can coating sprayer	0.89	1.04	0.14
can coating oven			0.09
can coating oven			0.01
metal coating oven			0.03
metal coating oven		1.04	
magnetic tape coater		1.18	
can coating sprayer & oven	0.97		
can coating sprayer & oven	0.97	1.15	0.16
can coating afterburner	1.15		
can coating sprayer & oven	0.95	1.22	0.22
can coating afterburner	1.71		
can coating sprayer & oven	0.90	1.87	0.52 ^a
litho oven	1.15		
automobile painting			
av of 16 sources <125 ppm	1.52		
av of 4 sources >250 ppm	0.59		
automobile painting		1.49	0.62 ^a
automobile painting		0.98	0.23
glass container mfr. afterburner	1.09		
glass container mfr. afterburner (inlet)	1.13		
glass container mfr. afterburner (inlet)	2.42		
fiberglass sprayer		0.95	
fiberglass sprayer		1.35	
fiberglass sprayer		1.01	
fiberglass sprayer		0.97	
can coating sprayer & oven		1.14	
can coating sprayer & oven		1.14	
metal coating afterburner	0.89		
metal coating afterburner	0.82		
metal coating oven	1.86	1.99	0.06
can coating sprayer & oven		1.02	
can coating afterburner	2.20		
litho oven			0.05
no. of data	18	18	12
mean	1.23	1.19	0.18 ±
SD	0.50	0.30	0.10 ^b
no. of data ≥ 0.90	14	18	
hypothesis	scrubbing method yields higher than FID?	subtractive method yields higher than FID?	
conclusion	yes	yes	
confidence	97%	99%	

^a If these data disregarded, mean = 0.11 ± 0.05. ^b 90% Confidence limit.

Table V. Comparison of Field Performances of FID/CO Combination with Combustion Methods

source and process	ratios of total carbon analyses	
	scrub FID + CO	subtr FID + CO
fiberglass sprayer		0.97
can coating afterburner	1.54	
can coating sprayer		1.19
can coating sprayer		1.24
metal coating oven		1.04
metal coating afterburner	1.37	
magnetic tape coater		1.10
can coating sprayer & oven	0.98	
can coating sprayer & oven	1.13	0.97
can coating afterburner	1.50	1.22
can coating afterburner	1.50	
can coating sprayer & oven		1.79
litho oven	1.16	
automobile painting		
av of 16 sources <125 ppm	1.14	
av of 4 sources >250 ppm	0.54	
automobile painting		1.38
glass container mfr. afterburner		1.90
glass container mfr. afterburner (inlet)	1.07	
glass container mfr. afterburner (inlet)	1.30	
fiberglass sprayer		0.95
fiberglass sprayer		1.35
fiberglass sprayer		1.01
fiberglass sprayer		0.97
can coating sprayer & oven		1.19
can coating sprayer & oven		1.22
metal coating afterburner	0.90	
metal coating sprayer & oven		2.20
metal coating afterburner	0.86	
metal coating sprayer & oven		1.94
litho oven	1.03	
can coating sprayer & oven		1.02
can coating afterburner	1.44	
no. data	14	19
mean	1.14	1.30
SD	0.28	0.38
no. data ≥ 0.90	12	19
hypothesis	scrubbing yields higher TOC than FID/CO?	Subtractive yields higher TOC than FID/CO?
conclusion	yes	yes
confidence	96%	99.5% +
*CO ₂ background / total carbon <0.80		**CO ₂ background / total carbon <0.80

afterburners are likely to have lower molecular weight organics than the data sources and since afterburner emissions are not likely to contain alcohols, the loss of carbon in the scrubbing medium may be less in actual field use than the data in Table IV suggest.

Overall Field Performance. In actual use of the combustion method, if background CO₂ exceeds 80% of the total (organic plus inorganic) carbon in a sample, the sample is

scrubbed of CO₂ before passing through the combustor. For data from cases that met this criterion, the ratio was taken of scrubbing technique results (including oxidized CO) to the sum of FID analysis plus CO measurement (by IR instrument). Similarly, for all cases in which the CO₂ background was less than 80% of the total carbon, the ratio was taken of subtractive technique results to the sum of FID analysis plus CO. The point of comparison is between the actual performances of the techniques as source test tools to generate TOC data. All available data were included except a few in which sampling time was insufficient.

The data and statistics in Table V are consistent with all previous data. These hypotheses may be accepted, with 96% and 99% confidence, respectively: that under general field conditions the scrubbing technique and the subtractive technique each yield higher average TOC values than the FID/CO instrument combination. In 12 of 14 cases, the scrubbing technique yielded at least 90% of the FID/CO value; the subtractive technique did so in all cases.

An interesting field test of the combustion method was conducted at the Ford Motor Co.'s Milpitas assembly plant. Plant personnel used a FID to monitor emissions from a duct that received exhaust gases from several ovens and paint booths. The FID was calibrated with a standard prepared from the solvents being applied in the various paint booths. The BAAPCD simultaneously monitored the same duct using the combustion subtractive technique and with a FID calibrated with a propane standard. Results are shown in Table VI.

If the FID calibrated with the solvent mix is accepted as a reliable analytical method for this particular source, then the test indicated that the combustion method yielded an accurate analysis of total organic carbon. The slightly lower values for the combustion method relative to the solvent-calibrated FID may be attributed to losses in 400 ft of sampling line between the FID and the BAAPCD's instruments.

Summary

The BAAPCD combustion method for total oxidizable carbon (total organic carbon plus carbon monoxide) is a useful source testing procedure well-suited to sampling many sources

Table VI. Field Comparison to FID's with Different Calibration Gases

	subtractive	FID (calibrated with solvent mix)	FID (calibrated with propane)
test A	145 ppm (as C ₃)	165	94
test B	210	228	143

of organic emissions. The method reduces the laboratory analyses and much of the labor in the field inherent in the use of integrated sampling techniques.

Caution should be used in applying the method to analyzing high-molecular-weight organics (>C₉) if CO₂ scrubbing is necessary and to analyzing organic carbon against a high CO background.

The accuracy of the method has been demonstrated in the laboratory against the gas chromatograph and in the field against a FID calibrated with a standard similar in composition to the sample gas. When compared with the propane-calibrated FID in extensive field testing, the method has yielded higher results for TOC, consistent with its greater accuracy in detecting oxygen bearing organics. If the sample must be scrubbed of CO₂ before analysis, some organic material is lost (in favor of the source), but the losses are generally less than the negative errors resulting from use of the FID.

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Received for review February 1, 1978. Accepted April 13, 1978.

Removal of Ammonium Sulfide from Wastewater by Liquid Membrane Process

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■ A novel separation process, which is a combination of liquid membrane permeation and conventional steam stripping, is devised to effectively remove ammonium sulfide from wastewater. In principle, this process is applicable to removal of any salt of a weak acid and a weak base from its aqueous solution. The liquid membrane emulsion can be tailor-made to remove either the weak acid or the weak base. At the same time, the other species is stripped from the solution by steam or an inert gas. Also, it is possible to devise a process based on a different combination of two separation techniques that can effectively remove a salt of a weak acid and a weak base that is difficult to remove by the individual separation techniques alone.

In many industrial applications the ammonia is present in conjunction with hydrogen sulfide, and the resultant ammonium sulfide solution, called "sour water", creates some peculiar problems for the conventional steam stripping process. The possible use of the liquid membrane technique was therefore studied for handling sour water and to achieve both water cleanup and ammonia recovery in a novel and economical way (1).

The industrial sour water is usually a purge stream resulting from the treatment of a number of refinery gas streams. Water is used to scrub both ammonia and some H₂S out of feeds going to regenerative gas cleanup units that do not tolerate ammonia. The high H₂S level of these water streams is the direct result of the presence of the ammonia which, by its neutralizing action, strongly enhances the solubility of H₂S in water. There are, in addition, relatively small amounts of other anions present, e.g., phenol, cyanide, aliphatic and

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Table I. Typical Ammonia-Containing Waste Streams

source	quantity (gpm)	NH ₃ (ppm)	acid
refinery			
sour water	1000	2 000	H ₂ S, phenol, HCN
recycle water	600	10 000	...
steel mills			
coke oven	500	2-6 000	HCl, phenol, HCN
municipal	1000's	20-50	misc

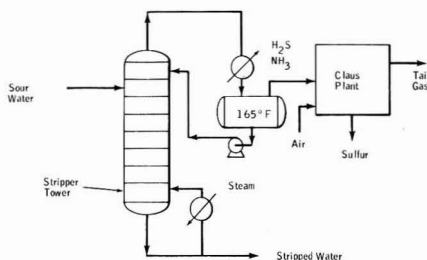


Figure 1. Conventional steam stripper

naphthenic acids, etc. Some typical ammonia and acid-containing streams are listed in Table I.

Conventional Techniques and Their Disadvantages

The conventional way to handle ammonia removal is either by exhaustive steam stripping or by air blowing after liming the effluent to make it alkaline. In refinery practice, shown in Figure 1, exhaustive steam stripping is used for ammonium sulfide removal. The ammonia is taken overhead, together with the H₂S, and both are then fed to the Claus plant for elemental sulfur recovery. Exhaustive steam stripping is needed since neither NH₃ nor H₂S is particularly volatile when they are present in neutralized form as the salt in dilute aqueous solution.

With this process scheme, there are many problems that provide incentives for developing a better process. Some of these problems are briefly discussed below.

First, the ammonia taken overhead to the Claus plant with the H₂S being burned, resulting not only in a loss of valuable by-product, but also in a large increase in air, heat removal, and tail-gas cleanup requirements. Also the stripper distillate drum, to prevent solids deposition and excessive recycle of ammonium sulfide salt with the overhead reflux, has to be operated at elevated temperature, such as 160-190 °F. This means that very wet vapor is sent to the Claus plant, putting an additional burden on that facility and on the Claus equilibrium. In addition, the high ammonium sulfide content of the tower reflux increases the stripping load on the tower and necessitates alloy construction around the tower top and overhead equipment. Finally, as mentioned earlier, the very fact that NH₃ and H₂S are present as a partially neutralized salt makes them more difficult to strip.

This can be made clear by Figure 2 which shows the percent undissociated H₂S and NH₃ in dilute aqueous solution as a function of pH. Since H₂S is a weak acid and NH₃ a weak base, their degrees of dissociation are highly pH-dependent. The dissociation constant of ammonia is about 2 × 10⁻⁵, and the first dissociation constant of H₂S is about 10⁻⁷. With this information one can calculate the pH of the system as a function of the NH₃/H₂S ratio, provided they are the only acids and bases present. This relationship is plotted as the dotted line in Figure 2. At the resultant pH, the percent undissociated

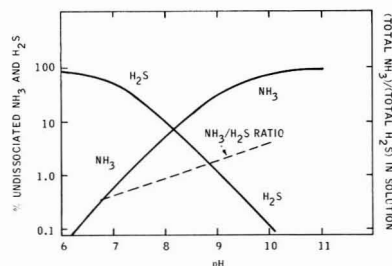


Figure 2. Effect of pH on NH₃ and H₂S dissociation

H₂S and NH₃ can easily be read from their respective curves.

Since only the undissociated compounds, not their ions, exert a vapor pressure over the solution, the plot of percent unionized NH₃ and H₂S vs. pH, therefore, can be transformed to a plot of vapor pressure, or partial pressure vs. pH, which will show the ease of stripping as a function of pH. The exact stripping rates, however, cannot be predicted from these concentration-vapor pressure equilibrium curves.

To convert concentration to partial pressure, Henry's law constant is used. For example, the partial pressure of H₂S over a solution is calculated below:

$$\begin{aligned} \text{partial pressure of H}_2\text{S} &= H_{\text{H}_2\text{S}} \times \text{concentration of} \\ &\quad \text{undissociated H}_2\text{S} \\ &= H_{\text{H}_2\text{S}} \times [\text{H}_2\text{S}_{\text{total}}] \times \text{fraction H}_2\text{S undissociated} \end{aligned}$$

where H_{H₂S} is the Henry's law constant, and [H₂S_{total}] is the total H₂S concentration in the solution. The same type of equation holds for NH₃. Therefore, at a given concentration level of H₂S and NH₃, the two curves in Figure 2 indicate the trend in value of the H₂S and NH₃ partial pressure above the solution as pH changes. Henry's law is assumed to be valid here because the sour water usually contains low concentrations of NH₃ and H₂S, i.e., less than 0.2%.

At the stoichiometric equivalence point of 2 mol of NH₃ to 1 mol of H₂S, i.e., at a pH of about 8, H₂S is only 1% undissociated and ammonia about 25%. Neither is easily stripped out of solution, H₂S being mostly in ionic form and NH₃ being highly water soluble. This is borne out by practical experience with sour water strippers, where a high steam-to-sour water ratio is required to get to the specification level of sulfur in the water product taken off the bottom of the tower.

As H₂S is stripped, the NH₃/H₂S ratio becomes greater, increasing the pH and decreasing the percentage of undissociated H₂S. As a result, the partial pressure of H₂S will drop off sharply, because both the concentration of total H₂S and the fraction undissociated are decreasing. At the same time, ammonia becomes easier to strip since its percentage undissociated is enhanced by the increasing pH. Accordingly, a complex check-and-balance interplay among pH, ammonia being stripped, and H₂S being stripped will be set up throughout a sour water stripping tower, resulting in difficulties to achieve low concentrations of both constituents in the treated water leaving the bottom of the tower.

Proposed Process Scheme Using "Liquid Membranes"

For the above reason, the liquid membrane technology (2-9) was investigated for sour water cleanup. The proposed process scheme (1) is to extract the ammonia out of the aqueous solution by a liquid membrane system and, simultaneously, to strip off H₂S with air or steam for producing an ammonium sulfide-free water effluent. Since a proper description of the proposed technique is quite wordy—simultaneous liquid

membrane extraction and air or steam stripping—a shortened name, “extripping”, is used in referring to the process.

Figure 3 represents a magnified schematic illustration of a liquid membrane system, specifically, a drop of water-in-oil emulsion, which is in contact with sour water. When the emulsion is agitated with the wastewater, it breaks up into emulsion drops (as shown in the figure), which stay essentially intact as long as reasonable agitation is maintained. In this dispersed water-in-oil emulsion system, the oil film is the liquid membrane through which permeation can occur from the wastewater into the small aqueous droplets within the emulsion drops or vice versa. Two conditions have to be met for this permeation to take place: whatever diffuses must have a reasonable solubility in the oil “liquid membrane”; and there must be a driving force of some kind in the direction of permeation.

While the oil membrane surrounding the aqueous droplets has a low solubility, and therefore low permeability, for ions, it is a good solvent for undissociated H_2S and NH_3 . Both will readily permeate through the oil into the aqueous droplets in the emulsion as long as there is a concentration gradient of undissociated species.

To confer the desired selectivity to this process, a strong, highly dissociated acid, e.g., sulfuric acid, is used as the internal phase of the emulsion. This acid, because it is highly ionized, is fully confined inside the emulsion droplets because the oil membranes are not permeable to hydrogen and sulfate ions. This was confirmed by the analysis of the wastewater for acid leakage while it was being treated with the acid-containing emulsion. Leakage was found to be extremely small—less than 5 ppm in the first 10 min of all the experiments reported here. The acid inside the emulsion droplets will effectively neutralize and ionize every ammonia molecule permeating across. This maintains an essentially zero concentration of undissociated ammonia within the droplets, allowing ammonia in the external wastewater phase to continue diffusing across the membrane into the emulsion droplets as long as the concentration of undissociated ammonia in the external phase is higher than inside the emulsion droplet.

The rate at which ammonia permeates through the membrane into the internal acid droplets of the emulsion is proportional to the concentration difference of undissociated ammonia outside and within the membrane. Since undissociated ammonia is essentially zero in the acid droplets, permeation is proportional to the fraction of undissociated ammonia in the wastewater. Consequently, Figure 2 will not only show the trend vs. pH of the ease of H_2S stripping, but also of NH_3 permeation.

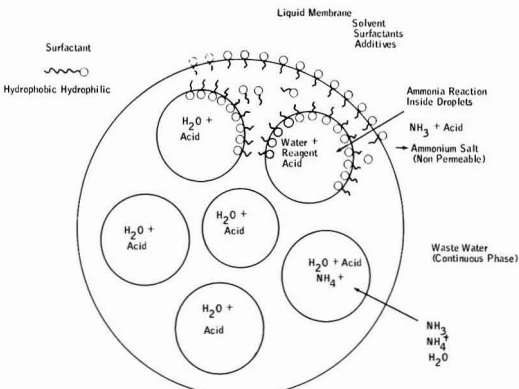


Figure 3. Schematic diagram of liquid membrane system for ammonia removal from wastewater

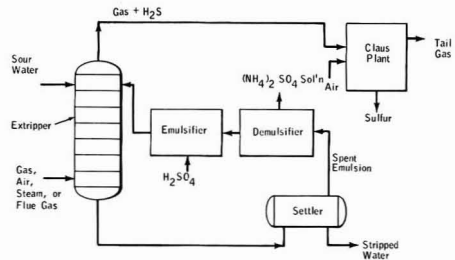


Figure 4. Extripper achieves permeation with stripping

It should be noted that there is very little driving force for the H_2S to permeate into the acidic emulsion droplets since the strong acid will not suppress the concentration of undissociated H_2S inside the droplets. This concentration, therefore, will quickly build up to the level outside. Consequently, permeation can be a very effective way of separating NH_3 from H_2S .

When NH_3 permeates out of the wastewater into the liquid membrane emulsion by the mechanism just explained, say at a pH = 8, undissociated NH_3 is about 7%; therefore, its permeation is reasonably fast. However, as ammonia leaves, the NH_3/H_2S ratio in the wastewater will drop, and so must the pH. This means that undissociated NH_3 , the species able to transfer across the membrane, will rapidly be used up. The undissociated H_2S will then increase, with a consequent enhancement in its ease of stripping. On the other hand, when H_2S is stripped out, the exact opposite will occur. At pH = 8, also about 7% of the H_2S is undissociated; therefore, the partial pressure and rate of stripping are reasonably high. As H_2S leaves the solution, though, NH_3/H_2S increases and pH goes up, suppressing undissociated H_2S and consequently making stripping increasingly difficult. But undissociated NH_3 will rise, making it more susceptible to removal by permeation.

Clearly, what this points to is simultaneous liquid membrane permeation to remove ammonia while the H_2S is being vapor stripped overhead, since either process alone is rapidly self-limiting.

The proposed process scheme is illustrated in Figure 4. The “Extripping” tower, which is operated at 80 °C, is fed at the top a mixture of sour refinery wastewater and an acidic liquid membrane emulsion, i.e., suspended drops of water-in-oil emulsion containing an aqueous solution of 20% H_2SO_4 in the fine emulsion droplets. A stripping gas, which can be air, steam, or flue gas, flows in from the bottom of the tower. The overhead gas, laden with H_2S and a small amount of ammonia, passes through a condenser that removes and refluxes all the contained ammonia, and is fed to the Claus plant for sulfur recovery. At the bottom of the tower, the cleaned wastewater is separated from the spent emulsion from which the ammonia values can be recovered. The spent emulsion is separated from the treated water in a settler. When a regenerable acid is used in the emulsion, it can be reused after the acid has released ammonia upon heating. When a nonregenerable acid such as sulfuric acid is used, the emulsion is broken to recover the ammonium sulfate solution, which may be used as fertilizer. In this case, the oil phase is reused by combining it with fresh dilute sulfuric acid to form the feed emulsion.

Experimental Materials and Procedure

The following experiments were designed to demonstrate that simultaneous gas stripping to remove H_2S and liquid membrane extraction to remove NH_3 by permeation can effectively reduce the ammonium sulfide content of a dilute aqueous solution.

Table II. Sour Water Stripping Experiments

1450 cc sour water, 185 °F, 245 rpm stirrer speed

run no. type of operation	1 stripping only			2 permeation only			3 extripping			4 extripping with encapsulated acid			5 extripping without encapsulated acid		
	NH ₄ ⁺	S ²⁻	pH	NH ₄ ⁺	S ²⁻	pH	NH ₄ ⁺	S ²⁻	pH	NH ₄ ⁺	S ²⁻	pH	NH ₄ ⁺	S ²⁻	pH
emulsion/sour water, w/w			0.25			0.25			0.243			0.240		
boil-up rate, % vaporization/h	17.4			...			20.0			15.3			17.1		
emulsion composition															
oil/aqueous, w/w			1.2			1.2			1.2			oil only		
oil type (wt % in oil phase)			solv 100 N (88%)			solv 100 N (88%)			solv 100 N (88%)			solv 100 N (88%)		
additive type (wt % in oil phase)			lubr 3702 (12%)			lubr 3702 (12%)			lubr 3702 (12%)			lubr 3702 (12%)		
NH ₃ in aq phase, wt %			5.2			5.2			5.2			no aqueous		
succinic acid in aq phase, wt %			30.0			30.0			30.0			emulsion		
NH ₃ /succ acid, mol/mol			1.2			1.2			1.2			phase		
sour water composition, wppm															
Initial	1520	2120	8.8	1760	1760	8.7	2040	1560	9.0	1720	1960	8.8	1720	2000	8.7
after 1 min	1560	672	9.2	1600	1580	8.7	1170	500	9.1	1120	276	7.8	1620	640	9.1
after 4 min	1400	420	9.4	1370	1200	8.4	530	220	8.8	420	240	8.3	1380	366	9.3
after 9 min	1180	306	9.4	1020	1072	8.3	160	74	7.6	210	106	8.0	1220	294	9.3
after 19 min	860	194	9.4	820	848	7.7	115	<20	7.6	180	<20	7.9	1040	234	9.5
after 29 min	610	126	9.5
% removal			NH ₃	H ₂ S	NH ₃	H ₂ S	NH ₃	H ₂ S	NH ₃	H ₂ S	NH ₃	H ₂ S	NH ₃	H ₂ S	NH ₃
after 1 min			0	68	9	10	43	68	35	86	6	68			
after 4 min			8	80	22	32	74	86	76	88	20	82			
after 9 min			22	86	42	39	92	95	88	95	29	85			
after 19 min			44	91	53	52	94	99	90	99	40	88			

The liquid membrane emulsion was prepared by adding an aqueous solution of 30 wt % weight sulfuric acid and 5.3 wt % of ammonia with vigorous stirring slowly to an oil phase which was composed of 12 wt % Lubrizol and 88% S100N. Lubrizol, made by the Lubrizol Co., is a styrene-maleic anhydride copolymer with 95% of the groups esterified with C₁₀-C₁₈ alcohols. It has a dual function of surfactant and stabilizer in the membrane phase. S100N, miscible with Lubrizol, is a shortened name for Solvent 100 Neutral made by Exxon. It is an isoparaffin having an average molecular weight of 386.5, a cloud point of 93 °F, a pour point of 90 °F, and a specific gravity of 0.85 at 75 °F.

In all runs discussed in this paper about 1450 g of dilute aqueous solution containing about 1500-2000 ppm by weight each of ammonia and hydrogen sulfide (the exact concentrations in each run are specified in Table II) was contacted with the emulsion at a temperature of 185 °F. The contact was carried out with a mechanical stirrer in a batch treater. A vacuum was applied during the mixing to achieve the necessary boil up, simulating steam stripping in a column. No control of pH of the water phase was needed because of the simultaneous removal of acid (H₂S) and base (NH₃).

From time to time, the mixing was stopped, and the two phases were allowed to settle. A sample of the aqueous solution of ammonium sulfide was taken for determination of the concentrations of both ammonia and hydrogen sulfide by the standard ion electrode method.

The spent emulsion was separated from the treated water in a settler and was then broken to recover the ammonium sulfate solution and the oil phase.

Results and Discussion

Some of the typical separation results of ammonia and hydrogen sulfide are summarized in Table II. For easy analysis of the separation, the data in this table are also plotted in Figures 5 and 6. In both figures three cases are shown: gas stripping only, permeation into emulsion only, and combined stripping and permeation, i.e., "extripping".

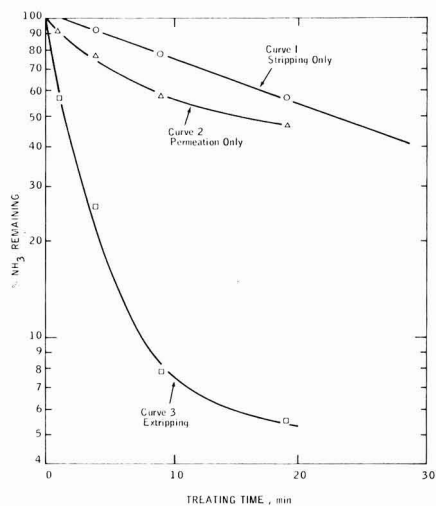


Figure 5. NH₃ removal from sour water

Figure 5 shows that when steam was passed through an (NH₄)₂S solution at pH of about 8.5-9.5 and at 85 °C, ammonia was slowly stripped out, but 35% still remained after half an hour. Ammonia simply is hard to strip. Using a similar feed but treating with an acid emulsion removed the NH₃ somewhat faster, initially, but after 20 min the removal appeared to essentially stop. However, when the two operations were carried out simultaneously, very rapid removal was achieved—only 7.5% of ammonia remained after 10 min. The slowdown after that point was due to some accidental spillage of emulsion acid into the wastewater, which neutralized the ammonia.

Figure 6 indicated a similar, yet much more pronounced

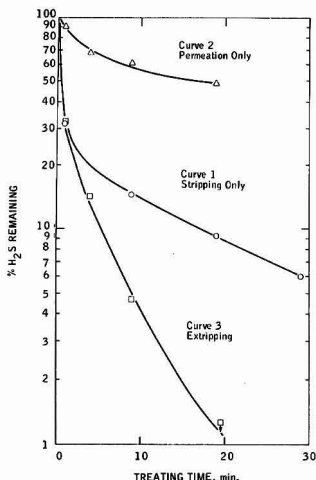


Figure 6. H₂S removal from sour water

pattern with H₂S. Permeation alone only removed about half of the H₂S in 20 min probably mostly by venting from the surface of the stirred vessel plus some H₂S solubility in the emulsion phases.

Stripping did a reasonably adequate, yet slow job, and 94% removal was achieved in 1/2 h. However, "extripping" was very rapid, with 95 + % removal in 10 min and 99 + % in 20 min.

These curves clearly demonstrate the effectiveness of "extripping" vs. stripping and extraction alone. Therefore, the proposed process is an effective way of producing an essentially ammonia-free H₂S stream and an H₂S-free ammonia product. It should be noted that in the future, long-term stability of the emulsion at the operating temperature of 80 °C and in the 30% H₂SO₄ environment should be studied. The emulsions were stable in all the experiments reported here. No significant entrainment of the emulsion and the dissolution of surfactants in the treated water phase was noticed.

This principle of treating NH₄S solution with two different separation processes simultaneously can be used with other salts of weak acids and bases such as CO₂, many organic acids, and amines. Also, of course, gas stripping and LM permeation are not the only two processes that can be combined. Other processes which can be considered are distillation, extraction, precipitation, ion exchange, and adsorption.

In evaluating laboratory data for designing the necessary equipment, the following diffusion equation is used to describe permeation into a liquid membrane emulsion.

$$\frac{dc}{d\theta} = -D \left(\frac{\Delta c}{\Delta t} \right) A \quad (1)$$

where c = concentration of permeating species, θ = time, Δt = thickness of membrane, A = area through which permeation occurs, and D = effective diffusion rate constant.

For liquid membrane systems, the effective thickness of the membrane and the area available for permeation are difficult to measure. For any given system, the membrane area is replaced by the treat ratio of emulsion to water. This is based on the assumptions that this ratio is proportional to the area through which permeation takes place and that the emulsion drop size is constant. The thickness, Δt , has been included in the permeation rate constant, D' . The new rate equation is therefore

$$\frac{dc}{d\theta} = -D' \left(\frac{V_e}{V_w} \right) \Delta c \quad (2)$$

Table III. Extripping Rate Data

(V_e/V_w) = 0.25; 182 °F

time (min)	H ₂ S (ppm)	NH ₃ (ppm)	pH	NH ₃	
				% undissoc.	D' corr.
0	1560	2040	9.0	96	
1	500	1170	9.1	97	2.9
4	220	530	8.8	94	1.5
9	74	160	7.6	51	2.8
19	<20	115	7.6	51	~1.0

where V_e , V_w = volume, or weight of emulsion and water, respectively, and D' = permeation rate constant.

Now, Δc is the concentration differential of the permeating species across the oil membrane, or, to put it in a different way, it is the difference between the concentration of unionized ammonia in the wastewater and that in the internal emulsion droplets.

Inside the emulsion, in the acidic droplets, the pH is below 1 or 2 until the acid is practically completely spent. Therefore, since the dissociation constant of NH₃, K_b , is about 2×10^{-5} , i.e.,

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 2 \times 10^{-5} \quad (3)$$

and the ionization constant of water at the temperature of operation is about 10^{-13} , one can easily calculate that the concentration of undissociated NH₃ is zero inside the emulsion for all practical purposes. On the other hand, the fraction of ammonia undissociated in the wastewater at 85 °C is about 75% at pH of 8.1 and about 60% at pH = 7.8.

Therefore, one can rewrite the NH₃ rate equation

$$\frac{dc}{d\theta} = -D' \left(\frac{V_e}{V_w} \right) (0.75)c \quad (4)$$

where c = total ammonia concentration in the wastewater.

The rate Equation 4 can be integrated over the residence time in the stripping tower to give

$$\ln \frac{c_1}{c_2} = 0.75 D' \left(\frac{V_e}{V_w} \right) \theta \quad (5)$$

By measuring the rate at which ammonia is removed by liquid membrane permeation in a batch experiment in the laboratory, one can calculate D' from Equation 5. This information can then be used to estimate the contribution liquid membrane permeation will make to the rate of ammonia removal in a steam stripping tower.

Table III shows some of the D' values based on the permeation data in Figures 5 and 6. The values vary approximately between 1 and 3. Based on tower design calculations, at D' of 2, about a 1-2-min residence time of emulsion is needed in the stripper to get adequate ammonia permeation.

It should be noted that ammonia removal actually takes place via two mechanisms. While the liquid membrane permeation takes the ammonia into the emulsion as water and emulsion descend down the tower, some vapor stripping of ammonia will occur along with the H₂S. The net effect of this vapor stripping is a transport of ammonia from regions of low concentration to regions of higher concentration in the tower where removal by permeation occurs more rapidly.

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Received for review August 20, 1976. Accepted April 14, 1978.

Qualitative Model of Heterogeneous Equilibria in a Fly Ash Pond

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■ Laboratory experiments conducted with various fly ash samples collected at the Columbia Energy Center near Portage, Wis., indicate that in ash ponds the dissolved concentrations of the major (Al, Fe, and Si) and minor (Ca, Mg, Na, and K) elements in fly ash are controlled by metastable equilibria with solid phases. Adsorption reactions have an important influence over the dissolved concentrations of the trace constituents cadmium and phosphorus. The most clearly defined isoelectric point (pH_{IEP}) of the fly ash occurs at $pH \sim 7.55$ where essentially 100% of the aluminum and iron are incorporated into solid phases on the fly ash particle. The constant negatively charged ash surface at low pH may result from isomorphic replacement of aluminum for silica in the $SiO_{2(s)}$ matrix, whereas calcium and magnesium carbonates or hydroxides probably contribute to the negative surface charge at high pH.

The enriched presence of major, minor, and trace elements in fly ash produced from coal combustion processes has been well established (1-3). Short duration solubility studies conducted by Natusch et al. (4) have shown that certain toxic trace elements may become directly available to the external environment when fly ash is leached by waters draining into streams or groundwaters. Nevertheless, fly ash has been proposed for use in lake restoration projects (5, 6) and in the neutralization of acidic mine wastes (5, 7). Its excellent pozzolanic properties also make it a desirable material for concrete fabrication and highway construction (8-10). Appropriately, these applications have been designed to alleviate the solid waste disposal problem associated with our nation's seventh most abundant raw material—coal (11).

Recently, Bertine and Goldberg (12) emphasized the need for detailed studies of the sedimentary record in the Northern Hemisphere for those elements that are selectively volatilized as a result of fossil fuel burning. Yet, the largest quantity of trace elements involved in coal combustion remains associated with those fly ash particles that are deposited into ash ponds near power plant facilities. This study was designed to identify those heterogeneous reactions that control the chemical composition of ash pond waters.

Extensive equilibrium leaching experiments were conducted to study dissolved and solid phase interactions that occur in ash ponds. These experiments permitted us to define the metastable equilibrium conditions that influence the observed elemental distribution. Using results obtained from the laboratory experiments, a qualitative equilibrium model for this complex heterogeneous system is described.

Plant Description

The Columbia I coal-fired power plant located along the Wisconsin River near Portage, Wis., has a peak capacity of 527 MW. It began operation in May 1975 and utilizes low-sulfur pulverized coal obtained from the Colstrip field (Rosebud seam), Montana. Operating at peak capacity, this plant consumes 5 000 tons/day of coal with a typical ash content of 7-8%. High-efficiency electrostatic precipitators are employed for particulate pollution abatement. The fly ash collected by stages II-IV of the precipitators is discharged into a 0.3 km² ash pond adjacent to the plant.

Sampling

Composite samples of fly ash used in the laboratory experiments include:

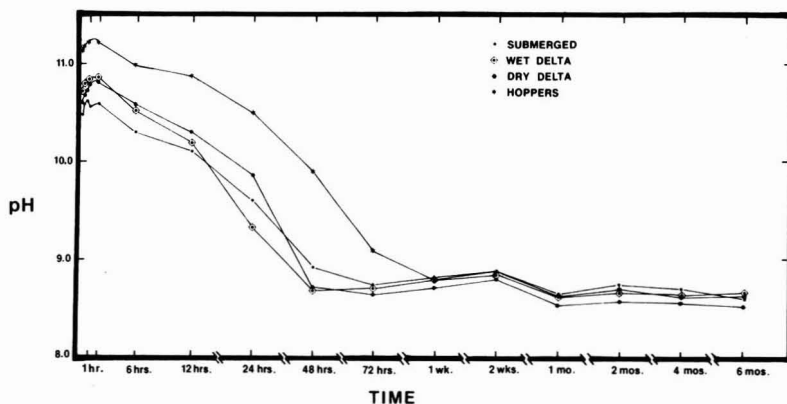


Figure 1. Change in pH with leaching time in a system open to atmosphere

1. Fly ash collected underwater off the end of the ash delta (submerged)
2. Freshly deposited fly ash on the ash delta (wet delta)
3. Fly ash deposited on the ash delta but dewatered (dry delta)
4. Fly ash from stages II and III of the electrostatic precipitator hopper bins (September 5, 1975).

Samples 1, 2, and 3 were collected from the ash delta at selected locations indicative of various stages of leaching by pond waters or rainfall. After collection, each composite sample of fly ash was air dried at room temperature (20 °C) and subsequently sieved through a U.S. Standard #325 sieve. The fly ash fraction collected from sieving consisted of particles less than 44 μm in diameter. Drying of the sieved fly ash was completed in a desiccator where the samples were stored until use.

Experimental

Duplicate equilibrium leaching experiments were conducted in large polyethylene containers. A solid-solution ratio of 1 g ash/L of doubly distilled water was utilized for each fly ash sample. These slurries were stirred for several months at a constant rate using electric stirrers equipped with polyethylene blades. At selected time intervals an aliquot was removed from each slurry and the pH measured with a low-junction potential electrode (Sargent-Welch Model S-30072-25). Each aliquot was then filtered through a prewashed 0.4- μm Nuclepore filter and the filtrate divided for analysis. Dissolved aluminum (13), dissolved reactive phosphorus (14), and dissolved reactive silica (15) were determined colorimetrically from one fraction. The remaining filtrate was acidified to 0.5% nitric acid for later analysis by atomic absorption spectroscopy (Perkin-Elmer Model 603) for Ca, Cd, Fe, K, Mg, and Na.

To facilitate electrophoretic mobility measurements, large volumes of fly ash slurries were prepared using the same four fly ash samples. The slurries were stirred for one week to obtain stability with respect to pH. At this time, 12 aliquots from each ash slurry were dispensed into 250-mL linear polyethylene bottles. The pH was adjusted from 1.0 to 12.0, respectively, with perchloric acid or potassium hydroxide. These slurries were then shaken at a constant temperature (20 °C) for one additional week. The final pH was recorded and the electrophoretic mobility determined with a Lazer-Zee Meter (Pen-Kem Inc.). The remaining slurry was filtered and elemental analysis conducted on the filtrate as previously described. Additional electrophoretic mobility experiments were conducted in the same manner, but using hydrochloric acid and sodium or ammonium hydroxide for pH adjustment. These experiments were performed to determine if the excess Na^+ or K^+ ions affected the metastable equilibrium state of this system.

Results

pH. Figure 1 illustrates that a dramatic increase in pH occurred when each of the fly ash samples was dispersed in doubly distilled water. The most significant pH rise was caused by the hopper fly ash. The pH of all four fly ash slurries stabilized at approximately the same value after one week of leaching. Similarly, Figure 2 shows the same pH increase with time when the experiment was conducted under a nitrogen atmosphere to exclude CO_2 from the system. In this instance, however, several weeks were required for the pH to decline to lower values.

Elemental Leaching with Time. The change in the dissolved concentrations of several major and minor elements in fly ash with time is shown in Figure 3a-i. The largest amount of leachable Al, Ca, Fe, Mg, Na, and Si was derived from the hopper fly ash. Nearly constant dissolved concen-

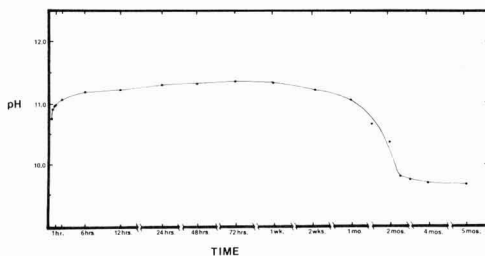


Figure 2. Change in pH with leaching time in a system closed to atmosphere

trations of Al, Ca, Cd, Fe, P, and Si are maintained for each fly ash sample after one month of equilibration, whereas K, Mg, and Na undergo a steady increase in solution following an initial rapid dissolution. Potassium, unlike other matrix elements, was leached from the submerged ash in the largest amount (Figure 3h). Figure 3e shows that dissolved reactive phosphorus concentrations increased slowly from the hopper fly ash and were lower than those derived from the other ash samples. Cadmium was quickly dissolved from the fly ash surface with the highest concentrations appearing from the hopper ash (Figure 3d).

Mobility. Electrophoretic mobilities of the four fly ash suspensions are shown as a function of pH in Figure 4. A constant solid-solution concentration of 200 mg/L was used in all cases. Although the particles appear to experience two charge reversals, (pH \sim 2.90 and 7.55), the most clearly defined isoelectric point (pH_{IEP}) lies between pH 7.5 and 7.6. Electrophoretic mobility measurements below pH 3.0 were difficult to obtain owing to the extreme negative surface charge of the ash particle. Measurements at pH 1.0, therefore, are not reported.

The change in the dissolved concentrations of several major and minor elements in fly ash with pH is shown in Figure 5a-h. Dissolution of the major matrix constituents of fly ash occurs below pH 5.0 with sharp increases in the dissolved Al, Fe, and Si concentrations (Figure 5a-c). Likewise, the fly ash particle dissolves gradually above pH 8.5 with increasing pH. Aluminum and iron exhibit the lowest dissolved concentrations in the pH regions where their hydrous-oxide phases are most stable. The concentration of dissolved silica depicted in Figure 5b remains constant except at extreme pH values where the ash particle dissolves. Calcium and magnesium (Figure 5e and f) exhibit identical behavior in the bulk solution below pH 10.0 and appear to be incorporated into the same solid phase.

The pH dependence of dissolved reactive phosphorus and dissolved sodium is shown in Figure 5g and h. Maximum loss of phosphorus and sodium from solution occurs near pH 5.0. Further pH increases result in higher dissolved concentrations for both species. At high pH, however, sodium is released into solution while phosphorus is removed from the dissolved phase.

Cadmium remains fairly constant in solution between pH 4.5 and 8.0, but is slowly removed from the dissolved phase as the pH increases (Figure 5d). In fact, above pH 11.0 cadmium is almost completely removed from the bulk solution.

Potassium was not measured over the pH range 1.0-12.0 in the same series of experiments shown here. Its behavior with pH was determined by additional experiments using sodium or ammonium hydroxide for pH adjustment. Potassium exhibits the same behavior in solution with pH as sodium (16). The dissolved concentrations of all other elements of interest in this study were monitored in these additional experiments, using sodium or ammonium hydroxide for pH adjustment,

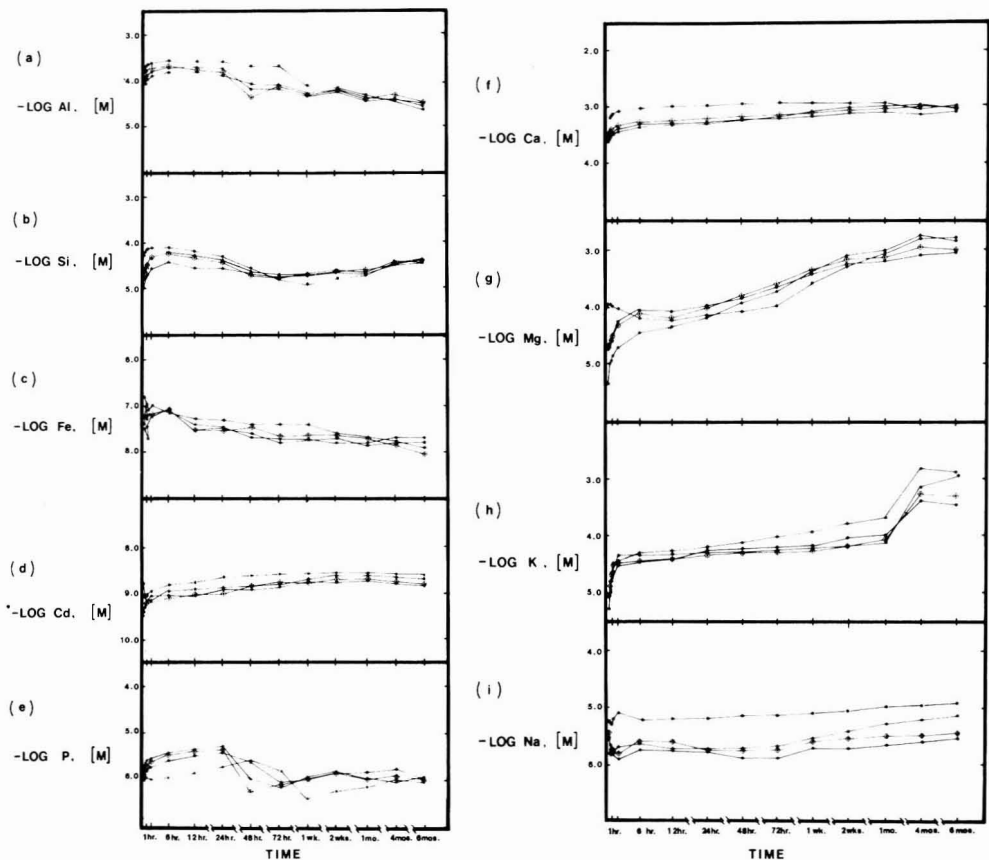


Figure 3. Change in dissolved concentrations with leaching time
 ★ Submerged off delta, ⊙ wet delta, ◻ dry delta, ✕ hoppers

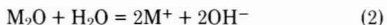
and demonstrated the same behavior with pH as reported above.

Discussion

pH Effects. The water-soluble layer surrounding a fly ash particle most likely contains various oxides of calcium, magnesium, potassium, and sodium (4, 17). The precise chemical forms of these oxides on fly ash have not been firmly established. In addition, some conversion (e.g., Equation 1) to their respective carbonates may have occurred during particle formation.



The dissolution of these oxides or carbonates from the fly ash surface should occur when fly ash is dispersed in doubly distilled water (16, 17). The highly electropositive character of potassium and sodium oxides permits them to be readily hydrolyzed by water as follows:



Analogous reactions may also be written describing the hydrolysis of the carbonate forms of these elements. Likewise, the hydrolysis of soluble calcium oxides or carbonates takes place upon water contact, whereas most magnesium oxides are essentially inert and are not expected to be appreciably hydrolyzed (18). The magnesium that enters the bulk solution at this time is most likely associated with soluble calcium compounds or magnesium compounds other than the oxide.

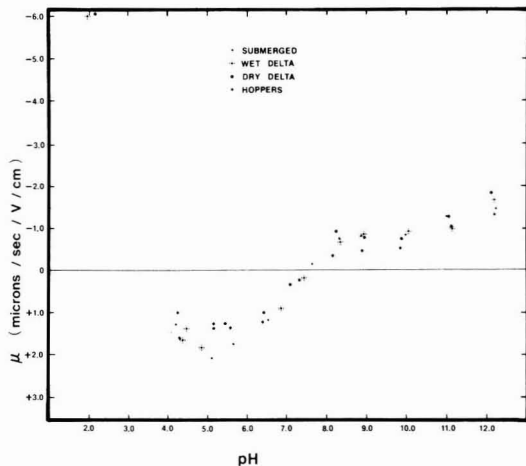


Figure 4. Electrophoretic mobilities of Columbia fly ash suspensions as a function of pH

The high pH of water extracts collected during fly ash leaching has been attributed to concurrent hydrolytic reactions of calcium, magnesium, potassium, and sodium (17). Talbot (16) found that hydrolysis of potassium and sodium compounds is most important during the first few minutes of ash leaching. In addition, the continued pH increase after the

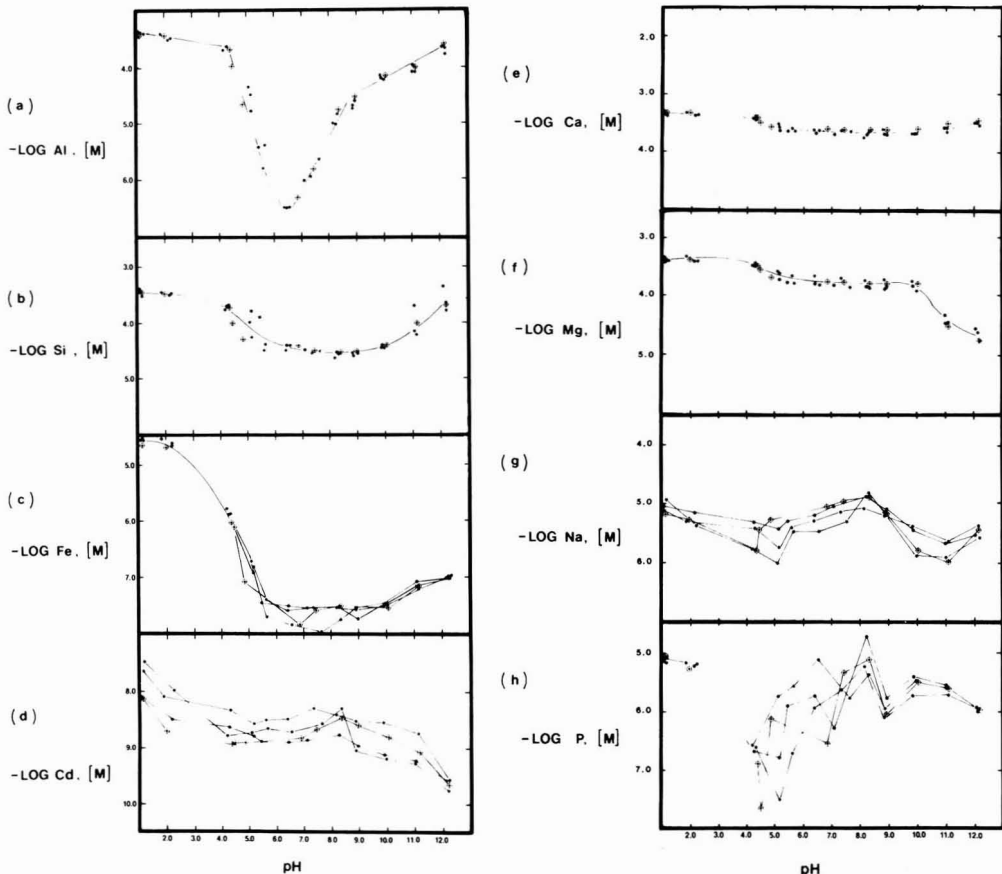


Figure 5. Change in dissolved concentrations with pH
 ★ Submerged off delta, ⊙ wet delta, • dry delta, * hoppers

initial leaching was ascribed to the hydrolysis of calcium compounds. The elemental depth profiles of fly ash reported by Linton et al. (2, 19) parallel these findings.

The hopper ash, as expected, produced the highest pH values since it had not undergone previous leaching by pond waters or rainfall. The drop in pH after 1 h of leaching is believed to result from atmospheric CO₂ entering this highly alkaline system. When CO₂ was excluded, the pH remained near 11.0 for several weeks before declining to lower values.

Major Matrix Elements. When placed in water, solid phase dissolution reactions control the dissolved concentrations of the major elements in fly ash, i.e., aluminum, iron, and silica. The presence of a single, well-defined solid phase is questionable owing to the suite of elements composing fly ash and to its random formation upon leaving the combustion zone of the furnace. Instead, a complex aluminosilicate mixture has been postulated with condensed trace elements surrounding the ash particle (2, 3, 19). It is possible that Al₂O₃ and Al₄C₃ may serve as additional precursors to hydrous aluminum oxides as shown in Equations 3 and 4.



Iron may initially be present on the fly ash as complex oxides (20) and possibly carbonates, sulfates, or carbides (e.g., Fe₄C₃). Brimblecombe and Spedding (20) suggest that iron originally combined with calcium and aluminum oxides on the ash

surface should be readily released to the bulk solution. The presence of iron sulfates may also enhance its dissolution rate (19). Results from this work indicate that these various components of the fly ash are dissolved by hydrolysis reactions and ultimately form hydrous iron oxides which are best described by Fe₂O₃·nH₂O.

Figure 5a-c indicates that incongruent dissolution of the fly ash occurs between pH 4.0 and 9.0 in an aqueous system. Aluminum, iron, and silica are released as dissolved components, while amorphous or microcrystalline Al(OH)₃ was formed concurrently as a surface precipitate (16). In addition, direct precipitation of aluminum and iron hydrous oxide phases from the bulk solution is expected within this pH region. As evidenced by Figure 5a, aluminum responds with pH (4.5-8.5) in a manner similar to that reported by Parks (21) for aluminum hydroxide systems. Although the solubility of iron is also controlled by its hydrous oxide phase (16), the bulk solution values below pH 3.0 are lower than expected with respect to Fe(OH)₃ equilibria. Nevertheless, the solubility of iron shown in Figure 5c is in good agreement with that observed by Byrne and Kester (22) and Schindler (23) for freshly precipitated hydrous ferric oxide.

Figure 6 shows that at the pH_{IEP} essentially 100% of the aluminum and iron is associated with various solid phases on the fly ash particle. This would suggest that the presence of iron hydrous iron and aluminum oxides, along with the aluminosilicate matrix, control the surface characteristics of the fly ash particle over the pH range 4.0-9.0. This heterogeneous

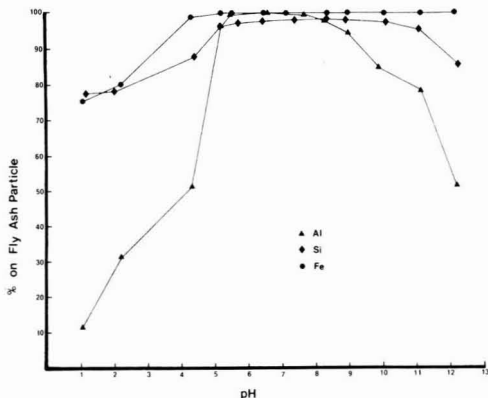


Figure 6. Percent of Al, Fe, and Si incorporated into fly ash particle as a function of pH

mixture comprising the ash surface corresponds well with the pH_{IEP} values reported for $Al(OH)_3$, $Fe(OH)_3$, and several aluminosilicate phases (24, 25). The pH_{IEP} of this complex surface mixture occurs at pH 7.55, although some shift in the pH_{IEP} toward a lower pH has undoubtedly occurred due to adsorbed anions (26, 27). Further electrophoretic mobility experiments conducted with fly ash leached at high pH indicate that the dip in the mobility curve at pH 9.0 (see Figure 4) is related to the presence of hydrous iron and aluminum oxides on the ash surface (16).

The correlation of dissolved silica and aluminum below pH 4.0 and above pH 9.0 suggests congruent dissolution of the aluminosilicate phase(s) in these pH regions. Table I shows the total elemental concentrations in the Columbia fly ash. However, supporting evidence for congruent dissolution cannot be obtained directly from these data since aluminum and silica exist in other solids on the ash particle in addition to the aluminosilicate phase.

At pH values less than 3.0, amorphous $SiO_{2(s)}$ probably controls the dissolved silica concentration. Figure 6 illustrates that at these low pH values, silica is the only major element present in sufficient concentration on the ash particle to effectively dictate its surface characteristics. Isomorphous replacement of aluminum for silica in this SiO_2 matrix may be responsible for the extremely negative charge at low pH (Figure 4). The constant dissolved silica concentrations appearing between pH 4.0 and 9.0 might be caused by adsorption onto the hydrous aluminum oxide phase. Silica would otherwise be expected to increase in the bulk solution as incongruent dissolution proceeded.

Alkaline Elements. Reference to oxide hydrolysis of alkali and alkaline earth elements during the initial ash leaching has previously been emphasized. The solubility diagram depicted in Figure 7 shows the theoretical relationships, based on thermodynamic considerations, between calcium and magnesium in this heterogeneous system. The appropriate equations describing the distribution of these solid phases were derived from the basic equilibrium expressions presented in Table II. These solid phases are stable above pH 8.5.

It is apparent from Figure 7 that the dissolved calcium and magnesium concentrations are controlled by carbonate and hydroxide solid phases. If the phase boundary is extended between calcite and dolomite into the dissolved phase on Figure 7, the experimentally determined dissolved calcium and magnesium values fall along this line. This linear relationship in the bulk solution strongly suggests that metastable equilibrium is maintained between these solid phases even at pH values where they are unstable. The dissolved calcium and

Table I. Total Elemental Concentrations^a in Columbia Fly Ash Expressed as % Dry Weight

element	submerged	wet delta	dry delta	hoppers
Al	6.3	5.7	6.5	6.3
Ca	11.4	11.7	11.2	11.8
Cd	<0.001	<0.001	<0.001	<0.001
Fe	3.0	2.7	3.2	3.3
K	0.46	0.40	0.43	0.45
Mg	3.4	3.4	3.5	3.8
Na	0.26	0.34	0.28	0.21
P	0.12	0.13	0.12	0.11
Si	23.0	20.6	22.4	21.6

^a Determined from HF-HNO₃-HCl digestion.

Table II. Log Equilibrium Constants at 25 °C and Log $P_{CO_2} = -3.52$

	ref
$CaCO_{3(s)} = Ca^{+2} + CO_3^{-2}$	-8.35 29
$MgCO_{3(s)} = Mg^{+2} + CO_3^{-2}$	-8.00 28, 30
$CaMg(CO_3)_{2(s)} = Ca^{+2} + Mg^{+2} + 2CO_3^{-2}$	-16.70 31
$Mg_4(CO_3)_3(OH)_{2(s)} = 4Mg^{+2} + 3CO_3^{-2} + 2OH^-$	-34.90 28
$Ca(OH)_{2(s)} = Ca^{+2} + 2OH^-$	-5.43 31
$Mg(OH)_{2(s)} = Mg^{+2} + 2OH^-$	-11.15 28
$H_2O = H^+ + OH^-$	-14.00 23
$H_2O + CO_2 = HCO_3^- + H^+$	-7.82 23
$HCO_3^- = H^+ + CO_3^{-2}$	-10.33 23

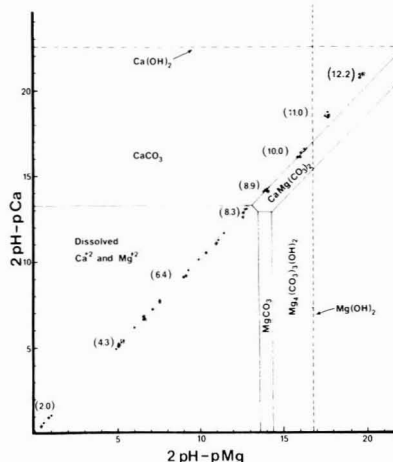


Figure 7. Solubilities of Ca^{+2} and Mg^{+2} carbonates and hydroxides at 25 °C

Numbers in parentheses correspond to pH values observed during electrophoretic mobility experiments

★ Submerged off delta, ⊙ wet delta, • dry delta, * hoppers

magnesium concentrations appear to be controlled exclusively by these solid phases. Figure 7 also shows that as the pH increases, the solubility of brucite- $Mg(OH)_2$ is exceeded. Above pH 10.0 magnesium probably precipitates from the dissolved phase by this reaction. As a result, the mixed carbonate solid phase, e.g., dolomite, is forced to release calcium and magnesium to the incongruent solution due to mass balance constraints. The bulk solution then contains calcium in excess, and calcite (or aragonite) would then form on the ash surface as described by Bricker and Garrels (32).

The dissolved potassium and sodium concentrations appear to be controlled by a feldspar or mica-type solid phase (Figure 8). The low abundance of these mineral phases (16), however,

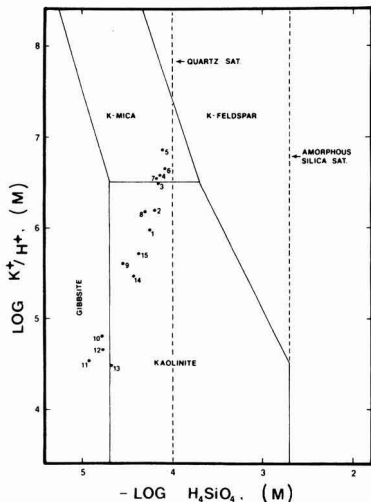


Figure 8. Silicate stability diagram with data points for K^+/H^+ (wet delta ash) from leaching experiments superimposed. Numbers are in consecutive order with respect to sampling intervals (short to long equilibration times) during leaching experiments

makes the interpretation of these elements difficult since their heterogeneous processes are overshadowed by reactions involving more prevalent solids. Figure 8 shows that this system is at disequilibrium with respect to K^+ -aluminosilicate phases. Similar values are given by Bricker and Garrels (32) for natural water systems in metastable equilibrium with feldspars or micas.

The initial ash dissolution proceeds toward equilibrium with either feldspar or mica-type phases, but the exact nature of the mineral remains uncertain. The reaction path followed by potassium indicates that equilibrium between a feldspar and mica phase would have been established with a logarithmic K^+/H^+ molar ratio between 7 and 8. The decreasing K^+/H^+ molar ratio after 2 h of equilibration occurs since more predominant mineral equilibrium processes involving aluminum, iron, and silica are controlling the bulk solution composition. The movement into the gibbsite stability field (Figure 8) coincides with incongruent dissolution of the aluminosilicate phase (16). After about 4 months, i.e., point 14 on Figure 8, the dissolved silica concentration is again increasing, but the reaction rates are very slow due to incongruent dissolution. Consequently, the bulk solution begins to reestablish metastable equilibrium with the feldspar or mica-type phase(s).

Minor Elements. Results from these experiments indicate that the behavior of cadmium and phosphorus in the ash pond is controlled exclusively by the major solid phase components of this heterogeneous system. The slow release of phosphorus to the solution by the hopper ash indicates that some prior dissolution of surface constituents is necessary before phosphorus becomes directly available to the bulk solution. The delta fly ash contained more leachable phosphorus than the hopper ash. This must result from the accumulation of additional phosphorus on the fly ash from the slurry water (Wisconsin River water) during discharge into the ash pond or from rainfall upon the ash delta.

Figure 5h shows that phosphorus is removed from solution between pH 4.0 and 8.5 onto the ash particle with decreasing pH. Huang (33) has observed a similar pH dependence for phosphorus adsorption on amorphous aluminum hydroxide. At higher pH, phosphorus is most likely removed from solution as a hydroxyapatite-type solid phase or by occlusion into

coprecipitating magnesian calcites (34). The appearance of phosphorus in the dissolved phase at low pH results from ash particle dissolution.

Cadmium is quickly dissolved from the fly ash surface with the highest solution concentrations appearing for the hopper ash. This behavior is expected since cadmium is volatilized during combustion, and subsequently condenses onto the outer layers of the particle after leaving the combustion zone (3). The slight increase in dissolved cadmium with leaching time is most likely caused by the gradual decline in the negative surface charge of the ash particle together with dissolution of a solid phase as the pH decreases. The nature of the solid phase with which cadmium is associated is presently unknown. Below pH 4.0 (Figure 5d) cadmium is readily released into the bulk solution with concurrent ash particle dissolution. The slight variations in the dissolved cadmium concentrations between 4.0 and 8.5 might be caused by solid phase rearrangements on the fly ash surface. At pH values above 8.5, adsorption and precipitation reactions are most likely responsible for the rapidly decreasing dissolved cadmium concentrations.

Summary

Dissolution of the major elemental components of fly ash begins immediately upon water contact. The dissolved behavior of Al, Ca, Fe, K, Mg, Na, and Si has been shown to be a function of their solubility relationship with solid phases under metastable equilibrium conditions. Cadmium and phosphorus are also incorporated into solid phases, but adsorption strongly influences their behavior in the appropriate pH regions.

The complex nature of the resulting heterogeneous solution and the different kinetic controls on solid phase predominance makes the existence of metastable phases highly likely. The conversion of metastable phases to more thermodynamically stable phases is expected to continue with longer equilibration times. The aluminosilicate and carbonate phases are primarily responsible for controlling the bulk solution composition. However, incipient phases like $Al(OH)_3$ and $Fe(OH)_3$ may play important roles in controlling the dissolved concentration of some species—particularly the trace elements. The diffusion of CO_2 into the system initially decreases solution pH, but incongruent reactions gradually exert pH control and a trend toward the pH_{IEP} is shown under a CO_2 -free environment.

Nucleation and crystal growth of mineral phases is expected to occur on the fly ash surface. Solids analysis on the samples collected during these experiments has been initiated in the hope of identifying various mineral phases. Knowledge of the composition and structure of these solid phases is vital for a rigorous explanation of the heterogeneous reactions occurring in this system and ultimately in predicting the composition of the aqueous phase.

Acknowledgment

The authors thank Owen T. Bricker for his critical evaluation and review of this manuscript.

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Received for review November 14, 1977. Accepted April 20, 1978. This project financed in part by funds from the Wisconsin Power and Light Co., Madison Gas and Electric Co., and Wisconsin Public Service Corp., and with funds from the Environmental Protection Agency under grant number R803971. The contents do not necessarily reflect the views and policies of the Environmental Protection Agency or the power companies, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Bioaccumulation Potential and Acute Toxicity of Synthetic Fuels Effluents in Freshwater Biota: Azaarenes

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■ The extent to which three polycyclic aromatic bases, isoquinoline, acridine, and benz(a)acridine, are accumulated from aqueous solution by *Daphnia pulex* was evaluated. Bioaccumulation kinetics were described as a first order approach to equilibrium in a two-compartment model (water and *Daphnia*) using a two-stage technique to resolve uptake and elimination rates while accounting for decreasing aqueous concentrations. The 24-h acute toxicities of the compounds were also determined. Equilibrium concentration factors increased dramatically with increasing molecular weights within the series of compounds and were also highly correlated with the calculated *n*-octanol/water partition coefficient. Benz(a)acridine, acridine, and isoquinoline were concentrated about 350-, 30-, and 2.5-fold, respectively, by *Daphnia*. Acute toxicity exhibited the same relationship with changing molecular weight, with 24-h LC₅₀'s of 0.4, 2.9, and 39.9 mg/L for benz(a)acridine, acridine, and isoquinoline, respectively.

The possible future development of a large-scale synthetic fuels industry in the U.S. creates the potential for release of substantial quantities of organic wastes to aquatic ecosystems (1). The effluents and products from such processes are ex-

ceedingly complex mixtures of organic compounds of varying molecular weights and chemical classes. One of the major differences between natural petroleum and synthetic liquid fuels derived from coal is the higher organic nitrogen content of the synthetic fuels (2). A portion of this nitrogenous material consists of polynuclear heterocyclic bases containing a single basic nitrogen within 2, 3, 4 or more aromatic ring systems (azaarenes). Some members of this class of compounds are known mutagens (3) and/or carcinogens (4-6). Results of Ames' test mutagenesis screening or fractionated synthetic fuels and aqueous effluents from their manufacturing processes indicate that the ether soluble base fraction (which should contain acridine and related compounds) exhibits high mutagenic activity (7).

Other industrial processes, such as coking (8, 9), currently release polycyclic bases in their effluents. Total concentrations of quinolines and larger azaarenes have been observed to range from 1 to 100 mg/L in effluents and raw wastewaters from coking and coal conversion processes (8, 10). The fate and effects of such compounds in receiving waters have received very little study, and little is known of their propensity to accumulate in aquatic organisms.

The objective of this study was to investigate the potential for accumulation in aquatic biota of three representative compounds from this class, ranging from two to four aromatic rings. The compounds studied were isoquinoline, acridine, and benz(a)acridine. Concurrent with bioaccumulation studies, acute toxicity determinations were carried out to ensure that

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bioaccumulation data were not obtained at concentrations close to toxic levels and to explore the relationship between bioaccumulation and acute toxicity across a chemical structure gradient within a particular class of chemicals.

The zooplankter, *Daphnia pulex*, was selected as the test organism due to its widespread use in the study of other toxicants and its ability to rapidly accumulate lipophilic organics from water (11-14). The importance of *Daphnia* as a food source for other aquatic organisms makes it a representative step in the possible food chain accumulation of toxicants in higher organisms, including man.

Methods

Isoquinoline and acridine were obtained from Aldrich Corp., while benz(a)acridine was obtained from Pfaltz and Bauer. Isoquinoline and acridine were purified by recrystallization from water, followed by dissolution in pesticide grade hexane (Burdick and Jackson Laboratories). The materials were then extracted from hexane into 0.1 M H₃PO₄, and the hexane phase was discarded. The aqueous phase was adjusted to pH 9-10 with 0.1 M NaOH and extracted with hexane. The hexane phase was evaporated to dryness under nitrogen to recover the azaarenes. Benz(a)acridine was purified by recrystallization from anhydrous methanol. Acid-base extraction was not employed due to unfavorable partitioning of benz(a)acridine. Analyses of the azaarenes in water and methanol extracts of *Daphnia* were conducted using a Beckman Model DB-G spectrophotometer and a Perkin-Elmer MPF-44 fluorescence spectrophotometer. Fluorescence analysis of acridine and isoquinoline was carried out in a mixture of 80% pH 3.0 H₂O/20% methanol (by volume) to take advantage of the enhanced fluorescence of the conjugate acids of these two bases. Calibration curves in pure H₂O, methanol, and 80% pH 3.0 H₂O/methanol were verified by the method of standard additions to test water and *Daphnia* extracts. The slopes were the same in all cases. Azaarenes were extracted from *Daphnia* by placing five intact organisms in 1 mL of methanol and gently shaking 30 min. Homogenization and reextraction of the *Daphnia* indicated that the initial extraction was essentially complete.

Bioaccumulation studies were carried out at 21 ± 1 °C in a 3000-mL pyrex beaker, using spring water filtered through a Whatman #40 glass fiber filter. Adult *Daphnia*, ~0.6 mg wet weight, per individual, were placed in the container at an initial density of about 67 animals per liter. Replicate samples of five animals each were randomly selected at periodic intervals, isolated by filtration, and extracted. Mean weight per individual of the test population was determined by selecting 10 organisms at random, isolating them by filtration, and rapidly weighing individually on an Ainsworth Model 24N balance. Elimination rates were measured by placing animals that had been exposed to test solutions long enough to reach equilibrium in filtered spring water and periodically removing and extracting two five animal replicates. Initial concentrations were: isoquinoline, 6.2 ppm; acridine, 245 ppb; and benz(a)acridine, 18 ppb.

Acute toxicity determinations were carried out by placing 10 animals in 400 mL of spring water containing a fixed concentration of the toxicant for 24 h. Five concentrations of each toxicant were tested in duplicate at each concentration following preliminary range finding tests, spanning levels from 0 to 100% mortality. Toxicant concentrations were measured at the start and conclusion of each run, and did not change appreciably. Environmental conditions for both toxicity and bioaccumulation studies were: temperature, 21 °C; dissolved oxygen, 6.5-8 ppm; pH, 7.5-7.9; and total alkalinity, ~80 ppm. LC₅₀ values were obtained from the concentration-mortality data using probit analysis (15).

Bioaccumulation data were analyzed as a first order approach to equilibrium in a two-compartment model (water and *Daphnia*). Uptake was assumed to be a first order process with respect to aqueous azaarene concentration, and the elimination rate first order with respect to azaarene concentration in the *Daphnia*. These assumptions lead to the following differential equation as our model:

$$\frac{dY(t)}{dt} = CZ(t) - kY(t) \quad (1)$$

where $Z(t)$ = aqueous azaarene concentration at time t after the start of the experiment ($\mu\text{g/g}$); $Y(t)$ = *Daphnia* azaarene concentration at time t after the start of the experiment ($\mu\text{g/g}$, wet weight); k = *Daphnia* elimination rate constant, h^{-1} ; and C = uptake constant, h^{-1} . Since aqueous benz(a)acridine concentration tended to decrease with time at very low concentrations due to uncharacterized removal and degradation processes, $Z(t)$ was approximated by the function

$$Z(t) = \alpha + \beta e^{-\lambda t} \quad (2)$$

to give a description of the behavior of the aqueous concentration over time. The decrease was about 15% in 48 h. Substitution of Equation 2 into 1 and integrating this differential equation yields the expression

$$Y(t) = \left(\frac{C\beta}{\lambda - k} - \frac{C\alpha}{k} \right) e^{-kt} - \frac{C\beta}{(\lambda - k)} e^{-\lambda t} + \frac{C}{k} \alpha \quad (3)$$

For an unchanging aqueous concentration, i.e., $Z(t) = \alpha = Z(0)$, $\beta = 0$ and $\lambda = \infty$, the expression takes the form

$$Y(t) = \frac{CZ(0)}{k} (1 - e^{-kt}) \quad (4)$$

The estimates of the parameters C and k were obtained using a two-stage iterative least-squares technique. The first stage used the observed $[t, Z(t)]$ values to obtain estimates of α , β , and λ or $Z(0)$ for the unchanging aqueous concentration case (16). [The estimate of $Z(0)$ was equal to the sample average of the observed $Z(t)$ values]. By substituting the parameter estimates from the first stage into Equation 3 or 4, a nonlinear iterative least-squares procedure was used to determine the estimates of C and k (16). The bioaccumulation curve (concentration factor vs. time) was derived from the ratio of Equation 3 to 2, and approached C/k as a limit with increasing time.

Since the properties of organic bases such as these would be expected to vary with pH, it was necessary to verify that the unchanged molecular species was dominant at the pH of the experimental system. The dissociation constants (pK_a) for isoquinoline and acridine obtained from the literature were found to be 5.62 for acridine (17) and 5.05 for isoquinoline (18). No literature value was found for benz(a)acridine; therefore, its pK_a was determined to be 5.25 by monitoring the UV absorbance of its conjugate acid at 400 nm in 0.001 N phosphate buffer over pH 3-8 (17). Unprotonated benz(a)acridine does not absorb appreciably at 400 nm. Since the pK_a 's of the three compounds are significantly lower than 7.5-8.0, all were >99% unprotonated at the pH range observed in this study.

Aquatic organisms may accumulate contaminants directly from water or through ingestion of contaminated food. To assess the importance of the latter pathway, one group of *Daphnia* was exposed to 18 ppb benz(a)acridine in filtered spring water containing trout chow suspension in the concentration used to feed stock *Daphnia* cultures (19). Benz(a)acridine uptake rates were determined for each treatment over a 3-h exposure period (the linear portion of the bioaccumulation curve).

Results

All three compounds were rapidly taken up by *Daphnia*, and the concentration factor (concentration of substance in *Daphnia*/concentration of substance in water) reached equilibrium within several hours (Figure 1). Equilibrium concentration factors increased slightly more than one order of magnitude with each ring structure added to a basic two-ring structure. A plot of log equilibrium concentration factor (CF) vs. molecular weight (MW) (Figure 2) clarifies this relationship, yielding the equation

$$\log(\text{CF}) = 0.0216(\text{MW}) - 2.408, R^2 > 0.999 \quad (5)$$

Individual kinetic parameters are given in Table I. It can be seen that the differences in bioaccumulation potential among the three compounds are associated primarily with the decrease in elimination rate (k) with increasing molecular weight. Elimination half lives range from ~ 70 min for benz(a)acridine to ~ 1 min for isoquinoline. The concentration independent uptake constant (C) varies relatively little with structural changes, ranging from 82 to 208 h^{-1} . Independent estimates of elimination rates agree fairly well with those obtained from the uptake experiments. The large differences in elimination rate with increasing molecular weight and the first order kinetics of the elimination process are evident (Figure 3).

The results of 24-h toxicity tests are summarized in Table I. LC_{50} values for isoquinoline and acridine agree with previously published values of 52 and 5.0 mg/L for isoquinoline and acridine, respectively (20). Benz(a)acridine was highly toxic, killing organisms at a concentration of 449 ppb. The aromatic bases appeared to have a narcotic effect on *Daphnia*; thus, toxic effects could also be expressed as immobilization as well as death. Applying this criterion reduced the critical concentration by roughly 20% (Table I). The relationship between acute toxicity and molecular structure is shown in Figure 2. Toxicity increases by roughly an order of magnitude with each additional aromatic ring and yields the expression

$$\log \text{LC}_{50}(\text{mg/L}) = -0.0194(\text{MW}) + 4.0471, R^2 = 0.991 \quad (6)$$

When toxicity is expressed on a molecular (molar) basis, the expression becomes

$$\log \text{LC}_{50}(\text{mol/L}) = -0.0219(\text{MW}) - 0.7478, R^2 = 0.992 \quad (7)$$

In both expressions the absolute value of the slopes of the toxicity relationship is nearly identical to the slope of the bioaccumulation relationship, suggesting an interrelationship, though not necessarily cause-effect, between toxicity and bioaccumulation potential. Statistical comparison of the absolute values of the slopes of the three data sets indicates that both toxicity curves have slopes that do not differ significantly from the bioaccumulation curve at the 10% level of significance.

The uptake of benz(a)acridine by *Daphnia* from water containing food did not differ significantly ($P > 0.10$) from the uptake from filtered water, with slopes of the uptake phase of the bioaccumulation curve of 1.50 and 1.67 $\mu\text{g g}^{-1} \text{h}^{-1}$, respectively. Centrifugation of the water containing food and subsequent analysis of the supernatant indicated that $< 5\%$ of the benz(a)acridine was sorbed to food particles. While uptake of contaminated particulates was not consequential in this experiment, it remains possible that under certain conditions of particulate type and loading, this pathway may be important.

While differences in bioaccumulation factor and toxicity were highly correlated with molecular weight, it must be noted that the molecular weight variations observed consisted of a single structural unit. Thus, properties such as molecular

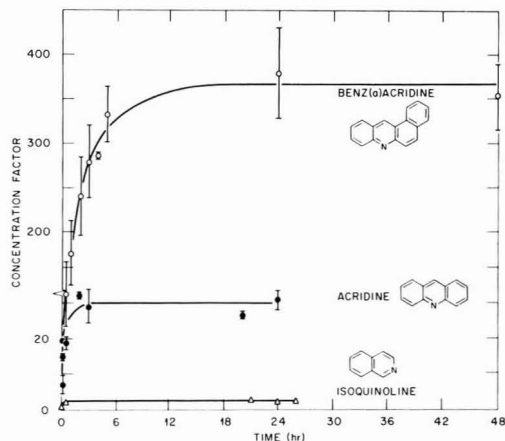


Figure 1. Uptake and equilibrium bioaccumulation of isoquinoline, acridine, and benz(a)acridine by *Daphnia pulex* at 21 °C. Initial concentrations: isoquinoline, 6.2 ppm; acridine, 245 ppb, benz(a)acridine, 18 ppb

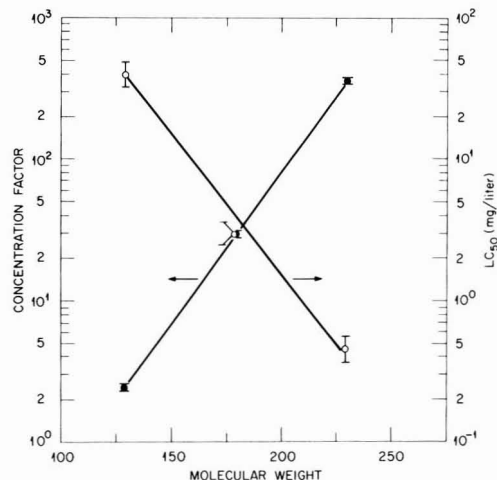


Figure 2. Variation in toxicity and bioaccumulation of azaarenes with molecular weight

Absolute value of slopes of log concentration factor and log acute toxicity (mg/L) vs. molecular weight is similar. Error bars are ± 1 standard error

volume and n -octanol/ H_2O partition coefficient would also be highly correlated with bioaccumulation (21). If calculated log partition coefficient (P) (22) is used in place of molecular weight in Equation 5, the expression becomes

$$\log \text{CF} = 0.819(\log P) - 1.146, R^2 = 0.995 \quad (8)$$

The fit of this expression to the data is not as good, but the mechanistic rationale for applying it is more sound (21). Applied to Equation 6, we get

$$\log \text{LC}_{50}(\text{mg/L}) = -0.742(\log P) + 2.940, R^2 = 0.999 \quad (9)$$

and applied to Equation 7,

$$\log \text{LC}_{50}(\text{M/L}) = -0.837 \log P - 1.999, R^2 = 0.999 \quad (10)$$

While use of these two approaches (MW vs. $\log P$) to estimate the bioaccumulation potential of a compound formed by adding another terminal aromatic ring would give essentially the same answer, applying them to a structure formed by adding a different substituent (such as $-\text{CH}_3$) would not, since such a substituent increases P more than it increases

Table I. Toxicity and Bioaccumulation Kinetics of Azaarenes. Test Organism, *Daphnia pulex*, 21 °C

	isoquinoline	acridine	benz(a)acridine
molecular weight	129	179	229
equil concn factor ± SE	2.41 ± 0.13	29.6 ± 1.4	352 ± 12
uptake constant ± SE, h ⁻¹	82 ± 16	109 ± 15	208 ± 24
elimination rate constant ± SE, h ⁻¹	34.2 ± 7.3	3.68 ± 0.55	0.590 ± 0.077
independent elimination rate ± SE, h ⁻¹	18.4 ± 2.6	2.15 ± 0.19	0.577 ± 0.063
LC ₅₀ , mg/L	39.9	2.92	0.449
95% confidence limits	33.0–47.7	2.37–3.56	0.365–0.590
IC ₅₀ , mg/L	33.6	1.71	0.362
95% confidence limits	26.4–42.0	1.36–2.41	0.290–0.472
log octanol/H ₂ O partition coefficient (calcd) (from Leo, 1975)	1.82	3.30	4.45

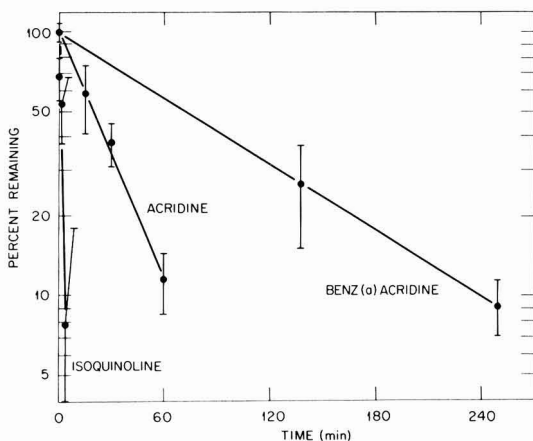


Figure 3. Elimination of benz(a)acridine, acridine, and isoquinoline by *Daphnia pulex* at 21 °C
Error bars are ± 1 standard error

molecular weight. In the absence of corroborative evidence evaluating the effect of side chains such as —CH₃, use of Equations 8–10 probably provides the best, though necessarily rough, estimate of bioaccumulation and toxicity, since *P* approximates lipid/water partitioning.

Discussion

The bioaccumulation potential of these polycyclic bases is highly correlated with the number of aromatic rings composing the molecule; thus, high molecular weight materials such as benz(a)acridine present a far greater likelihood of accumulating in aquatic biota than substances such as isoquinoline. The significance of a 352-fold accumulation of benz(a)acridine by *Daphnia* can be inferred by comparing it to bioconcentration factors (live weight basis) for other toxicants. DDT was concentrated 16 000-fold by immature *Daphnia magna* (12), while another pesticide, γ -hexachlorocyclohexane was magnified 60–350-fold by the same species (13). Methyl mercury was accumulated ~4000-fold by *D. pulex* (14), while anthracene, a three-ring PAH, was accumulated ~750-fold by *D. pulex* (11). It can be seen that the

direct bioaccumulation of azaarenes of four rings or less is 1–2 orders of magnitude lower than DDT and CH₃Hg⁺, two compounds whose bioaccumulation is an ecological hazard. If the observed trend is followed upon addition of another aromatic ring to benzacridine, a bioaccumulation factor of roughly 4000 would be expected for dibenzacridines, carcinogenic members of this class (6).

Comparison of uptake rates observed in this study with others points out an interesting trend. Applying our bioaccumulation model to the above data, the polar organo-metallic compound, methyl mercury, exhibits an uptake constant of 14–17 h⁻¹ at 20 °C (14). Nonpolar anthracene, on the other hand, had an uptake constant of about 750 h⁻¹ at 23 °C (11). The uptake constants of azaarenes (82–208 h⁻¹) were intermediate between these two compounds.

The increase in uptake rate with decreasing polarity is consistent with observations on the relationship between membrane permeability and polarity and lipophilicity (23). Biological membranes are less permeable to electrolytes and polar materials; thus, both uptake and elimination rates could be reduced by membrane transport behavior. If the equilibrium concentration factor is primarily a result of equilibrium lipid/water phase partitioning of a contaminant, restricted uptake and elimination rates caused by membrane transfer mediation would be manifest as slower equilibration kinetics (i.e., longer time to equilibrium) but not as an increase or decrease in equilibrium concentration factor (assuming it were possible to accumulate such materials without intervening membranes). Thus, electrolytes such as methyl mercury (14) equilibrate much more slowly in *Daphnia* than less polar substances such as benz(a)acridine.

The uptake rates observed in this study did not vary greatly with chemical structure of the azaarenes, an observation consistent with a mass transfer process limited by physical factors within the aqueous phase, such as filtering or swimming rate (22). Uptake rates exhibited in this study are roughly 5% of a typical *D. pulex* filtration rate (24).

Elimination rates were inversely correlated with partition coefficient, as was expected from theoretical considerations. Thus,

$$\log \frac{1}{k} = 0.67 \log P - 2.76, R^2 > 0.999 \quad (11)$$

This is consistent with the consideration of bioaccumulation of organics as a water:lipid partitioning mediated by phase boundary transfer kinetics (25). Elimination rate clearly is the most important kinetic factor associated with bioaccumulation behavior of azaarenes in *Daphnia*. Thus, molecular structures that are more likely to bioaccumulate in *Daphnia* will also exhibit longer turnover times within the animals. Analysis of water from benz(a)acridine elimination experiments indicated that it was primarily eliminated without undergoing chemical transformation. A concurrent but slower transformation of benz(a)acridine by *Daphnia* or their associated microflora is likely (11) but was not observed.

The differences between elimination rates obtained from uptake curves and those measured directly are greatest for isoquinoline, which was the most difficult to measure due to its rapidity ($T_{1/2} \sim 1$ min) and the low initial concentration within the animals due to the low bioaccumulation factor. Benz(a)acridine, in which time and analytical measurements could be made with relatively greater precision, demonstrated close agreement between the two techniques.

The acute toxicity data established that bioaccumulation data were not collected at acutely toxic concentrations, and also indicated that toxicity of these compounds is determined more by differences in delivery of the various toxicants to the organism than by variation of toxic action within the animal. While LD₅₀ measurements were not made, the product of

Equations 8 and 10 provides an estimate of 24-h LD₅₀. The coincident slopes of toxicity and bioaccumulation curves indicate that acutely toxic doses to *Daphnia* do not vary greatly with chemical structure within this class of compounds, with estimated LD₅₀'s of 6.6×10^{-7} and 6.0×10^{-7} mol/g for isoquinoline and benz(a)acridine, respectively, representing the extremes. If these data are used to infer the toxicity of 5-ring azaarenes, an LC₅₀ of about 5 ppb is estimated for dibenzacridine. Thus, direct toxicity may in fact be a problem associated with trace releases of high molecular weight azaarenes. The longer residence time of such compounds due to lower elimination rates would also enhance the likelihood of their producing subacute or long-term toxic effects.

The combined hazards of high bioaccumulation potential, high toxicity, and possible mutagenicity and/or carcinogenicity make minimization of releases of azaarenes to aquatic ecosystems a necessary objective of developing synthetic fuels technologies.

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Received for review August 16, 1978. Accepted April 18, 1978. Research, carried out at Oak Ridge National Laboratory, sponsored by the Division of Biomedical and Environmental Research, Department of Energy, under contract W-7405-eng-26 with Union Carbide Corp.

Modes of Metal Transport Above and Below Waste Discharge on the Haw River, North Carolina

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■ Modes of Cr, Sb, Fe, and Co transport were examined for differences between control and polluted stations within a selected small drainage area of the Haw River, North Carolina. Five modes of transport were operationally defined by sequential leaching of suspended particulates and analyses by neutron activation analysis. A Mann Whitney U-test was used to test for significant differences between the two station classes. Differences appeared among a greater number of transport modes for Cr and Sb, elements suspected of being added to the river as industrial wastes than for Fe and Co, elements with no known industrial input.

Significant transport of trace metals by particulates is found in most rivers of the world (1). Solid surfaces may control trace metal concentrations and account for the observed under-saturation of metals in oxic environments (2-4). Their importance to transport, control, and biological availability requires understanding of sorption-desorption mechanisms. The experimental approach commonly used for studying transport and availability of metals on solid phases is extraction with various leaching procedures. In many cases this amounts to

a one-step dilute mineral acid extraction, but in others elaborate partitioning schemes are used (5, 6). These schemes have been criticized because of their poor selectivity and because the results appear to reflect more the nature of the leaching reagents and extraction conditions than they do the nature of the solid phases affected (7). The danger inherent in interpreting leaching procedures is in placing undue emphasis on absolute phase identification. Despite its limitations, partitioning may provide information about relative differences in metal availability and metal transport for two environments differing greatly in water quality.

Studies of trace metal transport near municipal waste outfalls (6, 8-11) have almost always employed some extraction technique for solid phases, but only Burrows and Hulbert (11) have compared polluted to nonpolluted areas, and their study was limited to bottom sediment. They examined metal partitioning among adsorbed, reducible (oxides and carbonates), oxidizable (sulfides and organics), and crystalline fractions in clean and polluted sediments from a New Jersey estuary and observed that in clean sediments Pb, Zn, and Cd were found mainly in the adsorbed, reducible, and oxidizable phases, respectively. In the polluted sediments, Zn and Cd

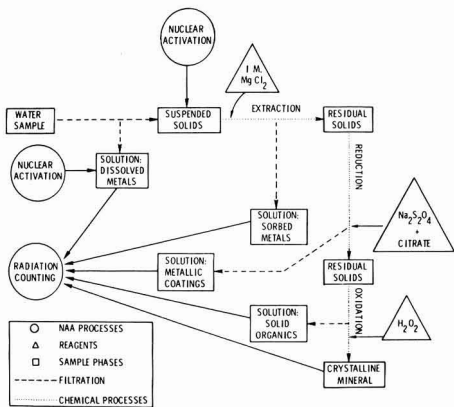


Figure 1. Procedures for defining modes of transport

were found primarily in reducible phases, and Pb was principally associated with crystalline phases.

As part of a larger study (12), we examined the modes of transport of Co, Cr, Fe, and Sb in the Haw River under different conditions of water quality using a sequence of leaching procedures adapted from Gibbs (5). A comparison was made between unpolluted waters and waters which receive both domestic wastewater and metal input. The objective of this work was to determine whether metal transport modes as identified by leaching procedures showed significant differences between polluted and unpolluted portions of the Haw River, North Carolina.

Materials and Methods

Five stations were selected in the upper Haw River watershed near Reidsville, N.C. (pop. 14 000). Three stations upstream of any known contamination served as control stations, and two stations located below the Reidsville sewage treatment plant served as polluted stations. The polluted stations had a point source of wastewater containing treated domestic sewage and industrial wastes. This choice of stations within a drainage area of about 10 square miles minimized variations in the geochemistry of solid phases.

Samples were collected January through May 1974. On each sampling date, water samples were taken from midstream with a Nalgene bucket and immediately transferred to a 1-L polyethylene bottle and frozen upon return to the laboratory. Prior to sampling, the containers and bucket were rinsed with 1:1 nitric acid, leached overnight in approximately 1:10 nitric acid, and finally rinsed three times with distilled water and allowed to drain.

The leaching procedure adapted from Gibbs (5) is diagrammed in Figure 1. Phase nomenclature is also that of Gibbs and is used here merely for ease in discussion. The entire thawed water sample was filtered through an acid washed and tared 0.45- μ m Millipore filter into an acid-washed filter flask containing 1 mL of Ultrex nitric acid. The acidified filtrate was returned to its original bottle to provide an opportunity for the acid to desorb any metal ions that might have previously been adsorbed on the container wall. Metals in water soluble forms were present in the filtrate, while metals bound to the sediment were retained on the filter. The filter was then oven dried at 105 °C for 2 h, desiccated, and weighed. Duplicate 100-mL aliquots of the filtrate and the entire filter were then irradiated, and metal concentrations determined as described below. Further separations were performed on the suspended sediment only after irradiation to eliminate the

possibility of contamination from the many reagents.

After counting, the irradiated filters were transferred from their irradiation vials to 50-mL Pyrex Erlenmeyer flasks with 15 mL of 1 M magnesium chloride at pH 7 and extracted for 4 h on a shaker table. The use of $MgCl_2$ as the adsorption reagent rather than the standard reagent, ammonium acetate ($NH_4CO_2CH_3$), was suggested by Gibbs (5) who found evidence that $NH_4CO_2CH_3$ tends to dissolve or complex metallic oxide coatings. At the end of the 4-h extraction, each solution was vacuum filtered through a 0.45- μ m membrane filter directly into a 125-mL polyethylene bottle for counting. The transfer from flask to filter was completed with 10 mL of $MgCl_2$ solution, and the filter was washed several times with another 10-mL aliquot of $MgCl_2$ solution. The filtrate, containing exchangeable (adsorbed) metals, was analyzed for metal concentrations. Metals bound by other mechanisms were retained on the filter. The solids on the filter, along with the initially irradiated filter, were transferred back to the flask with 10 mL of 0.3 M sodium citrate.

The next step in the separation scheme was to reduce the metallic oxide coatings. The procedure followed was that of Jackson (13) in which 10 mL of 0.3 M sodium citrate and 1 mL of 1 M sodium bicarbonate were added to the sample and heated to 80 °C on an electric hot plate. One-tenth gram of sodium dithionite, approximately the weight of the sample, was added with stirring, and the solution was kept at 80 °C for 15 min. At this point, the Fe and Mn coatings were dissolved, and the metals complexed in solution by citrate. The solution was then filtered through a 0.45- μ m membrane filter directly into a 125-mL polyethylene bottle for metals analysis, the flask and filter each being washed with 10 mL of distilled water to complete the transfer. The solids remaining on the filter were then transferred back to the flask with 10 mL of distilled water.

The third separation was the oxidation of organic matter with 30% hydrogen peroxide. The method used was that of Jackson (13) in which the flask containing distilled water and solids was heated to approximately 95 °C on an electric hot plate. Three drops of bromocresol green indicator solution were added to the flask, and then 0.1 M hydrochloric acid was added dropwise until the indicator turned yellow (pH 5.4 or less). Ten milliliters of H_2O_2 was added to rinse down the sides of the flask, and the oxidation continued for 15 min longer. Finally, the solution was vacuum filtered using the same procedure followed in the previous step and counted to determine the amount of organically bound metals. The filter was oven-dried at 105 °C and transferred to a polyvinyl vial for counting. The metals left with the solids on the filter after the three extractions were considered to be constituents of the crystalline mineral lattices.

The concentrations of Co, Cr, Fe, and Sb were determined using neutron activation analysis (NAA). Samples were placed into linear polyvinyl vials and subjected to a neutron flux of 3×10^{13} neutrons/cm²-s at the North Carolina State University Pulsar Reactor. Aqueous standards were prepared from the salts of the metals. Filter standards were made by drying aqueous standards on layered filter paper. Filter blanks were also analyzed, and their metal concentrations subtracted from sample concentrations. Following an appropriate decay time (usually 2–3 days), water, filters, and standards were transferred to nonirradiated containers for counting. The isotopes ⁶⁰Co, ⁵¹Cr, ⁵⁹Fe, and ¹²⁴Sb were counted after approximately 21 days for 2000–4000 s on large volume 17 and 21% Ge(Li) detectors coupled to a Nuclear Data 2200 or 4420 computerized multichannel analyzer.

A Mann Whitney U-test (one-tailed) (14) was selected for testing differences at various levels of significance. This nonparametric test is useful for small populations with unknown distributions.

Results and Discussion

Table I gives the mean concentrations of Cr, Sb, Co, and Fe in suspended particulates at each station for the entire sampling period September 1973 to May 1974, as well as the mean concentrations for the two classes of stations. Statistical analyses indicated significantly lower Co concentrations and significantly higher Fe, Cr, and Sb concentrations at polluted stations. While industrial input of Cr and Sb was suspected, no such input was known for Fe. Higher Fe concentrations may result from mobilization of iron from reducing bottom sediments or from input with domestic sewage. Elevated concentrations of Cr and Sb have been observed near other municipal sewage outfalls (15). Lower Co could result from dilution with organic solid wastes. Each mode of transport expressed as percent metal concentration is given in Table II and Figure 2. These data are from samples collected January to March 1974. Table II also contains statistical results.

At control stations Cr was transported principally as crystalline minerals. Transport with oxide coatings and as adsorbed ions was also important, whereas transport as soluble or organically bound species was not important. At polluted stations Cr was associated principally with oxides and with the organically bound fraction. The percentage Cr adsorbed and in crystalline minerals was small, and the soluble portion was negligible.

Significant differences between control and polluted stations were found among all Sb transport modes except the adsorbed fraction. At control stations nearly all Sb was in crystalline minerals, whereas downstream of waste discharge, Sb was associated with oxides.

The major fraction of Co was adsorbed or found with crystalline minerals. No significant differences between control and polluted stations were noted among any of the Co transport modes except for the organically bound fraction which was larger at polluted stations.

Fe was transported principally as oxides at all stations, and its transport in crystalline minerals was also important. The percentage of Fe in oxide coatings was significantly larger at polluted stations, while the percentage in crystalline minerals was significantly smaller. There were no differences in soluble, adsorbed, or organically associated Fe.

These data agree with several other studies (5, 16, 17) that indicate suspended sediment is important to fluvial transport of metals; transport in soluble forms was found important only for Co. The nature of the association between metal and solid phases appeared to depend both on the metal and the station class but not on flow. In multiple regression analysis giving consideration to flow and sample location, flow did not alter the primary association between location and metal concentration.

It is interesting to compare the control station data with other investigations. Gibbs (5) found less Fe in oxide coatings (44%) and more Fe crystalline minerals (47%) in the Amazon and Yukon rivers. He also found much less Cr in the oxide coating (5%) and more in crystalline structures (70%). The percentages of soluble, adsorbed, and organically bound Fe

Table I. Mean Suspended Sediment Metal Concentrations in $\mu\text{g/g}$

station	Cr	Sb	Co	Fe ($\times 10^2$)
control				
1	83	11.1	11.2	541
2	112	16.5	23.6	504
3	125	7.0	18.6	775
overall mean	106	12.5	17.8	607
polluted				
4	163	123	10.1	661
5	240	79	10.2	768
overall mean	202 ^a	101 ^a	10.2 ^a	714 ^a

^a Significant difference at $\alpha = 0.05$ between overall mean control and polluted station metal concentrations.

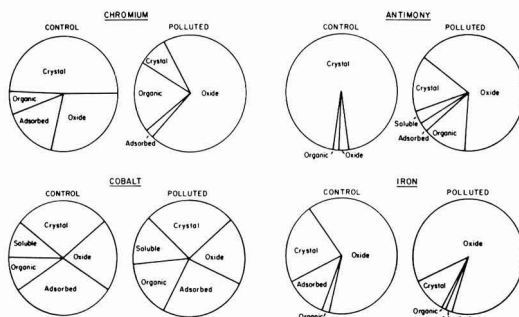


Figure 2. Fraction of metal in each mode of transport

were lower, and the percentages of Co in the soluble and adsorbed form were considerably less than those found in the present study. Angino and Schneider (18) found Co distributed almost equally between oxide coatings and organic + adsorbed phases and found no Co in crystalline minerals. Strong correlations between Fe and Co concentrations have been noted in several studies (19, 20), suggesting the importance of precipitation and dissolution reactions of Fe hydroxides and oxyhydroxides in regulating Co concentrations through sorption and coprecipitation reactions. All these studies were performed in areas removed from waste inputs, and the differences in the modes of metal transport likely reflect geochemical and geological differences.

Data from polluted stations reflect transport modes resulting from anthropogenic inputs of metals and domestic wastes. Association with oxide coatings was the principal mode for Cr (70%) and Sb (65%) at polluted stations. The remaining portion of these materials was transported with organic matter and crystalline minerals. Analytical concentrations in the crystalline form were similar for control and polluted stations, but the percentage of total metal in this form was much smaller at polluted stations presumably because Cr and Sb wastes were added in other forms. No significant differences

Table II. Percentage of Metal Transported in Each of Five Transport Modes at Control and Polluted Stations

transport mode	Cr		Sb		Co		Fe	
	control	polluted	control	polluted	control	polluted	control	polluted
soluble	0.0 (0.0) ^a	0.0 (0.0)	0.0 (0.0)	3.7 (0.6) ^b	10.3 (4.9)	14.6 (1.6)	0.0 (0.0)	0.0 (0.0)
adsorbed	15.7 (6.2)	2.4 (1.6)	0.0 (0.0)	2.6 (1.1)	32.0 (4.8)	25.1 (2.1)	12.2 (7.5)	2.2 (0.6)
oxide coating	29.2 (8.9)	69.9 (5.9) ^b	1.6 (1.6)	64.0 (2.5) ^c	19.9 (3.6)	18.2 (3.6)	63.6 (7.0)	86.8 (1.2) ^b
solid organics	6.8 (4.6)	19.8 (3.1) ^d	3.3 (3.3)	10.3 (1.5) ^b	10.8 (1.0)	16.1 (2.8) ^b	1.8 (0.5)	1.0 (0.4)
crystalline mineral	48.3 (8.5)	7.9 (4.0) ^c	95.2 (3.4)	12.6 (1.2) ^c	28.3 (4.1)	25.2 (1.8)	22.4 (4.3)	10.0 (1.1) ^d

^a Standard error of the mean given in parentheses. ^b Significant difference at $\alpha = 0.01$ between control and polluted station metal concentrations in each given transport mode. ^c Significant difference at $\alpha = 0.001$ between control and polluted station metal concentrations in each given transport mode. ^d Significant difference at $\alpha = 0.05$ between control and polluted station metal concentrations in each given transport mode.

in soluble or adsorbed Cr were noted between station classes. On the other hand, a significantly larger percent of Co was transported with organics at polluted stations, with soluble and adsorbed forms accounting for about 40%. These results agree with a model for Cr and Co in sewage (21) which suggests that Cr exists as the solid Cr (III) hydroxide and that Co exists principally in soluble and adsorbed forms. In general, Co, which had no known waste input, showed a high degree of phase stability between station classes, whereas Cr and Sb, elements which had large concentration increases due to waste inputs, showed large differences among modes of transport between station classes.

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Received for review April 16, 1976. Resubmitted January 23, 1978. Accepted May 5, 1978. Funding for this project received from the Water Resources Research Institute of the University of North Carolina, Project No. A-070-NC.

Application of the Rotated Disk Electrode to Measurement of Copper Complex Dissociation Rate Constants in Marine Coastal Samples

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■ A rotating disk electrode technique was used to estimate dissociation rate constants of copper chelates formed in marine coastal samples, to measure the extent of Cu chelation in these samples, and to establish an operational definition for labile and nonlabile metal complexes based on a kinetic criterion. Samples collected off the mid-Atlantic coast showed various degrees of chelation toward copper. A first order dissociation rate constant for copper chelates was estimated to be of the order of 2 s^{-1} .

Anodic stripping voltammetry (ASV) procedures are used to estimate the degree of metal-organic complexation in marine and fresh waters and the concentration of organic ligand sites in solution available for binding with added metal (called the water's "complexation capacity"). Complexed metal is estimated from the ratio of the ASV current at natural pH values to the current obtained after sample oxidation or at some low pH value where the metal is assumed uncomplexed (1-4). Complexation capacity is determined from the endpoint of a titration of the organic chelates with metal (4, 5). Shuman and Woodward (6, 7) demonstrated that this titration could be used for estimating conditional formation constants. All these procedures rely on the assumption that ASV can distinguish between "labile" and "nonlabile" complexes. The use of the terms labile and nonlabile is unfortunate because lability refers to the ability of a complex in solution to make and break bonds rapidly and to rapidly exchange a ligand within the metal coordination sphere for one outside this

sphere. Lability as a term applied to the ASV experiment has an operational definition related to the observed stripping current. Reduction of the metal ion during ASV pre-electrolysis at the mercury electrode lowers its concentration near the electrode and disturbs the equilibrium between the complex and its components. A complex that dissociates rapidly enough to maintain equilibrium is called a labile complex, and requires a rate of dissociation at least as rapid as the rate of metal mass transfer to the electrode surface. ASV currents result from the reduction of metal ions supplied by dissociation of labile complexes. A nonlabile complex in this terminology is one that dissociates very slowly and does not produce a current.

Complexes with dissociation rates that fall between the operational definition of labile and nonlabile complexes contribute to ASV currents to an extent that depends upon their dissociation rate and their concentration. Shuman and Woodward (6) corrected for these contributions by varying ligand concentration, but the procedure is not recommended for natural water samples because it necessitates dilution or concentration of the sample.

Shuman and Michael (8) introduced a technique that has sufficient sensitivity for kinetic measurement at very dilute solutions. It combines ASV with the rotating disk electrode (RDE) and provides a method for measuring kinetic dissociation rates in situ and a method for distinguishing labile and nonlabile complexes kinetically, consistent with the way they are defined. The RDE is essentially a flow system with solution transported across the face of the disk electrode in lam-

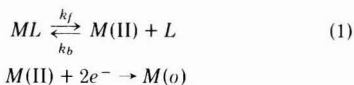
inar flow at a rate dependent on the rate at which the electrode is rotated. The time available for a complex to dissociate as it moves across the disk can be manipulated by varying the rotation rate. The dichotomy between "labile" and "nonlabile" complexes is operationally and unambiguously defined, and information about metal speciation is obtained from one series of experiments without resort to unrelated procedures such as photo-oxidation or drastic reduction of solution pH. In addition, rate constants for kinetic dissociation of complexes are obtained.

Copper toxicity to fresh water and marine phytoplankton in metal buffer solutions (TRIS or EDTA) has been studied as a function of Cu activity measured with an ion selective electrode (9, 10). In this media noncomplexed Cu as opposed to total Cu appears responsible for inhibiting growth. Related evidence indicates humic materials in natural waters suppress metal toxicity by complexation (11, 12). Duursma and Morgan (13) have suggested that metal availability to organisms may not be influenced simply by metal complex stability but may be related to the kinetic dissociation rates of complexes as well. Testing this hypothesis has been hampered by the lack of techniques capable of measuring kinetics at concentrations as low as those found in natural waters.

No in situ measurements of complex dissociation rates in natural waters have been reported to date although the dissociation rates of iron-humate complexes in synthetic solutions of high concentration have been estimated by a stopped flow method (14). The objectives of the work reported here were to demonstrate the utility of the RDE technique for estimating dissociation rate constants of copper chelates in natural waters, for measuring the extent of Cu chelation in these samples, and for establishing an operational definition for labile and nonlabile complexes based on kinetic measurements.

Procedures

The utility of a mercury-plated rotated disk electrode for measuring dissociation kinetics of metal complexes in natural waters was suggested by earlier work with model systems of Cd-NTA and Cd-EDTA solutions (8). A detailed description of the technique, its mathematical development, the equipment, and the general procedures used for each experiment is available in that reference. Briefly, anodic stripping voltammetry is combined with the RDE to allow kinetic measurements at a very low metal concentration. Electrolysis of the uncomplexed metal (the complex itself is not reduced at the applied potential) is described by the overall reaction:



and is carried out at constant potential for a period of 5–10 min for a series of electrode rotation rates, ω , in the range of about 50–3000 rpm. The amount of electricity passed during electrolysis, Q_k , is measured by integrating the oxidation (stripping) current and is a function of the kinetic dissociation constant of the complex, k_f , the ratio of uncomplexed to complexed metal, K , and the rotation rate. In general, Q_k increases as k_f and K increase (increased availability of M) and decreases as the experimental parameter, ω , is increased (less time for dissociation). The data are plotted as the ratio Q_k/Q_o , or its inverse, as a function of rotation rate where Q_o is the amount of electricity that would be passed during electrolysis if all the metal present were reducible. When Q_k/Q_o is plotted against ω or $\omega^{1/2}$, $Q_k/Q_o \rightarrow 1.0$ as $\omega \rightarrow 0$ because at very slow rotation rates all complexes have time to dissociate. At the limit of high rotation rates, there is no time for dissociation

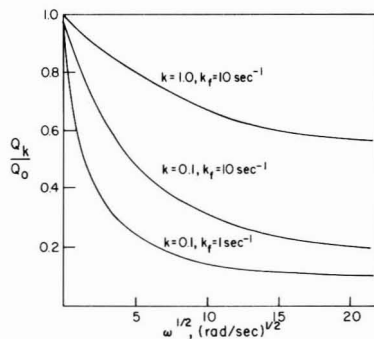


Figure 1. Q_k/Q_o vs. $\omega^{1/2}$ for two values of K and of k_f

and only uncomplexed metal is reduced at the disk. Therefore

$$Q_k/Q_o \rightarrow \frac{[M]}{[M] + [ML]} = \frac{K}{K + 1}$$

as $\omega \rightarrow \infty$. Kinetic information is obtained from data between these two limits.

Surface samples were collected during a cruise of the R/V *Columbus Iselin*, 28 March–2 April 1976. Samples from three stations, #2, #8, and #20, were run immediately after collection. Stations #2 and #20 were located on the western edge of the Gulf Stream off Cape Romain and Jekyll Island, respectively, and station #8 was on the western edge of the Sargasso Sea. Copper was added to the aliquot placed in the electrolysis cell to make stations #2 and #8, 50 ppb Cu(II) and station #20, 10 ppb Cu(II). Another aliquot of each sample was spiked with copper to 5×10^{-5} M Cu(II) to obtain Q_o at each rotation rate. These two concentrations were run for each sample at six rotation rates, and each rotation rate was run in triplicate. Collection of one data set for one sample required 8–12 h.

For comparison another surface sample from the continental shelf, about 20 miles south of Cape Lookout, was collected on the R/V *Machapunga*, the University of North Carolina Institute of Marine Sciences vessel. This sample was frozen immediately and returned to the laboratory in Chapel Hill. Aliquots were spiked with Cu(II) to concentrations of 7.5, 8.5, and 10 ppb.

All samples were filtered through thoroughly acid washed 0.45- μm filters prior to copper addition. Pre-electrolysis was carried out at -0.500 V vs. a Ag/AgCl reference electrode.

Results and Discussion

Analysis of the data was based on both the theory of Levich (15) and of Hale (16). According to Levich (15) k_f can be obtained by plotting Q_o/Q_k vs. $\omega^{1/2}$ according to

$$\frac{Q_o}{Q_k} = 1 + \frac{D^{1/6}\omega^{1/2}}{1.61 K \left[k_f \left(1 + \frac{1}{K} \right) \right]^{1/2} \nu^{1/6}} \quad (2)$$

The diffusion coefficient, D , used to calculate k_f is obtained by plotting Q_o vs. $\omega^{1/2}$ (15), and K can be obtained by plotting Q_k/Q_o vs. rotation rate. Hale's theory (1964) for kinetic dissociation is more general than the theory of Levich, but it is in the form of a numerical solution. Theoretical plots of Q_k/Q_o vs. $\omega^{1/2}$ using Hale's theory are shown in Figure 1 for two values of K and k_f and for rotation rates ranging from zero to about 3500 rpm. Two features are notable. First, the lines tend toward a constant value of Q_k/Q_o at high rotation rate, and second, for a given K , the approach to this limit is faster for smaller dissociation rate constants. The limiting value of

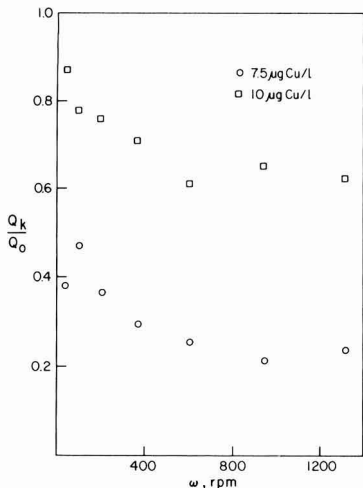


Figure 2. Q_k/Q_o vs. ω for 7.5 and 10 μg Cu/L additions to coastal sample

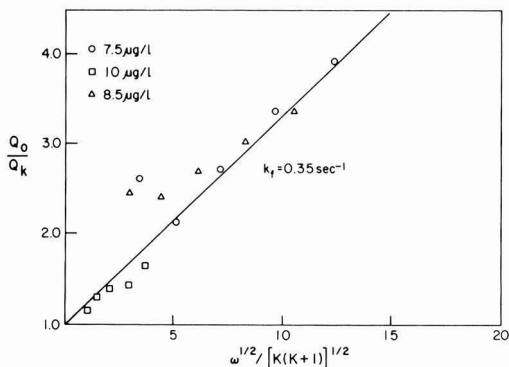


Figure 3. Q_o/Q_k vs. $\omega^{1/2}/K^{1/2}(K+1)^{1/2}$ for coastal sample and three Cu additions

Q_k/Q_o is simply the ratio $[M]/M_{\text{Total}}$, that is, the ratio of kinetically labile metal to total metal. The value of K is understood then as the ratio of "labile" to "nonlabile" metal and is related to the limiting value of Q_k/Q_o by $Q_k/Q_o = K/(K+1)$.

Figure 2 shows the RDE data for 7.5 and 10 ppb additions to the sample of coastal water. Both concentrations show a decrease in Q_k/Q_o with increasing rotation rate as expected for kinetic dissociation and the higher concentration levels off at a higher value indicating a larger K . From the limiting values, K was determined to be 0.22 for 7.5 ppb, 0.28 for 8.5 ppb, and 1.2 for 10 ppb. The value of Q_o/Q_k for each rotation rate and for each of these three concentrations was plotted vs. $\omega^{1/2}/K^{1/2}(1+K)^{1/2}$ (Figure 3) in accordance with Equation 2, and a dissociation rate constant $k_f = 0.35 \text{ s}^{-1}$ was calculated from the slope. Hale's theory and the experimental data were compared using a multiparametric curve fitting routine adapted from McCullough and Meites (17). The lines of best fit are presented with the data points in Figure 4. The value of k_f obtained from the fit of the data was $k_f = 1.8 \pm 0.7 \text{ s}^{-1}$ using D of $1.3 \times 10^{-6} \text{ cm}^2/\text{s}$.

The data from the three cruise stations are plotted in Figure 5. Station #20 shows a nearly constant value of 1.0 indicating no complex formation. For station #2 a value of $K = 3.0$ was obtained indicating about 25% of the added metal was com-

plexed, but no kinetic dissociation was observed. Station #8 showed a marked drop-off of Q_k/Q_o with ω and these data gave $k_f = 2.3 \text{ s}^{-1}$ (Figure 6) when 0.25 was used for the value of K .

Finally, the method of comparing experimental data with Hale's theory was evaluated by applying it to the model chemical system of CdEDTA and data reported earlier (8). The curve fitting routine returned a value of $k_f = 11.3 \text{ s}^{-1}$, which compares very favorably with 10.8 s^{-1} obtained by polarography (18) and 12.5 s^{-1} obtained by using Levich's theory (8). A good fit between theory and experiment was obtained (Figure 7).

In summary, the RDE technique is capable of distinguishing labile and nonlabile complexes by virtue of its ability to measure metal availability for reduction over a wide range of time scales. At high rotation rates only free metal and metal from complexes with large dissociation rates are available, whereas at low rotation rates, all metal except complexes with slow dissociation rates is available. The limiting values of k_f that can be measured depend on K , D , k_f , and the range of rotation rates employed. For example, for the diffusion coefficient and the range of rotation rates used in this work, if the metal is 50% complexed ($K = 1.0$), dissociation rate constants

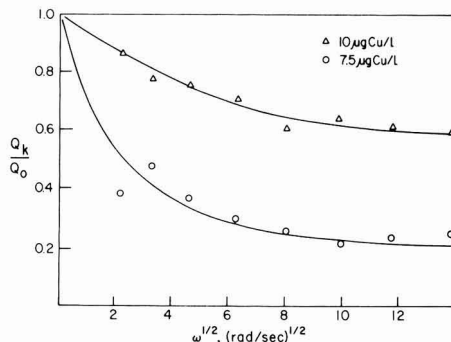


Figure 4. Q_k/Q_o vs. ω for 7.5 and 10 μg Cu/L additions to coastal sample

Line is fitted theory for 10 μg Cu/L, $K = 1.2$, $k_f = 3.8 \text{ s}^{-1}$, and for 7.5 μg Cu/L, $K = 0.22$, $k_f = 0.95 \text{ s}^{-1}$

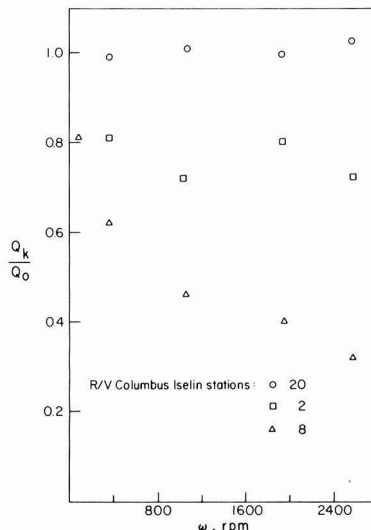


Figure 5. Q_k/Q_o vs. ω for Columbus Iselin stations 2, 8, and 20

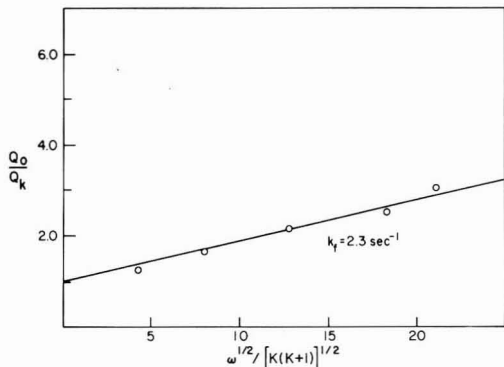


Figure 6. Q_0/Q_k vs. $\omega^{1/2}/K^{1/2}(1+K)^{1/2}$ for Ileslin station 8

between 0.2–400 s^{-1} can be estimated. A small degree of complexation limits the measurements to large rate constants. For example, the rate constant for station 2 where $K = 3.0$ can only be estimated to be less than about 1.5 s^{-1} .

These results demonstrate the capabilities of the RDE technique to obtain information about metal chelation in seawater. The RDE is capable of giving quantitative information about the extent of metal chelation; it can operationally separate "labile" from "nonlabile" metal complexes; and it estimates the dissociative rate constants of "nonlabile" complexes. The power of this technique resides in its ability to measure both equilibrium concentrations and kinetic availability of soluble metal in an aqueous environment and should be useful for studies of metal toxicity to aquatic and marine organisms.

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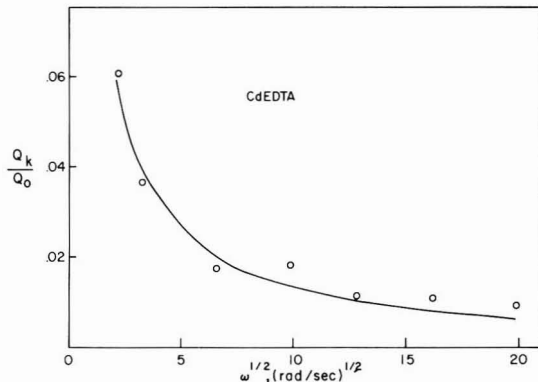


Figure 7. Comparison between Hale's theory, $k_f = 11.3 s^{-1}$ and $K = 9.8 \times 10^{-5}$, and CdEDTA data from ref. 8

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Received for review January 13, 1978. Accepted April 24, 1978. Work supported by the Oceanographic Section, National Science Foundation, NSF Grant OCE 73-21045.

Chemiluminescent Method for Determination of Hydrogen Peroxide in the Ambient Atmosphere

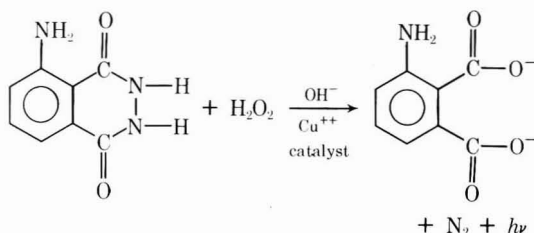
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The quantitative determination of hydrogen peroxide (H_2O_2) in the ambient atmosphere is important because of the role that H_2O_2 plays in the formation of photochemical smog (1–3). The two analytical methods currently in use for atmospheric H_2O_2 determinations are wet chemical methods involving the formation of a colored Ti(IV) complex (4–6). These methods have marginal sensitivity for atmospheric H_2O_2 determinations. As an alternative to these analytical methods, we have developed a chemiluminescent method for H_2O_2 determination in the ambient atmosphere. This chemiluminescent system has been successfully employed in studies of ambient H_2O_2 concentrations (7).

The chemiluminescent oxidation of 5-amino-2,3-dihydro-1,4-phthalazinedione (luminol) by H_2O_2 in the presence of a

metal ion catalyst has been studied extensively as an analytical system for metal ion determinations (8–10). The luminol reaction is shown in Equation 1.



■ A chemiluminescent method was developed for the determination of low concentrations of hydrogen peroxide (H_2O_2) in the ambient atmosphere. The analytical system was based on the oxidation of 5-amino-2,3-dihydro-1,4-phthalazinedione (luminol) by H_2O_2 in the presence of a Cu(II) cat-

In these systems (8-10) the metal ion has been used as the limiting reagent, and the H_2O_2 and luminol have been present in excess. The chemiluminescent oxidation of luminol can also be used for the determination of H_2O_2 when luminol and the metal ion catalyst are present in excess (11, 12). These systems have been used for the determination of H_2O_2 produced through enzymatic oxidation of glucose.

Experimental

Figure 1 is a diagram of the basic instrumentation for the determination of H_2O_2 using the chemiluminescence technique. The design goal was to provide a system compatible with the two types of sampling methods, impingers and continuous extraction, available for the determination of atmospheric pollutants by wet chemical methods.

Semicontinuous Analytical System. The analytical system shown in Figure 1 is designed for the determination of H_2O_2 in the liquid phase. For the determination of atmospheric H_2O_2 , samples are collected in aqueous solution using midjet impingers. The reagent flow in the system is maintained with a Technicon Auto Analyzer Type II pump. Technicon Flow Rated pump tubing is used to ensure reproducibility when the pump tubes are changed. The flow rates for each of the reagents are selected to give a moderate flow velocity with minimum dilution effects on the sample. The reagent concentration is adjusted to give optimum sensitivity commensurate with these flow rates. The entire flow system is constructed of $1/16$ -in. o.d. Teflon tubing, with the exception of the pump tubes.

Impinger collected and calibration samples of H_2O_2 are injected into the system using an Altex 201-06 slide injection valve with a 1-mL sample loop. Mixing of H_2O_2 solution and reagents takes place simultaneously at the reaction cell. The reaction cell is a flat spiral constructed from 4-mm o.d. glass tubing. To optimize light collection from the chemiluminescent reaction, the cell is positioned within 2 mm of the photomultiplier tube face. The chemiluminescent emission from the luminol reaction is centered at about 450 nm, making the use of a blue sensitive, high gain, RCA-4507 photomultiplier tube practical. No optical filtering is used, since no other chemiluminescent reactions are known to give spectral interference. The photocurrent is amplified using a Kiethly 414S picoammeter and displayed on a strip chart recorder.

Reagents. All reagent solutions were prepared using distilled and deionized water. Hydrogen peroxide standard solutions were prepared fresh daily by dilution of a 1% stock

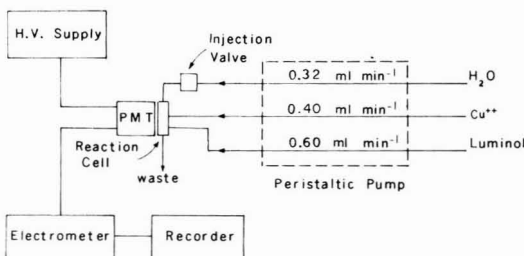


Figure 1. Analytical system for measurement of H_2O_2 in liquid phase

alyst. The sensitivity for gas-phase H_2O_2 was better than 1 ppb. Measurement of atmospheric H_2O_2 can be done using impinger or continuous gas-phase sampling techniques. The instrumentation was tested with a wide range of interfering species, and no significant interferences were observed.

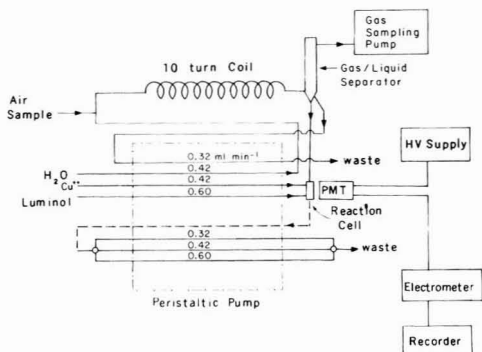


Figure 2. Analytical system for measurement of H_2O_2 in gas phase

H_2O_2 solution. The concentration of the H_2O_2 stock solution was established by titrating it with standard $KMnO_4$ solutions. Copper (II) nitrate was prepared by dissolving high-purity copper wire in nitric acid.

The purity of the luminol is crucial in obtaining optimum sensitivity from the analytical system. Luminol as supplied by the chemical manufacturer has an unknown impurity, which causes elevated background signals and reduced chemiluminescence activity. For purification of the luminol, the commercial material (Eastman) is dissolved in NaOH, the insoluble material is filtered off, and the luminol precipitated as the monosodium salt (13). The monosodium salt of luminol has better stability and dissolves readily in solution. Further mention of luminol assumes it is as the monosodium salt.

Continuous Analytical System. A modification of the inlet system of the instrument permits H_2O_2 to be determined directly from the gas phase. Figure 2 shows the modified system and reagent flow rates. This system uses a continuous extraction process to sample the H_2O_2 from the atmosphere and concentrate it in the liquid phase. The H_2O_2 in solution is analyzed using chemiluminescence instrumentation identical to that previously described. To differentiate between the two sampling systems, using impingers or continuous gas-phase sampling, they will be referred to as liquid-phase or gas-phase methods, respectively.

In the continuous analytical system sample, air and distilled water are continuously drawn through an absorbing coil, and the atmospheric H_2O_2 is extracted into the aqueous solution. The absorbing coil is made by shortening a stock NO_2 absorbing coil, Technicon No. 181-G012-02, to 10 turns and adding a Laboratory Data Control No. GC-1 glass to Teflon connector for the solution inlet. Air/ H_2O / H_2O_2 enter the gas/liquid separator through a 4-mm glass nipple located near the bottom of the separator. The bottom of the separator is formed to provide a small reservoir of solution with the excess solution being drawn off through the overflow. To minimize residence time for the H_2O_2 solution in the system, the connection between the gas/liquid separator and the reaction cell is kept as short as possible. This requirement made it impossible to pump the H_2O_2 solution into the cell; thus, solution is drawn into the cell by pumping solutions out from the cell.

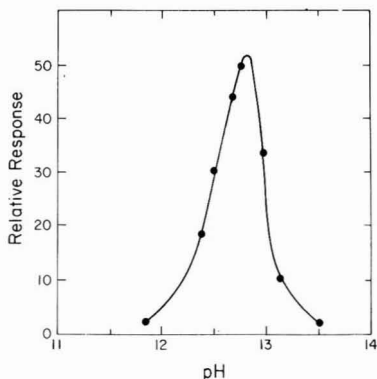


Figure 3. Response of chemiluminescence system to variations in pH

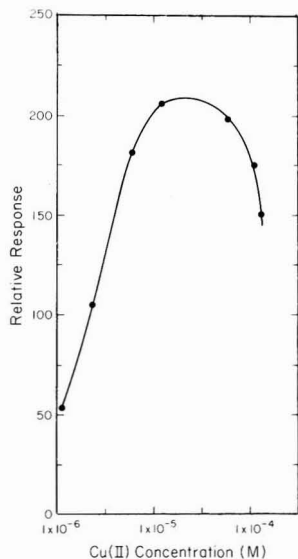


Figure 4. Response of chemiluminescence system to variations in Cu(II) concentrations

An examination of Figure 2 shows that both Cu(II) catalyst and luminol solutions are pumped into the reaction cell. The combined flow rate of these reagents is 1.02 mL min^{-1} . A total flow rate of 1.34 mL min^{-1} is pumped out of the cell; thus, 0.32 mL min^{-1} of H_2O_2 solution is drawn into the cell. The liquid flow rate into the absorbing coil is 0.42 mL min^{-1} ; the excess, 0.10 mL min^{-1} , is withdrawn through the overflow in the side of the gas/liquid separator. While a large amount of sample is essentially wasted, the overflow ensures that no bubbles enter the reaction cell.

Results and Discussion

Optimization. The liquid-phase H_2O_2 analytical system was used for optimization and linearity studies. The gas-phase system differs only in the sample absorbing coil; therefore, results obtained with the one system will apply to the other. In previous work (11, 12) on the determination of H_2O_2 using luminol chemiluminescence, potassium ferricyanide had been used as the catalytic reagent. Initial investigations with our system using ferricyanide as the catalytic reagent showed good sensitivity for H_2O_2 but high background signals, typically two

orders of magnitude above the photomultiplier tube dark current. Further investigations showed that Cu(II) is an excellent catalyst, providing high sensitivity for H_2O_2 with minimal background signal.

The sensitivity of the analytical system is very dependent on the concentrations of the various reagents. To optimize the sensitivity of the analytical system for H_2O_2 , a systematic study of the effect of varying pH, luminol, and Cu(II) concentrations was done. Figures 3 and 4 show the relative response of the system for variations in Cu(II) concentration and pH, respectively. The concentrations shown in Figures 3 and 4 are for the reagents as they are drawn into the analytical system. These concentrations are diluted at the reaction cell by the ratios of the various flow rates to the total reagent flow rate. The system does not show large changes in sensitivity with changes in luminol concentration. The maximum sensitivity for H_2O_2 is obtained at a luminol concentration of $2.4 \times 10^{-4} \text{ M}$. Over the luminol concentration range of 2.4×10^{-3} to $4.8 \times 10^{-5} \text{ M}$, the system sensitivity for H_2O_2 changes less than 50%.

Since the chemiluminescent reaction of luminol- H_2O_2 occurs only in basic solution, both the Cu(II) catalyst and luminol are prepared in solutions adjusted to pH 12.8 by the addition of NaOH. The concentration of Cu(II) used for analytical work is $1.5 \times 10^{-5} \text{ M}$.

Linearity. The linearity of the system is excellent as shown in Figure 5. Additional points not shown on this figure extend the linearity to 1 ppm. The sensitivity of the system for H_2O_2 in the liquid phase is better than 1 ppb. The standard deviation for samples at the 20 ppb level is about 4%. After approximately 30 min of operations the baseline drift for the

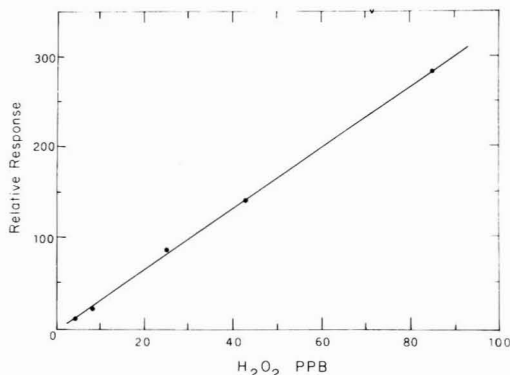


Figure 5. Linearity of H_2O_2 analytical system

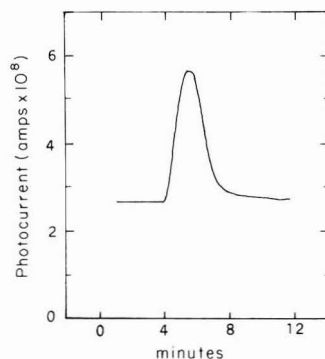


Figure 6. Response of liquid-phase analytical system to 10 ppb H_2O_2

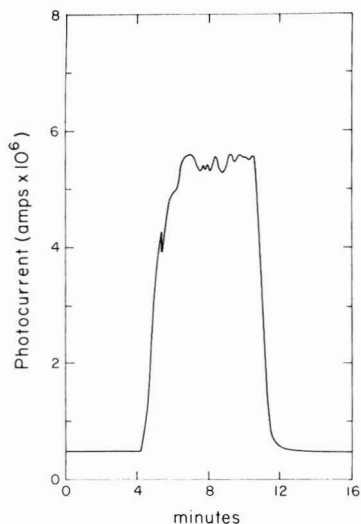


Figure 7. Response of gas-phase analytical system to input of approximately 20 ppb H_2O_2

system is essentially zero. Typically, the calibration shift for both systems was less than 10% per day. Figure 6 shows the response of the liquid-phase system to a 10 ppb H_2O_2 sample. The response of the gas-phase sampling system to a 20 ppb H_2O_2 sample is shown in Figure 7. At a sample flow rate of 2 $L\ min^{-1}$, the signal rise and fall times are about 1.5 min.

Sampling System Efficiency. Careful studies on the sampling system showed no loss of H_2O_2 during the sampling operation. The impingers were checked by placing a sample of 10 ppb H_2O_2 in the impinger and bubbling clean air through the impinger for 30 min at 1 $L\ min^{-1}$. Analysis of the H_2O_2 sample from the impinger showed no loss of H_2O_2 . The gas-phase sampling system was checked in a similar manner. A sample of 10 ppb H_2O_2 was injected into the absorbing coil, along with clean air at 2 $L\ min^{-1}$. Comparison of the system response with a standard 10 ppb H_2O_2 solution showed no loss of H_2O_2 .

The sampling efficiency of the impingers was checked by placing two impingers in series and sampling gas-phase H_2O_2 at a concentration of approximately 20 ppb. Analysis of both impingers for H_2O_2 showed that better than 95% of the H_2O_2 had been trapped by the first impinger.

The efficiency of the absorbing coil on the gas-phase sampling method was checked by observing the response of the

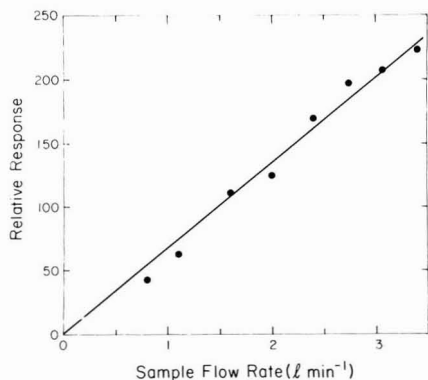


Figure 8. Response of gas-phase system to sample flow rate

Table I. Comparison of H_2O_2 Measurements^a by Chemiluminescence Using Impinger and Continuous Sampling Methods

Impinger sampling		continuous sampling	
period of measurement	H_2O_2 (ppb)	time at which reading was taken	H_2O_2 (ppb)
1:00-1:20	18	1:30	10
2:00-2:20	15	2:30	14
2:25-2:45	14	3:00	12
3:55-4:15	14	4:00	11
4:25-4:45	13	4:30	10

^a Ambient air samples July 27, 1977.

Table II. Effects of Interfering Species on Gas-Phase Sampling System for Chemiluminescent Determination of H_2O_2 ^a

compound	concn	% interference ^b
benzene	1 ppm	0
hexane	1 ppm	0
hexane	1 ppm	0
PAN	1 ppm	+2 ^c
NO_2	1 ppm	0
NO	1 ppm	0
SO_2	50 ppb	0 ^d
O_3	0.3 ppm	0

^a A gas-phase H_2O_2 concentration of approximately 20 ppb was present during these tests. ^b The percent value listed times the concentration of the interfering species is the response observed in terms of H_2O_2 concentrations. ^c The PAN was produced by photolysis of Cl_2 , NO_2 , and CH_3CHO in air (15). The PAN was not separated from the reaction mixture, and it is possible that the observed response is due to H_2O_2 produced as a side product in the reaction. ^d At higher concentrations of SO_2 (1 ppm), a strong negative interference is observed.

system while sampling 20 ppb gas-phase H_2O_2 as the sample flow rate was varied. These results are shown in Figure 8. Above a flow rate of 1600 $mL\ min^{-1}$, the response appears essentially invariant with flow rate. In addition, these points fit very well to a line which extrapolates through the origin. If the sampling efficiency were significantly less than 100%, nonlinear behavior as well as a nonzero intercept would be expected for this plot. The possible loss of sampling efficiency for the absorbing coil at flow rates less than 1600 $mL\ min^{-1}$ may be due to inefficient mixing of sample air and water absorbing solution. Typically, a sample flow rate of 2 $L\ min^{-1}$ is used with this system. In studies of H_2O_2 concentrations in the ambient atmosphere (7) using both the liquid- and gas-phase sampling systems, good correlation between the systems was noted. The gas-phase system typically gave a slightly lower response (approximately 10%) than the liquid-phase system. A comparison of the data obtained by the two sampling systems is shown in Table I.

Interference Tests. The exact mechanism of the chemiluminescent oxidation of luminol is not known, but is connected to the decomposition of H_2O_2 by the metal catalyst (8, 14). This specificity, coupled with the low solubility of other potentially interfering species under the sampling condition used, helps create an analytical system that is relatively interference free.

Table II shows the potentially interfering species tested on the gas-phase analytical system. These tests were made by doping a gas flow, containing approximately 20 ppb H_2O_2 with one of the listed potentially interfering species and observing the response. The only potentially interfering species tested which showed any response was peroxyacetyl nitrate (PAN).

Table III. Effect of Interfering Species on Chemiluminescence Analysis of H₂O₂ Using Impinger Sampling^a

compound	concn	% interference ^b
benzene	1 ppm	0
hexane	1 ppm	0
PAN	1 ppm	+4 ^c
NO ₂	1 ppm	0
NO	1 ppm	0
SO ₂	50 ppb	0
O ₃	0.3 ppm	0
C (particulate)	5 mg/m ³	0

^a A liquid-phase H₂O₂ concentration of 10 ppb was present during these tests.

^b The percent value listed times the concentration of the interfering species is the response observed in terms of H₂O₂ concentrations. ^c The PAN was produced by photolysis of Cl₂, NO₂, and CH₃CHO in air (15). The PAN was not separated from the reaction mixture; it is possible that the observed response is due to H₂O₂ produced as a side product of the PAN synthesis.

It is possible that a small amount of H₂O₂ was produced along with the PAN and that the observed response is not due to PAN.

The potentially interfering species tested on the liquid-phase sampling system are shown in Table III. Benzene and hexane were tested by making up a solution of 1 ppm benzene or hexane in a 10 ppb H₂O₂ solution. The checks on NO₂, NO, SO₂, and PAN were made by placing 10 mL of 10 ppb H₂O₂ in a midget impinger and pulling clean air, doped with one of the potentially interfering species, at 1 L min⁻¹ through the impinger for 10 min. Analysis of the solution gave the interference data shown in Table III. The interference response for the liquid-phase system is defined in the same terms as the gas-phase system. In these interference studies as well as in conducting ambient measurements (7), the impingers were cooled to 0 °C with an ice bath. This helps to minimize the reaction of H₂O₂ with an easily oxidized species that might be trapped. Some loss of H₂O₂ is noted as samples of ambient H₂O₂ are permitted to stand at room temperature for extended periods of time (e.g., 30 min).

Conclusions

The detection limit of the liquid-phase analytical system for H₂O₂ in the liquid phase is about 1 ppb. The use of an impinger for sampling ambient H₂O₂ provides preconcentration of the H₂O₂. Based on a sample flow rate of 1 L min⁻¹

for 15 min with a solution volume of 10 mL, the detection limit for H₂O₂ in the gas phase is about 0.5 ppb. For the gas-phase sampling system the preconcentration of H₂O₂ is slightly less than with impinger sampling, giving a detection limit of about 1 ppb in the gas phase.

The system described here has been employed in a study of H₂O₂ levels in ambient air (7). Comparison of the results obtained in the measurement of atmospheric H₂O₂ by the three currently available methods, TiSO₄, TiCl₄, and luminol chemiluminescence, shows relatively good correlation. The measured H₂O₂ levels, averaged over a 4-h period, were 12, 10, and 15 ppb H₂O₂ for the TiSO₄, TiCl₄, and luminol analytical methods, respectively. The differences observed in these data can be attributed to the difficulty in obtaining measurements at the trace levels observed in the atmosphere (i.e., generally ≤25 ppb).

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Received for review January 20, 1978. Accepted April 27, 1978. Work sponsored in part by the National Science Foundation-RANN (Grant No. ENV-76-14702). The contents do not necessarily reflect the views and policies of the NSF-RANN, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Ambient Air Measurements of Hydrogen Peroxide in the California South Coast Air Basin

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■ Hydrogen peroxide (H_2O_2) concentrations were measured at two locations (Claremont and Riverside) in the California South Coast Air Basin during the months of July and August 1977. Three different analytical methods were employed: a chemiluminescent method and two colorimetric procedures. Typical midafternoon concentrations of H_2O_2 during moderate smog episodes (i.e., $\text{O}_3 \sim 150\text{--}200$ ppb) ranged from approximately 10 to 30 ppb. These values were significantly lower than those measured in a study in Riverside in 1970. In general, maximum H_2O_2 concentrations were observed at about the time of the ozone maximum, but in the course of a day H_2O_2 levels did not occur in a fixed ratio to O_3 concentrations, and in a number of cases the concentrations of H_2O_2 declined more slowly than those of ozone following the O_3 maximum. During this investigation signals corresponding to elevated levels of H_2O_2 (i.e., ~ 100 ppb) were observed by all three methods when grass or forest fire plumes impacted on the measurement site.

Hydrogen peroxide (H_2O_2) is expected to be a mechanistically significant species in photochemical smog as a chain terminator and as an index of hydroperoxyl radical (HO_2) concentrations (1-3). Thus, knowledge of the concentration of H_2O_2 in both polluted ambient atmospheres and in simulated atmospheric systems is of considerable interest, particularly to atmospheric modelers (2-6). However, due to the analytical difficulties encountered in measurements of part per billion (ppb) concentrations of H_2O_2 , there have been relatively few laboratory or smog chamber studies in which H_2O_2 was monitored. In the laboratory studies H_2O_2 has been shown to be a product of the NO_x -photooxidation of formaldehyde (1, 7, 8) and of hydrocarbons (9-11). There has been only one set of atmospheric measurements, that of Bufalini et al. (8, 9, 12) in 1970. These workers reported H_2O_2 concentrations of up to 40 ppb in Hoboken, N.J., and of up to 180 ppb in Riverside, Calif.—in the latter case during a very severe smog episode in which the oxidant concentration reached 0.65 ppm.

Until recently, only the wet chemical titanium sulfate (TiSO_4) colorimetric method of Purcell and Cohen (7) has been available for measurement of trace quantities of H_2O_2 ; with long-path infrared spectroscopy, H_2O and CH_4 interferences substantially raise the detection limits for H_2O_2 . Recently, however, Kok et al. have developed a chemiluminescent method for the determination of H_2O_2 (13), and Pilz and Johann have put forward a titanium tetrachloride (TiCl_4) colorimetric method (14), which has been adapted (15) at the Statewide Air Pollution Research Center (SAPRC) of the University of California for chamber and ambient air measurements of low H_2O_2 concentrations.

We report here a joint investigation by workers from Harvey Mudd College, the UC-SAPRC and the Environmental Protection Agency (EPA) whose purpose was to obtain new

measurements of H_2O_2 levels at receptor sites in the California South Coast Air Basin (SCAB) (in conjunction with the measurements of other pollutants) using three different methods of analysis. An unanticipated outcome of the present study was the observation of elevated H_2O_2 concentrations in wildfire plumes which impacted the sampling sites during ambient air monitoring.

Experimental

In an initial study, H_2O_2 measurements were made at the Harvey Mudd College campus at Claremont, Calif., using the luminol-based chemiluminescent method, which has been described in detail elsewhere (13). Briefly, the analytical system is based on the chemiluminescent oxidation of luminol by hydrogen peroxide in the presence of a metal catalyst. This reaction is carried out in a solution buffered to about pH 12. The reagents are metered by a peristaltic pump and mixed at the reaction cell. A high gain photomultiplier tube and associated electronics are used for measurement of the chemiluminescent light intensity. With this basic system a detection limit for hydrogen peroxide in the liquid phase of about 1 ppb is observed. Atmospheric H_2O_2 can be sampled by trapping the H_2O_2 in a midjet impinger and analyzing the solution directly. In the present study sampling intervals were 15-20 min, and this gave a detection limit of approximately 0.4 ppb for gas phase H_2O_2 .

A modification to the sampling system of the chemiluminescent H_2O_2 analyzer permits continuous determination of atmospheric H_2O_2 . In place of the liquid sampling valve, a scrubbing coil is added to the sampling inlet of the basic chemiluminescent analyzer. Air and distilled water are continuously drawn through the coil, and the H_2O_2 is concentrated in the aqueous solution. The concentration of hydrogen peroxide in this solution is determined directly by the chemiluminescent analyzer. The sensitivity of this system for atmospheric H_2O_2 is approximately 1 ppb. Other atmospheric gases do not interfere significantly in the analysis for hydrogen peroxide with either of these analytical systems. In this study a glass and Teflon sampling system was used to bring outside air into the instrument laboratory. A Dasibi UV analyzer was used for the ozone measurements.

In Riverside, Calif., a series of measurements was made at the Statewide Air Pollution Research Center located on the University of California campus. In addition to measurements with the chemiluminescent method described above, H_2O_2 was monitored by two methods employing titanium salts, the Cohen and Purcell, TiSO_4 -8-quinolinol, method, which has been described previously (6, 8, 10, 12), and a TiCl_4 method developed by Pilz and Johann (14) and modified by SAPRC workers (15).

Briefly, the TiSO_4 -8-quinolinol method involves passing the air sample through a coarse fritted bubbler containing an aqueous $\text{TiSO}_4/(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ solution at a concentration of $\sim 50 \mu\text{g mL}^{-1}$ of Ti(IV) . After sampling, the pH of the so-

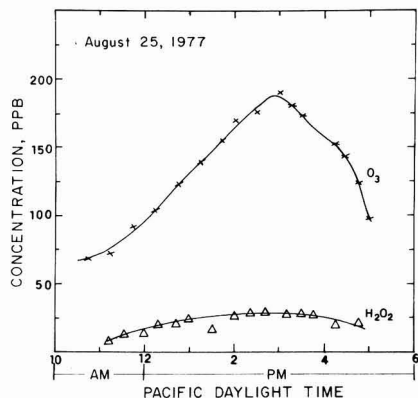


Figure 1. Ambient H_2O_2 and O_3 concentrations measured at Claremont, Calif.

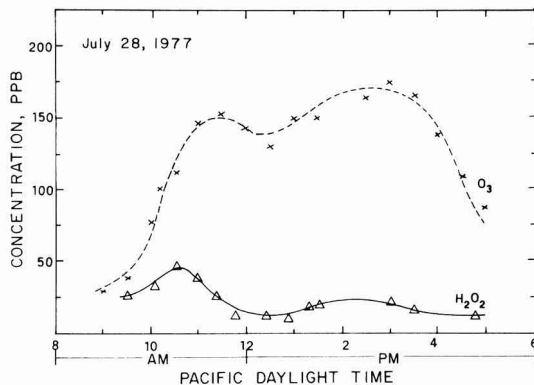


Figure 2. Ambient O_3 and H_2O_2 concentrations measured at Riverside, Calif.

lution is adjusted to 4.2 ± 0.2 using a sodium acetate buffer, and the mixture is then shaken with an aliquot of 0.1% 8-quinolinol in chloroform. The absorbance at 450 nm of the $\text{Ti(IV)}\text{-H}_2\text{O}_2\text{-8-quinolinol}$ complex in chloroform is determined ($\alpha = 3060 \text{ M}^{-1} \text{ cm}^{-1}$).

The TiCl_4 method involves sampling through a midjet impinger containing an aqueous TiCl_4/HCl solution at a concentration of $\sim 8 \text{ mg mL}^{-1}$ of Ti(IV) . A stable $\text{TiCl}_4\text{-H}_2\text{O}_2$ complex is formed immediately, and after dilution to a known volume, the absorbance of the complex at 410 nm is determined ($\alpha = 735 \text{ M}^{-1} \text{ cm}^{-1}$). For H_2O_2 concentrations less than 100 ppb, 5-cm cells and a 0.05 A full-scale range were used. The principal difficulty encountered with this method was the formation of a fine precipitate, presumably consisting of either atmospheric particulates or TiO_2 formed in the solution. The presence of such precipitates contributes to scattering in the visible spectra with, as expected, the effect being more pronounced at shorter wavelengths. In the Riverside study NO and NO_2 were determined with a Bendix NO-NO_x analyzer, and O_3 measurements were made with a Dasibi UV analyzer.

Results and Discussion

Ambient Air Measurements. Measurements of H_2O_2 levels in the ambient atmosphere were made on July 19 and August 10 and 25, 1977, in Claremont, Calif., and in Riverside, Calif., during the week of July 25–29, 1977. Figures 1 and 2 show typical O_3 and H_2O_2 time-concentration profiles observed at Claremont and Riverside during the measurement periods. The majority of the H_2O_2 data reported here were gathered by the chemiluminescent method (8) since data points could either be recorded continuously or at 15–20-min intervals. The sampling periods for the TiSO_4 and TiCl_4 methods were from 40 to 60 min.

For the low ambient H_2O_2 concentrations encountered in this study, there were often significant differences between

results obtained with the three analytical methods, although generally these were not greater than the combined uncertainties associated with the respective methods. In general, the data from the two colorimetric techniques were more erratic and usually somewhat lower than concentrations obtained with the chemiluminescent method. Table I compares data obtained by the different analytical methods for one monitoring period. The uncertainties for the concentrations of H_2O_2 observed are assigned as approximately ± 5 ppb for the chemiluminescence method and ± 8 and ± 6 ppb for the TiSO_4 and the TiCl_4 methods, respectively. Of the two colorimetric methods the TiCl_4 procedure was experimentally most straightforward and appeared to provide more consistent data.

Differences between H_2O_2 concentrations obtained by the three methods (see Table I) are indicative of the substantial difficulties encountered attempting to quantitatively determine ambient concentrations H_2O_2 which were generally < 20 ppb. Sampling and handling procedures were somewhat more difficult in the field measurements than in laboratory experiments, and in the case of the colorimetric methods, signal-to-noise ratios and/or signal-to-background (for example, due to scattering by particles) ratios were low. For these reasons any one H_2O_2 concentration reported here may be uncertain by as much as a factor of two. Thus, the major contribution of the present study is to definitively establish the order of magnitude of H_2O_2 concentrations in moderate to severe photochemical smog episodes at downwind receptor sites as being of the order 10–20 ppb, rather than 1–2 or 100–200 ppb. Thus, for the purposes of those modeling photochemical smog formation, a value for H_2O_2 concentrations of 20 ± 10 ppb for times near ozone maxima of $\sim 0.15\text{--}0.35$ ppm seems appropriate on the basis of the data obtained here.

H_2O_2 concentrations obtained in the present study are very substantially lower than those obtained in the earlier work of Bufalini et al. (8, 10, 12). For example, in the former study at

Table I. Comparison of H_2O_2 Measurements^a by Three Different Analytical Techniques

TiSO_4^b		TiCl_4^c		chemiluminescent ^d	
period of measurement	H_2O_2 (ppb)	period of measurement	H_2O_2 (ppb)	period of measurement	H_2O_2 (ppb)
11:15–12:00	17	11:40–12:20	10	11:30–11:45	12
12:00–1:00	4	12:40–1:20	14	12:30–12:50	10
1:00–2:10	6	1:40–2:20	7	1:15–1:35	19
2:10–3:00	20	2:40–3:20	8	2:40–3:00	19

^a Ambient air samples July 28, 1977. ^b Refs. 6 and 8. ^c Refs. 14 and 15. ^d Ref. 13.

maximum oxidant concentrations of 0.6 and 0.3 ppm, H₂O₂ levels of 180 and 60 ppb, respectively, were reported. In contrast, on July 25 and 26, 1977, ozone concentrations reached approximately 0.3 ppm in Riverside, but H₂O₂ concentrations observed with the chemiluminescent method were between 25 and 30 ppb; whereas on July 28, O₃ peaked at approximately 0.2 ppm, but H₂O₂ concentrations were less than 20 ppb as measured by all three methods. These differences in concentrations of H₂O₂, relative to O₃ or oxidant, between the 1970 and 1977 studies are probably actually greater than indicated by the raw data cited, since in the earlier study oxidant rather than ozone was measured, and in the time between the two studies the calibration procedure in the Federal reference method for oxidant has been shown to result in oxidant measurements approximately 10–20% too high (16, 17).

Whether or not the apparent decline in ambient H₂O₂ concentrations between 1970 and 1977 is real is difficult, if not impossible, to establish. Recent long-path infrared measurements at SAPRC (18, 19) have shown that ambient HCHO concentrations during smog episodes in Riverside are low, in the range of 2–20 ppb. This is consistent with low H₂O₂ levels since formaldehyde is both a direct and indirect precursor of H₂O₂ via Reactions 1 and 3 shown below. These same infrared measurements have established an upper limit for H₂O₂ in Riverside ambient air of approximately 50 ppb (20), which is consistent with the chemiluminescent and titanium salt measurements in the sense that none of these exceeded 50 ppb.

An important conclusion from our simultaneous measurements of H₂O₂ and O₃ is that the H₂O₂ levels observed do not occur in a fixed ratio to O₃. Thus, in a number of cases the concentrations of H₂O₂ were observed to decline more slowly than those of O₃ following the O₃ maximum, and in some cases H₂O₂ concentrations remained essentially constant into the early evening hours (see Figure 3). This is consistent with the fact that major loss processes for H₂O₂ are photolysis (21, 22) and reactions with the hydroxyl radical (23) whose concentration tends toward zero after sunset (24, 25). To date no overnight studies have been conducted to obtain complete diurnal concentration-time profiles for H₂O₂.

H₂O₂ levels observed in the mornings tended to be in the range 5–10 ppb, although in several cases (see Figure 3) concentrations between 25 and 35 ppb were observed. It would be of considerable interest to determine H₂O₂ levels in the early morning prior to sunrise, since, if substantial H₂O₂ were present at this time, it would undergo photolysis to produce hydroxyl radicals which would accelerate the production of photochemical oxidant.

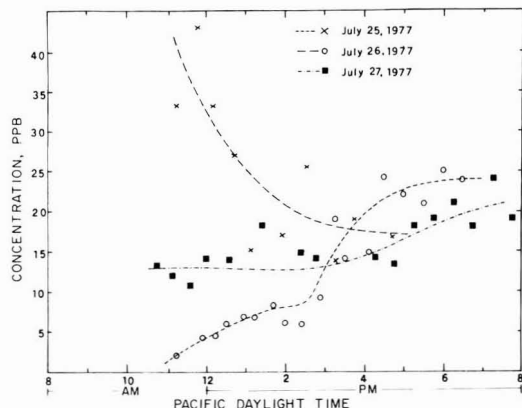


Figure 3. Ambient H₂O₂ concentrations measured at Riverside, Calif., on July 25–27

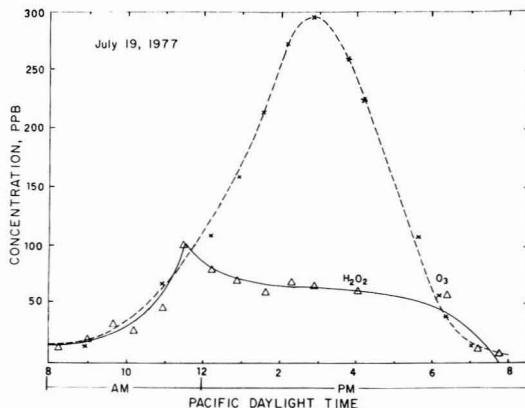
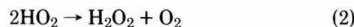
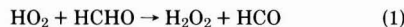


Figure 4. H₂O₂ and O₃ concentrations measured in ambient air at Claremont, Calif., during impact of grass fire plume

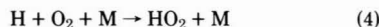
The mechanism of formation of H₂O₂ in NO_x–hydrocarbon photooxidation systems has been discussed in detail elsewhere (3, 8). Possible reactions leading to the production of H₂O₂ are



with Reaction 2 probably being the more important since Reaction 1 is known to be slow (26). Thus, any source of H atoms for example



can contribute to H₂O₂ formation via



Hydrogen Peroxide Concentrations in Fire Plumes. On two of the days for which H₂O₂ measurements were being made, wildfires were occurring directly upwind of the sampling sites. In the first of these cases (July 19), a small brush fire occurred approximately 6 miles west of the Claremont sampling site. The fire started at approximately 8:00 a.m. in the morning, and burned 3 acres before being extinguished at 12:30 p.m. H₂O₂ and O₃ data obtained for this day are shown in Figure 4. Hydrogen peroxide concentrations observed on this day were substantially higher than during any other monitoring period at Claremont. In particular, the H₂O₂ concentration reached a maximum of 100 ppb several hours before the O₃ maximum, observed at ~2:30 p.m. The H₂O₂ level decayed slowly from 11:30 on but remained high relative to H₂O₂ levels observed on other days.

On July 29 the plume from a wildfire in the Cleveland National Forest, located approximately 20 miles southwest of Riverside, was blown over the Riverside area. This fire had been burning out of control for approximately two days prior to the 29th. Results from the H₂O₂ and O₃ measurements for this day are shown in Figure 5.

The observation in both of these cases of relatively low levels of O₃ compared to H₂O₂ concentrations is of considerable interest, since it provides the clearest example of the deviation of H₂O₂ time-concentration profiles from those for O₃ or oxidant that has been reported to date. The occurrence of some unknown interference leading to these observations of elevated H₂O₂ levels cannot be definitively ruled out at this time; however, Kok et al. (13) have shown that their chemiluminescent method is not subject to interference by particles. Moreover, the good correlations obtained between the TiCl₄ method (an absorption technique) and the chemiluminescent

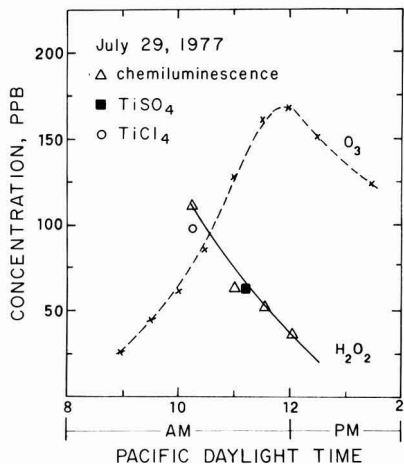
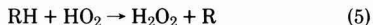


Figure 5. H₂O₂ and O₃ concentrations measured in ambient air at Riverside, Calif., on July 29, 1977, during impact of forest fire plume

method (a luminescence technique) suggest that elevated H₂O₂ levels are present in the fire plume.

Further support for concluding that the H₂O₂ measurements made here in wildfire plumes are not artifacts arises from cool flame combustion kinetics. At cool flame temperatures (<400 °C) the reaction R + O₂ produces HO₂ radicals and unsaturated products rather than RO₂ radicals (27, 28). The HO₂ becomes active in propagating chains via abstraction reactions of the type (27, 28)



Unlike RO₂ radicals, HO₂ is thermally stable at cool flame temperatures, and hydrogen peroxide is likewise much more stable than organic hydroperoxides (27, 28). Thus, it appears quite plausible that the measurements we have obtained do in fact result from elevated concentrations of H₂O₂ produced during combustion in the wildfires whose plumes were sampled. To our knowledge this is the first such observation associated with wildfires, although recent attention has been given to other products formed in the burnings of forests (29).

Acknowledgment

SAPRC workers acknowledge the assistance of G. Breuer and L. Willis in development of the TiCl₄ analytical method. One of us (G.L.K.) thanks M. Lopez and H. Nachtrieb for their help in conducting the chemiluminescent ambient air measurements.

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Received for review January 20, 1978. Accepted April 27, 1978. This study sponsored in part by the National Science Foundation-RANN (Grant No. ENV-76-14702-Harvey Mudd and Grant No. ENV73-02904-A04-Statewide Air Pollution Research Center). The contents do not necessarily reflect the views and policies of the NSF-RANN, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

SO_x Removal and Acid Neutralization with Its By-Product

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■ A solid by-product from a new sulfur dioxide removal process consists of a core of lime surrounded by a shell of anhydrous calcium sulfate (CaSO₄), which has a plurality of cracks. The unspent lime in the by-product is suitable for sulfuric acid neutralization. The calcium sulfate coating serves as the nucleus for acceleration of the growth of particles to a size that settles rapidly, forming a compact sludge. Scale formation due to CaSO₄ supersaturation is also prevented by the adsorption of the reaction product by the CaSO₄ coating. The by-product can also effectively and advantageously neutralize H₂CO₃, H₂SO₃, and H₂SO₄ in SO₂ scrubbing. CaSO₄ scale formation is absent in the SO₂ scrubbing with the by-product, and other types of scale can be controlled.

A process for controlling atmospheric pollution and recovering useful products has been reported (1, 2). The potential production of the by-product has been described, and the solid disposal problems have also been discussed (3). The laboratory-produced by-product has been demonstrated to be suitable for phosphate and turbidity removal from wastewater (3, 4), for floor plaster (5), and for a binder for fly ash to produce construction materials (5). This paper describes a method that uses the waste product for acid neutralization and SO₂ scrubbing.

SO_x Removal System and By-Product

Figure 1 shows the dry SO_x removal process developed by the author (2). Briefly, combustion gases from fuel-burning furnaces are treated in order to separate solid particles as fly ash and to oxidize the sulfur dioxide gas (SO₂) contained therein into sulfur trioxide (SO₃). The SO₃ is reacted with lime (CaO) in a fluidized lime reactor to form a coating of calcium sulfate over the external surfaces of calcium oxide particles. The particles are then quenched rapidly from reactor temperature to ambient or below ambient temperature, and many cracks result in the lamination of calcium sulfate. Figure 2 is the diagrammatic cross-section view of the solid product particle, having a core of unspent lime with a cracked CaSO₄ coating.

Acid Neutralization

Acidic plant effluents are serious sources of stream pollution. The choice of an alkaline reagent for neutralization of acidic wastewater is generally among sodium hydroxide, sodium carbonate, and various limes. The limes have the advantage of relatively low cost. If the sulfuric acid in the wastewater is neutralized with dolomitic or high calcium lime, the resulting product, CaSO₄, is highly insoluble and forms scale and sludges (6-8).

Comparison of By-Product and Lime in Acid Neutralization

The unspent lime in the by-product is considered to be very useful for acid neutralization, particularly for sulfuric acid. To test the merit of the unspent lime, a series of experiments was conducted on a laboratory scale, comparing the by-product with high calcium lime in sludge volume produced, CaO dosage used, and scale formation characteristics. Four

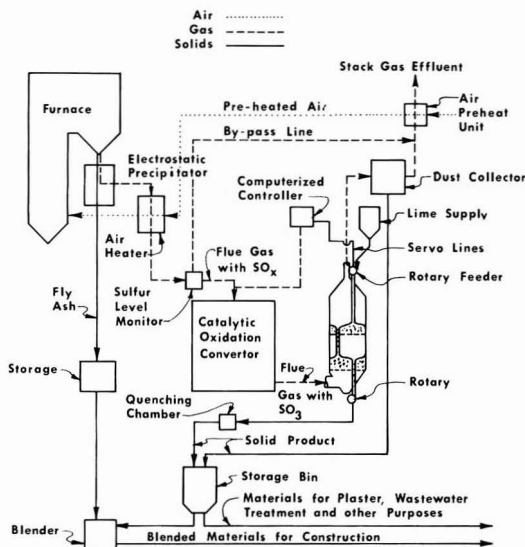


Figure 1. SO_x removal and waste product reclamation system

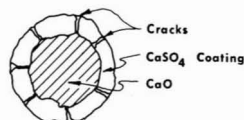


Figure 2. Cross-sectional view of solid product particle

types of the by-product produced from different SO_x removal procedures were compared with a high calcium lime.

The tests were conducted on 1 wt % sulfuric acid solutions. The by-product and lime powders in dry form were added to 500 mL of an agitated 1% sulfuric acid solution until the desired pH value was reached. The neutralized solutions were then transferred to a 500-mL graduated cylinder for sedimentation. Since the equivalent point for sulfuric acid is pH 4.2, it was decided that the pH value of the acid solution should be adjusted to 4.2 in the neutralization tests. At this pH the addition of a small amount of alkaline reagent will appreciably raise the pH of the solution.

Test Results and Proposed Reaction Mechanism. The results of the experiment are found in Table I and Figures 3 and 4. A comparison of the results clearly indicates that the by-product is a superior chemical for neutralization with regard to the volume of sludge produced, dosage of chemical on a CaO basis required, and scale formation.

CaO Dosage. During sulfuric acid neutralization with the by-product, the acid solution seeps through the cracks of the CaSO₄ coating and comes in contact with the CaO in the core. The chemical reaction between lime and water is represented as follows:



Table I. Comparison of Sludge Volumes Resulting from Neutralization of 1 wt % Sulfuric Acid Solution^a by High Calcium Quicklime and By-Products, Respectively

type powder	powder dosage (g/L)	pH value after neutralization	CaO in powder ^b (wt %)	CaO dosage ^c (g/L)	sludge ^d vol (%)	remarks
by-product LF-B1B	13.00	4.6	61.72	8.02	12.5	concd sludge
by-product LF-1A	9.14	4.8	69.00	6.31	8	concd sludge
by-product LF-2A	9.58	5.2	71.30	6.83	5	concd sludge
by-product LF-A2A	16.46	4.9	44.30	7.29	7	concd sludge
high-cal-cium lime	10.78	4.9	96.36	10.39	28.5	fluffy sludge

^a Acid volume = 500 mL, acid temperature = 27 °C. ^b These values represent content of both calcium and magnesium oxides as CaO. ^c The stoichiometrical weight of CaO needed to neutralize 1 wt % of 95% H₂SO₄ solution = 5.42 g/L. ^d Expressed as percent of original volume after 1 h sedimentation.

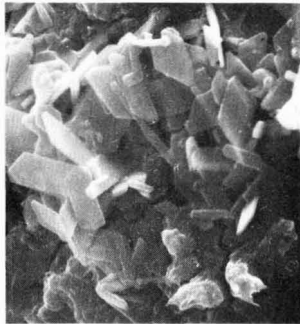
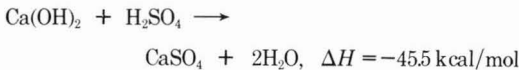


Figure 3. Electron micrograph showing surface structure of dry sludge particle from neutralization of 1% H₂SO₄ solution by by-product LF-B1B (5000X magnification)

The hydrated lime in the core reacts with the sulfuric acid in accordance with the following reaction:



It is believed that the intense heat generated by the chemical reactions is reflected by the refractive CaSO₄ coating, resulting in a sudden temperature rise in the core of the by-product. The high-temperature thermal shock causes the lime at the center of the core to crack under high tensile stresses, and the cracks continuously propagate in all directions in a short period of time. Consequently, the lime in the core of the by-product becomes a porous material that has a higher surface area, and is more reactive chemically.

On the other hand, when the acid solution is neutralized with high calcium lime, a coating of CaSO₄ forms on the surface of the lime particle. The coating acts as a barrier that prevents the acid solution from reaching the lime inside. As a result, the lime in the core is wasted.

It is interesting to note from Table I that the CaO dosage of the by-product is invariably smaller than that of high cal-

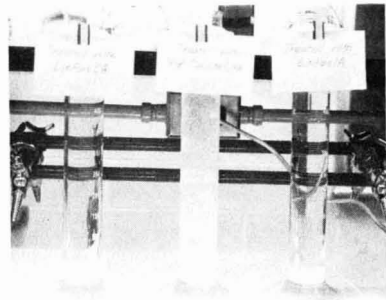


Figure 4. Comparison of scale forming characteristics of H₂SO₄ solutions treated with by-products and high calcium lime, respectively

cium lime for the same degree of acid neutralization. This fact demonstrates that the lime in the by-product is more effectively utilized in acid neutralization than high calcium lime.

Sludge Volume Produced. Figure 3 is a photomicrograph showing partly the surface structure and cracks in the CaSO₄ coating of a by-product particle. This figure also shows that the CaSO₄ produced by neutralization with the by-product is composed of rhombic crystals that are adsorbed on the surface of the CaSO₄ coating.

It is proposed that the calcium hydroxide within the by-product diffuses through the cracks to react with sulfuric acid to form very tiny calcium sulfate crystals on the surface of the by-product as shown in Figure 3. The formation of the large CaSO₄ sludge particles is due to the growth of the CaSO₄ crystals; the insoluble anhydrous CaSO₄ coating of the by-product serves as the nucleus in particle growth. When the mixture is slightly agitated, the collision of these growing calcium sulfate nuclei is promoted so that the nuclei will combine into lumps and effect a higher settling velocity of calcium sulfate particles and a more compact sludge.

Table I shows that in all of the cases the by-product produced a smaller sludge volume than high calcium lime. In addition, by-product LF-2A produced the least sludge volume, only 5% of the volume of the acid solution. The high sludge volume (28%) produced from acid neutralization by conventional lime is due to poor compaction characteristics of the sludge which has been attributed to the typical acicular shape of calcium sulfate crystals (9).

Scale Formation. As was pointed out, when the by-product is added to a sulfuric acid solution, a large amount of heat is generated from the chemical reactions inside the particle. A portion of the chemical product (CaSO₄) is expected to crystallize inside the particle, even though the temperature there is very high. However, some of the CaSO₄, in dissolved form, will flow out from the particle through the cracks with the hydrated lime. The outflowing hydrated lime reacts with the acid to form CaSO₄ in the immediate vicinity of the particle. The diffusion of the chemical through the cracks is facilitated by the high temperature and the high chemical concentration gradients. Once the outflow reaches a point just outside the by-product, supersaturated CaSO₄ solution is temporarily formed, due to the high concentrations of the reactants and the sudden drop of temperature in the solution. However, the CaSO₄ coating of the by-product, serving as nuclei, may immediately adsorb the supersaturated CaSO₄. As a consequence the CaSO₄ concentration in the solution can rapidly reduce to the level of its solubility. Therefore, the scale formation is prevented. Scale formation is mainly due to the slow crystallization of the supersaturated chemical reaction product in a solution.

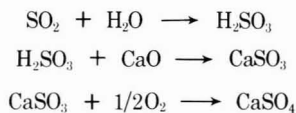
Table II. Neutralization of H₂SO₃ Solution by High Calcium Lime and By-Product, Respectively (Initial pH Value of Solution = 1.9)

chemical used	dosage (g/L)	CaO in powder (wt %)	CaO dosage (g/L)	final pH value	sludge vol (%)	remarks
by-product LF-B1B	19.8	61.04	12.09	8.5	9	spotty scale
	20.2	61.04	12.33	12.2	9	spotty scale
	20.0	61.04	12.27	7.1	8	no scale
high calcium lime	32.2	95.50	30.85	7.0	11	spotty scale
	35.8	95.50	34.19	12.6	12	spotty scale
	35.6	95.50	34.00	8.8	12	spotty scale

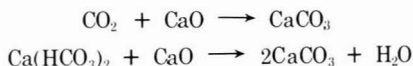
Figure 4 is a photograph taken three days after sedimentation, in the sulfuric acid neutralization experiment. The picture shows no evidence of scale formation when the by-products are used, a clear indication that supersaturation of CaSO₄ is absent from the solution. As expected, scale was formed on the graduated cylinder containing the solution neutralized with high calcium lime. Scale formation in acid neutralization (6) can be extremely troublesome when lime is used. By using the by-product, scaling can be eliminated or minimized.

Comparison of By-Product and Lime in SO_x Scrubbing

In recent years, SO_x removal from stack gas by the lime scrubbing process has been popular. The chemical reactions are represented by the following formulas (10):



Since scrubbed gas contains CO₂ and scrubbing water sometimes has bicarbonate alkalinity, the following reactions also take place:



Field experience with the scrubbing is not satisfactory, and the operations are plagued with numerous problems (11, 12). Scaling of the scrubber has led to clogging problems and other downtimes. The large amount of sludge generated by the process constitutes a serious disposal problem (11, 12).

The by-product has been considered as a scrubbing agent for SO₂ removal. A series of jar tests designed to compare the SO₂ scrubbing efficiency of high calcium lime and by-product LF-B1B, respectively, was conducted on 1000-mL H₂SO₃ solutions that were produced by aerating the lake water from Angola, Ind., with SO₂ until the pH value was 1.9. The chemical (by-product LF-B1B or high calcium lime) was added to the H₂SO₃ solution while the sample was being stirred at a mixing speed of 100 rpm. The addition of the chemical was terminated when the pH value of the solution reached a desired level, and the contents of the jars were then transferred to a series of 1000-mL graduated cylinders for sedimentation. The results of the experiment are presented in Table II, which shows that a smaller dosage of the by-product, compared with high calcium lime, is required to achieve the same degree of neutralization. The CaO dosage from by-product LF-B1B is about 37% of high calcium lime, indicating that CaO in the by-product is effectively utilized. The by-product produces smaller sludge volume.

The equivalent point of the H₂SO₃ solution is at the pH value of 7.0. At this equivalent point the addition of a small

amount of high calcium lime will increase the pH precipitously. This explains why there are large variations in pH value (about 7) for nearly identical CaO dosages as shown in Table II.

In lime scrubbing, scaling can be caused by calcium sulfate, sulfite, or calcium carbonate. The remedy for sulfite scaling is to keep the pH value of the scrubbing solution at a level on the order of 9 or less (13). Adjustment of the pH to 8.0 or below essentially completes conversion of carbonate to bicarbonate, thus eliminating carbonate scaling. Sulfate scaling is normally the most difficult to control. Unlike sulfite and carbonate, the decrease in pH value in a solution does not help hold sulfate in solution.

Table II shows that no scale was found when the final pH value of the solution treated with the by-product was less than 8.0 (7.1), and spotty scaling took place when the pH value was above 8.0 (8.5, 12.2). These facts clearly indicate that when the by-product is used in the treatment, the scale resulting from chemical reactions is due to calcium sulfite and carbonate, not calcium sulfate. As expected, scale was found at all pH levels (7.0, 8.8, 12.6) when the solution was neutralized with high calcium lime, indicating that the scale was due to calcium sulfite, carbonate, and sulfate. Therefore, by the adjustment of the pH value of the solution to a level not over 8.0 with the by-product, scaling can be completely prevented or eliminated.

Conclusions

The crystals formed from neutralization of sulfuric acid solution by the by-product are rhombic in form and are adsorbed on the surface of the cracked CaSO₄ coating. The volume of sludge produced in the laboratory neutralization of a sulfuric acid solution by the by-product is considerably less than that by high calcium lime. The CaO dosage of the by-product is smaller than that of high calcium lime, for the same degree of H₂SO₃ neutralization. Under laboratory conditions the by-product did not produce scale in acid neutralization. The by-product can also be used advantageously for scrubbing SO₂.

Acknowledgment

The author thanks C. S. Yeh, E. J. Kirsh, and Carolylin Brendel of Purdue University for their assistance.

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Received for review January 6, 1977. Resubmitted November 11, 1977. Accepted March 27, 1978.

Observations on Boron Release from Coal-Fired Power Plants

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■ The boron content of coal and power plant process ashes is investigated. Calculation of mass balances suggests that a large fraction of the boron is being released to the atmosphere.

Trace element emissions from industrial sources, especially coal-fired power plants, have been the subject of a number of recent studies (1-6). Mass balances on as many as 37 elements have been measured (4), and in-stack particle size distributions have been determined for 34 elements (1, 2). These measurements have been performed almost exclusively by instrumental neutron activation. Several potentially toxic elements (e.g., B, Cd, F, Pb) cannot be satisfactorily determined in power plant effluents by neutron activation. Among this group, boron is of particular interest.

Coal-fired power plants are often constructed in rural, agricultural areas where social and economic factors are favorable. There is a growing literature (7-11) that suggests boron has a rather narrow range of tolerance in plants. Outside this concentration range it can have severe effects on vegetation. Concern about boron in agricultural fertilizers and pesticides is evident (12-15). Sources of airborne boron have not been carefully studied, but adverse effects of boron release from appliance manufacturing have been reported (7, 16).

This note reports an investigation of the behavior of boron during the combustion of coal at two large coal-fired power plants. It includes a discussion of boron partitioning in coal and power plant process ashes.

Experimental

A complete description of the Chalk Point Electric Generating Station (Maryland) and of sampling techniques is given by Gladney (1). Similar data for the Four Corners plant may be found in Wangen and Wienke (17). The thermal neutron prompt gamma-ray facility at the Los Alamos Omega West Reactor (18, 19) was used for all boron determinations in the present work. The details of the analytical procedure may be found in ref. 18.

Results and Discussion

The 9-day average boron content of Chalk Point coal and process ashes is shown in Table I. Similar 3-day averages are given for the Four Corners plant. An approximate mass balance for an element may be determined in the following manner. The boron concentration in the feed coal is divided by the ash content (%) of the coal. This yields the "total possible in ash" boron concentration (i.e., as if the coal were ashed without loss of boron). The boron concentration in each pro-

Table II. Mass Balance for Boron at Two Coal-Fired Power Plants (Fraction·ppm)

Plant	Bottom slag	Economizer ash	Precipitator fly ash	Accountable in ash	Total possible in ash	Accountable/total possible
Chalk Point	1.5	2.3	25	29	100	0.29
Four Corners						
This work	24	...	190	214	390	0.55
SWES	24	...	180	204	415	0.49

cess ash is multiplied by the fraction of the total ash collected at that location. The sum of the latter figures should equal the boron concentration in the "coal ash" if all the boron is being collected in the plant ("Accountable in ash"). The ratio of the accountable boron to the total possible boron is the fraction of boron collected by the emission control system.

The ash contents of coal burned at Chalk Point and Four Corners at the time of sampling were 13 and 23.6%, respectively (1, 20). Therefore, the coal ash boron concentrations are 100 and 390 ppm. Using process ash distributions of 9, 12, and 75% for bottom, economizer, and precipitator fly ash, respectively at Chalk Point (1) and 20, 0, and 80%, respectively, at Four Corners (17), the data in Table II may be calculated. This excludes the 4% of ash released from the stack at Chalk Point.

If the mass balance shown in Table II is correct, then boron becomes one of the most enriched elements in power plant emissions, in a class with Br, Cl, Hg, Se, and As (1). A similar depletion for boron in the process ashes with implied loss to the stack is seen in the Southwest Energy Study (17, 20). The SWES data for boron content of coal are highly variable. Using the lowest error limit, one still calculates a loss of 30% of the boron.

One in-stack cascade impactor sample set from Chalk Point was analyzed for boron. Only the filter stage showed a positive indication for boron: 0.4 μg or 2.0 $\mu\text{g}/\text{m}^3$ of stack gas. This provides a hint that the boron is condensing only on the smallest particles and that most of it is being emitted in the gas phase. It has been suggested that boric acid or boron halides would be the most probable volatile species in the emissions (21). Another study (22) provides data that indicate higher boron concentrations on stack particulates of 12 μm and less.

Float-sink data on organic affinities as studied in coals by the Illinois Geological Survey (IGS) (23) are also suggestive. Their conclusions break trace elements into three groups: organic: Ge, B, Be, Sb, Br; intermediate: Co, Ni, Cu, Cr, Se; and inorganic: Zn, Cd, Mn, As, Mo, Fe.

Data indicated that most of the elements having high organic affinities (23) become preferentially enriched in the fly ash (1-6) and are emitted to the atmosphere. Our data support this for boron. However, significant quantities of As have also been measured leaving the plant (1-4), and IGS identifies this element as clearly inorganic associated. The more "volatile" material found in the coal, the higher the average boron concentration on a coal ash basis. Ray and Parker (24) report the following average coal ash boron concentrations (ppm): Anthracite, 90; low volatile bituminous, 123; medium volatile bituminous, 218; high volatile bituminous, 770; and lignite,

Table I. Boron Concentrations in Power Plant Coals and Process Ashes (ppm)

Plant	Coal	Bottom slag	Economizer	Precipitator fly ash
Chalk Point, Md.	13 \pm 2	17 \pm 3	19 \pm 2	33 \pm 3
Four Corners, N.M.				
This work	92 \pm 1	120 \pm 12	...	240 \pm 5
SWES (20)	98 \pm 32	120	...	230

1020. The apparently large amounts of boron lost to the environment through stack emissions may be closely related to the organic association of boron in the coal.

While these data are hardly definitive, they imply that coal-fired power plants are a significant source of atmospheric boron. These results indicate a need for more detailed studies of the behavior of boron during combustion and the effects, if any, of boron releases on agriculture.

Acknowledgment

We thank Glen E. Gordon and William H. Zoller of the University of Maryland for supporting the collection of samples at Chalk Point in 1973, and the staff of the Los Alamos Omega West Reactor for their assistance with the irradiations.

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Received for review January 13, 1978. Accepted March 27, 1978. Work performed under the auspices of the Department of Energy. Sample collection at Chalk Point supported by NSF-RANN Grant GI-36338X to the University of Maryland.

Dispersion of Plutonium from Contaminated Pond Sediments

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■ Sediment-water distributions of plutonium as a function of pH and contact time are investigated in a holding pond at the Rocky Flats plant of the Department of Energy. Although plutonium has been shown to sorb from natural waters onto sediments, the results of this study indicate that under the proper conditions it can be redispersed at pH 9 and above. Concentrations greater than 900 pCi Pu/L result after 34 h contact at pH 11 or 12 and the distribution coefficient, defined as the ratio of concentration in the sediment to that in the liquid, decreases from 1.1×10^5 at pH 7 to 1.2×10^3 at pH 11. The plutonium is probably dispersed as discrete colloids or as hydrolytic species adsorbed onto colloidal sediment particles whose average size decreases with increasing pH above pH 9. About 5% of the total plutonium is dispersed at pH 12, and the dispersion seems to readsorb on the sediment with time. Consequently, migration of plutonium from the pond should be slow, and it would be difficult to remove this element completely from pond sediment by leaching with high pH solutions.

The behavior of plutonium in aquatic environments has received considerable attention because of nuclear weapons tests in the Pacific and concern about potential radioactive releases from nuclear energy facilities and waste burial sites. At the pH conditions found in natural waters, plutonium hydrolyzes (1-4) and sorbs onto bottom sediments (5-9). Little effort has been expended in determining in what form and how permanently the plutonium is fixed, even though changes in pH would be expected to change the character of both the plutonium and the sediment particles.

In this paper we report on a study of the dispersion of plutonium from the sediments of a freshwater holding pond at the Rocky Flats Plant of the Department of Energy near Golden, Colo. This pond, known as B-1, was selected for study because it had measurable concentrations of plutonium in the sediment. This pond has been receiving treated sewage effluent since 1952 and laundry wastewaters from that date until late 1973. Most of the element now present in the sediment is believed to be from the latter stream, which was contaminated in the laundering of protective clothing used in a plutonium processing facility. Pond B-1 has a maximum depth of approximately 4 m and a volume of about 3×10^6 L. The residence time for water in the pond is approximately 34 h (10). Although the results reported here are specific to waters and sediments from Pond B-1, they should be at least quali-

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Table I. Activity and Particle Size Distribution of Sediment in Pond B-1

size fraction, μm	% of total wt	Pu pCi/g	% of total Pu
+74	0.33	380	0.08
+52-74	0.32	2300	0.45
+37-52	0.48	320	0.09
+26-37	2.5	570	0.86
+19-26	2.7	890	1.4
+13-19	7.4	780	3.5
+9-13	13	1000	8.1
+6.5-9	39	2000	49
+4.6-6.5	19	2100	25
+2.3-4.6	7.0	1600	6.7
-2.3	7.5	1000	4.6

tatively applicable to other freshwater systems of similar pH and sediment composition.

Experimental

The sediments used in this study were collected from the bottom of Pond B-1 using a coring device that penetrated only the top few centimeters of sediment. Plant fragments and other debris were removed prior to homogenizing with an electric mixer. The homogenized sediment had an average concentration of 1620 pCi Pu/g based on dry weight. A Stokes law sedimentation procedure indicated that 75% of the plutonium was associated with particles in the 4.6-9- μm size range, which comprised 74% of the total sediment weight. About 3% was associated with particles larger than 19 μm , and less than 5% with those smaller than 2.3 μm . Complete results are shown in Table I.

The water used in the experiments was collected from Pond B-1 at the same time as the sediment and was not filtered. The water had a pH of 7.8 and contained 2.3 pCi Pu/L. The following anions were determined by standard methods (11, 12) and were present in concentrations expressed as milligrams/liter: nitrate, 25; sulfate, 120; bicarbonate, 37; total phosphate (as PO_4^{3-}), 1.9; chloride, 18; fluoride, 0.6.

Extraction experiments were conducted at room temperature by shaking 35 mL of Pond B-1 water with B-1 sediment in 50 mL polycarbonate centrifuge tubes on a Burrell wrist-action shaker. Before shaking commenced, the sediment-water mixtures were adjusted to the specified pH with dilute HCl or NaOH. Generally 5 mL of wet sediment, equivalent to approximately 1.2 g of dry sediment, was used in each extraction except in the runs involving filtration. In the latter runs, in which it was desirable to minimize the amount of material retained on the filters, only 1 mL of wet sediment was

used. At the end of the specified extraction time, the tubes were centrifuged at 5000 rpm for 5 min and a 5-mL sample of the supernate withdrawn for analysis. In those experiments involving extraction for successive time intervals, the tubes were then shaken vigorously by hand to resuspend the sediment and replaced on the shaker for additional extraction; this procedure was repeated at each specified time period. At the conclusion of the experiments, the residues were dried and analyzed for plutonium. From these values and the concentrations of the element in the extraction supernates, the apparent distribution coefficients (K') for each supernate sample were calculated by the expression

$$K' = \frac{\text{pCi Pu/g residue}}{\text{pCi Pu/mL solution}}$$

The term *apparent distribution coefficient* is used in this paper to describe the distribution of plutonium between sediment and water since results will show that the plutonium is not in true solution; hence, its behavior cannot correctly be described by thermodynamic terms such as distribution coefficient.

In the runs involving filtration the tubes were not centrifuged but were allowed to stand for 57 min, the calculated time to allow particles with a density of 2.5 g/cm³ and a diameter larger than 5 μm to settle. Nuclepore membrane filters of the specified pore size were used in all filtrations except the 0.4- μm separations at pH 12, which were accomplished with 0.45- μm Nalge membrane filters.

Supernate samples were evaporated on stainless steel planchets, flamed and analyzed by alpha spectrometry using the 5.15 MeV alpha peak for plutonium-239, 240. The samples were counted on a Nuclear Data 4420 pulse height analysis system with ORTEC surface barrier detectors.

The solid residues from the extraction runs were leached with 1:1 HNO₃-HCl solution containing a small amount of HF. The plutonium was separated by anion exchange and thenoyltrifluoroacetone (TTA) extraction and analyzed as above.

Results and Discussion

Concentrations and distribution coefficients of plutonium in pond water after contacting with sediment for various time periods in the pH 3-12 range are shown in Table II. Extraction remained relatively constant between pH 3 and 8, but from pH 9 to 12 it increased rapidly, yielding concentrations greater than 900 pCi Pu/L after 34 and 68 h at pH 11 and 12. The values at pH 9 and 10, although not as high, are perhaps of more practical concern since they are still considerably above normal concentrations for pond water and are more likely to be attained by an accidental pH excursion.

The increased dispersion at high pH values suggests that

Table II. Plutonium Sediment Extraction Results

Plutonium concentration in supernate, pCi/L, and apparent distribution coefficient, K' , after extraction time shown^a

Initial pH	2 h		8 h		20 h		34 h		68 h		final pH
	Pu concn	$K' \times 10^{-2}$	Pu concn	$K' \times 10^{-2}$	Pu concn	$K' \times 10^{-2}$	Pu concn	$K' \times 10^{-2}$	Pu concn	$K' \times 10^{-2}$	
3	10 (5)	1200 (120)	33 (6)	480 (66)	29 (6)	540 (140)	34 (6)	450 (100)	55 (10)	290 (61)	3.4
4	20 (9)	850 (360)	9 (5)	1600 (990)	5 (2)	3600 (1500)	26 (5)	510 (200)	43 (8)	370 (61)	3.8
5	5 (2)	3100 (1300)	8 (4)	1800 (960)	3 (0)	5000 (500)	8 (1)	2000 (270)	34 (4)	450 (82)	5.1
6 ^b	6 (5)	2300 (2500)	11 (7)	1000 (96)	11 (2)	1500 (170)	11 (1)	1600 (160)	18 (5)	1100 (200)	7.0
7	11 (1)	1200 (350)	8 (5)	1900 (1200)	12 (7)	1600 (1300)	14 (2)	1100 (130)	12 (1)	1200 (110)	7.2
8	49 (16)	360 (160)	23 (6)	830 (180)	18 (1)	1000 (300)	19 (5)	740 (86)	20 (5)	920 (340)	7.1
9 ^b	120 (46)	120 (40)	180 (42)	80 (16)	120 (14)	120 (15)	36 (3)	400 (52)	27 (7)	520 (170)	7.6
10	200 (15)	-69 (28)	340 (58)	46 (10)	670 (61)	23 (3)	380 (57)	41 (8)	36 (4)	420 (99)	8.6
11	220 (23)	75 (10)	350 (99)	44 (12)	420 (29)	41 (4)	1400 (200)	12 (2)	1200 (270)	15 (0.8)	10.7
12	100 (21)	150 (43)	210 (44)	79 (20)	720 (210)	23 (5)	910 (100)	18 (2)	4500 (700)	4 (1)	12.0

^a Parenthetical values are standard deviations. ^b Values in these rows are means of four replicates; all others are means of five replicates.

Table III. Filtrate Particle Size DeterminationConcentration in filtrate after filtration through pore size shown^a

pH	Pu, pCi/L			
	5 μ m	1 μ m	0.4 μ m	0.2 μ m
3	50 (\pm 2)	6.6 (\pm 2.5)	4.1 (\pm 1.1)	2.4 (\pm 0.8)
8	59 (\pm 6)	4.3 (\pm 0.9)	4.3 (\pm 1.7)	2.7 (\pm 1.0)
9	44 (\pm 7)	41 (\pm 6)	25 (\pm 6)	2.7 (\pm 1.0)
12	50 (\pm 2)	38 (\pm 6)	41 (\pm 6) ^b	8.2 (\pm 3.2)

^a Parenthetical values are standard deviations. ^b These samples filtered through 0.45- μ m filters.

Table IV. Successive 20-h Extractions of Single Sediment Sample with Fresh Pond Water

extraction	Pu concentration, pCi/L ^a	
	pH 9	pH 11
first	170 (\pm 38)	1100 (\pm 230)
second	74 (\pm 45)	1200 (\pm 170)
third	9 (\pm 3)	400 (\pm 53)
fourth	15 (\pm 5)	198 (\pm 150)

^a Parenthetical values are standard deviations.

Table V. Successive 20-h Extractions of Fresh Sediment with Single Pond Water Sample

extraction	Pu concentration, pCi/L ^a	
	pH 9	pH 11
first	170 (\pm 38)	1100 (\pm 23)
second	180 (\pm 12)	1700 (\pm 310)
third	86 (\pm 30)	890 (\pm 170)
fourth	34 (\pm 16)	390 (\pm 120)

^a Parenthetical values are standard deviations.

the plutonium was present in colloidal form. To explore this possibility a series of 20-h extractions was conducted with four replicate samples each at pH values of 3, 8, 9, and 12. After extraction and settling, portions of the supernates were filtered through Nuclepore filters of pore sizes 5, 1, 0.4, and 0.2 μ m. As shown in Table III, the plutonium in the 0.2- μ m filtrates, which was the only concentration that could be in true solution, did not vary significantly at pH 3, 8, and 9 from the original pond water. There was a tendency toward smaller size particulates at pH 9 and 12, and at the latter pH there was a small but real increase in plutonium concentration in the 0.2- μ m filtrate. These results strongly suggest that the plutonium was present as a discrete radiocolloid or was adsorbed onto dispersed colloidal sediment particles. Since there was little or no increase in the 0.2- μ m filtrate, the absence of soluble complexes is indicated, a finding that is consistent with the reported inability of plutonium to form soluble complexes with natural fulvates (13), a likely source of anions in the sediment.

The relatively large concentration of plutonium in the water phase at high pH values raised the question of whether the amount of the element that could be dispersed was limited by its availability in the sediment or whether saturation of the water was the limiting factor. The results of a series of "cascade" extractions suggest that both factors were involved. Four replicate samples at pH 9 and four at pH 11 were extracted for 20 h, centrifuged for 5 min at 5000 rpm, and the water was removed by decantation and sampled. The initial sediment was again extracted for 20 h with fresh pond water at pH 9 or 11, while the initial water phase was contacted for 20 h with fresh sediment at pH 9 or 11. After centrifugation and liquid-phase sampling, the above procedure of contacting the initial water with fresh sediment and initial sediment with fresh water was repeated two more times. Thus, the initial sediment was successively contacted with four portions of fresh pond water, and the initial pond water was successively contacted with four portions of fresh pond sediment. The results are shown in Tables IV and V.

The data in Table IV indicate that the amount of plutonium dispersed from the sediment decreased with each successive contacting, suggesting that only a fraction of the plutonium present in the sediment is available for dispersal. Perhaps this fraction is less tightly bound to the sediment, or is associated with smaller, less dense sediment particles that are more readily dispersed.

The dispersions formed in these experiments not only have a saturation value, but tend to readsorb or reprecipitate as indicated by Table V. The decrease in plutonium concentration with successive contactings with fresh sediment is additional evidence that the element is largely present in a colloidal dispersion.

The following conclusions can be drawn from these experiments: Plutonium is dispersed from the sediment into the water as either discrete radiocolloids or adsorbed onto dispersed colloidal sediment particles; it is not in true solution.

The absence of soluble complexes is indicated. Since most of the plutonium in this system is not in true solution, thermodynamic equilibrium concepts are not applicable, and the need to establish the nature of any plutonium aqueous system before attempting to apply such concepts is clearly indicated. Finally, migration of plutonium from the pond sediment should be slow, and it would not be feasible to remove the element completely from the sediment by leaching with high pH solutions.

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Received for review August 11, 1977. Accepted April 6, 1978. Work performed at the Rocky Flats Plant under contract to the Department of Energy.

CORRESPONDENCE

SIR: Carpenter and coworkers (1) have reported that the iodometric titration procedure for residual oxidants in chlorinated seawater can underestimate the true value by three-fold or more. Their results indicate that the amperometric standard method also badly underestimates the residual oxidant concentration in chlorinated seawater. Workers at our laboratory and other marine science facilities were disturbed to read that the accepted method for analysis of residual oxidants in seawater may be greatly in error.

During the seawater oxidant analysis, the order of addition of the chemicals is of paramount importance. Our experimental results are in agreement with those of Carpenter et al. (1) if we follow the mixing order that they reported. However, when we use a method that differs solely in the order of addition of reagents, the results are an accurate and precise estimate of the residual oxidants in seawater.

"Standard Methods" (2) reports two different mixing orders for residual chlorine analysis in water. With regard to the mixing order, we have included three examples from the literature. Carpenter et al. (1) reported, "Adjust the pH of the sample to 4 with acetate buffer, add KI solution and titrate with either sodium thiosulfate or phenylarsine oxide solutions." "Standard Methods" (2, page 111) recommended under iodometric method, to place the pH buffer in the titration container, add KI, then pour in the sample, mix and titrate. Also, "Standard Methods" (2, page 116) recommended under amperometric titration method to treat the sample with KI followed by buffer and titrate. All these procedures work properly for fresh water, but we have found that only the mixing order reported by "Standard Methods" (2, page 111) is reliable for residual oxidant determination in chlorinated seawater.

The "mixing order" we have been using consists of adding 2 mL of buffer (2, page 115) and 2 mL of KI solution (2, page 115) to an empty beaker. Swirl the reagents for a few seconds, then rapidly pour in 200 mL of sample and titrate immediately with phenylarsine oxide, using either the amperometric method (2, page 112-6) or the potentiometric method described by Eppley and coworkers (3).

To determine the accuracy of our method, both fresh water and seawater were spiked with known concentrations of calcium hypochlorite or sodium hypochlorite. At the 2 ppm chlorine level, the measured levels are within 10% of the predicted level if the analysis is performed immediately before the natural chlorine demand of the seawater has much effect. As a check of our procedure, we have also analyzed spiked seawater samples by the back titration procedure (2, page 382) which Carpenter et al. (1) found to be accurate for chlorinated seawater. Over the range of 0.01-1.0 ppm chlorine, these two methods agree within 5%. The precision of both of these procedures is $\pm 10\%$ or better for one SD over the range of 0.010-1.0 ppm oxidant as chlorine. The reagent blank in seawater is less than 0.002 ppm oxidant as chlorine.

We conclude that the "Standard Methods" (2, pages 112-6) can be used for seawater if the mixing order we have reported here is used. J. C. Goldman and J. M. Capuzo (private com-

munication) have had satisfactory results with oxidant analysis of seawater using the same mixing order as we use. Data reported in the past by this laboratory and others using our identical mixing order should not be considered in error due to analytical methods, since this method has been shown to produce consistent and accurate results.

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Based on work performed under Department of Energy Contract EY-76-C-06-1830.

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SIR: The report of Crecelius et al. that premixing of the buffer and KI solutions in the procedure for the determination of residual oxidants in chlorinated seawater eliminates the errors due to spurious iodate formation suggests that an easily performed change in the procedure will produce accurate results. However, it should be emphasized that in contrast to present practice, particulars of the procedure used by various investigators will need to be reported. The errors described by Carpenter et al. occur with the "standard" amperometric method as described in "Standard Methods" (1, page 116), EPA Environmental Protection Technology Series (2), and the instructions for commercial amperometric titration equipment (3), which has been widely used.

If these errors have been fortuitously avoided by using the premixing procedure or the back titration procedure (1, page 382), this fact should be specifically noted in research reports.

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ES&T

INDUSTRY TRENDS

Air Products and Chemicals, Inc. has received a patent for a process that "effectively eliminates phosphates, nitrates, ammonia, and biological components from wastewater."

Arizona Public Service Co. has awarded a contract for engineering/construction of a \$220 million emission abatement project at Four Corners to United Engineers and Constructors, Inc. (Philadelphia, PA).

Kerr-McGee Nuclear Corp. (Oklahoma City, OK) has received an award from the Izaak Walton League for efforts to clean up wastewater at an underground uranium mine in Wyoming.

Church & Dwight Co., Inc. (New York, NY) said that a recent survey showed that sodium bicarbonate is preferred over lime to combat operating upsets at wastewater plants. The company also established a technical assistance "hotline" number, (800) 526-3652, for plant operators.

Du Pont announced that its reverse osmosis technology is in use at a 600 000-gpd water desalting system in the Arabian Gulf nation of Bahrain to make water for concrete manufacture.

Converse Ward Davis Dixon (Pasadena, CA) is the new name of a geo-technical consultant firm formed by the merger of Converse Davis Dixon Associates, and Joseph P. Ward and Associates. A major specialty is soil engineering.

The American Boiler Manufacturers Association (Arlington, VA) forecasts that an additional 4500 MW of nuclear units, and 14 000 MW of coal-fired units will be ordered in 1978.

Arizona Public Service Co. said that reduced short-term forecasts of electricity demand has led the firm to delay by one year the completion dates of two units at the Cholla Power Plant. These dates will now be May 1980, and mid-1981, respectively.

Ecology Consultants, Inc. (Fort Collins, CO) general manager Burton

Kross is now a vice president of Environmental Research & Technology, Inc., parent firm of Ecology Consultants.

Schleicher & Schuell, Inc. (Keene, NH) will provide glass-fiber ultra-pure filters for the EPA's nationwide network of air monitoring stations. Initial delivery: 400 000 sheets, with additional option of 1.2 million filter sheets.

Slickbar, Inc. (Southport, CT) will make 21 oil pollution control workboats for the U.S. Navy. They will be 26-ft tri-hull folding boats, with sufficient platform for up to 3000 ft of oil boom.

The **Chlorine Institute, Inc.** (New York, NY) announced an improvement in design/material of gaskets for sealing and temporarily containing chlorine leaks. The material is known as VITON®.

The **Insurance Information Institute** (New York, NY) announced that nuclear insurers have declared a \$2 million refund to nuclear power plants, and related facility operators because of their excellent safety record over the last 21 years.

Research-Cottrell, Inc. (R-C) said, with respect to the Willow Island, WV cooling tower construction accident in which 51 workers died, that R-C was supplied with defective concrete, and is suing the firm that supplied it, as well as the firm which tested the concrete.

Grumman Energy Systems, Inc. (Bethpage, NY) is offering its "Sunstream" solar hot water systems at \$500 off list price to compensate for Congress' having failed, so far, to pass an expected tax credit for solar energy purchases.

United McGill Corp. (Columbus, OH) has installed a 43 000-acfm electrostatic precipitator for N.V. Philips Gloeilampenfabrieken at Winschoten, Holland—UMIC's first European installation. Performance exceeds 98%. Cost was \$720 000.

Solarex Corp. (Rockville, MD) will participate in four major Dept. of Energy demonstration projects, more than any other photovoltaic solar cell manufacturer. One such project, in Oklahoma, will have a peak output of 400-500 kW.

Jacobs Engineering Group has established a new, expanded 12 000-ft² analytical laboratory at Pasadena, CA, to offer a broad spectrum of environmental, quality assurance, and chemical testing to industries and municipalities.

MikroPul Corp. (Summit, NJ), a subsidiary of U.S. Filter Corp., will supply five dust collection systems to Bethlehem Steel Co., at Bethlehem, PA. These fabric systems will total 180 000 acfm. Value: \$1 million.

Neptune International Corp.'s subsidiary, Neptune Engineering & Research Corp., will design, engineer, and construct sewage sludge dewatering and disposal equipment for the Patapsco Waste Water Treatment Plant, Baltimore, MD, to handle over 280 000 lb/d of sludge.

Environmental Data Corp. (Monrovia, CA), together with Exxon, has received a \$100 000 extension contract to continue an industrial boiler fuel conservation program for the U.S. Dept. of Energy (DOE).

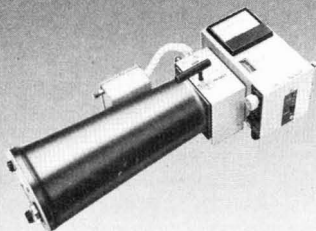
AEL Industries, Inc. (Lansdale, PA) has a DOE contract, through a subsidiary, for flue gas desulfurization system development. The approach involves no "dumping" of material; rather, the spent scrubbing material would be used to make sulfuric acid.

Autotrol Corp. (Milwaukee, WI) has received its largest municipal contract for air-driven wastewater treatment equipment for the City of Eau Claire, WI. The plant capacity will increase to 16.3 mgd.

Wheelabrator-Frye, Inc. and **Air Products and Chemicals, Inc.** have formed a joint venture to design, build, and operate a solvent-refined coal plant near Newman, KY—6000 tpd, initially.

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CIRCLE 23 ON READER SERVICE CARD

Chevron U.S.A., Inc. has begun construction of a modified wastewater discharge system to treat waste from oil/gas production wells in the Santa Barbara Channel. The system will be at Carpinteria, CA.

Mitsubishi Heavy Industry, Ltd. has opened a "pollution-free" foundry at Futami, Japan, near Kobe. There is water reuse, and casting sand reuse (95%), as well.

Alron Industries, Inc. (Rochester, NY) president W. Alan Burriss has won an "Inventor of the Year" Award, from the Rochester Patent Law Association, for making possible ozone water purifiers for home applications.

Hitachi Zosen (Japan) has a U.S. EPA order for a 1700 Nm³/h (0.5 MWe) demonstration plant for flue gas denitrification at coal-fired boilers. The principle is a proprietary catalyst. Envirotech/Chemico is also working on this project.

Research Appliance Co., which manufactures precision instruments for sampling/monitoring pollutants in ambient air and process emissions, is moving headquarters and production facilities to Cambridge, MD.

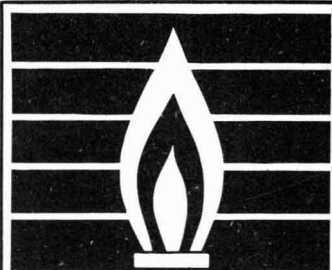
Envirotech/Chemico Air Pollution Control will furnish two Electrodynamic Venturi (EDV) scrubber systems to U.S. Steel. Chemico says that the EDV system saves 80–90% of energy necessary for particulate removal. A total of 1.68 acfm will be handled at two mills.

Stanley Consultants, Inc. will design a 400-MW steam electric plant, including fabric filters and flue gas desulfurization, for Colorado-Ute Electric Association, Inc. (Montrose, CO).

C-E Power Systems (Windsor, CT) and **Gulf States Utilities Co.** have begun negotiations with DOE for a gasification plant to handle 1344 tpd of high-sulfur, midwestern bituminous coal. The gas would be 100–125 Btu/scf.

Davy Powergas (Lakeland, FL) has received Florida's top safety award for 1 million man-hours without an accident involving lost time.

Clean Rivers Cooperative and Willamette-Western Corp. (Portland, OR) have announced a \$1.5 million system for prompt oil spill cleanup of the Columbia and Willamette Rivers.



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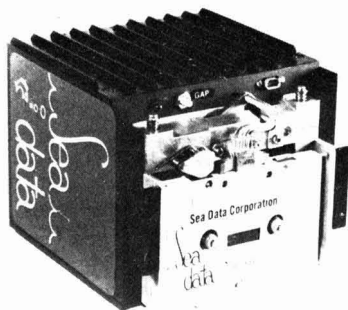
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The rigid discharge electrode is designed for service in electrostatic precipitators at utility power generating stations and industrial plants. This electrode is a long, slim, bean-like member, which provides both mechanical strength and good electrical performance, according to the manufacturer. Research-Cottrell 105

Pumped dye laser

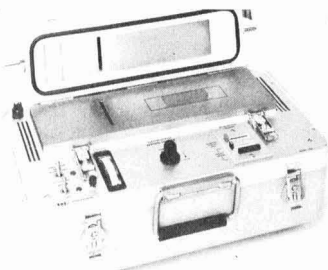
The solid-state laser produces a peak power output of 0.5 MW over the 500–900 nm range. The laser oscillator produces an output of 100 mJ/pulse at a wavelength of 1064 nm (near infrared), which is converted by a generator to 28 mJ/pulse at 532 nm (green). It finds application in in situ and remote pollution studies. International Laser Systems 106

Gas sampling bags

The "Tedlar" fluorocarbon bags are unaffected by nearly all chemicals; the bags have very low absorption and adsorption properties. Permeation is also low. Carborundum 107

Temperature controller

Features of this unit include high stability and digital set point. Thermocouple break protection and cold junction compensation are standard. Eurotherm 108



Aerosol sampler

The electrostatic aerosol sampler collects particles in the 0.02–10 μm diameter range. Collection can be made on glass, plastic or metal surfaces. It finds application in air pollution sampling. TSI Inc. 109

Hi-vol timer

This electronic timer is designed to satisfy the timing requirements of the EPA 6-day cycle. Accuracy is 0.01% over 6 days. Environmental Measurements 110

Evaporation retardants

These additives can modify the evaporation characteristics of volatile organic liquids; evaporation suppression can be controlled precisely by choice of additive and its concentration. Kyros Corp. 111

Glass-fiber filter

This micro-quartz filter can be used for the accurate analysis of air pollutants, especially sulfates and trace metals. Its features include: no interaction with sulfur dioxide, organic binder free and neutral pH. Gelman Instrument 112

Dissolved oxygen analyzer

The analyzer uses a polarographic membrane sensor to generate a current proportional to the dissolved oxygen content in water. It finds application in wastewater aeration tanks and effluent monitoring. Delta Scientific 113

Butterfly valve

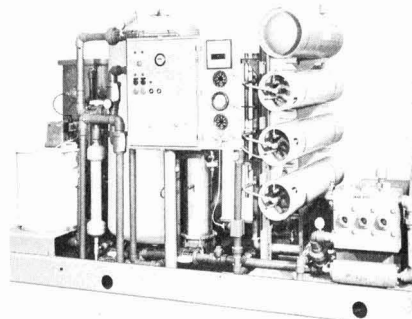
The valve finds application in continuous ion-exchange towers. Tomoe Valve Company 114

High-volume air sampler

This system samples suspended particulates at 40–60 cfm and fractionates the particles into as many as eight size fractions. The system uses a cyclone preseparator/cascade impactor combination. Sierra Instruments 115

pH converter

The system can be connected directly to a digital panel meter to transform the meter into a precision digital pH instrument. Or, the system can be connected to the input terminals of a strip-chart recorder to make the resulting system a self-contained pH recording unit. Lazar Research Laboratories 116



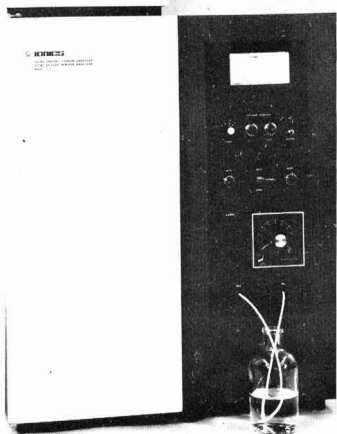
RO desalting system

The reverse osmosis equipment is rated to produce up to 15 000 gal of fresh water daily from seawater in a single pass. Aqua-Chem 117

Gases/liquids analyzer

The unit measures trace level pollutants in gases and liquids with a response time measured in seconds. The manufacturer claims that readings are "immune" to background gases or liquids and that levels less than 1 ppb can be determined. Houston Atlas

118



TOC/TC/TOD analyzer

This combined instrument uses ASTM and EPA-approved techniques to measure one of these parameters. Features include automatic sample injection, digital electronic sequence control and automatic zero function. Ionics, Inc.

119

NO/NO_x analyzer

This chemiluminescence-based analyzer is capable of online measurement of nitric oxide and total oxides of nitrogen. Response time is less than 1 s to 90% full-scale. The built-in molybdenum NO_x converter operates at a lower temperature to extend operating life. Environmental Tectonics

120

Oil-water separator

The unit consists of a separate sludge or separation compartment/area, a main separation chamber and a third chamber through which purified water is discharged to a weir-type outlet. McTighe Industries

121

Submicron filter

This filter will remove the finely divided silt that is present in most surface water. The filter element is a spiral-wound roll of oleophilic polyester fabric. The water is forced to pass between tightly compressed layers of fabric for the length of the roll; submicron openings on the surface of the layers entrap the particulates. Motor Guard

122

Disposal air sampler

The sampler is a matched-weight aerosol monitor consisting of a polystyrene filter holder that contains a pair of membrane filters. Air passes through both filters but the contaminants are trapped on the top filter. Millipore

123

"Settleometer"

The meter provides complete curves of the settling characteristics of sludges on a strip-chart recorder. The unit consists of a settling column, electronic sensors and a microprocessor. Tech-Line Instruments

124

Dry electrostatic precipitator

Features of this precipitator include roll-formed collecting plates, a maintenance-free rapping system and weighted strip discharge electrodes. The unit is recommended for applications requiring high-collecting plates or where dust is difficult to remove. MikroPul

125

A spectroscopy auto sampler

The automatic sampler injects either 50 μ L or 100 μ L samples directly into the instrument nebulizer. The sampler is compatible with all the manufacturer's atomic absorption instruments. Perkin-Elmer

126

Scrubber dewatering tanks

The tanks accept particulate-laden slurries from gas scrubbers, and retain them to allow solids to settle. Processed water can be recirculated to the scrubbing system or sent to the sewers for disposal. W.W. Sly Manufacturing

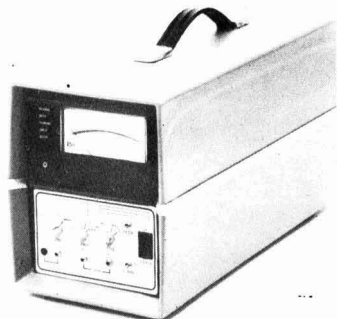
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Liquid chromatographs

The new 5000 series incorporates CRT and keyboard for instantaneous display of analysis programs. The CRT provides a continuous readout of all important operating conditions. The unit stores up to 9 complete analysis programs. Varian Associates

128



Portable NO_x meter

The unit measures NO, NO₂ and NO_x accurately to within 10 ppb. Zero drift is less than 0.01 ppm/8 h; span drift is held to 5%/day or less. Four ranges, from 0.0-0.5 ppm to 0.0-5.0 ppm, are offered. Columbia Scientific Industries

129

Water reference samples

These certified reference samples can be used to test the accuracy of a laboratory's potable water analysis technique. A complete set contains the values for 27 common parameters, including those regulated under the Safe Drinking Water Act. Environmental Resource Associates

130

Wet scrubber

This filtration-augmented wet scrubber has been developed for submicron particulate removal under corrosive conditions that prevent the use of baghouses or precipitators, or where the particulate matter is hygroscopic or sticky. Andersen 2000

131

Conductivity meter

The portable total dissolved solids meter has three test ranges; the low range tests boiler condensate; the mid-range tests make-up water and the high range is used to adjust cooling tower bleed and boiler blowdown rates. Presto-Tek

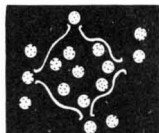
132

Aerosol generator

The spinning disk aerosol generator produces large volume, high concentration aerosols. Particle sizes range from 1-25 μ . It is suitable for use in pollution control equipment efficiency measurements. Environmental Research

133

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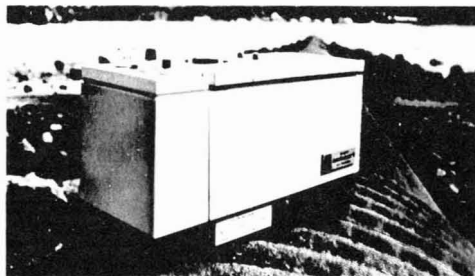
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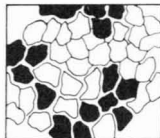
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ES&T LITERATURE

Water treatment. Brochure explains how water can be treated by identifying and correcting the cause of the problem, rather than by treating the effect. Covers boiler and cooling systems. UOP Inc. **151**

Water filtration. Bulletin NP-177 explains how ordinary newsprint paper can be a filter medium on a continuous rotary vacuum drum-type filter. Can be used with wastewater. Technical Fabricators, Inc. **152**

Wastewater measurement. Brochure describes the UFM-200 non-contact wastewater measurement system. Principle is sonar-in-air. Explosion-proof. WESMAR **153**

Laboratory services. Fact file details services in water, wastewater, and solid waste. Includes sampling/analysis, and completion of federal, state, and local environmental forms and permits. Arro Laboratories, Inc. **154**

Precious metals. Precious metals for catalysts, aircraft ozone abators, and many other applications are described. Engelhard **155**

Filter systems. Bulletin EF/18a describes tough tubular filter systems for services too corrosive for even stainless steel. Some are fluorocarbon-lined, rated up to 200 °F at 150 psi. The Duriron Co., Inc. **156**

Wind measurement. Brochures describe 011-3 Wind Speed, and 012-15 Wind Direction Transmitters. Applicable to air pollutant spread studies. Advice on determining airborne particle size/distribution also available. Climet **157**

Analytical laboratory. Bulletin 030 describes full range of services to help clients define and solve water/wastewater problems. TECSULT LABS **158**

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Fabric filters. Brochure describes Sky-Kleen pulse jet side access fabric filters. Air volumes 15 000 cfm, up; temperatures to 450 °F. No moving parts; self-cleaning. Johnson-March Corp. **159**

TV for sewers. Literature tells how closed-circuit TV detects inflow, severe infiltration, and major structural problems in a sewer system in a mid-western community. National Power Rodding Corp. **160**

Mud removal. Mud Remover Bulletin 507 describes mud removal and anti-foulant products for cooling systems, long runs of piping, and heat exchangers. Zimmite Corp. **161**

Pumps, filters, controls. Catalog gives information on pumps, filters, and controls for many wastewater applications, including pH control, total dissolved solids, and many others. SERFILCO **162**

Submicron emissions. Brochure describes wet scrubbing systems for controlling submicron emissions and capacity problems for many different industries. RP Industries, Inc. **163**

Desalination. Literature describes reverse osmosis water desalination system for up to 15 000 gpd of fresh water from seawater in a single pass. Aqua-Chem, Inc. **164**

Air cleanup maintenance. Brochure "ESP" describes retrofit, conversion, repair, and maintenance services for air pollution control equipment, including emergency help. Envirotech/Buell. **165**

Flyash collection. Bulletin E-17144 describes use of fluorocarbon fibers for filtering out flyash and other particulates generated by use of coal. Fabric is called "Armalon". Du Pont **166**

Refuse transfer. Bulletin No. SWH-72544-578 offers solutions to problems of hauling high tonnages of solid waste to distant disposal sites. The Heil Co. **167**

Glass capillaries. "GC Reporter" for June 1978 tells about glass capillaries

especially selective for measuring pesticides and aromatic hydrocarbons, as well as crude oil in water. Supelco, Inc. **168**

Ion exchange. Forms 177-1294 and 177-1296 explain how to select anion and cation exchange resins for water treatment applications, so that a knowledgeable choice can be made. Du Pont **169**

Pollution control. Brochure describes process systems for the pollution control industry; includes water and gas conditioning, fluids processing, and process heating. C-E Natco **170**

Automatic weighing. Brochure describes KWT10 Automatic Weigher and others, for fast, automatic sample weighing coupled to computer modules or other data receivers. Mettler Instrument Corp. **171**

Liquid chromatography. Catalog features full line of products for liquid chromatography analysis, including packings, columns, and the like. Glenco Scientific, Inc. **172**

Nuclear Services. Brochure, "Wyle Nuclear Services", discussed the company's "Nuclear Environmental Qualification" approach to a large variety of nuclear power services. Wyle Laboratories. **173**

Liquid chlorine changeover. Literature describes the Series 50-204 System for automatic changeover for liquid chlorine, ammonia, or SO₂ supplies. Pennwalt/Wallace & Tiernan **174**

Air quality models. Brochure will interest managers concerned with air-quality impact assessment, including Prevention of Significant Deterioration. TRC **175**

Sample preparation. Brochure describes grease-free methods for putting together necessary apparatus to prepare samples for analysis, including those for semi-micro, and micro scale. Wheaton Scientific **176**

Water treatment. Buyer's guide focuses on standard package-size treatment, and details water impurities and

methods of treatment. Covers ion exchange, reverse osmosis, and other methods. Permutit 177

Scale elimination. Brochure tells how scale eliminators can avoid build-up of calcium, iron, magnesium, and other deposits in heat exchangers, filters, nozzles, and other such equipment. Sonic Development Corp. 178

Chlorinator. Literature Series 20-057 describes chlorinator that operates solely from cylinder gas pressure, with no other power supply. Range 22-30 psi. Pennwalt/Wallace & Tiernan. 179

Navigation/positioning. Chart service provides electronic navigation/positioning grids for precise surveys, including those aimed at pinpointing pollution. ENDECO 180

Chlorine monitoring. Data sheet PDS-E400 describes a system that can monitor total free, or residual chlorine. Sample temperature limits 50-85 °F. Polarographic wet chemistry is the principle. Envirotech/National Sonics 181

Slurry conditioning. Brochure tells how to chop, shred, accelerate, mix, and condition slurries in pipes, ducts, tanks, or pumps, with use of Pipeline Delumper® DSC®. Franklin Miller, Inc. 182

Sludge pasteurization. Bulletin 2200-2 tells how sludge exposure to temperatures up to 200 °F deactivates pathogenic organisms, and renders sludge safe for land disposal. Zimpro 183

Pesticide respirators. Data Sheet 10-00-06 describes pesticide respirators and gas masks for protection to those who handle and spray pesticides and certain fumigants. Mine Safety Appliances Co. 184

Cassette recorders. Brochure describes ICT Series of ultra-low-power incremental digital cassette data recorders. Uses for air/water quality monitoring, and oceanographic buoys, as well as others. Datal Systems, Inc. 185

Reverse osmosis. Tech Bulletins 108 and 109 describe applications of reverse osmosis and ultrafiltration, as well as membranes. New areas of use are listed. Osmonics, Inc. 186

N-P detectors. Application Note AN 228-4 (Pub. 5952-5771) describes simplified ways of nitrogen-phospho-

rus (N-P) detection, with applications including toxicology. Hewlett-Packard 187

Visible emissions. Bulletin G1305 describes EPA-approved visible emission monitor system for stack or duct mount. Checks out compliance. Esterline Angus Instrument Corp. 188

Chlorination. Bulletins 3006 and 3007 discuss chlorine gas feed rates at multiple, and at single points of injection, respectively. Capital Controls Co. 189

Water monitor. Brochure describes monitors that measure pH, conductivity, dissolved oxygen, temperature and other important parameters. Series 8000 is featured. HYDROLAB™ CORP. 192

Air purification. Brochure with chart tells how to remove contaminants from air in many indoor environments. Batson Machinery, Inc. 194

OSHA safety supplies. June 1978 catalog lists equipment for sale or lease to meet OSHA regulations, as well as laboratory services available. Interex Corp. 195

FBC technology. Fluidized-Bed Combustion (FBC). FBC Environmental Review is now available. Discusses many aspects. Periodical. Industrial Environmental Research Laboratory, EPA, Research Triangle Park, NC 27711 (write direct).

German environment. "German Studies Notes" covers toxics and citizen participation in environmental affairs, U.S., and W. Germany. Institute of German Studies, Ballantine Hall 666, Indiana University, Bloomington, IN 47401 (write direct).

Toxic substances. Free ACS Service literature covers symposium entitled, "Implementation of the Toxic Substances Control Act". American Chemical Society, Special Issues Sales, 1155 16th St., N.W., Washington, DC 20036 (write direct).

Engineer listing. First national register of officially recognized chemical engineers and chemists in practice, by National Certification Commission in Chemistry and Chemical Engineering. The American Institute of Chemists, 7315 Wisconsin Ave., N.W., Washington, DC 20014 (write direct).



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Environment International: A Journal of Science, Health, Monitoring, and Policy. A. A. Moghissi, Editor-in-Chief. Periodical. Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, NY 10523. \$72.60 (libraries); \$30 (individuals whose library subscribes), for annual subscription.

This journal offers a forum for up-to-date data, causes of pollution, and methods for protection. Control technologies, description/interpretation of laws, health effects, pollutant transport, and many other relevant topics are discussed.

Disposal and Decontamination of Pesticides. Maurice V. Kennedy. 158 pages. American Chemical Society, 1155 16th St., N.W., Washington, DC 20036.

Misuse of pesticides, or their overuse, has led to the necessity to decontaminate them and dispose of them. But there has been a whole variety used, and much lack of information as to their proper disposal. Moreover, no standard disposal method exists. But here is a collection of papers providing the latest information that has been accrued to date. It is No. 73 in the ACS Symposium Series.

Environmental Science. Amos Turk et al. xiii + 597 pages. W. B. Saunders Co., West Washington Square, Philadelphia, PA 19105. 1978. \$15.95, hard cover.

This work is a textbook, complete with instructor's manual, of environmental science. It offers an in-depth survey of many aspects of this broad field but, despite the breadth and depth of coverage, the language is easily understandable. Each topic is illustrated with case histories from various parts of the world.

Stalking the Wild Taboo. Second edition. Garrett Hardin. ix + 284 pages. William Kaufmann, Inc., One First St., Los Altos, CA 94022. 1978. \$11.95, clothbound.

This book updates the first edition published in 1973. It questions, for example, whether there really is a pressing need for rapid nuclear power

expansion, how environmental disruption can be precisely defined, and to what extent population control is really critical. The author presents a series of essays, including 17 since the last edition came out.

Industrial Water Pollution: Origins, Characteristics, and Treatment. Nelson L. Nemerow. xii + 738 pages. Addison-Wesley Publishing Co., Inc., Reading, MA 01867. 1978. \$14.95, hard cover.

This work covers sources of pollution, sewers, sludge, treatment plants, and monitoring. Numerous case histories are given. Economics are discussed, and various types, and treatments for municipal and industrial wastes are categorized and explained.

International Engineering Directory. Document No. 61. American Consulting Engineers Council, 1155 15th St., N.W., Washington, DC 20005. 1978. \$10.

Need help in designing a wastewater plant in California? An air pollution cleanup system in Japan? This directory lists, in 3 languages, consulting engineers and firms which are Council members, worldwide. Services, capabilities, personnel, and other necessary and pertinent information is included.

Environmental Law Handbook. 576 pages. Government Institutes, Inc., 4733 Bethesda Ave., Washington, DC 20014. 1978. \$34.50.

This book is the fifth edition. It covers latest court decisions, air/water/noise pollution, land use, pesticides, and resource conservation. Especially covered are the latest Clean Air and Clean Water Amendments, and the Toxic Substances and Resource Conservation and Recovery Acts.

Bio-Energy Directory. The Bio-Energy Council, Suite 204, 1337 Connecticut Ave., N.W., Washington, DC 20036. 1978. \$24.

This directory presents more than 200 entries concerning bio-energy programs in the public and private

sectors. They cover operations, sponsors' financial commitments, and names/addresses of personnel. Listed are: Systems to produce/harvest renewable biomass; techniques for burning biomass; and processes to convert biomass to a wide variety of solid, liquid, and gaseous fuels.

Water in Synthetic Fuel Production. 296 pages. The MIT Press, 28 Carleton St., Cambridge, MA 02142. 1978. \$14.95, hard cover; \$9.95, paper.

To beneficiate oil shale, and to make synfuels from coal, much fresh water will be required, and much dirty water will be produced. Problems of supply will be most acute in western states. Water use, cleanup, recycle, and reuse for these fuel-making processes are thoroughly discussed in this book, which resulted from a National Science Foundation-supported study.

Growing and Saving Vegetable Seeds. Marc Rogers. iv + 139 pages. Garden Way Publishing Co., Charlotte, VT 05445. 1978. \$4.95, paper.

Pesticide and artificial fertilizer use could be curtailed somewhat through saving vegetable seeds. The idea is that succeeding generations of these plants become accustomed to local conditions, and resistant to insect and fungus pests indigenous to the area. This book tells why this is the case, and explains how healthier "regional" varieties may be developed and propagated.

Gold Dust. Periodical. The Mellvaine Co., 2970 Maria Ave., Northbrook, IL 60062. 1978. \$106/year, U.S., \$116/year, foreign (except Canada and Mexico).

This periodical is a management newsletter for the world's air pollution control industry. It reports on market projections for various industries and countries, and advises concerning placement of promotional dollars. Financial information is given for various companies, and new legislation is analyzed for market effects. New opportunities in the air pollution control field are discussed.

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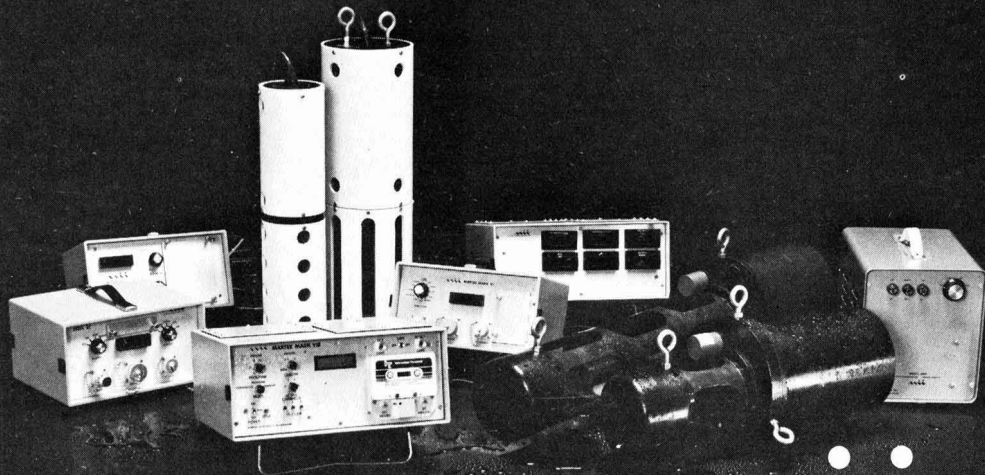
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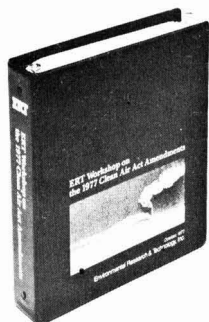
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ERT Handbook on Industrial Expansion and the 1977 Clean Air Act Amendments. 29 pages. ERT, 696 Virginia Road, Concord, MA 01742. 1978. \$2, paper.

For interests affected by the latest clean air laws, here is a précis of what they must face, if they desire to expand their activities. New source, prevention of significant deterioration, Classes I, II, and III, and other pertinent matters are covered.

The Reclamation of Disturbed Arid Lands. Robert A Wright, Ed. x + 196 pages. Dr. Max Dunford, Executive Secretary, Southwestern and Rocky Mountain Division of AAAS, P.O. Box 3 AF, Las Cruces, NM 88001. 1978. \$4.95, hard cover.

Mining activity can disturb many arid lands and their highly fragile ecological balances. But this damage can be minimized and, in many cases, reversed, if the proper efforts are expended. This book explains what research is being done in these directions, and presents several specific project case histories.

Fungi, Man and His Environment. R. C. Cooke. ix + 144 pages. Longman, 19 W. 44th St., New York, NY 10036. 1978. \$15.50, hard cover.

Some fungi are edible. Others are toxic. Yet others are pests. Still others are beneficial against pests. This book lists many fungi, and explains beneficial and detrimental aspects of them. Interactions between fungi and other organisms is also covered.

Handbook of Air Pollution Analysis. Roger Perry, Robert J. Young, Eds. xiv + 506 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1978. \$37.50, hard cover.

In order to gauge air pollution, one must determine its location and components. This book explains in great detail how to accomplish those tasks. Sampling techniques and analysis methods are discussed, as are pollution origins.

Petroleum Refining Industry: Energy Saving and Environmental Control. Marshall Sittig. x + 372 pages. Noyes Data Corp., Mill Road at Grand Ave., Park Ridge, NJ 07656. 1978. \$39, hard cover.

The petroleum refining industry is now called upon to solve many pollution problems. This book explains how a refinery works, what the pollutants are, and what the latest technology is to address these problems. New energy conservation technology is also discussed.

Highly Hazardous Materials Spills and Emergency Planning. J. E. Zajic, W. A. Himmelman. 240 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, NY 10016. 1978. \$24.50, hard cover.

Millions of pounds of toxic and hazardous substances are carried by many means of transportation, but little information about their handling is in print in a systematic manner. This book answers the need for such information; it identifies toxic chemicals, and outlines known procedures/technology for handling toxic spillages. Latent hazards are also examined. Case histories are given.

Handbook of Pollution Control Management. Herbert F. Lund, Ed. 444 pages. Prentice-Hall, Inc., Englewood Cliffs, NJ 07632. 1978. \$39.95.

Coming: toxic effluent standards; "best available technology"; tough clean air and hazardous materials regulations, among other things. Can business and industry meet those tough rules without adding severely to overhead, and disrupting normal operations? "Yes" is the answer given by 22 top experts in the pollution control field, and they explain why and how, in very great depth.

Engineering for Nuclear Fuel Reprocessing. Justin T. Long. 1036 pages. American Nuclear Society, 555 North Kensington Ave., La Grange Park, IL 60525. 1978. \$68, hard cover.

This book fully explains methods of processing spent nuclear reactor fuel elements in order to recover valuable unburned fuel. Radiochemical plant design, process data, engineering principles, and other pertinent topics are covered. Shielding, criticality control, waste disposal, fuel element storage/handling, and materials accountability are among the many topics discussed.

Microphysics of Clouds and Precipitation. Hans R. Pruppacher. xvi + 706 pages. D. Reidel Publishing Co., Lincoln Building, 160 Old Derby St., Hingham, MA 02043. 1978. \$39.

Acid rain. How does it actually form? What other pollutants might one expect to be washed down with rain? Answers to these and related questions can be found in this book, which covers cloud and drop formation, atmospheric chemistry, aerosols, and other related topics. The book presents very important basic information on cloud and precipitation formation, even though it assumes no special knowledge of meteorology on the reader's part.

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September 19-23 San Francisco, Calif.

Seventh Congress on Waste Management Technology and Resource and Energy Recovery. National Solid Wastes Management Association (NSWMA)

Write: NSWMA, 1120 Connecticut Ave., N.W., Suite 930, Washington, D.C. 20036

September 20-21 Phoenix, Ariz.
Third International Fabric Alternatives Forum. Arizona State University and American Air Filter Co.

Write: R. C. Braverman, American Air Filter Co., 215 Central Ave., Louisville, Ky. 40277

September 20-22 Lexington, Ky.
Third Annual Governor's Conference on the Environment. Commonwealth of Kentucky

Write: Kentucky Dept. for Natural Resources and Environmental Protection, 4th Floor, Capital Plaza Tower, Frankfort, Ky. 40601

September 20-22 Minneapolis, Minn.

Fourth National Ground Water Quality Symposium. National Water Well Association

Write: Dr. Jay H. Lehr, National Water Well Association, 500 W. Wilson Bridge Rd., Worthington, Ohio 43085

September 21-22 Boston, Mass.
Wasteworks '78: Waste Management Alternatives. National Wildlife Federation and Environmental Action Foundation

Write: Solid Waste Project, National Wildlife Federation, 1412 16th St., N.W., Washington, D.C. 20036

September 23-28 Baltimore, Md.
National Environmental Sanitation and Maintenance Educational Conference & Exposition. Environmental Management Association

Write: Environmental Management Association, Harold C. Rowe, executive director, 1701 Drew St., Clearwater, Fla. 33515

September 25-27 St. Louis, Mo.
1978 Midwest Meeting of the American Geophysical Union. American Geophysical Union

There will be sessions on meteorology and water resources. *Write:* American Geophysical Union, 1909 K St., N.W., Washington, D.C. 20006

September 26 Atlanta, Ga.
Air Quality Committee's Seminar. TAPPI's Environmental Division

Write: Mrs. C. A. Zippay, Technical Association of the Pulp and Paper Industry (TAPPI), One Dunwoody Park, Atlanta, Ga. 30338

September 26-29 Denver, Colo.
Environmental Aspects of Nonconventional Energy Resources. American Nuclear Society

Write: Richard A. Petzke, public information chairman, Public Service Company of Colorado, 5900 E. 39th Ave., Denver, Colo. 80207

September 27-29 Chicago, Ill.
Sixth Annual Illinois Energy Conference on Electric Utilities in Illinois. University of Illinois at Chicago Circle/Energy Resources Center

Write: Energy Resources Center, University of Illinois at Chicago Circle, Box 4348, Chicago, Ill. 60680

October 1-6 Anaheim, Calif.
1978 Annual Conference. Water Pollution Control Federation

Write: Water Pollution Control Federation, 2626 Pennsylvania Ave., N.W., Washington, D.C. 20037

October 3 Chicago, Ill.
Health Hazards of Pregnant Women in the Workplace. National Safety Council

Write: Julian B. Olishifski, National Safety Council, 444 N. Michigan Ave., Chicago, Ill. 60611

October 3-4 New York, N.Y.
Energy Management in Buildings. New York University School of Continuing Education

Write: Heidi E. Kaplan, Dept. 20NR, New York Management Center, 360 Lexington Ave., New York, N.Y. 10017

October 3-5 Philadelphia, Pa.
Fifth International Electric Vehicle Symposium and Exposition. Electric Vehicle Council and the International Union of Producers and Distributors of Electrical Energy

Write: Electric Vehicle Council, 90 Park Ave., New York, N.Y. 10016

October 4-5 Minneapolis, Minn.
Reverse Osmosis/Ultrafiltration for the Production of Pure Water. Osmonics, Inc.

Write: Mrs. Patricia A. Letson, Osmonics, Inc. 15404 Industrial Rd., Hopkins, Minn. 55343

October 4-6 Atlanta, Ga.
Solar Energy Seminar. New York University's School of Continuing Education

Write: Heidi E. Kaplan, Dept. 20NR, New York Management Center, 360 Lexington Ave., New York, N.Y. 10017

October 5-9 Washington, D.C.
First Annual National Energy Expo. National Society for Energy Awareness

Write: National Society for Energy Awareness, Suite 700, 1010 16th St., N.W., Washington, D.C. 20036

October 8-13 New Orleans, La.
Disposal of Oil and Related Materials and Debris Resulting from a Spill Clean-up Operation. American Society for Testing and Materials, Committee F-20

Write: Sam W. Bowman, American Society for Testing & Materials, 1916 Race St., Philadelphia, Pa. 19103

October 9-12 Las Vegas, Nev.
1978 American Mining Congress's International Mining Show. American Mining Congress

Environmental issues will be discussed. *Write:* American Mining Congress, 1100 Ring Building, Washington, D.C. 20036

October 10-12 Rolla, Mo.
UMR-DNR Conference and Exposition on Energy. University of Missouri-Rolla and the Dept. of Natural Resources

Write: Dr. J. Derald Morgan, Electrical Engineering Dept., University of Missouri-Rolla, Rolla, Mo. 65401

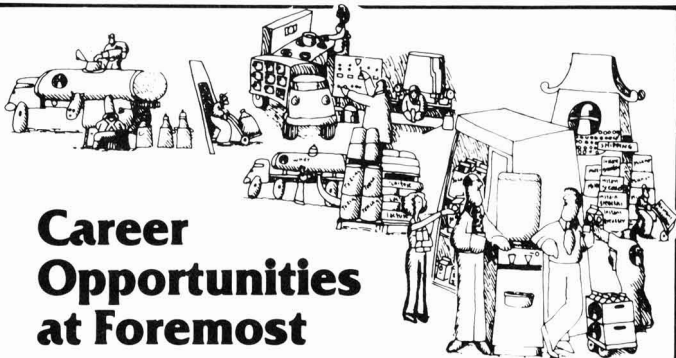
October 12-14 Los Angeles, Calif.
22nd Annual Western Occupational Health Conference. American Industrial Hygiene Association and others

Write: William M. Taylor, M.D., Medical Dept., Standard Oil Co. of California, 324 West El Segundo Blvd., El Segundo, Calif. 90245

October 12-14 Atlanta, Ga.
Second Human Hair Symposium. Human Hair Symposium Program Committee

There will be a paper on scalp hair as a monitor of environmental pollutants. *Write:* A. C. Brown, M.D., 960 Johnson Ferry Rd., N.E., Atlanta, Ga. 30342

(continued on page 1103)



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Send resume and salary requirements to **Executive Director, V. I. Water and Power Authority, P. O. Box 1492, St. Thomas, V. I. 00801.**

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MEETINGS (continued)

October 15-17 Dundee, Ill.
Coal Gasification: Current Status and Future Prospects. Gorham International Inc.

Write: Dr. Andrew C. Nyce, vice president, Gorham International Inc., P.O. Box 8, Gorham, Me. 04038

October 15-19 Los Angeles, Calif.
APHA's 106th Annual Meeting. American Public Health Association

Write: Annual Meeting Program Coordinator, APHA, 1015 18th St., N.W., Washington, D.C. 20036

October 16-18 Washington, D.C.
Symposium on Statistics and the Environment. Research Council's Committee on National Statistics and Committee on Toxicology

Write: Fred Leone, American Statistical Association, 806 15th St., N.W., Washington, D.C. 20005

October 16-18 Philadelphia, Pa.
1978 ISA Conference & Exhibit. Instrument Society of America

There will be a symposium on instrumentation and control in the water and wastewater industry. *Write:* Dr. Harry A. Fertik, Leeds & Northrup Co., Dickerson Rd., North Wales, Pa. 19454

October 16-18 Reston, Va.
Air Quality and Aviation: An International Conference. Society of Automotive Engineers and the Air Pollution Control Association

Write: Anthony J. Broderick, AEQ-10, Federal Aviation Administration, 800 Independence Ave., S.W., Washington, D.C. 20591

October 16-18 Houston, Tex.
Third International Conference on Waste Oil Recovery and Reuse. Association of Petroleum Re-refiners

Write: Association of Petroleum Re-refiners, 1730 Pennsylvania Ave., N.W., Washington, D.C. 20006

October 16-19 Washington, D.C.
92nd Annual Meeting. Association of Official Analytical Chemists (AOAC)

There will be a 2-day long toxicology symposium. *Write:* Luther G. Ensminger, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044

October 17-18 New Orleans, La.
Third ASTM Symposium on Aquatic Toxicology. American Society for Testing and Materials

Write: ASTM, 1916 Race St., Philadelphia, Pa. 19103

(continued on page 1105)

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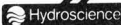
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MEETINGS (continued)

October 17-19 Houston, Tex.
Coal Technology '78: International
Coal Utilization Exhibition and Conference

Write: David I. Johnson, executive director, Coal Technology '78, 6006 Bellaire Blvd., Suite 101, Houston, Tex. 77081

October 18-20 Tulsa, Okla.
National Conference on Energy and the Future of America's Communities.
Tulsa Chamber of Commerce and the Economic Development Commission of Tulsa

Write: Bruce Carnett, Metropolitan Tulsa Chamber of Commerce, 616 S. Boston Ave., Tulsa, Okla. 74119

October 19-20 Chicago, Ill.
Health Hazards in the Arts and Crafts.
Society for Occupational and Environmental Health (SOEH)

Write: SOEH, 1341 G St., N.W., Suite 308, Washington, D.C. 20005

Courses

September 18-22 Cincinnati, Ohio
Analytical Methods for Trace Metals,
Course No. 107.4. EPA

Fee: \$175. *Write:* Registrar, National Training and Operational Technology Center, U.S. EPA, Cincinnati, Ohio 45268

September 19-22 Seattle, Wash.
Control of Particulate Emissions,
Course No. 413. EPA

Fee: \$88. *Write:* Registrar, Air Pollution Training Institute, MD-20, Environmental Research Center, Research Triangle Park, N.C. 27711

September 19-December 5 Los Angeles, Calif.

Solar Energy—Technology and Applications. UCLA Extension's Continuing Education in Engineering and Mathematics

Fee: \$135. *Write:* Continuing Education in Engineering and Mathematics, UCLA Extension, P.O. Box 24902, Los Angeles, Calif. 90024

September 20-22 Houston, Tex.
Environmental Health Management.
International Safety Academy

Fee: \$325. *Write:* International Safety Academy, P.O. Box 19600, 10575 Katy Freeway, Houston, Tex. 70024

September 21 Boston, Mass.
Hazardous Waste Workshop. National Wildlife Federation

No fee. *Write:* National Wildlife Federation, Attention: Solid Waste Project, 1412 16th St., N.W., Washington, D.C. 20036

(continued on page 1106)

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September 23 Davis, Calif.
Solar Energy. University of California-Davis

Fee: \$43 (non-credit). Write: University Extension, University of California, Davis, Calif. 95616

September 25-28 Kansas City, Mo.

Atmospheric Sampling, Course No. 435. EPA

Fee: \$140. Write: Registrar, Air Pollution Training Institute, MD-20, Environmental Research Center, Research Triangle Park, N.C. 27711

September 25-29 Cincinnati, Ohio
Analytical Quality Control, Course No. 151. EPA

Fee: \$110. Write: Instructional Resources Center, National Training and Operational Technology Center, U.S. EPA, Cincinnati, Ohio 45268

September 25-29 Atlanta, Ga.
Legal Aspects of the Occupational Safety and Health Act of 1970, Course No. 599. NIOSH

Fee: \$250. Write: Donna Welage, training registrar, NIOSH, Division of Training & Manpower Development, 4676 Columbia Pkwy., Cincinnati, Ohio 45226

September 27-28 Newark, Del.
Microprocessor Applications. Instrument Society of America

Environmental applications will be discussed. Fee: \$225 (member); \$260 (non-member). Write: ISA Short Courses, 400 Stanwix St., Pittsburgh, Pa. 15222

September 27-29 Denver, Colo.
Solar Energy Opportunities for Public Power Systems.

Fee: \$285 (members); \$335 (nonmembers). Write: Nancy Mooney, APPA, 2600 Virginia Ave., N.W., Suite 212, Washington, D.C. 20037

September 29-30 Anaheim, Calif.
Processes for Wastewater Reclamation and Reuse. University of California Extension

Fee: \$250. Write: Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

October 9-11 Chicago, Ill.
Applications of Air Quality Models for Impact Assessment. A. J. Ranzieri

Fee: \$325. Write: Andrew J. Ranzieri, 64 Cavaleade Circle, Sacramento, Calif. 95831

October 16 Boston, Mass.
Impact of Metals on Environmental Health and Industry. Environmental Sciences Associates, Inc.

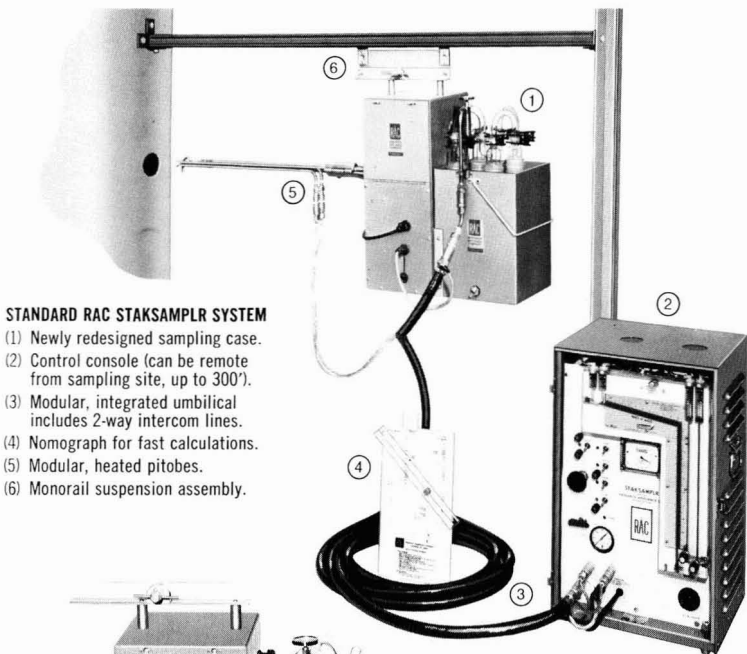
Fee: \$125. Write: Dr. Reginald M. Griffin, ESA Laboratories, Inc., 43 Wiggins Ave., Bedford, Mass. 01730

For sampling
stacks by
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RAC Staksamplr is No. 1 in versatility

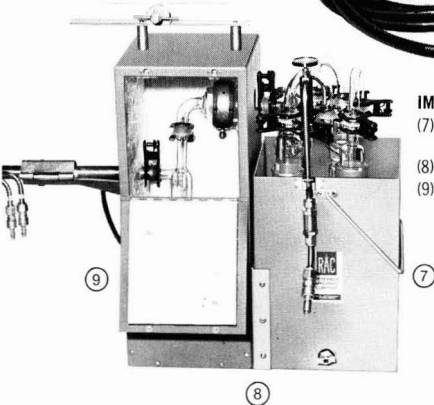
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- (1) Newly redesigned sampling case.
- (2) Control console (can be remote from sampling site, up to 300').
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- (4) Nomograph for fast calculations.
- (5) Modular, heated pitobes.
- (6) Monorail suspension assembly.



IMPROVED 2-MODULE SAMPLE CASE

- (7) New carrying handle for detachable impinger compartment.
- (8) New slip-fit interconnection.
- (9) New door for quicker access to components in heated compartment.



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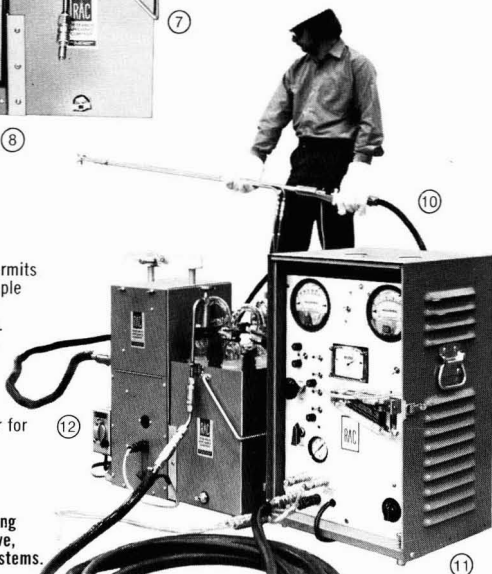
RAC's continuous improvement program is based on the most extensive in-the-field operating experience in the industry, with hundreds of units now in use around the world. That's why **Staksamplr's** performance meets—or exceeds—all accepted standards for sampling emissions from stationary sources.

RAC's modular design concepts also permit easy adaptation of many new components to **Staksamplr** systems already in service . . . enhancing their overall capabilities with minimal effort and cost.

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- (11) New console with magnetic gages for reading differential pressures across orifice & in pitot tube (optional).
- (12) Remote temperature regulator for flexible line (optional).

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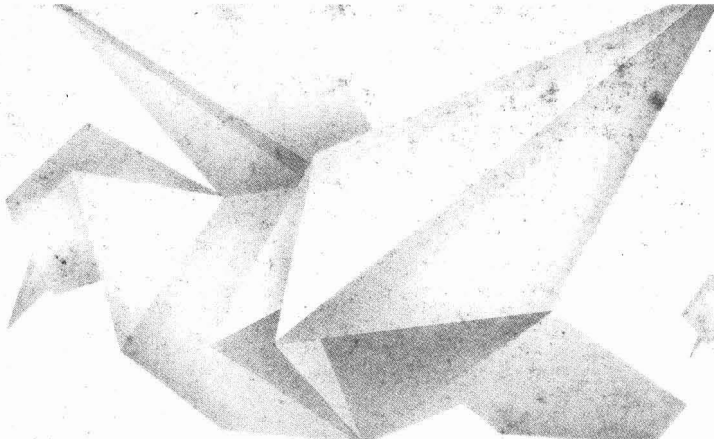
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