

AUGUST 1985

ENVIRONMENTAL PROGRESS



Three Mile Island Cleanup

Experiences, Waste Disposal, And Environmental Impact

Lester J. King and James H. Opelka,
Editors

"The papers included in this book deal with the experiences and problems in cleaning up Three Mile Island Unit-2 (TMI-2) following the accident . . . and the waste disposal and environmental impacts of the cleanup.

The material damages and losses resulting from the accident are very high. Cleanup will take many years and . . . costs will certainly be somewhere near \$1 billion" (from the foreword).

Contents:

- Three Mile Island Unit 2 (TMI-2) Reactor Building Venting Experience.
- TMI Containment Entry Program.
- Water Decontamination Process Improvement Tests and Considerations.
- TMI-2 Technical Information and Examination Program.
- Generation, Classification, Treatment and Disposal of Solid Waste Forms Resulting from Cleanup of TMI-2.
- Three Mile Island Waste Management: A DOE Perspective.
- Radiation Effects on Ion Exchange Materials Used in Waste Management.
- Three Mile Island Zeolite Vitrification Demonstration Program.

Material presented was selected from papers presented at AIChE's National Meeting in Detroit, Michigan, August 16-19, 1981.

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Photo courtesy Fluid Systems, one of the Signal Companies, San Diego, Calif.

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Acid Rain and the Chemical Engineer

by Richard D. Siegel

Acidic deposition is one of the most controversial environmental issues in the United States, largely due to incomplete scientific information that accurately describes the magnitude and extent of its impact on aquatic and terrestrial resources and the relationship between anthropogenic sources and sensitive receptors. At the present time, U.S. policy makers have been unable to achieve a consensus amongst the scientists, engineers, economists, and numerous special interest groups required to develop and adopt an appropriate legislative response to the problem. Proposed legislation ranges from mandated use of flue gas desulfurization systems on all large electric utility plants to programs permitting selection of the most cost effective means to achieve compliance with designated emission limitations in only those regions proximate to sensitive receptors.

The first question that policy makers must resolve is whether we should impose control now, recognizing the significant uncertainty associated with the effectiveness of any control program. A significant economic burden will be associated with any action; one must weigh the possibility and concomitant political risk that the selected control program may ultimately be found unwarranted or inappropriately focused against the potential risk of continued environmental and material damages. Should that issue be resolved in favor of control, one must then resolve the even thornier questions of control procedures and cost allocation.

By mandating technology, for example by requiring use of flue gas desulfurization on most of the older large utility boilers, legislators will deny an owner/operator the freedom of choice to select the lowest cost option for his facility. Such a strategy will protect the high sulfur coal interests in Appalachia by not permitting many facilities to switch to lower sulfur eastern or western fuel sources to achieve a desired emission reduction. But it will impose an incremental cost burden on consumers, and probably eliminate the incentive for development of new control technology.

The American Institute of Chemical Engineers' Government Program Steering Committee (GPSC) has considered this latter question in the context of our responsibility to contribute to this discussion in our area of expertise—control technology. GPSC concluded in its recent *Commentary, Technology Recommendations for the Reduction and Abatement of Acid Rain*, "... that if an emission reduction program is required, it should be based on the most cost-effective control technology applicable to the specific facility (system) in question." The report further states that if legislation is enacted, it should provide incentives for in-

dustry to adopt advanced technologies for precombustion, *in situ* and post combustion control to achieve system wide objectives.

Given the foregoing flexibility, many organizations will choose to achieve compliance with specified emission limits through fuel switching. The societal impact of such a choice must, therefore, be considered by the Congress in its development of such legislation. That is, the Congress must not only address the issue of allocation of the direct costs for control (e.g., the consumer of the "product" from affected facilities, individuals in those areas currently impacted by acidic deposition, or the country as a whole) but the indirect costs associated with loss of livelihood, relocation, etc., as fuel use patterns are modified to meet demand.

It is our duty to make sure that the foregoing issues are thoroughly understood by the policy makers, our friends, and our associates as we deal with this complex issue. Further, although most of us lack expertise related to source-receptor relationships, we must not be afraid to speak out as we see factual distortions perpetrated by non-technically trained individuals in their zeal to develop a case for their cause. For example, the public press is currently strongly implying that the damages now being seen throughout the forest systems in Europe and portions of the Eastern United States are due to acidic deposition. While this possibility exists, one must call attention to the fact that responsible scientists from both sides of the acid rain debate freely admit that the specific source(s) of this problem cannot be determined at this time. That is, a variety of stresses may be causing the observed damages, including climactic stress (drought) and other atmospheric contaminants such as ozone.

Whether you agree or disagree with GPSC's recommendations, I hope you agree with the necessity for chemical engineers to participate in this dialogue in order to help assure that (1) the decisions reached by our policy makers are based on accurate representations of the facts of the matter, and (2) the perspectives and needs of all affected parties are fairly considered in the establishment of said policy.

Richard D. Siegel is Senior Environmental Consultant with Environmental Research and Technology Inc. He is a founding member of Environmental Progress' Advisory Board and is past chairman of the AIChE Environmental Division and is current chairman of the air section. He is vice-chairman of the Government Programs Steering Committee.

Ethyl, in Agreement with Dupont, To Sell Antiknock Compound Overseas

Ethyl Corp. has made a joint arrangement with E. I. duPont deNemours & Co. under which Ethyl will sell and distribute lead antiknock compounds to the export market.

Du Pont will produce the compounds at its plant in Deepwater, N.J., and Ethyl will supply the export market, using its personnel and facilities for sale and distribution.

"As a result of current and anticipated further restrictions on the allowable use of lead antiknocks in gasoline, this is an essential step if compounds produced in the United States are to compete successfully in the international market," Floyd D. Gottwald, Jr., chairman of the board of Ethyl said.

The Ethyl executive also said that the firm will shut down the remaining units of its Baton Rouge, La., manufacturing facilities. According to company plans, the lead antiknock unit will be shut down as soon as practical and the intermediate sodium unit will be phased out over the next several months. Current lead antiknock inventory and similar long-term antiknock purchase arrangements will assure adequate supply for its U.S. customers.

Shutdown of the Baton Rouge manufacturing facilities will involve the layoff or retirement of approximately 250 employees. Research and development activities will continue, however, at the Baton Rouge site.

Environment Award for 3M

The 3M Co. received the World Environment Center's first award for International Corporate Environment Achievement.

Presented in Washington, D.C., May 10, the award was in recognition of the company's pioneering Pollution Prevention Pays (3P) program. The 3P Program seeks to eliminate industrial pollution at the source — in product development and manufacturing processes.

Begun in 1975 as a key element in 3M's worldwide manufacturing efforts, 3P has resulted in annually preventing 98,000 tons of air pollutants, 10,500 tons of water pollutants, 150,000 tons of sludge and solid waste, and 1.5 billion gallons of wastewater. The company estimates that a 10-year savings through the 3P Program saved them \$235 million. This program is in effect in the United States as well as 20 foreign countries where 3M manufactures consumer, industrial, technical, and health care products.

Lewis W. Lehr, 3M chairman and chief executive officer, in accepting the award, said the only sensible course for industry is to anticipate and prevent product and process pollution problems — not to clean up pollution after it has been created. He called for the cooperation of industry and government in addressing environmental problems.

The World Environment Center award was the second recent major recognition the 3P program received. A special award from the governor of Minnesota was presented to the company April 29 in recognition of the 10th anniversary of 3P.

Japan Joins Ocean Drilling Program

The National Science Foundation and the Ocean Research Institute of the University of Tokyo signed a Memorandum of Understanding for cooperation in the Ocean Drilling Program, June 5. The ODP is an international partnership of scientists and governments who have joined resources to explore ocean basins to find clues on how the earth was formed and developed.

The agreement calls for Japanese participation, in principle, for the nine year duration of the ODP. The primary purpose of the program is to provide core samples from beneath the oceans' floors to enable researchers to study sediments and rocks that underlie them and thus learn about the structure of the planet, earth's interior, life in the oceans, and changes

in global climate. ODP scientists use the 470 ft. drillship JOIDES Resolution to conduct their research.

The memorandum stipulates that Japan will contribute \$2.5 million in U.S. currency annually to the project. This entitles Japanese researchers to have two scientific representatives on each cruise and one co-chief scientist a year. The Japanese also will take part in ODP planning, including the selection of cruise sites.

Members of the ODP, in addition to the United States and Japan, are Canada, France, and the Federal Republic of Germany. Negotiations are in progress with the United Kingdom, and a European consortium which includes Belgium, Denmark, Greece, Italy, the Netherlands, Norway, Spain, Sweden, and Switzerland.

Weston Awarded \$3.7 Million for Technology Development

Roy F. Weston, Inc. has been awarded a \$3.7 million contract to provide research and development services for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) over the next three years.

Weston's work under the contract will support USATHAMA's Installation Restoration program, which was organized several years ago in response to requirements for correcting current environmental problems caused by past disposal practices. Tar-

gets include disposal sites, waste lagoons and contaminated groundwater left from past industrial operations, some of which pre-date World War II. The program's objectives are to stop pollution from moving off Army property and restore selected Army real estate to a condition that allows unrestricted use.

Under the new contract, the major focus of Weston's activities will be the development, design, construction, and field demonstration of innova-

tive hazardous waste treatment technologies. The firm will develop new or innovative soil and groundwater decontamination technology that is more cost-effective and efficient.

Weston has been under contract to USATHAMA since 1982 and has developed technology for them including the removal of solvents, pesticides, and heavy groundwater and incinerating sludge contaminated with explosives.

Books

Contaminant Removal from Public Water Systems, Houck, D.C. *et al*, Noyes Publications, Park Ridge, NJ, 1985, 524 pp. \$52.

Safe Storage of Laboratory Chemicals, Repitone, D. A., ed., John Wiley, New York, NY, 1984, 280 pp. \$60.

Handbook of Toxic and Hazardous Chemicals and Carcinogens, 2nd ed., Sitty, M., ed., Noyes Publications, Park Ridge, NJ, 1985, 950 pp. \$96.

Biotechnology: A Textbook of Industrial Microbiology, Creyger, M. and Creiyer, A., Sinauer Associates, Sunderland, MA, 1984, 308 pp. \$30.

Incineration Systems—Selection and Design, Brunner, C. R., Van Nostrand Reinhold, New York, NY, 1984, 417 pp. \$52.50.

Recovery Recycle and Reuse of Industrial Wastes, Noll, K. E., Haas, C. H., Schmidt, C. and Kodukula, P., Lewis Publishers, Chelsea, MI, 1985, 196 pp. \$24.95.

Multi-Media Compliance Inspection Manual, USEPA, Government Institute, Washington, DC, 1985, 195 pp. \$35.

Mineral Impurities in Coal Combustion: Behavior, Problems and Remedial Measures, Raask, E., Hemisphere Publishing, New York, NY, 1985, 484 pp. \$69.

Corrosion and Deposits from Combustion Gases: Abstracts and Index, Radway, J. F., ed, Hemisphere Publishing, New York, NY, 1985, 575 pp., \$95.

Conferences

November 10-14, 1985 AIChE

The American Institute of Chemical Engineers will hold its Annual Meeting in Chicago, Illinois with the Environmental Division having a major fraction of the program. Almost 30 sessions will be held on air, water, and hazardous waste problems and control. Contact AIChE, 345 E. 47th St., New York, NY 10017

December 2-6, 1985 Polmet-85

The First Asia/Pacific Conference on Pollution in the Urban Environment will be held in Hong Kong under the sponsorship of the government and the Hong Kong Institute of Chemical Engineers. The focus of the meeting and exhibition will be on policies, programs, technologies and practices and solutions to urban pollution problems. Contact Interport, P.O. Box 333, Sunset Beach, CA, 90742.

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Treatment of an *In-Situ* Oil-Shale Retort Water

An experimental study of the effectiveness of coagulation-sedimentation and activated-carbon systems.

D. J. Kocornik, W. F. McTernan, and S. L. Williams, Western Research Institute, Laramie, Wyoming 82071

The oil shale in the Green River formation in Colorado, Utah, and Wyoming represents an immense potential energy resource. It has been estimated [6] that there are approximately 1.8 trillion barrels of oil stored in western oil shale, and that about 80 billion barrels are currently recoverable. One major environmental issue related to utilizing this resource is the large amounts of water that are produced, consumed, and/or contaminated during retorting. Different retorting processes produce between 0.1 and 22 barrels of contaminated retort water for every barrel of oil produced [7]. Although these waters may present a significant water treatment problem for a large-scale shale oil industry, it should be understood that the water does not necessarily have to be treated enough to meet environmental discharge requirements. It may be more practical to treat the water to a level of purity suitable for reuse in the oil shale plant. Potential uses include spent shale wetting, dust control, and cooling water make-up [10].

The specific retort water addressed in this paper is Geokinetics-17, a product of a true in situ retort operated south of Vernal, Utah, in 1979. The oil-to-water production ratio reported at this retort was 0.97 [16]. This water has

been stored in barrels at the Western Research Institute's Refrigerated Research Sample Repository at 4.5°C since it was collected [16]. The water sample is characterized by high levels of organic carbon, ammonia, dissolved solids, and alkalinity [15]. Some representative contaminant levels for Geokinetics 17 water as well as for three other retort waters produced by other processes are presented in Table I.

The objectives of this study were to evaluate the effectiveness of coagulation-sedimentation and activated carbon systems, alone and in combination, as possible steps in the treatment of this water.

EXPERIMENTAL

Coagulation-Sedimentation

Three inorganic salts and four synthetic organic polymers were tested as primary coagulants. These were: $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $CaCl_2$, Nalco polymer 7731, Nalco polymer 7736, Allied Clarifloc C305P, and Allied Clarifloc C303. These experiments were structured to evaluate the direct removal of organic microemulsions as

TABLE I. EXAMPLE WATER QUALITY DATA FOR SELECTED OIL SHALE RETORTS

Constituent	1 Surface Retort	2 Simulated Modified In Situ Retort	3 Modified In Situ Retort	4 True In Situ Retort
Alkalinity (as $CaCO_3$)	26,600	6,690	7,190	12,900
Calcium	708	7.6	11	4.1
Carbon, inorganic	223	1,186	1,040	2,580
Carbon, organic	40,800	3,910	2,890	2,280
Chloride	32,800	2,190	392	3,180
COD	136,000	13,700	14,000	—
Conductivity (μ mhos/cm)	63,000	17,600	13,000	19,000
Ammonia	2,180	1,340	1,320	1,350
Oil and Grease	2,210	1,020	391	—
pH (SU)	8.35	8.65	8.84	8.69
Phenols	6.1	—	47	37.3
Potassium	57	16	104	138
Sodium	308	270	2,600	4,830
Sulfate	8,720	1,860	1,430	1,100
Total Dissolved Solids	—	5,240	8,900	14,000

Notes: a) Concentrations in mg/l except as noted; b) Retort water LETC Designations are 1) 79-Paraho-77778-00W-00C; 2) 79-150T-S1SR-R17-00W-U01-17-00W-00-U01; 3) 79-OXY-6-02W-00-C; and 4) 79-Geokinetics-17-00W-00-U.

well as the secondary adsorption and precipitation of dissolved organics. These processes were evaluated to determine individual unit operation performance as well as to identify possible pretreatment approaches to enhance adsorption and activated carbon capacity.

The following jar tests were performed in sequence:

1. pH response (pH 2-10)
2. dose response (100-2000 mg/liter inorganics, 25-90 mg/liter organics)
3. Gt (where G is the mixing intensity [sec^{-1}] and t is time [sec]) variation in the rapid mix and slow mix

As each optimum was determined, it was incorporated into subsequent tests.

Jar test apparatus consisted of a Phipps and Bird six-paddle gang stirrer and 600-ml beakers containing 400 ml of wastewater each. Samples were initially rapid mixed at 80 rpm for 1 minute, slow mixed at 20 rpm for 15 minutes, and settled for 20 minutes. The supernatant was filtered through a 0.45μ filter. Jar test results were evaluated in terms of the dissolved organic carbon (DOC) content of the effluent samples. Organic carbon was measured by high temperature combustion on a Coulometrics Model 5010 CO_2 Coulometer and a Model 5020 Total Carbon Apparatus manufactured by Coulometrics, Inc.

Three organic polymers were tested as coagulant and/or flocculant aids. These were Betz 1125-L, Poly-floc 3, and Betz 1190. Coagulant aids were added for the last thirty seconds of the rapid mix and flocculant aids were added for the last five minutes of the slow mix.

Activated Carbon Adsorption

Two commercially available activated carbons were used for tests in this phase of the study. These were Filtrasorb 400 (F400), an eastern coal-based carbon made by Calgon Corporation, and Carborundum 1240 (C1240), a western coal-based carbon manufactured by CECA, Inc. Powdered forms of both carbons were prepared by pulverizing the granular form and sifting 100% of it through a #200 mesh screen (U.S. sieve size).

Standard equilibrium uptake and isotherm batch tests were conducted as detailed below with both powdered carbons on untreated Geokinetics water, water previously coagulated by the optimum primary coagulant, and water treated by the optimum coagulant-coagulant aid combination.

Equilibrium uptake tests were conducted using a constant amount of powdered activated carbon (PAC) (2000 mg/liter) added to a constant volume of water (100 ml) in sealed flasks in 25°C shaker water baths. The agitation rate was adequate to maintain constant motion of the water and PAC. Flasks were removed at specific time intervals. PAC was removed by 0.45μ filtration and DOC analysis was performed on the sample. System equilibrium was assumed when DOC concentration remained constant over several intervals.

Isotherm tests were conducted with the same apparatus, with the PAC dose varied from 0 to 10,000 mg/liter. The samples were left on the shaker at least one and one half times the equilibrium time that was established in the equilibrium uptake tests. Isotherm data were collected at both 25°C and 50°C.

Experiments with granular activated carbon (GAC) (U.S. sieve size number 12/number 40) were conducted only on untreated retort water and included batch equilibrium uptake tests (2000 mg/liter) and isotherms tests (0-50,000 mg/liter GAC; 5°C, 25°C, 50°C) paralleling those outlined above. A dynamic granular carbon system was also evaluated. The flow-through column apparatus used in the continuous flow study consisted of five plexiglass carbon columns, each with a 5.08-cm inside diameter. Each column contained 186.6 g GAC before backwashing. Flow through

the system was 75 ml/minute ($4.5 \times 10^{-3} \text{ m}^3/\text{hr}$) moving in a downflow mode, which is within the low range of feed rates recommended by Calgon Corporation [3]. Sampling valves at the bottom of each column allowed the DOC concentration to be monitored throughout the study. Samples were stored under refrigeration prior to analysis.

RESULTS

Coagulation-Sedimentation

The seven primary coagulants achieved overall TOC reductions of between 8 and 19 percent in the untreated water. Of these, 1000 mg/liter ferrous sulfate at pH 4, which achieved 19 percent TOC reduction, was selected for further study. This treatment is hereafter referred to as "coagulated water."

The results of the coagulant aid and flocculant aid experiments showed that, in general, polymers functioned more effectively as coagulant aids (26 to 36 percent TOC removals) than as flocculant aids (19 to 22 percent TOC removals). Overall, 1000 mg/liter ferrous sulfate with 50 mg/liter B1190 coagulant aid at pH 4 was selected as the best approach, based on consistency and reproducibility of results. This treatment is hereafter referred to as "coagulated with coagulant aid water."

When the mixing parameters were varied, rapid mix Gt values from 1451 to 10,200 achieved TOC reductions between 16 and 18 percent. Slow mix Gt values ranging from 19,440 to 144,240 achieved TOC reductions between 16 and 20 percent.

The purpose of the Gt variation phase of the study was to establish what level of power input to the system resulted in the optimum floc formation. This power level needed to be great enough to accomplish mixing of the particles subject to coagulation (i.e., increase their contact opportunities), but not so great that the floc particles would be sheared apart by the turbulence produced. Since there were no statistical differences (one-way analysis of variance) between the results obtained under the various mixing conditions tested, the data indicated that sufficient energy input to achieve coagulation and flocculation is readily obtained. Once established, floc and effluent conditions are apparently stable.

Activated Carbon

The two activated carbons in the PAC equilibrium uptake tests are compared in Figure 1 and are shown to be equally effective in all three cases. The results of all the PAC batch isotherms done at 25°C and 50°C are presented

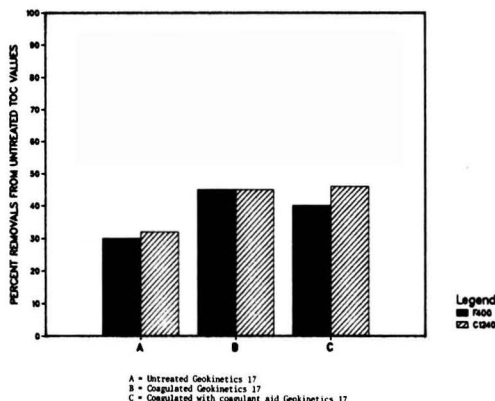


Figure 1. Comparison of carbons—percent removal from untreated water TOC values by 2000 mg/liter of F400 and C1240 powdered activated carbons.

in Tables 2 and 3. Again, the two types of PAC performed equally; different DOC values noted on the same test and PAC dose are largely due to the variable DOC influent concentration. The results from the GAC isotherm tests at 5°C, 25°C, and 50°C are shown in Table 4. These GAC batch isotherm tests were more extensive because the data were to be used in the design of the continuous-flow GAC study that followed. Equations fitting two models to all of the 25°C isotherm data are presented later in this paper.

The breakthrough curves for the carbon column data are found in Figure 2. The slopes of these curves progressively decrease between the first and last columns. Influent, exhaustion, and breakthrough TOC concentrations are all noted on the figure. Ultimate capacities were calculated for each column according to Humenick's [12] graphical integration procedure and are expressed as a unitless parameter (mg TOC adsorbed/mg adsorbent). The average ultimate capacity for all five columns was 0.30.

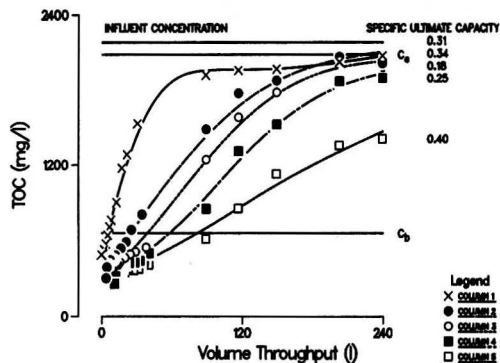


Figure 2. Plot of TOC breakthrough curves, including column specific ultimate capacities.

DISCUSSION AND CONCLUSIONS

Coagulation-Sedimentation

The best TOC removals obtained for all three coagulation systems (primary coagulant [19 percent], coagulant and coagulant aid [30 percent], coagulant and flocculant aid [20 percent]) indicate that coagulation will not be an effective sole treatment process for this water. These re-

sults do not preclude coagulation as a useful pretreatment to another treatment process.

Coagulation processes primarily removed charged colloids [1], so activated carbon, which acts mainly on large organic molecules in solution [1, 5] was chosen as a process likely to complement the coagulation step.

TABLE 2. EQUILIBRIUM DOC VALUES (MG/LITER) FOR VARYING POWDERED ACTIVATED CARBON DOSAGES UNDER ISOTHERMAL CONDITIONS 25°C

Water	Carbon	PAC doses (mg/liter)						
		0	100	500	1000	1500	2000	10,000
Untreated	F400 PAC	1849	1789	1675	1587	1483	1428	740
	C1240 PAC	1884	1847	1774	1654	1561	1483	731
Coagulated	F400 PAC	1523	1446	1374	1272	1173	1016	449
	C1240 PAC	1680	—	1518	1400	1202	1193	504
Coagulated with Coagulant Aid	F400 PAC	1560	—	—	1289	1203	1101	403
	C1240 PAC	1508	—	1330	1178	1126	1013	432

TABLE 3. EQUILIBRIUM DOC VALUES (MG/LITER) FOR VARYING POWDERED ACTIVATED CARBON DOSAGES UNDER ISOTHERMAL CONDITIONS 50°C

Water	Carbon	PAC doses (mg/liter)						
		0	100	500	1000	1500	2000	10,000
Untreated	F400 PAC	1934	—	1762	1661	1503	1509	768
	C1240 PAC	1964	1887	1854	1687	1614	1520	782
Coagulated	F400 PAC	1419	1388	1302	1245	1153	1102	459
	C1240 PAC	1726	1687	1536	1361	1187	1157	542
Coagulated with Coagulant Aid	F400 PAC	1552	1501	1396	1258	1138	1113	438
	C1240 PAC	1486	1454	1308	1212	1061	1091	454

TABLE 4. EQUILIBRIUM DOC VALUES (MG/LITER) FOR VARYING GRANULAR ACTIVATED CARBON DOSAGES UNDER ISOTHERMAL CONDITIONS

Water	Temperature	Carbon	PAC doses (mg/liter)								
			0	500	1000	1500	2000	10,000	20,000	30,000	50,000
Untreated	5°C	F400 GAC	1810	1737	1676	1604	1533	821	507	437	330
	25°C	F400 GAC	1832	1749	1633	1513	1405	658	477	379	312
	50°C	F400 GAC	1735	1605	1568	1385	1283	613	486	403	317

Activated Carbon

Batch

The equilibrium uptake studies conducted on both the untreated and coagulant-pretreated Geokinetics water showed that the two processes, used in the sequence, had a cumulative effect on total organic carbon removal (Table 5).

The equilibrium uptake data were plotted on semi-log paper and analyzed for the DOC transfer coefficient according to the method suggested by Gilbert and Libby [9]. The slopes of linear portions of the curves are equal to the rate coefficient, *K* (Table 6).

$$\text{Overall DOC transfer coefficient} = K = \frac{\text{Ln}C_1 - \text{Ln}C_2}{t_2 - t_1}$$

This analysis shows that there are two or three identifiable sections of each curve, with each section being adsorbed at a different rate. The relative rates for each section of these curves remain consistent throughout the study. These sections of the curves appear to correspond to homologous groups of organic molecules which are each adsorbed at different rates [4]. The highly heterogeneous nature of this retort water increases the plausibility of applying this physical description to these adsorption systems.

The system-specific parameters affecting adsorption rate are also clarified in Table 6. For this wastewater, the adsorption rate decreased with increasing adsorbent particle size, was faster for C1240 PAC than for F400 PAC, and increased when the water was pretreated by coagulation. It seemed that increasing the rate of adsorption was the only nonadditive contribution of pretreatment by coagulation. This change in adsorption rate may be explained if coagulation is assumed to have removed a portion of the colloids and turbidity that could interfere with and retard adsorption.

It was thought that the removal of colloids might also favorably affect the ultimate capacities of the carbons (again by the removal of interferences), but this effect was not observed (Table 7). Linearized equations along with corre-

TABLE 5. PERCENT DOC REMOVALS WITH SINGLE AND COMBINATION TREATMENT APPROACHES

Treatment	F400	C1240
1000 mg/l PAC Adsorbed	30%	30%
Coagulated	20%	13%
Coagulated with Coagulant Aid	17%	23%
Coagulated Plus PAC Adsorbed	45%	45%
Coagulated with Coagulant Aid Plus PAC Adsorbed	41%	46%

TABLE 6. RATE CONSTANTS FROM BATCH EQUILIBRIUM UPTAKE STUDIES

Water	Carbon	<i>K</i> ₁ (hr ⁻¹)	<i>K</i> ₂ (hr ⁻¹)	<i>K</i> ₃ (hr ⁻¹)
Untreated	F400 GAC	0.19	0.02	—
	F400 PAC	1.38	0.18	0.04
	C1240 PAC	3.14	0.14	0.04
Coagulated	F400 PAC	1.92	0.17	0.08
	C1240 PAC	4.80	0.47	—
Coagulant with Coagulant Aid	F400 PAC	1.35	0.71	0.13
	C1240 PAC	4.40	0.41	0.06

TABLE 7. 25°C ISOTHERM DATA FIT TO FREUNDLICH AND LANGMUIR MODELS. UNITS AS INDICATED IN TEXT

Water	Carbon	Linearized Freundlich Equation Log(x/m) = Log K + 1/n Log C	Ultimate Capacity	Linearized Langmuir Equation 1/(x/m) = 1/b + 1/abc	Ultimate
Untreated Water	F400 PAC	Log(x/m) = 5.48 + 1.56 Log C <i>r</i> = 0.88	0.41	1/(x/m) = -1.75 + 8144 1/c <i>r</i> = 0.96	0.38
	F400 GAC	Log(x/m) = -4.34 + 1.18 Log C <i>r</i> = 0.98	0.30	1/(x/m) = -1.96 + 9434 1/c <i>r</i> = 0.96	0.31
Coagulated Water	C1240 PAC	Log(x/m) = -3.53 + 0.91 Log C <i>r</i> = 0.88	0.28	1/(x/m) = 0.64 + 5952 1/c <i>r</i> = 0.95	0.26
	F400 PAC	Log(x/m) = -3.12 + 0.79 Log C <i>r</i> = 0.86	0.41	1/(x/m) = 0.05 = 4107 1/c <i>r</i> = 0.94	0.36
Coagulated with Coagulant Aid Water	C1240 PAC	Log(x/m) = -3.37 + 0.91 Log C <i>r</i> = 0.97	0.36	1/(x/m) = 0.37 + 4090 1/c <i>r</i> = 0.98	0.36
	F400 PAC	Log(x/m) = -2.80 + 0.71 Log C <i>r</i> = 0.99	0.30	1/(x/m) = 1.75 + 2788 1/c <i>r</i> = 1.00	0.28
	C1240 PAC	Log(x/m) = -3.77 + 1.06 Log C <i>r</i> = 0.98	0.39	1/(x/m) = 0.08 + 4053 1/c <i>r</i> = 0.99	0.38

sponding correlation coefficients for both the Freundlich [8] and the Langmuir [14] models are also presented in Table 7. Figures 3 and 4 are representative graphs showing the 25°C F400 GAC data fit to the Freundlich and Langmuir models. The equations commonly presented for these models are [1]:

Freundlich:

$$x/m = KC^{1/n}$$

- x = amount of solute adsorbed (mass)
- m = amount of adsorbent (mass)
- C = equilibrium concentration of solute after adsorption (mass/vol.)

K, n = constants evaluated for each system

The Freundlich model is empirical [1] but corresponds to multiple monolayer adsorption sites.

Langmuir:

$$x/m = \frac{abc}{1 + ac}$$

- x = amount of solute adsorbed (mass)
- m = amount of adsorbent (mass)
- c = equilibrium concentration of solute after adsorption (mass/vol.)

a, b = constants evaluated for each system

The Langmuir model is based on the assumptions that monolayer adsorption is occurring, that all adsorption sites are independent and equally attractive to the sorbate, and that adsorption is irreversible.

All of the 25°C isotherm data fit both models with correlation coefficients ranging from 0.88 to 1.00 (Table 7). Ultimate capacities, $(x/m)_{\text{influent}}$, calculated from the lines fit to both models were reasonably similar, ranging from 0.26 to 0.41, with an average of 0.34. Ultimate capacities were calculated from the variable influent DOC concentration and did not change when the water was pretreated by coagulation, so coagulation can be considered not useful for improving activated carbon capacity on a batch basis. It is possible that, in a non-equilibrium system such as a packed bed, system performance could be improved by emulsion destabilization.

Carbon Column Study

The breakthrough curves presented in Fig. 2 reveal several things about the dynamic system. The TOC concentration at exhaustion, C_e , represents 95 percent of the influent TOC value. Some removal still occurs beyond this point, possibly due to very slow adsorption and/or biological degradation [18]. C_b represents 30 percent of the influent TOC value, a level arbitrarily chosen as breakthrough concentration for the purposes of this study. The level actually required by industry will have to be determined for the specific intended use of the effluent.

Because these columns were operated in the downflow mode, the hypothesis is that there were two phenomena occurring in the series. Apparently the first column served largely as a microemulsion filter, with subsequent columns providing progressively less filtration and more adsorption. Because the influent to and the function of each individual column is unique, separate ultimate capacities were calculated for each by graphical integration of the breakthrough curves [12]. The last column showed the highest ultimate capacity, presumably because any compounds that may have interfered with adsorption were removed by either the filtration or adsorption occurring in the preceding columns. A similar breakthrough curve pattern was observed in an activated carbon column study performed on underground coal gasification process water by Johnson and McTernan [13]. The average ultimate capacity for the five columns was 0.30, which corresponds closely to the batch values obtained for F400.

Rate of transfer calculations performed on the column data provide further insight into the physics of this retort water-activated carbon system. The adsorption process is generally acknowledged to involve three steps [1, 11].

1. Film diffusion—movement of the sorbate molecule from the bulk fluid phase to the outer surface of the solid sorbent molecule (external diffusion).
2. Pore diffusion—movement of the sorbate molecule through the pores to the point of adsorption (internal diffusion).
3. Reaction—adsorption of the sorbate molecule onto the sorbent.

The reaction step is generally extremely fast and is considered negligible [11], so either of the remaining two steps may be rate limiting for a given system. Resistance values for both of these may be calculated as suggested by Summers *et al.* [18].

1. Aqueous-phase (bulk) diffusivity = $D = 2.74 \times 10^{-9} (MW)^{-1/2} = 5.5 \times 10^{-10} \text{ m}^2/\text{sec}$. [2], where MW = average molecular weight of pollutant molecules, determined for Geokinetics-17 to be 130 by gas chromatography [17].
2. Internal resistance

$$\text{pore diffusivity} = D_p = \frac{D\epsilon_i}{\chi} = 1.17 \times 10^{-10} \text{ m}^2/\text{sec}.$$

[18],

where

$$\epsilon_i = \text{internal porosity} = 0.64 \text{ cm}^3/\text{g} \text{ for F400}$$

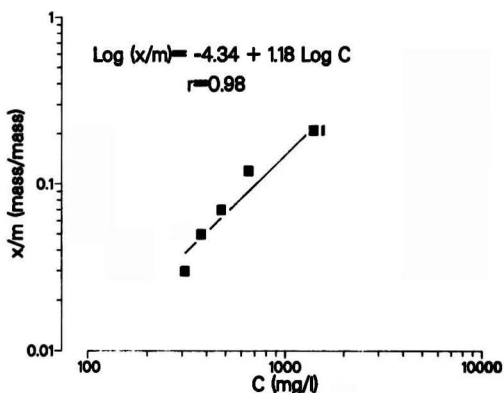


Figure 3. Freundlich model of the 25°C F400 isotherm data.

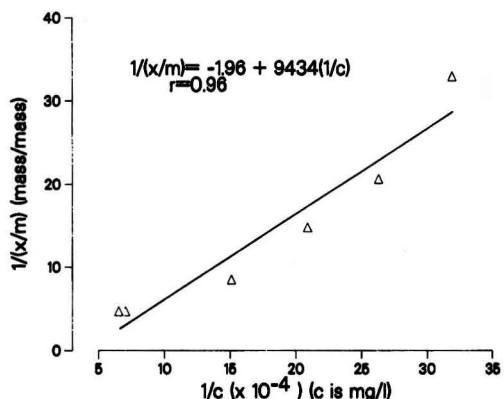


Figure 4. Langmuir model of the 25°C F400 isotherm data.

χ = tortuosity of pores = 3 for F400; this parameter accounts for irregularity of pore shape (F400 values from Reference [2]).

Internal resistance to mass transfer = R_p

$$R_p^{-1} = k_p a = 60D_p \frac{(1 - \epsilon_b)}{d^2} = 3.52 \times 10^{-3}/\text{sec.} \quad [19]$$

Where

k_p = pore mass transfer coefficient (m/sec)
 a = external surface area of sorbent particles (m^2/m^3)

ϵ_b = bed void fraction = 0.5

d = diameter of particles = $1 \times 10^{-3}\text{m}$

$R_p = 284$ seconds

3. External resistance

$$Sh = 2 + 1.1 Re^{0.6} Sc^{1/3} \quad [20],$$

$$\text{Where } Sh = \frac{k_f d}{D}, Re = \frac{d v \epsilon_b}{\nu}, Sc = \frac{\nu}{D}$$

k_f = film mass transfer coefficient (m/sec)

ν = kinematic viscosity = 1.01×10^{-6} (m^2/sec)

d = sorbent particle diameter = 1×10^{-3} (m)

D = bulk diffusivity = 5.5×10^{-10} (m^2/sec)

ν = fluid velocity = 5.33×10^{-4} (m/sec)

ϵ_b = bed void fraction = 0.50.

This approach gives $k_f = 4.33 \times 10^{-6}$ m/sec.
 External resistance to mass transfer = $R_f = \frac{d}{6k_f} = 39.5$ seconds.

These calculations indicate that the Geokinetics 17-granular F400 system is rate limited by the pore diffusion step. This is consistent with experiments conducted by other investigators [2, 18] working with approximately linear isotherms derived from other heterogeneous wastewaters.

CONCLUSIONS

The following conclusions can be drawn from this investigation.

1. Coagulation-sedimentation is not an effective one-step treatment process on this water.
2. Pretreatment by coagulation followed by activated carbon treatment does have an additive effect on total DOC removal and also increases the rate of adsorption in batch systems, but does not affect the ultimate capacity of the carbon when evaluated in a batch mode.
3. The dynamic granular carbon-untreated retort water system was rate limited by pore diffusion of the sorbate. Analysis of the breakthrough curves showed an unfavorable slope in the first section of column bed. The hypothesis for this behavior is that organic microemulsions interfere with adsorption until they are either filtered or adsorbed.

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Maleic Anhydride via Butane Oxidation

Substitution of *n*-butane for benzene in the production of maleic anhydride has led to the solution of a serious environmental problem.

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The commercial synthesis of maleic anhydride was originally developed with benzene as feedstock by Allied Chemical Company in 1931 and had a long distinguished history before alternative feedstocks were introduced. After some early difficulties, including low yields, poor plant operating performance and substantial corrosion problems were overcome, the benzene to maleic process showed a vigorous growth, rising from 5MM lb/yr (2.3 MM kg/yr) in 1940 to 300 MM lb/yr (136 MM kg/yr) in 1975.

Benzene maintained its prime position as feedstock for MAN due to the advanced state of development of the process, primarily high reactor selectivity at high conversion, providing excellent yields at high productivity. In addition, engineering improvements made throughout the years in energy recovery, crude product handling and distillation techniques gave increased back end yields and provided safe, efficient operation.

Recently, however, several major factors have combined to increase the attractiveness of butane over benzene. These factors include: environmental considerations, economics, and process technology.

FACTORS AFFECTING BUTANE REPLACEMENT OF BENZENE

Environmental

Up to very recently, increasingly tighter emission control standards for benzene have been proposed by the EPA and OSHA, since benzene was recognized as a hazardous chemical. The original OSHA standard for benzene adopted in 1971 called for an 8 hour time-weighted average of 10 ppm with a ceiling limit of 25 ppm and a maximum peak concentration of 50 ppm for a 10 minute period. This standard was based on concern for the development of aplastic anemia, but not on concern for development of cancer.

In February 1978, OSHA promulgated a new permanent standard for occupational exposure to benzene at 1 ppm on an 8 hour time-weighted average with a ceiling limit of 5 ppm for any 15 minute period. This was based on evidence of a causal connection between benzene exposure and leukemia.

However, the U.S. Court of Appeals vacated this standard based on two cases and asked for additional evidence of significant risks. The 10 ppm ceiling on benzene remained in effect during this interim period.

In July 1983, the Federal Register announced that OSHA was reconsidering the 10 ppm standard for benzene and had set up a schedule for review and promulgation of a new standard by May 1984.

In a somewhat surprise move, the most recent step by the EPA was a proposal published in March 1984 to withdraw all standards for benzene vent gas emission from MAN plants (as well as for EB-styrene plants and benzene

storage tanks). This proposal to withdraw was made because of the very good self regulation of maleic producers. It was found that the potential number of sources of emission and the quantity of benzene emitted had decreased significantly due to:

- 1) Plant Closures
- 2) Process Changes (mainly substitution of butane for benzene)
- 3) Application of Benzene Controls (including carbon bed adsorption and thermal and catalytic incineration).
- 4) Better estimates of emission and risks of incidence of disease.

Thus, of all 11 U.S. plants originally considered, 5 have shut down, 4 have converted partially or completely to *n*-butane and 2 were originally based on butane feed.

In contrast to benzene, butane presents no environmental problem. In fact, according to a proposed EPA Maleic Anhydride Manufacturing Standard of April 1980, *n*-butane is recommended as a substitute for benzene in all new plants built after April 18, 1980.

As stated above, it is expected that in the U.S., all existing plants will ultimately be converted to butane feed. In addition, it is expected that any new plants built will be *n*-butane based. The only recent new plant constructed in the U.S., Monsanto at Pensacola (started up in 1983) is butane-based.

Economics

In the same time period as the promulgation of the stricter benzene emission standards, a rapid increase in the price of benzene was occurring in parallel with the world wide oil price increases. Benzene price surged from around 65¢/gal (19.5¢/kg) in 1978 to \$1.85/gal (55¢/kg) in 1979 and only recently has slacked off to \$1.55/gal (46¢/kg). Further shortages, however, could bring the price back to the former high levels.

Butane was available at 10-11¢/lb (22-24¢/kg) in 1979, up from 6¢/lb (13.2¢/kg) and is currently 13-15¢/lb (29-33¢/kg) except for captive situations, where it can be charged at a lower price.

Process Technology

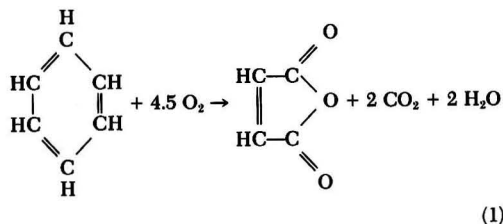
Spurred by the economic and environmental problems with benzene, intensive research and development work has undertaken on improved butane to MAN catalysts. Currently, a number of commercial catalysts have been developed by Monsanto, Denka, and Halcon SD in the U.S.A. as well as at least one Western European company. In addition, new processing techniques, i.e., fluid bed reaction, vent gas recycle, and use of non-aqueous absorption are being studied.

PROCESS CHEMISTRY—HALCON SD PROCESS

Maleic anhydride is produced by the partial oxidation of benzene or a C₄ hydrocarbon (such as n-butane) over a promoted vanadium oxide catalyst.

The chemical reactions are as follows:

For Benzene:



The principal secondary reactions are the oxidation of benzene to water, carbon monoxide, and carbon dioxide:



Approximately 73% of the benzene feed to the reactor is converted to maleic anhydride. About 26% is burned to CO₂, CO, and H₂O, and the remainder is unconverted. The overall yield to purified maleic anhydride is approximately 88 percent by weight.

The reactions in the manufacture of maleic anhydride are highly exothermic—approximately 5400 kilocalories are released per kilogram of benzene converted.

In addition to CO₂, CO, and water, certain higher molecular-weight substances are formed in the reaction; other byproducts including fumaric acid are formed in the recovery, dehydration, and purification steps of the process.

For n-Butane:



The principal secondary reactions are as follows:



The overall yield to purified maleic anhydride is approximately 90 percent by weight based on present catalyst.

Newer catalysts studied in our laboratory have given yields several points higher.

The heat of reaction is approximately 6300 kilocalories per kilogram of butane converted.

PROCESS DESCRIPTION

The HSD process for the manufacture of maleic anhydride from benzene or n-butane is best followed by reference to Figure 1. Basically, the process scheme is the same for the two feedstocks. As shown, ambient air is passed through a filter and then compressed to the reaction pressure by the air compressor. Feed benzene or butane is vaporized, superheated, mixed with the compressed air, and fed to the reactor.

The salt pump circulates molten heat transfer salt through the reactor shell to remove the heat of reaction and to control the temperature. A portion of the molten salt passes through the salt cooler where the reaction heat is efficiently recovered by steam generation. The reaction effluent gases pass through the gas cooler where additional heat is recovered by heating boiler feed water and generating steam.

The reaction gases are then cooled below the maleic anhydride dew point in the aftercooler by heat exchange with a tempered water stream.

Careful control is required because maleic anhydride solidifies at approximately 53°C, and, if this temperature is reached, there is danger of plugging the equipment and lines. The partially condensed reaction gases are then fed to a specially designed separator where the condensed maleic anhydride flowing in fine droplet form is separated from the gases and uncondensed vapors.

The condensed crude maleic anhydride passes to the crude MAN tank from which it is pumped to the refining section for further processing. The off-gas from the separator is fed to the scrubber where countercurrent scrubbing with water absorbs the remaining maleic anhydride by conversion to maleic acid. The overhead gases containing unconverted feedstock benzene or butane, plus traces of lower aldehydes and acids, are exhausted to the atmosphere or disposed of by a suitable incineration unit, either thermal or catalytic.

Maleic acid solution accumulates in the acid storage section at the base of the scrubber from which it is pumped to the refining section for further processing.

The following operations are carried out in sequence in the dehydrator/refiner.

The first step is the azeotropic dehydration of the ma-

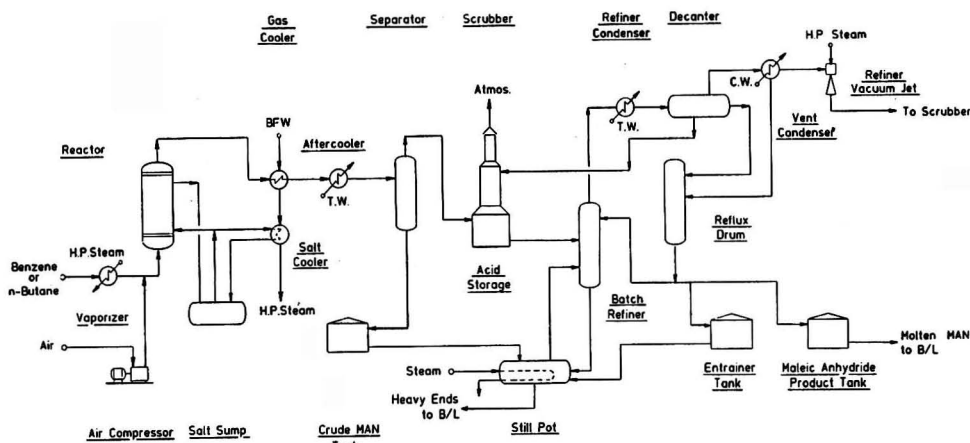


Figure 1. Maleic anhydride process flowsheet.

leic acid solution. Initially, xylene entrainer and some molten crude are transferred to the still pot, and column equilibrium is established.

Maleic acid solution is next introduced into the column for dehydration and the resultant crude molten maleic anhydride accumulates in the still pot. Water from dehydration of maleic acid is recovered overhead, decanted, and recycled for use in the scrubber, while the entrainer is stored in the entrainer tank. After dehydration, additional crude maleic anhydride is added and the refining step is begun.

In the refining operation, column pressure is reduced below atmospheric and a forecut is first taken overhead at high reflux.

Collection of the heartcut at a lower reflux ratio then begins. Molten MAN is accumulated in the MAN product tank for testing. The molten MAN may be sold as such or transferred to a pastillation or briquetting system, where product MAN in its finished form is produced.

Residues left in the still pot following the heartcut operation are rerun with the next charge. After several batches, water is added to the residue in the pot, the column is boiled out, and the washings drained from the distillation system for disposal. Disposal methods include incineration or discharge to a biological pond, both methods having been practiced in SD-designed plants.

PROCESS ECONOMICS

As previously discussed, the flow schemes for the benzene and butane-based MAN processes are basically the same. However, the process design bases and equipment sizes are different for a given plant capacity, and hence the equipment and plant costs differ for the two feedstocks.

At the present state of development, the butane based catalyst operates at a somewhat lower productivity than the benzene catalyst when each is operated at optimum conditions. However, laboratory and pilot plant development work currently in progress on the butane catalyst systems have improved yields and productivity, and thus differences in equipment sizes and capital and operating costs are tending to diminish.

CAPITAL COSTS

The battery limits capital cost for a U.S. Gulf Coast location for the production of molten refined MAN versus plant capacity is shown in Figure 2. The capital cost for the butane feedstock is observed to be greater than for benzene feedstock because of the productivity difference previously discussed. However, the capital costs are closer for small capacity plants since only a single reactor train is needed for each plant, but for larger plants a greater divergence occurs due to the requirement for additional reactor trains for the butane-feed case. Thus, for the 20 MM lb/yr (9070 MT/yr) case, the capital cost for the butane feedstock is 13% higher than for benzene, while for 60 MM lb/yr (27,200 MT/yr), the capital cost is 22% higher.

The effect of this difference in capital cost on the MAN transfer price will be observed in the comparison of maleic anhydride economics for the two feedstocks.

MAN TRANSFER PRICE

The elements of manufacturing cost per 1,000 lbs. of maleic anhydride are given in Table 1. The maleic anhydride yield from benzene is shown as 88 weight percent while, for butane, it is shown as 90.5 weight percent, expressed as lbs. of MAN product per lb. of feedstock. As indicated earlier, however, recent laboratory catalyst studies have indicated an improved overall yield several points higher. The cost of catalyst is an annual cost, obtained by dividing the initial cost of catalyst by its life. The chemical costs reflect the actual annual consumption.

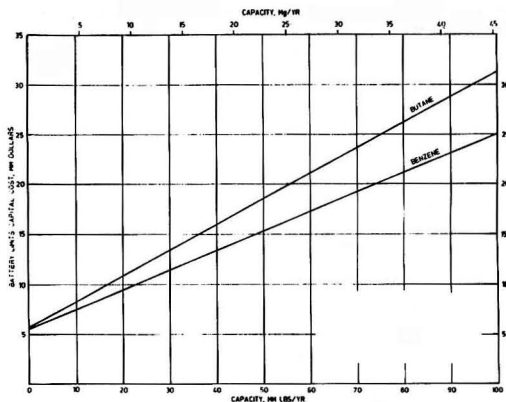


Figure 2. Battery limits capital costs for maleic anhydride and butane. U.S. Gulf Coast basis (Jan. 1985) (1 lb = 0.454 kg).

Under the utilities, high pressure steam, 300 to 475 psig, is shown as a credit and represents the net excess of steam exported to battery-limits after deducting the steam used for process heating and steam tracing. Condensate return to battery-limits is also shown as a credit.

Based on these raw material and utility consumptions, together with the labor requirements and capital related expenses, the transfer prices for benzene and butane-based plants at various capacities have been calculated using the typical feedstock and utility unit costs as shown in Table 2. Unit costs of 13 and 15¢/lb have been used for n-butane while for benzene, 21¢/lb has been taken as a representative cost.

The comparative economics for a moderate size plant, 20 MM lb/yr (9070 MT/yr) and a large plant, 60 MM lb/yr (27,000 MT/yr) have been presented in the table. In all cases, the transfer price for the butane-derived MAN is lower than for the benzene feedstock in spite of the higher capital and utility costs. This is due to the lower feedstock costs.

TABLE 1. ELEMENTS OF MANUFACTURING COSTS

Per 1000 lbs. of MAN

Raw Materials	Benzene	Butane
Benzene	1,136 lb.	
n-Butane (100%)	—	1,105 lb.
Catalyst & Chemicals	\$6.8 (U.S.)	\$30.4 (U.S.)
Utilities		
Steam, H.P. (Credit)	(5,000 lb)	(5,200 lb)
Power	426 KWH	616 KWH
Cooling Water	20,200 Gal.	27,500 Gal.
BFW	1,300 Gal.	1,260 Gal.
Cond. Return (Credit)	(480 Gal.)	(490 Gal.)
Process Water	50 Gal.	60 Gal.
Inert Gas	200 SCF	200 SCF
Labor		
Operators, Men	9	9
Foreman, Men	5	5
Supervisor, Man	1	1
Capital Related Expense	0.195 × BLCC	
Return on Investment	0.200 × BLCC	
Conversion Factors:		
1 lb.	= 0.454 Kg.	
1 Gal.	= 0.00379 CuM	
1 SCF	= 0.0283 NcuM	

TABLE 2. COMPARATIVE MALEIC ANHYDRIDE ECONOMICS

Capacity MAN	20 MM Lb/Yr			60 MM Lb/Yr		
	Butane		Benzene	Butane		Benzene
Feedstock						
BLCC \$M	10,800 (In ¢/lb of MAN)		9,500	21,000 (In ¢/lb of MAN)		17,200
Raw Materials @ ¢/lb	13	15	21	13	15	21
Feedstock	14.40	16.60	23.90	14.40	16.60	23.90
Catalyst & Chemicals	3.04	3.04	0.68	3.04	3.04	0.68
Total Raw Materials	17.44	19.64	24.58	17.44	19.64	24.58
Utilities	(0.57)	(0.57)	(1.15)	(0.57)	(0.57)	(1.15)
Labor Related Cost	2.40	2.40	2.40	0.80	0.80	0.80
Capital Related Costs (19.5%)	10.53	10.53	9.26	6.83	6.83	5.59
Cost of Production	29.80	32.00	35.09	24.50	26.70	29.82
R.O.I. (20%)	10.80	10.80	9.50	7.00	7.00	5.73
Transfer Price	40.60	42.80	44.59	31.50	33.70	35.55

Conversion Factors

1 lb. = 0.454 Kg.

However, wide variations have been occurring in the prices of benzene and butane. In 1981, typical prices were 23¢/lb (51¢/kg) for benzene and 10¢/lb (22¢/kg) for n-butane, while more recently the price of n-butane has risen to 13-15¢/lb (29-35¢/kg) while benzene has fallen to 21¢/lb (46¢/kg). It is noted that the difference in transfer

price becomes quite small at the higher butane price of 15¢/lb. It is quite clear therefore that the projected feedstock prices for a given manufacturer is a very significant factor in the choice of the process to be selected.

The effect of raw material price on transfer cost can be visualized by reference to Figure 3, which shows MAN transfer price vs. raw material cost at the two selected capacity levels. The data plotted are taken from the calculations made in Table 2. With this chart, the MAN transfer price for any given feedstock can be obtained at the 20 MM and 60 MM lb/yr levels, and the economic choice can be made.

A further use of this chart is to obtain the comparative benzene and butane prices for a desired MAN transfer price. Thus, at 60 MM lb/yr capacity and a MAN transfer price of 35¢/lb, butane would be priced at 16.5¢/lb, while the benzene price would be 21¢/lb, a differential of 4.5¢/lb in favor of butane. Thus butane would have to be 4.5¢/lb cheaper to compete with benzene as feedstock.

The same feedstock price differential is found at the 20 MM lb/yr capacity for an equal MAN transfer price, i.e., at 40¢/lb transfer price, the butane cost would be 12.5¢/lb while the benzene price would be 17.0¢/lb, or a 4.5¢/lb difference.

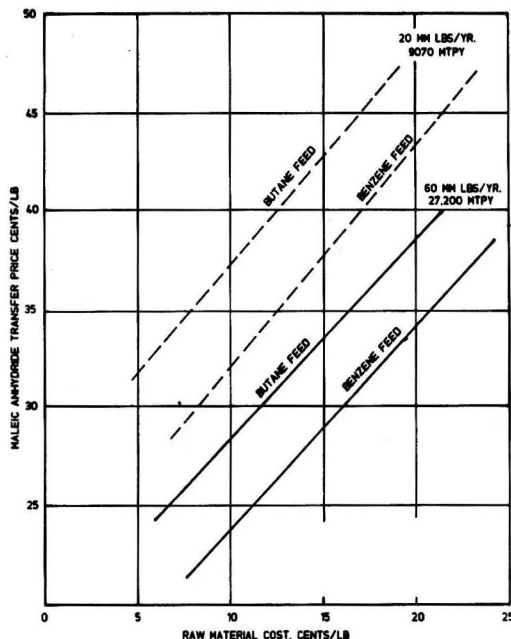


Figure 3. MAN transfer price vs. raw material cost for 20 and 60 MM lb/yr plants (1 lb = 0.454).



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THE WISE PROGRAM

The WISE (Washington Internships for Student of Engineering) is a program sponsored by AIChE, ANS, ASAE, ASHRAE, ASME, ASTM, NSPE, and SAE. The program is coordinated by the American Society for Engineering Education (AEE) with the overall sponsorship of the American Association of Engineering Societies (AAES) and the University of Washington.

Each year, the sponsoring societies subsidize a summer internship for approximately 15 students who are juniors in various engineering disciplines. Interns conduct studies and research in areas of engineering public policy, selecting topics relevant to the interests of the sponsoring organization. Interns are based and housed at the George Washington University in Washington, DC and are guided and monitored by: Dr. Michael D. Devine, Faculty Member in Residence for 1984, University of Oklahoma, and John Lisack, Jr., WISE Project Coordinator, ASEE.

In 1984, AIChE selected William Wescott, a Chemical Engineering student at Princeton, as the AIChE intern. Additionally, Miss Lynn Anzenberger, a ChemE student at Lafayette requested that she be accepted as a non-subsidized intern since she has a great interest in policy and engineering affairs. Both interns worked closely with Dr. Martin Siegel, Staff Director of Government Relations at the Washington AIChE office and members of GPSC.

Mr. Wescott researched the management and recycling of hazardous wastes generated by the electroplating industry. Wescott interviewed a number of administrators and scientists in EPA, OTA and other agencies and they reported that his sincerity, dedication and knowledge of the subject was impressive.

Ms. Anzenberger chose to do a review of EPA's regulatory policies to determine if and how a holistic approach to regulation could be more effective in the control of air, water and waste pollutants. Ms. Anzenberger also spent a good deal of time talking with officials and engineers at EPA, where her topic and approach were of real interest.

Martin Siegel
AIChE Staff Director
Government Relations

The Environmental Protection Agency's Regulatory Practices: The Impact of a Holistic Approach

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The Environmental Protection Agency has been the target of much criticism since its inception in 1970. EPA, unlike other similar federal agencies, was established by a presidential reorganization plan rather than a legislative act of Congress. Consequently, EPA operates under and answers to a multitude of congressional subcommittees and, as a result of the lack of a spelled out generic statute from which to administer, the agency cannot always act in an efficient manner. Quality leadership, technically valid statistics and regulations, and research activities have been problematic areas which have plagued the agency for some time now.

One key issue of concern relates to the internal operating procedures of certain regulatory offices within EPA. The lack of effective communication between the Office of Water, the Office of Air and Radiation, and the Office of Solid Waste and Emergency Response, has created doubt as to whether resulting regulations are technically, economically, and moreover, environmentally appropriate.

Currently, the regulatory offices within EPA function according to the medium addressed—air, water, solid waste, with a fourth office regulating pesticides and toxic substances (Fig. 1). This separation of responsibility is largely due to the fact that the legislation concerning these areas is also distinguished in this manner. For example, the Clean Air Act set standards for air quality and the Clean Water Act determined the desirable conditions for water. EPA is responsible for developing regulations that comply with these and other legislative mandates such as the Re-

source Conservation and Recovery Act and the Toxic Substances Control Act.

Some officials within EPA and others external to the agency have felt that, with respect to environmental regulation, a "holistic" approach to environmental control would be more appropriate. This approach would promote greater consideration and communication between the Offices when developing regulations. An example is evident in the case of ocean incineration where, initially, solid waste is disposed of under direct regulation by the Solid Waste Office. However, once the waste is burned, the gases generated enter the atmosphere and thus the Office of Air and Radiation becomes involved. Critics feel that situations of this sort could be better handled if the agency could tailor its approach to environmental regulation with the recognition that the media specific regulatory areas are dependent and interrelated. A combined effort put forth by the Offices could provide environmental protection in the most sensible, efficient manner.

An integrated approach to environmental regulation has met with opposition in the past and present. As mentioned before, the separation of responsibility within EPA has been viewed as a direct result of the separate and distinct legislative acts. Some believe it is not only inconvenient but impractical to structure the EPA any other way because of the existing legislative organization. Other sources voice their skepticism concerning the implementation of a holistic approach for different reasons. Industry, for one, feels comfortable with the relationships it has es-

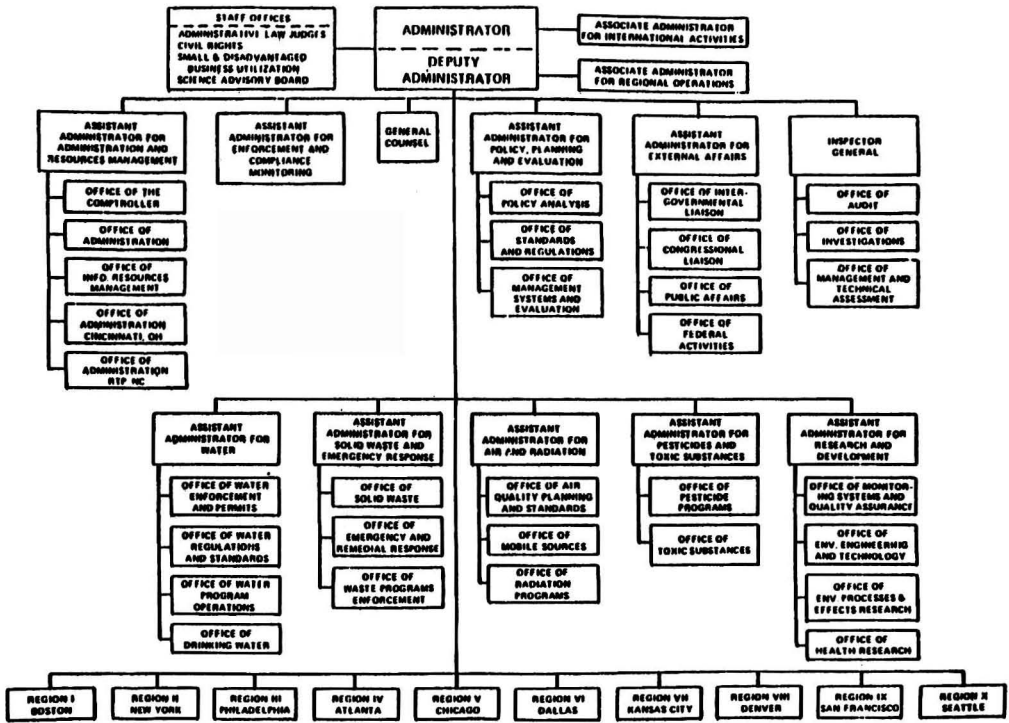


Figure 1. U.S. Environmental Protection Agency.

established with the regulatory offices it must deal with and is wary of any changes. In addition, industry often recruits experts in the major area of regulation it operates under and to change to a holistic approach might involve keeping a whole range of experts on hand.

Committees in Congress also oppose this idea for reasons stemming from political control concerns. As it stands, each committee has an "established" jurisdiction over certain offices within EPA. However, with a holistic approach, control territories may become less sharply delineated and a loss of power to another committee could result.

The purposes of the author in writing this report were to describe the separation of responsibility for the current environmental regulations and some of the regulatory problems this creates. As one possible solution to these regulatory problems, an integrated or "holistic" approach to regulation will be investigated, paying specific attention to cross media concerns. EPA's current efforts in addressing this issue will be described and recommendations for further action will be presented.

STATEMENT OF PROBLEM

As indicated, the EPA was created to regulate pollutants in an efficient, sensible, and consistent manner. Health and environmental risks are the two primary concerns. The Agency's organizational chart reveals the existence of media specific regulatory offices. Each office regulates in what is viewed as a semi-autonomous fashion. These offices are semi-autonomous in that they each strive to uphold the statute which they administer. The principal issue at hand is whether cross media concerns are receiving the attention necessary to develop the most effective regulations.

As of this date, there are several programs in which the

consideration of cross media effects are required. The air program is required under the Clean Air Act to consider "non-air quality health and environmental impact" in setting new source performance standards. Under the Clean Water Act, "non-water quality environmental impact" must be considered when setting various technology based guidelines. However, these considerations only go as far as to price the alternate media control. Other statutes contain the very general criteria to "protect human health and environment"⁽⁴⁾. This apparently is the extent of any legislative direction to promote holistic considerations. The need for a more comprehensive approach has been recognized by EPA.

The EPA is attempting to bring together these loose ends to develop within the Agency, managerial as well as procedural consistency. In this paper, the author examines two major efforts undertaken by the EPA as part of their process investigating how holistic considerations could be incorporated into their regulatory practices. These two studies are the Toxics Integration Project and the Statutory Review Project.

The Toxics Integration Project

Under the Carter administration, an intensive study was begun by EPA to address the issue of a holistic approach to environmental regulation. The study was entitled the Integrated Environmental Management Program. The study is still under way and is receiving much attention, because of one particular project stemming from the original study. This particular project, the Toxics Integration Project, is run by the Office of Policy Analysis, and was initiated as a result of a call from OMB to develop an integrated approach for dealing with toxics. A 1981 report on the Toxics Integration Project updating the progress of this study revealed some key recommendations. One comprehensive

suggestion made was that the Associate Administrator for Policy and Resource Management should manage all aspects of the integration process, not just the toxic integration project. This was not only a call for toxic integration, but more importantly, a realization of the need for an agency wide holistic attitude.

In specific, the report researched ways in which to centralize and integrate the toxic program. Under this project, three specific modes of regulating toxics were studied. Each of these modes exemplified the use of a holistic approach in various forms—chemical by chemical, by industry, and by geographic locations. The strategic goal of the project was to find an “organizationally effective way to build a network among the three approaches, setting each in a context that plays to its strengths, but defining interlocking responsibilities in such a way as to implement an integrated set of Agency priorities” [6]. Although this study dealt specifically with toxics, more generally it made available and tested workable models for holistic environmental regulation.

Integrated Approach: Chemical-by-Chemical

The chemical-by-chemical approach was designed to identify toxic chemicals and track them throughout their life cycle (Fig. 2). This approach was also applied to non-toxic problem chemicals with widely dispersed uses and thus common to various industries and various media. The crux of the chemical approach is the materials balance concept. A thorough tracking of a problem chemical from its production through its process, distribution, use, and disposal lends to a comprehensive and exhaustive record of its release, exposure, and resultant health effects. This approach is the most obvious in its cross media considerations. By devising regulations on a chemical present in commerce or which is a byproduct of a commercial process, health and environmental hazards can be nationally assessed in all environmental media.

Toxics are often dealt with by all of the various offices since they are present in all media. Duplication of scientific studies and analyses has occurred in the past, as in the case of ethylene dichloride. Between 1978 and 1980 nine separate studies by the various offices were conducted on the chemical. Officials now see that essentially the same results were obtained concerning health effects, production and use, sources or release, and exposure [6]. A similar problem occurred with early studies done on arsenic. Surely, one report may not be the answer, but clearly the inefficiency of nine reports dealing with the same chemical in different environmental media became apparent. Using the chemical integrator approach, these duplications could be prevented.

Once all aspects of the life cycle of a chemical, such as ethylene dichloride, have been explored, a complete and

detailed control option analysis is performed. The use of this analysis provides the mechanism by which the chemical hazards are determined in every media into which it enters. The analysis naturally incorporates cross media concerns and explicitly assesses in which media a specific pollutant poses the highest/lowest risks, control costs, etc.

The chemical-by-chemical approach to regulation, the most directly obvious integrated approach, was studied through the implementation of several chemical work groups. Each of these work groups was to develop strategic options for a certain problem chemical, to collect data, and perform in-depth analysis including cost effectiveness considerations. The work groups would also monitor whether their proposed strategic options were operable under current regulations or whether changes in regulations would be necessary to implement their options. An evaluation was also made as to whether the options presented would result in stricter or less stringent regulatory controls.

The cross media transfer of toxics received significant attention and this also has a wide pollutant applicability. These issues often arise from volatility problems and how the present, one-medium centered regulatory practices can overlook the risk present on the total environment. Potentially, the Agency, with the use of the results from these work groups, could implement integrated regulatory practices that reduce overall risk posed by all pertinent toxic and non-toxic chemicals.

Thus far, a tentative intermedia priority pollutants list has been drawn up that contains the major organic and inorganic chemicals that often cross media, such as arsenic, asbestos, lead, benzene, chloroform, and toluene. However, a broader result has been the strong suggestion to the Agency that improved control strategies incorporating holistic considerations can be implemented without necessarily disrupting Agency activities.

Integrated Approach: By Industry

Another mode of regulation investigated in the Toxics Integration Project was by industry. The project attempted to comprehensively analyze the environmental and economic factors inherent to an industry, in efforts to develop options for regulatory practices [6]. The purpose of this mode of approach was to provide a simultaneous review of all effluents from one industry (e.g., chlorinated solvents plants, copper smelters) while making a point to consider cross media and economic factors. The industry’s risk to society would then be assessed based on a full picture of all its hazards. Implementation of regulations could then be carried out in the most environmentally effective manner with the most economic control technologies. The project was able to incorporate risk, exposure, and cost in-

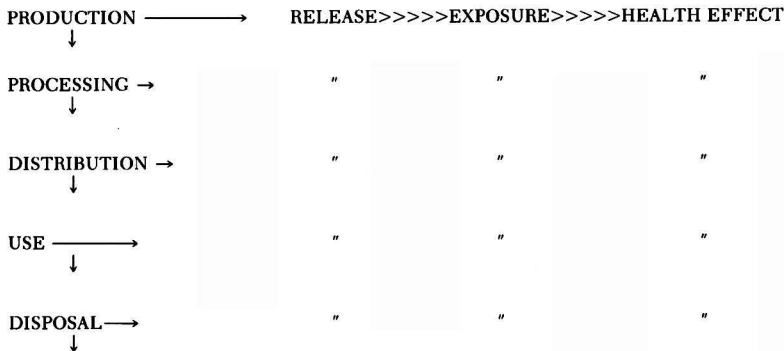


Figure 2. The toxics "cycle."

formation to compute the effectiveness of each alternative control option available to an industry [6].

With the same basic objectives of strategic option development, data gathering analysis, and strategy review and tracking, industry work groups were established to study industries with complex toxic cross media concerns. It was found that uncoordinated one medium controls could easily allow costly adverse shifts of toxics from one medium to another. By a holistic analysis of various waste streams of one industry, it could be determined which streams should, or should not be controlled, or to what degree and at what cost—the ultimate goal being net risk reduction.

While the studies done on copper smelting and the chlorinated solvent industries emphasized reducing adverse health effects, a specific study done on the Northern Ohio iron and steel industries was aimed at reducing both health and environmental effects. The iron and steel industries are a big source of air, water, and solid waste pollution. This study was performed with certain purposes in mind:

- To determine the effectiveness of current controls in achieving health and environmental risk reduction.
- the relative merit of a variety of additional control strategies
- the implications of different priorities for health and environmental effects
- the cross media impacts of different control actions.

The objectives were achieved through a step by step process of production analysis, health, and environmental analysis. Then, the results of these analyses were integrated into a comprehensive regulatory scheme.

The industry work groups provided estimates on present and potential regulatory costs along with the respective release exposure, and risk of current and potential regulations. A synthesis of this data enabled the work groups to devise an economically and environmentally sound attack on an industry's pollution problems, again by proposing several control options. Again in support of holistic consideration, the media which deserved the most

regulatory attention were specified, when possible, and an evaluation conducted of how the consideration of intermediate transfer affected regulations.

Certain limitations of this industry approach were recognized. Resultant risks were hard to quantify from the various data collected and a lack of highly accurate models caused somewhat inconclusive results (Figure 4). One drawback to these models was that, because of time and resource restrictions, the models usually placed emphasis upon assessing health effects more than environmental effects. However, the work study groups generated a sound process to deal with assessing risks, prioritizing data collection and enforcement, and establishing a consistent public health protection levels, while at the same time incorporating cross media considerations. They also recognized the need for change in some regulations to sensitize them both to human effects as well as the economic vitality of the industry.

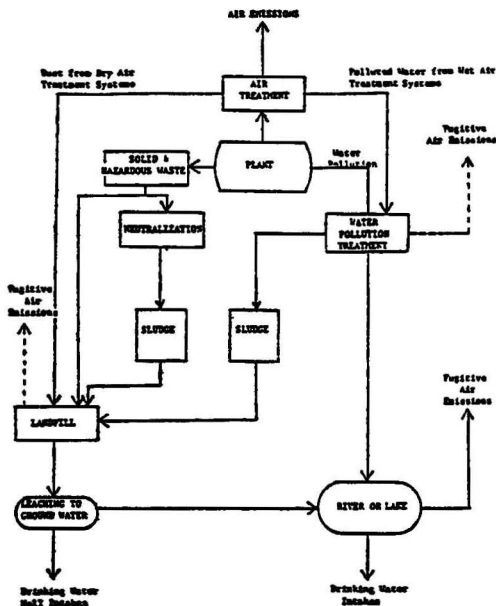
Integrated Approach: By Geographic Locations

The third and final mode including holistic considerations in the Toxics Integration project is the geographical approach to environmental regulation. To achieve integration in the geographic mode, the work group identified geographic localities where industry posed a significant threat to both the environment and the population. Federal, state, and local powers were called upon to meet the needs of the designated localities, such as the present study taking place in Philadelphia. The Philadelphia work group was to gather and analyze pertinent toxic data on the location, to perform an integrated analysis on the life cycles of pollutants throughout all media, and to assess the risk posed to the population of that area. This approach received much attention because of its suitability in treating the nationwide distribution of population and industry.

Typically, regulations are set using nationwide averages of exposures, risks, climatic conditions, and so on. However, there are several atypical regions of the country with highly concentrated industrial sites coupled with dense population and unusual environmental conditions. The geographical approach would reveal the aggravated environmental conditions particular to that region or locality. Once these geographically specific problems were identified, regulation could then be tailored to suit that locality by the states, industry, and the public in the most cost-effective environmentally sound manner. Naturally, multimedia concerns are inherent in this analysis, yet emphasis was placed on the primary environmental problem. For example, areas that have significantly more problems with air quality would receive attention in that area as areas with unusual water/groundwater problems. An example of how a geographical attack is conceptualized can be seen in Figure 5. This figure illustrates the initial scan on the Kanawha Valley, a highly industrialized region near Charleston, West Virginia. The scan reveals how humans, fish, and wildlife are exposed to the 4 selected pollutants by various (usually multiple) pathways [6].

Particular to this move of integration, the importance of the state and local involvement in developing and implementing regulations takes on unprecedented significance in the success of this geographic approach. With state, local, and industrial cooperation, effective communication can occur and all parties become involved in working together to improve their environment. Thus, the need for Federal, state, and local cooperation is the key to the future success of the geographic approach and its nationwide applicability.

Some problems with the geographic approach centered around the crucial need for extensive data collection and analysis. However, officials feel the approach could prove to be the single most effective way to treat a region with a small number of highly troublesome sites. The work group



Source: "Analysis of Cost Effective Pollution Control Strategies in the Steel Industry.: Volumes I and II.

Figure 3. Typical pollutant flows and exposure routes from integrated iron and steel plants.

Component of Analysis	Models/Data Used	Estimated Accuracy
Production	Process Flows, Manufacturing Cost Data	± 30 to 50%
Pollution	Emission Rates	± 30% to Order of Magnitude
Exposure	Pollution Control Flows, Costs Air Dispersions Exposure Models Water Models	± 30 to 35% ± 20 to 100%
Health Effects Environmental Effects	Solid Waste Models Dose-Response Scores Dose-Response Data Water Quality Index	± 500% Order of Magnitude Order of Magnitude Order of Magnitude Rough Approximation

Source: Toxics Integration Report

Figure 4. Accuracy of data and models.

determined that a three to five month preparation period during which data and analytical work would be done would be necessary.

The Toxics Integration Project is both a financial and time intensive project. The significance of the results obtained through this project was the development of three basic approaches to integrated regulatory practices. At this date, toxic chemicals are by and large regulated by chemical largely to the success of the chemical approach. The industry approach did not meet with much success because of the unreliable and limited data the analysis used to predict risks, costs, etc. The geographic approach is currently being tested on site in California and Philadelphia. The Toxics Integration Project did not help determine the applicability of these three modes of regulatory integration and also, perhaps more importantly, revealed certain obstacles that have been hindering progress towards more holistic regulatory practices.

STATUTORY REVIEW PROJECT

One set of obstacles identified through the Toxics Integration Project was in the area of statutory guidelines and deadlines. A second study of interest ongoing at EPA regarding statutory reform in order to improve the holistic approach is the Statutory Review Project. This project is currently being run by both the Office of Policy Planning and Evaluation and the Office of Policy and Resource Management.

In the summer of 1983, EPA's Administrator, William D. Ruckelshaus, asked the Office of Policy Planning and Evaluation to begin a long range inquiry into the effectiveness of EPA as a direct function of current statutory guidelines. As Ruckelshaus pointed out, the statutes from which the EPA administers direct EPA to deal with pollution of the land, the air, and the water each in a separate fashion. The full list of principle statutes that EPA regulates from is given below:

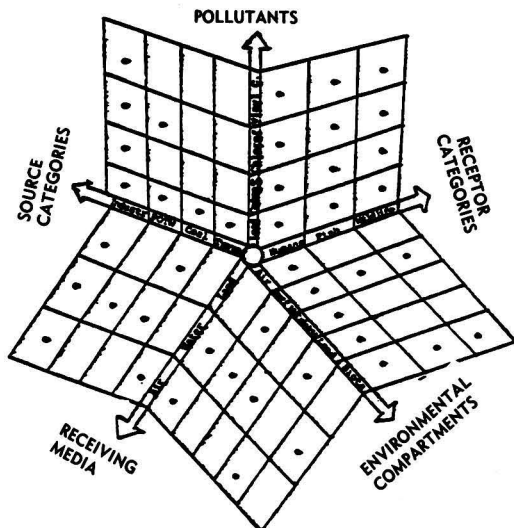
- THE CLEAN AIR ACT
- THE FEDERAL WATER POLLUTION CONTROL ACT
- THE SAFE DRINKING WATER ACT
- THE MARINE RESEARCH PROTECTION AND SANCTUARIES ACT
- THE RESOURCE CONSERVATION AND RECOVERY ACT
- THE TOXICS SUBSTANCES CONTROL ACT
- THE FEDERAL INSECTICIDE, FUNGICIDE, AND RODENTICIDE ACT
- THE COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION, AND LIABILITY ACT

These acts have been instituted over a period of ten years or so and officials feel it is time to ascertain whether the existing forms of legislation are appropriate and effective in reducing the net risk to the environment and human health.

The project initially identified six areas where a change in legislation could lead to better regulatory practices. The change in legislation would not attempt to significantly increase or decrease the strength and importance of any single statute, but rather fill any gaps, omissions, or inconsistencies found to exist. The six areas under consideration for reform are:

1. An Integrated Enforcement Act
2. Cross Media Effects
3. New Source Emphasis
4. Deadlines
5. Consistency in Agency Decision Making
6. Citizen Suits

The first area targeted will assess the advantages and disadvantages inherent in integrating all of EPA's enforce-



Source: Toxics Integration Report

NOTE : The dots indicate categories selected for consideration in this study.

Figure 5. Kanawha Valley initial scan.

ment authorities into a single enforcement act [9]. Apparently the nature and severity of a regulatory decision or fine can vary drastically with the media the pollution enters and thus also depends directly on the respective state administered from and the Office the regulations originated from.

Cross media effects also have a predominant area of concern because, under present statutes, pollution can simply be moved from one medium to another without ever really being cleaned up. Examples include stack gas scrubbers that generate toxic sludges that then are disposed of in land fills. Also, volatile organic compounds removed from water often end up evaporating into the air. Under this project, troublesome cross media situations will be identified and recommendations will be made for necessary statutory changes that will address the cross media problems directly.

The remaining four problem areas do not directly consider holistic considerations and are not within the scope of this report. However, a push for statutory reform in all of these areas can alleviate inconsistencies, duplication of effort, and omissions that result from the present statutory forms.

An "Organic EPA Act" has also been suggested by some who see the problems with having the Agency responsible to numerous legislative mandates with no unifying piece of legislation. Earnest Abbott, who heads the Review Project within the Office of Policy Planning and Evaluation, feels the conceptual difficulties that would arise when drafting an organic act would overwhelm the potential benefits that a unifying "generic" act would give [1]. He feels that perhaps the best way to achieve risk reduction and holistic practices through legislative changes would be through the legislative amendment process. For example, RCRA would be amended to remove restrictions that hamper EPA in treating flyash waste, bottom ash waste, and slag waste as hazardous materials. The current legislation exempts RCRA from dealing with these environmental problems because it does not consider them "hazardous" [9, 10]. The amendment process would not only leave the current statutes, such as RCRA, intact, but also prevent disruption to the Agency while incorporating holistic consideration into law. As illustrated by the Toxics Integration Project the regulation of toxics is also an area more easily regulated in an integrated fashion. The Statutory Reform Project is currently wading through the difficulties in assessing whether net risk reduction is obtained through holistic regulatory practices, or whether the risk reduction would remain virtually the same with current legislation and regulatory practices. Unfortunately, Abbott does not expect to recommend the introduction of any amendments in 1984-1985.

CONCLUSIONS AND RECOMMENDATIONS

The aim of this report thus far has been to provide a brief account of two major efforts by EPA to examine the need for agency-wide holistic and integrated regulatory practices. The two projects discussed, the Toxics Integration Project and the Statutory Report Project, both illustrate the serious inquiry EPA has made in this area. The EPA has tried to determine the feasibility of modifying regulatory practices through both procedural and/or statutory reform. Through this report it has been determined that under the present statutory deadlines, the EPA is making commendable progress in addressing this issue. The Toxics Integration Project provided the testing and ground work for three potential modes of integrated regulatory practices (chemi-

cal, industry, and geographical). The Statutory Reform Project also provides ongoing insights into how the EPA can be held accountable by law for integrating their regulatory processes.

While the concept of "holistic" or integrated environmental management is sound, the problems of identifying workable, effective means for accomplishing this is a difficult task. Thus, action by all interested parties is called for. The AIChE, among other societies, can contribute and support the effort for legislative change through the amendment process. The EPA's Statutory Review Project is being conducted openly and invites participation from any and all interested state, environmental, and business organizations. The EPA feels broad participation will help ensure that their empirical studies are complete, objective, and credible [9]. The AIChE can play an active role by representing industrial, academic, as well as engineering considerations due to its wide and diverse membership. With statutory reform as a first step in attempting to integrate environmental legislation the EPA, along with industrial and public support, can realistically hope for a net risk reduction for the environmental as well as human health.

ACKNOWLEDGEMENT

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Recovery and Reuse of Solvents from VOC Air Emissions

Actuated carbon fiber solvent systems are found to be a cost-effective approach to recycle or reuse of recovered solvents.

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Solvents found in air emissions from chemical processing operations can be recovered and reused economically. The use of activated carbon adsorbers to accomplish this has been commercially practiced for over 50 years. However, the recovery of solvents which are corrosive and/or reactive has been a risky art as practiced using conventional granular carbon adsorption technology. The risk can of course be reduced, but at a high cost in operating and/or capital expenditures.

This paper describes technology developed in Japan using an activated carbon fiber, which has all of the adsorbing micropores at the carbon surface. This gives the carbon high adsorption capacity relative to granular carbon as well as providing high adsorption/desorption rates. When used in a system designed for short desorption cycles, the carbon fiber system, called KF, provides advantages over conventional granular systems for recovery of corrosive solvents such as 1,1,1-trichloroethane, and methylene chloride and recovery of reactive solvents such as methyl ethyl ketone.

Some of these advantages are:

1. Higher quality of recovered solvent.
2. Less system corrosion problems.
3. Less risk of carbon bed fires.
4. Less wastewater treatment problems.
5. More compact and lighter systems.

In Figure 1A, a flow schematic of an activated carbon fiber based solvent recovery system is shown. The vessel shown on the left side is in the adsorbing stage. The air containing solvent is forced into the adsorbing vessel (left) with a blower, and cleaned by the cylindrically wound filter element adsorbing almost 100% of solvent.

The cleaned air exits through the outlet at the top of the equipment. Meanwhile, the desorbing vessel (right) takes

the adsorbed solvent from the filter element and desorbs it by steam at 212 F/100°C. The solvent is then recovered in the condenser and separated in the separator.

In Figure 1B, an actual unit in service on a chlorinated solvent stream is shown.

CHLORINATED SOLVENT RECOVERY

The recovery of highly corrosive solvents such as 1,1,1-trichloroethane and methylene chloride has had mixed success when granular carbon technology is used. During carbon regeneration, the presence of steam and the catalytic action of the transition metals (Fe, Cu, etc.) in the carbon at regeneration temperature (120-150°C) hydrolyzes a small portion of the solvent heel to form hydrochloric acid, chloroalcohols, and other organics. The acid, in the presence of condensed steam, causes stress corrosion cracking when alloy or carbon steels are used for system construction. Disastrous failure of systems have occurred in less than a year of service in some cases.

Protective polymeric liners have been tried, but liner integrity cannot be guaranteed with the alternate heating/cooling cycles that the adsorption vessels are subject to. Some users have found that exotic alloys such as titanium, Hastelloy, and Monel are the only suitable materials for vessel construction where corrosive chlorinated solvents are to be recovered. The resulting high capital cost and long lead time required to obtain such alloys have discouraged their use when the user is examining the cost-effectiveness of his installed system.

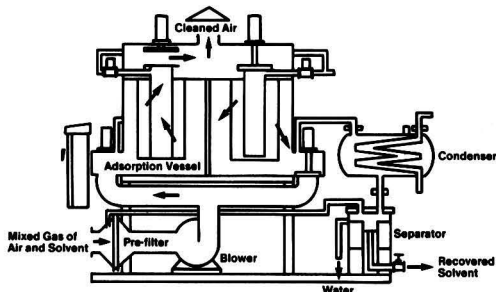


Figure 1a. Flow schematic of activated carbon fiber based solvent recovery system.

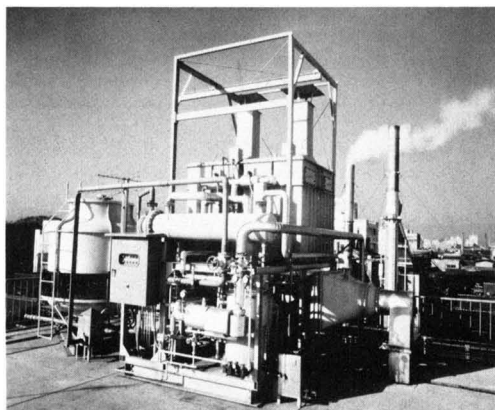


Figure 1b. Installed activated carbon fiber based solvent recovery system.

Even if the system integrity can be maintained when granular carbon systems are recovering corrosive chlorinated solvents, the quality of the recovered solvent is poor. In printed circuit board manufacture, 1,1,1-trichloroethane is a popular solvent and has a high cost. However, 1,1,1-trichloroethane recovered from granular activated carbon systems not only contains hydrochloric acid but also has lost much of the inhibitor used to stabilize it to prevent hydrolysis during storage. To reuse this recovered 1,1,1-trichloroethane, electronics companies must redistill it (at high capital and operating cost) and either re-add an inhibitor package or blend a small amount of recovered solvent into fresh solvent. This total recycle approach is therefore very difficult to use when 1,1,1-trichloroethane must be reused in high technology operations.

Activated carbon fiber-based solvent recovery systems have been applied in the electronics industry, for example, with a high degree of success. A number of installations in the United States and Japan have shown some of the advantages of this unique activated carbon form and system operating cycle.

First of all, the activated carbon fiber contains 1/2 to 1/10 of the metals content of granular carbons, so that catalysis of hydrolysis is inhibited. Second, the desorption cycles with the carbon fiber are 5-10 minutes whereas 30-60 minutes are required to regenerate a granular activated carbon bed satisfactorily. The result is that the quality of solvent recovered is far better than that from granular carbon recovery systems.

A side benefit is that system corrosion is reduced because of the reduced concentration of hydrochloric acid formed, so that vessels, valves and piping can be made of readily available 304L or 316L stainless steel rather than exotic alloys.

The quality of recovered solvent is good enough so that, in many installations, 1,1,1-trichloroethane can be reused directly in the printed circuit board process without distillation and only requires the addition of a small amount of inhibitor or fresh solvent to make it acceptable for reuse. When the closed-loop economic payback is examined, solvent recovery systems based on activated carbon fiber are generally more cost-effective than granular activated carbon systems.

In Table 1, data from a typical electronics-industry application of activated carbon fiber for recovery of 1,1,1-trichloroethane, is shown. In Table 2, a comparison of the purity of recovered trichloroethane from carbon fiber and from granular carbon based solvent recovery systems is shown. The carbon fiber-based system has been found to be extremely cost-effective when corrosive chlorinated solvents such as 1,1,1-trichloroethane, methylene chloride, chloroform and carbon tetrachloride are recovered from process exhausts for customer reuse.

The compact modular concept of the carbon fiber-based system, where more vessels can be added to a basic system to increase solvent/process flow capacity, can be integrated with some innovative purification concepts for the solvent and the steam condensate. These concepts can include:

1. Solvent dryers using zeolites, organic resins, or silica gel to remove traces of water from the solvent. This

TABLE 1. APPLICATION OF ACTIVATED CARBON FIBER SOLVENT RECOVERY SYSTEM TO ELECTRONICS MANUFACTURE

Solvent:	1,1,1 Trichloroethane
Concentration:	2,700-3,700 PPMV
Mass Emissions:	20 Kgs/Hr (45 Lbs/Hr)
Exhaust Flow:	14 M ³ /Min (480 Ft ³ /Min)
KF Size:	2N-6 (2 Vessels-6 KF Elements)
Adsorption Time:	10 Minutes
Desorption Time:	8 Minutes
Elimination Efficiency:	98%
Steam Consumption:	86 Kgs/Hr (189 Lbs/Hr)

TABLE 2. QUALITY OF SOLVENT RECOVERED WITH GRANULAR CARBON AND ACTIVATED CARBON FIBER
SOLVENT: 1,1,1-TRICHLOROETHANE

Parameter Tested	Value For Recovered Solvent Using:		
	Fresh Solvent	Activated Carbon Fiber	Granular Carbon
pH	7	6-6.7	—
Acids (mgs/liter)	5	1.5	25-75
Decomposed Solvent	Not Detectable	Not Detectable	Detectable
Stabilizer Concentration	1%	0.6%	0.2%

has been used to dry methylene chloride, for example, for reuse without recourse to distillation. Substantial capital and energy costs can be saved using this solvent purification concept with a solvent recovery system.

2. Condensate air strippers, where air is bubbled through the condensed steam to remove volatile solvents from the condensate so that it can be reused for cooling water or steam generation and thus achieve nearly zero discharge. The air containing the solvent vapors is sent back through the solvent recovery system for solvent recovery. This has been applied to methylene chloride, for example, which has a significant solubility in water. In Figure 2, a diagram of a typical air stripper is shown. They have a one-hour storage time based upon the volume of steam condensate generated in one hour of solvent recovery system operation. They can be used with any type of carbon adsorption system. Typical performance data obtained from chlorinated solvent recovery installation at a 60:1 air/liquid ratio is as follows:

Solvent	Inlet Solvent Concentration	Outlet Solvent Concentration
Methylene Chloride	5460 mgs/liter	<10 mgs/liter
Methylene Chloroform	300 mgs/liter	< 5 mgs/liter

3. Liquid carbon adsorbers to remove traces of organics which are water soluble from the steam condensate. The carbon can be returned to the supplier for regeneration after use in the carbon bed adsorber. This has been used to remove phenol from the steam condensate, for example, after the phenol has been desorbed from a KF activated carbon fiber solvent recovery system.
4. Mechanical vapor recompressors to reuse the condensate, as well as the latent heat remaining in the KF steam, in a total steam condensate recycle system. This can result in the solvent recovery system having

CONDENSATE AERATOR SYSTEM

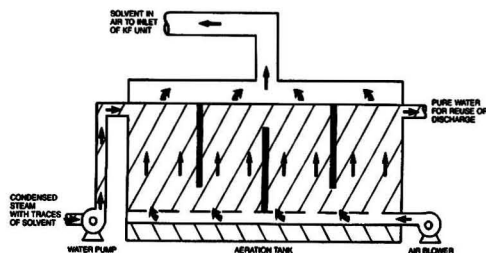


Figure 2. Condensate aerator system.

a "zero" wastewater discharge. In addition, fifty percent or more of the energy in the steam can be recycled with resulting fuel cost savings for the steam boiler.

In Figure 3, a solvent recovery system utilizing concepts 1-4 is illustrated. A system using the process flow schematic shown in Figure 3 is presently in operation recovering toluene from a plastic film coating operation. The solvent recovery system uses an activated carbon fiber as the adsorption media for the solvent. This total recycle concept alleviates the problem caused by the plant being located on a scenic river. No wastewater discharge is permitted.

KETONE RECOVERY

The recovery of ketones using granular activated carbon has resulted in numerous cases of bed fires caused by heat buildup from the reaction of the ketones on the granular activated carbon. The worst of these ketones appear to be cyclohexanone and methyl ethyl ketone. These break down on the carbon, in the presence of air and/or steam and the transition metals of the carbon to form adipic acid and biacetyl, respectively. The exothermic heat of reaction is retained by the carbon granule and if reaction continues through nonregeneration of the carbon for extended periods with low air flow, smoldering fires result. Usually the first warning is black smoke pouring from the exhaust stack even though exhaust gas and carbon bed thermocouples show nothing unusual in the temperatures observed.

Pressure from insurance companies and their own safety personnel has forced granular carbon systems users to install expensive, complicated fire prevention systems. The most cost-effective system has been found to be continuous monitoring of the CO content of the exhaust gas and overhead spray nozzles in the vessels to blanket the carbon system with water to cool it. Low ash metal content carbons have also been developed for ketone recovery. However, the required interlocks, operating procedures and frequent "false alarms" have frustrated many of the companies recovering ketone solvents. Freedom to operate the process to optimize company profitability must take a backseat to keeping a good safety record and public image.

The activated carbon fiber solvent recovery system has been applied to ketone recovery with a great degree of success. The reasons for this are as follows:

A. The low metals content of the carbon fiber results in lower reaction rate of the solvent heel with air and/or steam.

B. The frequent, but short, regeneration cycles of the carbon fiber-based system, plus the thoroughness of regeneration, leaves only a small heel of solvent on the bed to react and build up heat in the carbon bed.

C. The small fiber diameter, which gives accessibility to the vent stream, plus low total weight and low fiber

density, allow quick removal of exothermic reaction heat from the carbon bed into the exhaust stream.

The use of carbon fiber-based systems with ketones such as cyclohexanone and methyl isobutyl ketone has resulted in recovery of good quality solvents with few or no bed fire problems. Although the activated carbon fiber solvent recovery systems can be equipped with fire prevention systems, they are more to please the insurance companies and safety departments than to solve a serious problem.

In Table 3, results of the laboratory testing of bed fire potential for a granular carbon and the activated carbon fiber are shown. This was done by passing an air stream containing 1800 ppmv methyl ethyl ketone through a steel tube containing equal volumes of each type of carbon at a linear velocity of 0.5 meters/second (100 feet/minute). The tube is heated by a tubular furnace from ambient temperature to 500°C at a rate of 2.5°C/minute. The amount of carbon monoxide exiting the carbon is taken as an indicator of the degree of combustion of the carbon occurring. A serious potential for bed fire was found for granular carbon at temperatures of 200°C or above, whereas the carbon fiber had no serious bed fire potential below the carbon ignition temperature of 425°C.

In Table 4, data from a typical application of activated carbon fiber to recovery of a mixed solvent emission containing methyl isobutyl ketone and cyclohexanone as major components is shown. The system has been operating for almost seven years without serious bed fire problems. Other activated carbon fiber-based solvent recovery systems used on ketone containing air emissions have shown similar results.

The technical benefits of using a low metals content carbon such as the activated carbon fiber in ketone solvent recovery included a significantly reduced bed-fire risk. Another benefit of the activated carbon fiber-based solvent recovery systems is better recovered solvent quality. Oxidation products in the recovered ketone can result in additional expense to purify it for reuse or make it totally unacceptable for reuse. Less oxidation products occur when the short regeneration cycle (approx. 10 minutes) of the activated carbon fiber-based systems is used *versus*

TABLE 3. CARBON MONOXIDE PRODUCED BY ADSORBING METHYL ETHYL KETONE * ON CARBON

	PPMV CO produced by:	
	Granular Carbon	Carbon Fiber
100°C	80	140
150°C	80	195
200°C	2,000	200
250°C	7,200	180
300°C	33,000	90
425°C	4,000 (Ignition Temperature)	1,000 (Ignition Temperature)

*At 1,800 PPMV in air.

TABLE 4. APPLICATION OF ACTIVATED CARBON FIBER SOLVENT RECOVERY SYSTEM TO KETONE RECOVERY

Solvent Mixture:	Toluene Ethyl Acetate Methyl Isobutyl Ketone Cyclohexanone
Concentration:	2,000 PPMV
Mass Emissions:	12.6 Kgs/Hr (27.7 Lbs/Hr)
Exhaust Flow:	30.5 M ³ /Min (1037 F ³ /Min)
KF Size:	2N-4 (2 Vessels-4 KF Elements)
Adsorption Time:	10 Minutes
Desorption Time:	8 Minutes
Elimination Efficiency:	98%
Steam Consumption:	42 Kgs/Hr (92.5 Lbs/Hr)

TOTAL RECYCLE SOLVENT RECOVERY SYSTEM

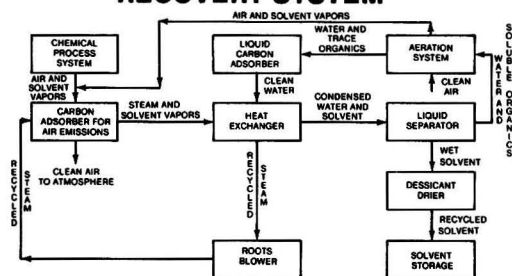


Figure 3. Total recycle solvent recovery system.

the long cycle (approx. 1 hour) of granular carbon-based systems.

4.0 SUMMARY

Activated carbon fiber solvent recovery systems have been found to be a cost-effective approach to recycle/reuse of recovered solvents where the reactivity and/or corrosivity of the solvent makes it difficult to make granular carbon systems work. The recovered solvent quality and durability of system components has shown to over 150 users worldwide that activated carbon fiber solvent recovery systems are a good, long-term investment for high technology industries such as electronics, pharmaceuticals, speciality chemicals and fiber/films manufacturing. Numerous installations in the United States are for corrosive chlorinated solvent applications where recovery/reuse is possible.

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Alkylate Sludge Reuse Potential

A detailed discussion of the pros and cons of alternative methods.

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Alkylation units came on stream in the petroleum refining technology of the 1940's to yield a critical blending component for high-octane aviation gasolines. Although their popularity diminished when jet fuel took over the aviation market, alkylation processes are enjoying a revival because of the need to have higher-octane blending streams as a result of the lead phase-out.

An HF (hydrofluoric acid) alkylation unit is made up of a number of parallel reactors which accept a feed of isobutane and olefins (predominantly butylenes), and produce a higher molecular weight mixture of iso-octanes and other components. The reaction is catalyzed by the liquid HF, and must be kept cool. The reactor products are then passed through downstream separation, as shown in the Figure 1 schematic, to split off acid for recycle and to separate various reacted and unreacted components. A key distillation unit, the isostripper, separates crude alkylate in the bottom from an overhead stream of isobutane/propane/HF. Both the HF and isobutane are recovered downstream for recycle to the reactors. (Some configurations use an HF stripper prior to the isostripper).

The primary waste stream from an HF alkylation unit is produced as a bottoms draw from the acid regenerator, which is designed to return a purified HF acid component into the acid recycle. The waste stream is a sludge made up of acid soluble oils (ASO), together with varying fractions of water, HF, tars, and trace amounts of organic fluorides and sulfides. This paper incorporates a survey of methods used in practice to reuse or dispose of the ASO waste as well as an analysis of the advantages and disadvantages of various disposal options. The uncontrolled landfill disposal practices of the 1940 and 1950 era have led to a few of the Superfund sites of today.

REQUIREMENTS FOR HANDLING ASO SLUDGE

ASO sludge is drawn from the acid-regeneration tower in a batch or continuous mode (Figure 1). The feed to the regenerator is not the entire acid recycle, but only a slip stream. One typical separation method uses hot isobutane as a stripping medium. Some regenerators are provided with reboilers. The bottoms draw from the regenerator

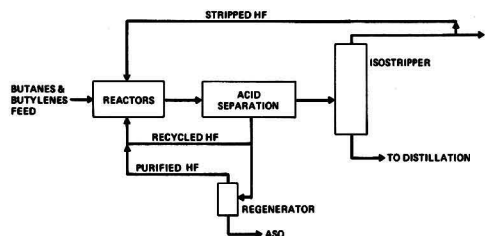


Figure 1. Schematic of HF alkylation unit.

may be a two-phase material in some operations, with a tar-like "polymer" separated out from the ASO (which is collected as an azeotrope of hydrocarbons, acid, and water). Butadiene impurities in the feed stock are at least one of the sources of polymer. In other cases, there is no separate polymer in evidence. Both ASO and the polymer are very viscous and must be kept hot to prevent the material from setting up. They are also corrosive, particularly the ASO, with HF concentrations ranging anywhere from five to forty percent. Metal surfaces and pump seals are readily attacked.

The quantities of ASO and polymer that are generated, per unit of production, vary considerably from one HF alkylation unit to another. Some recent control optimization studies [1] have demonstrated that ASO formation can range from one to several kg per metric ton of alkylate produced, with lower ASO generation associated with appropriately high values of the feed composition ratio of isobutane/olefins. In spite of the appreciation refiners have had for control of alkylation feed composition [2], operating performance in various units has resulted in substantial quantities of ASO generation (and resultant acid consumption), caused by feed impurities, limited control capabilities and unit design limitations.

REUSE AND DISPOSAL OPTIONS

There are two general approaches with regard to reuse of the alkylate sludge materials. Since their hydrocarbon content provides a reasonable heat of combustion, a number of refiners have attempted to use ASO and polymer wastes as fuel, either in alkylation unit furnaces or in other refinery units. ASO is reported to be a complex mixture of partially olefinic ring compounds [3]. Together with typical amounts of HF and water, the sludge heat of combustion is estimated at around 36,000 kilojoules/kg, or about 85 percent of the combustion value of residual fuel oils. Another approach (Figure 2) to take advantage of the hy-

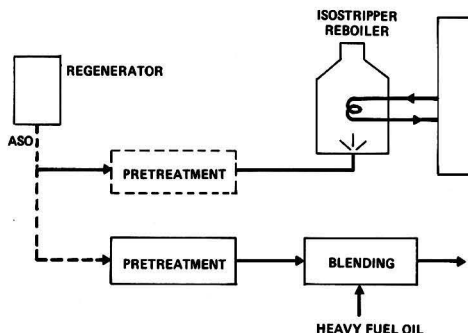


Figure 2. Alkylate sludge used as a fuel vs. recycle to product streams.

drocarbon content is to reintroduce the waste into the refinery product stream (either the alkylate or various fuels).

Disposal options can generally be thought of as either reuse, or disposal where no reuse value is gained. Disposal may occur either onsite or offsite, so that reuse is a special case of onsite disposal. The various options are discussed in detail below.

PRETREATMENT MAY BE NECESSARY

Pretreatment of the waste products may be required before reuse or other disposal routes are taken. The regeneration step, in which HF is stripped from the acid purge stream, is a form of pretreatment which is integrated with the overall alkylation process. The regenerator bottoms section can also act as a separator for ASO and polymer. Once these two components are split, they can be handled independently.

One of the more unpleasant characteristics of these alkylation unit wastes is their high acidity. They would be classified as hazardous wastes if they were disposed offsite. Neutralization pits or vessels have been designed to neutralize ASO with either lime or caustic (Figure 3). The residual HF will drop out in the neutralizer as calcium fluoride if lime is used. The odor generation from the neutralization step (which probably yields disulfides) requires containment and scrubbing of the exhaust fumes. Both aqueous and solid absorbent scrubbing can be effective. Polymer neutralization is sometimes used also, but successful polymer disposal options may be carried out without pretreatment.

ASO REUSE AS A REFINERY FUEL

A number of refineries have attempted to use ASO as a fuel, with varying degrees of success. Usually, the ASO

burner is installed in the reboiler of the isostripper column. Other less frequent fuel reuse applications include catalytic crackers, atmospheric crude units, and coker units. Very few of these uses of untreated ASO have reported success over a long period.

The chief problem of using ASO as a fuel is corrosion and fouling in the convection section of the reboiler, since the ASO sludge combustion products include HF vapor and water. Burner corrosion is also likely, although burner changeouts can be done fairly often without too much expense. The loss in capacity and eventual replacement of corroded tube bundles is an unacceptable penalty. Polymer has also been used occasionally as a fuel in refinery heaters.

RECYCLE INTO ALKYLATE PRODUCT

By far the most common reuse tactic is to recycle ASO and polymer back to the isostripper feed (Figure 4). The recycle stream may be taken from the bottom of the regenerator, or as a slip stream from the acid recycle loop (without the regenerator in service). The idea is to use the isostripper as a regenerator as well, since HF will be stripped from the ASO in the column, and the stripped ASO, together with the polymer, will leave the unit as part of the alkylate.

This method is certainly not trouble-free and has some built-in compromise. Corrosion and fluoride plugging in the isostripper have been experienced by a number of alkylation unit operators.

The acid purity will progressively degrade in this mode of operation, as water content increases, which, in turn, will increase corrosion rates. Operators differ on the impact on alkylate quality when recycle is used [2]. Color and odor problems are frequently encountered, and octane degradation occurs in a number of cases. The quality and

TABLE I. COMPARISON OF REUSE AND DISPOSAL OPTIONS

<u>Option</u>	<u>Technical Considerations</u>	<u>Environmental Attributes</u>	<u>Cost Comparison</u>
Reuse as Refinery Fuel	Potential for fouling of convection tubes. Energy savings could be offset by capacity reduction.	Avoids solid and wastewater loading. HF, sulfate emissions.	Low installed cost; can be high maintenance cost.
Recycle to Alkylate	Potential fouling of isostripper and impacts on alkylate quality. Probably requires pretreatment.	Avoid solid and wastewater loading. Fluorides and sulfides appear in motor fuels.	Low installed cost; maintenance cost can be significant.
Recycle to Refinery Fuels	ASO requires neutralization. Feasible choice.	Sulfides appear in fuels. Neutralization requires odor control.	Installed and operating costs of neutralization and blending units
Incineration without Heat Recovery	Special incinerator design features. Further investigation required.	Generates emissions without heat recovery.	Cost of separate incinerator. Probably most expensive on-site disposal option.
Neutralization and Disposal	Common practice.	Liquid waste requires further treatment or special disposal. May generate solid waste.	Moderate cost, uncomplicated process; cost of nonhazardous waste disposal.
Disposal without Treatment	Storage and transfer.	Disposal of hazardous waste liquid. Must conform to RCRA requirements.	High cost.

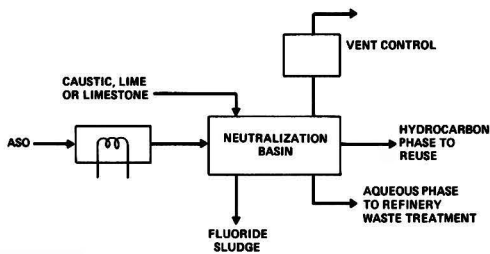


Figure 3. Pretreatment of waste.

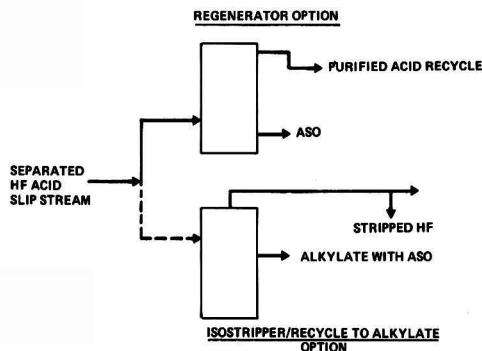


Figure 4. ASO separation vs. recycle options.

amount of ASO appears to determine the impact on alkylate quality.

RECYCLE INTO REFINERY FUELS

Polymer has occasionally been introduced into heavy fuel oil stocks, particularly for shipboard consumption. Organic fluorides in polymer material amount to several thousand ppm, yielding HF vapor on combustion. ASO must be neutralized to successfully blend into heavy fuel, dropping out the free HF, and perhaps some organic fluorides. The sulfides will remain, but the overall quantity of ASO is quite small compared to heavy fuel oil production. Neutralization with caustic or other alkalis will require some means to keep the ASO hot and pumpable.

INCINERATION WITHOUT HEAT RECOVERY

The same problems with corrosive combustion products will occur with separate incineration of alkylation wastes. The impacts of attack on metal surfaces can be moderated by firebox design that minimizes residence time, impeded stack gas flow, or low stack temperatures.

TREATMENT AND DISPOSAL OF WASTE PRODUCTS

As noted previously, neutralization of the waste products is typical, which will also generate a fluoride sludge when calcium-based alkalis are used. The resultant liquid will have to be treated in the refinery waste treatment plant because of the hydrocarbon content. Recovery of the hydrocarbons should be investigated. Landfarming of the

TABLE 2. COST ESTIMATES ASSOCIATED WITH REUSE AND DISPOSAL OPTIONS

Basis: 945 metric tons/day (8000 bpd)
Alkylation Unit; 1.2 metric
tons/day ASO sludge

- Fuel Use (Untreated) in Isostrripper Reboiler**
Cost of replacement of fouled reboiler convection section tubing and burners—\$50,000 to \$60,000 every four months, or \$200,000 to \$240,000 per year.
- Recycle to Alkylate (Untreated)**
Cost of repair and replacement of isostrripper internals—\$75,000 to \$100,000 per year maintenance cost during annual turnaround.
- Neutralization for Pretreatment or Offsite Disposal**
Installed cost of neutralizing basin and associated chemicals storage and handling system—\$250,000 to \$300,000 capital cost; O&M cost minimal.
- Incineration on Site**
Annualized cost of incinerator, supplementary fuel, maintenance—\$500/day or \$150,000/year.
- Disposal as Hazardous Waste**
At \$200/metric ton storage, transportation, disposal—\$72,000/year.
- Disposal as Treated Nonhazardous Waste**
At \$20/metric ton—\$7,200/year.

treated waste may also be feasible. Untreated alkylate wastes will be categorized as a hazardous waste, and its disposal will be limited by the current ban on liquids in landfills. The amount of waste disposed of on-site or off-site (as a fluoride sludge) will be about the same; a typical figure would be 1.3 metric tons of waste for every thousand tons of alkylate product.

CONCLUSIONS

The technical, environmental, and cost attributes of the alternative methods are given in Table 1. The reuse and disposal cost estimates for a 945 metric ton/day alkylation unit basis are summarized in Table 2. The cost of pretreatment (prior to fuel use or recycle to product) will evidently pay out in a few years, by avoiding the damage to the alkylation equipment that would otherwise occur.

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New Approach to *In-Situ* Treatment of Contaminated Groundwaters

***In-situ* treatment of contaminated groundwaters using positive control and treatment techniques may prove to be an important method as remedial action at waste-disposal and treatment facilities becomes more widespread.**

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The problem of soil and groundwater contamination resulting from industrial waste storage, treatment and disposal practices, and from accidental spills is of widespread concern. Present technologies for remedial action most often consist of retrieval of ground water for treatment and disposal. The disadvantages of this method include the inability to capture the contaminants, high pumping and treatment costs, large volumes of produced water to be safely disposed of, and depletion of groundwater resources as a result of pumping clean water in conjunction with contaminated water. A second popular method, containment with low permeability slurry walls, only achieves a delay in the contamination reaching an impact point until some future date.

The focus of the ongoing research described in this paper is the *in situ* treatment of contaminated groundwater. The goal is to establish a technology and methodology capable of removing hazardous constituents from the groundwater without the liabilities of resource depletion, treated water disposal, expensive and energy-intensive withdrawal well fields, or expensive surface treatment facilities. Among the possible subsurface treatment processes are sorption, ion exchange, precipitation, and nutrient and/or oxygen-enhanced microbiological degradation. It is suggested that an interceptor trench containing an appropriate treatment media can be placed in the ground such that the quality of the contaminated groundwater flowing through it will be significantly improved. Such treatment media could include activated carbon for sorption of organics, ion exchange resins to capture inorganic ionic species, substances for pH control of solubility, media for fixed-film biological reactions enhanced by nutrients and/or oxygen supplies, or combinations of these and many other treatment techniques.

CONCEPTUAL DESIGN

The conceptual design of the *in situ* treatment facility involves three phases: physico-chemical treatment, hydraulic, and geotechnical design. The chemical characteristics of the contaminated groundwater must be adequately understood at the outset to decide on a treatment method, and the effects of atmospheric contamination of the samples must be accounted for. In addition, the geochemical effects of the subsurface environment must be known. Most groundwater treatment cases will be in isothermal, anaerobic, reducing environments. Once the mechanism of an applicable treatment process has been identified, it may be evaluated for use *in situ*. The most feasible use of this technology, in its present state, is a

passive design using natural groundwater flow and a treatment media which can capture or treat the contaminants without the need for regeneration or replacement, although more complex designs and treatment formats should be possible as experience with the system complexities is developed.

In approaching the second phase of the design process, it is necessary to understand that the hydraulic characteristics of the groundwater flow regime must meet certain requirements. The hydrogeology at a prospective site must be such that the water flow is essentially horizontal, that is, there must be a layer of restrictive permeability at a relatively shallow depth to minimize vertical seepage. There are two basic variations of horizontal flow conditions from a source of contamination: 1) there is significant regional flow such that a plume is formed, or 2) the regional flow is low and contaminant movement is essentially radial. In either case, the amount of treatment media required to provide sufficient bed depth for removal of contaminants in a trench whose length is dictated by a wide plume, as in the first case, or by a large diameter, as in the latter, may be uneconomical. To solve this problem, it is proposed that a collector-barrier system of low permeability slurry cut-off walls be installed to channel the contaminated water through smaller, more efficient and cost effective treatment beds as shown in Figure 1.

An essential consideration in the design of such systems will be the hydraulics of the cut-off walls and treatment areas. In order to accept the accumulated flow from the collector-barrier dikes without causing the water to back up and either overtop the treatment bed and slurry wall and seep out at the surface or to flow around the ends of the cut-off wall, the flow through the treatment beds must be equal to or greater than the natural flow across the entire width of the plume. This can only be accomplished by increasing the hydraulic gradient across the beds and the formation immediately adjacent to the beds. Therefore, the size of the treatment bed perforations in the cutoff wall must be determined on the basis of allowable up-gradient head increases. These parameters can be determined using either analytical or numerical modeling techniques. The present state of the analytical modeling research uses potential flow theory and complex variable mapping techniques to arrive at dimensionless design parameters relating the bed and barrier wall lengths as a function of the regional flow, up-gradient head increase, and formation permeability.

Finally, the geotechnical considerations of feasibility must be considered. This area of design will depend upon the soil characteristics, required depth, and available

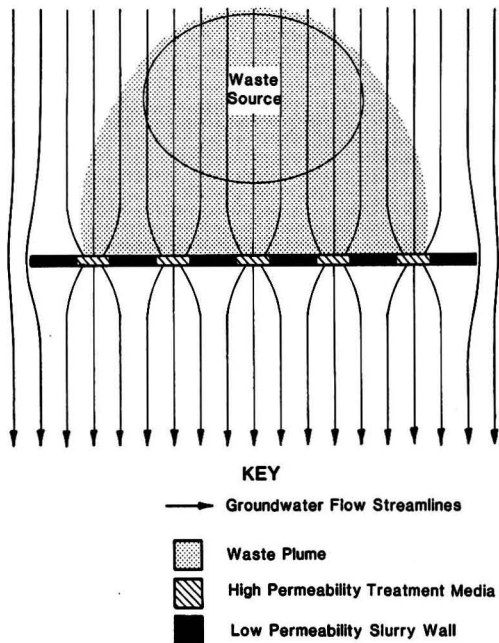


Figure 1. Schematic representation of treatment/barrier facility for conditions where plume has formed.

equipment at each site. The technology used in slurry wall construction is relatively well known; however, a significant complication arises in the need to install treatment media.

One method of installing the treatment media is similar to conventional slurry trench construction utilizing a bentonite slurry to provide stability during excavation below the water table. Since this method would be used to install the cut-off walls, it would also be the most convenient and economical method of placing the treatment media. The slurry serves two basic purposes: 1) it provides stability because the high viscosity slurry, maintained at levels above the water table, resists the hydrostatic forces of the groundwater and the horizontal soil forces, and 2) it forms a low permeability filter cake on the trench wall. The latter function would be detrimental to the operation of the treatment zone since the inflow of groundwater would be resisted. Therefore, a slurry which does not form a permanent, low permeability filter cake must be found in order to utilize this particular construction technique. Certain organic polymer drilling fluids have the ability to form a high viscosity, low permeability slurry which degrades with time to the viscosity of water. Such characteristics would be ideal for the treatment trench construction, however, the polymer might tend to sorb onto activated carbon or other treatment media, reducing their adsorptive capacity.

An alternative technique for the treatment zones is the installation of a rigid cage constructed of perforated sheet piles or plates to hold the treatment media. The media could then be removed for regeneration, recycling, or disposal and replaced with fresh material without collapse of the trench. The use of this construction technique for this type of operation in anything but a very shallow application, however, has not yet been developed and would represent an extension of current technology.

HYPOTHETICAL EXAMPLES

Although Underground Resource Management, Inc. has not yet applied the techniques described in this paper, the examples described are based on conditions at existing fa-

cilities. These examples are intended to illustrate the potential uses of this *in-situ* approach to groundwater treatment.

Case 1. Leaking Surface Impoundment

A petrochemical manufacturing plant, located along a small river, has used surface impoundments to store and dispose of process wastewater and heavy organic sludges. Although the process wastewater discharged to the ponds since 1980 is of significantly better quality than that discharged in the past, a plume of shallow groundwater contamination is moving from beneath the ponds toward the river. Samples from monitor wells indicate that the groundwater contains TOC concentrations of 1,000 to 7,000 mg/L and specific constituents including benzene, toluene, xylene, phenols, and other heavier organic compounds.

The stratigraphy beneath the ponds is 30 feet (9 m) of silty sand underlain by a thick clay bed. The next lower aquifer is under artesian conditions with flowing wells at the surface. The ponds are built on top of the silty alluvium. Since there is a low permeability clay bed beneath the site and because the net flow from the lower aquifer is upward, there is a minimal risk of contamination of the lower aquifer by vertical seepage. The leakage from the ponds infiltrates to the water table on the clay layer, then migrates laterally toward a discharge boundary at the river as shown in Figure 2.

The plant's wastewater treatment system is currently overloaded and has experienced periodic permit violations in its effluent quality and flow rate limitations. There appears to be little chance of upgrading the facility to handle any produced groundwater.

A hydrogeologic investigation has indicated that a conventional recovery system, consisting of a line of wells between the ponds and river, could intercept all contaminated flow. However, due to the proximity of the river, approximately 40 percent of the recovered water would be clean river recharge water. The total flow rate for the well system would be over 100 gpm (545 m³/day), with estimated concentrations of TOC of 500 to 3,000 mg/L. A feasibility study indicated that the design, construction, and permitting of additional water treatment facilities to handle the contaminated groundwater would be a major undertaking in terms of both capital expense and time. A less costly and more rapid solution, if available, would be better from both environmental protection and management points of view.

An *in situ* treatment system consisting of a low permeability slurry wall perforated with beds of granular activated carbon (GAC) has been proposed. Treatability studies including batch isotherm and continuous column studies were performed to design the beds. Techniques similar to those used for standard upflow packed bed column design were used, except that the flow velocities in the column were kept low (laminar flow approximately 0.5-1.0 feet/day, or 0.1 to 0.3 m/day) and the head and tail

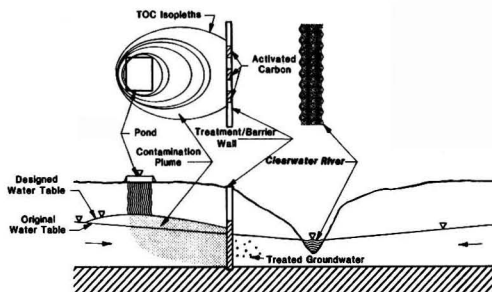


Figure 2. Hypothetical case 1.

waters were isolated from the atmosphere. The bed depth, or width in this case, was determined not by contact time, since the groundwater velocities are low, but by total adsorptive capacity. The mass of organic carbon in the groundwater was found by estimating the volumes of contaminated ground water within TOC isopleths in the plume. These volumes were multiplied by the TOC concentration to give total mass and the volume of GAC required to capture this mass was determined. Once the length and vertical height of the carbon bed was determined in the hydraulic analysis, the bed depth, or width of the trench, was determined.

Hydraulic studies using a finite difference groundwater flow model were conducted to find the proper ratio of treatment slot length to total slurry wall length. It was determined, based on an allowable head increase behind the wall of 9 feet (2.7 m), that a ratio of approximately 15 percent of the containment wall as treatment beds was adequate and that the length of the barrier-treatment wall must be at least two to three times the width of the existing plume.

It was predicted that this passive treatment system would remove over 95 percent of the organics as the plume moved through it. After a period of several years, the carbon could be excavated and removed for regeneration and re-use or disposal. The system would require no new treatment or pumping facilities, no maintenance, and minimal monitoring down-gradient from the treatment zones.

Case 2. Emergency Spill of Lead Contaminated Acid Waste

An accident occurred involving the spill of a tank truck loaded with 5,000 gallons (19 m³) of acid waste. The waste had a low pH and contained high concentrations of lead, chromium, and other heavy metals. The site of the spill was a hillside underlain by clean quartz sand on the surface and a hard shale at shallow depths of 1 to 3 feet (.3 to .9m). A residential development is located at the base of the hill.

An emergency response team of geologists and engineers quickly saw that all of the waste had seeped into the sandy soil and was moving down slope. Hand-dug excavations yielded water with a pH of 2. The engineer promptly ordered a trench dug at the toe of the slope down to the shale layer. Crushed, washed limestone was placed in the trench to neutralize the liquid and cause the metals to precipitate, and clean water was used to flush residual waste down the hill and through the treatment media. The limestone and surrounding 2 feet of soil were later removed from the site.

The design of such an emergency treatment response could be quick and effective. A simple calculation of groundwater velocity based upon assumed values of hydraulic conductivity, gradient, and porosity would allow the engineer to estimate where the trench should be placed to intercept the plume. Since the treatment medium in this case is inexpensive, it could be used throughout the entire length of the trench.

Case 3. Existing Hazardous Waste Site

A hazardous waste landfill closed after promulgation of the §264 land disposal regulations by the Environmental Protection Agency was known to be causing groundwater contamination localized in the area of the landfill. The analysis of the leachate from the landfill for Appendix VIII constituents indicated that several volatile organic contaminants exist at levels requiring remedial action in order to obtain a permit for the facility during post closure operations.

Because the facility is located in relatively impermeable soils, a multi-point wellfield to control the seepage has been determined to be very expensive and of suspect efficiency because of the very large number of wells which would be required. In addition, the production of

the water from such a system would require surface treatment facilities and an NPDES surface discharge permit in order to dispose of the treated water. Local opposition to surface water discharge permitting can be expected.

An alternate approach is the *in situ* treatment of the leachate utilizing a slurry wall to control the plume and treatment zones composed of coarse gravel on top of a diffused air injection manifold to provide for both air stripping of the problem organics as well as possible biological removal. The trench would be lined with an envelope of geotextile filter fabric to prevent migration of fine soils into the gravel. The potential problem of biofouling of the media by excessive biological growth has been identified, and measures have been taken to provide for shock-chlorination of the media should this occur. Piezometers or monitor wells on each side of the facility would monitor the head loss through the wall to identify any significant reduction in permeability.

The hydraulic design of this system is similar in form to that in Example One except for the specifics of the treatment zone and process design.

The use of this system of leachate migration control and treatment has definite advantages in the acquisition of the facility permit for operation in terms of groundwater monitoring. The "point of compliance" is easily defined as the area immediately down-gradient from the treatment zone outlet. One or more monitor wells equipped with submersible pumps can be used for compliance monitoring at the outlet, and if off-specification groundwater is found in the effluent from the treatment zone, it can be pumped out for alternate disposal or storage until any treatment problems are solved and the system is operating at full efficiency again.

CONCLUSIONS

In situ treatment of contaminated groundwaters using passive control and treatment techniques may prove to be an important method as remedial action at waste disposal and treatment facilities becomes more widespread. This technology will be limited to sites where migration of contaminants is shallow and essentially horizontal.

Further research is needed to develop methodology for the design of the barrier wall/treatment zone hydraulic controls and for the geotechnical considerations during construction. At this time, numerical modeling is the most appropriate approach in most real world applications for the former aspect. Pilot scale installations are needed to determine the practicality of several techniques being considered under the latter.



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Since joining URM, he has directed the URM staff in projects related to hazardous waste disposal and the impact of such activities on groundwater and the subsurface environment, as well as industrial and municipal wastewater treatment, injection well permitting and system design, groundwater supply, and the recovery of spilled or leaked hydrocarbons and organics, often profitably, from the groundwater environment.

Wet Air Oxidation of Hazardous Organics in Wastewater

Wet air oxidation can be used effectively to treat aqueous waste streams which are too dilute to incinerate and yet too toxic to biotreat.

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Recent awareness of the potentially harmful effects of hazardous organic substances present in many industrial wastewaters have generated interest in establishing effective treatment technologies for these wastes. Technologies used for treatment of such wastes should preferably accomplish destruction of the hazardous waste components to innocuous end products. An established technology proven to be effective for destruction of a wide variety of hazardous organics contained in wastewater is Wet Air Oxidation (WAO).

Wet Air Oxidation can effectively treat hazardous organic waste streams which are too dilute to incinerate and yet too toxic to biotreat. The WAO process has been used extensively for the treatment of both municipal and industrial wastes [1-4, 7-9]. A listing of the various categories of wastes treated by Zimpro full-scale Wet Air Oxidation systems is presented in Table 1.

More than thirty years have been spent on detailed research and development work with the WAO process. Studies have included reaction kinetics, mass and heat transfer, catalysis, and reaction mechanisms. All of the above have taken into account three-phase flow encountered in continuous systems. Materials of construction studies and practical tests to quickly establish the most economical materials have been developed. All of the above have been refined and further developed in the construction and operation of the 186 units listed in Table 1.

The purpose of this paper is to outline the ability of Wet Air Oxidation to destroy hazardous organic compounds as demonstrated in numerous bench, pilot, and full-scale studies. Bench and pilot-scale work has included both

TABLE 1. ZIMPRO WET AIR OXIDATION INSTALLATIONS

No. Plants	Type Waste
109	Municipal Sludge
29	Night Soil
12	Carbon Regeneration
7	Acrylonitrile
6	Metallurgical Coking
6	Petrochemical
3	Paper Filler
2	Industrial Activated Sludge
2	Pulping Liquor
2	Hazardous Waste
1	Paper Mill Sludge
1	Explosives, 345-T, Malathion
1	Monosodium Glutamate
1	Polysulfide Rubber
1	Textile Sludge
1	Chrome Tannery Waste
1	Petroleum Refining
1	Misc. Industrial Sludges
186	

pure compound and actual industrial waste oxidations. Full-scale installations to detoxify hazardous organic wastes are in operation. These bench, pilot, and full-scale applications of Wet Air Oxidation for treatment of hazardous organic wastes will be discussed.

THE WET AIR OXIDATION PROCESS

Wet Air Oxidation refers to the aqueous phase oxidation of organic and inorganic materials at elevated temperatures and pressures. Oxidation takes place through a family of related oxidation and hydrolysis reactions at temperatures of 347 to 608°F (175 to 320°C) and at pressures of 300 to 3000 psig (2169 to 20708 kPa). The enhanced solubility of O₂ in aqueous solution at elevated temperature provides a strong driving force for oxidation. The source of oxygen is compressed air or high pressure pure oxygen.

Elevated pressures are required to keep water in the liquid state. Liquid water catalyzes oxidation so that reactions proceed at relatively lower temperatures than would be required if the same materials were oxidized in open flame combustion. At the same time water moderates oxidation rates by providing a medium for heat transfer and removing excess heat by evaporation.

Figure 1 is a basic flow scheme for a WAO system. First, a stream containing oxidizable material is pumped to the system using a positive displacement, high pressure pump. The feed stream is preheated by heat exchange

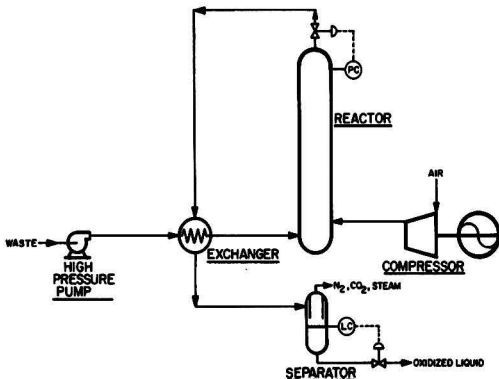


Figure 1. General schematic-Zimpro Wet Air Oxidation.

with hot oxidized effluent. Air or oxygen is introduced at the high pressure pump discharge or injected directly into the wet oxidation reactor. The reactor is a vertical bubble column which provides holding time for the oxidation reactions. The reaction time varies from a few minutes to several hours depending on the type of the wastewater and the treatment objectives. The heat of oxidation raises the reactor temperature to the desired operating level. Injection of steam into the reactor may be necessary to maintain the operating temperature for systems not generating enough heat due to low degree of oxidation. Hot oxidized effluent is cooled by heat exchange with the feed before pressure letdown through a control valve. Liquid and non-condensable gases are disengaged in a separator drum and discharged separately.

Wet oxidation is intrinsically energy conservative. Heat released in the oxidation process can be harnessed to produce steam or hot water. Mechanical energy can be produced when off-gases are expanded.

Wet oxidation consumes far less fuel than other forms of thermal oxidation. In incineration, for example, one has to supply not only the sensible heat and heat of vaporization of the liquid, but also heat for elevating the water vapor, combustion products, and excess air to combustion temperatures of between 1500° and 2000°F (816° and 1093°C). With WAO, however, the only energy required is the difference in enthalpy between the incoming and outgoing streams.

For wet oxidation to proceed autogenously (self-sustaining, with no auxiliary fuel), feed chemical oxygen demand (COD) concentrations of approximately 15,000 milligrams per liter are required compared to 300,000 to 400,000 mg/liter for autogenous incineration.

The wet oxidation process is simple, exceptionally adaptable to changes and variations in feed characteristics and can process a wide variety of oxidizable materials. The oxidation products are innocuous. The primary products of oxidation are carbon dioxide and water. Sulfur is oxidized to sulfate which remains in the aqueous phase. Organic ni-

trogen is converted primarily to NH₃. No SO_x or NO_x is formed. Metals generally are converted to their highest oxidation state and remain in the aqueous phase as dissolved or suspended solids. Halogens also stay in the aqueous phase. The gas discharged from a WAO unit consists mainly of spent air and CO₂ and is essentially free of any air polluting constituents. There is extensive published literature describing wet oxidation [1-9].

BENCH-SCALE STUDIES

Bench-scale studies were performed using batch autoclaves having a total volume of 500 to 750 ml, constructed of 316L stainless steel, nickel, or titanium. The autoclave alloy used depended on the expected corrosiveness of the sample to be tested.

Autoclaves were charged with 100 to 300 ml of the sample to be oxidized, sealed, charged with air or oxygen sufficient to satisfy the sample oxygen demand, and placed in a heater/shaker mechanism. Resistance heater strips in autoclave holders heated the autoclaves while rocking of the holder assembly provided continuous agitation. Thermocouples were inserted in autoclave thermal wells to provide continuous temperature monitoring and control. Following treatment at the desired temperature and time autoclaves were removed from the holders and quenched with tap water.

Pure Compound Oxidations

Bench-scale Wet Air Oxidations of a number of pure compounds have been reported by Randall and Knopp [5] and Randall [6]. The compounds studied represented various categories from the EPA priority pollutant list. Results are summarized in Table 2. This summary includes information on several compounds which has not been reported elsewhere. In most cases, greater than 99 percent destruction, as determined by analysis of starting material, was observed. Improved oxidation efficiencies were generally observed upon increasing temperature or using a catalyst. The last three compounds in Table 1—kepone,

TABLE 2. BENCH-SCALE WET AIR OXIDATION OF PURE COMPOUNDS

Compound	Wet Oxidation Conditions, °C/Minutes	Starting Concentration, mg/liter	Final Concentration, mg/liter	Percent Destroyed
Acenaphthene	275/60	7000	0.5	99.99
Acrolein	275/60	8410	<3	>99.96
Acrylonitrile	275/60	8060	80	99.0
2-Chlorophenol	*275/60	12410	15	99.88
2,4-Dimethylphenol	275/60	8220	0.1	99.99
2,4-Dinitrotoluene	275/60	10000	26	99.74
1,2-Diphenylhydrazine	275/60	5000	6	99.88
4-Nitrophenol	275/60	10000	40	99.6
Pentachlorophenol	*275/60	5000	135	97.3
Phenol	275/60	10000	20	99.8
Formic Acid	300/60	25000	410	98.3
Chloroform	275/60	4450	3	99.9
Carbon Tetrachloride	275/60	4330	12	99.7
1,2-Dichloroethane	275/60	6280	13	99.8
N-Nitrosodimethylamine	275/60	5030	22	99.6
Hexachlorocyclopentadiene	300/60	10000	<15	>99.9
Toluene	275/60	4330	12	99.7
Nitrobenzene	*320/120	5125	255	95.0
Chlorobenzene	*275/60	5535	1550	72.0
Pyridine	*320/120	3910	570	85.4
2,4-Dichloroaniline	*275/60	259	<0.5	>99.8
2,4,6-Trichloroaniline	*320/120	10000	2.5	99.97
Dibutylphthalate	275/60	5230	26	99.5
Isophorone	275/60	4650	29	99.4
1-Chloronaphthalene	*275/60	5970	5	99.92
Pyrene	275/60	500	0.26	99.95
Malathion	250/60	11800	18	99.85
Kepona	*280/60	1000	690	31.0
Arochlor 1254	320/120	20000	7400	63.0
1,2-Dichlorobenzene	*320/60	6530	2017	69.1

* Catalyzed

the PCBs in Aroclor 1254, and 1,2-dichlorobenzene—showed relatively lower destruction efficiencies.

Based on these results, and as discussed by Randall (6), observations can be made on the susceptibility of various compound classes to destruction by conventional Wet Air Oxidation:

- Inorganic and organic cyanide compounds are easily oxidized.
- Aliphatic and chlorinated aliphatic compounds are easily oxidized.
- Aromatic hydrocarbons such as toluene, acenaphthene, and pyrene are easily oxidized.
- Aromatic and halogenated aromatic compounds containing non-halogen functional groups e.g., phenols and anilines, are easily oxidized.
- Halogenated aromatic compounds without other non-halogen functional groups, e.g., chlorobenzene and PCBs, are relatively resistant to conventional Wet Air Oxidation.

In acute static toxicity tests using *Daphnia magna*, Randall and Knopp [5] showed 15 to 4000-fold reductions in the toxicity of solutions of a number of the compounds listed in Table 2, following Wet Air Oxidation.

Phenolic Wastes

Results of bench-scale Wet Air Oxidation studies performed on seven phenolic wastewaters are reported in Table 3. Feed phenols concentrations ranged from 204 to 11750 mg/liter. Wet Air Oxidation at 280 to 320°C resulted in phenols reductions of 95.1 to 99.7 percent. In study "A" the use of a catalyst at 300°C provided only marginal improvement in phenol removal compared to the non-catalyzed oxidation—96.3 percent versus 95.1 percent, respectively. The 99.7 percent phenols reduction was achieved at conditions of 320°C and 120 minutes, indicat-

TABLE 5. BENCH-SCALE WET AIR OXIDATION OF ORGANICS IN WASTEWATERS

Compound	Removal, %
Dinitrobenzamine	90.6
2,4,6-Trichlorophenol	99.9+
1,2-Dichloro-3-nitrobenzene	80.6
3-Nitrophenol	99.9+
Dinitrophenol	82.5
2,4,6-Trinitrophenol	99.9+
Dinitrochlorobenzene isomer	
No. 1	99.8
No. 2	93.8
Dinitrochlorophenol isomer	
No. 1	99.9+
No. 2	99.9+
No. 3	99.9+

* Wet Air Oxidation conditions were 285°C for 120 minutes.

** Removal efficiencies calculated based on changes in mass spectral specific ion counts upon treatment.

ing that higher temperatures and longer reaction times can yield more complete phenols destruction.

In two cases, studies "B" and "C", ozone and hydrogen peroxide- post-treatments were performed to further reduce residual phenols. Results indicated that ozone was much more effective in reducing residual phenols than hydrogen peroxide. Phenols reductions of greater than 99.9 percent were achieved with Wet Air Oxidation/ozone treatment.

Specific Organics

In a number of bench-scale Wet Air Oxidation studies performed on industrial wastewaters the fate of specific organic compounds was evaluated. In Tables 4 and 5 data from eleven such studies are reported.

TABLE 3. BENCH-SCALE WET AIR OXIDATION OF PHENOLIC WASTES

Study	Treatment Conditions		Feed Phenols, mg/liter	Product Phenols, mg/liter	Phenols Removal, %
	Wet Air Oxidation, °C/Minute	Other			
A	300/60	—	204	10.0	95.1
	*300/60	—	204	7.5	96.3
B	280/60	—	6140	34.3	99.4
	280/60	250 mg/liter O ₂	6140	<1.0	99.9+
C	280/60	900 mg/liter H ₂ O ₂	6140	21.2	99.6
	280/60	—	11750	106	99.1
	280/60	330 mg/liter O ₃	11750	1.8	99.9+
	280/60	900 mg/liter H ₂ O ₂	11750	128	98.9
D	280/60	—	10090	70	99.3
E	280/60	—	10014	135	98.6
F	280/60	—	5290	70.5	98.7
G	320/120	—	1223	4.0	99.7

* Catalyzed

TABLE 4. BENCH-SCALE WET AIR OXIDATION OF ORGANICS IN WASTEWATERS

Study	Compound	Wet Air Oxidation Conditions, °C/Min.	Feed Concentration, mg/liter	Product Concentration, mg/liter	Removal, %
A	Dimethylaniline	280/60	1300	1.6	99.9
B	1,2-Dichlorobenzene	320/120	590	150	74.6
C	Toluene	320/60	5.0	<0.5	90.+
D	Acetonitrile	*275/60	1040	17	98.4
	Propionitrile	*275/60	391	7	98.2
E	2,4-Dichlorophenol	320/60	500	2	99.6
F	Dipropylformamide	250/60	219	1	99.5
G	Mercaptans	225/60	151	<1	99.3+
H	N-nitrosodimethylamine	320/60	510	1	99.8
I	5,5-Dimethylhydantoin	280/60	2254	16	99.3
J	Trichloroethylene	320/60	500	1.7	99.7

* Catalyzed

In Table 5 absolute concentrations of compounds were not determined due to a lack of analytical standards. Removal efficiencies were determined based on differences in total ion counts for mass spectral ions specific to each compound. Concentrations of these compounds were expected to be in the 20 mg/liter and lower range.

Results of specific compound analyses generally agree with the conclusions drawn from Wet Air Oxidations of pure compounds. Even at 320°C for 120 minutes the chlorinated aromatic 1,2-dichlorobenzene was reduced by only 74.6 percent. Other compounds which showed less than 98 percent destruction were dinitrobenzeneamine (90.6 percent), 1,2-dichloro-3-nitrobenzene (80.6 percent), dinitrophenol (82.5 percent), and a dinitrochlorobenzene isomer (93.8 percent). Many of these compounds would likely have been destroyed to a greater degree at more severe oxidation conditions or with the use of a catalyst.

These results and the results of the pure compound studies seem to indicate that the presence of electron with-

drawing groups, such as chlorine and nitro groups, on aromatic rings provides stability and hence resistance to Wet Air Oxidation. Electron donating constituents such as hydroxyl, amino, and methyl groups appear to make aromatic rings more susceptible to destruction by Wet Air Oxidation.

Solvent Recovery Wastewater

A wastewater generated by a solvent recovery process was subjected to wet oxidation at 280 and 320°C for 60 minutes. Results in Table 6 show excellent removal, with the exception of methanol, for a variety of low molecular weight solvents. In general, these materials are considered biotreatable, but they are also amenable to Wet Air Oxidation.

Nonchlorinated Pesticide Wastewaters

Several Wet Air Oxidation studies performed on wastewaters generated in the production of non-chlorinated pesticides indicated these classes of compounds were very amenable to Wet Air Oxidation (Table 7). In study "A" greater than 94 percent destruction of organophosphorus pesticide and by-product compounds was demonstrated by conversion of organic phosphorus to inorganic phosphate.

In study "B" the phthalimide based by-product of a pesticide production process was 99.0 percent removed at relatively mild Wet Air Oxidation conditions—225°C for 60 minutes. In study "C" two organonitrogen/phosphorus pesticides and an organonitrogen/sulfur pesticide showed greater than 99 percent destruction at relatively mild 260°C/60 minute conditions.

TABLE 6. SOLVENT WASTE WET AIR OXIDATION

Compound	Diluted Raw Waste (mg/liter)	Oxidized 280°/60 min. (mg/liter)	Oxidized 320°/60 min. (mg/liter)
Methanol	3230	1380	290
MEK	276	1	3
Toluene	80	<1	<1
Ethanol	1530	60	10
Acetone	1680	<10	<10
2-Propanol	2230	40	30

TABLE 7. BENCH-SCALE WET AIR OXIDATION OF NON-CHLORINATED PESTICIDE WASTEWATER

Study	Compound Type	Wet Air Oxidation Condition, °C/Min.	Feed Concentration, mg/liter	Product Concentration, mg/liter	Removal, %
A	Organophosphorus	300/60	8320	<490	94.+
B	Phthalimide	225/60	13000	132	99.0
C	Organonitrogen/phosphorus	260/60	1887	7.6	99.6
	Organonitrogen/phosphorus	260/60	2585	13.5	99.5
	Organonitrogen/sulfur	260/60	6.7	0.038	99.4

TABLE 8. BENCH-SCALE SCREENING FOR COMMERCIAL WAO UNIT, CONDITIONS: 280°C/60 MINUTES

Study	Compound	Feed Concentration, mg/liter	Oxidized Concentration, mg/liter	Removal, %
A	2,4-Dichlorophenol	23.5	0.38	98.4
B	Mercaptan-S	238	0.24	99.9
C	2-(α -naphthoxy)-N,N-diethyl propionamide	362	0.88	99.8
D	MEK	8200	<1	>99.98
	2-Propanol	9900	170	98.3
	Ethanol	2800	1200	57.2
E	1,2-Propanediol dinitrate	*	*	99.+

*Ion intensities by GC/MS

TABLE 9. AUTOCLAVE OXIDATIONS OF CHLORINATED ORGANICS SPIKED WASTEWATER
OXIDATION CONDITIONS: 280°C/60 MINUTES

Compound	⁽¹⁾ Input	Product	% Removal
Chloroform, mg/liter	270	<1	>99
Chlorobenzene, mg/liter	792	61	92.3
1-Chloronaphthalene, mg/liter	1524	8	99.5
2,6-dichlorobenzonitrile, mg/liter	498	39	92.1
Trichloroethylene, mg/liter	300	2	99.3
Dichloromethane, mg/liter	252	<1	>99

(1) Input based on GC and HPLC assay of spiking stock solution

Screening Tests of Industrial Wastewaters

Bench-scale screening tests were performed for a commercial treater who is using a Wet Air Oxidation unit to treat toxic and hazardous wastes. A variety of specific compounds were monitored in wastes subjected to the bench-scale screening tests. The conditions employed for screening were 280°C for 60 minutes. The results, shown in Table 8, demonstrate excellent removals for a number of specific compounds including 2,4-dichlorophenol, methyl ethyl ketone (MEK) and 1,2-propanediol dinitrate.

Oxidation of Spiked Wastewater

Laboratory autoclave oxidations were performed on a mixture of organic wastewaters after addition of the chlorinated organic compounds listed in Table 9. This study was performed to investigate the removal of relatively high concentrations of chlorinated organics by wet oxidation. The listed input concentrations of individual compounds were based on analysis of the stock spiking solution. Following oxidation at 280°C for 60 minutes, each product was analyzed for the six added compounds.

Reductions of 99+ percent were observed for chloroform, 1-chloronaphthalene, trichloroethylene, and dichloromethane. Chlorobenzene was reduced by 92.3 percent while 92.1 percent reduction of 2,6-dichlorobenzonitrile was obtained. These results are consistent with previous Wet Air Oxidation experience in that chlorinated aliphatic compounds are generally very easily oxidized, whereas chlorinated aromatic compounds are more resistant. The removal observed for chlorobenzene in this study was greater than observed in single compound oxidation studies. Such results are often observed for complex mixtures compared to single compound oxidations.

PILOT-SCALE STUDIES

Pilot-scale, continuous flow Wet Air Oxidation Studies have been performed on a number of industrial wastewaters from the classes of hazardous organic materials discussed above. The flow rates of systems used in these

TABLE 10. PILOT-SCALE WET AIR OXIDATION OF COKE PLANT WASTEWATER

Wet Air Oxidation Conditions:	
Temperature, °C	279
Flow, GPH	6.3
Residence Time, min.	69
Pressure, PSIG	1558
Catalyst	Yes
COD	
Feed, g/liter	5.52
Effluent, g/liter	0.48
% Removal	91.3
Cyanide	
Feed, mg/liter	309
Effluent, mg/liter	<6
% Removal	99+
Phenols	
Feed, mg/liter	743
Effluent, mg/liter	1.05
% Removal	99.8
Cresol	
Feed, mg/liter	188
Effluent, mg/liter	<0.2
% Removal	99.9+
Quinoline	
Feed, mg/liter	38
Effluent, mg/liter	13
% Removal	65.8

S. I. Conversion:
 $m^3/d = GPH \times 0.0908$
 $kPa = PSIG \times 6.89$

TABLE 11. PILOT-SCALE WET AIR OXIDATION OF ORGANIC COMPOUNDS IN INDUSTRIAL WASTEWATER

Wet Air Oxidation Conditions:	
Temperature, °C	314
Flow, GPH	2.6
Residence Time, Min.	128
Pressure, psig	1943
COD	
Feed, g/liter	77.5
Effluent, g/liter	9.4
% Removal	87.9
1,2-dichlorobenzene	
Feed, mg/liter	2213
Effluent, mg/liter	29
% Removal	98.7
Methylene Chloride	
Feed, mg/liter	60
Effluent, mg/liter	0.01
% Removal	99.9+
Perchloroethylene	
Feed, mg/liter	4000
Effluent, mg/liter	0.9
% Removal	99.9+
Freon TF	
Feed, mg/liter	3000
Effluent, mg/liter	2
% Removal	99.9+
Xylene	
Feed, mg/liter	8385
Effluent, mg/liter	<20
% Removal	99.8+
Toulene	
Feed, mg/liter	30
Effluent, mg/liter	0.5
% Removal	98.3+
Phenols	
Feed, mg/liter	1556
Effluent, mg/liter	2.1
% Removal	99.9
Isopropyl Alcohol	
Feed, mg/liter	1700
Effluent, mg/liter	400
% Removal	76.5
Methyl Ethyl Ketone	
Feed, mg/liter	6000
Effluent, mg/liter	1.0
% Removal	99.9+

S.I. Conversion
 $m^3/d = GPH \times 0.0908$
 $kPa = PSIG \times 6.89$

studies ranged from 2.5 to 28.9 GPH (0.23 to 2.6 m^3/d). Pilot systems were constructed of materials ranging from stainless steel to titanium. Some of the studies were run in trailer mounted mobile pilot units. Performance data reported were based on analyses of composite samples taken during steady state operation.

Coke Plant Wastewater

Results from the 279°C catalytic oxidation of a coke plant wastewater are reported in Table 10. Greater than 99 percent removals of cyanide, phenol, and cresol were observed along with a 91.3 percent COD reduction. Quinoline was apparently more resistant to Wet Air Oxidation and showed a 65.8 percent removal.

Specific Organic Compound Oxidation

The Wet Air Oxidation of a number of specific organic compounds was evaluated in a pilot-scale study with an industrial wastewater containing a complex mixture of materials. Results of oxidation at 314°C (Table 11) indicate removal efficiencies similar to those expected based on bench-scale pure compound Wet Air Oxidations. With the exception of isopropyl alcohol, aliphatic compounds had

removals of greater than 99 percent. Low molecular weight alcohols such as isopropyl alcohol are frequently seen in the residual organics following Wet Air Oxidation. In this study some of the isopropyl alcohol in the product may actually have been a by-product from oxidation of other compounds. These alcohols are, of course, highly biodegradable and these Wet Oxidation biological treatment would be expected to remove them from the treated wastewater.

The aromatic compounds xylene, toluene, and total phenols had removals of 99.8+, 98.3, and 99.9 percent, respectively. The 98.7 percent removal of 1,2-dichlorobenzene was much higher than expected based on pure compound and other oxidation studies. This enhanced removal efficiency may have been the result of matrix effects not seen in the bench-scale studies.

Pesticide and Herbicide Wastes

Pilot-scale Wet Air Oxidation studies have been performed on several pesticide and herbicide production wastewaters. A wastewater containing organonitrogen/phosphate and organonitrogen/sulfur pesticides was oxidized at 240 and 260°C. Results (Table 12) indicated greater than 99.9 percent removals of the compounds of interest.

This wastewater contained organic materials not measurable by the dichromate COD test but which exerted an oxygen demand upon Wet Air Oxidation. Thus, removal of oxygen demanding materials was measured by the reduction in autoclave oxygen demand (AOD). The AOD test involves a high temperature catalyzed batch autoclave oxidation in which offgas analyses are used to calculate oxygen uptake. AOD reductions for this wastewater were 30.4 and 65.2 percent at 240 and 260°C, respectively. Higher AOD removal efficiencies would be expected at higher oxidation temperatures. However, the main objective of the study was destruction of the pesticide compounds and was accomplished by oxidation at relatively low temperatures.

Wet Air Oxidation of an AMIBEN® production wastewater was performed at 281°C for 60 minutes with catalyst

TABLE 12. PILOT-SCALE WET AIR OXIDATION OF PESTICIDE PRODUCTION WASTEWATER

Wet Air Oxidation Conditions:		
Temperature, °C	240	260
Flow, GPH	4.54	4.45
Residence Time, Min.	120	120
Pressure, PSIG	848	1200
*AOD		
Feed, g/liter	15.8	15.8
Affluent, g/liter	11.0	5.5
% Removal	30.4	65.2
Organonitrogen/Phosphate Pesticide No. 1		
Feed, mg/liter	900	900
Affluent, mg/liter	0.032	0.022
% Removal	99.9+	99.9+
Organonitrogen/Phosphate Pesticide No. 2		
Feed, mg/liter	1500	1500
Affluent, mg/liter	<0.001	<0.001
% Removal	99.9+	99.9+
Organonitrogen/Sulfur Pesticide		
Feed, mg/liter	2.0	2.0
Affluent, mg/liter	<0.001	<0.001
% Removal	99.9+	99.9+

*AOD—Autoclave Oxygen Demand

S.I. Conversion:
m³/d = GPH × 0.0908
kPa = PSIG × 6.89

TABLE 13. PILOT-SCALE WET AIR OXIDATION OF AMIBEN® HERBICIDE PRODUCTION WASTEWATER

Wet Air Oxidation Conditions:	
Temperature, °C	281
Flow, GPH	6.4
Residence Time, Min	60
Pressure, PSIG	1558
Catalyst	Yes
COD	
Feed, g/liter	30.5
Affluent, g/liter	2.9
% Removal	90.5
2,5-dichloro-6-nitrobenzoic acid and 2,5-dichloro-3-nitrobenzoic acid	
Feed, g/liter	19.1
Affluent, g/liter	<0.1
% Removal	99+

S.I. Conversion
m³/d = GPH × 0.0908
kPa = PSIG × 6.89

TABLE 14. PILOT-SCALE WET AIR OXIDATION OF HERBICIDE PRODUCTION WASTEWATER

Wet Air Oxidation Conditions:		
Temperature, °C	224	243
Flow, GPH	4.11	4.15
Residence Time, Min.	131	130
Pressure, PSIG	1580	1582
COD		
Feed, g/liter	58.4	58.4
Affluent, g/liter	18.8	17.0
% Removal	67.8	70.9
*AOD		
Feed, g/liter	107	107
Affluent, g/liter	66.4	66.3
% Removal	37.9	38.0
Dipropyl Formamide		
Feed, mg/liter	484	484
Affluent, mg/liter	20	<5
% Removal	95.9	99.0+

*AOD—Autoclave Oxygen Demand

S.I. Conversion
m³/d = GPH × 0.0908
kPa = PSIG × 6.89

(Table 13). The components of interest in this wastewater were 2,5-dichloro-6-nitrobenzoic and 2,5-dichloro-3-nitrobenzoic acids. Greater than 99 percent removal of these compounds was demonstrated.

Wet Air Oxidation was performed on a herbicide production wastewater containing dipropyl formamide. Results (Table 14) showed reductions of 95.9 and greater than 99 percent for this compound at 224 and 243°C, respectively. This wastewater was another in which the dichromate COD test did not measure all of the oxygen demand. Both COD and AOD data are presented in Table 14. Although COD reductions in the 70 percent range were observed, reductions in oxygen demand as measured by the AOD test were in the 38 percent range. Higher reductions in oxygen demand would likely have been obtained at higher oxidation temperatures. However, removal of dipropyl formamide was the main study objective and was accomplished at relatively low temperatures.

FULL-SCALE UNITS FOR WET AIR OXIDATION OF HAZARDOUS ORGANICS

The wet oxidation of wastes containing a number of hazardous organic compounds has been demonstrated on a full-scale basis as well. The commercial units employed in

TABLE 15. FULL-SCALE WET AIR OXIDATION OF HAZARDOUS ORGANICS

Study	Waste Type	Compound/Parameter	Oxidation Conditions °C/min.	Feed Concentration mg/liter	Effluent Concentration mg/liter	Removal, %
A	Herbicide	Herbicide by-product	245/60	735	< 5 to 13.3	98.2 to >99.3
B	Spent Caustic	COD	268/113	108,100	11,600	89.3
		Total Phenols		15,510	36	99.8
		Organosulfur		3,010	180	94.0
C	Rocket Fuel	COD	271/117	42,130	2,540	94.0
		Hydrazine		12,700	<0.1	>99.99
		1,1-Dimethylhydrazine		9,250	<0.7	>99.99
D	Pesticide	COD	281/182	110,000	5,200	95.3
		DOC		26,600	1,070	96.0
		Dinoseb		37.1	0.186	99.5
		Methoxychlor		8.84	<0.018	>99.8
		Carbaryl		30.0	0.59	98.0
		Malathion		93.1	0.13	99.9

this respect are the skid-mounted type, capable of 10 gpm flow rates for a material with COD of 40 g/liter. The cases where specific organics were monitored include spent caustic scrubber waste, rocket fuel waste, and pesticide and herbicide wastes. Nominal oxidation conditions were 280°C with residence times varying from 60-180 minutes. Results of full-scale oxidation runs are shown in Table 15.

In study "A" a skid-mounted wet oxidation system treated wastewater from a herbicide production process. Performance data for this unit indicated destruction in the range of 98.2 to >99.3 percent for the herbicide by-product component.

Study "B" represents full-scale treatment of a spent caustic wastewater generated by various petroleum refining processes. Oxidation of this waste at an average temperature of 268°C for 113 minutes resulted in 89.3 percent COD reduction, 99.8 percent phenols reduction, and 94.0 percent organosulfur reduction.

A waste rocket fuel mixture containing hydrazine and 1,1-dimethylhydrazine was treated in Study "C" at average conditions of 271°C for 117 minutes. Wet air oxidation of this waste resulted in >99.99 percent removals of both hydrazine and 1,1-dimethylhydrazine. COD reduction for this study was 94.0 percent.

In the final study (Study "D"), an organic wastewater containing propylene glycol and various organic ethers and esters was spiked with four commonly used pesticides—dinoseb, methoxychlor, carbaryl and malathion—in order to demonstrate the destruction of pesticides by wet oxidation. High levels of destruction were observed for the four pesticides with removals ranging from 98.0 to greater than 99.9 percent. COD and DOC removals of 95.3 and 96.0 percent, respectively, were also observed during Study "D".

CONCLUSIONS

Bench, pilot, and full-scale performance data have indicated that Wet Air Oxidation can be very effective in treating various toxic and hazardous industrial wastewaters. In particular, wastes containing phenols, pesticides, herbicides, and other hazardous organic compounds are amenable to Wet Air Oxidation. Wastewaters with high concentrations of these materials can generally be detoxified to allow subsequent biological treatment, or, in some cases, direct discharge.

Full-scale performance data for systems treating wastewaters containing hazardous organic materials have confirmed results obtained in bench and pilot-scale studies.

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The Role of Environmental Site Assessments in Reducing Lender Risk in Massachusetts

An insider's view of the legal complications arising with the application of the Massachusetts "Superfund" law relating to the clean-up of hazardous wastes.

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Love Canal. Virtually overnight, engineer William Love's ill-fated attempt to construct a navigable power canal between branches of the Niagara River became synonymous with hazardous waste. Within a matter of months, the discovery of other major sites in Grey, Maine; Lowell, Massachusetts (Silresim); and West Point, Kentucky ("Valley of the Drums"), catapulted the question of how industries dispose of their wastes from the purview of a few regulatory agencies into the public eye. Sunday supplements, made-for-TV movies, and even comic strips all reflected the country's preoccupation with the real, potential, or imagined threats to public health and safety which chemical wastes—and, by extension, the companies which produced these wastes—represented.

Despite the continued focus on the hazardous waste issue through the end of the 1970's and into the 1980's, at least one segment of society remained relatively insensitive to the issue: the real estate community. In 1981, Goldberg-Zoino & Associates (GZA) attempted to market pre-lending site investigations to the major commercial lenders in Massachusetts, on the theory that it was better to know about a hazardous waste problem on a site before investing in it rather than after. This marketing effort elicited negligible response from the several dozen institutions contacted, despite the fact that the problems of the bank involved in the Silresim site were well publicized. (Eventually, its involvement with Silresim resulted in a loss to this bank of approximately \$300,000.)

THE MASSACHUSETTS "SUPERFUND" LAW

The laissez-faire attitude of the real estate community changed rapidly and dramatically in March 1983, when the Massachusetts "Superfund" Law (Mass. General Laws Chapter 21E) was passed. In many respects, this law was similar to the federal "Superfund" law (CERCLA). Provisions for reporting "releases" of hazardous material or oil into the environment were set forth, and a pot of money was established for the Commonwealth to use in cleaning up sites where the responsible parties would not take on this task.

Of particular interest to the real estate community, however, were the provisions for cost-recovery by the Commonwealth. The assessment of treble damages against the responsible parties was not a new concept, but the use of a priority lien as a means of cost recovery was. Under the priority lien (soon referred to as the "superlien") provision, the Commonwealth's claims against the liable parties could be satisfied in whole or part by a lien on the parties' property (both the cleaned-up site and other properties not

involved in the clean-up) which took priority over all other liens on the property, including mortgages.

An equally controversial aspect of the Massachusetts Superfund Law was the way in which it dealt with "innocent owners" (owners who were not responsible for the wastes on the site, i.e., who had unknowingly purchased, foreclosed on, or otherwise acquired a former waste disposal area). Under 21E, current site owners, innocent or not, shared in the joint and several liability for the costs of remediation with the responsible parties. While innocent owners would not be assessed treble damages, they could be assessed by the Commonwealth for an amount equivalent to the value of the property (and improvements) after clean-up. This provision was insisted on by the Commonwealth, which claimed that in several previous situations public funds had been spent to clean up a site, which was then sold at a substantial profit by the owners.

The superlien provision of 21E served as a highly effective mechanism for gaining the attention of the real estate community. Almost immediately, efforts were begun to modify 21E to make it more palatable. As a result of these efforts, the Commonwealth agreed that certain modifications should and could be made. In December 1983, the Governor signed an amendment to the Superfund Law which limited the priority lien to the actual property involved in the clean-up (although the Commonwealth could still obtain a normal lien on other property of the responsible parties), and which removed from the priority lien provision property which was wholly or primarily residential in nature. These provisions forestalled an imminent threat to the origination of residential mortgages in Massachusetts because of the unwillingness of the secondary mortgage market to deal with the risks created by the superlien provision.

Continuing efforts of the real estate community to eliminate the superlien provision entirely and to provide protection for innocent owners have not yet met with success. At one point, it appeared that the income from a tax on real estate transactions might be used to augment the pot of cleanup money, so that innocent owners could be relieved of any involvement; this proposal is no longer being considered. An alternate amendment, submitted by the Governor in May 1984, would both eliminate the superlien provision and exclude an innocent owner from any liability to the Commonwealth for its cleanup costs if "due diligence" had been used by the innocent owner in trying to determine, prior to purchase, whether there had been a release of hazardous material or oil on the site. While this amendment satisfies some of the concerns of the real estate community, it is perceived by some of the environ-

mental groups involved in the amendment process as a serious weakening of the law. As of January 1985, a final version of the amendment had not been agreed to.

Somewhat curiously, the group within the real estate community most affected by the fallout of 21E is the group which stands to benefit least from any individual real estate transaction: the title insurance companies. Commercial lenders are generally willing to provide money in those situations in which the priority lien would be insured over by the title company involved. After some initial debate, the major title companies in Massachusetts have settled on their current policy, under which they will provide coverage for defects in title resulting from a superlien if 1) the "release" resulting in the imposition of a superlien occurred prior to the date of the policy, and 2) an evaluation of the site with regard to 21E concerns had been conducted by a qualified firm prior to issuance of the policy. This evaluation is the environmental site assessment which, for better or worse, has come to play a pivotal role in Massachusetts real estate transactions.

DEFINITIONS

The term "site" is defined in Section 2 of Chapter 21E as a "place or area where oil or hazardous material has been deposited, stored, disposed of, or placed, or otherwise come to be located." "Assessment" is defined in this same section as those investigations, etc., carried out to identify the nature and extent of the contamination problem; to determine the impact of this problem on public health, safety, welfare, and the environment; to identify those persons liable under the act; and to remediate the problem.

As it is currently used by those involved in resolving site-specific superlien concerns, the term "environmental site assessment" has a significantly different connotation. In the first place, the site is not necessarily the locus of an actual or potential release of hazardous material into the environment; it is whatever building or parcel of land is under consideration, whether a release is actually suspected or not. Secondly, the focus to date has been on a "preliminary" site assessment, the purpose of which is to determine whether there is a potential problem. Once a 21E problem has been detected on a site, the site assessment may move on into the more rigorous phases referred to in the law.

TECHNICAL BACKGROUND

Broadly speaking, the geology of Massachusetts consists of glacial deposits overlying bedrock. Where a significant water-saturated thickness of permeable glacial deposits (sand and gravel) is involved, the deposit is considered an aquifer, a source of water supply. Although many private wells and occasional municipal and industrial wells draw water from fractures in bedrock, most large-yield production wells in Massachusetts are located in these sand and gravel aquifers.

Hazardous materials released onto or into the ground will tend to move downward under the force of gravity through the unsaturated zone until the water table (the top of the saturated zone) is reached. In most cases, the introduced materials will move with the groundwater as it slowly moves toward a downgradient discharge point such as a river or lake. The rate of movement will generally be very slow, on the order of a foot per day, although the rate may be substantially higher or lower depending on such factors as the nature of the soils involved and the nature of the introduced material.

The situation is complicated when the amount of material introduced exceeds the amount which can be dissolved in the groundwater. In certain situations, large releases of undiluted material may result in lenses of the

material "floating" on top of the water table or sinking through the uppermost permeable unit to move as a body along the bottom of the unit, depending on whether the material in question is less or more dense than water. This phenomenon commonly occurs in situations involving gasoline or oil spills, where the lens on top of the water table may be thick enough to recover as pure product. The movement of introduced material as discrete bodies is much less amenable to analysis than the movement of this material dissolved in groundwater.

The situation is further complicated by the fact that materials introduced into the ground may interact with the soils involved in any number of ways. The soils may result in significant attenuation of the material or may merely retard its movement. A release involving a mixture of materials may thus result in the formation of a number of contaminant "plumes", each with a slightly (or significantly) different size and shape. Some contaminants (e.g., metals, PCBs) tend to be retained in the soil, and may not even reach the water table.

Predicting the rate and direction of movement of contaminant plumes is one of the key elements of a complete site assessment. This information is obviously critical in evaluating the impacts of the contamination and the necessary remedial action. However, as noted in the preceding section of this paper, most of the site assessments currently being commissioned are preliminary in nature. It is the attempt to provide a definition of a complex three-dimensional subsurface situation with little or no subsurface information which makes preliminary site assessments more a question of "opinion" than of "certification," as discussed below.

THE NATURE OF A SITE ASSESSMENT

Site assessments are a means of reducing the level of risk in a real estate transaction related to MGL Chapter 21E. Site assessments will not eliminate the risk entirely, but in general the level of risk reduction will increase with the time and budget available for the site assessment.

For analytical purposes, the hydrogeologic environment is often considered to be a readily definable, fully predictable entity. This, of course, is science fiction; while the general rules of hydrogeology are clear, their application to any individual parcel of land is somewhat ambiguous. Coupled with this uncertainty is the often haphazard nature of releases of materials into the environment, which are seldom uniform in rate, consistent in location, or constant in composition.

Another factor to consider is the interpretation of the term "release." As of this writing, it is the position of the Department of Environmental Quality Engineering (DEQE—the Massachusetts environmental regulatory agency) that this term refers not only to such obvious cases as a leaky lagoon or a spilled drum, but also to the movement of released material within the environment.

Under DEQE's interpretation, the movement of contaminated groundwater away from its source area may be considered as a series of releases. In other words, as groundwater containing hazardous materials moves from upgradient source A to downgradient property B there is a release, and as the contaminated groundwater moves beyond B to further downgradient property C there is another release. It then is up to the owner of B to show that he is not responsible for the contamination of C's well by chemicals originating at A. In fact, both B and C, as owners of sites on which there has been a release, are in theory jointly and severally liable for the Commonwealth's cleanup costs.

Given the uncertainties inherent in defining the hydrogeologic framework, the irregular nature of many releases of hazardous materials, and the currently operative interpretation of "release" by DEQE, it should be clear

that a routine preliminary site assessment will not provide sufficient information to completely eliminate the risk related to 21E. In a similar vein, it should be clear that a consultant hired to perform a routine site assessment, costing on the order of a few thousand dollars, will be unwilling to "certify" (i.e., "guarantee") that there has not been a 21E release on the site. For this reason, site assessments should be considered closer in nature to the environmental opinions provided by attorneys than to the certifications provided by surveyors.

THE SCOPE OF THE SITE ASSESSMENT

As noted above, the purpose of the site assessment is to reduce the risk involved in a real estate transaction. While the correspondence is not always linear, it will generally be the case that the level of risk reduction will be proportional to the time and budget available for the assessment.

The establishment of an "acceptable" level of risk reduction has been key to the development of site assessment procedures in Massachusetts. The several parties involved in the real estate transaction have to agree on the definition of "acceptable": the buyer (who is most often the party commissioning the site assessment), the lender, the title insurer, and, in some cases, the seller. Moreover, the consultant performing the site assessment has to decide on what a technically appropriate minimum standard would be, since there is as yet no "industry standard" for this type of work. GZA's approach to site assessments is described below; other firms' approaches are similar in general form, although they may differ considerably in detail.

There are certain basic elements of a site assessment which will be performed in virtually every case. Some of these are described in the following paragraphs.

1. Observation of present site conditions. The site and any buildings on it should be viewed by the person conducting the site assessment. Signs of contamination should be looked for in surface water on or adjacent to the site, in the site soils (e.g., staining or discoloration), and in the site vegetation (e.g., stressed or dead vegetation). In addition, possible sources of past or ongoing releases should be noted, such as lagoons, landfills, or carelessly handled drums. Since 21E also covers releases of oil, buried oil tanks (and their ages) should also be noted. Finally, although not specifically covered under 21E, apparent significant threats to health and safety (e.g., concrete floors saturated with pesticides) should be noted.
2. Review of site history. An attempt should be made to determine what the previous land uses were on the site. The availability of the chain of title is useful, but not in itself sufficient, for this purpose, since owner names are not always indicative of actual use and lessees are not indicated. Information on the raw materials, waste products, and manufacturing and waste disposal practices of present and past owners and tenants should also be sought. State and local authorities should be contacted as to any information they may have regarding previous releases on or near the site.
3. Land use on adjacent properties. Activities on property adjacent to or in the vicinity of the subject property may also be indicative of at least the possibility of past or ongoing releases. For instance, the presence of a gas station upgradient of a site suggests the potential for gasoline or oil in the groundwater beneath the site. This is particularly important given DEQE's current definition of "release" which, as discussed above, could result in liability attaching to the site owner for the activities of the gas station. Note, how-

ever, that it is generally not feasible to examine adjacent sites as carefully as the subject site.

The requirement for subsurface explorations as part of a site assessment has been the subject of much discussion by both the real estate and consultant communities. In January 1984, after eight months of "walkover" site assessments, GZA instituted an internal policy of generally requiring subsurface investigations as part of site assessments except where the land had no history of industrial usage or, at the other extreme, where the site was located in downtown Boston or a similar urban setting. Even in these cases, however, borings could be required if site observations or the review of site history indicated their necessity.

GZA's decision in this matter was based on an increasing uneasiness about calling sites "clean" on the basis of a limited assessment, when in the vast majority of cases where borings were executed some level of soil or groundwater contamination was encountered. While in most cases the observed levels of contamination were insignificant in terms of actual impact, the detection of even low levels often concerned the parties involved in the transaction. In GZA's opinion, the potential liability involved in performing site assessments required a higher level of care in evaluating the presence of hazardous material or oil on site than a simple walkover could provide.

A significant decline in site assessment business volume was anticipated as a result of the decision to require subsurface explorations, since these explorations added to both the project budget and time required. In fact, the decline in volume was negligible. Most of the major title companies, and many developers and real estate lawyers, began to appreciate the significance of the potential liability which could attach to even innocent owners. As of this writing, the requirement for subsurface explorations appears to have been adopted by additional consultants, so that subsurface explorations are currently more the norm than the exception in site assessments.

As with subsurface explorations, the role of chemical analyses in site assessments varies with the consultant involved. GZA uses in-house screening capabilities for volatile organic compounds and indicators of inorganic contamination to evaluate the need for more quantitative analyses, since quantitative analyses can add significantly to project cost and duration. Other consultants have quantitative analyses of one sort or another performed on all samples.

The variations in approach with regard to subsurface explorations and chemical analyses reflect differences in opinion regarding "acceptable" risk, as well as the differences in approach and capability of the various consultants performing site assessments. Somewhere between no borings and deep borings across the site on a 10-foot grid pattern, and between no chemical analyses and full priority pollutant analyses on all soil and water samples, lies a level of investigation which is the appropriate balance between risk reduction and the constraints of realistic budgets and schedules. While the "ideal" level of investigation may eventually be prescribed for regulatory purposes in amendments to 21E, the technical community has yet to agree on it.

THE SITE ASSESSMENT REPORT

The site assessment report is the culmination of whatever investigative activities were carried out to evaluate the presence of releases of hazardous material or oil on the site. It is subject to intense scrutiny by all the parties involved in the pending transaction, particularly the title in-

surers, and must be carefully worded in terms of both what it purports to say and what it does not purport to say.

The report should provide a full description of the observations and research carried out by the site investigator, including the dates of site visits, the names or titles of people contacted for site history information, the locations and number of subsurface explorations, the types of chemical analyses performed and the results, and other pertinent information. There should be an opinion (not a certification) as to the presence of hazardous material or oil on the site. Given the variety of legal theories among environmental attorneys in Massachusetts regarding what the courts will eventually decide "release" really means, GZA's practice is to report the "presence in the environment" of some substance, rather than to attempt to establish a definition of "release" of its own.

While the scope of the preliminary site assessment report is usually contractually limited to evaluating the possibility of a release on the subject site, GZA commonly provides a preliminary risk analysis in those situations in which something is detected on the site. This includes a discussion of both on-site and off-site impacts (e.g., water quality impacts on downgradient wells) of the site in its present condition and, if excavation or similar earthmoving procedures are planned, the precautions which should be taken to protect workers on the site and passersby.

The report may also include a section on limitations regarding the use of or reliance on the report designed to protect the consultant. Many consultants, including GZA, are reluctant to take on without reservation what could amount to millions of dollars worth of liability to a potentially large number of parties in exchange for a modest fee. It is somewhat ironic that the parties who have the smallest financial stake in any transaction—the site assessment consultant and the title insurer—are most likely to be considered as casualty insurers if there is a subsequent problem on the site.

"VOLUNTARY" SITE ASSESSMENTS

MGL Chapter 21E, at least in its present form, does not specifically require the completion of a site assessment prior to a real estate transaction; as discussed above, site assessments come into being to satisfy the real estate com-

munity rather than the regulatory community. In a limited number of situations, site assessments have been requested by the owners or operators of facilities at which there may have been a release without any specific impetus (e.g., pending sale or regulatory enforcement action).

In these cases, it is the intent of the owner/operator to determine, in advance of a specific need, whether the site might at some point present a significant environmental problem. If a release is detected, such remedial actions as may be necessary may be undertaken on a voluntary basis by the owner/operator, often with the cooperation of the regulatory agency. While any remedial action is more expensive in the short term than no remedial action, the near inevitability of the eventual detection of a significant release, and the high remedial costs which may accompany this detection, can make this "voluntary" site assessment economically attractive.

CONCLUSION

The Massachusetts Superfund Law has been hailed as a major boon by some, and as a misguided attempt to tinker with free enterprise by others. There are clearly arguments to support both sides, along with the argument as to whether the environmental benefits of the law have been worth the attendant costs, delays, and aggravation. While the form of the superlien provision may be altered substantially, the environmental site assessment, created out of desperation to serve as a tool for reducing the risks inherent in the implementation of 21E, will, in one form or another, persist.

Lawrence Feldman is an Associate of Goldberg-Zoino & Associates. His experience has encompassed a wide variety of groundwater related issues, ranging from groundwater quality and contamination to groundwater resource evaluation. Projects completed under his direction include studies of groundwater contamination by industrial wastes, hydrogeologic evaluations of sewage disposal sites, environmental assessments prepared as part of wetlands submissions, and town-wide water resource studies. He has been particularly active in multiphased studies aimed at locating, evaluating, and controlling groundwater contamination by organic chemicals.



Design and Implementation of Groundwater Recovery Systems

Three case-history studies illustrate the problems involved in the implementation of existing government regulations.

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The status of many existing interim status hazardous waste facilities involved in the storage, treatment, and disposal of hazardous materials, with respect to groundwater impact has been prominently exhibited during the last two years. Based on experience and raw statistics, it is apparent that a far greater proportion of facilities than originally expected have been forced into Groundwater Quality Assurance Programs. This is due, at least in part, to the rigid and often improper application of statistical procedures set forth in the interim status regulatory program. Although many of these facilities may ultimately show that no "hazardous wastes or hazardous waste constituents" have entered the groundwater, the probability is high that the groundwater investigations which demonstrate the lack of such constituents will also show such facilities to be contributing other "non-hazardous" materials and contaminants to the groundwater systems. The long-term implications of such findings are significant, both in the preparation and implementation of final hazardous waste permits, and to addressing groundwater contamination and impacts in states where regulatory programs other than the Resource Conservation and Recovery Act and associated state regulations (herein generically referred to as RCRA) are pertinent.

The RCRA permitting regulations divide groundwater monitoring into a three-phase program. These phases are logically arranged to proceed from a monitoring program designed to detect the occurrence of hazardous constituents (detection monitoring) to a program designed to track the extent and level of contamination in an affected aquifer in comparison to a defined standard of groundwater quality (compliance monitoring), to the design and implementation of remedial activities when groundwater quality in affected aquifer is degraded beyond the defined standard (corrective action).

Within the regulatory description of these programs, particularly compliance monitoring, there is considerable discussion of a "groundwater protection standard," which identifies specific hazardous constituents and the allowable concentrations for such contaminants in the monitored aquifer. The concentrations specified for such constituents are to be set as:

- The background concentration in the groundwater, or
- The concentration set forth as a drinking water standard for eight metals and six pesticides, or
- An alternate concentration established by the Regional Administrator.

Many people have put faith in the use of discretion by the "Regional Administrator" in order to avoid costly corrective action programs where data and studies can be developed to indicate a substantial lack of environmental need

for groundwater clean-up. However, the recent regulation climate and specific project negotiations indicate that there is little real probability that such exceptions will be granted. Thus, there appears to be little hope of avoiding eventual corrective action for many facilities. Given this scenario in the RCRA program and adding to it groundwater recovery programs associated with hydrocarbon leakage and spills from tanks, which are also expected to increase dramatically, it is apparent that many facilities may be in need of basic information on the engineering and design of groundwater retrieval systems. The purpose of this paper is to describe several recent case histories where groundwater recovery has been implemented, and to use these case histories to describe some of the difficulties encountered in such a process.

SERVICE STATION LEAK, SAN ANTONIO, TEXAS

Upon filling one of its gasoline tanks for the first time, a new service station in San Antonio, Texas, discovered that the entire contents of the tank had escaped from a hole in the tank caused by an oversized rock in the granular support bed. It was determined that an investigation was necessary to carefully delineate the geology and hydrology of the extensively fractured bedrock in the project area. The gasoline was found in a formation known as the Buda Limestone at depths of 0 to approximately 24.4 meters (m); confined by the Del Rio Clay below the Buda. The Edwards Aquifer, a sole-source aquifer supplying San Antonio's drinking water, is located at depths of 36.6 m to 109.7 m in the project area. Because of the sensitivity of the area in terms of proximity to the Edwards Aquifer, the spill, though low in volume (41,600 liters), was considered to have the potential to become a major environmental problem.

By installing multiple groundwater monitoring wells and exploratory borings in the vicinity of the source tank, and by collecting samples from private water wells in the area surrounding the service station, it was possible to define the approximate limits of contamination. Analyses of samples collected for contaminants such as benzene, toluene, and the more soluble MTBE, allowed distal edges of the spill to be identified.

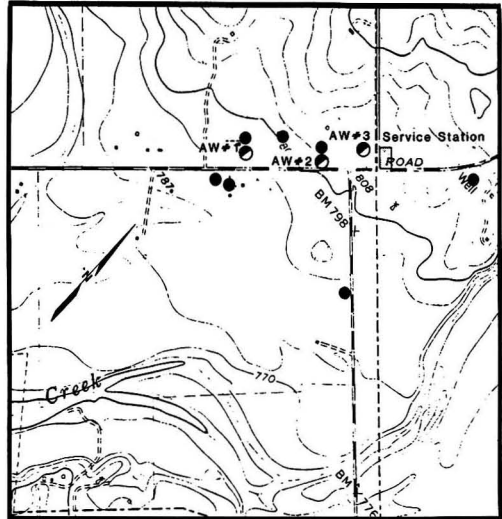
Contaminants were identified in several nearby Edwards Aquifer water wells. Since the major concern of the investigation was the potential for contamination of the aquifer, several steps were immediately undertaken to determine the path followed by the contaminants invading these wells. Borehole camera surveys were used to determine whether the well casings had failed, allowing dissolved hydrocarbon constituents to migrate from the Buda

Formation to the Edwards Limestone via wellbore crossflow. Pumping tests were also completed on the problem wells to determine whether, upon pumping, the water quality problems were eliminated. Based on these studies, it was determined that, in all cases, the path of contamination into the wells was via casing failure and down the wellbore. All impacted wells were either plugged, or casing liners were installed to eliminate crossflow into the Edwards Aquifer.

The preliminary investigation was utilized to determine the approximate area of spill impact, a difficult task in the fractured Buda Formation. The basic hydrogeology of the area was analyzed from the exploratory borings and monitor wells, and analyses of groundwater samples for gasoline components were completed to develop a concentration profile for hydrocarbons in the groundwater system. A base map of the area with the concentration profile for MTBE is shown in Figure 1.

These investigations were completed in order to develop a comprehensive approach to recovering both free hydrocarbons and contaminated water. Because of the fractured aquifer in which the gasoline was spilled and local water table gradients, the movement of contamination toward nearby water wells had rapidly proceeded from the point of spill to a distance of over 600 m in six months. This made it very important to arrest further contaminant spreading in order to prevent additional water wells from being impacted with the potential for further Edwards Aquifer contamination. In addition, it was determined that an attempt should be made to recover any free hydrocarbons and associated contaminated water near the point of spill.

To accomplish these goals, a two-phased recovery system was designed and installed. As shown in Figures 2 and 3, two water recovery wells were installed at the down-gradient edges of the plume. These wells were installed through the Buda Formation and terminated in the upper Del Rio Clay. These wells are intended to remove contaminated groundwater, which is subsequently treated to remove free and dissolved hydrocarbons prior to discharge to the City of San Antonio sewer system. In addition, a third recovery well located in the vicinity of the point of maximum hydrocarbon concentration was installed in an attempt to recover any free hydrocarbons and high concentrations of dissolved constituents in the groundwater. This well is located to effectuate the maximum rate of removal of contaminants, as opposed to the other two wells, which are located to arrest plume movement. The intent of the third well is to decrease, as quickly as possible, the mass of



- Private Water Supply Wells
- Arresting and Recovery Wells

Figure 2. Area water well location map.

hydrocarbons in the groundwater in order to reduce the driving force for down-gradient migration, reduce the ultimate volume of contaminated water requiring removal and treatment, and reduce the time required to complete the groundwater clean-up program was well. Water and hydrocarbons produced from the third well are treated to remove free hydrocarbons by gravity separation, with subsequent absorptive and adsorptive processes to remove dissolved and emulsified contaminants.

In completing such a project, it is also important to define a cutoff point in order to prevent continued operation beyond reasonable, cost effective goals. In this case, the well system will be operated, maintained, and monitored until all wells consistently produce groundwater with total hydrocarbon concentrations below 100 ug/L. Once this goal is achieved, the system will be dismantled and all wells plugged.

HAZARDOUS WASTE IMPOUNDMENT LEAK

A Texas chemical manufacturer used a system of dike-walled lagoons for treatment of liquid wastes. The lagoons, which are unlined, are located in the floodplain of a major river system. In 1969, a waste treatment lagoon was constructed immediately adjacent to the river. On the side facing the river, a dike was built to form one side of the lagoon. The dike was constructed of sand, silt, and clay scraped from the area that would eventually become the impoundment bottom.

The lagoon has been used as a solar evaporation basin for high strength waste. Shortly after the lagoon was filled in 1969, a number of seeps began discharging contaminated water to the river adjacent to the impoundment. In 1975, a slurry wall was installed along the length of the dike to stop the seepage, but was effective only in reducing the amount of seepage. The lagoon remained in operation until 1979, when water was pumped from the lagoon and discharged to the wastewater treatment system. By 1981, the lagoon was empty, as it remains today, however, some contaminated seepage continues to enter the river adjacent to the now empty lagoon. Recently, the adjacent river was sampled at locations both up and downstream of the seeps. Waste-specific constituents were analyzed and a statistical comparison was made of the up and downstream

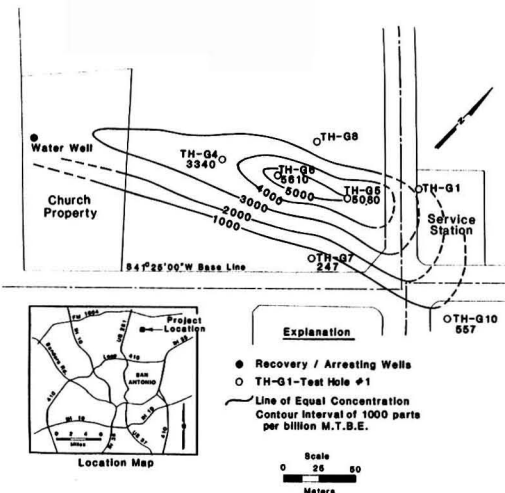


Figure 1. MTBE concentration isopleth (1/26/84).

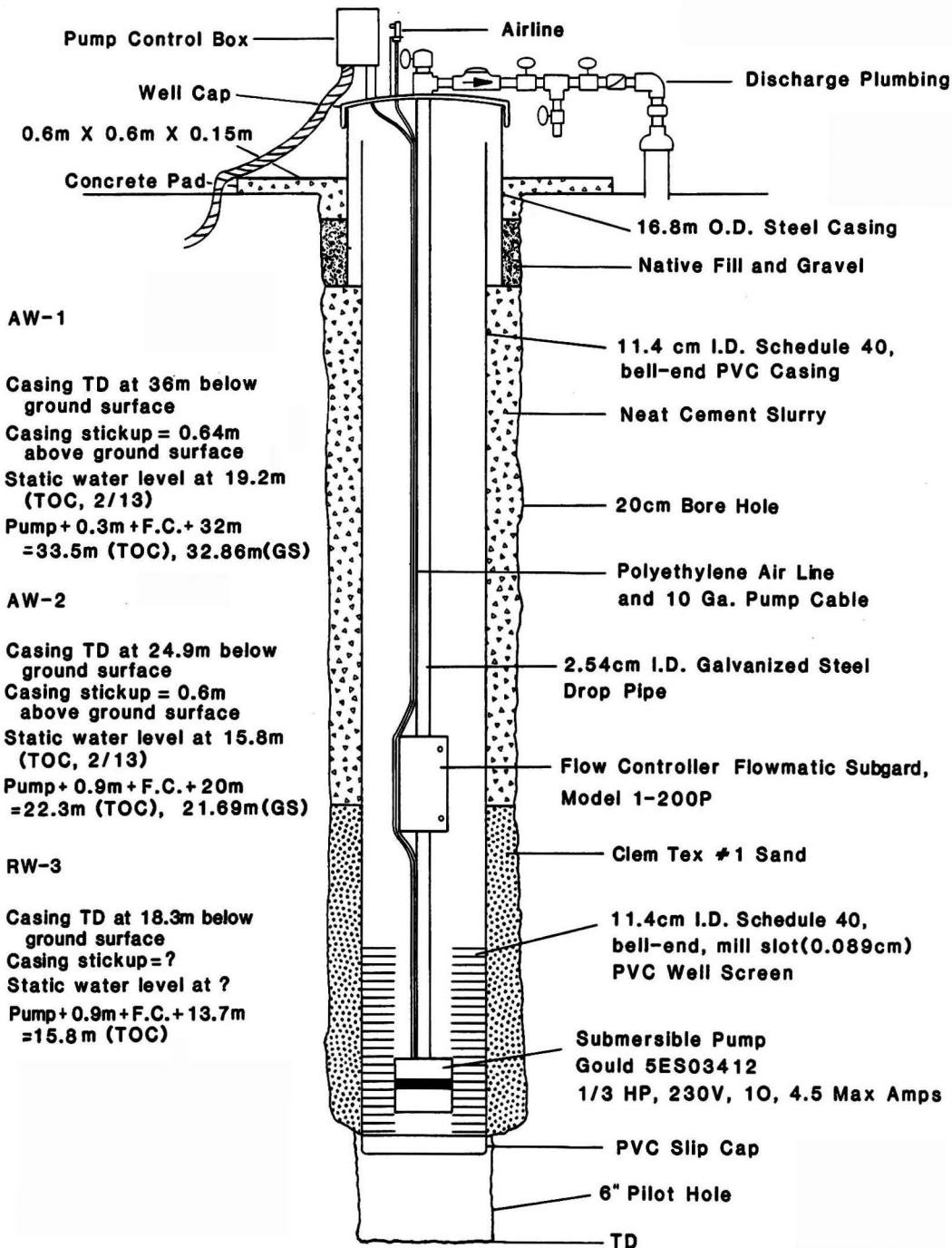


Figure 3. Arresting recovery well design.

sample concentrations. The results indicated that certain waste-specific constituents were increasing significantly above background levels probably as a result of the seepage entering the river. A decision was made to design and implement a groundwater recovery system that would eliminate or control seepage to the river.

A cross section of shallow geology in the area where seepage is occurring is shown in Figure 4a. The shallow saturated zone occurs in a coarse sand in the lower part of

the alluvium. Seeps occur at the point where the potentiometric surface intersects the river bank. The alluvium is 10.7 to 12.2 m thick and rests upon an underlying Tertiary Clay. On the river side of the existing slurry wall, the saturated thickness of this sand, above the bedrock, varies from 3.0 m to 3.7 m. On the up-gradient side of the slurry wall, however, the saturated thickness is from 5.2 to 7 meters. A map of the piezometric surface is shown in Figure 5. Water level data indicate that the slurry wall acts as a

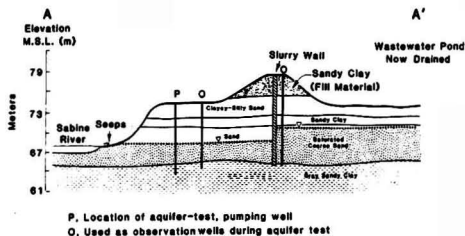


Figure 4a. Configuration of piezometric surface before pumping.

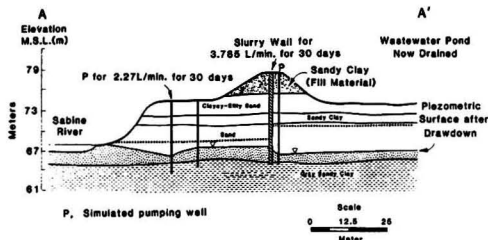


Figure 4b. Simulated drawdown after 30 days pumping at rates of 2.27 L/min using a computer assisted thesis non-equilibrium solution and image wells to simulate boundaries.

groundwater dam, with the difference in head between the up and down-gradient sides being about 1.8 vertical meters over the 1.2-meter thickness of the wall.

Recently, two test wells were installed on the down-gradient side of the slurry wall, as shown in Figure 2. Aquifer tests were run to determine the transmissivity and storage coefficient. Two observation wells were installed with each pumping well, one near the pumped well on the down-gradient side of the slurry wall, and a second observation well located on the up-gradient side of the slurry wall. Due to the low permeability of the aquifer material

and the limited saturated thickness, the wells could not sustain pump rates greater than 5.7 L/min. The nearby observation wells showed appreciable drawdown, but the observation wells on the opposite side of the slurry wall showed no measurable response, probably due to the limited length of the pump tests and the greater distances from the pumped wells. Analyses of the observation well data yield estimates of transmissivity values from 7.2 m²/day to 10.8 m²/day, and an estimated storage coefficient of 2.8 × 10⁻³.

Results of the aquifer test have been used to determine well spacing and pumping rates for a recovery system. A computer-assisted analysis of drawdown, solving a non-equilibrium flow equation for several wells pumping simultaneously, was used to analyze the drawdown response at various well spacings and pumping rates, with wells placed on both sides of the slurry wall. The slurry wall was treated as a no-flow boundary, and the boundary condition was simulated by using discharging image wells. Likewise, the river and a fresh-water lake adjacent to the northern part of the wastewater pond were treated as constant head boundaries, and simulated by using injecting image wells. The east and west sides of the slurry wall were simulated using separate simulation runs for drawdown on each side of the wall.

A no-flow boundary simulated with image wells presumes that the aquifer ends at the no-flow boundary, and therefore the solution is valid only for the aquifer-side of the boundary. A limitation of modeling each side independently is that there is no recognition of interaction of water levels across the slurry wall which would occur during actual long-term pumping.

The results of a 30-day simulation indicated that four wells on the down-gradient side and five wells on the up-gradient side of an 800-foot long section of the slurry wall would reduce the head in the aquifer below the elevation of the river bottom. Simulated pumping rates on the down-gradient side were varied from 2.3 L/min to 3.0 L/min. On the up-gradient side of the slurry wall, where the saturated thickness is greater, simulated pumping rates of 3.8 L/min to 7.6 L/min produced the desired drawdown in the model. Figure 3 shows a cross section of the projected drawdown after 30 days of simulated pumping.

The final recovery well system design includes nine wells. Pumps capable of pumping low volumes (1.9 L/min to 7.6 L/min) will be installed, and a float-switch system will be included with each well to provide automatic shutdown and restart if the wells pump off. Wastewater will be routed to the plant waste treatment facility for disposal.

TEXAS GULF COAST CHEMICAL PLANT

Another case history which demonstrates the potential of the CFR 264 corrective action program requirements is demonstrated by a study of a chemical manufacturing facility located near the Texas Gulf Coast. This facility has been in operation in excess of 50 years and, prior to the installation of a biological treatment system in the past 10 years, the facility utilized solar evaporation ponds for waste disposal. At the time of initial plant construction, solar evaporation ponds constituted state-of-the-art technology for disposal of process wastewater, and use of such ponds was consistent with the emerging industry's wide recognition of the necessity for environmental protection of surface waters. During this period, when water quality control attention was focused on surface water considerations, the potential for long-term impact on groundwater associated with surface impoundment use was not fully recognized nor appreciated. The shift in focus to groundwater concerns in the late 1960's and 1970's resulted in a recognition that significant long-term potential impact of shallow groundwater was associated with surface impoundment usage.

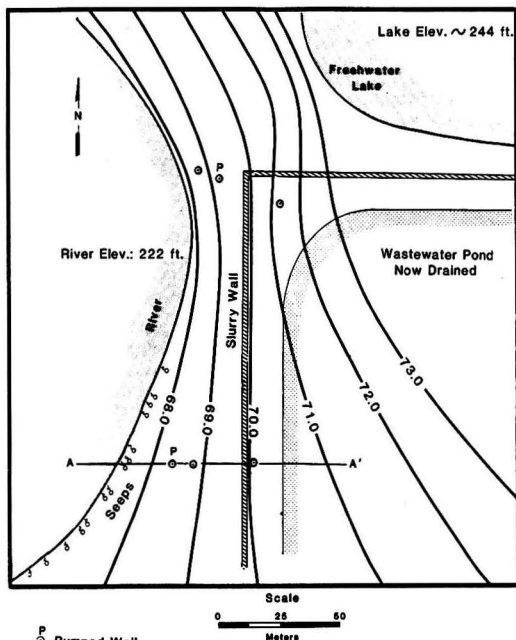


Figure 5. Plan view of wastewater pond-slurry wall river.

Prior to the initiation of a biological treatment system, the waste disposal practices ultimately resulted in the utilization of over 283 hectares (ha) of solar evaporation lagoons at this facility. Although located in the Texas Gulf Coast region, the climatic conditions at the site are such that annual average evaporation exceeds rainfall. The 283 ha of surface impoundment had been reduced to approximately 162 ha by the time an extensive groundwater assessment at the plant site was initiated.

The groundwater assessment consisted of the installation of in excess of 100 monitor wells over the entire 283-hectare area, with monitor well locations concentrated in the area of the 162 ha of currently in-use solar evaporation ponds. The monitor well system revealed that shallow groundwater impact had occurred with an aerial extent of 162 to 202 ha, and depths extending 9.1 m to 21.3 m below the ground surface. Total Organic Carbon (TOC) concentrations within the contaminated groundwater exceeded 20,000 mg/L in some cases. Many issues were involved in assessing the environmental consequences of the groundwater impact. The shallow groundwater system in which the impact had occurred is naturally saline, the total dissolved solids are in excess of 10,000 mg/L, and it is not utilized in the regional area surrounding the facility. In addition, further contributions to the groundwater contamination were being eliminated as alternative disposal methods which did not utilize lagoons were being implemented. Further migration of the contaminated groundwater would be mitigated by the removal of the ponds and the imposed hydraulic heads, plus the fact that the local and regional shallow groundwater gradients are extremely flat. The organics involved in the groundwater contamination at this particular site did not represent priority pollutants, nor EPA-defined hazardous waste constituents.

An evaluation of the feasibility of recovery of the contaminated groundwater was made at the facility. The stratigraphy at the site consists of typical Gulf Coast sediments with lenticular sand and clay beds, and an absence of extensive continuity in any sand units across the site. Permeabilities in the clays are on the order of 1×10^{-7} cm/sec., and in the sand are as high as 1×10^{-4} cm/sec. To fully evaluate the feasibility of recovery, trial recovery systems were installed at various locations around the facility. These systems consisted of several pumping wells plus a number of observation wells for monitoring the groundwater response to the operation of the recovery system. Extensive pump tests were performed on the recovery test wells to evaluate hydraulic conductivities and aquifer parameters for theoretical assessment of the retrieval systems. Extensive theoretical modeling using finite element techniques was performed to assist in evaluating the response of the groundwater system to the retrieval efforts.

Many operational problems were encountered in testing the retrieval systems. The nature of the sediments, and lack of extensive inter-connected highly permeable units resulted in relatively low yields, less than 7.6 L/min, from any of the wells. The characteristics of the naturally saline groundwater plus the nature of the organic contamination lead to operational difficulties with the submersible pumps which were utilized.

Results of the assessment of the retrieval systems indicated that in excess of 90 percent of the flow from any well generally came from relatively thin, high permeability, 1×10^{-3} cm/sec sand units. The conclusions from the feasibility assessment of recovery at the site can be summarized as follows:

- At a 3.8 L/min average production rate it would take in excess of 6,000 well-years to retrieve the volume of recoverable contaminated groundwater estimated to be present (one well-year is one recovery well in operation for one year).

- The water which could be recovered would be produced from only the more permeable units. As a result, in excess of 60 percent of the contaminated groundwater is essentially non-recoverable.

This case history represents a situation where recovery of impacted groundwater would, at best, be a perpetual operation. Had this been a situation where Federal EPA hazardous wastes constituents were involved in a CFR Part 264 Corrective Action Program, then such a perpetual operation would be mandated in spite of the fact that such recovery operations would probably never achieve the intended result. This conclusion is particularly relevant today, in an environment where regulatory agencies are reluctant to assess groundwater usage and local groundwater conditions in establishing compliance limits for hazardous waste constituents. The thrust of present regulatory actions is to use background concentrations as compliance limits. Accordingly, there will be many cases where corrective action programs, though required and implemented, will never be successful in achieving the intended results.



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Modeling Ammonia Gas Transport from Solidified Hazardous Waste

Ammonia off-gassing from solidified waste in modeled using transport theory, numerical methods, and computer simulation.

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Donald O. Hill, Mississippi State University, Miss. 39762

Application of transport theory to the movement and fate of chemicals in the environment is becoming more widely appreciated by scientific professionals whose training traditionally has not included the principles of transport phenomena. Chemical engineers, by virtue of their education and practical experience, have had a better appreciation for the theoretical power of the fundamental principles. The current interest among environmental professionals in theoretically derived models of the environmental fate of chemical contaminants reflects a growing appreciation of the potential of transport theory to improve our understanding of the behavior of chemicals in the environment.

One hindrance to the application of transport phenomena theory to environmental problems is the complexity of the environment. More often than not, the simplifying assumptions applied in the design of chemical reactors cannot be used to simplify environmental chemical transport problems without seriously limiting the usefulness of the results. Without simplifying assumptions, however, certain problems may not be solvable. If they can be solved, the specific problem of interest may not justify the human and computer resources required to arrive at a solution. The process of selecting appropriate assumptions involves a consideration of the mathematics needed to describe the problem, the quantity and quality of the data that are available, and the human and computer resources that can be assigned to the problem. In the final analysis the selection of a set of simplifying assumptions is a subjective judgement of what is reasonable versus what is unreasonable. For these reasons it is important that the user of a model derived from analytical considerations know what assumptions were made and how these assumptions constrain the utility of the analysis. In the model described in this paper, several simplifying assumptions were made. They were necessary for the following reasons: 1) certain data were not available; 2) the results of the analysis were to be used at the planning level and not for design or detailed assessment, and 3) the problem was to be solved by simulation on a microcomputer.

Time dependent environmental chemical transport problems can not be adequately described without the use of partial differential equations (PDE). For many environmental applications, exact solutions to the PDE's are not available. However, numerical approximations can be carried out on a computer. At one time simulations were carried out on mainframe computers after considerable effort and expense. Today this is no longer the case, nor is it always desirable to use a large computer in order to obtain information. Practically every professional that deals with

the fate of chemicals in the environment has access to a microcomputer. It is the purpose of this paper to describe the use of the principles of transport phenomena and a microcomputer to develop the technical input needed for planning level assessment of a selected environmental problem.

Hazardous Waste Solidification

One treatment/disposal option that has been considered for cleanup of uncontrolled hazardous waste sites involves solidification processing of the waste followed by secure landfilling of the solidified material. Solidification processing is a technology that is used to treat liquids and sludges that for technical reasons cannot be detoxified or treated by more conventional methods. Solidification typically provides three major advantages over raw waste management and disposal; these are 1) removal of free liquid, 2) development of structural integrity, and 3) improved contaminant isolation and containment.

There are several commercially available solidification processing systems available today [1]. A generic classification of the major solidification systems in use in the United States is as follows:

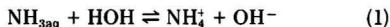
- Portland cement.
- Bentonite-Portland cement.
- Soluble silicates-Portland cement.
- Kiln dust.
- Kiln dust-flyash.
- Flyash.
- Flyash-Portland cement.
- Flyash-lime.
- Lime.
- Gypsum cement-soluble silicates.

Generic descriptions of these and other solidification technologies have been published by Malone, Jones, and Larson [2]. Patents have been issued for some of the solidification processes listed above. Applicable patents include US RE 29 783, US Patent 4 149 968, US Patent 3 837 872, US Patent 4 028 240, US Patent 4 079 003, and UK Patent 1 485 625; additional patent applications are reportedly pending, and there may be others the authors are unaware of.

PROBLEM STATEMENT

Most setting agents required for solidification are alkaline materials. Thus, the product of most solidification processes is basic on the pH scale. The exact pH depends on the type and amount of setting agent used. This is im-

portant for wastes that contain ammonia. For ammonia there is an equilibrium between the dissolved gas or aqueous ammonia, $\text{NH}_{3\text{aq}}$, and the ammonium ion, NH_4^+ , according to the following equation:



Raising either pH or temperature shifts the equilibrium toward aqueous ammonia. The pH and temperature dependency of the partitioning between aqueous ammonia and ammonium ion for a 2.2 molar solution is shown in Figure 1. When the pH is greater than 10, practically all of the ammonia nitrogen exists as aqueous ammonia. A final pH greater than 10 is typical of many solidification processes, especially those that use lime. In addition to yielding basic pH conditions, most, if not all, setting reactions involve exothermic hydration that increases the temperature of freshly prepared solidified waste. Hydration of setting agents rapidly consumes the liquid phase and reduces it by several orders of magnitude. The combined effect of basic pH conditions, exothermic reactions, and reduced liquid phase in the release of ammonia.

Preliminary feasibility studies on solidification processing of a hazardous liquid containing 31,100 mg/liter ammonia nitrogen (2.2 molar) have been conducted. As expected, significant quantities of ammonia gas were released with the addition of various process additives. This was particularly true for alkaline additives that shift the equilibrium in favor of aqueous ammonia and, in turn, gaseous ammonia. Laboratory studies showed that the amount of ammonia released could be reduced by chemi-

cally sequestering ammonia prior to the addition of solidification reagents by precipitation as ammonium magnesium phosphate hexahydrate. The amount of ammonia released after various degrees of chemical sequestering for ammonia control are as shown in Table 1. The hexahydrate complex is substantially insoluble in water and effectively isolates the ammonia from further reaction. It is formed by adding magnesium sulfate heptahydrate, commonly known as Epsom salt, and concentrated phosphoric acid to a waste containing ammonia nitrogen.

A solidification/landfill project has been proposed for treatment and disposal of the above waste. The proposed landfill design involves placement and compaction of 0.40m lifts of solidified waste. After a lift has been placed, it will be allowed to cure for 24 hours before another layer is added. The total depth of solidified waste will be 6.0m when the landfill is completed. Below the landfill will be a compacted clay liner of 1 meter thickness. Information for planning level assessments of potential ammonia concentrations on the landfill surface during construction and of ammonia flux at the landfill perimeter after closure is needed in order to properly evaluate work-place health safety hazards and environmental impacts associated with the proposed project.

Presented below is a one-dimensional mathematical model that describes ammonia off-gassing during construction of the proposed solidified waste landfill. The numerical methods used to effect a solution of the model on a microcomputer and the results obtained are also discussed.

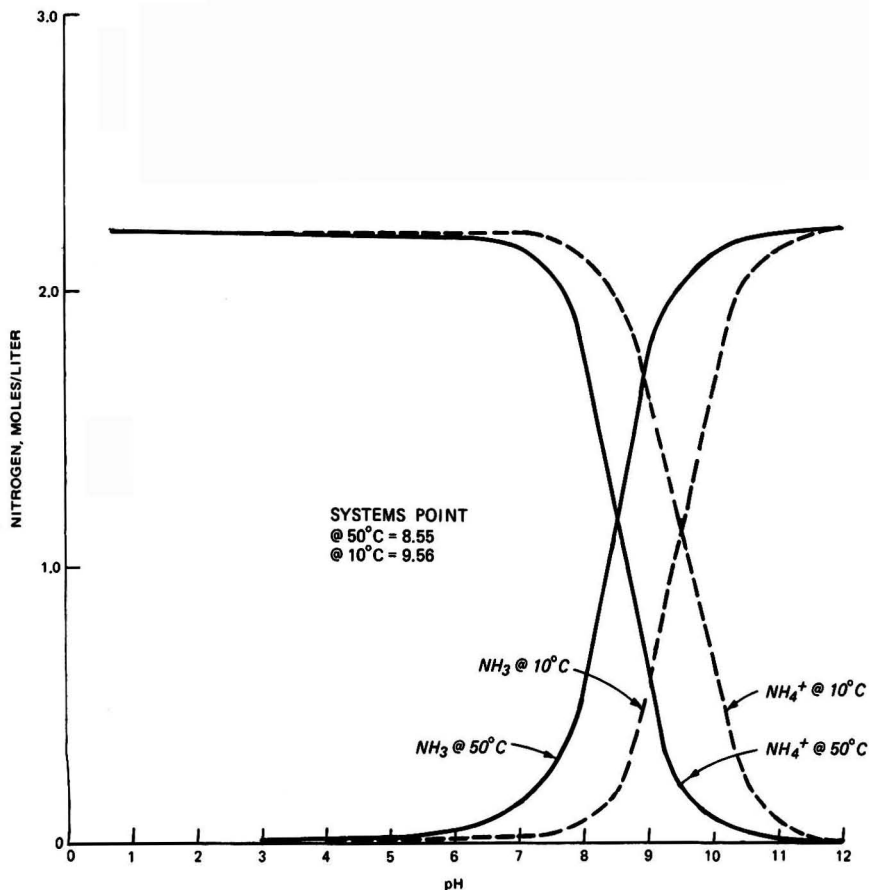


Figure 1. Equilibrium diagram for the ionization of aqueous ammonia.

TABLE I. AMMONIA RELEASED FROM SOLIDIFIED WASTE IN LABORATORY STUDIES AFTER PRE-TREATMENT FOR AMMONIA SEQUESTERING^a

Stoichiometric Ratio (SR) of Sequestering Reagent to Ammonia in Raw Waste	Ammonia Released From Solidified Waste (mg/m ³)
1.0	2.9×10^6
1.5	1.2×10^6
2.0	1×10^4

^a Reported as nitrogen per unit volume of solidified waste.

MODEL DEVELOPMENT

A definition sketch for the ammonia off-gassing problem stated above is shown in Figure 2. Several simplifying assumptions were made as follows:

- Air between surface of solidified waste and surface of the ground is stagnant.
- No free convection in the stagnant air column; air temperature is a constant 298°K.
- Constant sea level barometer of 1.013 Bars; no pressure gradients exist.
- Each Lift is instantaneously placed to 0.4m thickness.

- Diffusivity of ammonia is not concentration dependent.
- Constant soil temperature of 291°K.
- Variable but defined solidified waste temperature.
- Heat transfer by radiation and convection is ignored.
- Conservation of ammonia throughout; gaseous ammonia does not react with constituents in the air, solidified waste, or clay soil used as a liner.

The equation for mass transport by ordinary diffusion is a second order partial differential equation [3, 4], Equation 2 below.

$$D_A(\partial^2 c / \partial z^2) = \partial c / \partial t \tag{2}$$

where D_A is the molecular diffusivity of ammonia, c is the concentration of ammonia, z is the length dimension in Figure 2, and $\partial c / \partial t$ is the accumulation term for ammonia. Exact mathematical solutions for certain problems described by Equation 2 are available in the works of Carslaw and Jaeger [5] and Crank [6]. In this paper numerical evaluation is emphasized because three different regions must be analyzed for which different diffusivities, different and varying temperatures, different boundary conditions, and different and varying initial conditions apply. The general diffusion equation as written for the region encompassing the clay liner beneath the landfill, the region consisting of solidified waste, and the column of air above the solidified waste is, respectively, as follows:

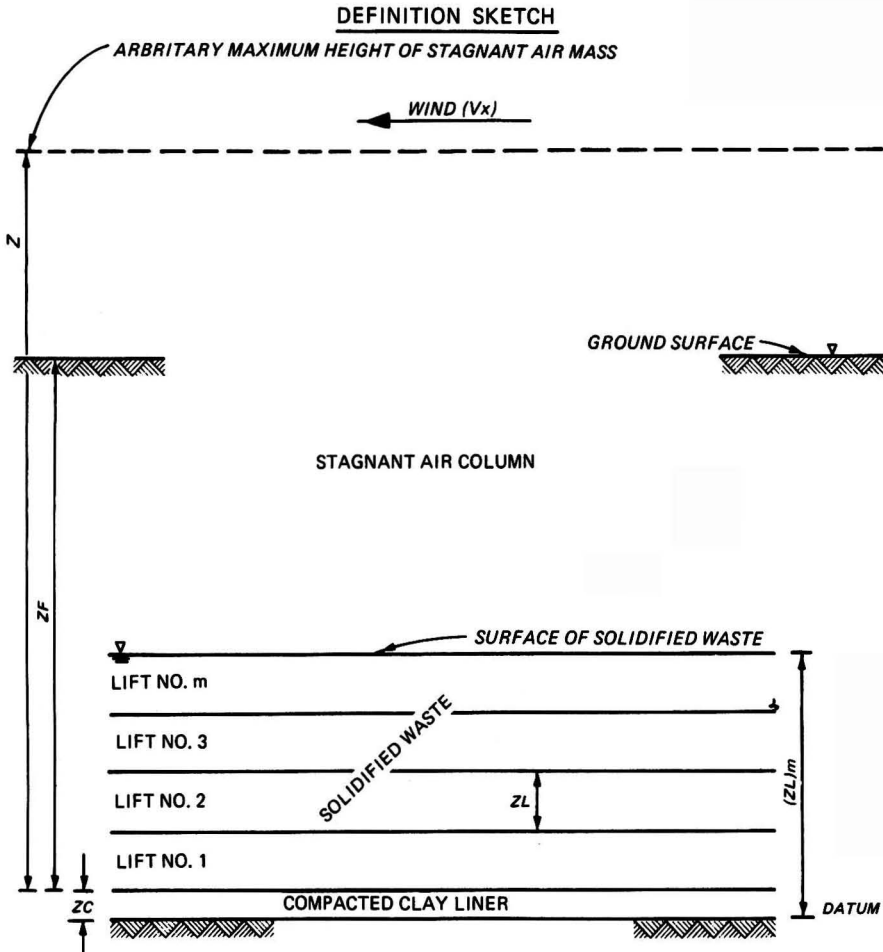


Figure 2. Definition sketch.

$$D_{AC} \left(\frac{\partial^2 c_c}{\partial z^2} \right) = \frac{\partial c_c}{\partial t} \quad (3)$$

$$D_{AS} \left(\frac{\partial^2 c_a}{\partial z^2} \right) = \frac{\partial c_a}{\partial t} \quad (4)$$

$$D_{AB} \left(\frac{\partial^2 c_B}{\partial z^2} \right) = \frac{\partial c_B}{\partial t} \quad (5)$$

where D_{AC} is the molecular diffusivity of ammonia in the clay soil, D_{AS} is the molecular diffusivity of ammonia in the solidified waste, and D_{AB} is the molecular diffusivity of ammonia in air. Note that D_{AA} is not used to designate the diffusivity of ammonia in air in order to avoid confusion with notation used elsewhere [3, 4] in which D_{AA} designates the self diffusivity of substance A in A.

The mathematic model consists of three separate equations that described the diffusion process in three distinct regions. The differences that characterize the different regions are stated in mathematical terms in Table 2. These conditions are restated in general terms as follows: The ammonia concentration at the bottom of the clay liner is zero for all time, and the ammonia concentration at the top of the stagnant air mass is zero for all time. Initially there is no ammonia in the clay liner below the solidified waste or in the air above the solidified waste. When a lift of solidified waste is placed, the ammonia concentration is instantaneously some initial value, C_0 , in that lift. Ammonia is introduced to the system by the placement of new lifts of solidified waste. Ammonia generated during the curing process is assumed to be negligible. Furthermore, the distribution of ammonia is continuous, i.e., the flux on one side of the solidified waste-air interface is equal to that on the other side and likewise for the linear-solidified waste interface. Since emphasis is on worst case conditions in the landfill excavation during placement of the solidified waste, atmospheric transport above the excavation was not modeled.

The temperature regime presents special problems. For the intended use of the model developed here, it was adequate to assume constant temperatures at the soil and air boundaries. The temperature regime in the solidified waste, however, was allowed to vary with time. During the curing of solidified waste, heat is released as a hardened solidified mass develops. This heat development is due to hydration of setting agents and is called heat of hydration [7]. As a consequence of the heat of hydration, the temperature in a mass of solidified waste will rise and then fall as heat is developed and dissipated during setting and curing. Quick setting materials tend to develop heat very rapidly, beginning when the solidification reagents and waste are first brought into contact. This is particularly true for lime based solidification processes. Gaseous diffusion of ammonia is temperature dependent. Due to the cyclic nature of the solidified waste temperature, it was necessary to run a heat transfer model side-by-side with the ammonia transfer model in order to adjust the diffusion coefficient for temperature. In order to keep the problem as reasonably constrained as possible, a very simple conductive heat transport model was developed that neglects radiation and convection.

Temperature in the solidified waste varies with position and time. It is described by the second order partial differential equation given below [5].

TABLE 2. BOUNDARY AND INITIAL CONDITIONS FOR PROPOSED LANDFILL AMMONIA OFF-GASING PROBLEM

REGION	Boundary condition	Initial condition
Clay liner	$c(0, t) = 0$	$c(z, 0) = 0$
Solidified waste	$N_{AC} = N_{AS}; N_{AS} = N_{AB}$	$c(z, 0) = C_0$
Air	$c(Z, t) = 0$	$c(z, 0) = 0$

See text for definition of N_{AC} , N_{AS} , N_{AB}

$$\alpha \left(\frac{\partial^2 T}{\partial z^2} \right) + KH = \frac{\partial T}{\partial t} \quad (6.a)$$

where KH is the generation term for the development of the heat of hydration, T is temperature, and α is the thermal diffusivity of the solidified waste. If $KH = 0$, i.e., the heat of hydration is developed instantaneously, Equation 6.a reduces to the well known [3, 4, 5, 6] one-dimensional, conductive heat transfer equation for an isotropic material, Equation 6.b below.

$$\alpha \left(\frac{\partial^2 T}{\partial z^2} \right) = \frac{\partial T}{\partial t} \quad (6.b)$$

For processes in which the rate of heat development is mono-modal and is essentially complete within a short period of time, Equation 6.b provides a good approximation of the conductive heat transfer process. Because the problem statement requires simulation of the landfill construction scenario, a numerical method is required in order to calculate temperatures in the solidified waste, even though only one region of the landfill is being modeled for changing temperature.

In addition to simulating ammonia transport within each region, the computer model must tie the regions together into a simulation of continuous transport of ammonia and heat. Since the media in which transport is occurring can be regarded as continuous, the distributions of ammonia and temperature are also continuous. Continuity considerations required that the flux on each side of an interface must be the same. Continuity of ammonia is provided in Equations 7.a and 7.b below,

$$N_{AC}|_{ZC} = N_{AS}|_{ZC} \quad (7.a)$$

$$N_{AS}|_{ZL_m} = N_{AB}|_{ZL_m} \quad (7.b)$$

where in Equation 7.a

N_{AC} is the ammonia flux at ZC on the clay side.

N_{AS} is the ammonia flux at ZC on the solidified waste side.

and in Equation 7.b

N_{AS} is the ammonia flux at (ZL)_m on the solidified waste side.

N_{AB} is the ammonia flux at (ZL)_m on the air side.

Z_C and (ZL)_m are as defined in Figure 2.

A similar consideration applies to heat transport across the solidified waste boundaries. The interface transport phenomena will be dealt with in a greater detail below.

NUMERICAL APPROXIMATION

A finite difference approach to the solution of differential equations is a technique that is often applied because it is one of the simplest and most straightforward approaches in use. The numerical solution procedure described below is an explicit finite difference technique taken largely from Carnahan's work [8]. The explicit finite difference approximations for Equations 3, 4, and 5, respectively, are as follows:

$$c_{i,k+1} = D_{AC} \lambda c_{i-1,k} + (1 - 2 D_{AC} \lambda) c_{i,k} + D_{AC} \lambda c_{i+1,k} \quad (8.a)$$

$$c_{i,k+1} = D_{AS} \lambda c_{i-1,k} + (1 - 2 D_{AS} \lambda) c_{i,k} + D_{AS} \lambda c_{i+1,k} \quad (8.b)$$

$$c_{i,k+1} = D_{AB} \lambda c_{i-1,k} + (1 - 2 D_{AB} \lambda) c_{i,k} + D_{AB} \lambda c_{i+1,k} \quad (8.c)$$

where $\Delta k = \Delta t$, $\Delta i = \Delta z$ and $\lambda = (\Delta k / \Delta i)^2$. Figure 3 is a grid representation of the z:t plane that is numerically approximated by Equations 8.a, 8.b, and 8.c. The ammonia concentration at any z in Figure 2 and for any time greater than $t = 0$, is designated $c(z, t)$. Each dot in Figure 3 represents a numerically approximated (computer) solution of $c(z, t)$. The squares in Figure 3 indicate boundary conditions (on the left and right vertical margins) and initial conditions (horizontal bottom margin). If all the $c_{i,k}$ are known at any time level t_k then the next level, t_{k+1} , can be calculated

BOUNDARY AND INITIAL CONDITIONS

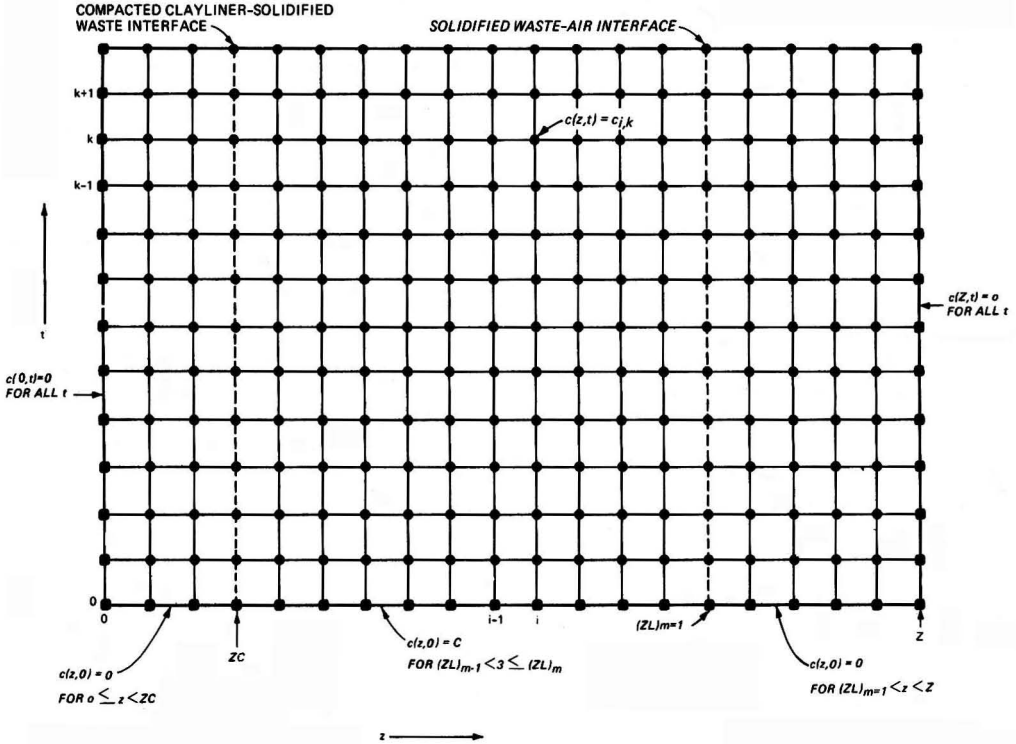


Figure 3. Numerical model of landfill.

using Equations 8.a, 8.b, and 8.c. Thus, the computer solution begins at the known initial condition on level $t_k = 0$ ($k = 0$) and proceeds upward one level at a time. When a lift of solidified waste is placed in the landfill, the ammonia concentration in that lift is assumed to be uniformly equal to C_m . Below the new lift the model uses the most recently calculated value of $c(z, t)$. Each time a new lift of solidified waste is placed in the fill the air mass is raised from the bottom by the depth of the new lift. The top air layer is assumed lost through the boundary so that the total z -dimension under consideration remains constant.

The interfaces require special consideration [8, p. 462]. Finite difference approximations for the new ammonia concentrations at the interfaces after a time increment Δk (equivalent to Δt) can be derived from the conditions stated in Equations 7.a and 7.b [8]. The explicit finite-difference approximation of the solidified waste-air interface concentration after a time increment Δk is given in Equation 9.a below, and the explicit finite-difference approximation of the clay liner-solidified waste interface after a time increment Δt is given in Equation 9.b below.

$$c_{i,k+1} = c_{i,k} \left[1 - \frac{D_{AS} + D_{AB}}{\lambda} \right] + \frac{D_{AS}c_{i-1,k} + D_{AB}c_{i+1,k}}{\lambda} \quad (9.a)$$

$$c_{i,k+1} = c_{i,k} \left[1 - \frac{D_{AS} + D_{AC}}{\lambda} \right] + \frac{D_{AS}c_{i+1,k} + D_{AC}c_{i-1,k}}{\lambda} \quad (9.b)$$

To calculate $c(z, t)$ after a time increment Δk the following equations are used:

For $z = 0$, $c(0, t) = 0$ for all t .

- For $0 < z < ZC$ use Equation (8.a).
- For $z = ZC$ use Equation (9.b).
- For $ZC < z < (ZL)_m$ use Equation (8.b).
- For $z = (ZL)_m$ use Equation (9.a).
- For $(ZL)_m < z < Z$ use Equation (8.c).
- For $z = Z$, $c(Z, t) = 0$ for all t .

In order to simulate temperature in the solidified waste a numerical approximation of Equation 6.b of the same form as in Equation 8.b was used to model changing temperature in the solidified waste. The equation used for this numerical approximation is as follows:

$$T_{i,k+1} = \alpha \lambda T_{i-1,k} + (1 - 2\alpha \lambda) T_{i,k} + \alpha \lambda T_{i+1,k} \quad (10)$$

Heat transfer through the clay liner-solidified waste interface is modeled like a classical composite wall problem. An explicit finite difference equation analogous to the form developed for ammonia transfer at the clay liner-solidified waste interface (Equation 9.a) was developed. Assuming that the liner beneath the landfill acts as a heat sink (the clay liner is at constant temperature), Equation 9.a reduces to Equation 11 below.

$$T_{i,k+1} = T_{i,k} \left(1 - \frac{2\alpha}{\lambda} \right) + \frac{\alpha(T_{i-1,k} + T_{i+1,k})}{\lambda} \quad (11)$$

where

- T_i = temperature at interface
- α = thermal diffusivity of the solidified waste
- $T_{i-1,k}$ = liner temperature, a constant 291°K

In Equation 11, which is the clay liner-solidified waste interface heat transfer equation, the thermal diffusivity of the liner is assumed to be the same as that in the solidified waste. If the thermal diffusivity of the liner is known, then an equation of the general form of Equation 9.a can be written such that interface heat transfer is a function of two thermal diffusivities.

Heat transfer at the solidified waste-air interface was modeled using Newton's Law of Cooling. At the interface a heat balance equation can be written as follows:

$$\left[\begin{array}{l} \text{Rate of Heat} \\ \text{In by Conduction} \\ \text{from the Solidified} \\ \text{Waste} \end{array} \right] - \left[\begin{array}{l} \text{Rate of Heat} \\ \text{Out} \\ \text{at the Interface} \end{array} \right] = \left[\begin{array}{l} \text{Rate of} \\ \text{Change of} \\ \text{Enthalphy} \\ \text{at Interface} \end{array} \right] \quad (12)$$

The rate of change in enthalpy is given by

$$\frac{\Delta H}{\Delta k} = \frac{A_{\Delta} \rho c_p}{\Delta k} (T_{i,k+\Delta k} - T_{i,k})$$

Where

$$\frac{\Delta H}{\Delta k} = \text{Time rate of change in enthalpy}$$

T_i = Temperature at the interface

A = Area through which heat is transferred

Δ_i = Δs defined in Figure 3

ρ = Density

c_p = Specific heat of solidified waste

The rate of conductive heat transfer to the interface through the solidified waste is given by

$$\text{RATE IN} = \frac{k_w A}{\Delta i} (T_{i-1,k} - T_{i,k})$$

Where

k_w = Thermal conductivity of solidified waste

and the rate of heat loss from the interface to the air is given by

$$\text{RATE OUT} = hA(T_{i,k} - T_a)$$

Where

h = Heat transfer coefficient

By substituting into Equation 12 the above quantities for rate of change in enthalpy, rate of heat transfer in, and rate of heat transfer out, the solidified waste-air interface heat transfer equation, Equation 13 below, is obtained.

$$\frac{k_w}{\Delta i} (T_{i-1,k} - T_{i,k}) - h(T_{i,k} - T_a) = \frac{\Delta i \rho c_p}{\Delta k} (T_{i,k+1} - T_{i,k}) \quad (13)$$

This can be arranged to yield

$$T_{i,k+1} = T_{i,k} + (T_{i-1,k} - T_{i,k})(k_w/\Delta i) - h(t_{i,k} - T_a) \frac{\Delta k}{\Delta i \rho c_p} \quad (14)$$

Equation 14 is the explicit finite difference equation for approximating the change in surface temperatures at the solidified waste-air interface.

The heat transfer coefficient, h , in Equation 14 is an empirical quantity usually associated with a moving fluid. It can also involve radiation, depending on usage. In the problem addressed in this paper, h was taken to be the overall heat transfer coefficient.

One final note on explicit finite difference approximations is needed. It can be shown that for the explicit finite difference method to have "stability" the following stability criterion must be met [8]:

$$0.5 \leq \lambda$$

DATA REQUIREMENTS

In order to analyze an ammonia off-gassing problem using the model developed in the preceding paragraphs, specific data pertaining to the solidified waste, the landfill, and other site specific factors are needed. Some of the required data were provided in the definition of the problem, e.g., the dimensions of the landfill and the thickness of the liner. In practice the material used for the liner and the thickness will most likely be established by regulatory criteria applicable to the specific problem. The values assumed for ambient air temperature and for the liner temperature can be based on the local meteorology and soil conditions. Certain chemical and physical properties data on the solidified waste are also required. These data can be determined by laboratory testing, or, where specific laboratory data are not available, typical values can be assumed for selected parameters.

The one datum that cannot be assumed is the initial ammonia concentration in fresh solidified waste. This quantity can be determined experimentally. The data in Table 1 were obtained from laboratory studies on the effectiveness of sequestering reagents. In the model, these data were extrapolated to field conditions by assuming that a selected percentage of the ammonia released during solidification processing is lost before the waste is landfilled. Thus, if it is assumed that 80 percent of the ammonia is lost by the time the waste is landfilled, for $SR = 2.0$ in Table 1, C_s is 2×10^3 mg/m³. In an actual operation the percentage lost could vary significantly from those used in this model, depending on the materials management practices in effect.

In order to relate laboratory data to the actual landfill, the in-place density of the solidified waste must be estimated. An in-place density can be estimated on the basis of experience, or by using a compaction test such as the Corps of Engineer standard compaction test [9] that approximates the in-place field density. For the landfill problem solved in this paper, an in-place density of 1600 kg/m³ (100 lbs/ft³) was assumed.

Another key parameter that is required is the diffusivity of ammonia in the various components of the system. Empirical values available in the published literature [3, p. 458, 10, p.31] indicated a diffusivity of ammonia in air of 2.0×10^{-5} m²/sec at 273°K. Ammonia diffusivity in the solid components of the system should be determined by laboratory testing if possible. Various techniques for determining the diffusivity of a gas in a porous solid have been reported [6, 11, 12]. If specific information is not available, then the relationship for diffusivity of a gas in a porous solid to the diffusivity in air reported by Thibodeaux can be used [3, p. 337]. In this paper the following equation suggested by Thibodeaux [13] was used to estimate the diffusivity of ammonia in the clay and in the solidified waste:

$$D_{AS} = D_{AB} e^{4.13}$$

where D_{AB} is the diffusivity of ammonia in air, e is the porosity of the solid medium, and D_{AS} is the diffusivity of ammonia in the porous solid. Porosity can be determined using standard soil testing procedures [9]. In this paper a porosity of 0.5 was assumed for the solidified waste, and a porosity of 0.2 was assumed for the compact clay liner.

As previously discussed, the diffusivity of a gas is temperature dependent. For low density gases (such as is the case for atmospheric conditions) a temperature correction for diffusivity can be inferred from the Chapman-Enskog kinetic theory of molecular diffusion of gases to follow a 3/2 power law [3, 4]. Equation 15 below was used to apply temperature correction factors.

$$D_2 = D_1(T(2)/T(1))^{3/2} \quad (15)$$

T is temperature in degree Kelvin, D_1 is the diffusivity at temperature = $T(1)$, and D_2 is the diffusivity at temperature = $T(2)$.

The heat transfer coefficient, h , in Equation 14 is another variable that requires estimation. The heat transfer coefficient is dependent on the thermal properties of the solid and the fluid and also certain system parameters such as the fluid velocity. In an excavation, the fluid velocity or wind speed near the surface of the solidified waste for a stagnant air mass is zero. The heat transfer coefficient under such conditions is not exactly known, but typical values for hot slabs in contact with a virtually stagnant air mass range from 5.44 to 22.6 J/m²/sec°K (1 to 4 BTU/hr ft² °F). For the simulations developed in this paper a value of 22.6 J/m²/sec°K was assumed.

Actual data is always preferred over assumed values. When it is necessary to make assumptions as is usually the case for making planning level assessments, the sensitivity of the computed results to the assumptions made can be determined by running the model for different assumptions. Table 3 is a listing of the default values used in the computer simulation of the proposed landfill simulated in this paper.

COMPUTER SIMULATION

A computer program was written to simulate Fickian diffusion of ammonia in solidified waste and side-by-side heat transfer from the solidified waste to the clay liner beneath the solidified waste and to the air above the solidified waste. The program was run on five popular microcomputers. Three had the following basic configuration: 64K RAM, 8 bit CPU, printer and one 5¼-inch floppy disk (optional). The other two computers were 16 bit machines. The source code was written in the particular version of BASIC that was available on each microcomputer. Commercially available compilers were used where available to compile the source codes in order to speed execution. Run times varied from 6 hours for interpretive BASIC on one 8 bit machine to 30 minutes for compiled BASIC on one 16 bit machine.

TABLE 3. DATA REQUIRED AND DEFAULT ASSIGNMENTS

Quantity	Units	Value Assigned
D_{Ab} , Diffusivity of ammonia in air	m ² /sec	2.0 E-5
e_r , Porosity of clay liner	—	0.2
e_s , Porosity of solidified waste	—	0.5
k_s , Thermal conductivity of solidified waste	(J/sec · m · k)	2.25
c_p , Specific heat of solidified waste	(J/Kg° · K)	921
ρ_s , Density of solidified waste	Kg/m ³	1600
h , Solidified waste—Air Interface heat transfer coefficient	(J · m/m ² /sec°K)	22.6
ZC, Thickness of clay liner	m	1.0
ZF, Final depth of solidified waste	m	6.0
ZL, Lift thickness	m	0.40
ZA, Height of stagnant air column ground level	m	0
T_a , air temperature	°K	298
T_c , clay liner temperature	°K	291
T_s , Initial temperature of a fresh lift of solidified waste	°K	318
C_o , Initial ammonia concentration in a fresh lift of solidified waste	mg/m ³	Various percentages of the values in Table 1
CT, Cure time between lift placements	sec	86400
Δk , time increment	sec	200
Δz , z increment	m	0.20

The general conceptualization and utilization of the computer model is shown in Figure 4.a, and the general logic flow of the program is shown in Figure 4.b. Conceptualization consists of problem definition, interpretation on physical grounds, and mathematical description of the physical interpretation. Utilization consists of numerical approximation of the governing equations on a microcomputer and interpretation of the results. Numerical approximation is the sole function of the microcomputer in the model presented in this paper.

The microcomputer program consists of two distinct steps. First, the governing equations for ammonia transport are numerically approximated for the appropriate boundary conditions by an explicit finite difference technique. Then, the governing equations for heat transport are numerically approximated for the appropriate boundary conditions, also using a finite difference technique. From the heat transfer approximation a new temperature profile for the landfill is constructed. The new temperature profile is then used in the next iteration of the ammonia transport equations. Numerical simulations of ammonia diffusion and then conductive heat transfer is repeated until the lift cure time has elapsed for the most recently placed lift of solidified waste. The program then simulates placement of a new lift, establishes new boundary conditions associated with placement of the new lift, and returns to the numerical approximation of the governing equations for ammonia and heat transport. A program listing is available from the authors.

Computer simulations were run for various initial ammonia concentrations and lift cure times. The initial ammonia concentration, C_o , is the residual ammonia in a new lift of solidified waste as it is placed in the landfill. Ammonia concentrations at various locations in the landfill for selected stages of landfill construction are shown in Figures 5, 6, 7, for selected percentages of the ammonia released when $SR = 2.0$ as per Table 1. These percentages were 80% for Figure 5 ($C_o = 8000$ mg/m³), 40% for Figure 6 ($C_o = 4000$ mg/m³), and 20% for Figure 7 ($C_o = 2000$ mg/m³). The selection of these percentages was based on the authors' personal experiences with treatment efficiencies. The above percentages probably represent the range of percent ammonia losses that could be accomplished by temporarily stockpiling the solidified waste and allowing it to offgas before landfilling. In an actual operation these numbers could change significantly, depending on mixing time during solidification, haul distance to a conditioning pad, surface area to volume ratio of the stockpiled waste, pile temperature, meteorological conditions, and perhaps other site specific parameters.

These figures indicate how ammonia concentration varies with the initial ammonia concentration in the solidified waste when the waste is placed in the landfill. In each figure the ammonia concentrations at 20 cm above the bottom of the landfill, at the clay liner-solidified waste interface, and at a point 140 cm above the solidified waste-air interface are plotted. The horizontal line in each figure at 370 mg/m³ ammonia represents a specific worker exposure limit that is discussed below. Graphs were used because it is sometimes difficult to comprehend reams of sequential data output.

DISCUSSION

The graphs show that the general form of the concentration versus time curves are not altered by changing the initial ammonia concentration, C_o . Changes in C_o affect in a significant way the scale on the vertical axis. The graphs also show that after the landfill is approximately one-third completed, 120 hours (5 days), the landfill ammonia concentrations approach a maximum. As additional lifts of solidified waste are placed in the landfill, and the solidified waste-air interface is pushed closer to the top of

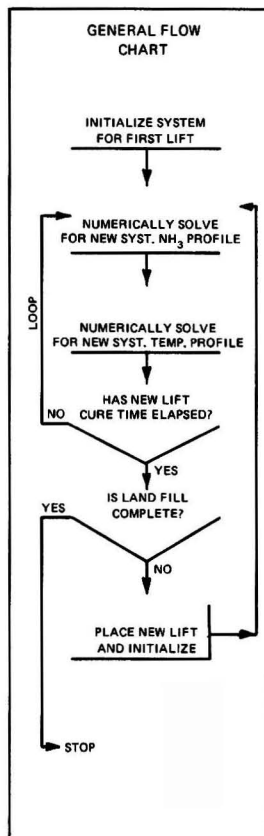
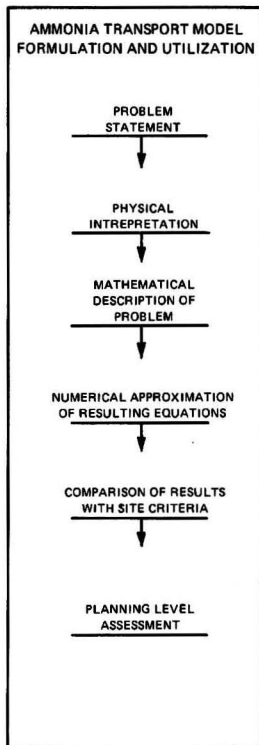


Figure 4. Conceptualization and utilization of transport model and general flow chart for computer model.

the excavation, the length of the stagnant air column decreases. As a consequence, the gradient in ammonia concentration between the solidified waste and the zero boundary condition at the tip of the excavation increases. Due to the increased gradient, ammonia is transported away from the landfill at a faster rate, and ammonia concentrations in the solidified waste and in the air above it begin to diminish. Computed results beyond the curing of the sixth lift are not presented because, as the solidified waste-air interface gets closer to the top of the excavation, the model assumptions become less and less realistic. In particular, the assumption of a stagnant air column becomes less supportable. The simulations presented describe worst case conditions for each assumed initial ammonia concentration, C_0 , that are likely to occur during the construction of the solidified waste landfill.

The concentration of ammonia above the solidified waste surface at worker level is of special interest for planning level assessments. These concentrations determined what equipment is needed to provide adequate protection of worker health safety. The safety measures that are required in turn significantly affect worker productivity and consequently the overall cost of a solidification/landfill project.

Permissible ammonia work-place concentrations for selected personal safety equipment is listed in Table 4. As indicated in Table 4, the continuous exposure limit for an unprotected worker is 37 mg/m^3 . For concentrations in excess of 370 mg/m^3 , supplied air is required. In between these concentrations a face mask with the proper filter cartridge is sufficient. By comparing these limits to the simulated workplace environment, the percentage of the time that a worker needs a specific type of protection can be estimated. Assuming that 1.4 meters above the surface of the solidified waste is a reasonable height for making an assessment, Figure 5 shows that for a C_0 of 8000 mg/m^3 , supplied air for the landfill workers will be a requirement practically from the start of solidified waste placement until the finish of landfill construction. If C_0 can be lowered to 4000 mg/m^3 , Figure 6 shows that after the first day of operation supplied air will be a continuing requirement. Figure 7 shows that, if the ammonia concentration in the solidified waste as it is placed in the landfill can be lowered to 2000 mg/m^3 , then supplied air will not be required until after the fourth lift is placed. Considering that the model scenario simulates worst case conditions (convective transport within the excavation is not included), on-site air monitoring during an actual operation would prob-

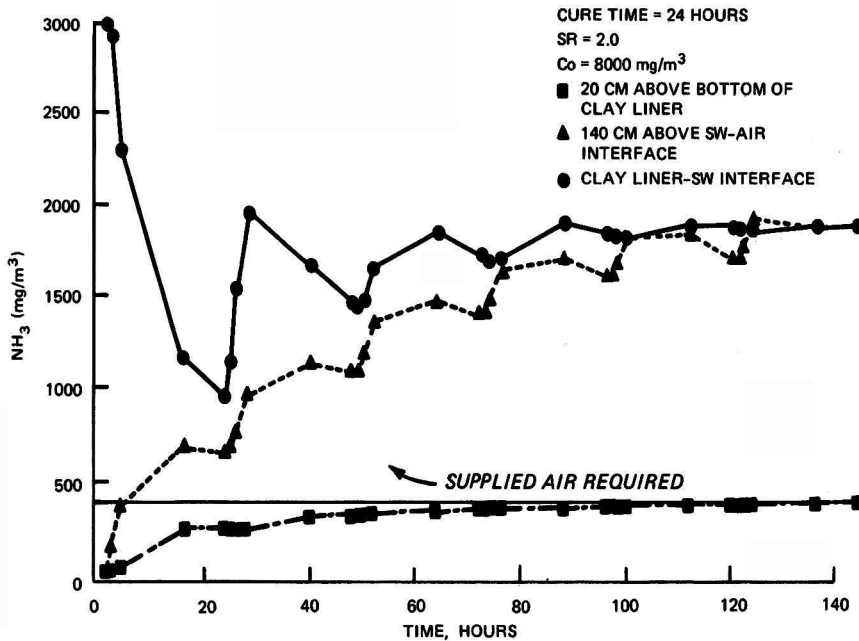


Figure 5. Landfill ammonia concentrations for $C_0 = 8000 \text{ mg/m}^3$, cure time = 24 hours.

ably show that the workplace ammonia concentrations were below those computed in this paper.

An alternative to chemical sequestering for ammonia control could involve a conditioning step in the solidification processing operation in which ammonia is stripped from fresh solidified waste before it is

landfilled. The effect would be to reduce the concentration of ammonia in the air column above the landfill. This and other ammonia control strategies can be simulated by changing the appropriate constants in the computer program.

For example, if a 48 hour lift cure time were utilized in-

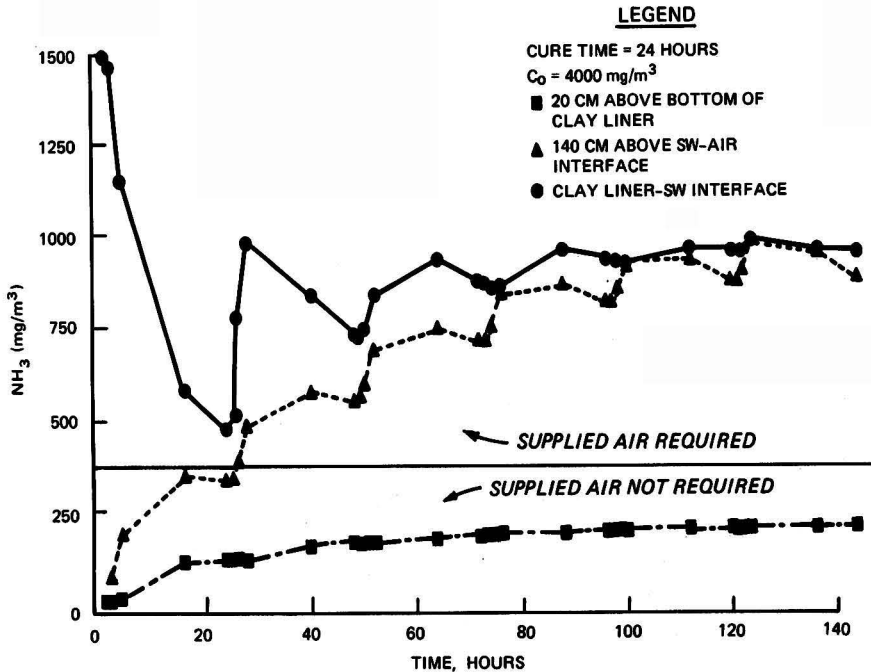


Figure 6. Landfill ammonia concentrations for $C_0 = 4000 \text{ mg/m}^3$, cure time = 24 hours.

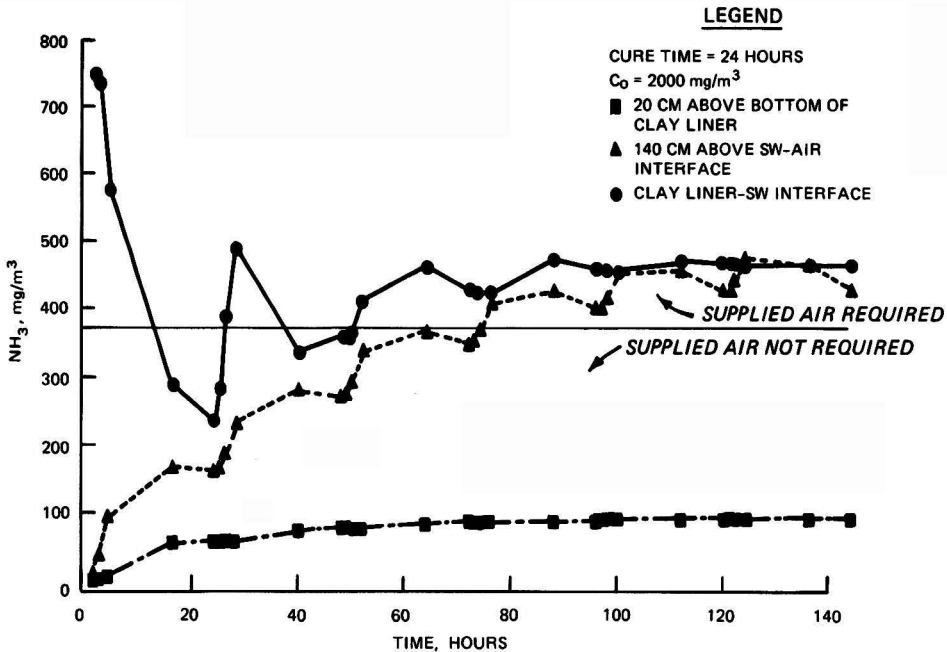


Figure 7. Landfill ammonia concentrations for $C_0 = 2000 \text{ mg/m}^3$, cure time = 24 hours.

stead of the 24 hour period used previously, the simulation represented in Figure 8 indicates that the concentrations of ammonia at the worker level can be improved. The graph shows that the worker-level ammonia concentration reaches a relative maximum between lifts and then decreases until the next lift is placed. Increasing the lift cure time lowers the average and the maximum ammonia concentration at the worker level. For this particular scenario, however, it did not reduce the number of lifts for which the worker-level ammonia concentration exceeds the supplied air limit. In general, the computer simulations indicate that increasing cure time does not affect ammonia concentrations as much as reducing the initial concentration of ammonia.

Although the supplied air requirement will probably be less than that indicated by Figures 5 through 8, the computer simulations help establish an upper bound for the seriousness of the problem. This is the type of information needed for planning level assessments of health safety problems. It is also important information for planning level assessments of over-all costs for a solidification/landfill project. Supplied air is a stringent field requirement that significantly reduces worker productivity. The actual dosage rates for sequestering reagents would have to be determined by trade-off analysis of materials cost for sequestering reagents and worker productivity.

The computer simulations in Figure 5 through 8 also

show significant ammonia transport through the clay liner. These results indicate that an ammonia vapor gradient will develop in the soil beneath the solidified waste and that ammonia will be transported down the gradient. Computer simulations indicate that porous solids such as solidified waste and natural liner materials are poor barriers to vapor transport. Unless a vapor tight jacket system is employed ammonia will diffuse into the soils beneath the site. This type of information is important for planning level assessment of the potential impact of various ammonia control strategies on groundwater resources.

The simulations discussed above represent a worst case situation. A more realistic model would include convective transport processes. Convective transport mechanisms can have significant effect on the outcome of trade-off analyses for various ammonia off-gassing control alternatives.

CONCLUSIONS

Ammonia off-gassing from solidified waste was modeled using transport theory, numerical methods, and computer simulation. Because the model was used to provide technical input to planning level assessments, transport theory was constrained to a one-dimensional analysis, and a simple numerical method was applied on a micro-computer. The computer simulations, which were intended to describe a worst case situation, indicate that for the ammonia concentrations considered precautions will be needed in order to protect worker health. In order to assess the alternatives, analysis of trade-offs and costs will be required. In addition, consideration should be given to stochastic meteorological conditions relating to atmospheric transport that may eliminate or reduce the need for stringent safety measures.

ACKNOWLEDGEMENT

The authors received administrative, clerical, and typing support from the US Army Engineers Waterways Experiment Station and from Mississippi State University.

TABLE 4. PERMISSIBLE EXPOSURE LIMITS FOR AMMONIA IN THE WORK-PLACE^a

NH_3 (mg/m ³)	Protection Required
<37	None
<74	Respirator with filter cartridge
<370	Full face mask with filter cartridge
>370	Supplied air, full face mask

^a Source: Occupation Safety and Health Administration, DHEW (NIOSH) Publ. No. 78-210, GPO Stock No. 017-033-00342-4

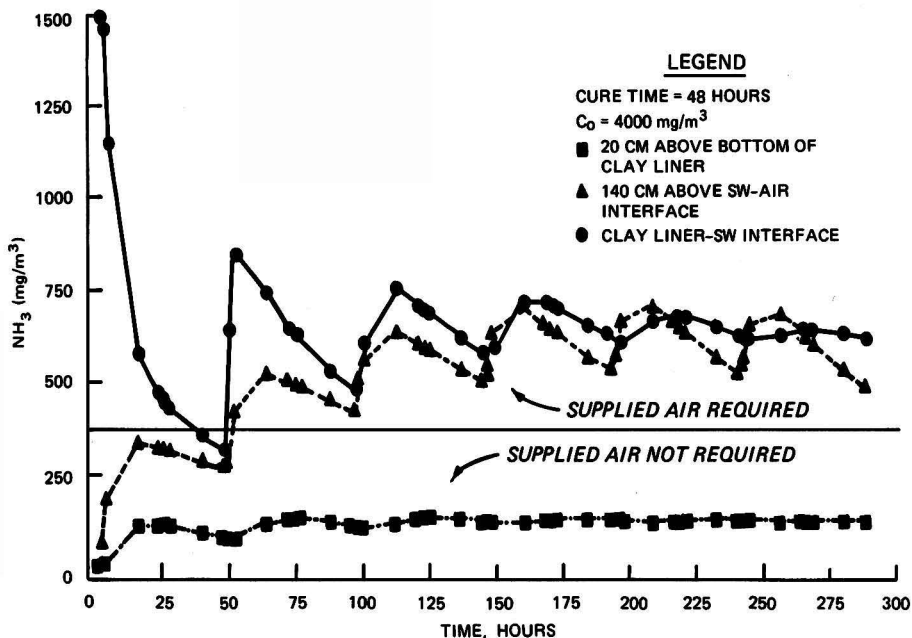


Figure 8. Landfill ammonia concentrations for $C_0 = 4000 \text{ mg/m}^3$, cure time = 48 hours.

One of the computers was provided by the authors and the remainder were provided by Mississippi State University.

NOMENCLATURE

A = area (m^2)
 C_0 = initial ammonia concentration in a newly placed lift of solidified waste (mg/m^3)
 CL = clay liner (no dimension)
 CT = lift cure time (sec)
 c = ammonia concentration (mg/m^3)
 c_p = specific heat of solidified waste ($\text{J/Kg}^\circ\text{K}$)
 D_{AB} = diffusivity of ammonia in air (m^2/sec)
 D_{AC} = diffusivity of ammonia in the clay liner (m^2/sec)
 D_{AS} = diffusivity of ammonia in solidified waste (m^2/sec)
 e_c = porosity of clay liner (dimensionless)
 e_s = porosity of a solidified waste (dimensionless)
 k = thermal conductivity of solidified waste ($\text{J} \cdot \text{m}/\text{sec} \text{m}^2\text{K}$)
 KH = generation term for heat of hydration (J/sec)
 h = solidified waste-air interface heat transfer coefficient ($\text{J}/\text{m}^2 \text{sec}^\circ\text{K}$)
 N_{AB} = ammonia flux on the air side at the solidified waste-air interface ($\text{mg}/\text{m}^2 \text{sec}$)
 N_{AC} = ammonia flux on the clay liner side at the clay liner-solidified waste interface ($\text{mg}/\text{m}^2 \text{sec}$)
 N_{AS} = ammonia flux on the solidified waste side as applied to either the clay liner-solidified waste interface or the solidified waste-air interface ($\text{mg}/\text{m}^2 \text{sec}$)
 SR = stoichiometric ratio (moles of sequestering reagents used/moles of ammonia-nitrogen present in untreated waste)

SW = solidified waste (no dimension)
 T = temperature of solidified waste ($^\circ\text{K}$)
 T_a = temperature of air ($^\circ\text{K}$)
 T_c = temperature of clay liner ($^\circ\text{K}$)
 T_s = initial temperature of a new lift of solidified waste ($^\circ\text{K}$)
 t = time (sec)
 Z = total depth of landfill model (m)
 ZA = height of air column above ground (m)
 ZC = thickness of clay liner (m)
 ZF = final depth of solidified waste (m)
 ZL = lift thickness (m)
 α = thermal diffusivity of solidified waste (m^2/sec)
 Δz = incremental change in z-dimension (m)
 Δk = incremental change in time (sec)
 λ = stability criterion (sec/m^2)
 ρ = density of solidified waste (g/m^3)

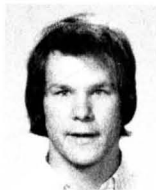
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Measurement of Fugitive Volatile Organic Emission Rates

The enclosure approach is shown to be well suited for determining emission rates from a variety of sources.

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Emission measurements at hazardous waste sites provide a means by which existing and potentially hazardous conditions can be assessed. Emission measurements are used to estimate the amount of a single species or multiple species being emitted from a given surface area of waste per unit time. These data can then be used in predictive models for population exposure assessments and for remedial action design.

A number of sampling approaches [1], both direct and indirect, have been used to obtain emissions data at hazardous waste sites. One of the most promising of these is a direct approach — the enclosure approach using an emission isolation flux chamber. Emission measurements using flux chambers have been performed to assess the need to control gas emissions from subsurface contamination, to define the levels of air emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs), and at a number of remedial action sites. This paper presents the procedures for the use of an emission isolation flux chamber and the results of volatile species rate measurements at two spill sites, three landfills, several surface impoundments, a landfarm operation, and a remedial action site.

THEORY

The enclosure approach has been used by researchers to measure emission fluxes of sulfur, nitrogen, and volatile organic species [2-7]. The approach uses an enclosure device (flux chamber) to sample gaseous emissions from a defined surface area. Clean dry sweep air is added to the chamber at a fixed controlled rate. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber. The emission rate is expressed as:

$$E_i = C_i R / A \quad (1)$$

where, E_i = emission rate of component i , $\mu\text{g}/\text{m}^2\text{-sec}$
 C_i = concentration of component i in the air flowing from the chamber, $\mu\text{g}/\text{m}^3$
 R = flow rate of air through the chamber, m^3/sec
 A = surface area enclosed by the chamber, m^2

All parameters in Equation 1 are measured directly.

A diagram of the flux chamber apparatus used for measuring emission rates is shown in Figure 1. The sampling equipment consists of a stainless steel/acrylic chamber with impeller, ultra-high purity sweep air, and rotameter for measuring flow into the chamber, and a sampling manifold for monitoring and/or collection of the specie(s) of interest. Concentrations of total hydrocarbons are monitored continuously in the chamber outlet gas stream using portable flame ionization detector (FID)-

and/or photoionization detector (PID)-based analyzers. Samples are collected for subsequent gas chromatographic (GC) analysis once a steady-state emission rate is obtained. Air and soil/liquid temperatures are measured using a thermocouple. The system pressure is monitored using a pressure gauge.

To determine the emission rate for a source much greater than that isolated by the flux chamber, a sufficient number of measurements must be taken at different locations to provide statistical confidence limits for the mean emission rate. The area sources measured are gridded and a minimum of six (6) measurements made (when possible) to account for spatial variability. Additionally, a single point should be selected as a control point to define temporal variability. On-site GC analyses are performed for all flux chamber measurements and canister samples are collected for each area to allow off-site detailed GC analysis [8]. Prior to using the chamber, blank and species recovery data are obtained.

OPERATION/QUALITY CONTROL

The generic sampling procedure for emission measurements using the enclosure technique is summarized below:

- 1) Establish grid system over area to be sampled.
- 2) Randomly select six or more points to be sampled.
- 3) Locate equipment instruments at the sampling location and document location, time, conditions, air, and surface temperatures.
- 4) Begin sweep air flow and address instruments and recorders.
- 5) Place enclosure on waste; record time.
- 6) Monitor emissions documenting steady-state concentration after 3-5 residence times.

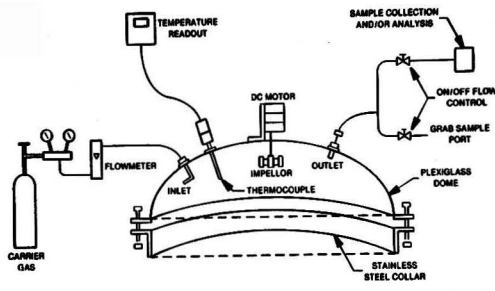


Figure 1. Cutaway side view of emission-isolation flux chamber and sampling apparatus.

$$\text{One residence time} = \frac{\text{Chamber Volume}}{\text{Sweep Air Flow Rate}}$$

- 7) Record air and surface temperatures inside chamber.
- 8) Collect grab samples for speciation studies.
- 9) Remove enclosure; end determination.
- 10) Relocate to next sampling location.

The following quality control tests are normally performed daily:

- system blank,
- duplicate sampling at one point,
- sampling at background point,
- repeat sampling at one point (control) at various times to determine temporal variability of site emissions.

Prior to the flux chamber's initial use, additional quality control tests should be performed to determine the characteristics and suitability of the flux chamber. First, the residence time and mixing efficiency of the flux chamber is determined. The chamber is placed over a flat surface (Teflon plug) containing an inlet port and operated in a typical manner (i.e., sweep air flow rate). An inert tracer gas, carbon monoxide (CO), is introduced into the chamber. The CO flow is shut off and the rate of decay of the CO concentration is measured. A comparison of the observed decay versus the theoretical decay (Figure 2) can then be made to determine the number of sampling residence times necessary to reach steady-state operation (i.e., 95% of full scale) and to ensure that there is proper mixing within the enclosure. The second quality control test involves introducing a multi-component organic standard into the enclosure via the plug/inlet port, operating the chamber in a typical manner (i.e., sweep air flow rate), and measuring the concentration of the various organic species in the output line of the flux chamber. These values are compared to the theoretical values to determine the percent recovery for each species in the flux chamber (Table 1).

RESULTS

The sampling and analytical results for each site are shown in Table 2. All results are given in the total hydrocarbons, $\mu\text{g-C}/\text{m}^2\text{-sec}$, for the sake of clarity. Speciation studies permit calculation of emission rates for individual compounds of interest. Included in the table are the corresponding annual emission rates for each site. These values are shown for comparison purposes only.

The sites sampled are briefly described below:

Site A is a jet fuel spill caused by a transportation ac-

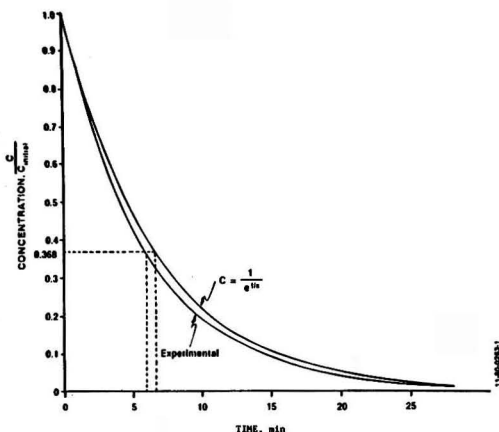


Figure 2. Residence-time distribution (RTD) for an enclosure where $\tau = 6.7$ min.

TABLE 1. COMPOUNDS TESTED IN THE EMISSION ISOLATION FLUX CHAMBER AND THE MEASURED % RECOVERY

Compound	% Recovery	Compound	% Recovery
Total C ₂	100	3-methyl-hexane	106
Total C ₃	108	2,2,4-trimethyl-pentane	106
Isobutane	109	n-heptane	103
1-butene	108	Methyl-cyclohexane	103
n-butane	106	Toluene	103
t-2-butene	107	Ethyl benzene	94.7
c-2-butene	109	mtp-xylene	88.5
Isopentane	112	o-xylene	97.3
1-pentene	105	n-nonane	99.4
2-methyl-1-butene	124	n-propyl-benzene	95.5
n-pentene	103	p-ethyltoluene	92.5
c-2-pentene	105	1,3,5-trimethyl-benzene	93.5
Cyclopentene	105	1,2,4-trimethyl-benzene	88.7
Isohexane	107	2-methyl-2-butene	103
3-methyl-pentane	106	Methyl-mercaptan	107
Methylcyclopentane	105	Ethyl-mercaptan	107
Benzene	106	Butyl-mercaptan	101
1,2-Dimethyl-pentane	105	Tetrahydrothiophene	115

cident. Sampling took place six months after the spill occurred. The site soil was nearly saturated with water and this probably reduced emissions by increasing the gas transfer resistance term of the soil. Site B is a jet fuel spill site. Leakage of fuel occurred over several years. Sampling took place six months after the leakage problem was identified and rectified.

Sites C and D are receiving ponds that are part of the wastewater treatment systems at hazardous waste disposal facilities.

Site E is an inactive landfill at a hazardous waste disposal facility. The landfill is covered with several feet of compacted clay.

Sites F and G are active landfills at hazardous waste disposal facilities.

Site H is a landtreatment operation for refinery sludge.

Site I is an uncontrolled hazardous waste site currently undergoing remedial action.

Tables 3 and 4 show a comparison of the organic species detected in product, headspace, and flux chamber samples. This fingerprinting procedure is useful for identifying the source of air emissions at a site.

CONCLUSIONS

The enclosure approach has been shown to be well suited for determining VOC emission rates from a variety of sources. The theoretical range of hydrocarbon emissions that can be measured is 5.4 to $5.4 \times 10^5 \mu\text{g-C}/\text{m}^2\text{-sec}$ with the current analytical capabilities. The enclosure approach is simple, straightforward, and reproducible. The method has been shown to be simpler to execute than indirect sampling techniques, possesses greater sensitivity, and it is less affected by environmental factors (especially meteorological conditions) [1]. The enclosure approach

TABLE 2. RESULTS FROM EMISSION ISOLATION FLUX CHAMBER SAMPLING AT NINE HAZARDOUS WASTE SITES

Emission Measurement	Emission Rate $\mu\text{g-C}/\text{m}^2\text{-sec}^{-1}$								
	Site A ^a	Site B ^b	Site C ^a	Site D ^a	Site E ^a	Site F ^a	Site G ^b	Site H ^a	Site I ^b
1	0.304	11.3	6.58	142	0	11.4	121	181	3.43
2	0.0895	11.2	4.73	1060	0	4.72	113	32.4	0.568
3	1.22	5.21	10.1	95.3	—	12.4	204	574	0.116
4	0.316	5.60	7.33	2430	—	11.7	81.7	97.8	—
5	0.0895	4.18	20.9	—	—	9.70	101	26.3	—
6	0.0895	5.28	11.3	—	—	—	83.0	20.8	—
7	0.0895	12.3	—	—	—	—	19.9	47.4	—
8	0.0895	6.48	—	—	—	—	46.3	—	—
9	1.57	12.0	—	—	—	—	18.7	—	—
10	—	9.92	—	—	—	—	—	—	—
11	—	12.3	—	—	—	—	—	—	—
12	—	9.53	—	—	—	—	—	—	—
Average Emission Rate	0.429	8.78	10.1	931	0	9.97	87.6	140	1.37
Confidence Interval	-0.0041 to 0.862	6.76 to 10.8	4.09 to 16.2	-806 to 2670	—	6.12 to 13.8	43.3 to 132	-44.7 to 325	—
Annual Emissions (kg-C/yr)	10.4	33	422	2220	—	6	38,700	1460	—

^aAnalysis by field portable GC-FID
^bAnalysis by capillary GC-FID/PID

may alter the environment at the sampling location and as such have an effect on the true emission rate. Future studies will attempt to optimize chamber design and operating conditions by performing parametric studies on a simulated spill site. Another study is planned to find a chamber design and operation suitable for agitated liquid surfaces.

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TABLE 3. COMPARISON OF AIR AND LIQUID SAMPLES WITH COMPOSITION OF JP-4 AVIATION FUEL AT SITE A

JP-4 Jet Fuel ^a	Product from Well ^b		Air Sample from Well ^c	Flux Chamber from Grid Point ^b				Ground Probe from Grid Point ^c		
	P-2	P-6	P-7	4	6	8	23	8	17	25
n-pentane	X		X		X	X		X	X	
2/3-methylpentane	X	X		X	X	X		X	X	
n-hexane	X	X	X		X	X		X	X	
methylcyclopentane	X	X	X		X	X		X	X	X
cyclohexane	X	X	X		X	X		X	X	X
2,3-methylhexane	X	X			X					
n-heptane	X	X	X		X			X		
methylcyclohexane	X	X	X		X			X	X	
toluene	X	X	X		X			X	X	
2,3-methylheptane	X	X			X					
n-octane	X	X	X		X			X	X	
o-xylene	X	X			X	X	X			
n-nonane	X	X	X		X		X			
1,2,4-trimethylbenzene	X	X	X		X	X	X	X		
n-decane	X	X			X	X	X			
n-undecane	X	X			X		X			
n-dodecane							X			
n-tridecane										

^aCompounds present at greater than 1 percent by weight in JP-4 aviation fuel
^bAnalysis of capillary GC-FID/PID
^cAnalysis by field portable GC-FID

TABLE 4. COMPARISON OF AIR AND LIQUID SAMPLES WITH JP-4 COMPOSITION AT SITE B

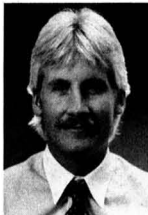
Primary Components of JP-4 ^a	Liquid Sample Well #24 ^b	Headspace Sample Well #24 ^b	Flux Chamber Sample Grid Point 2B ^b
n-Pentane		X	X
2/3-methyl-pentane		X	X
n-hexane		X	
methylcyclo-pentane	X	X	X
cyclohexane	X	X	X
2/3-methyl-hexane	X	X	X
n-heptane	X	X	X
methyl-cyclo-hexane	X	X	X
toluene	X	X	X
2/3-methyl-heptane	X	X	X
n-octane	X	X	X
o-xylene	X	X	X
n-nonane	X	X	X
1,2,3-trimethyl-benzene	X	X	X
n-decane	X	X	X
n-dodecane			
n-tridecane			

^aCompounds present at greater than 1 percent by weight in JP-4 aviation fuel

^bAnalysis by capillary GC-FID/PID

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Liquid-Phase Mass Transfer Coefficients for Surface Impoundments

The liquid-phase mass transfer coefficient can be described as a function of the square of the wind velocity.

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As hazardous wastewater resides in surface impoundments, volatile organic chemicals (VOC's) enter the air phase. Under turbulence enhanced environmental conditions, significant amounts of dangerous chemicals can be released into the atmosphere in a short period of time.

Accurate predictions of the VOC emission rate from surface impoundments are necessary to develop appropriate regulations for the control of such emissions and to assess the potential threat to the public. Although the Two-Resistance Theory [1] has been found to be a sufficient quantitative tool to describe interphase desorption of VOC's from a surface impoundment, the method requires the estimation of up to six individual gas and liquid film coefficients, in addition to a Henry's Law Constant for the chemical of concern.

The Two Resistance Theory for a batch operated, hazardous wastewater impoundment is given by Equations 1, 2, and 3.

$$1/K_L (f) = 1/k_L (f) + 1/k_G (f)m \text{ forced convection zone} \quad (1)$$

$$1/K_L (zof) = 1/k_L (zof) + 1/k_G (zof)m \text{ zone of influence} \quad (2)$$

$$1/K_L (n) + 1/k_L (n) + 1/k_G (n)m \text{ natural convection zone} \quad (3)$$

Successful application of the theory to a surface impoundment requires recognition of the existence of a zone of greatly enhanced mass transfer in the vicinity of an operating surface aerator, a "zone of influence" in the proximity of the aerator, and a "natural zone" in which the mass transfer rate is determined by environmental conditions, such as the surface wind velocity. In the case of a nonaerated lagoon or holding pond, only the natural zone is present.

The problem of predicting VOC emissions from wastewater impoundments reduces to the determination of the individual liquid and gas phase coefficients presented in equations 1, 2, and 3 for prevailing environmental and operating conditions.

Accurate, reliable correlations are available for determining the forced and zone-of-influence gas and liquid-film coefficients, as well as the natural zone gas phase coefficient [2]. The majority of chemicals classified as "volatile priority pollutants," however, are liquid phase controlled, i.e., the major resistance to mass transfer by volatilization is present in the liquid film. Thus, the individual liquid phase coefficient for the natural zone is probably the single most important parameter for predicting VOC emissions.

Several expressions for the individual liquid film coefficient are in the literature, and new expressions ap-

pear often. These expressions can be classified either as 1) quantitative models or 2) empirical/semi-empirical expressions. A number of these models are presented in Tables 1 and 2.

The quantitative models presented on Table 1 represent the earliest attempts to describe the liquid phase mass transfer coefficient in a turbulent fluid. These expressions are generally unsuitable because they contain input parameters not subject to direct measurement. Included in this group are the film (3), penetration (4), and surface renewal theories (5).

Brtko and Kabel [6] developed two quantitative models from modern mass transfer theories amenable to direct calculation. The importance of these models lies in the specification of variables which affect the liquid film coefficient based on theoretical considerations. The "eddy cell" and "large eddy" models developed by Brtko and Kabel appear as Equations 4 and 5, respectively, of Table 1, and specify the liquid phase depth and the wind shear velocity as important environmental variables.

Empirical and semi-empirical expressions for the liquid-film coefficient are presented in Table 2. These expressions were developed from simulation studies,

TABLE 1. QUANTITATIVE MODELS FOR THE LIQUID PHASE MASS TRANSFER COEFFICIENT: TURBULENCE ENHANCED CONDITIONS

Expression	Description	Reference
1. $k_L' = \frac{D_r}{\delta}$ where D_r = liquid diffusivity, L^2/t δ = film thickness, L	Film Theory	3
2. $k_L' = 2(D_r/\pi\theta_c)^{1/2}$ θ_c = eddy contact time	Penetration Theory	4
3. $k_L' = (D_r s)^{1/2}$	Surface Renewal Theory	5
4. $k_L' = 0.4 (D_r/\nu_2)^{1/2} \left\{ \frac{\nu_2 u_*^3}{kZ} \left(\frac{\rho_1}{\rho_2} \right)^{3/2} \right\}^{1/4}$ ν_2 = kinematic water viscosity, cm^2/s u_* = wind shear velocity, cm/s k = von Karman constant ρ_1 = air density, g/cm^3 ρ_2 = water density, g/cm^3 Z = unspecified reference depth, cm	Eddy Cell Model	8
5. $k_L' = 1.46 \left\{ \frac{D_r u_*^3}{0.1Z} \left(\frac{\rho_1}{\rho_2} \right)^{3/2} \right\}^{1/2}$	Large Eddy Model	8

TABLE 2. EMPIRICAL EXPRESSIONS FOR THE LIQUID PHASE MASS TRANSFER COEFFICIENTS FROM LABORATORY SIMULATIONS

Original Reference	Expression	Units of variables
1. Kanwischer [7, 8]	$k'_l = D_r / (200-60u^{1/2}) 10^{-6}$	k'_l , m/s u , m/s D_r , m ² /s
2. Banks [9]	$k'_l = 4.19E-6u^{1/2}$ (small u) $k'_l = 1.80E-6u^{1/2}$ (intermediate u) $k'_l = 0.32E-6u^2$ (large u)	k'_l and u m/s
3. Eloubaity and Plate [10]	$k'_l = \frac{Cu^* Z u_2^*}{\nu_2}$	C = constant of proportionality (0.0027) ν_2 = kinematic viscosity of water (m ² /s) u^* = wind surface shear velocity (m/s) Z = "normal depth," i.e., depth with uniform water flow (m) u_2^* = water shear velocity, $\sqrt{(ghSc)}$ (m/s) Sc = pressure adjusted channel slope, $So + \frac{1}{\rho g} \frac{\partial \rho}{\partial x}$ ρ = water density (kg/m ³) g = gravitational constant (m/s ²) So = channel slope for uniform flow (dimensionless) $\frac{\partial \rho}{\partial x}$ = air pressure gradient
4. Cohen, Cocchio, and Mackay [11]	$k'_l = 11.4 N_{Re}' (0.195) - 5$	k'_l (cm/hr) $N_{Re}' = (V^* y_0) / \nu_1$ u^* = friction velocity (cm/s) Z_0 = roughness height (cm) ν_1 = kinematic viscosity of air (cm ² /s)
5. Hwang [12]	$k_L = (1.3 N_{Re}^{0.195} 0.57)$	$\frac{D_r, H_2O}{D_r, H_2O}$ k_L in lb mol/ft ² hr D_r, H_2O = liquid diffusivity of chemical in water D_r, H_2O = liquid diffusivity of toluene in water
6. Shen [13]	$k_L = \left(\frac{78}{M_i} \right) \left(\frac{u}{4} \right) \left(\frac{Z}{0.6} \right)^{-0.85} (1.024)^{(T-20)}$	k_L and $k_L(O_2)$ in g mol/cm ² s M_i = molecular wt. of volatile Z = average water depth in lagoon (m) u = solution viscosity (cP) T = water temperature, °C $k_L(O_2)$ = coefficient for oxygen dissolution in water, g mol/cm ² s

mostly from laboratory measurements of the rate of oxygen reaeration.

A limited number of the expressions available for determining the liquid phase mass transfer coefficient have been developed from field measurements. Again, most of these expressions were developed from oxygen reaeration studies.

Kanwischer's open sea data [7] were fitted to the following equation for the transfer coefficient to produce an expression considered applicable to estuaries [14].

$$K'_l = 1.57 + 0.32 u^2 \quad (5)$$

in which K'_l has units of ft/day and u is in ft/sec. The usefulness of this expression has been investigated [15]. Banks [9] cited the expression

$$K'_l = (10.0 + 3.38 u) \times 10^{-6} \quad (6)$$

(with both K'_l and u in m/sec) based upon oxygen absorption data taken from the Thames Estuary in 1964.

Thibodeaux and Parker [16] assumed that the transport mechanisms operative in the zone of natural convection in a surface impoundment were analogous to those operative in flowing streams. Thus, a stream aeration equation developed by Owens and coworkers [17] was transformed to yield a mass transfer coefficient for any chemical absorbing or desorbing in the zone of natural convection:

$$k'_l (n) = 5.78 \frac{D_r}{D'_l} u^{0.68} Z^{-0.85} (1.024)^{(T-20)} \quad (7)$$

where D_r = chemical diffusivity in water, cm²/sec
 D'_l = oxygen diffusivity in water, cm²/sec
 u = average stream velocity, cm/sec
 Z = average stream depth, cm
 T = temperature, °C

The problem with this equation, apart from the assumption of stream characteristics being identical to those of a basin, lies in obtaining realistic values for u and Z , although suggested approximations are included in the original reference [16].

Certain correlations previously described are conceivably applicable to surface impoundments. Banks' correlation [9], based upon the authoritative measurements of Dowling and Truesdale [18], was developed for "shallow lakes," i.e., water systems in which the vertical turbulent diffusivity was constant throughout the depth of the system. Since most surface impoundments are constructed with a shallow depth, Banks' equations are possibly applicable, provided that the liquid film coefficient is corrected for the chemical of concern by the use of a suitable diffusivity correction factor.

Mackay's correlation [11] is popularly considered to be the most appropriate model for determining liquid film coefficients for surface impoundments [19]. The correla-

tion was based upon laboratory desorption experiments using benzene and toluene, which are typical of the low solubility, non-ionizable organic solutes found in hazardous wastewater.

Mackay and coworkers incorporated a "roughness" Reynolds number, Re^* , to describe wind generated turbulence. Since environmental values of this input parameter are difficult to obtain, Mackay suggested that the approximation

$$N_{Re^*} = \frac{7.07E-2(u_{10})^{5/4}}{\nu_1 \exp(56.6/u_{10}^{1/4})} \quad (8)$$

where u_{10} = wind velocity at 10 m height, cm/s
 ν_1 = kinematic air viscosity, cm²/s

Variations of this expression have appeared in the literature [12, 13]. Recently, Mackay introduced several new expressions for the liquid phase mass transfer coefficient which did not include the Roughness Reynolds number (20).

SIMULATION STUDIES TO DETERMINE THE COMBINED EFFECTS OF SURFACE WIND AND DEPTH UPON THE LIQUID PHASE MASS TRANSFER COEFFICIENT

The expressions appearing in Tables 1 and 2 were considered unsatisfactory for determining coefficients for surface impoundments. Simple theoretical considerations suggest that the liquid film coefficient should be a function of the wind's kinetic energy, i.e., the square of the surface velocity. This observation, which agrees with the overwhelming amount of laboratory evidence [7, 8, 18, 21, 22, 23], should appear as an input parameter in a general correlation for surface impoundments. Additionally, a general correlation should also include the hydraulic influences identified by several of the existing models presented previously. Finally, a correlation for surface impoundments should render laboratory coefficients comparable to field measurements.

Obviously, none of the expressions previously described satisfy all of these requirements. Mackay's correlation, for example, rejects the square of the velocity dependence and neglects the hydraulic considerations identified by theory. In order to develop a reliable emission model for wastewater surface impoundments, simula-

tion studies were performed in a wind tunnel-water tank (Figures 1 and 2) in which the wind velocity and the depth were varied.

Simulation Studies With a Fetch to Depth Ratio

The combined effects of the depth and wind velocity on the liquid phase mass transfer coefficient were characterized by performing simulation experiments with a wind tunnel-water tank of variable depth. Effective laboratory simulations of the environment require the existence of some identifiable, peculiar parameter shared in common by the laboratory apparatus and the environment which renders these entities dimensionally similar [24]. Thus, in order to compare these data to the results of other research groups and to the environment, a characteristic length scale had to be chosen for the simulator.

Previous research groups assumed that the fetch of the wind tunnel test section was a characteristic parameter that would render laboratory data comparable to the environment [22]. This assumption was unjustified because the wind fetches encountered in the environment are much greater than those of laboratory simulators. Moreover, this assumption neglected hydraulic effects on the mass transfer coefficient. Unsurprisingly, comparison of laboratory coefficients to field data for oxygen absorption was poor [22].

The fetch to depth ratio, F/D , is a quantity which would apparently serve well as a characteristic parameter for comparing wind tunnel-water tank data to each other and to the environment. Not only is the quantity dimensionless, it is also readily obtainable for most systems, especially surface impoundments. Furthermore, this dimensionless grouping has a theoretical basis. The fetch accounts for wind effects, whereas the depth accounts for hydraulic effects. Thus, the fetch to depth ratio is actually a measure of the relative importance of wind and hydraulic enhancements upon the liquid phase mass transfer coefficient.

Description of Equipment

The laboratory simulator consisted of two plywood wind tunnel sections, 3 ft wide, 2 ft high, and 8 ft long, divided by a Plexiglass water tank (Figure 1). The water tank test section was 3 ft wide, 4 ft deep, and 8 ft long, and was sup-

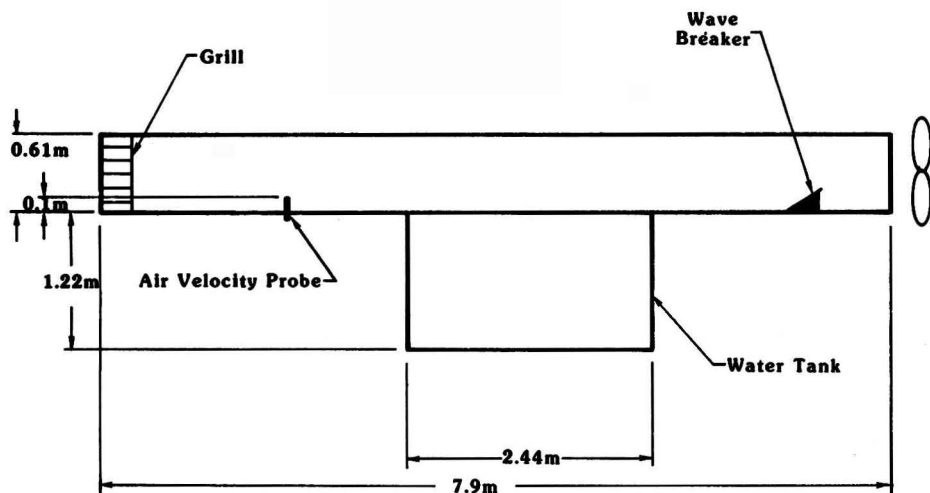


Figure 1. Schematic diagram: Wind tunnel/water tank system.

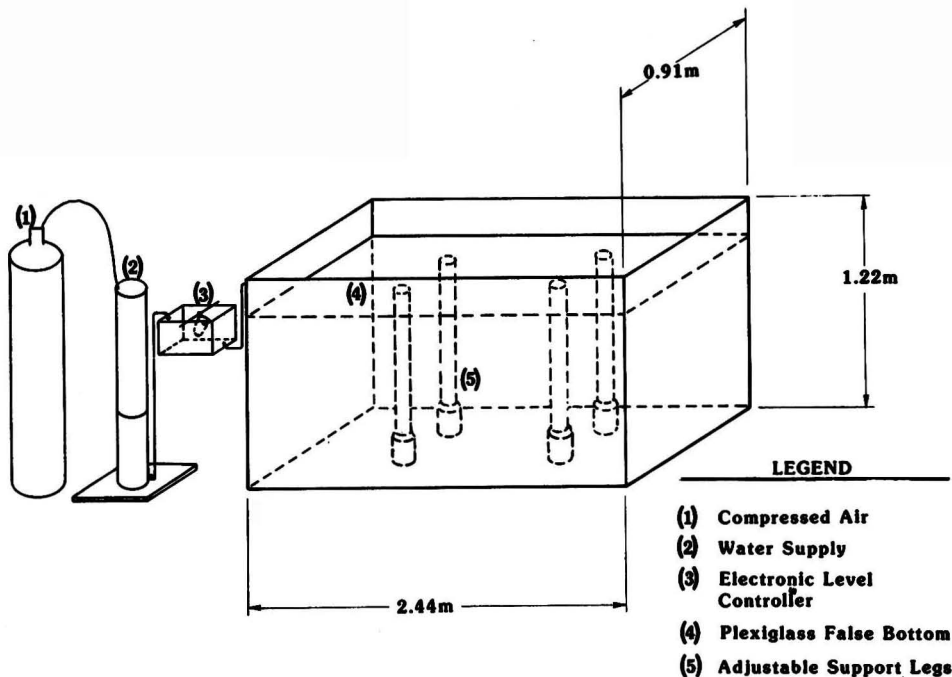


Figure 2. Water tank test section.

ported with steel angle supports. A Phelps Model CPW 270 fan with a 15 HP motor and a baffle arrangement provided wind speeds continuously variable up to 18 mph at 10 cm height without water entrainment (misting).

A wave damper was installed 8.5 inches from the downwind edge of the water tank to prevent water loss due to wave formation. Water loss by evaporation was measured and replaced by a constant level device (Figure 2), which was electrically controlled.

The distinctive, unique feature of this wind tunnel-water tank was the Plexiglass "false bottom" (Figure 2), which allowed the depth to be adjusted from extremes of 1.87 inches to 4.0 feet in less than 2 inch increments. Thus, with the fetch of the test section held constant at 8.0 feet, fetch to depth ratios from extremes of 51.3 to 2 were possible. In each set of experiments, the false bottom was sealed with silicone sealant to prevent interchange between the contents of the upper and lower tank sections. The lower tank section could then be filled with water in order to support the upper section and relieve the false bottom of the requirement of supporting the weight of the upper tank section.

The investigation of the depth and wind effects on the liquid film coefficient required desorption rate measurements for a suitable chemical. Ethyl ether (molecular weight 74.1) was chosen for these experiments for several reasons. Ethyl ether was considered safer than aromatic hydrocarbons for desorption measurements. Moreover, the chemical was relatively inexpensive and was generally more soluble in water than most other liquid phase controlled chemicals. Furthermore, the chemical had such a strong response for flame ionization detector analysis by gas chromatography that very dilute solutions could be prepared and analyzed easily. Finally, the high Henry's law constant for this chemical ($H_{FA} = 5.0$, mole fraction form) assured liquid phase control and affected rapid desorption, thus permitting a large number of experiments to be performed in a relatively short time period.

Experimental Procedure

The time period of the ethyl ether desorption experiments varied with the wind velocity and the particular fetch to depth ratio under observation, since high wind velocities and shallow depths resulted in extremely rapid chemical desorption. Generally, the experiments were continued until the major portion of the chemical initially present was desorbed (roughly 80 percent). Thus, in a particular experiment at 47.65 cm depth and at the lowest wind velocity setting (approximately 6-7 mph), six samples were collected over a 66 hr time period at roughly 12 hr intervals during which over 97 percent of the ethyl ether initially present was desorbed. In contrast, at 4.76 cm depth and the identical wind velocity setting, six samples were collected over a 2 1/2 hr period at half hour intervals during which 78 percent of the ethyl ether initially present was desorbed.

Prior to the start of an experiment, the test section of the apparatus was charged with enough ethyl ether to produce roughly a 100 ppm solution. Stirring with a paddle and at high wind speed for several minutes effected a uniform concentration.

Wind velocity profiles were measured at the leading edge of the test section with a Kurz Model 444 air velocity meter. Usually, two or more profiles were measured during the course of an experiment. The velocity at 10 cm height was obtained both by direct measurement and by interpolation of the average velocity profiles obtained during an experiment.

In each experiment six or more aqueous samples were collected with a 5 ml pipet placed directly in the center of the water tank at approximately mid-depth. The volatile samples were analyzed immediately after collection by gas chromatography. Liquid sample aliquots were injected directly into a Perkin Elmer Sigma 3B gas chromatograph equipped with a flame ionization detector, a Perkin

Elmer Model M-2 calculating integrator, and a Houston Instruments Omniscrite recorder.

Component separation and quantification were performed with a 10 ft long, Nickle column packed with Chromosorb 102, which was maintained isothermally at 185 C with 50 ml/min He carrier gas flow.

PRESENTATION AND DISCUSSION OF RESULTS

The coefficients measured for each depth at various wind velocities are presented in Tables 3-8. These coefficients were calculated from desorption data by assuming a first order rate process, i.e.

$$dC/dt = K_{des} C \quad (9)$$

where C = the chemical concentration, kg/m³
 k_{des} = the desorption rate constant, s⁻¹
 t = time, s.

The desorption constant for each experiment was thus determined by linear regression analysis of a semi-log plot of the ratio of the measured concentration at time "t" to the

TABLE 3. LIQUID PHASE MASS TRANSFER COEFFICIENT VS. WIND VELOCITY AT 10 CM HEIGHT, DEPTH = 47.7 CM, F/D = 5.1

u , m/s	k'_L , m/s* × 10 ⁶
2.65 ± 0.009	3.28 ± 3.19
4.65 ± 0.022	12.8 ± 0.14
6.08 ± 0.045	24.3 ± 0.50
6.80 ± 0.027	35.0 ± 0.78
7.78 ± 0.049	39.2 ± 1.58

* To obtain K_{Lr} (kmol/m² · s), multiply by 55.6

TABLE 4. LIQUID PHASE MASS TRANSFER COEFFICIENT VS. WIND VELOCITY AT 10 CM HEIGHT, DEPTH = 17.4 CM, F/D = 14.0

u , m/s	k'_L , m/s* × 10 ⁶
2.47 ± 0.089	3.36 ± 0.278
4.73 ± 0.112	19.3 ± 0.806
6.08 ± 0.483	21.6 ± 0.583
6.71 ± 0.308.	26.6 ± 0.806
7.64 ± 0.04	38.1 ± 0.583

* To obtain K_{Lr} (kmol/m² · s), multiply by 55.6

TABLE 5. LIQUID PHASE MASS TRANSFER COEFFICIENT VS. WIND VELOCITY AT 10 CM HEIGHT, DEPTH = 12.3 CM, F/D = 19.9

u , m/s	k'_L , m/s* × 10 ⁶
3.13 ± 0.443	5.31 ± 0.389
4.78 ± 0.031	17.6 ± 1.11
6.44 ± 0.219	24.7 ± 0.417
7.15 ± 0.031	33.3 ± 1.36
8.09 ± 0.188	44.7 ± 1.17

* To obtain K_{Lr} (kmol/m² · s), multiply by 55.6

TABLE 6. LIQUID PHASE MASS TRANSFER COEFFICIENT VS. WIND VELOCITY AT 10 CM HEIGHT, DEPTH = 6.91 CM, F/D = 35.3

u , m/s	k'_L , m/s* × 10 ⁶
2.33 ± 0.022	5.25 ± 0.167
4.65	19.6 ± 0.472
6.04 ± 0.013	31.4 ± 0.778
7.02 ± 0.004	41.9 ± 0.194
7.73	50.6 ± 1.97

* To obtain K_{Lr} (kmol/m² · s), multiply by 55.6

TABLE 7. LIQUID PHASE MASS TRANSFER COEFFICIENT VS. WIND VELOCITY AT 10 CM HEIGHT, DEPTH = 4.75 CM, F/D = 51.2

u , m/s	k'_L , m/s* × 10 ⁶
3.03 ± 0.112	6.64 ± 0.111
4.52 ± 0.058	17.7 ± 0.139
6.17 ± 0.072	30.8 ± 0.194
7.06 ± 0.215	49.2 ± 0.972
7.91 ± 0.170	56.9 ± 0.778

TABLE 8. EQUATIONS FOR THE LIQUID FILM COEFFICIENT AS A FUNCTION OF THE WIND VELOCITY AT 10 CM HEIGHT

F/D	Relationship, k'_L , m/s
51.2	5.78 E-7 $u^{2.2}$
35.3	1.10 E-6 $u^{1.9}$
19.9	4.08 E-7 $u^{2.2}$
14.0	5.85 E-7 $u^{2.1}$
5.1	4.09 E-7 $u^{2.3}$

initial concentration versus time. The mass transfer coefficient followed from the expression

$$k'_L = Z K_{des} \quad (10)$$

where Z = depth, m.

Curve fits of these coefficients for each depth studied are presented in Table 8. In each case, it was observed that the coefficient varied approximately with the square of wind velocity.

The effect of the depth on the mass transfer coefficient is evident from Figures 3 and 4, which present the coefficient as a function of the fetch to depth ratio for several wind velocities. Each of the points illustrated were produced from the appropriate empirical model contained in Table 8. These plots suggest that, at each wind speed, the coefficient is essentially constant at low fetch to depth ratios ($F/D < 14$), but increases significantly for fetch to depth ratios greater than 20. Moreover, the magnitude of this increase appears to reach a maximum value at F/D approximately equal to 50. This effect has been attributed to the existence of two distinct mass transfer mechanisms which are operative in water systems with high and low fetch to depth ratios [23]. In systems of great depth (low F/D), the establishment of an Ekman depth, as illustrated in Figure 5, separates the system into an upper layer of enhanced turbulence due to surface winds, and a relatively calm lower layer. Presumably, chemical desorption in such a system would result from two steps, transport of solute from the calm zone into the turbulent layer by molecular diffusion followed by rapid chemical desorption due to eddy motion. Since the first step is likely to be "rate determining," the overall desorption process is diffusion controlled and thus independent of depth.

Whereas the interaction of surface winds with relatively deep water systems establishes a limited zone of turbulence, in shallow systems ($F/D > 14$) the entire fluid is turbulent. An increase in the fetch to depth ratio, at constant fetch, intensifies the turbulence by compressing the turbulent water velocity profile and thus increases the coefficient. Presumably, for a fetch to depth ratio greater than 50, the rate of eddy transport is maximized, and further increases in the fetch to depth ratio at constant wind velocity merely increase the kinetic energy per unit volume of fluid, which is dissipated as internal energy.

DEVELOPMENT OF A GENERAL CORRELATION FOR SURFACE IMPOUNDMENTS

In order to produce a predictive correlation from the measured laboratory coefficients, it was necessary to ac-

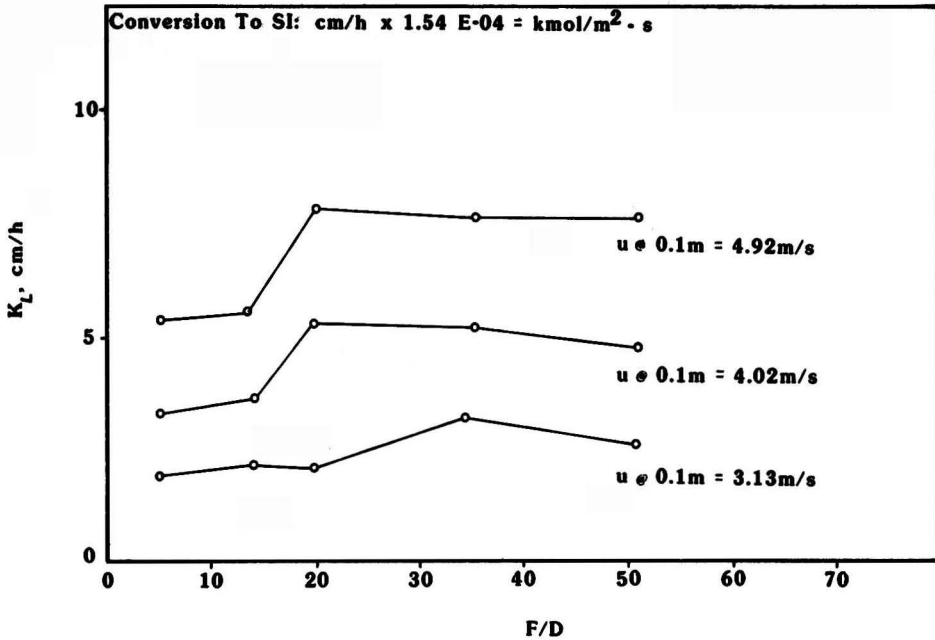


Figure 3. Model calculations, low wind speeds.

count for the different transport mechanisms operative in shallow as opposed to deep systems, as well as the requirements specified previously. Two correlations, representing the two possible mass transfer mechanisms, were developed from the laboratory coefficients.

The first correlation represents an unusual situation characterized by low fetch to depth ratios ($F/D < 14$), characteristic perhaps of a deep lake as well as most laboratory simulators, whereas the second expression represents the

shallow systems which characterize surface impoundments.

The "deep lake" correlation, in SI units, is

$$k'_L = (2.78E-6) (D_r/D_{r \text{ ether}})^{2/3} : 0 \leq u \leq 5.5 \text{ m/s} \quad (11a)$$

$$k'_L = (1.87E-7 u^2 - 1.3E-6) (D_r/D_{r \text{ ether}})^{2/3} : u > 5.5 \text{ m/s} \quad (11b)$$

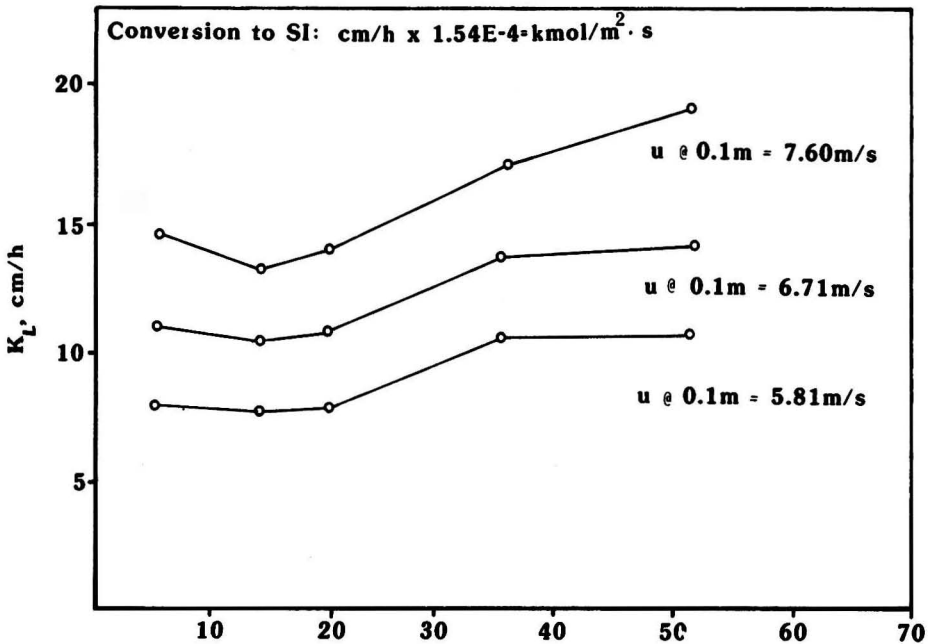


Figure 4. Model calculations, high wind speeds.

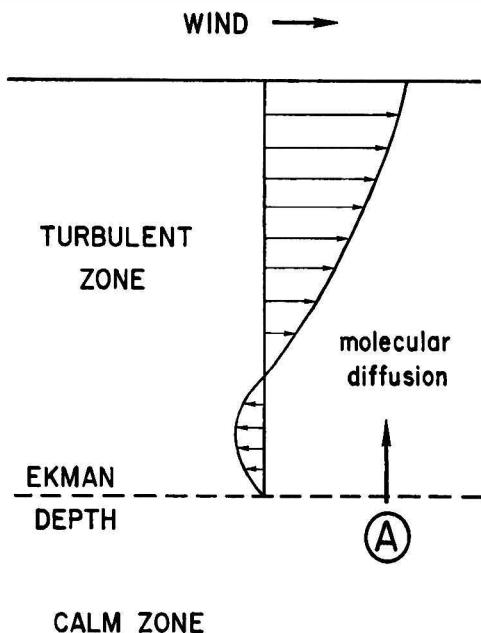


Figure 5. Establishment of an Ekman layer.

where D_r is the chemical diffusivity of the solute of concern, and $D_{r(ether)}$ is the diffusivity of ethyl ether in water, $0.85E-9 \text{ m}^2/\text{s}$ at 25°C [25].

The correlation which describes the coefficient for "shallow" systems ($F/D > 14$) is presented in Table 9. Of the three expressions included in this correlation, the third is probably the most useful or describing wind enhanced emission from surface impoundments.

Both the deep lake and the surface impoundment correlations were produced by fitting the laboratory data against the square of wind velocity by regression analysis. The deep lake expressions were developed from the data in Table 3, whereas multiple linear regression analysis of the data contained in Tables 4-7 produced the general correlation for surface impoundments. For this purpose, it was assumed that laboratory wind velocities could be converted to their environmental equivalents at 10 m height with the power law of Deacon (26).

$$u = u(0.1 \text{ m}) (10/0.1)^{1/7} \quad (12)$$

where $u(0.1 \text{ m})$ is the laboratory measurement of the wind velocity at 0.1 m. In the development of both correlations, it was assumed that the natural convection, "no wind" coefficient [27] was operative at wind speeds less than or equal to 5 m/s.

TABLE 9. A GENERAL CORRELATION FOR SURFACE IMPOUNDMENTS

SI units: k'_i and u in m/s , u is wind velocity at 10 m altitude

Expression	Scope and Limitations
$k'_i = 2.788E-6(D_r/D_{r(ether)})^{2/3}$	$0 \leq u < 5 \text{ m/s}$
$k'_i = 2.60E-9(F/D) + 1.277E-7 u^2(D_r/D_{r(ether)})^{2/3}$	$u > 5 \text{ m/s}$ $14 \leq F/D \leq 51.2$
$k'_i = 2.611E-7 u^2(D_r/D_{r(ether)})^{2/3}$	$u > 5 \text{ m/s}$ $F/D > 51.2$

* To obtain $k_{i,r}$ ($\text{kmol}/\text{m}^2 \cdot \text{s}$), multiply by 55.6

Note that these relationships "correct" the coefficient for the chemical of interest to that of ethyl ether with the ratio of the liquid chemical diffusivities raised to the two-thirds power. This correction, which represents a compromise to the extremes of the film and the penetration theories, is based upon turbulent boundary layer theory and has been confirmed experimentally in our laboratory [23].

Comparison of Model Predictions to Established Correlations and Field Estimates

Given the scarcity of reliable, published field measurements for VOC emissions, together with the apparent difficulty of obtaining such measurements from industrial sites, it is difficult to verify the general correlation's assumptions and predictive power. Certain evidence can be produced, nevertheless, that both the deep lake and surface impoundment correlations yield reasonable estimates of environmental coefficients, and that the fetch to depth ratio renders laboratory simulators dimensionally similar to the environmental systems.

Dowing and Truesdale [18] obtained their oxygen re-aeration data with a laboratory simulator of low fetch to depth ratio. Thus, Banks' correlation (2nd of Table 2), which was based upon this data, should be essentially equivalent to the deep lake correlation, Equations (11a) and (11b).

A statistical comparison of the predictions of these relationships for a reasonable range of wind velocities is presented in Table 10. The statistical procedure used to construct this table involved a pair data comparison [28], in which the average difference between corresponding predictions were used to calculate a Student's t according to the expression

$$t = (\bar{x} - m) \sqrt{n/\sigma}$$

where t = Student's t

- \bar{x} = Average difference between pairs
- m = true average difference
- n = number of observations
- σ = standard deviation

Since the true average difference was unknown, the hypothesis tested was " $m = 0$ ", i.e., there was no significant difference between the predictions. This hypothesis was confirmed by the fact that the calculated t was less than

TABLE 10. STATISTICAL COMPARISON OF DEEP LAKE EXPRESSION TO BANKS' CORRELATION

Note* Correction Factor, Ethyl Ether to Oxygen: 2.053
 D_r , ether = $0.85 \times 10^9 \text{ m}^2/\text{s}$
 D_r , oxygen = $2.50 \times 10^9 \text{ m}^2/\text{s}$
 $(D_r \text{ oxygen}/D_r \text{ ether})^{2/3} = (2.50/0.85)^{2/3} = 2.053$

Wind Velocity at 10 m, m/s	$k'_{i,r}$, $\text{m}/\text{s} \times 10^6$		
	Banks	Deep Lake	Difference
2	6.94	5.71	1.23
6	11.5	10.6	0.90
8	20.5	21.0	-0.50
10	32.0	34.3	-2.30
12	46.1	50.5	-4.40
14	62.7	69.8	-7.10
16	81.9	91.9	-10.0

Average Difference, $\text{m}^2/\text{s} \times 10^6$: -3.17

Standard Deviation, $\text{m}^2/\text{s} \times 10^6$

Calculated t : 1.980

Tabulated t for 6 degrees of freedom, 95% confidence = 2.447

Conclusion: No statistical difference at 95% confidence level

the tabulated value for 6 degrees of freedom at 95% confidence.

The significance of this comparison is that Banks' correlation, supposedly developed for "shallow lakes", is suited, rather, for "deep lakes" and is not generally suited for the usual shallow surface impoundment.

Comparison of the General Correlation to Reasonable Field Estimates

Recently, it was suggested that environmental or field coefficients would be different from those obtained from laboratory simulations [20]. Indeed, past comparisons of laboratory coefficients to field measurements for oxygen reaeration were disappointing [22].

This apparent discrepancy was probably due to the failure to identify a dimensionless parameter in laboratory simulators which rendered the artificial systems dimensionally similar, and hence directly comparable, to the environment. In the general correlation for surface impoundments, this requirement is fulfilled by the inclusion of the fetch to depth ratio.

Recently, Mackay [29] presented "reasonable estimates" of environmental coefficients for benzene desorption at various wind velocities. These values are compared statistically to the predictions of the general correlation in Table II. The calculated coefficients were determined by assuming a fetch to depth ratio greater than 50, which is reasonable for a typical surface impoundment.

Clearly, the results of this comparison support the validity of the general correlation and the assumption that the fetch to depth ratio is an appropriate parameter for comparing laboratory coefficients to field values.

Note that the agreement between the field coefficient and the value calculated from the general correlation improves with increasing wind velocity. Reliable, actual field values, however, are necessary to justify the validity of the correlation for a range of environmental conditions.

Laboratory Confirmation of the Correlation's Validity at Large Fetch to Depth Ratios

An obvious criticism of the general correlation's construction was that there was no experimental data to support the assumption that no increase in the magnitude of the mass transfer coefficient occurred when the fetch to depth ratio was greater than 50. Recently, experiments were performed to test this assumption [30].

The original wind tunnel was modified such that the fetch was increased by 2.44 m and was fitted with a new water tank measuring 4.88 m in length and 4.72 cm in

depth ($F/D = 103$). Desorption experiments were performed in the normal manner.

The results of these experiments are compared to the predictions of the general correlation in Table 12. The result of the comparison indicates that no significant difference exists between the laboratory values and the correlation's predictions.

These results are highly significant with respect to verifying the correlation's assumptions, especially when it is considered that the entire configuration of the original test apparatus was changed.

CONCLUSIONS

The following conclusions, based upon the observations and data presented in this test, appear justified.

1. In addition to the previously documented enhancement of the liquid phase mass transfer coefficient due to wind velocity, there is also an enhancement due to the depth of the water system.
2. The magnitude of the coefficient generally approaches a maximum value with decreasing depth for a system of constant fetch.
3. The liquid phase mass transfer coefficient can be described as a function of the square of wind velocity.
4. The depth enhancement of the coefficient can be described in terms of the dimensionless fetch to depth ratio, which apparently renders laboratory simulators comparable to each other and to the environment.
5. A general correlation, which was developed from laboratory measurements to describe emissions from surface impoundments with large fetch to depth ratios, produced mass transfer coefficients for benzene which were in agreement with reasonable field estimates.

The general correlation presented in this text is probably the only relationship which has the potential to explain the apparent discrepancy between field observations and laboratory data. Therefore, the use of this model is recommended to describe the liquid-phase mass transfer coefficient for environmentally enhanced VOC emissions.

DISCLAIMER

Although the information described in this article has been funded wholly or in part by the United States Environmental Protection Agency under Assistance Agreement CR-808161-02 to the University of Arkansas, it has not been subjected to the Agency's required peer review and administrative review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

TABLE 11. STATISTICAL COMPARISON OF THE GENERAL CORRELATION TO SUGGESTED ENVIRONMENTAL COEFFICIENTS FOR BENZENE

Wind Speed at 10 m, m/s	$k_L', \text{ m/s} \times 10^6$		
	Environmental	*Calculated	Difference
2	5	3	2
5	15	7	8
10	35	28	7
15	60	63	-3

Average Difference, $\text{m/s} \times 10^6$: 3.5

Standard deviation: 5.07

Calculated t : 1.38

Tabulated t for 3 degrees of freedom at 95% confidence: 3.182

Conclusion: No statistical difference at 95% confidence

*Coefficient correction factor, Ethyl Ether to Benzene:

D_r , benzene, 25°C: 0.902 E - 9 m^2/s (diffusivity in water)

CCF = $(0.902/0.85) = 1.04$

TABLE 12. COMPARISON OF THE GENERAL CORRELATION TO LABORATORY MEASUREMENTS FOR A LARGE FETCH TO DEPTH RATIO

Wind Velocity at 10 m, m/s	$k_L', \text{ m/s} \times 10^6$		
	Experimental	Calculated	Difference
3.43	5.67	2.78	2.89
8.83	21.8	20.3	1.50
11.8	35.8	36.2	-0.4
14.2	48.8	52.8	-4
15.69	65.8	64.3	1.5

Average difference, $\text{m/s} \times 10^6$: 0.298

Standard Deviation: 2.67

Calculated t : 0.249

Tabulated t for 4 degrees of freedom at 95% confidence: 2.776

Conclusion: No Statistical Difference

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Case History of a Major Nitric Acid Spill

Here is what actually happened on April 3, 1983, when a tanker car was accidentally punctured in downtown Denver.

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Early on the morning of Easter Sunday, April 3rd, 1983 a railyard switching mishap occurred in downtown Denver, Colorado. While coupling operations were being conducted in the switching yards, a tanker car was accidentally punctured and 55 cubic meters (14,500 gallons) of a 99-percent solution of nitric acid were spilled. The resulting vapor cloud of potentially toxic nitrogen dioxide (NO₂) forced the evacuation of nearly 5,000 residents during the early morning hours and closed the city's two major metropolitan highways for all holiday travelers.

This incident attracted national attention, because it involved a toxic waste spill in a major metropolitan area which required the orderly evacuation of a large number of people during one of the busier holidays of the year. Prompt action and excellent coordination among the responding groups were necessary to minimize the threat to public health and prevent public concern from escalating or otherwise impeding the safe and orderly resolution of the emergency.

Representatives from numerous governmental agencies responded, including the Denver Fire Department (DFD) and their Hazardous Materials Emergency Response Group (HAMER), the Denver Police, the State Highway Patrol, the Colorado Department of Health (CDH), City and County of Denver, Department of Health and Hospitals, the Office of Emergency Preparedness (OEP), and the Regional Transportation District (RTD). On the scene as EPA representatives was the Region 8 Technical Assistance Team (TAT), an organization of scientists under Contract #68-01-6669 to the U.S. Environmental Protection Agency (EPA) for response to oil and hazardous materials spills.

This paper presents the chronological events surrounding the spill and discusses the problems encountered during the initial response, the resolution of those problems, and the development and implementation of long-term remedial actions. The opinions expressed in this paper are the authors' and do not necessarily reflect official EPA policy.

CHRONOLOGY OF EVENTS

A. The Response

The spill occurred at 4:00 A.M. in the north yards of the Denver and Rio Grande Western Railroad. Within the next few hours, the Denver Fire and Police Departments and the TAT were on-scene, and evacuation of an area extending 1.6 kilometers (one mile) square downwind was underway. Segments of Denver's two major interstate highways were closed to traffic. The location of the spill and evacuation areas is shown in Figure 1. In addition, response teams were coordinating with the OEP, and plans were being implemented to neutralize the spill with soda ash. By 8:30 AM, a decision was reached to extend the

evacuation zone an additional 1.6 kilometers (one mile) square prior to neutralization.

The TAT was requested to assist in air monitoring at both the spill site and the evacuated zone during the neutralization process. Soda ash had been transported to the site in 91,000 kilogram (100-ton) cars, and by 10:30 A.M., was being offloaded and spread with front-end loaders. Approximately 273,000 kilograms (three hundred tons) of the material were further dispersed on the spill area by the use of snowblowers from Stapleton International Airport. Despite the operation being somewhat hampered by snow and low temperatures, the soda ash application was completed at noon and the evacuation was terminated at 12:30 P.M., when people were told they could return safely to their homes.

The TAT and CDH performed air monitoring throughout the duration of the neutralization process and continued monitoring until 1:00 P.M.

The remaining task in resolving the immediate problem was to off-load 1.89 to 2.27 cubic meters (500 to 600 gallons) of nitric acid that was still remaining in the ruptured tanker. Late in the day, several attempts were made to offload the tanker; however, darkness and worsening climatic conditions precluded completing this task on that day. Ultimately, the nitric acid was successfully transferred to a tanker on April 6th. Other measures taken during the afternoon of the spill in order to mitigate the problem included: neutralization of isolated pockets of nitric acid along the railroad tracks; checking of sanitary and storm drains; and diking of a marsh that receives runoff from the track area via a culvert.

With the emergency essentially resolved on the day in which the spill occurred, the remaining concerns related to the longer-term environmental impact and remedial measures.

Follow-up

On Monday morning, April 4th, a meeting of the various response groups was held to review strategies for investigating contamination of surface water, groundwater, and soils, as well as to identify potential remedial actions. Over the course of the next two weeks, many meetings were held with representatives of the Rio Grande Railroad and the response teams. During these meetings, the TAT served in an advisory capacity, providing technical assistance in delineating methods for efficient and appropriate mitigation of the spill. Field activities which occurred during this time period included the following:

1. Surface water sampling was conducted on and adjacent to the Rio Grande property and water collected in the parking lot was pumped to the already contaminated marsh.

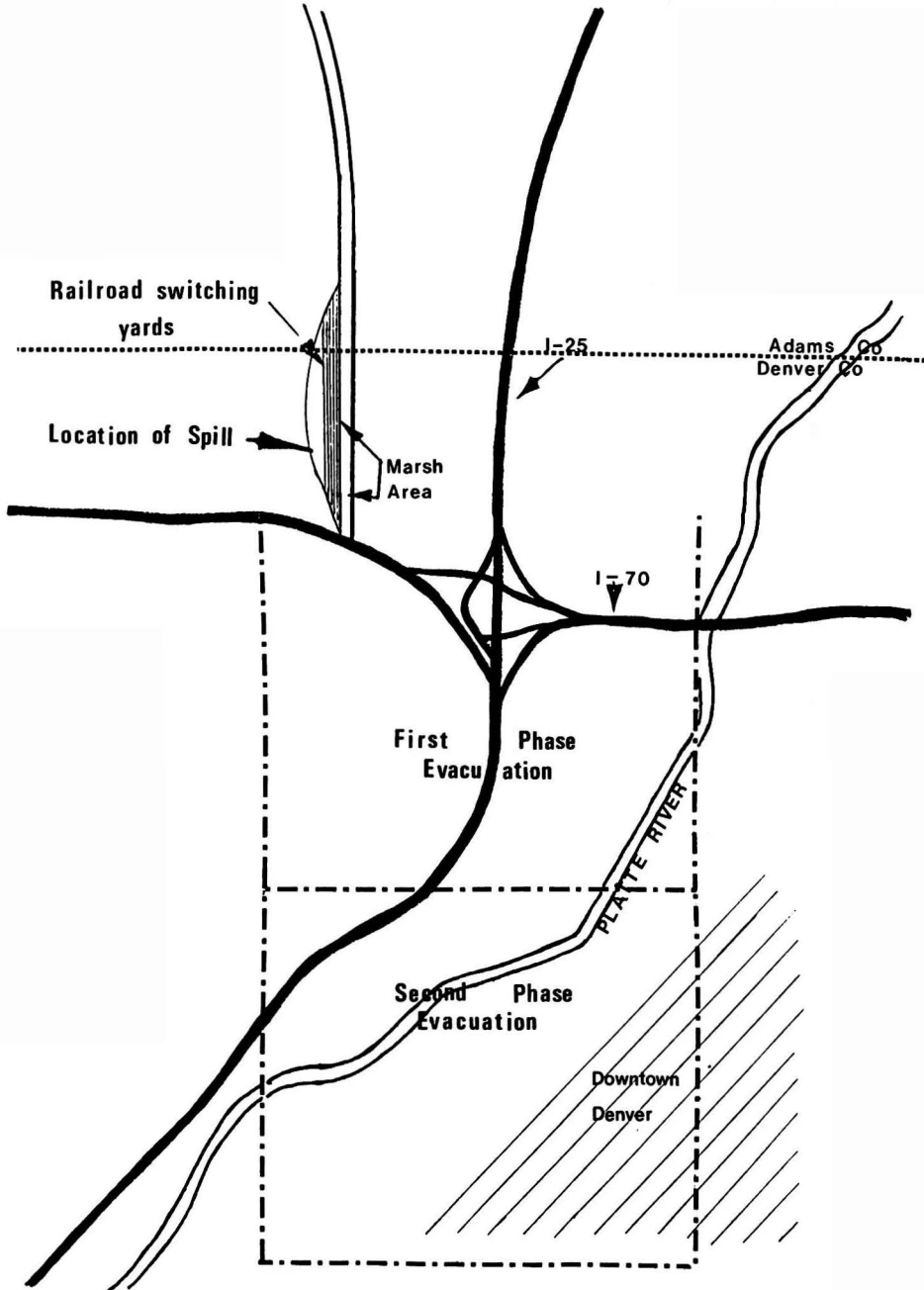


Figure 1. Schematic diagram

2. The TAT collected both surface water and soil samples for NO_2 analyses.

3. Backhoe excavations were dug at strategic locations in the spill and marsh areas, in order to determine soil excavation and disposal requirements.

4. Contaminated marsh waters were pumped into lined dumpsters.

By May, 1983, approximately 1100 cubic meters (1,450 cubic yards) of soil/soda ash had been disposed at Tower Landfill in Denver. Water collected from the contaminated marsh area had been treated and disposed. The following section of the paper provides a discussion of some of the logistical and technical problems encountered during the response and cleanup, and their resolution.

LOGISTICAL/TECHNICAL PROBLEMS

A. Initial Response

1. The first primary concern faced by the responders and the railroad authorities was the notification and evacuation of the residents potentially impacted by the vapor cloud. This cloud was formed by the volatilization and reaction of the acid, as it came into contact with carbonaceous materials and metal in the tracks area. Immediately upon their arrival at the scene, the police began effecting a local evacuation. As climatic conditions changed and the vapor cloud was carried south into the City, the evacuation encompassed an area 1.6 kilometers (one mile) square to the south of the spill. Later, the evacuation was extended an additional 1.6 kilometers (one mile) square south, as a precaution against the vapor release anticipated during neutralization. Denver policemen went door-to-door throughout the evacuation area, and with assistance from RTD busses to ambulances from local hospitals, transported people to schools for the duration of the evacuation.

EPA requested assistance from their Emergency Response Team in Edison, New Jersey, in modeling the plume. Unstable climatic conditions, coupled with physical site-specific restrictions (such as topographic lows and structural barriers) limited the applicability of the model's predictions for the site.

2. Railroad officials immediately began the search for the large quantity of a base substance required to neutralize the 55 cubic meters (14,500 gallons) of spilled acid. Through inter-company cooperation, Rio Grande located, on a competitor's line, a shipment of soda ash that was enroute to the Coors Brewery in Golden, Colorado (48 kilometers west of Denver). Rio Grande contacted the consignor and requested the shipment be rerouted to the Rio Grande yards. At this point in the response, it became evident that several hours would elapse before the shipment would arrive and neutralization could begin.

3. While awaiting the arrival of the soda ash, concern focused on identifying a method to rapidly disperse the large quantity of neutralizing materials on the spill. Denver's then-Mayor, Bill McNichols, suggested using Stapleton Airport's snowblowers. The snowblowers arrived on scene in advance of the soda ash shipment. Actual application and neutralization required less than one hour.

4. To complete neutralization, DFD personnel in protective clothing walked the track area and, with shovels, applied the ash to "hot spots." Appropriate protective clothing and equipment consisted of a fully encapsulated suit and self-contained breathing apparatus. Suits normally carried by the DFD were not chemically compatible with the acid; thus, special acid-resistant suits had to be procured and sent to the site.

5. As stated earlier, the evacuation was conducted in two phases. Unstable climatic conditions which continued to exist following the initial evacuation, coupled with concern over the extent of the vapor acid cloud during neutralization, necessitated a continuing evaluation of the adequacy of the extent of the evacuation zone. Winds that day were predominantly out of the north at 2.24-4.47 m/s (5-10 mph) but gusting to 17.88 m/s (40 mph). Wind patterns changed at approximately 11:30 A.M., when an arctic storm front moved into the area. Snow began falling during the late morning hours and continued to fall throughout the day, producing difficult conditions for the response teams working in the area.

CDH and TAT personnel assisted in air monitoring around the evacuation perimeter to assure that the extent of evacuation was adequate. The air monitoring was conducted using portable hNu and Draeger pumps. The hNu is a portable, non-specific vapor/gas detector employing the principle of photoionization to detect a wide variety of chemical compounds, both organic and inorganic. Because of the limited shelf life of the Draeger tubes, quanti-

ties of tubes are not stockpiled. Consequently, before air monitoring activities could begin, it was necessary to locate the appropriate tubes required to monitor the constituents of the vapor cloud. Through a resource list maintained by OEP, a dealer located in metropolitan Denver was identified, contacted and asked to assist. Coincidentally, the dealership was located just within the perimeter of the evacuation area. The necessary nitrogen dioxide tubes were procured for air monitoring.

While both nitric acid and nitric oxide vapors are irritants and have an Immediately Dangerous to Life or Health (IDLH) concentrations of 100 ppm, monitoring the vapor cloud for nitrogen dioxide reflected the most sensitive parameter of the three gases most likely to be present. Nitrogen dioxide has an odor threshold of 4 ppm, a Threshold Limit Value (TLV) of 5 ppm and IDLH of 50 ppm. TLV's refer to airborne concentrations of substances and are developed for a repeated day-to-day exposure in the workplace environment. IDLH's refer to concentrations of a maximum level from which one could escape within 30 minutes without escape-impairing symptoms or any irreversible health effects.

Downwind monitoring was conducted from approximately 10:30 A.M. to 1:00 P.M. at various locations throughout the evacuated zone. At one point, a reading of 20 ppm was obtained on the hNu only a few blocks from the actual spill site. While this reading generated immediate concern, its validity was uncertain in view of the calibration of the instrument and the affects of the changing climatic conditions. In fact, minutes later, this reading could not be duplicated in the same area.

Nitrogen dioxide readings obtained with the Draeger tubes at the spill site ranged from 0.5 ppm to 17 ppm in the area of the railroad car. The average perimeter reading, at the site, but away from the direct vapors, was 2-3 ppm of NO₂. However, it was apparent from the reddish-brown coloration of the cloud that pulses of higher vapor concentrations were probably present within the evacuated area in the early phase of the response.

6. During the course of the first day of response, inspections were made around the perimeter of the spill site to assess for avenues of possible movement of the acid off-site. Drains located around the site perimeter were checked and where appropriate, the drains were diked. The marsh which received the runoff waters and materials from the track area was dammed to prevent any surface migration of the contaminated material.

7. At the conclusion of the first day of the response, several attempts had been made to off-load the remaining 1.89 cubic meters (500 gallons) of acid from the damaged car. Pumps utilized in off-loading failed because they did not have Teflon diaphragms. Additional complications were encountered with the pumps due to the low ambient air temperatures; consequently the tanker was not successfully off-loaded until three days later when special equipment was flown in and weather conditions improved.

B. Follow-up

1. Following the initial mitigative measures and stabilization of the site, the task of evaluating the environmental impact and necessary cleanup had to be undertaken. Soils, surface water and ground water had to be addressed.

a. soils:

The immediate spill area was encrusted with a thick, black sludge resulting from the acid burning the railroad ties and carbon materials in the soil. The CDH and EPA determined that soils should be tested for pH and conductivity. The extent of contamination would be defined by the parameters of specific conductance at one percent (10,000 ppm) above background and/or a pH of less than 5 or greater than 10.

Before field work was initiated, an attempt was made to collect the appropriate background information. A shallow geologic/soil profile was obtained from a report prepared for the construction of the adjacent viaduct. This report, along with extrapolated soils maps for the adjacent county, indicated that the undisturbed portion of the site consisted of permeable clay-loam soils (pH range of 6.6 to 8.4) underlain by a sandy clay grading to claystone and shale. It was felt that the contaminants would migrate down to the cohesive clay lens.

Based upon this information, a sampling program was developed. Throughout the track area soil samples were taken using a .10 meter (four-inch) diameter hand auger to a depth of .61 meter (24 inches); pH readings ranged from 9.2 at a .05 meter (two-inch) depth to 8.5 at a .51 meter (20 inch) depth. In addition to the hand augering, two backhoe excavations were dug to determine the extent of the clay layer thought to underlay the railyard. One trench was excavated in the north area of the spill and one in the north marsh area. Rio Grande and its cleanup contractor, Emergency Environmental Services, then prepared a sub-surface soil investigation plan utilizing backhoe excavations to evaluate soil profiles and collect samples. The plan called for the excavation of four trenches in uncontaminated areas and three trenches in the heavily contaminated area.

After a soil profile was developed, soil samples were collected from all the trenches from .08 to .91 meter (3 to 36 inches) at .15 meter (six-inch) intervals, and a bottom sample was taken at 1.83 meters (72 inches). The soils in the immediate spill area, along with .10 to .15 meter (four to six inches) of topsoil from the marsh area, were removed and stockpiled, pending determination of a disposal site. Composite sampling of the removed soil and ballast material was analyzed as follows: pH—0.6; conductivity—163,000 ohms; nitrates—10,000 ppm; sodium—44,000 ppm; carbonates—68,000 ppm; and percent solubility—106,000 ppm (10.6%).

b. surface waters:

The pH in the contaminated marsh area the day after the spill ranged from 2 to 12. As soda ash, nitric acid, and runoff water from the snow melt washed from the Rio Grande property into the marsh area, mixing increased and the pH range narrowed. Approximately 28.4 to 45.4 cubic meters (7,500 to 12,000 gallons) of contaminated water were collected in the diked marsh area. Surface waters were sampled throughout the marsh and in the immediate spill area/site. The analytical parameters used to evaluate surface waters included pH, conductivity, and nitrate levels. Nitrate analyses were performed in the field using a diphenylamine colorimetric test. Seventeen locations were chosen for conductivity and pH measurements.

Based on the results of the field tests, Rio Grande proposed to CDH a plan for containerizing the surface waters from the contaminated marsh in plastic-lined, 18.9 cubic meters (5,000 gallon), roll-off dumpsters. The dumpsters would act as settling ponds for the solids. The effluent would then be discharged into the sanitary sewer by flow regulated release, as stipulated by the City and County of Denver Wastewater Management Division. The waters prior to discharge would have to meet certain criteria: pH of 6.0 to 9.5 and total solids of 0.4 to 0.5% or less. A trial discharge was conducted with no impact on the denitrification processes of the wastewater treatment plant. The remaining volume from the contaminated marsh area was then discharged at a daily rate of 4.54 m³/hr (20 gpm) in two-hour intervals.

c. groundwater:

Initially, a great deal of concern was expressed over the possibility of contaminated groundwater, both from the in-

itial acid spill and from neutralization by-products. The first course of action in assessing the potential impact was to ascertain groundwater use from existing wells in the immediate vicinity. Through a records search, it was learned that wells that lay in the downgradient groundwater flow direction were completed at depths in excess of 61 meter (200 feet). During trench excavation and soil augering, free water was observed at the sand/clay interface. The water was tested for pH with broad-range litmus paper and found to range between 5 and 8. Waters in the north spill trench were high in nitrate and specific conductance levels (10,220 ppm nitrate and 27,760 micro-ohms/cm conductance). To determine continuity or discontinuity of the near-surface groundwater in this area, several holes were augered to a depth of .61 meter (24 inches) throughout the track area and adjacent to the eastern edge of the culvert. Water was encountered at near surface in one hole and not at all in others. Based upon these findings, it was determined that further action directed to contaminated groundwater would be ineffective in this unique setting.

2. The remaining problem was disposal of the contaminated soils and soda ash. Approximately 272,000 kilograms (300 tons) of soda ash were sprayed on the spill area by the snowblowers during the initial neutralization activities. Calculations indicated that approximately 91,000 kilograms (100 tons) were required to neutralize the spilled acid, but additional soda ash was applied to insure adequate dispersal by the snowblowers. In fact, snowblower operations were more effective than anticipated. Therefore, at the conclusion of the neutralization, approximately 182,000 kilograms (200 tons) of excess soda ash remained on the Rio Grande property. Much of this material was still in pure form. The gross recovery of this material was performed using front-end loaders. The soda ash was stored in two railroad hopper cars and later given to the Public Service Company. Excess soda ash removal from around the rails, ties and ballast was accomplished by hand labor. Workers wore dust masks to eliminate exposure to the airborne soda ash particulates. The soil was ultimately classified as a hazardous waste under CDH's regulations and the 1100 cubic meters (1,450 cubic yards) was transported to Tower Landfill, just west of metropolitan Denver. Prior to the acceptance of this material, serious consideration was given to the effects that the soda ash may have on the clay liners present at the landfill. However, application figures indicated that the material would not produce any impact on the liner, and the material was transported to the facility.

SUMMARY

In summary, the TAT's responsibilities during the response and cleanup included air monitoring, development and implementation of sampling programs, assistance with decontamination procedures, evaluation of potential impacts of contamination, and provision of technical advice during multi-agency meetings. This spill incident provides an excellent example of multi-agency involvement in which local, state, and federal groups worked with the responsible discharger in the successful mitigation of a hazardous material spill. One of the factors that contributed to the effective and expeditious resolution of this serious incident was the prior training of groups designated as first-response agencies for chemical spills. Prior to this incident, EPA and the U.S. Coast Guard had conducted a "Scenario Spill Exercise" which depicted a hypothetical train accident in the downtown Denver area. The Scenario was presented to the local first-response agencies who were requested to respond according to their capabilities and authority. EPA and the U.S. Coast Guard showed foresight in understanding the importance of conducting trial exercises to ensure optimal preparedness for any chemical

emergency. This exercise proved to be a valuable precursor to the actual spill incident, in that it delineated each individual agency's area of responsibility and the necessity for interaction with other area responders.



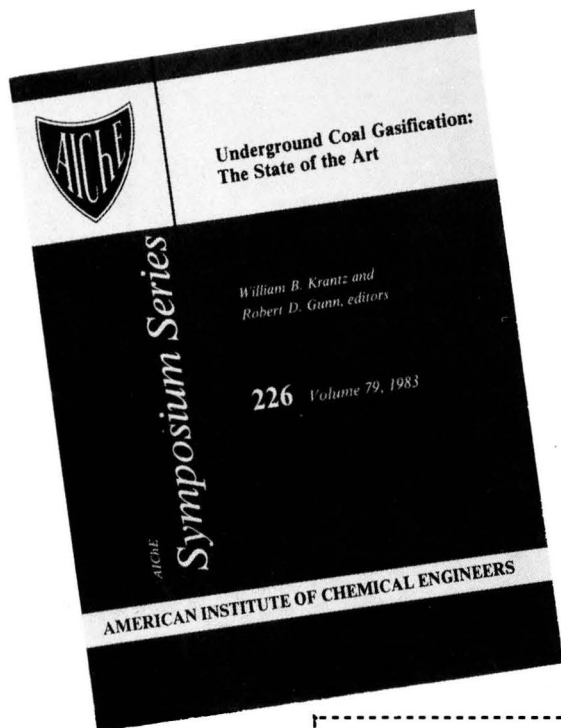
Thomas P. McVeigh graduated from Drexel University in 1972 with a B.S. in Civil Engineering. He owned and managed a construction company in Oregon for eight years. He was a member of the Technical Assistance Team (TAT), an emergency response and spill cleanup contractor to EPA, for four years; the last two as regional manager for the Denver office. He is presently employed by Jacobs Engineering Group, Inc. of Pasadena, California.



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John Zimmerman has more than nine years experience in the environmental field; five of which include work for U.S. EPA under the Field Investigation Team (FIT) and the Technical Assistance Team (TAT) contracts. He holds a degree in Environmental Science from Colorado State University in Fort Collins. He is currently employed by Jacobs Engineering Group in Denver, Colorado.

Underground Coal Gasification: The State of the Art



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- An Analysis of Permeation Models for *In Situ* Coal Gasification (Forward Combustion Mode)
- Sweep Efficiency Models for Underground Coal Gasification: A Critical Assessment
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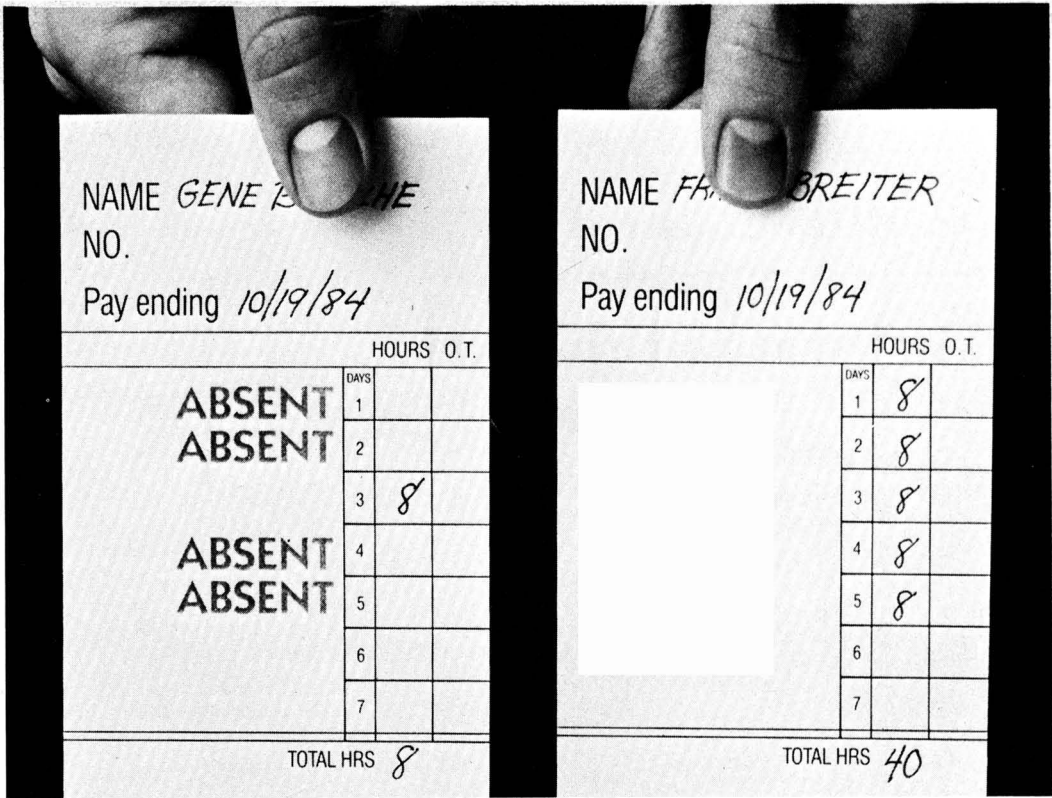
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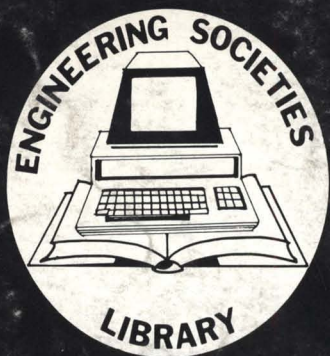
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