



NOVEMBER 1987

# ENVIRONMENTAL PROGRESS

# HANDBOOK OF AQUEOUS ELECTROLYTE THERMODYNAMICS

Theory & Application

Joseph F. Zemaitis Jr, Diane M. Clark, Marshall Rafal  
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**Cover: Laboratory-scale fluidized-bed bioreactor for treatment of coal gasification wastewaters. Photo courtesy T.L. Donaldson, Oak Ridge National Laboratory, Oak Ridge, Tennessee (see article on page 205).**

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# Landfilling of Hazardous Wastes: The End of an Era

Charles A. Wentz

Landfill has been the most commonly practiced method for disposal of waste materials in the United States. Many domestic generators have sent their hazardous wastes offsite for landfill disposal, since this was normally the least expensive alternative available. Generators were encouraged to landfill wastes by attractive economics and the short-sighted influence of government, industry, the general public and special interest groups. More recently, all concerned parties realize that the low initial costs of landfilling are merely a small portion of the true costs to human health and the environment. Many of the present day Superfund sites were acceptable landfills or surface impoundments for hazardous wastes in the past. Ultimately, this will cost taxpayers and consumers hundreds of billions of dollars more than what it would have cost to properly treat and incinerate the original hazardous wastes that have created the Superfund sites.

Refuse, trash and garbage are biodegradable in a sanitary landfill. For this reason, municipal landfills that have accepted only sanitary wastes should not present severe longterm threats to human health and the environment. The disposal of chemical substances in a landfill are an entirely different matter because of the persistence of many hydrocarbons and synthetic chemicals. These hydrocarbons and chemicals often require treatment or incineration to render them harmless.

Legislation and regulations are now in place to insure less adverse impact on human health and the environment from future landfill design, construction and operation. Because of poor management, however, by government and industry alike, there are numerous operating or abandoned landfills that were not designed under these more stringent regulations. Many of these older landfills have now become Superfund sites that must be remediated at tremendous costs to all concerned parties.

In the future, landfills for hazardous waste management will be more highly regulated than in the past. While significant cost increases are expected to begin to close the economic gap that has historically favored landfills, the lower initial cost of landfilling is expected to continue to provide a somewhat attractive alternative to other treatment and disposal techniques. Also, sanitary municipal landfills will become a more attractive target for hazardous waste disposal whenever relatively small, unnoticeable quantities of hazardous wastes can be incorporated into that disposal network.

Landfilling includes many factors that must be considered in the overall cost of disposal of hazardous waste.

- Capital investment for planning, design and construction.
- Operational and maintenance costs during the active service life.
- Closure costs at the end of the active service life.
- Maintenance and security costs for the postclosure period.
- Longterm liability costs which may occur at any time.

In order to obtain a true picture of disposal costs for landfilling hazardous wastes, an accounting must be made for all of the above factors. These individual cost segments should be analyzed through appropriate risk and probability assessment. These segments should then be discounted over the life of the project to obtain a true overall cost for the disposal of hazardous wastes. Even the most sophisticated, properly constructed and operated landfill will eventually leak to the detriment of human health and the environment. As a result, it is difficult to envision an economic situation that would favor landfill for longterm disposal of hazardous wastes that could otherwise be destroyed. Clearly, landfill technology should only be applicable for disposal of residual wastes that have no alternative treatment or incineration potential. While landfill capacity will continue to be needed in the United States to accommodate residual end products of our cradle to grave hazardous waste management system, other alternative disposal methods offer better solutions.

*Charles A. Wentz is currently manager of Technology Assessment at Argonne National Laboratory. He holds a PhD. in Chemical Engineering from Northwestern University and is the author of numerous technical papers related to the environmental field.*



## ERT To Manage Phase 2 Cleanup of New Jersey Superfund Site

ERT, Inc., a leading environmental consulting and engineering firm, is managing the second phase of cleanup of the Swope Oil Company Superfund site in New Jersey.

According to the EPA, the Swope Oil Company operated a chemical recycling operation from 1965 until it closed in December, 1979. Operations on the 2-acre site included the manufacturing and processing of oil, chemicals, chemical compounds and paints.

During active operations, waste liquids and sludge from the Swope Oil operation were discharged to an excavated unlined lagoon. Contaminated material was also ponded within a diked tank farm area and an exposed drum storage area. As a result of these operations, the property was listed as a Superfund site in 1983. The owner has declined to take action at the site due to limited finances. However, a group of potentially responsible parties (PRPs) have assumed responsibility for the cleanup.

ERT is managing phase 2 of the remediation program for the PRPs. ERT will direct the analysis of site soils to identify PCB contamination and oversee the excavation and disposal of PCB-contaminated soils found at the site. In addition, the company will oversee the contract for removal of forty-one above-ground tanks, an underground storage tank and septic tank, and an area of buried sludge disposal of two buildings.

Phase 1, which was conducted by the PRPs, involved the removal of contents from the site lagoon and drums from the surface of the site. Phase 2 is expected to be completed within the next two years.

## New Hazardous Waste Manual Available

A design manual entitled *Geosynthetic Design Guidance For Hazardous Waste Landfill Cells and Surface Impoundments*, by G. N. Richardson and R. M. Koerner has recently been published. The 247 page manual, which includes twenty-seven worked out example problems, was sponsored by U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio under Contract No. 68-03-3338. Included in the manual are an introduction to geosynthesis (geomembranes, geotextiles, geonets, geogrids, and geocomposites), design of linear systems beneath the waste cell, within the

cell as it is being filled, and above the cell after its capacity is reached. Sections on construction and fabrication considerations, long term service considerations and appendices are also included. The main appendix summarizes all of the test materials used in solid waste impoundments and disposal. The manual is available for \$40 domestic (\$50 foreign) from: Geosynthesis Research Institute, Drexel University, West Wing-Rush Building (#10), Philadelphia, PA 19104. Attn: Mrs. Marilyn Ashley. Checks should be made payable to "Geosynthetic Research Institute."

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(Continued on page N6)

# Washington Environmental Newsletter

## **National Dioxin Study Released**

EPA has recently announced the results of a two year Dioxin Report to Congress. This report gathered information on the extent of dioxin contamination in the country. Because of media and news stories that have appeared over the last few months on dioxin in paper products, the EPA pushed forward the release date of the study to help state environmental officials and state health officials answer questions from the public about dioxin in their respective states. Space limitations of this column prohibit any detailed discussion of findings, but you may obtain a full copy of the report by writing or calling this office (address and telephone number appear at the bottom of this page).

## **EPA Acts on Air Emissions**

EPA is now requiring controls on air emissions from MSW incinerators because available technologies can substantially reduce risks associated with these emissions. Conservative risk assessment shows that potential health risks to the public are generally small, but of enough concern to justify regulation. EPA will also propose guidelines to states for use in developing performance standards for all existing facilities, calling for the use of best available technologies. State implementation is subject to EPA approval and the agency can issue regulations for existing facilities if the states fail to act. EPA found that a combination of proper combustion conditions, an acid gas scrubber and particulate-matter-collection devices can reduce dioxins and furans by greater than 99%; other organics by more than 95%; HCl by 90%; and metals by 97 to 99%.

## **Congressional Hearing Held on MSW Incinerators**

Congressman Henry Waxman, Chairman of the House Health & Environmental Subcommittee, is evidently *not* satisfied with EPA's current regulatory stance on MSW incinerator emissions. Waxman opened the hearing by stating that "almost every incinerator in the country releases a mix of hazardous air pollutants that include three known human cancer causing substances, and eight probable human carcinogens, as well as mercury and lead." He supports Congressman Florio's bill HR 2787 that would require federal standards to regulate emissions of MSW incinerators. Florio's bill would require EPA to set emissions standards within one year for "some two dozen toxic air pollutants, including dioxins, PCB's, lead and other toxic substances."

Of ten witnesses (from both sides of the question) only EPA's Don Clay was questioned. In summary, Clay said that Section 111 of the Clean Air Act will be more than adequate to achieve this outcome without need for further regulation and that setting individual performance standards would be needlessly burdensome and time consuming. Further, he stated that adequate emission data are not available for some of the pollutants and that mandatory recycling is "problematic." He also said that the Florio bill would force some resource recovery systems to close and that continuous monitoring of emissions is not necessary.

It was clear that the Congressmen have limited confidence that EPA will take any aggressive actions during the remainder of the Reagan Administration. This office will continue to monitor actions on HR 2787.

*This material was prepared by AICHE's Washington Representative, Siegel • Houston & Associates, Inc.  
Suite 333, 1707 L Street, N.W., Washington, D.C. 20036. Tel. (202) 223-0650*

## 598 Waste Burning Projects Now in Construction and Planning Stage

The United States is decades behind European countries in terms of burning its garbage and waste but a combination of factors has culminated in a burst of activity. Presently the construction of waste burning plants is one of the major opportunities for manufacturers of boilers, fans, instrumentation and air pollution control equipment. In a report which is updated monthly entitled "Waste Burning Projects and People," the McIlvaine Company of Northbrook, Illinois is presently tracking 598 projects burning more than 40 tons per day which are in the construction or planning stage. This does not include nearly 200 projects which have already started full operation and are contained in a separate data base. New plants with an aggregate capacity of more than 40,000 tpd are scheduled for startup in each year in the 1988-1990 period. While the majority of the fuel being burned in these plants will be municipal garbage, there is a variety of other waste materials including anthracite

coal, wood waste, tires and various biomass wastes.

In terms of distribution of planned facilities among the various states, the largest number in the planning and construction stage is in California, where 74 projects are listed. Many of these projects involve municipal garbage and resource recovery. Several large tire burning plants are in the planning stage. Because of the large agricultural industry in California, projects are also planned where orchard prunings and their agricultural wastes are the planned fuel. One project is planning to generate 27 MW from the burning of cow manure. The second largest is Pennsylvania where coal mine wastes are available as fuel.

These 598 projects will require billions of dollars invested in grates, boilers, material handling, heat recovery and air pollution control systems. These plants already represent a substantial percentage of the order backlog for many U.S. companies and offer the largest immediate sales potential for many others.

## Biotechnology Impacts Environmental Contaminant Monitoring

A recent study of the economic impacts of biotechnology reveals many potential effects beyond those previously recognized. Overshadowed by the well-publicized benefits in human health care and agriculture are a number of developments which will heighten public awareness of potentially harmful contaminants in U.S. food, air and water supplies.

According to Consulting Resources Corporation, Lexington, MA which carried out the study, this heightened public awareness is

likely to lead to new restrictions affecting food companies, food importers, pesticide and other chemical producers, refineries, solvent users and office workers, among others. In fact, the recent Labor Department decision to order a 90 percent reduction in the allowable workplace exposure to the cancer-causing chemical benzene represents the beginning of a new phase of increased chemical monitoring and control which will extend into the next decade.

## New Orleans National Meeting

March 6-10, 1988

### Group 9: Environmental

Group Chairman: B. Mo Kim, General Electrical Co., P.O. Box 8, Bldg., K-1, Schenectady, NY 12301 (518/387-6596); Program Coordinator: Aysel Atimtay, Dept. of Chem. Eng. Tulane Univ.,

New Orleans, LA 70118 (504/865-5772)

**Area 9a: Air** — Area Coordinator: Richard D. Siegel, ERT, Inc., 696 Virginia Rd., Concord, MA 01742 (617/369-8910)

**Atmospheric Emissions from Refinery and Petrochemical Industries** — Chairman: Aziz A. Siddiqi, Resochem Corp., P.O. Box 669, Houston, TX 77001 (713/999-6111)

**The Ozone Non-Attainment Issue: Regulatory and Industry Perspective** — Chairman: Louis R. Roberts, 8611 Honeysuckle, Austin, TX 78759 (512/338-0337)

**Fugitive Emissions of Volatile Air Toxic Compounds from Chemical Facilities** — Chairman: Peter H. Anderson, ERT, Inc., 696 Virginia Rd., Concord, MA 01742 (617/369-8910)

### Area 9b: Water

**Causes and Cures for Groundwater Pollution Due to Land Disposal** — Chairman: Robert C. Knox, Univ. of Oklahoma, Civil Engineering Dept., 202 West Boyd St., Room 334, Norman, OK 73019 (405/325-4256)

**Biological Waste Treatment in Chemical Industries** — Chairman: Manuel P. DelPino, Union Carbide, Inc., P.O. Box 8361, Technical Center (770-Rm. 356), South Charleston, WV 25303 (304/747-5560)

**In-Plant Modifications for Waste Treatment** — Chairman: Andrew Englande, Jr., Dept. of Environmental Health Science, Tulane Univ., 1501 Canal St., Room 1507, New Orleans, LA 70112 (504/588-5374)

### Area 9c: Solid Wastes

**Alternative Treatment and Destruction Methods for Hazardous Wastes** — Chairman: F. Carl Knopf, Dept. of Chem. Eng., Louisiana State Univ., Baton Rouge, LA 70803-7300 (504/388-1426)

**Solid Waste Handling and Disposal** — Chairman: Robert E.C. Weaver, International Matex Terminals, 321 St. Charles Ave., New Orleans, LA 70130

**Incineration of Hazardous Wastes** — Chairman: Aysel T. Atimtay, Chem. Eng. Dept., Tulane Univ., New Orleans, LA 70118 (504/865-5772)

**Alternatives to Refinery Waste Disposal** — Chairman: Louis J. Thibodeaux, Chem. Eng. Dept., Louisiana State Univ., Baton Rouge, LA 70803-7300 (504/388-1426)



# Biooxidation of Coal Gasification Wastewaters Using Fluidized-Bed Bioreactors

Terrence L. Donaldson, Gerald W. Strandberg, Jimmie D. Hewitt,  
Glenna S. Shields, and R. Mark Worden

Chemical Technology Division, Oak Ridge National Laboratory,\* Oak Ridge, Tennessee 37831

*Process condensate wastewaters from two fixed-bed gasifiers have been treated successfully using a laboratory-scale, fixed-film, fluidized-bed bioreactor. Both dilute (1 to 2% raw wastewater) and more concentrated (50% stripped wastewater) were treated continuously for periods of one to three months. Biological activity was stable, recovery from upsets was rapid, and reaction rates were high due to the high concentration of microorganisms retained on the support particles. Removal of phenolics exceeded 99%, and removal of chemical oxygen demand was typically 75 to 85% for the 50% stripped wastewater with a hydraulic residence time in the bed of ~5 to 7 h. Sludge production rates were comparable to rates in suspended growth systems.*

## INTRODUCTION

Most coal gasification processes will use large quantities of water and generate wastewaters that require treatment prior to discharge or reuse. A major wastewater source in many gasification processes is the raw quench condensate. These wastewaters are characterized by high concentrations of suspended solids, ammonia, organics (notably phenols), tars, and oils. Treatment of wastewaters from synthetic fuels plants may require a train of operations such as clarification, extraction of tars and oils, hydrogen sulfide and ammonia stripping, removal of organics, and final polishing [1-3].

The major portion of the dissolved organics can be removed by biooxidation. Fixed-film, fluidized-bed bioreactors, which are being developed at Oak Ridge National Laboratory [4-7] (ORNL) and elsewhere [8, 9], offer several advantages relative to conventional biooxidation technologies. Relatively high concentrations of cells can be retained in the bioreactor as immobilized

films on the support particles, which leads to high reaction rates at low hydraulic retention times. This is somewhat analogous to long solids retention times via cell recycle in conventional suspended-growth systems. The columnar configurations of fluidized-bed bioreactors promote optimal hydraulic behavior. In addition, these bioreactors typically exhibit improved resistance to environmental stress and improved process stability relative to suspended-growth processes. These features are directly related to the immobilized films of microorganisms. The "washout" phenomenon that plagues suspended-growth systems does not occur because the microorganisms are immobilized. Biofilms tend to be more resistant to variations in substrate concentrations, toxic chemicals, heavy metals, etc. It is believed that the outer surfaces of the films absorb the insult and thus protect the inner regions of the films, which can then quickly reestablish normal bioactivity once the stress condition has passed. Several experimental studies have supported these hypotheses [10, 11].

Recognition of these potential advantages and recent process development work have led to increased utilization of fluidized-bed bioreactors for a variety of wastewater treatment applications. Previous work at ORNL [12, 13] using a laboratory-scale bioreactor has established that fluidized-bed bioreactors work well for biooxidation of dilute coal gasification wastewaters, and can produce effluent water with <1 mg/L of phenols. In this report, we describe the continuous treatment of dilute

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\* Operated by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy, under Contract No. DE-AC05-84OR21400.

and 50%-strength actual wastewaters from two coal gasification plants. The principal objective was to determine if relatively high-strength wastewater could be treated directly with minimal dilution and high degradation rates to simulate the front-end portion of a large-scale biooxidation process.

## EXPERIMENTAL PROCEDURES

**Coal gasification wastewaters:** Raw condensate wastewaters were obtained from the Holston Army Ammunition Plant in Kingsport, Tennessee, and from the Morgantown Energy Technology Center in Morgantown, West Virginia. Characteristics of these wastewaters are shown in Table 1.

The Holston plant has 12 air-blown Wilputte® fixed-bed gasifiers that produce low-Btu gas. Wastewater was collected from the decanter in 210-L drums, transported immediately to ORNL by truck, and stored at 4°C with no further treatment.

Wastewater from the fixed-bed gasifier at Morgantown was shipped to ORNL in 210-L drums by common carrier. The wastewater treated in this study was obtained from the recirculating decanter during air-blown gasification of a Blacksville (bituminous) coal, Test Run No. 102. It was stored at 4°C with no further treatment. Prior to biotreatment, the wastewater was passed through a cartridge fiber filter to remove a significant quantity of oil (~2%). Dilute wastewaters (<5%) could be treated without stripping to reduce sulfides and ammonia since dilution with process water lowered these inhibitors to noninhibitory levels. Stripping was necessary for treatment of higher-strength wastewaters.

The stripping unit consisted of a ~200-L stainless steel drum connected to a small reflux column of 0.6-cm Berl saddles and a partial condenser. Approximately 100 L of wastewater was transferred to the stripper and heated to ~90°C using band-type barrel heaters. Nitrogen gas was then introduced at the bottom at a flow rate of 15 L/min. After stripping for 8-9 h, the ammonia concentration decreased to ~1,500 and 2,000 mg/L from initial values of 15,000 and 16,000 mg/L, respectively, for two separate batches. The sulfides concentrations for both batches were reduced from 200-400 mg/L to <1 mg/L. After stripping, the wastewater was allowed to cool to ambient temperature and transferred to the bioreactor feed reservoir. Supplementary mineral salts and micronutrients were added prior to introducing the wastewater to the bioreactor.

**Bioreactor design:** The laboratory-scale bioreactor, shown in Fig. 1, was a 5-cm ID and 1.5-m tall glass column with a water jacket for temperature control, a solids disengaging zone at the top, and an angled effluent dis-

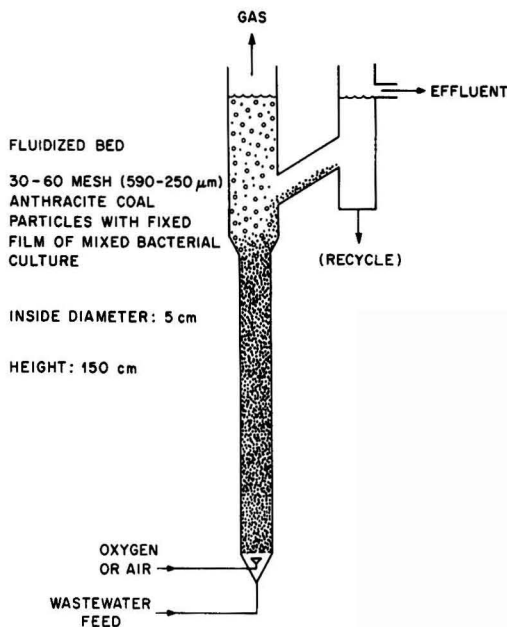


Figure 1. Fixed-film, fluidized-bed bioreactor

charge arm to allow solids to return to the main column. Recycle of solids or liquid was possible if desired. Total liquid holdup was ~10 L. An alternate configuration was used with 50%-strength wastewater in which the liquid effluent was taken from the RECYCLE location (see Fig. 1). This arrangement lowered the liquid to the overflow level in the angled side arm and reduced the liquid holdup to ~6 L.

The solid support particles were 30-60 mesh anthracite coal. Considerable earlier work at ORNL with other biological fluidized-bed applications indicated that anthracite coal is effective for retaining stable fixed films. Coal is less dense than sand (another common support), which allows fluidization at a lower liquid velocity and hence permits a smaller reactor for a given contact time. It also offers the potential advantages for coal gasification plants of being readily available (presuming other coals will work as well as anthracite) and of being readily disposable in the gasification process.

A minimum liquid flow rate of ~24 L/h was necessary to fluidize the bed and to allow adequate gas flow without slugging. This corresponds to a superficial linear velocity of ~13 m/h. The bioreactor was generally operated at a liquid flow rate of 35 to 40 L/h to improve liquid-solid mass transfer. Pure oxygen gas was introduced at the bottom of the bioreactor through a metal frit at a flow rate ~50% of the liquid flow rate, which was sufficient to maintain 1 to 2 mg/L of dissolved oxygen in the liquid phase in the bed. Use of air instead of pure oxygen caused a decrease in the reaction rate, presumably because of oxygen limitations. The bioreactor was equipped with a dissolved oxygen probe and a pH probe.

**Microbial cultures:** Phenobac® (Polybac Corporation, Berlin, N.J.) was selected as the inoculum. Earlier work at ORNL indicated this culture was effective for phenol degradation in a fixed-film mode [6]. A mixture of BICHEM® 1001 and 1002 (Sybron/Biochemical, Salem, Va.) also was evaluated [12]. Once fixed films are established on coal particles, samples of the cultures are readily preserved by lyophilization. The bioactivity of the cul-

TABLE 1. CHARACTERISTICS OF RAW WASTEWATERS<sup>a</sup>

Parameter	Holston	Morgantown
COD, mg/L	23,600	50,000
TOC, mg/L	6,800	6,700
pH	7.9	8.5
Phenols, mg/L		
4-AAP	2,300	6,000
HPLC	3,900	8,800
Resorcinol	940	(none detected)
Phenol	1,240	3,700
<i>m,p</i> -cresol	1,390	3,960
<i>o</i> -cresol	340	1,140
Ammonia, mg/L		15,000
Sulfides, mg/L		200-400

<sup>a</sup> Before stripping; see text for results of stripping.

tures was stable in the fluidized-bed bioreactor, and no supplementation/reinoculation was necessary.

**Analytical Techniques:** Five-milliliter samples of influent and effluent were collected and filtered immediately through a 0.45- $\mu$ m filter (Millipore). Analyses were usually done immediately; however, freezing and storage of the samples for several days had no effect on the phenol assay. Phenols were routinely determined colorimetrically using the 4-aminoantipyrine (4-AAP) method [14]. Chemical oxygen demand (COD) was determined using the Hach procedure [15]. Total organic carbon (TOC) was determined using a Beckman 915A TOC analyzer. Polyhydric phenols were determined periodically by high-pressure liquid chromatography (HPLC) [16] and by gas chromatography. A 2-mm ID, 1.8-m long glass column packed with 60- to 80-mesh Tenax GC (Alltech Assoc., Deerfield, IL), operated isothermally at 190°C, was used to separate the phenols. Ammonia and sulfides were estimated using CHEMets water analysis test kits (CHEMetrics, Inc., Warrenton, Va.). Total suspended solids (TSS) and volatile suspended solids (VSS) were determined according to methods 208D and 208E in *Standard Methods for the Examination of Water and Wastewater* [17].

**Bioreactor start-up:** The start-up procedure was based on experience at ORNL and consultations with vendors such as Sybron. First, the bioreactor was filled with clean coal plus a synthetic phenol feed solution containing ~0.2% whey and 0.2% dibasic sodium phosphate, and an inoculum of the culture was added. The bioreactor was then operated at total recycle at ~24 L/h. Phenol was added periodically to maintain a concentration of 50 to 100 mg/L. After ~4 d at 30°C, films could be seen on the coal with the aid of a microscope. At this point, a gradual change from total recycle to zero recycle was implemented over a several-day period while a constant flow rate of ~24 L/h through the bed was maintained. The growth of the films continued for 1 to 2 weeks, at which time a durable film was achieved. Thereafter, excess cell mass was shed naturally due to the mechanical shearing action; heavily loaded particles were removed occasionally from the top of the bed by aspiration and from the built-in clarifier when no recycle was employed. In addition, it is practical to shear excess films from the coal in a separate device if necessary [7]. This start-up procedure has also been successfully demonstrated using coal-biomass inocula that were removed from the operating reactor several months earlier and stored as lyophilized preparations.

To minimize stress on the culture, actual wastewaters were initially diluted to ~1% with process water as they were fed continuously to the bioreactor. The wastewater strength was increased gradually over ~3 weeks by reducing the process water diluent, and effluent recycle was initiated with higher-strength wastewaters to maintain the desired concentration of phenols in the bioreactor.

**Batch kinetic studies:** Batch kinetic studies were carried out in 500-mL Erlenmeyer flasks that were baffled at the base to promote mixing. Biomass-laden coal was removed from an operating bioreactor and washed three to five times with a mineral salts medium. Samples of 5 to 20 mL (settled volume) of the washed biomass-coal particles were combined with mineral salts medium to a volume of 90 to 95 mL in the flasks and agitated at 165 rpm in a temperature-controlled water bath. Air or O<sub>2</sub> (~5 L/h) was introduced through a tube extended below the liquid level. After temperature equilibration (5 to 10 min), phenol or wastewater was added to initiate the reaction. Aliquots were removed from the reaction flasks at intervals, briefly centrifuged to remove particulates, and analyzed for residual phenols using the 4-AAP assay.

## RESULTS

**Bioreactor performance:** The fluidized-bed bioreactor was operated under several different conditions to simulate segments of a commercial-scale biotreatment process. It is obviously desirable to operate a commercial process with minimum recycle to reduce liquid handling costs. This condition was investigated experimentally for high-strength wastewater at the expense of poor effluent quality. After start-up on synthetic wastewaters, dilute actual wastewaters were used to simulate the downstream treatment, and then several campaigns were conducted with more concentrated wastewaters to simulate the front-end of a biotreatment train.

Treatment of the Holston and Morgantown wastewaters was characterized primarily in terms of removal of phenolics. Reduction in COD was also monitored periodically. The reaction rate in the fluidized bed was expressed on a volumetric basis as the amount of phenolics degraded per unit time per volume of settled bed. The equation is:

$$\text{degradation rate} = (C_{in} - C_{out}) \times Q/V,$$

where  $C_{in}$  and  $C_{out}$  are the concentrations of phenolics entering and leaving the fluidized bed, respectively;  $Q$  is the volumetric flow rate of wastewater through the bed; and  $V$  is the settled bed volume in the absence of gas and liquid flow. The expanded bed volume during operation was typically 50% greater than the settled bed volume.

Typical bioreactor performance with diluted Holston wastewater is shown in Tables 2 and 3. In these experiments, the raw (unstripped) wastewater was diluted to 1 to 2% with process water as it was fed to the bioreactor. Prior to introduction of the Holston wastewater, the bioreactor had been operated on synthetic wastewater for several months. The dilute Holston wastewater was treated continuously for ~6 months as described above, with no operating difficulties or bioreactor instability. No liquid recycle was used. The phenolics degradation rate

TABLE 2. TREATMENT OF DILUTE HOLSTON WASTEWATER USING FLUIDIZED-BED BIOREACTOR<sup>a</sup>

Phenols concentration (mg/L)		Phenols degradation rate (mg/L bed · min)
Influent	Effluent	
20	2	7
33	4	11
32	13	9
66	23	11
83	39	12
95	58	12

<sup>a</sup> Bed volume, 1.7-2.8 L; temperature, 30°C; flow rate, 0.75-0.85 L/min; phenols determined by 4-AAP; no recycle; typical grab samples over a 6-month period.

TABLE 3. TYPICAL DEGRADATION OF INDIVIDUAL PHENOLS IN HOLSTON WASTEWATER<sup>a</sup>

Constituent	Concentration (mg/L)			Percentage degraded
	Raw wastewater	Bioreactor influent	Bioreactor effluent	
Resorcinol	942	18	14	22
Phenol	1236	32	8	75
<i>m,p</i> -cresol	1390	29	16	45
<i>o</i> -cresol	341	7	5	29

<sup>a</sup> Bed volume, ~2.8 L; temperature, 30°C; flow rate, 0.74 L/min; no liquid recycle; phenols determined by HPLC.



was typically 5 to 15 mg/L bed · min, depending on the condition of the culture. Growth of biomass caused bed expansion and necessitated removal of ~10% of the bed approximately twice per week. The more heavily loaded particles were more buoyant and thus rose to the top of the bed, where they were removed by aspiration. Clean coal was added after bioparticles were removed. The average solids retention time was ~5 weeks. Hence the biomass quantity was variable and led to variations in the degradation rate. Thin films were more active on a volumetric basis; the volumetric degradation rate was high shortly after clean coal was added, and low just before excess solids were removed.

Dilute Morgantown wastewater (filtered but unstripped) was treated in a similar manner. Typical operating data over several months are shown in Table 4. Partial effluent recycle was initiated in preparation for treatment of higher-strength wastewater. The recycle ratio is defined as the fraction of the effluent recycled to the bioreactor inlet to be mixed with fresh feed, divided by the fraction of effluent discharged from the bioreactor system. The phenolics degradation rates for Morgantown wastewater (Table 4) are similar to the rates for Holston wastewater (Table 2), and both rates are comparable to rates obtained with synthetic wastewater containing only monohydric phenol. No inhibition of biological activity was seen under these conditions.

TABLE 4. TREATMENT OF DILUTE MORGANTOWN WASTEWATER USING FLUIDIZED-BED BIOREACTOR<sup>a</sup>

Total phenolics concentration (mg/L)		Effluent recycle ratio	Degradation rate (mg/L bed · min)
Influent	Effluent		
25	3	3.0	9
40	8	0.7	12
38	12	1.6	16
39	19	1.3	9
52	25	0.5	11
66	35	0.7	10
65	41	3.7	10
147	129	3.7	8
202	180	3.7	11

<sup>a</sup> Bed volume, 1.3-1.7 L; temperature, 30°C; flow rate in bed, 0.52-0.87 L/min; phenols determined by 4-AAP; grab samples over several-month period.

TABLE 5. TREATMENT OF HIGHER STRENGTH MORGANTOWN WASTEWATER USING FLUIDIZED-BED BIOREACTOR<sup>a</sup>

Feed concentration, striped wastewater (%)	Phenolics degradation rate <sup>b</sup> (mg/L bed · min)	COD degradation rate (mg/L bed · min)	COD removal (%)
34	5	24	80
36	6	25	80
100	5	32	87
55	8	33	87
52	11	32	85
83	8	32	87
83	4	30	81
52	6	28	77
52	9	27	75
52	7	27	75
50	9	32	87
50	4		

<sup>a</sup> Bed volume, 1.3-2.0 L; liquid recycle, 0.6 L/min; oxygen flow rate, 85-130 mL/min; temperature, ~30°C; grab samples over a 3-week period.

<sup>b</sup> Phenol concentrations (4-AAP) in the bioreactor were generally 20-60 mg/L. Removal of phenols was >99%, as determined by HPLC analysis.

In several short-term campaigns, it was demonstrated that effluent phenolics concentrations of <1 mg/L could be readily achieved. The small fluidized-bed volume (1 to 2 L) required that the inlet concentration of phenolics be ≤10 mg/L or lower in order to achieve this effluent concentration. The reaction kinetics appear to follow a conventional saturation model [12] with a half-velocity constant ( $K_{1/2}$ ) for phenol of 1 to 5 mg/L, which is consistent with other published kinetic studies for suspended growth systems [18].

Stripped and filtered Morgantown wastewater was successfully treated up to 50% strength (Table 5) for several weeks, with sufficient recycle to maintain the phenols concentration at <100 mg/L in the fluidized bed. On several occasions, 80 to 100% wastewater was fed to the bioreactor for short periods during mechanical malfunctions. However, the hydraulic residence time in the total reactor system was 15 to 20 h, which moderated the effects of the brief periods of higher strength wastewater. Shedding of films occurred in these instances (discussed later), but the bioreactor recovered quickly.

The phenolics degradation rate was somewhat lower than the rate for dilute wastewater. Gas chromatographic (GC) analysis showed that the actual total concentration of phenol, *o*-cresol, and *m,p*-cresol was in the range of <1 to 5 mg/L in the effluent, which is substantially lower than the 20 to 40 mg/L indicated by the 4-AAP assay. However, the degradation rates were essentially the same based on changes in 4-AAP-reactive material and GC-analyzed phenols, which suggests that other components in the wastewater interfere with the 4-AAP assay for phenols. More than 99% of the GC-measured phenols were degraded.

Reduction of COD was ~75 to 80%. Effluent COD concentrations were generally in the range of 1150 to 2500 mg/L, and appeared to increase with feed strength. The theoretical COD for monohydric phenol is ~2.4 g O<sub>2</sub>/g phenol. Thus a comparison of the phenol and COD degradation rates in Table 5 indicates that about two-thirds of the COD reduction is attributable to phenol degradation, while one-third is attributable to biodegradation of other species.

Mild foaming occurred at wastewater strengths shown in Table 5. Foaming could be controlled with small quantities of Dow Corning Antifoam B<sup>®</sup> emulsion, or with a fine spray of water at the top of the bioreactor. It has been reported that foaming is reduced when the phenols are extracted prior to biooxidation [1].

The bioreactor was successfully operated for ~1 week with the phenolics concentration in the 500 to 900 mg/L range and 50%-strength stripped wastewater. These conditions are potentially representative of the front-end portion of a commercial-scale treatment process. The results of analyses of grab samples of influent and effluent are shown in Table 6. The phenolics degradation rates were comparable to those obtained previously at much lower phenolics concentrations (see Table 5). However, the COD degradation rates were ~50% lower than those reported in Table 5. The reason is unknown.

**Batch kinetic tests:** Experiments were performed to determine maximum degradation rates of monohydric phenol and wastewater phenols under more favorable, controlled conditions with an excess of dissolved oxygen. High initial degradation rates of 35 to 40 mg/L bed · min in all cases indicated that the acclimated culture was equally active on synthetic substrates and actual wastewaters. Preliminary batch treatability tests with Morgantown wastewater and unacclimated cultures showed degradation rates of 20 to 25 mg/L bed · min. However, the batch reaction rates were substantially greater than the rates in the continuous bioreactor. This same phenomenon had been noted earlier with synthetic feeds [12]. These results suggest that mass transfer of phenols and/or

TABLE 6. PERFORMANCE OF BIOREACTOR AT HIGH PHENOLICS CONCENTRATION<sup>a</sup>

Feed strength (%)	Phenolics <sup>b</sup> (mg/L)	Phenolics degradation rate <sup>c</sup> [mg/(L bed · min)]	Phenolics removal (%)	COD (mg/L)	COD degradation rate <sup>c</sup> [mg/(L bed · min)]	COD removal (%)	Organic carbon (mg/L)	Organic carbon degradation rate <sup>c</sup> [mg/(L bed · min)]	Organic carbon removal (%)
53	498	11	78	3792	27	54	1000	9	57
46	838	8	58	5713	10	21	1360	5	31
51	955	8	57	5646	14	29	1420	6	35
49	729	8	66	5192	15	32	1330	6	36
47	808	7	60	5257	12	29	1290	5	36
47	748	7	63	5133	12	30	1300	5	35

<sup>a</sup> Bed volume, 1.23 L; feed flow rate, 0.007 to 0.008 L/min; liquid recycle, 0.74 L/min; temperature, 27 to 28°C; O<sub>2</sub> flow rate, ~100 cc/min; grab samples over a 1-week period.

<sup>b</sup> Analyzed by gas chromatography.

<sup>c</sup> Degradation rates obtained from overall material balance on bioreactor system; the change in concentration across the bed is small relative to the concentration, and cannot be directly determined accurately.

oxygen is limiting the reaction rates in the fluidized-bed bioreactor. Increased reaction rates may be possible with improved bioreactor design and/or operating conditions.

**Sludge production:** An estimate of the sludge production rate can be obtained from the concentration of solids in the effluent and accumulation of biomass in the bioreactor. Effluent TSS and VSS concentrations were determined over a 25-d period in which 50% Morgantown wastewater was being treated. Negligible increase in bed volume occurred under these conditions and hence accumulation of biomass in the bioreactor can be assumed to be negligible.

The total suspended solids in the effluent shown in Fig. 2 are based on daily grab samples over a 25-d period, and those in Fig. 3 are based on the total effluent over a 10-h period. The normal concentration of dry solids appeared to be around 30 to 40 mg/L, but higher TSS values were common. Normal shedding of biomass, washout of materials with fluctuations in flow rates, and a variety of other factors are responsible for high solids outputs. The large discharge of solids over days 10-15 (see Fig. 2) are believed to be related to a pulse of full-strength wastewater on approximately day 10. Integration of the data shown in Fig. 2 leads to an average dry solids concentration of 55 mg/L in the bioreactor effluent. Similarly, the data in Fig. 3 are indicative of an average value of 51 mg/L. The VSS content was consistently ~90% of the TSS value. In addition, it was determined that ~0.1 g/d of dry volatile solids were discharged with the effluent but set-

tled out and were not included in the data displayed in Figs. 2 and 3. With an average effluent TSS value of 55 mg/L and an average effluent flow rate of 4.5 mL/min, the total estimated dry sludge production was 0.47 g/d.

During the sludge production study, the average phenol degradation rate was 7.3 mg/L bed · min and the settled bed volume was steady at 1.3 L, so that 13.7 g/d of phenol was degraded. Overall sludge production during the study was therefore 0.034 g dry solids/g phenol degraded, or ~0.34 g wet sludge/g phenol degraded. This value is typical of cell yields in suspended growth systems [18].

#### PROCESS STATUS AND EVALUATION

The fluidized-bed bioreactor is a proven technology in several applications, and is growing in use. For biooxidation of coal gasification wastewaters, we have found that the fluidized-bed bioreactor will operate continuously and remain stable over long periods of time. Continuous stable operation has been achieved experimentally for periods of months. Prolonged pulses or spikes of organics may cause temporary inhibition of biological activity, but the activity returns within 1 to 2 days. Similarly, biological activity picks up quickly after downtimes with no carbon substrate and no hydraulic flow.

High-strength wastewater (50% process condensate wastewater) can be treated successfully after stripping to remove ammonia and sulfides. The reaction rate appears to be reduced slightly compared to more dilute waste-

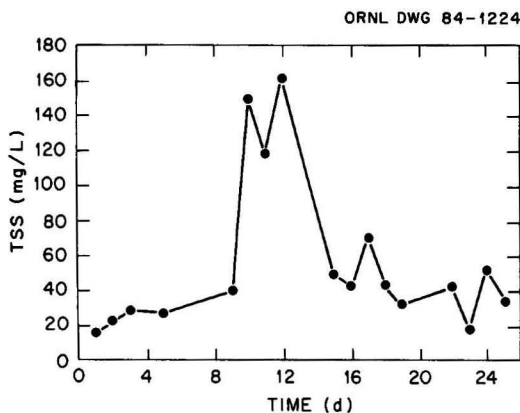


Figure 2. Total suspended solids in bioreactor effluent, as determined from daily grab samples.

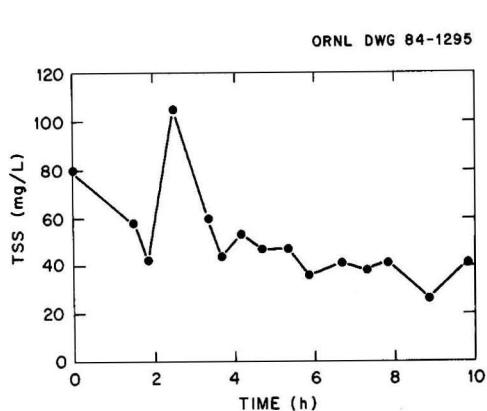


Figure 3. Total suspended solids in total bioreactor effluent over a 10-h period, measured in 100 to 200 mL fractions of effluent.

waters; however, the distinction between this effect and dependence on dissolved oxygen is not yet resolved. High-strength wastewater appears to slow the growth of biofilms and hence reduce the sludge for ultimate disposal compared to more dilute wastewaters. Sludge production appears to be comparable to that for suspended growth systems, such as activated sludge.

Dissolved organics in addition to phenols are degraded, as evidenced by decreases in COD and TOC in excess of the contributions from phenolics. The degradation rates depend upon the biofilm loading and characteristics (thin, dense films are best). Typical volumetric degradation rates are 10 mg phenolics/L bed · min with real wastewater at 25 to 30°C. This is  $\sim 2 \times 10^{-5}$  g phenol/g biomass · s, which is comparable to specific rates in activated sludge systems for biooxidation of phenolics in actual wastewaters [2]. Under controlled conditions and special efforts to maintain high concentrations of dissolved oxygen, rates of 20 and 100 mg phenolics/L bed · min have been obtained with actual and synthetic wastewaters, respectively. For comparison, laboratory-scale activated sludge systems with sludge recycle may exhibit volumetric phenol removal rates of 3 to 4 mg/L · min [2, 19]. Thus there is the potential for a five- to tenfold increase in the degradation rate with the fluidized-bed bioreactor under favorable operating conditions. This increase is due primarily to high concentration of microorganisms. The biomass loading on the support particles is typically >0.01 g VSS/g coal, which is equivalent to 5,000 to 10,000 mg/L of MLVSS in a suspended growth system without the need for cell recycle.

**R&D needs:** Maintenance of sufficient dissolved oxygen in the liquid phase to allow maximal reaction rates is a significant problem. The demand for oxygen is high. On a mass basis,  $\sim 2.4$  grams of oxygen are needed per gram of phenols to be degraded. Thus, the oxygen demand rate is  $\sim 25$  g/L bed · min, which is difficult to supply when the solubility of oxygen is only  $\sim 40$  mg/L (or less) at a partial pressure of 1 atmosphere. It is probable that oxygen will need to be supplied throughout the fluidized bed, by sparging or other means; presaturation of the feed will probably not be sufficient. This issue is particularly important because the overall degradation rate is quite sensitive to maintaining sufficient oxygen.

Occasional foaming and clumping of the bioparticles have been experienced. Foaming can be controlled in the laboratory bioreactors with the use of antifoam compounds. Clumping of the bioparticles, which leads to a loss of fluidization and severe channeling of liquid, was circumstantially related to buildup of unknown chemicals in the bioreactor; the problem was solved in the laboratory bioreactor by removing the agglomerated material and flushing the fluidized bed briefly with process water. These phenomena need to be investigated in larger scale equipment.

Physical characteristics of the biofilms, probably related to biological characteristics, appear to be related to biological activity. Denser biofilms, presumably containing more microorganisms and less "glue," are more active [20]. It is not known how to favor and promote such films. Circumstantial evidence suggests, not surprisingly, that environmental conditions such as nutrient levels play a role. There is much to be learned about biofilms to enable an engineering design approach.

**Economics:** The potential economics of the fluidized-bed bioreactor process were compared with a conventional activated sludge process outlined by other investigators [21]. The comparison of conceptual designs [13] indicated that the fluidized-bed process might require half the capital investment and half the operating costs of an activated sludge process. The principal reason for these lower costs is the higher reaction rate in the fluidized bed, which requires smaller reactor volume.

The key issues governing the costs for the fluidized bed process were (a) the strength of the wastewater to be treated, which affects reactor volume and recycle requirements; and (b) the reaction rate. The process design called for treatment of 50% strength wastewater in the front end of the biotreatment process. The technical feasibility of this strategy has been demonstrated.

The conceptual process design was also based on a degradation rate of 20 mg phenolics/L bed · min in the major bioreactors exclusive of a small polishing bioreactor. Efforts to determine the minimum requirements for dissolved oxygen and demonstrate degradation rates of 20 mg/L bed · min with actual wastewater have been inconclusive to date. This degradation rate has been achieved in small bioreactors with excess dissolved oxygen. However, it is clear that maintaining sufficient oxygen in bioreactors will not be a trivial matter. Neither is it obvious that it will be impossible to do so. Therefore, the economic picture remains uncertain. More development work with larger scale equipment and innovative oxygen supply methods is needed to resolve this issue.

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#### LITERATURE CITED

1. Luthy, R. G., V. C. Stamoudis, J. R. Campbell, and W. Harrison, "Removal of Organic Contaminants from Coal Conversion Process Condensates," *J. Water Pollut. Control Fed.*, **55**, 196 (1983).
2. *Technical Analysis of Advanced Wastewater Treatment Systems for Coal Gasification Plants*, Report No. D-TR-80/041-001, UOP/SDC, McLean, Va., 1981.
3. Frankel, I., Drabkin, M., "Wastewater Treatment Systems for Synthetic Fuels Plants Based on Peat and Oil Shale," *Environ. Progress*, **4** (1), 39-43 (1985).
4. Scott, C. D., and C. W. Hancher, "Use of a Tapered Fluidized Bed as a Continuous Bioreactor," *Biotech. Bioeng.*, **18**, 1393-1403 (1976).
5. Hancher, C. W., P. A. Taylor, and J. M. Napier, "Operation of a Fluidized-Bed Bioreactor for Denitrification," *Biotech. Bioeng. Symp. No. 8*, 361-78 (1978).
6. Lee, D. D., C. D. Scott, and C. W. Hancher, "Fluidized-Bed Bioreactor for Coal-Conversion Effluents," *J. Water Pollut. Control Fed.*, **51**, 974-84 (1979).
7. Walker, J. F., C. W. Hancher, R. K. Genung, B. D. Patton, and M. Kowalchuk, "Biological Treatment of Nitrate Wastewater Using Fluidized-Bed Bioreactors," *Biotech. Bioeng. Symp. No. 11*, 415-25 (1981).
8. Sutton, P. M., "Fluidized Bed Finds New Application in Wastewater Treatment," *Pollut. Eng.*, **13** (2), 38-40 (1981).
9. Melcer, H., S. Nutt, I. Marvan, and P. Sutton, "Combined Treatment of Coke Plant Wastewater and Blast Furnace Blowdown Water in a Coupled Biological Fluidized Bed System," *J. Water Pollut. Control Fed.*, **56**, 192-98 (1984).
10. Rivera, A. L., "Heavy Metal Removal in a Packed-Bed, Anaerobic Upflow (ANFLOW) Bioreactor," *J. Water Pollut. Control. Fed.*, **55**, 1450-56 (1983).
11. Kennedy, K. J., M. Muzar, and G. H. Copp, "Stability and Performance of Mesophilic Anaerobic Fixed-Film Reactors during Organic Overloading," *Biotech. Bioeng.*, **27**, 86-93 (1985).
12. Donaldson, T. L., G. W. Strandberg, J. D. Hewitt, and G. S. Shields, "Biooxidation of Coal Gasification Wastewaters," *Environ. Prog.*, **3**, 248-53 (1984).
13. Strandberg, G. W., R. M. Worden, J. D. Hewitt, and T. L., Donaldson, *Fixed-Film, Fluidized-Bed Bioreactors for Biooxidation of Coal Conversion Wastewaters: Progress Report for The Period October 1, 1983-September 30, 1984*, ORNL/TM-9395, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., March 1985.



14. *Standard Methods for the Examination of Water and Wastewater*, 14th ed., American Public Health Association, Washington, D.C., 1975, pp. 580-81.
15. *Wastewater Analysis Handbook*, Hach Chemical Company, Loveland, Colo., 1978, pp. 371-80.
16. Yeatts, L. B., Jr., C. B. Hurst, and J. E. Caton, "Determination of Hydroxybenzenes in Fossil Fuel-Derived Liquids and in Associated Process Waters," *Anal. Chem. Acta*, **151**, 349-58 (1983).
17. *Standard Methods for the Examination of Water and Wastewater*, 14th ed., American Public Health Association, Washington, D.C., 1975, pp. 94-95.
18. Stover, E. L., and D. F. Kincannon, "Biological Treatability of Specific Organic Compounds Found in Chemical Industry Wastewater," *J. Water Pollut. Control Fed.*, **55**, 97-109 (1983).
19. Kostenbader, P. D., and J. W. Flecksteiner, "Biological Oxidation of Coke Plant Weak Ammonia Liquor," *J. Water Pollut. Control Fed.*, **41**, 199-207 (1969).
20. Worden, R. M., *Dynamics of a Biological Fixed Film for Phenol Degradation*, Ph.D. Dissertation, University of Tennessee, Knoxville, 1986.
21. Neufeld, R. D., C. Moretti, F. Ali, and J. Paladino, *Pretreatment and Biological Digestion of METC Stirred Fixed Bed Gas Producer Wastewaters*, DOE/ET/14372-7, September 1981.



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# The Assessment of Risk at Superfund Sites

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*Risk assessments are one component in the evaluation of potential impacts of remedial alternatives at Superfund sites. They inherently involve uncertainty and incomplete scientific understanding. There is general agreement in the risk assessment community on the broad categories of activities to be performed (i.e., exposure, hazard, and risk assessments), but the method of analysis for each element within an activity is presently not uniformly established.*

*The objective of this paper is to describe judgmental decisions that must be made by the risk assessors during the design and execution of a Superfund site assessment, with a focus on the issues of uncertainty and exposure scenarios. The assessment at Western Processing, Washington, is used as an example of the substantial expert judgment required in choosing the analytical methods and appropriate assumptions.*

## INTRODUCTION

Today in the field of hazardous waste management, there are few engineering criteria upon which to base engineering assessments, alternatives, selections and designs. In the absence of promulgated standards, risk assessments have been employed to estimate the risk to human health and the environment. Risk estimates are used to compare the risk associated with alternative actions, or to estimate the risk reduction associated with implementing an action, or the risk of a single action or condition.

The risk assessment process is a systematic procedure that takes into account the chemical sources, intrinsic chemical properties, transport and fate, receptors, and dose-response elements. The process itself has been generally defined for some applications such as remedial alternatives comparison at Superfund sites [1]. There are, however, no universally accepted procedures for any specific risk assessment application. Neither are there any accepted definitions as to the scope and extent of the analyses required to develop an estimate of risk for the various applications of risk assessment.

Risk assessments are most effective when used as a tool for organizing the best available scientific and technical information about a particular exposure problem, to assist in informing decisionmakers about the consequences of alternatives, not when the objective is to obtain a specific risk value. Risk assessments inherently involve uncertainty and incomplete scientific understanding, and therefore are inexact. Assumptions are often employed as an approach to handling uncertainty, and these assumptions may severely limit the interpretation of an absolute risk level from any risk assessment. Comparative risk assessments between different alternatives may be viable because the assumptions may be the same across the alternatives.

Risk assessment is a very young discipline. Current efforts at improving risk assessments and the understanding

of potential effects of chemical exposure are products of the recent laws and regulations governing toxic and hazardous substances: the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, or commonly called "Superfund"), the Toxic Substances Control Act (TSCA), and the Resource Conservation and Recovery Act (RCRA).

The purpose of this paper is to provide a description of the current state of the practice of risk assessment, focusing on the process used in evaluating Superfund sites. The objective is to describe judgmental decisions that must be made by the risk assessors during the design and execution of a Superfund site assessment. Many of these decisions result from the fundamental infancy of the risk assessment process and the often limited data base, whereas others result from the objectives of site assessment under the Superfund requirements. The discussion of assessment design considerations later in this paper is based on the Superfund study objectives.

This paper is organized into four sections. The next section summarizes the general assessment categories and elements of a risk assessment. This is followed by a brief review of the current and potential future Superfund requirements, and then a discussion of the design consideration for a site-specific risk assessment. The paper closes with a discussion of a site-specific assessment design example for a Superfund site.

## RISK ASSESSMENT

### Background

There is no general consensus on the definition of terms in the field of risk. In this paper, harm is defined as an undesirable outcome of an action with respect to measures of public health, or of environmental values, particularly in the natural populations of animals, plants, and microorganisms. A hazardous activity is one that may lead to

harm. Risk, then, is the exposure to harm, and can be defined simply as the expected magnitude, in a probabilistic sense, of harm associated with an activity. Operationally, this means that a risk has three characteristics: a series of actions that may lead to harm, the probability that those actions may occur, and the magnitude of harm if they do occur.

Risk assessment will be defined here as the process of assessing the existence of chemical exposure and potential toxic effects, and estimating their nature and magnitude. Some authors have included the evaluation of human perception of risk as an element of risk assessment [2], but that is not included here.

Risk assessment is descriptive and analytical, not prescriptive. It provides a consistent framework in which information can be organized and logically considered. It does not value things or make choices. It cannot tell us what action to take, although it certainly can assist people in reaching decisions based on a full and complete understanding of the available evidence.

### Process

A risk assessment for chemical exposure consists broadly of the five categories shown in Figure 1. The process begins with a description of the chemicals that may result in exposure, and further details on the quantity and form of the chemicals, and the specific conditions of the location in which they are found (i.e., nature and extent of contamination).

The next category, fate and transport, characterizes the physical (e.g., groundwater dispersion), chemical (e.g., hydrolysis), and biological (e.g., biodegradation) processes that will alter the chemical concentrations before the chemicals contact human or environmental receptors. In some cases, contact may be immediate (e.g., humans walk on the contaminated area), whereas in other cases there may be major processes that occur before receptors contact the chemicals (e.g., leaching of chemicals from soil and subsequent groundwater migration to a domestic well). At this point of contact, receptors will be performing different activities (e.g., drinking water) that will lead to different levels of exposure to the chemicals through different exposure routes (ingestion, inhalation, dermal contact). This information is incorporated into the exposure assessment.

The toxicity assessment is concerned with the inherent toxicological properties of chemicals (e.g., carcinogenicity). Toxicity is also a function of the exposure route and the particular sensitivities of the individual receptor (e.g., human exposure to chemical). The chemical exposure is combined with the toxicity assessment to characterize the risk. This risk characterization includes a comparison to the applicable or relevant and appropriate requirements for Superfund sites. It will also likely include, for Superfund sites, an estimation of excess lifetime cancer risk based on exposure to chemical carcinogens, and a comparison to USEPA reference doses for chemical non-cancer effects. The risk characterization may be qualitative or quantitative, depending on the objectives and scope for a specific site.

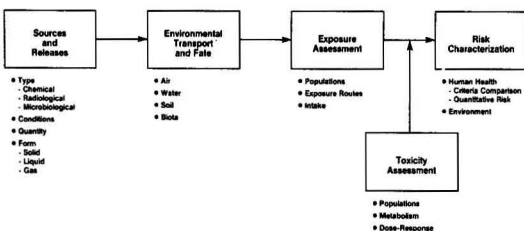


Figure 1. Risk assessment process.

There is general agreement in the risk assessment community that the broad categories in Figure 1 are appropriate for characterizing the risk assessment process. Each of these categories, however, consists of a number of elements (see Table 1), and the method of analysis for each of these elements is presently not uniformly established, although USEPA has issued two guidance documents [1, 3].

### CERCLA REQUIREMENTS

Under CERCLA and implementing agreements, the U.S. Environmental Protection Agency may act to provide for remedial action at an uncontrolled hazardous substances site when necessary to protect the public health or welfare, or the environment. The selected remedial responses are to be "to the extent practicable in accordance with the national contingency plan and which provide for that cost-effective response which provides a balance between the need for protection of public health and welfare and the environment at the facility under consideration, and the availability of amounts from the Fund . . ." Under the National Contingency Plan (NCP) [4], removal and remedial actions may be taken at sites where there is an actual or potential exposure to hazardous substances or pollutants. The detailed analysis of remedial alternatives requires an assessment of the extent to which the alternatives "is expected to effectively prevent, mitigate, or minimize threats to, and provide adequate protection of public health, welfare and the environment."

CERCLA provided no explicit acceptable chemical concentrations in the environment. Under the NCP, however, the analysis for remedial alternatives must include an evaluation of the extent to which the alternative "attains or exceeds applicable or relevant and appropriate Federal public health and environmental requirements. Where the analysis determines that Federal public health and environmental requirements are not applicable or relevant and appropriate, the analysis shall, as appropriate, evaluate the risks of the various exposure levels projected or remaining after implementation of the alternatives under consideration."

Applicable requirements are those "Federal requirements that would be legally applicable, whether directly, or as incorporated by a Federally authorized State program, if the response actions were not undertaken pursuant to CERCLA Section 104 or 106" (the sections that provide the authority to take response actions). Relevant and appropriate requirements are those "Federal requirements that, while not 'applicable,' are designed to apply to problems sufficiently similar to those encountered at CERCLA sites that their application is appropriate if they would be 'applicable' but for jurisdictional restrictions associated with the requirement." At this time, the USEPA considers only the drinking water maximum contaminant levels, national ambient air quality standards, and federally-approved state water quality standards developed under the Clean Water Act to be potentially applicable or relevant and appropriate requirements for environmental pollutant concentrations [1].

The Superfund Amendments and Reauthorization Act of 1986 (SARA) largely adopts this approach. Formally approved state standards and criteria, adopted to protect human health and the environment and not adopted simply to preclude land disposal, are also now legally applicable.

### ASSESSMENT DESIGN CONSIDERATIONS

The critical issues in performing a risk assessment are problem structure, choice of risk analysis tools, methods for handling uncertainty, and combining all these factors into a unified risk assessment. There is little agreement in the risk assessment community as to the proper approach under different conditions. Risk assessment is as much an

TABLE 1. ASSESSMENT ELEMENTS AND UNCERTAINTIES

Category	Element	Uncertainty
Sources and Releases	Type Quantity Concentrations Form Local conditions	Measurement error Sampling error Chemical use practices Historical conditions Sources Background concentrations Choice of chemicals to include for lab analysis Variability (temporal and spatial)
Environmental Transport and Fate	Environmental media (air, soil, water, biota) Transport within a medium Transfer between media Transformation	Environmental conditions Physical properties of media and chemicals Biological properties of chemicals Limits on chemicals to include in the assessment Advection, dispersion rates Partitioning between media Rates of mass transfer
Exposure Assessment	Exposure routes (inhalation, ingestion, dermal contact) Exposure point concentrations Receptor activities Intake rates of environmental media Populations	Intake rates: USEPA has used 2 L/day for water ingestion, 20 m <sup>3</sup> /day for air inhalation and 6.5 gm/day for fish ingestion (1) Exposure frequency Exposure duration Limits on chemicals to include in the assessment
Toxicity Assessment	Population Metabolism Dose-response relationships	Variety of effects Assessments available for relatively few chemicals Extrapolations Animal-to-man High-to-low dose Structure-activity relationships Synergism/antagonism Individual sensitivity Cancers have different impacts on expected lifetime Absence of quantitative toxicological data on tested chemicals
Risk Characterization	Combines all of the above elements	Combines all of the above uncertainties

art as a science. Experienced personnel may produce different assessments for the same problem. The three following sections describe some of the factors that result in these different assessment approaches. This is not an exhaustive list of potential factors, but focuses on some of the more significant.

#### Scope of Assessment

With five major environmental media (air, groundwater, surface water, soil, and biota), a large variety of inter- and intra-media transfer process for fate and transport assessments, three exposure routes, and a large number of known toxic chemical effects, the permutations and potential resource requirements for performing a "complete" risk assessment for a general site condition are quite large. Unfortunately, there is no generally accepted "stopping rule" that describes when there is enough information to perform a risk assessment that meets the study objectives. Clark [5] has pointed out that the only stopping rule, in the extreme, is "discovery of the sought-for effect, or exhaustion of the investigator (or his funds)."

A theoretical stopping rule would be one driven by the value of information, which would take into account the objectives of the analysis and the differences in the alternatives being considered (6). The stopping point would be when the marginal resource requirements of the risk assessment exceed the marginal gains in distinguishing between two alternative actions. Few applications in the risk assessment literature, however, have formally examined this point. Although not quantitatively examined, the USEPA have provided guidance on the scope by explicitly describing the tasks for a Superfund site risk assessment [1].

#### Uncertainty

Uncertainty is a significant issue in risk assessments. The approach to characterizing and dealing with these uncertainties is one of the central problems in risk analysis. Categories or technical uncertainty include [2]:

1. Functional relationships among parameters for the physical, chemical, and biological processes are unknown.
2. Functional relationships among parameters for the physical, chemical, and biological processes are known, but the values of the associated parameters are unknown.
3. Process parameters are known, but are inherently stochastic. (This may result from inadequate current knowledge of a truly deterministic process, an inherently stochastic process, or the practical need to simplify a very complex process.)

Morgan [2] describes several methods for dealing with these uncertainties, depending on the degree of uncertainty. The choice of a strategy involves professional judgment as to the type of uncertainty and the specific objectives of the analysis. Morgan also notes that the evidence for characterizing the uncertainty may come from different sources. These categories, with an increasing order of uncertainty, are:

1. Good, direct statistical evidence on the process(es) of interest is available.
2. The process may be disaggregated into subprocesses, for which good statistical data are available.
3. Good data are not available for the specific process of interest, but good data are available for a similar process.



4. Available direct and indirect evidence is poor or incomplete and it is necessary to rely on physical intuition and subjective judgment of technical experts.
5. There is little available evidence and experts have little basis on which to base a judgment.

As Morgan notes, a large fraction of quantitative risk assessment problems today fall in evidence categories 3, 4, and 5.

Most large and complex risk assessment problems need to be decomposed into various elements. Different strategies will be important for different elements, and the elements must be reconstituted to form the overall risk assessment. A corollary to this decomposition approach is that a risk assessment can be no stronger than its weakest link.

In the presence of substantial uncertainty, risk assessors have commonly used conservative assumptions (from a health protection perspective). Even this philosophy, however, leads to a form of additional uncertainty, because there is no clear definition of the appropriate level of conservatism, and different assessment professionals will use different levels. In addition, other assumptions will tend to lead to an underestimate of risks.

This issue is made more complex because the choice of assumptions is also a function of the study objectives and activity conditions being assessed. For example, some site-related conditions may be "so bad" that the choice of conservative assumptions may be immaterial in determining that the risk is very high, so a set of assumptions is chosen with little controversy. In contrast, those same assumptions may be inadequate for addressing whether some other site has very low risk.

Table 1 also provides an additional layer to the understanding of risk assessments. Types of uncertainties have been added to the broad categories and elements presented earlier. Some of the uncertainties come from fundamental limitations of scientific knowledge (e.g., carcinogenesis), others from limitations of data collection (e.g., sampling error), and still others from an effort to maintain a manageable assessment (e.g., limitations on the number of chemicals assessed). Carcinogenesis is a case in which the function relationships among parameters are unknown, whereas many of the elements of the exposure assessment involve known functional relationships, but unknown parameter values.

#### Exposure Scenarios

Table 1 noted several of the uncertainties in characterizing the exposure to chemicals. For a potential future exposure, there is the additional factor of estimating future site conditions, the future human activities that will take place on the site.

While many Superfund sites are so grossly contaminated that future unrestricted onsite activities may seem very unrealistic, an assessment of the "no-action" alternative includes a consideration of impacts as if the USEPA were to perform no response actions, walk-away from the site, and allow unrestricted use. This provides a baseline analysis against which the residual risks associated with response actions can be compared.

General future potential land uses include: current (which may be none or one of the following), residential, commercial, or industrial. The decisions as to which general use is applicable includes a consideration of the land use around the site. Within these general uses, however, are a number of additional elements that need to go into an exposure scenario: type of people, their activities (indoors and outdoors), and their habits. There is, again, potentially a large number of combinations, and decisions will have to be made to maintain a reasonable scope.

#### ASSESSMENT DESIGN EXAMPLE

The Western Processing site is located in Kent, Washington. The site is currently zoned for a limited industrial district. It is surrounded by undeveloped land, a creek, and land currently being developed according to the light industrial land use classification. From 1961 to 1983, the site was used for various chemical reclamation, industrial waste processing, and storage activities. The principal wastes received at the site included: electroplating solutions and sludges, pesticides/herbicides, spent acid and caustic solutions, waste oils and solvents, battery chips, flue dust from secondary smelters, aluminum slag, and galvanization skimmings. Prior to the risk assessment, there were three major remedial activities: emergency removal of onsite materials, stormwater control project, and a surface cleanup. During the emergency removal, 1,900 cubic yards of paint sludges and flammables, 920,000 gallons of organics and wastewater, and 127 drums were removed. During the surface cleanup, 2,400 truckloads of liquid, solid, and demolition wastes were shipped from the site.

Groundwater movement near Western Processing is influenced by three primary factors: regional westward flow with an upward flow component; groundwater recharge and mounding onsite with a downward flow component; and discharge to the nearby creek and an east drain.

TABLE 2. WESTERN PROCESSING SITE ISSUES AND ASSESSMENT DESIGN APPROACHES

Issue	Approach
Assessment scope Large number of chemicals	Demonstrate high risk, not total risk. Analyze for USEPA priority pollutants. Tentatively identified chemicals not included. Quantitatively evaluate only those with USEPA cancer potencies or acceptable daily intakes.
Sources and Releases Background concentrations Spatial distribution	Analyze nearby locations. Reasonably dense sampling distribution.
Transport and Fate Transport models	Groundwater migration distance was minimal, requiring only simple model. Minimal surface runoff, so not assessed. Other exposure pathways adequate to demonstrate risk.
Exposure point concentrations	Used sampling point concentrations, and no loss with time, as substantial portion of site risk was from inorganic compounds.
Exposure Assessment Actual Exposures Potential exposures Media intake rates	No one regularly working onsite. Defined future use scenarios: residential and worker. Water: 2 L/day for residential, and adjusted level for worker. Soil: Range from Schaum (8) to Kimbrough et al. (9). Additional adjustment for climatic conditions that would affect exposure frequency.
Toxicity Assessment Variety of effects	Assessment limited to excess lifetime cancer risk, and the effect associated with the reference doses.
Quantitative risk	Used USEPA cancer potencies and reference doses.
Synergism/antagonism	Noted the potential, but not quantitatively included.

Eighty-three USEPA priority pollutants were found in onsite soils and 57 were found in onsite groundwater monitoring wells. Average observed surface soil chemical concentrations included 310 ug/kg PCBs, 38,000 ug/kg benzo (a) anthracene, and 5,700 ug/kg lead. Average observed groundwater chemical concentrations included 18,000 ug/L trichloroethane, 2,100 ug/L chloroform, 75,000 ug/L phenol, 1,500 ug/L chromium, and 1,100 ug/L cadmium. Water and sediments in the creek are contaminated primarily with USEPA inorganic priority pollutants [7].

Table 2 summarizes the key issues in the assessment of the no-action assessment for this site, and the approaches adopted in this study. This study was performed under CERCLA, not SARA. Note the variety of approaches, from limitations imposed by sampling analysis to those used to maintain a manageable bounds on the breadth and depth of the analysis.

#### SUMMARY

Risk assessment is an evolving process. The general approach involves an assessment of the chemical sources and releases, transport and fate, exposure assessment, toxicity assessment, and risk characterization. The current state of the practice requires substantial expert judgment in the choice of methods because there is little agreement as to how the general approach should be adjusted to the assessment objectives and available data.

For Superfund sites, the USEPA has developed guidance manuals that describe the approach to be taken, which includes comparisons to applicable or relevant and appropriate requirements. Even so, there is still a substantial requirement for expert judgment in the specific application to a site. A summary of the judgments made for the risk assessment of the no-action alternative for the Western Processing site demonstrated this point.

#### LITERATURE CITED

1. U.S. Environmental Protection Agency, *Superfund Public Health Evaluation Manual*, Draft, Office of Emergency and Remedial Response (October 1986).
2. Morgan, M. G., "Risk Assessment and Risk Management Decision-Making for Chemical Exposure," in W. B. Neely and G. E. Blau (eds.), *Environmental Exposure from Chemicals*, CRC Press, Boca Raton, Florida (1985).
3. U.S. Environmental Protection Agency, *Endangerment Assessment Handbook*, Office of Waste Programs Enforcement (August 1985).
4. *Federal Register* 50:47950 (1985).
5. Clark, W. C., "Witches, Foods and Wonder Drugs: Historical Risk Management," in R. C. Schwing, and W. A. Albers, Jr. (eds.), *Societal Risk Assessment: How Safe is Safe Enough?* Plenum Press, New York (1980).
6. Raiffa, H., *Decision Analysis: Introductory Lectures on Choices under Uncertainty*, Addison-Wesley, Menlo Park, California (1970).
7. U.S. Environmental Protection Agency, *Feasibility Study for Subsurface Cleanup, Western Processing, Kent Washington* (1985).
8. Schaum, J., *Risk Analysis of TCDD Contaminated Soil*, Office of Health and Environmental Assessment, U.S. Environmental Protection Agency, Washington, D.C. (1984).
9. Kimbrough, R. D., H. Falk, P. Stehr, and G. Fries, "Health Implications of 2,3,7,8-TCDD Contamination of Residential Soil," *J. of Toxicology and Environmental Health* 14:47-93 (1984).

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# Prediction of Organic Chemical Fates in Biological Treatment Systems

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*Attention is presently being focused on the fates of organic chemicals in biological treatment systems. Most systems have been designed and operated to remove organic compounds from the aqueous waste stream and performance has been defined in terms of removal of a non-specific parameter from the wastewater. Parameters like total organic carbon, biochemical oxygen demand, and chemical oxygen demand have historically been used in treatability studies, in system design, and in determining system performance. Performance data using these approaches are inadequate for determination of the removal of specific compounds unless (fortuitously) the specific compound's biological activity is approximated by the generalized activity of the non-specific parameter.*

*The resulting assumption that the biokinetics, and therefore the fate of organic compounds, are similar and well-described by the biokinetics of the non-specific parameter does not hold for specific chemicals that possess strong stripping/volatilization and/or biomass sorption tendencies or for compounds that have biotransformation kinetics that differ from the idealized "BOD-like" compound.*

*Some compounds are likely to preferentially strip/volatilize or sorb onto biomass either if generally recalcitrant to biotransformation, or if the biotransformation process is variable and the rates of the competitive fate mechanisms are large relative to the low transient biotransformation rate. All of the above cases have been experimentally documented and will be discussed. The biotransformation rates have the greatest magnitude of variation of any fate-related parameter and therefore have a major influence on the compound fate. An equation coupling the competitive fates of organic chemicals in completely-mixed and steady-state biological treatment systems has been developed and is presented. This equation can be arranged to allow calculation of the fraction or percentage of an organic compound fed to a system that strips, sorbs onto biomass, biotransforms, or remains in the effluent if the stripping, sorption, and biotransformation rates are known. It can be used to correct experimental data to account for the competitive mechanisms and generate more reliable biotransformation data. Finally, it also serves as a unifying approach against which the specific fate performance of a given system may be compared. Therefore it may be used to estimate potential organic air emissions and the potential of toxic organics in sludge generated from the biological waste treatment process.*

## INTRODUCTION

In today's environmental climate, questions are being raised regarding the fate of specific organic compounds upon introduction to biological wastewater treatment systems. Compounds stripping with air added to the system contribute to organic air pollution and compounds partitioning in waste biomass that subsequently undergoes land disposal may ultimately migrate into groundwater.

This follows from the reality that nearly all systems now in operation have been designed from treatability data that focus on the removal of a non-specific analytical parameter from the wastewater fed to the system. Thus, a plant is considered to be performing well if, say, over 90 percent of a five-day biochemical oxygen demand (BOD<sub>5</sub>) fed to the system has been removed from the aqueous effluent.

The non-specific parameter approach has served well

in the effort to develop unstructured biomass design models to describe the biomass production kinetics and the removal kinetics of the non-specific parameter. Over the years it has led to a rational basis on which to design plants and there is every reason to expect that it will be an integral part of future design procedures. When the organic compounds present in wastewater individually behave similarly to the hypothetical "BOD-like compound" developed from treatability data on the specific stream, the unstructured model holds and adequately describes the overall performance. "BOD-like" compounds are generally highly water soluble, relatively easily assimilated by microorganisms, and generally have low volatility in terms of the Henry's law constant of the compound. When the feed composition is approximated by "BOD-like" compounds, removal from the treatment system is accomplished by a series of transformations leading to complete mineralization and the present rational design approach works. (Biotransformation is the enzymatic conversion of the original compound to a chemically-different metabolite, while mineralization is the complete conversion of the compound to CO<sub>2</sub>, CH<sub>4</sub>, water, and/or mineral salts.)

The organic component of the vast majority of waste streams either contains major fractions of "BOD-like" compounds or if biotransformation proceeds on non-"BOD-like" compounds, "BOD-like" compounds are formed as metabolites. However, when an organic has generally low solubility, is volatile, sorbs readily on biomass at high loadings (g of sorbed compound per g of dry weight biomass), or rapidly chemically or photochemically converts to a low solubility or highly sorbed compound as described above, the compound does not conform to the "BOD-like" compound description and cannot be assumed to be removed from the wastewater with the same efficiency as BOD removal. Large fractions of the compound may partition with the air or biomass even if high levels of BOD, COD, or TOC removal from the effluent can be demonstrated. Mathematical analysis and presentation of experimental data in this paper will demonstrate these effects for a completely-mixed, bubble diffusion, activated-sludge treatment system.

## EXPERIMENTAL DESCRIPTIVE EQUATIONS

Several related works have been published in this area [1, 2, 3, 4]. Included in reference 1 is a critical review of much of the related work done in the fate area over the last decade [5]. A reader interested in an overview of the general fate literature is referred here.

With the assumptions of continuous feed, complete mixing, steady-state operation and first-order biotransformation and stripping rate equations, a coupled-mechanism equation has been proposed that incorporates the fate mechanisms of sorption onto biomass, stripping from the reactor offgas, biotransformation, and loss in the effluent [6]. This equation relates to a system as shown in Figure 1.

With rearrangement and generalization this equation can be rewritten as follows:

$$\frac{C_a}{C_{ao}} = \frac{1}{1 + K^{sp} \cdot HRT + K^s \cdot HRT + K^b_2 \cdot X \cdot HRT} \quad (1)$$

Where:

- $C_a$  = Concentration of the specific organic compound in the reactor effluent
- $C_{ao}$  = Concentration of the specific organic compound in the feed stream to the reactor
- $K^{sp}$  = Rate constant describing removal of the compound sorbed to biomass in the waste biomass

- $K^s$  = Rate constant describing the removal of the compound into the reactor offgas
- $K^b_2$  = A biotransformation rate constant, first-order in compound concentration, and first-order in biomass concentration, but second-order overall
- $X$  = A measure of biomass concentration consistent with the units of  $K^b_2$
- $HRT$  = Hydraulic residence time in the reactor

If no biotransformation occurs in the clarifier (normally the clarifier is under anaerobic conditions) then the reactor effluent concentration equals the system effluent concentration or  $C_a = C_{ae}$ .

Equations can be derived from equation 1 to calculate the percent removal of the specific compound related to each fate mechanism [7]

$$R_{sp} = \frac{A}{1 + A + S + B} \cdot 100 \quad (2)$$

$$R_s = \frac{S}{1 + A + S + B} \cdot 100 \quad (3)$$

$$R_b = \frac{B}{1 + A + S + B} \cdot 100 \quad (4)$$

$$R_e = \frac{1}{1 + A + S + B} \cdot 100 \quad (5)$$

Where:

- $A$  = Sorption Rate Parameter,  $K^{sp} \cdot HRT$
- $S$  = Stripping Rate Parameter,  $K^s \cdot HRT$
- $B$  = Biotransformation Rate Parameter,  $K^b_2 \cdot X \cdot HRT$
- $R_{sp}$  = Percent removal of the specific compound by biomass sorption and sludge wastage
- $R_s$  = Percent removal of the specific compound into the offgas
- $R_b$  = Percent conversion of the specific compound to subsequent metabolites
- $R_e$  = Percent removal of the specific compound in the effluent

The sorption and stripping rate constants  $K^{sp}$  and  $K^s$  can be determined by careful experimental measurement of the rates of removal of the specific compound in the waste biomass and offgas and by dividing by  $C_a$ . For example, the sorption rate constant,  $K^{sp}$ , equals the measured flux of specific compound leaving in the waste biomass ( $\text{mg L}^{-1} \text{hr}^{-1}$ ) divided by the aqueous concentration ( $\text{mg L}^{-1}$ ), and has units of  $\text{hr}^{-1}$ . In the case of using experimentally-derived sorption concentrations or loadings, one must be careful to include only the fraction of compound actually associated with the biomass (or solids) and not the frac-

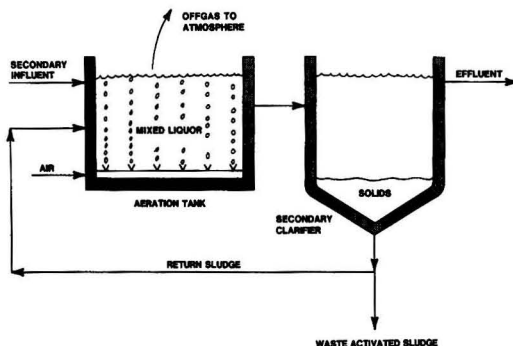


Figure 1. A model activated sludge process.



tion of compound residing in extracellular water in the waste biomass [8]. Similarly, the stripping rate constant for a compound can be calculated from the measured stripping rate and the aqueous phase concentration of the compound.

The sorption process has been proposed to be related to "extraction" of the compound into cellular lipids [9]. Even though this is an equilibrium process (mass-transfer reaches equilibrium rapidly), this concept can be related to the biomass production and wasting process with the following equation.

$$K^{sp} = \frac{X \cdot K_{ow} \cdot f_L}{1000 \rho_L \theta_c} \quad (6)$$

Where:

- $K_{ow}$  = Octanol-water partition coefficient
- $f_L$  = Fraction of lipid in biomass
- $\rho_L$  = Density of the cellular lipids (g/L)
- $\theta_c$  = Mean cell residence time (days)

This equation represents the minimum sorption related to "passive" partitioning. It can be modified for compounds that undergo biochemical binding (usually seen with polar or ionic compounds) or active cellular transport.

As mentioned before, the stripping rate constant can be experimentally determined in small systems by sampling and analysis of the off-gas calculation of the stripping rate and dividing by the aqueous concentration at the stripping location. For low Henry's law constant compounds, for mass-transfer limited stripping/volatilization processes, or for large open reactors, (like wastewater treatment systems) direct measurement becomes complicated and prone to uncertainties. Predictive equations can also be used, sometimes with greater accuracy.

An equation for stripping from coarse-bubble diffuser systems has been developed [3, 10]. It can be converted to units consistent with this present analysis.

$$K^s = 6.18 \cdot 10^{-5} \frac{Q_{air}}{V} (H_c)^{1.045} \quad (7)$$

Where:

- $Q_{air}$  = Air flow into the reaction (L/day)
- $V$  = System volume (L)
- $H_c$  = Henry's law constant (torr · L · gmole<sup>-1</sup>)

This equation was found to be accurate in pure water (tap water) systems for compounds with Henry's law constants varying over four orders of magnitude. Variation found in various contaminated (abiotic) aqueous matrices was less than 50 percent of the pure water values.

Other relationships may be used for different kinds of aeration systems as long as the stripping rate equation remains first-order in aqueous concentration,  $C_a$ .

#### DIRECT DETERMINATION OF BIOTRANSFORMATION RATE CONSTANTS

In principle, the biotransformation rate constant,  $K^s \cdot X$ , can be determined by measuring the biotic disappearance of the parent compound or the appearance of the metabolic product. In practice, parent compound disappearance is only a measure of biotransformation when other competitive mechanisms are controlled, predicted, or eliminated from the experiment. Measurement of the metabolite production requires either axenic culture studies (single organism) at high cell densities or labeling the parent compound and measuring both the concentration of the metabolite and the rates of conversion of the first metabolite to the second metabolite(s) in the biotransformation series.

Normally in functional cells, the rate of conversion of the first metabolite to the second metabolite proceeds similarly as the rate of production of the first metabolite from the parent compound. Therefore, concentrations of the first metabolite are low and difficult to analyze in mixed culture biomass. In organisms that are genetically well understood, mutants defective in conversion of the first metabolite to the second metabolite can be used to establish the initial biotransformation rate and the approach can be applied to each successive metabolite conversion. This approach leads to elucidation of the degradation (catabolic) pathway as shown for toluene in Figure 2. These are necessarily axenic culture studies and kinetics that also may be under genetic control can differ greatly in the mutant organisms. Mutant studies may not be representative of organisms in the mixed culture ecosystems.

#### INDIRECT CALCULATION OF BIOTRANSFORMATION RATE CONSTANTS

As discussed, direct measurement of  $K^s \cdot X$  is very difficult in real treatment ecosystems. If the reactor effluent concentration can be measured and the other competitive mechanism rates can be measured or predicted, the biotransformation rate can be indirectly calculated.

Beltrame and his associates used conventional kinetic plotting techniques to interpret biotransformation rate constants for 2,4-dichlorophenol [11]. This study is a typical example of the present status of developing specific compound biokinetic rate constants. Four runs were completed with phenol and glucose added in addition to the 2,4-dichlorophenol and various MCRT's and HRT's were employed.

Experimental conditions for this work are found in Table 1. Table 2 compares a disappearance rate constant calculated using conventional empirical techniques that tend to "average" the values for all runs with the

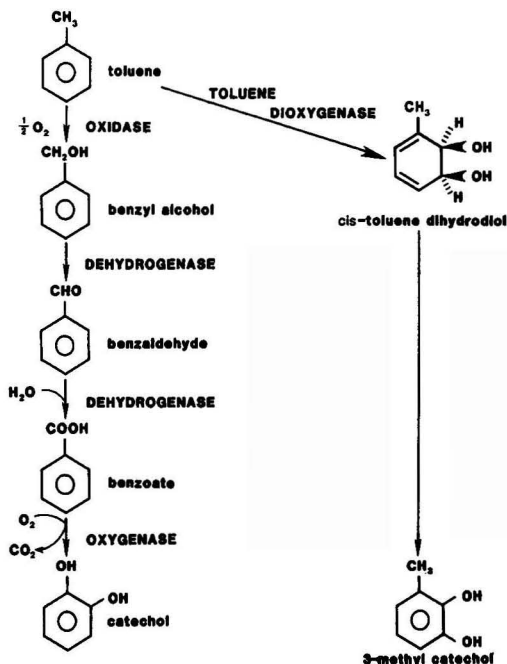


Figure 2. Biochemical pathway for toluene biotransformation.

TABLE 1. SYSTEM PARAMETERS FOR 2,4-DICHLOROPHENOL BIOTRANSFORMATION\*

Run	Substrate	Mean Cell Residence Time (hr)	Hydraulic Residence Time (hr)
1	phenol/2,4-dichlorophenol	257	25
2	phenol/2,4-dichlorophenol	42	6.25
3	glucose/2,4-dichlorophenol	109	6.25
4	glucose/2,4-dichlorophenol	20	6.25

\*See Reference 11.

biotransformation rates corrected for stripping and sorption by use of equations 1-7 for each of the runs and the average for all runs. In addition, the fate calculations using equations from this paper are also presented. Calculated values for biotransformation rate constants using the equations proposed in this study show both wider variance and potential relationships between the biotransformation rate constant and the mean cell residence time.

In general, if adequate data on system parameters are reported in the literature, the use of this approach on the existing data base may lead to a biotransformation rate constant data base retroactively corrected for possible sorption and stripping mechanisms.

#### VARIATIONS IN BIOTRANSFORMATION RATE CONSTANTS

The preceding example highlights the potential variability in biotransformation rates in several runs of a controlled laboratory test system. The compound studied, 2,4-dichlorophenol, was neither very volatile nor significantly sorbed (using predictors presented here).

If a combined microbiological and ecological view is taken of the biomass (as opposed to the unstructured model where the biomass is a uniform, homogenous catalyst and is measured as mixed liquor suspended solids), one can imagine an active subpopulation of organisms in which the parent compound, e.g., 2,4-dichlorophenol, is enzymatically transformed to a series of subsequent metabolites. Some of the metabolites may be released to the aqueous medium and be taken up by other organisms not able initially to degrade 2,4-dichlorophenol. This subpopulation competes for common nutrients with subpopulations using other carbon sources and is prey for higher microorganisms. This is a structured biomass conceptual model and incorporates important ecological and organism variables.

Strong evidence for active degrader subpopulations has been developed for batch, fill-and-draw (sequencing batch reactor), and continuous systems [4, 11, 12, 14]. These subpopulations generally represent a small frac-

tion of the total viable cells and range from one hundred-fold to ten thousand-fold less than the total viable cells.

Using a structured model for biotransformation, then, the biomass variable,  $X$ , in our biotransformation rate constant,  $K^b_2 \cdot X$ , is the number of cells actively biotransforming the substrate and  $K^b_2$  may have units of  $\text{mL} \cdot \text{organism}^{-1} \text{day}^{-1}$ .

With this model, variations in biotransformation rates can be considered in terms of: (1) relatively longer term changes in the subpopulation (i.e., number of cells capable of biotransformation of the specific organic) related to selective biological and ecological pressures, and (2) shorter term changes in the expression of the biotransformation activity within a cell. The latter possibility becomes important when the molecular biological machinery that cells use to regulate or control biotransformation activity is considered. This control can be at the genetic or the operating enzyme level and be exquisitely sophisticated and very rapid. Subpopulation related changes in biotransformation rates may occur over time frames of hours to weeks or months. The molecular control process is important with time intervals as small as seconds or minutes.

What evidence exists that supports the variability and mechanism of the structured biotransformation model? In earlier work with toluene in a continuous reactor, measured variations in the percent of the toluene stripped occurred over a time frame of 1 to 3 hours and were reliably monitored by measuring toluene in the feed and offgas. Toluene can be shown not to sorb strongly on biomass. For cases where sorption can be neglected and no other competitive fates such as chemical or photochemical conversion are active, equation 3 can be shown graphically in terms of S and B. The solutions of the equation are shown in Figure 3. By using equation 7 to calculate  $K^b_2$  for the test reactor, by knowing that the HRT was 1 day, and by knowing that the percent of toluene that stripped during this period ranged from near zero to 75 percent (Figure 4), the biotransformation rate parameter,  $B = K^b_2 \cdot X \cdot \text{HRT}$ , can be seen to vary over 3 orders of magnitude. Further, the expected variation in the stripping rate parameter (shown by error bars) is insignificant relative to the variation in the biotransformation rate parameter. The huge variation of  $K^b_2 \cdot X \cdot \text{HRT}$  over such a short time frame (1-3 hours) cannot be related to an equivalent change in the subpopulation,  $X$ . Rather, it has to be related to cellular regulatory controls that "switch-on-and-off" the toluene biotransformation as a result of some ecological or environmental influence on the cellular needs.

Recent data on naphthalene degradation in a 0.35 L continuous, "steady-state" reactor shows naphthalene stripping removal varying from 7 to over 80 percent over a time frame of several weeks [13, 14]. Naphthalene sorption can also be neglected by calculation and measurements. Figure 5 shows that the biotransformation rate

TABLE 2. BOKINETIC RATE CONSTANTS AND FATE PREDICTIONS FOR 2,4-DICHLOROPHENOL BIOTRANSFORMATION

Run	Disappearance Rate Constant <sup>a</sup> (hr <sup>-1</sup> )	Biotransformation Rate Constant (hr <sup>-1</sup> )	Percent Removal by <sup>b</sup>			
			Sorption	Stripping	Biotransformation	Effluent
Overall	0.045 (±0.005)	0.052 <sup>c</sup>				
1		0.075	0.008	0.034	63.0	33.6
2		0.043	0.67	2.0	21.6	76.8
3		0.070	0.25	1.8	29.8	68.1
4		0.020	0.78	2.2	10.8	86.2

a. Conventional empirical methods, Reference 11  
 b. Using equations 1-7 from this work  
 c. Average for all runs

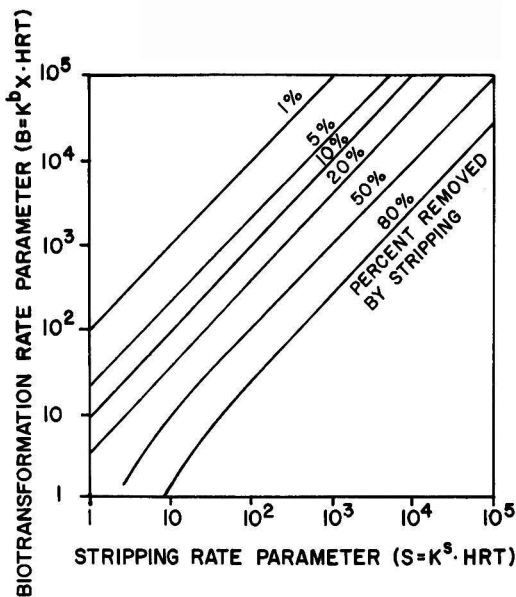


Figure 3. Relationship between the stripping and biotransformation rate parameters and the percent removal by stripping.

parameter again varies over two orders of magnitude and that the variation in  $B$  dwarfs variations in the stripping rate constants. Because of the longer time frame, longer-term subpopulation changes may be the cause of the biotransformation rate variation. Measurements of the naphthalene-degrading subpopulations support these suppositions.

#### APPLICATION OF THIS APPROACH FOR EMISSION ESTIMATION

For a given system and system parameters and a given compound Henry's law constant, the stripping rate pa-

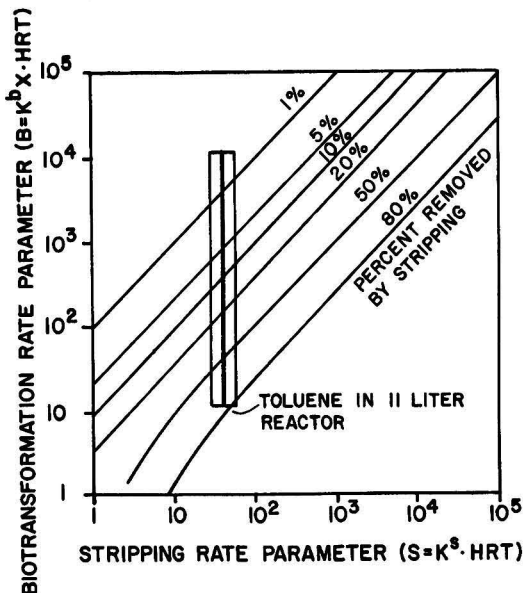


Figure 4. Results from toluene biotransformation in an eleven liter, continuous activated sludge reactor.

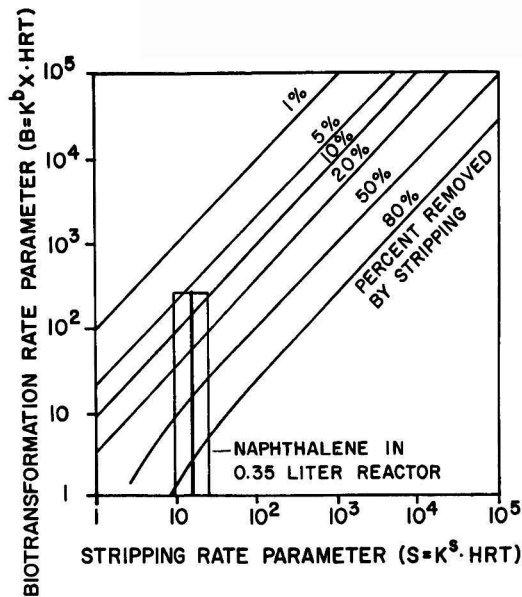


Figure 5. Results from naphthalene biotransformation in a 0.35 liter, continuous activated sludge reactor.

rameter may be calculated using equation 7. If the distribution of the two system variables air flow,  $Q_{air}$ , and volume,  $V$ , for all operating treatment systems in a region were known and the distribution of biotransformation rate parameters for a given compound were known (experimental testing and treatability studies), emission estimates would be possible for individual systems or for the region.

For example, a "most probable" scenario of likely values for the system parameters can easily be formulated. A set of such values can be found in Table 3. Note that these values are simply chosen and could be adjusted based on any given plant design or any probability distribution of system variables. Having chosen these variables, the abscissa of the relationship of the relationship plotted in Figures 1-4 can be amended to be a function of only Henry's law and any volatile compounds can be located on the graph (Figure 6). The biotransformation rate parameter required to achieve a given percent stripping removal (assuming no significant compound sorption) can be determined. If, for instance, a stripping fate of less than 10 percent of the feed was desired in a plant with "most probable" system parameters, the biotransformation rate parameter required for naphthalene would be near 20, while a transformation of around 1000 would be required for trichloroethylene. A biotransformation rate parameter of approximately 1 million would be required if only 10 percent of vinyl chloride were to be stripped and 90 percent biotransformed.

The impact of a compound's stripping potential on the required biotransformation rate parameter can place ma-

TABLE 3. VARIABLES FOR "MOST PROBABLE" TREATMENT PLANT SCENARIO

Biomass Concentration -	
Mixed Liquor Suspended Solids, $X$	2000 mg/L
Volume, $V$	day $10^6$ L
Air Flow to Liquid Volume Ratio,	
$Q_{air}/V$	144 day $^{-1}$
Mean Cell Residence Time, $\theta_c$	2.5 day
Hydraulic Residence Time, HRT	1 day

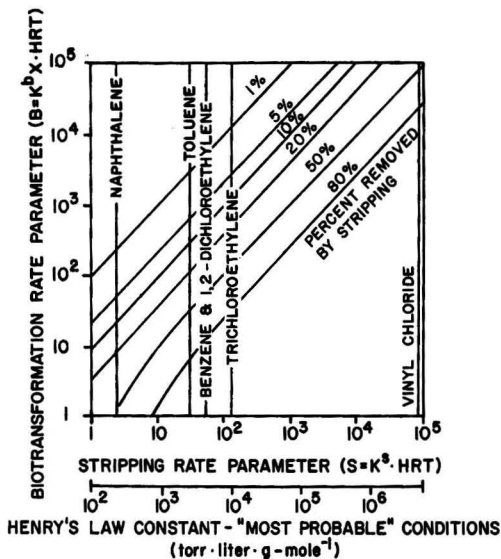


Figure 6. Stripping removal for several compounds for "Most Probable" systems.

for demands on the enzymatic process. An organism degrading 90 percent of the vinyl chloride (in the absence of sorption) would have to use an enzyme system with kinetics 50,000 times faster than the naphthalene biotransformation enzyme, an active subpopulation 50,000 times larger than in a naphthalene-degrading system, a residence time 50,000 times greater than the naphthalene-degrading system, or a combination of each factor. These are serious constraints to place on nature or on a man-made treatment process and may offer insight as to why certain compounds (in this case, very highly volatile compounds) may not readily degrade.

#### THE EFFECTS OF SORPTION

Using both the sorption model presented in equation 6 for the compound of interest and "most probable" values for the model variables as shown in Table 3, a relationship between the octanol-water partition coefficient,  $K_{ow}$ , the sum of the stripping and biotransformation rate parameters,  $S+B$ , and the percent removal by sorption on the waste biomass can be derived from equation 2. This is presented in Figure 7. For our "most probable" system, we wish to limit the amount of a specific compound that sorbs on waste biomass and then is disposed of in non-hazardous waste land disposal to 10 percent of that fed to the system. The minimum-required  $S+B$ , to achieve less than 10 percent sorption would be 0.01 for a compound with a  $K_{ow}$  of 10, 1 for a  $K_{ow}$  of  $10^3$ , and 100 for a  $K_{ow}$  of  $10^5$ . Minimal  $S+B$  levels are required for lower  $K_{ow}$  compounds and generally can be easily achieved. Thus, for lower  $K_{ow}$  compounds sorption is not important in biological processes unless specific sorption reactions (ionic or polar compounds) or active uptake is at play. For medium-to-higher  $K_{ow}$  compounds, however, sorption can be important 1) if biotransformation rates vary widely, 2) if stripping processes are minimized (by reducing the air flow, for example), or 3) if the compounds are recalcitrant in terms of biotransformation.

It has been suggested that, in general, biological catalytic activity decreases with increasing  $K_{ow}$ . Since  $K_{ow}$  and aqueous solubility are inversely related, stripping potential may hold steady or increase with increasing  $K_{ow}$ .

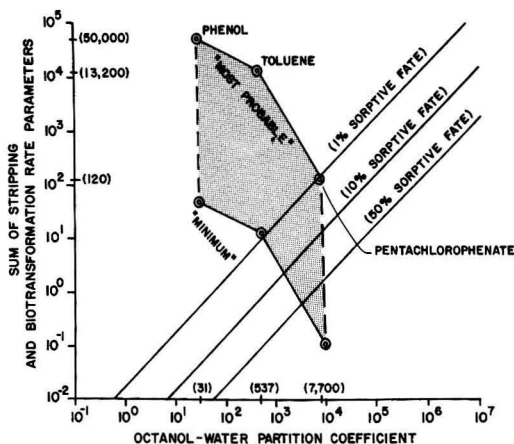


Figure 7. Sorption as a function of octanol-water partition coefficients and the sum of stripping and biotransformation rate parameters for the "Most Probable" systems.

Use of structure-activity relationships in the context of the coupled mechanism equations presented here may provide useful further generalizations regarding the effect of  $K_{ow}$  on fates.

#### CONCLUSIONS

A coupled mechanism equation and related fate equations provide a basis for estimating organic compound fates from a single or a group of biological wastewater treatment systems. This approach can be used to correct existing treatability data for stripping and sorption processes and, in new treatability experiments, can provide for an indirect measure of the biotransformation rate mechanism. Use of existing data in the proposed equations suggests strong ecological subpopulation control and enzyme regulation effects resulting in major variations in biotransformation rates. Biotransformation rates are the most sensitive parameters in the fate prediction model.

The coupled kinetic approach can also help elucidate the limits of an existing process to treat various specific compounds and also to establish the minimum stripping and biotransformation rates required to achieve a given concentration of a specific compound in waste biomass. In summary, this tool should find application at the design, construction, operation, and regulatory levels of biological treatment of wastes containing specific organics with hazardous or toxic properties.

#### LITERATURE CITED

- Blackburn, J. W., W. L. Troxler, K. N. Truong, R. P. Zink, S. C. Meckstroth, J. R. Florence, A. Groen, G. S. Saylor, R. W. Beck, R. A. Minear, A. Breen, and O. Yagi, 1985, "Organic Chemical Fate Prediction in Activated Sludge Treatment Processes," EPA/600/S2-85/102, (NTIS PB 85-247674).
- Blackburn, J. W., W. L. Troxler, and G. S. Saylor, 1984, "Prediction of the Fates of Organic Chemicals in a Biological Treatment Process—An Overview," *Env. Prog.*, Vol. 3, No. 3, pp. 163-176.
- Truong, K. N., and J. W. Blackburn, 1984, "The Stripping of Organic Chemicals in Biological Treatment Processes," *Env. Prog.*, Vol. 3, No. 3, pp. 143-152.
- Saylor, G. S., A. Breen, J. W. Blackburn, and O. Yagi, 1984, "Predictive Assessment of Priority Pollutant Bio-Oxidation Kinetics in Activated Sludge," *Env. Prog.*, Vol. 3, No. 3, pp. 153-163.



5. Blackburn, J. W., et al., 1985, "Organic Chemical Fate Prediction in Activated Sludge Treatment Processes," EPA/600/S2-85/102, (NTIS PB 85-247674), pp. 31-60.
6. Ibid., pp. 292-303.
7. Ibid., pp. 303-308.
8. Ibid., pp. 138-139.
9. Ibid., p. 301.
10. Ibid., pp. 75-118.
11. Beltrame, P., P. L. Beltrame, P. Carniti, and D. Pitea, 1982, "Kinetics of Biodegradation of Mixtures Containing 2,4-Dichlorophenol in a Continuous Stirred Tank Reactor," *Water Res.*, Vol. 16, pp. 429-433.
12. Blackburn, J. W., et al., 1985, "Organic Chemical Fate Predictions in Activated Sludge Treatment Processes," EPA/600/S2-85/102, (NTIS PB 85-247674), pp. 166-220.
13. Blackburn, J. W., R. K. Jain, and G. S. Sayler, 1986, "Optimization of a Continuous Mixed-Culture Microbial System Using Monitoring and Control of a Critical Catabolic Genotype," Presented at the Eighth Symposium of Biotechnology for Fuels and Chemicals, Gatlinburg, Tennessee.
14. Jain, R. K., J. W. Blackburn, and G. S. Sayler, 1986, "The Use of Gene Probes to Monitor Catabolic Genotypes in a Contin-

uous Mixed Culture Microbial System," Presented at the Southeastern Symposium on In-Situ Treatment and Immobilization of Hazardous and Radioactive Wastes, Knoxville, Tennessee.



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# Ozonolysis of Organic Compounds In A Two-Phase Fluorocarbon-Water System

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*Ozone, due to its characteristics as a powerful oxidant, has found use in the destruction of toxic organic compounds in wastewater. Its use has been limited however, because of ozone's rapid decomposition and low solubility in water. The ozonation process may be more efficiently carried out in a two-phase system. The second phase consists of a reusable, fluorinated hydrocarbon, with an ozone solubility of 12-14 times that of water. The fluorinated solvent serves as both an ozone source and a non-aqueous phase in which the oxidation occurs. With this novel two-phase process, it is also possible to perform selective oxidation. The experimental results are presented for organic compounds such as phenol, naphthol, etc. The extent of degradation is measured in terms of pH changes, HPLC, and TOC.*

## INTRODUCTION

Chemical oxidation in wastewater treatment serves as a method of removing various organic materials that are resistant to other methods, such as biological treatment. Liquid phase oxidation of organics can be carried out in two ways: (1) Wet oxidation [1] at high temperature (150-250°C) and pressure (20690 kPa); and (2) ozonation at room temperature. The high temperature and pressure required by the wet oxidation process warrants further investigation of ozonation as an alternative oxidation technique.

Ozone (O<sub>3</sub>) has long been used as a chemical oxidant due to its rapid reaction with various organic compounds. One group of organics that react rapidly with ozone are phenolic compounds. Single phase studies indicate that phenolic oxidation is controlled by the rate of ozone mass transfer rather than reaction kinetics [2]. However, the products of phenolic oxidation often include a variety of low molecular weight organic acids and their aldehydes which react much slower with ozone [3]. For designing a proper contacting system one must consider reaction kinetics as well as mass transfer. A two-phase system is proposed as an alternative to single-phase ozonolysis.

Providing a second reusable solvent phase with high ozone solubility, and in which a typical organic is partially extractable, would enhance both mass transfer and reaction kinetics. Since oxidation would occur in the sol-

vent phase, only extractable compounds would oxidize, allowing selective oxidation and reducing ozone demand. This report details the results of two-phase ozonolysis of phenol, naphthol, and phenol in the presence of sodium sulfite.

## OBJECTIVES

The overall objective of this research is to establish the feasibility of a novel two-phase ozonation process. The specific objectives are: (1) to establish solubility of ozone in fluorocarbon solvent, (2) to show the efficiency of performing ozonation reactions in a "two-phase" system, (3) to perform a preliminary experiment to determine possible use as a selective oxidation technique, (4) to determine the effect of contact time on pH drop and destruction of phenol and 2-naphthol, and (5) to show formation of reaction intermediates.

## BACKGROUND

Ozone (O<sub>3</sub>), an allotropic form of oxygen, is a colorless gas at room temperature. With a molecular weight of 48, it is approximately one and one-half times as dense as oxygen. From microwave spectra, the ozone molecule has been described as a resonance hybrid [3]. Ozone is one of the most powerful oxidants known (only F<sub>2</sub>, F<sub>2</sub>O, and O<sup>•</sup> are better) and is thought to exhibit free radical oxidation via the following reaction:



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## Ozone Generation

Ozone is typically produced by subjecting oxygen or air to an electrical or corona discharge [4]. In a recent study by Foller and Goodwin, ozone was produced electrochemically in amounts 8 to 15 times that possible by air-fed Corona discharge [5]. Another less popular method is ultra-violet excitation. Air or oxygen is irradiated with ultra-violet light producing low concentrations of ozone.

## Ozonolysis Reactions

The reaction of ozone with organic molecules has been studied extensively in the development of alternative wastewater treatment techniques. Reactions involving aromatic compounds are of particular interest due to their frequent occurrence in wastewater from industrial processing. Ozone reacts with aromatic compounds to form catechol and hydroquinone, which in turn react with various organic acids such as muconic, maleic, glyoxylic, glycolic, oxalic, and formic [6, 7]. Japanese workers observed that the major product of phenolic oxidation was formic acid [8]. A detailed study was conducted by Devlin and Harris [1] of the oxidation of phenol at elevated temperature and pressure. The reaction pathway involves formation of dialcohols and ketones, followed by opening of the aromatic ring to form various acids. Further decomposition often involves CO<sub>2</sub> production and degradation to formic acid, which reacts much more slowly to give CO<sub>2</sub> and water. It must be noted that the pathway includes compounds too short-lived to isolate, but which are consistent with the sequential reaction scheme [1].

## Ozonation Reaction Kinetics in Single Phase Systems

The reaction of ozone with organics has been expressed as a second order reaction [9, 10]:

$$r = k_1 C_A [O_3] \quad (2)$$

$r$  = rate of reaction of organic per unit volume, mol l<sup>-1</sup>t<sup>-1</sup>

$k_1$  = reaction rate constant, l mol<sup>-1</sup>t<sup>-1</sup>

$C_A$  = aqueous concentration of organic reactant, mol l<sup>-1</sup>

$[O_3]$  = aqueous concentration of ozone, mol l<sup>-1</sup>

In the presence of excess ozone, Equation (2) can be considered pseudo-first order. Measurements of the rate constant ( $k_1$ ) indicate that as pH increases above 3, ozone decomposes to form highly reactive hydroxyl radicals and the reaction rate increases. In addition, phenol ionizes to form the more reactive phenolate ion at pK = 9.9.

Alternative expressions have been reported by Gould [11] and Eisenhauer [12] describing phenol concentration profiles during ozonation as:

$$\frac{dC_A}{dt} = K_c F C_A \quad (3)$$

$K_c$  = combined rate constant, mol phenol (mol O<sub>3</sub>)<sup>-1</sup>

$F$  = dosage rate, moles of ozone per minute per mol phenol initially present, mole of O<sub>3</sub> mol<sup>-1</sup>t<sup>-1</sup>

$C_A$  = phenol concentration, mol l<sup>-1</sup>

Equation (3) considers the effects of both mass transfer and reaction. Thus, the combined rate constant  $K_c$ , is system-specific [6].

## Ozonation Techniques

Ozone stability decreases with temperature, thus most ozonation reactions are carried out at room temperature since ozone is a powerful oxidant even at these temperatures [1]. A typical contacting system involves bubbling

ozonized gas through aqueous solutions containing a hazardous organic. Other systems have been used involving packed columns, jet scrubbers, pressure injectors, and turbine agitated reactors [13]. A major difficulty associated with this system is the low solubility of ozone in water. An alternative technique has recently been proposed [5] in which ozone is dissolved directly into a stream of pure water at high pressure. The ozone-rich water stream is then mixed with the wastewater to be treated. This method resembles wet oxidation processes in which oxygen-rich water is mixed with wastewater at high temperature and pressure. Both ozonation techniques rely on a comparatively slow mass transfer rate in comparison with reaction kinetics.

## THEORY

An extensive literature review produced no articles concerning two-phase ozonation reactions. The ideas presented in this section are grounded in well-established oxidation and extraction theory [14-18].

## Two Phase Oxidation

The two-phase oxidation process consists of a chemical extraction from the aqueous phase followed by oxidation by ozone in the solvent phase. The intermediate oxidation products of many organics often include highly polar acids which diffuse back to the aqueous phase due to their high solubility.

The relative rates of extraction/oxidation determine whether the system is "diffusion controlled" or "kinetically controlled." If oxidation is rapid compared to mass transfer of solute to solvent phase, the system is "diffusion controlled." In a "kinetically controlled" system the converse is true. The extraction/oxidation process can be modeled using the "two film theory" proposed by Lewis and Whitman.

## Oxidation/Extraction: An Overall Model

Oxidation of an organic solute A, in the solvent phase is described as a second order reaction as expressed in Equation (2). Under conditions of excess O<sub>3</sub>, the reaction is assumed to be pseudo-first order, thus Equation (2) reduces to:

$$r = k_2 C_A \quad (4)$$

In order to formulate an overall model, diffusion of organics from aqueous to solvent phase must be considered:

When an aqueous solution containing a dissolved organic solute is brought into contact with an immiscible nonpolar solvent like FC 77, partial solute distribution may occur between the two phases. Solute distribution is expressed as a distribution coefficient  $K_D$ , defined as:

$$K_D = \frac{C_A (\text{solvent phase})}{C_A (\text{aqueous phase})} \quad (5)$$

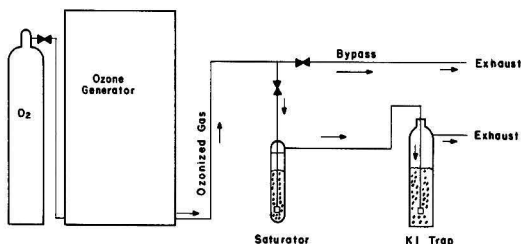


Figure 1. Flow diagram of experimental setup.

TABLE I. FC 77 SOLVENT PROPERTIES [19]

Boiling point	97°C
Thermal stability	270°C
Solubility in H <sub>2</sub> O	negligible
Specific gravity	1.78
Vapor pressure at 25°C	42 mm Hg
Avg. molecular weight	415
Solubility of O <sub>2</sub> at 25°C	56 ml/100 ml solvent

K<sub>D</sub> values vary with pH for ionizable solutes such as phenol and are solute specific. For example, at a high pH level (pH > pK<sub>a</sub>) organics containing hydroxyl group ionize and thus exhibit higher affinity for the aqueous phase.

A differential material balance with respect to the solute (A), combined with K<sub>D</sub> as defined in Equation (5) results in the rate expression (14):

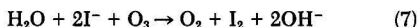
$$\frac{d(C_A)_{AQ}}{dt} = - \frac{V_{solvent} K_D k_2 (C_A)_{AQ}}{(K_D V_{solvent} + V_{AQ})} \quad (6)$$

by defining  $k_{apparent} = \frac{V_{solvent} K_D k_2}{(K_D V_{solvent} + V_{AQ})}$ .

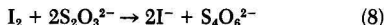
Equation (6) can be rewritten as a pseudo-first order reaction. From experimental determinations of k<sub>app</sub>, the first order rate constant k<sub>2</sub> can be approximated.

**EXPERIMENTAL**

A Welsbach T-816 ozonator with pure oxygen feed provided a continuous supply of ozone for saturating the solvent liquid (Figure 1). Ozone concentration was determined by bubbling a known amount of ozonized gas through a 2% KI solution using a medium pore diffuser mounted in a 100 ml test tube. Ozone reacted with iodide ion (I<sup>-</sup>) to form free iodine as follows [11]:



The resulting solution was acidified with 1N sulfuric acid to convert any iodates that were formed to iodine. Free iodine was then titrated with .005N sodium thiosulfate solution according to the reaction:



Tests for ozone solubility in the fluorocarbon solvent were conducted in a similar manner. The fluorocarbon solvent (designated as FC 77) was obtained from the 3M Company. Forty ml samples of the FC 77 solvent were saturated by bubbling ozonized oxygen through the sol-

vent for periods of up to 60 minutes. A 10 ml sample of the ozonated solvent was then removed and contacted with 100 ml of 2% KI solution. After vigorous shaking for several minutes, the two phases were transferred to a separatory funnel and 50 ml of the aqueous KI solution was titrated with sodium thiosulfate solution. Since the fluorocarbon solvent was insoluble in water, separation was quick and complete. Spent solvent was separated and contacted a second time with fresh KI solution to detect any unreacted ozone remaining.

Ozonolysis of aqueous solutions was conducted with phenol, 2-naphthol, and a 5:1 (molar) ratio of sodium sulfite and phenol. Each trial was performed identically by saturating 40 ml of fluorocarbon solvent with ozone and contacting with 10 ml of aqueous solution for 2, 5, 10, 30, or 60 minutes while shaking them vigorously. All runs were performed at the ambient temperature of 25°C. Aqueous samples were then separated for pH measurement, HPLC (High Performance Liquid Chromatography) and TOC (Total Organic Carbon) analysis.

Stock solutions and aqueous phases after contacting with ozonated solvent were analyzed using a Beckmann 915 Total Carbon Analyzer for changes in organic carbon content. Temperatures of 950 and 150°C were used in total carbon and inorganic carbon columns, respectively. HPLC analysis of aqueous phases was performed using a

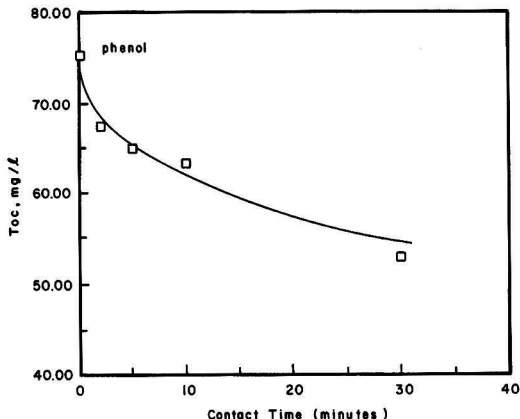


Figure 3. Effect of oxidation time on TOC removal for phenol.

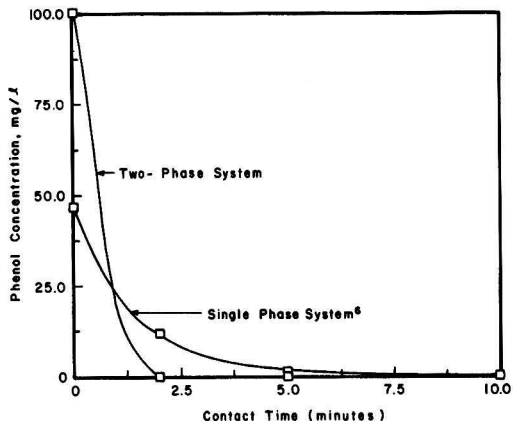


Figure 4. Disappearance rate of phenol in single and two phase systems.

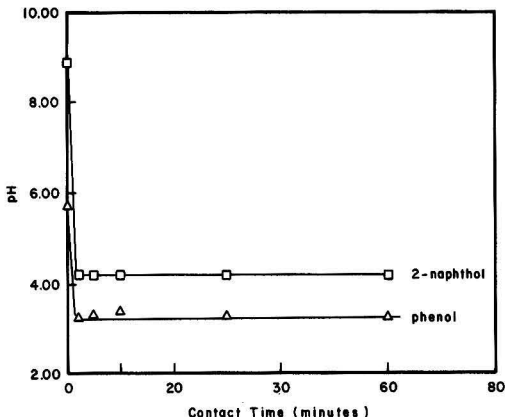


Figure 2. pH change with oxidation time for phenol and 2-naphthol.



Varian Model 5000 with a variable UV detector and a Vista computer system. The HPLC column Varian Micropak MCH-10 contained a stationary phase of 10  $\mu\text{m}$  silica with a monomeric layer of octyldecylsilane. The carrier solvent consisted of an acetonitrile/water mixture in proportions of 20:80 for phenol solutions and 45:55 for 2-naphthol solutions. The ultraviolet detector was operated at a wavelength of 220 nm for phenol solutions and 226 nm for 2-naphthol solutions. Intermediate organic acids were also detected at these wavelengths.

## RESULTS AND DISCUSSIONS

The ozonation experiments were conducted at an initial pH of 5.7 for 100 mg/l phenol, and at pH 8.9 for 55 mg/l 2-naphthol. Aqueous solutions were contacted with an ozone saturated fluorocarbon solvent to determine the effect of contact time on pH, intermediate product formation, and changes in total organic carbon content. Ozone concentration and solubility in the solvent were also established by the iodometric method.

### Ozone Concentration, Solubility, and Solvent Properties

Ozonated samples of aqueous KI solution were collected at a gas flow rate of 0.2 l/min; an ozone concentration of 2% (57 mg  $\text{O}_3$ /l Air) was found. The solvent used in the ozonolysis experiments was an immiscible fluorinated hydrocarbon manufactured by 3M Company and is typically used in the electronics industry due to its inertness and high thermal stability.

Table 1 contains pertinent physical properties of the solvent, which is designated as "FC 77" [19]. The oxygen solubilities listed in Table 1 assume an oxygen partial

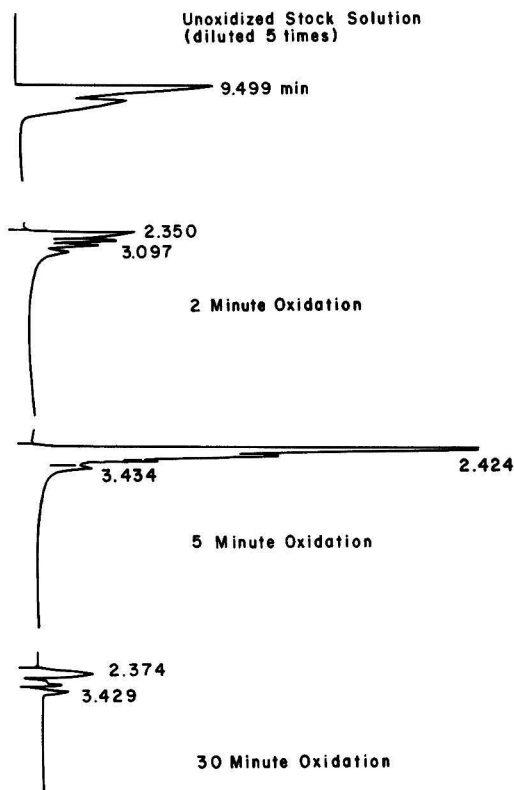


Figure 5. HPLC spectra of phenol oxidation.

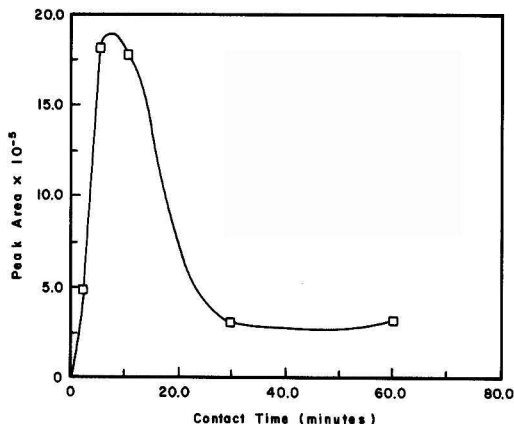


Figure 6. Peak area counts from HPLC spectra for phenol oxidation.

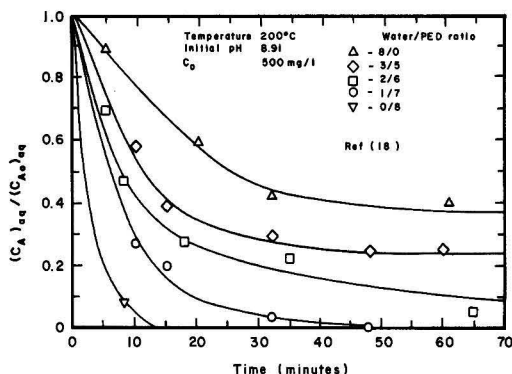


Figure 7. The effect of the water/PFD ratio on the disappearance rate of  $\beta$ -naphthol.

pressure of 1 atmosphere above the liquid. Since ozone concentration in ozonized gas is only 2%, solubility tests will not reflect true solubility limits, only that for our system. Solubility tests involving water and the solvent show ozone to be approximately 12-14 times more soluble in FC 77 than in water. Water is found to dissolve 0.29 ml  $\text{O}_3$ /100 ml  $\text{H}_2\text{O}$  while the solvent dissolves 3.7 ml  $\text{O}_3$ /100 ml FC 77.

### Oxidation of Phenol

Over the range of pH values studied, the effect of pH on extraction for the two-phase oxidation process was constant. The distribution coefficient  $K_D$  remains constant at about 0.1 for this pH range (pH 3-6) since (pH <  $\text{p}K_a = 9.9$ ). At pH = 10,  $K_D$  decreases to 0.05 due to phenol ionization to form the more soluble phenolate ion.

Aqueous samples were contacted with ozonized solvent in a ratio of 10 ml aqueous solution/40 ml solvent for 2, 5, 10, 30 and 60 minute periods. From solubility measurements, ozone dosage was determined to be about 8 mols  $\text{O}_3$ /mol phenol, which is about 57% of the stoichiometric amount for total oxidation assuming ozone reacts with phenol as follows:



The formation of organic acids was suspected when pH measurements showed a sharp drop after contacting with

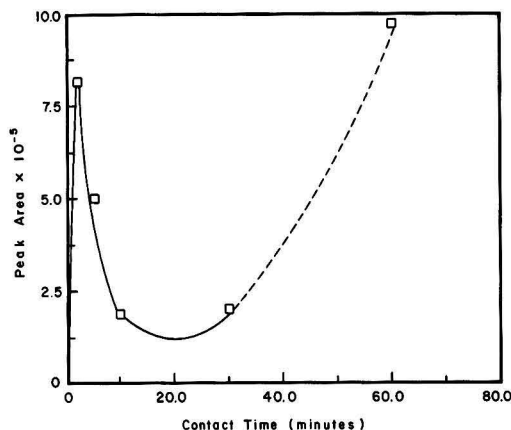


Figure 8. Peak area counts from HPLC spectra of 2-naphthol oxidation.

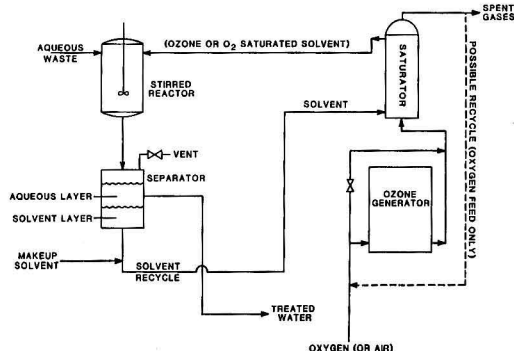


Figure 9. Proposed continuous process for a two-phase ozonation system.

ozone rich solvent. Figure 2 shows that after 2 minutes of contact pH had dropped to about 3.25 and remained relatively unchanged during further oxidation. pH stabilization occurs due to the formation of low molecular weight organic acids which oxidize very slowly.

TOC analysis of aqueous phases showed a significant drop in total organic carbon content with increasing contact time (Figure 3). Assuming that changes in organic carbon content were due mainly to  $\text{CO}_2$  formation, not extraction, reaction order can be deduced. Log organic carbon content was plotted vs. contact time yielding a straight line indicating that reactions involving the formation of  $\text{CO}_2$  were approximately first order. The pseudo-first order rate Equation (4) appeared to be valid for reactions of this type. The first order apparent rate constant for  $\text{CO}_2$  formation was  $0.05 \text{ min}^{-1}$ .

In Figure 4, two-phase ozonation of 100 ppm phenol is compared with that of single-phase [6] ozonation of 46 ppm phenol. In the two-phase system, destruction of phenol to concentrations below the detection limit (0.5 ppm) were obtained after only two minutes' contact, while in the single phase experiment, about 12.5 ppm of phenol remained after a 2-minute ozonation.

Comparison of initial reaction rates for one- and two-phase systems show that the reaction rate for two-phase ozonation is at least eight times that of the single-phase system. The relative rates could be much greater. Proof of this requires additional experiments with contact times < 2 min.

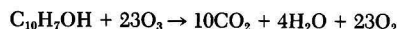
Ozonation of phenol is characterized by the formation of intermediate organics followed by decomposition to organic acids, such as oxalic, formic, etc., and eventually  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The rise and fall of various acid profiles correspond to the appearance and disappearance of sharp peaks in the 2-3.5 minute elution band of HPLC spectra in Figure 5. Comparing spectra from stock solution and ozonated samples, the phenol peak at 9.4 minutes vanishes after only 2 minutes of contact with ozonated solvent. Phenol oxidation must be very rapid.

Peak area counts in the 2-3.5 minute elution band were plotted vs. contact time in Figure 6. The rapid formation of intermediates were seen for ozonation time < 10 min. by the increase in peak area counts from  $5 \times 10^5$  to  $16 \times 10^5$  for 2 and 5 minute ozonations, respectively. The plateau encountered after 30 minutes suggested a slow oxidizing compound such as formic acid had been formed.

A 5 to 1 molar ratio of sodium sulfite to phenol was prepared (100 mg/l phenol) and contacted with ozone-rich solvent for 10 minutes to observe the oxidation changes for phenol. HPLC spectra showed that all of the phenol has been oxidized. Selective oxidation was achieved since oxidation of sulfite would have consumed a major portion of the available ozone. This prevented complete oxidation of phenol because such selective oxidation would not be possible with a single phase system.

### Oxidation of 2-Naphthol

The effect of extraction should be more pronounced for 2-naphthol since  $K_{D_{\text{naph}}} (= .3) > K_{D_{\text{phenol}}} (= .1)$ . Greater extractability should increase the efficiency of this process. Aqueous samples were contacted in the same manner as in phenol oxidations. However, 8 mols  $\text{O}_3/\text{mol}$  naphthol represents only 34.7% of the stoichiometric (for complete oxidation) ozone requirement, assuming ozone reacts with 2-naphthol as follows:



Again, organic acid formation was suspected due to pH drop. Figure 2 shows that the pH dropped from 8.9 to 4.2 after contacting for two minutes and remained unchanged during further oxidation. TOC analysis of aqueous phases showed an insignificant drop in organic carbon content, thus  $\text{CO}_2$  formation was negligible.

Concentration profiles of various aqueous/solvent ratios for high temperature (at  $200^\circ\text{C}$ ) [18] oxidation of 2-naphthol with oxygen using perfluorodecalin (similar to FC 77) as the solvent are shown in Figure 7. The advantage of the two-phase ozonation process over the high temperature oxidation process is demonstrated by observing that an aqueous/solvent ratio of 1/4, the high temperature oxidation process destroys only 60% of aqueous naphthol. The two-phase ozonation process destroyed all the 2-naphthol within 2 minutes according to the observed HPLC spectra. The feed solution naphthol peak observed at 7.7 min vanished completely after 2 minutes of oxidation time. Peak area counts of intermediates for 2-3.5 min elution band showed basically the same trends as for phenol (Figure 8).

### CONCLUSIONS

An innovative two-phase ozonation system for the destruction of organics was investigated. This two-phase ozonation process provides higher efficiency of organic destruction compared to a single-phase oxidation, or wet air oxidation process. The ozonation results indicate that the process is indeed feasible.

The specific conclusions are:

- (1) Use of an inert fluorocarbon solvent, which has

high ozone solubility, reduces mass transfer resistance in contrast to single-phase processes.

- (2) Ozone solubility in FC 77 solvent is approximately 12-14 times that in water.
- (3) Two-phase ozonation at room temperature is found to be more effective than two-phase wet air oxidation reported at 200°C.
- (4) Complete degradation of phenol (100 mg/l) and 2-naphthol (55 mg/l) is accomplished in less than 2 minutes' contact with ozonated FC 77 solvent.
- (5) Complete degradation of phenol (100 mg/l) is achieved even in the presence of a high concentration of sodium sulfite.
- (6) A reduction of 29% in total organic carbon content is observed after 30 minutes contact with ozonated FC 77 solvent.
- (7) Phenol reactions resulting in CO<sub>2</sub> formation exhibit pseudo-first order kinetics.
- (8) Negligible reduction in total organic carbon content for 2-naphthol (55 mg/l) is found after 60 minutes' contact with ozonated FC 77 solvent.
- (9) Formation of intermediate reaction products (organic acids) result for both phenol and 2-naphthol.
- (10) Reusability of solvent is established by resaturation and subsequent contact with an aqueous organic solution.

Future work should include further experiments on selective oxidation of hazardous organics from mixed solute systems. A continuous two-phase ozonation system (Figure 9) should be tested with model compounds as well as actual hazardous wastewater.

#### LITERATURE CITED

1. Devlin, R. D. and I. J. Harris, "Mechanism of the Oxidation of Aqueous Phenol with Dissolved Oxygen," *Ind. Eng. Chem. Fund.*, **23**, 4 (1984).
2. Rice, R. G. and M. E. Browning, "Ozone for Industrial and Wastewater Treatment: A Literature Survey," U.S. Environmental Protection Agency Report, EPA-600/2-80-060 (1980).
3. Bailey, P. S., "Organic Groupings Reactive Toward Ozone: Mechanisms in Aqueous Media," *Ozone in Water and Wastewater Treatment* (ed. by F. L. Evans III), Ann Arbor Science Publ. (1972).
4. Layton, R. F., "Analytical Methods for Ozone in Water and Wastewater Applications," *Ozone in Water and Wastewater Treatment*, (ed. by F. L. Evans III), Ann Arbor Science Publ. (1972).
5. Foller, D. C., and M. L. Goodwin, "Electrochemical Generation of High Concentration Ozone for Waste Treatment," *Chemical Engineering Progress*, **81**, 4 (March 1985).
6. Baillod, C. R., B. M. Faith, and O. Masi, "Fate of Specific Pollutants During Wet Oxidation and Ozonation," *Environmental Progress*, **1**, 3 (1982).
7. Rice, R. G., "Ozone for the Treatment of Hazardous Materials," Paper presented at 73rd Annual Meeting, AIChE, Chicago (1980).
8. Yamamoto, Y. E., H. Shiokawa, and Y. Kamiya, "Ozonation of Organic Compounds. 2. Ozonation of Phenol in Water," *J. Org. Chem.*, **44** (13), 2137-2142 (1979).
9. Hoigne, J. and H. Bader, "The Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous Solutions," *Water Research*, **10** (1976).
10. Gurol, M. D., "Kinetic Behavior of Ozone in Aqueous Solution: Decomposition and Reaction with Phenol," Ph.D. Thesis, Univ. of N. Carolina, Chapel Hill (1980).
11. Gould, J. P. and W. J. Weber, "Oxidation of Phenols by Ozone," *J. Wat. Poll. Cont. Fed.*, **48** (1), 47-60 (1976).
12. Eisenhauer, H. R., "Increased Rate and Efficiency of Phenolic Waste Ozonation," *J. Wat. Poll. Cont. Fed.*, **43**, 200 (1971).
13. Opatken, J. O., A. D. Venosa, and M. C. Meckes, "Contractor Evaluation for Ozonation of Wastewater," Paper presented at US/USSR Joint Symposium (1978).
14. Klien, E., McKelvey, and B. G. Webre, "The Simultaneous Measurement of Distribution Coefficients and Hydrolysis Rates," *J. Chem. Phys.*, **62**, 286-288 (March 1958).
15. Kuo, C. H. and C. J. Huang, "Liquid Phase Mass Transfer with Complex Chemical Reaction," *AIChE Journal*, **16**, No. 3, 493-496 (May 1970).
16. Merchuk, J. C. and I. H. Farino, "Simultaneous Diffusion and Chemical Reaction in Two Phase Systems," *Chem. Eng. Sci.*, **31**, 645-650 (1976).
17. Sharma, M. M. and R. D. Mhaskar, "Extraction with Reaction in Both Phases," *Chem. Eng. Sci.*, **30**, 811-818 (1975).
18. Glynn, W. K., "Two-Phase Oxidation of Toxic Organic Compounds," M.S. Thesis, University of Kentucky, Lexington, KY (1984).
19. 3M Products Manual "Fluorimert<sup>tm</sup> Electronic Liquids," (1982).

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# Recent Changes in Superfund Policy and Guidance: Alternative Technology

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*Engineering practices applicable to Superfund sites, as viewed in the context of the institutional policies that guide them are discussed below. Past practice has relied heavily on land disposal of wastes removed from uncontrolled hazardous waste sites. The requirements of the 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act however, have caused land disposal to be the option of last choice. Indeed, the HSWA's general policy directives have established the overall environmental goal of drastically reducing dependence on land disposal for all forms of hazardous waste. As a result, a new set of waste treatment/disposal priorities has been implemented for Superfund site Remedial Actions. The first priority is reuse or recycling of waste, the second is waste destruction, and the third is waste immobilization. The paper outlines the steps for selecting waste treatment processes for Superfund sites and distinguishes between in situ and mobile technologies.*

## INTRODUCTION

In 1984 EPA Administrator William D. Ruckelshaus reminded the International Solid Waste Association that "ten years ago, for all practical purposes, we were unaware that there was a hazardous waste problem." Putting the rapid development of the EPA hazardous waste regulatory structure in perspective, Mr. Ruckelshaus pointed out that to address this newly-recognized problem "we are building a set of very large national institutions from the ground up" to handle "an immense *physical* undertaking . . . a civil engineering operation of staggering proportions. Quite literally, we are moving mountains" [1].

The purpose of this paper is to discuss Superfund's engineering practices, setting them in the context of the institutional policies that guide them. Even within the short history of the Superfund program, engineering within the program has evolved and matured. In part, changes in engineering approach reflect a greater technical understanding of the problems we face. But in addition, they reflect significant new emphases in underlying Congressional and EPA policy, changes that are altering the basic structure of the national hazardous waste management system.

## LONG-TERM PERSPECTIVE

The last six years have underscored the immensity of Superfund's cleanup obligations. Early expectations that the program would be a short term quick fix have given way to the reality of a major long term effort. There is considerably more awareness today of the ultimate environmental effects of cleanup programs, particularly in regard to containment practices. We now recognize more clearly that, in the worst case, we may simply be moving

Superfund sites from one place to another; today's landfills can become tomorrow's new generation of uncontrolled sites. Even if landfills are properly managed, they require careful supervision and long-term monitoring if they are not to become vehicles for shifting contaminants to other environmental media. Such realizations have significantly modified the way the Superfund program budgets its resources and views its environmental responsibilities.

In the past, containment technologies have had relatively low initial capital costs, but the initial capital costs of land disposal are projected to climb as the design provisions of the 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) are implemented. HSWA and RCRA have also significantly increased costs of operation and maintenance. The overall effect is to make land disposal far less attractive economically than it has been in the past. For example, pre-HSWA land disposal costs (at commercial rates) have been estimated at \$30 to \$66 per metric ton; projected rates for land disposal under current HSWA requirements are estimated at \$100 per metric ton (for wastes that do not require solidification) and \$350 per metric ton (for wastes that require cement solidification)\*.

\* These higher figures include all technical improvements required under part 264 of HSWA (including double synthetic and clay liners, leachate collection systems, and monitoring) as well as closure costs and post-closure care. Current regulations do not require solidification, but the new amendments *will* require it. The estimates shown here cover changes related to liquid solidification requirements, but do not include consideration of supply and demand effects. Sources: "Regulatory Impact Analysis of Restrictions on Land Disposal of Certain Solvent Wastes," November 1986, EPA; "Regulatory Impact Analysis of Restrictions on Land Disposal of California Wastes," October 27, 1986, EPA.

Costs for alternative approaches to managing CERCLA wastes—through recycling, reuse, destruction, and other forms of treatment—are therefore far more cost-effective now than in previous years, especially when long term costs are calculated. This has created a powerful incentive to move away from containment technologies and toward an array of treatment alternatives.

Yet cost considerations are only part of the picture. HSWA's general policy directions have been even stronger than the economic impacts of its engineering standards. These set the overall national environmental goal of drastically reducing dependence on land disposal for all forms of hazardous waste. HSWA encourages many alternatives to land disposal, emphasizing resource reuse and recovery as well as treatment. These same themes appear in reauthorization language for Superfund's statute (the Comprehensive Emergency Response, Compensation, and Liability Act, or CERCLA). The general trend of environmental policy as set by Congress is unmistakable. Land disposal has become the waste management option of last resort.

The long-term challenge to superfund is to implement this policy as an integral part of the program's obligation to provide rapid, safe, and reliable response to the threats posed by uncontrolled sites.

#### APPLICABILITY OF TREATMENT TECHNOLOGIES TO CERCLA

One aspect of Superfund that deserves some discussion is the difference between removal and remedial actions as they affect waste treatment. The purpose of removal actions is to respond to imminent hazards; as the name implies, they emphasize physical *removal* of any wastes that could cause acute risks to health or the environment. When treatment is used as part of a removal action, it therefore usually occurs off site. Opportunities for onsite treatment are limited: occasionally wastes may be neutralized to reduce handling risks and the possibilities of containment ruptures, but more ambitious treatments are very seldom used. On the other hand, removal actions are more likely than remedial actions to employ recycling or resource recovery. This is simply because removal actions are more likely than remedial programs to encounter intact drums containing concentrated wastes suitable for recycling. Remedial actions usually must deal with wastes after they have escaped containment and are mixed with soil, water, or debris, making recycling of constituents neither cost-effective nor technically feasible.

When we discuss the use of treatment at CERCLA sites, we do so with reference primarily to remedial actions, not removals. Procedurally, the process by which remedial actions are evaluated and selected must include detailed evaluations of treatment options for all remedial actions.† This has always been the case, but despite the intent of this policy, actual use of treatment has been considerably lower in the past than it will be in the future, for the reasons discussed above. A review of current statistics on frequency of use of treatment alternatives is presented in Figures 1a and 1b.

Although superfund emphasis on recycling and treatment of wastes is moving in parallel with RCRA, Superfund's use of treatment is not simply an extension of RCRA policy. The two correspond closely in some ways, but programmatic and technical differences are often highly significant. Similarities and differences are explored below.

Specific regulatory requirements of CERCLA for offsite and onsite treatment of Superfund wastes form one of the closer links between CERCLA and RCRA. Offsite treatment, storage, and disposal of Superfund wastes must occur at a RCRA-approved facility, operated according to RCRA standards. Hazardous substances from a Superfund site may be transferred to a land disposal facility only if (1) the unit receiving such hazardous substances is not releasing any hazardous wastes into the ground water, surface water, or soil and (2) all releases of hazardous wastes from other units at the facility are being controlled by a corrective action program approved by EPA under Subtitle C of RCRA. In addition, there must be no unusual conditions at the site or facility that would adversely affect that facility's ability to protect human health, welfare, or the environment.

Onsite treatment requirements set forth in the National Contingency Plan for Superfund wastes, while linked to RCRA, have some significant differences. The treatment process involved must meet any RCRA technical performance operational and design standards that would otherwise apply if the treatment were used off site, but at

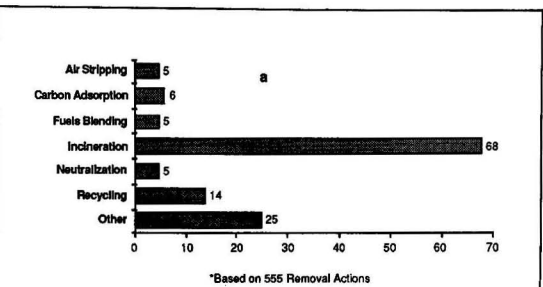


Figure 1a. Use of treatment technologies as part of removal programs.

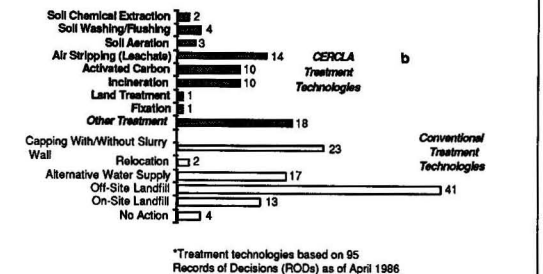


Figure 1b. Use of treatment technologies at remedial action sites.

Fig. 1a presents similar statistics for remedial actions, based on review of 95 Records of Decision. Note that recycling is not specifically identified as a treatment technology for any action, probably reflecting less frequent encounters with concentrated wastes in containers. The most frequently used technology has been air stripping to remove volatile organics from ground water, followed by incineration and carbon adsorption. Although only one site has been listed as using fixation, this may reflect that option's recent availability on a commercial basis; we expect fixation to be much more widely used in the future (see text). Several sites are using numerous approaches to soil treatment—a process that often occurs *in situ*—including soil flushing, soil aeration, and chemical extraction.

†This process is formally known as the Remedial Investigation and Feasibility Study (RI/FS) process.



present such technology-specific standards are limited (additional standards are in preparation by the Office of Solid Waste).<sup>†</sup> Facilities that treat hazardous wastes on site may also have to comply with other requirements related to safety, insurance coverage, training, and preparation of contingency plans for spills of hazardous materials.

Although they have to follow RCRA standards, treatment installations at Superfund sites do not have to obtain a RCRA permit if the cleanup response is undertaken under the authority of CERCLA, Section 104 (i.e., if it supports a removal action or is a remedial action at a National Priority List (NPL) site).

Differences between Superfund and RCRA begin to emerge when we consider the range of conditions under which treatment technology is actually used in the field. For newly generated RCRA wastes, for instance, treatment can generally occur within well-controlled facilities, often even within the premises of the waste generator. In contrast, a typical Superfund site is usually not a convenient setting for evaluating or managing hazardous materials or for applying complex industrial technologies. Moreover, Superfund wastes and sites vary widely among themselves.

Other special technical requirements related to the performance of treatment technologies at CERCLA sites derive from the inherent characteristics of uncontrolled sites. CERCLA sites seldom contain single-constituent, homogeneous waste streams. Treatment options must therefore often handle a heterogeneous mixture of wastes—a “soup” of combined solids, liquids, and sludges including both organic and inorganic compounds. Treatment must respond to these mixtures without breakdowns or losses of efficiency that might create uncontrolled shifts of pollution to other environmental media. A breakdown of an incinerator, for instance, could result in serious air pollution; a failure in a fixation process could cause serious surface-water or ground-water contamination.

In addition to handling mixtures of wastes, treatment at Superfund sites must often handle very large volumes of material, since constituents have often escaped into surrounding soil or bodies of water. To handle such volumes, these treatment installations must have correspondingly high throughput capacities and must be able to operate reliably for long periods of time. They must also deal effectively with whatever objects are found in the soil or water—logs, rocks, or discarded automobiles or machinery. Any of these problems can rule out a treatment process that is otherwise technically suited to the waste in question.

Another aspect of selecting technologies for use at Superfund sites is a conservative bias toward reliable and proven techniques, and away from unproven ones. This arises out of the need (1) to predict and control costs and (2) to ensure acceptable minimum levels of performance. Superfund resources must be stretched over many more sites than originally anticipated, so cost control and performance predictability are strong priorities. But there is also a third potential element of bias toward conservatism: this has to do with public perceptions of the risks of treatment. Where unusual technologies have been tried, many communities have expressed concern over what

they perceive as an experimental procedure, with themselves as guinea pigs.\*\*\*\*

These biases toward conservative technologies have been reinforced to some extent by the regulatory community. The Office of Technology Assessment report on the need for new Superfund strategy observed that both the regulations under the National Contingency Plan dealing with remedial actions and EPA's own “Guidance on Preparation of Feasibility Studies,” prepared in 1985 encourage a bias toward containment and, to a lesser extent, innovative technology. When established technologies are used as a standard against which all other technologies are measured, a resulting “predilection for short term costing and reluctance to reach beyond comfortable traditional technology favors the status quo.” (OTA, “Superfund Strategy,” April 1985).

This OTA report also suggested that “without adequate R&D and demonstration funding, no technology will reach the stage where it can demonstrate an acceptable level of reliability and effectiveness under field conditions.” Shortages of reliability and effectiveness data translate into administrative barriers for RI/FS technology reviews. The conclusion is that innovation in Superfund treatment technology—so badly needed as a way of increasing treatment efficiency, lowering treatment costs, and treating a wider variety of wastes—needs special attention and cultivation. Existing incentives will be slow to provide either that attention or that cultivation.

#### ACTUAL APPLICATION OF TREATMENT TECHNOLOGIES UNDER CERCLA

A review of the entire list of treatment technologies applicable to Superfund sites is not possible in a short paper. Even if only well-established technologies are covered, the list is still long. Some generalizations however, are possible and useful.

The various types of treatment available can be grouped into functional categories. The category of first priority is *recycling, including reuse*. This is actually a recent development. In parallel with HSWA, Superfund is putting greater stress on possibilities for recovery of useful materials from abandoned sites. This is frequently more practical during removal actions than during long-term remedial actions, but data available now do not provide much insight into the ultimate potential for waste recovery. It will take several years to determine the potential for increased waste recovery from abandoned sites; clearly, rates of recovery will vary greatly from site to site.

After recycling and reuse, the next priority is placed on *destruction* of wastes, wherever and to whatever extent that may be possible. Most frequently, at least for organic wastes, destruction implies incineration, commonly with rotary kilns, since these can accommodate the widest range of physical forms of wastes. Where wastes are in liquid form (such as from lagoons or impoundments), liquid injection incinerators may be used. Destruction can also be accomplished by biological processes, though to date this is far less common at CERCLA sites than incineration. One possibility for biological destruction of

<sup>†</sup>The only current RCRA performance standard for treatment is for incineration. It requires 99.99 percent destruction and removal for most wastes (the so-called 4-9's standard), and 99.9999 percent destruction and removal (the 6-9's standard) of extremely hazardous wastes such as dioxins; it also includes some additional operating conditions and particulate limits.

\*\*\*\* Frustratingly, there are instances of the opposite community reaction when innovative technologies are *not* used. The public has sometimes asserted that the cleanup could be more effective and safe if only EPA would use such and such a method. Occasionally the method in question does exist, but has been ruled out for one of the many reasons—unpredictable efficiency, reliability, inability to cope with throughput rates or nonhazardous debris, etc.

wastes is direct application of microorganisms *in situ*. There are a number of commercially sponsored processes of this nature in the development stage. In addition, wastes from a handful of sites have been transported to activated sludge treatment plants; since activated sludge is certainly a well-established process, we may expect it to be used more frequently in the future.

In a more limited sense, chemical processes can be used to destroy hazardous wastes, though here the term "destroy" more accurately implies modification of those properties that account for a waste's original designation as hazardous. Whereas thermal and biological processes transform organic materials into different chemical forms (e.g., carbon dioxide and water), chemical processes like neutralization do not destroy compounds themselves, but change some aspect of them (such as pH) that accounts for their hazardous properties.

If destruction of wastes is impossible or impractical (as it is, for instance, for metals), then *immobilization* is the next priority. Under current CERCLA practice, immobilization implies much more than simple landfilling. It usually involves chemical and/or physical bonding of wastes into solid matrices. The process is commonly referred to as "solidification," "stabilization," or "fixation," though technical distinctions among these terms are vague. Another form of immobilization is encapsulation of wastes with reliable and impermeable materials such as glass, resins, or plastics. Currently, however, the most economical and dependable approaches appear to be common pozzolan or lime-based (cement) fixation processes. Encapsulation techniques do not yet appear to be cost-effective for most applications.

So far there are few examples of actual or proposed use of fixation on active sites. However, it is expected to play a much broader role in the future.

Finally, there is a wide variety of other technologies that do not qualify as either destruction or immobilization, but that are indispensable to CERCLA operations. As a group, these can be characterized as *pre- or post-treatments*, since they are necessary adjuncts to the primary objective of either destroying or immobilizing wastes. For instance, chemical precipitation can be used to separate metals from organic solvents prior to incineration of the solvents; the metals could then be solidified prior to placement in a landfill. Physical processes can also be used: a common approach for treating ground water contaminated with organics is to air strip the light organics from the water, then to capture the stripped organics using activated carbon. (The carbon should then be incinerated or reclaimed.)

The general steps used in determining what treatment processes are applicable to a particular site are outlined in Fig. 2. The practical complexities of treating wastes at CERCLA sites simply underscore that treatments are almost always used in "trains"—sequences of physical, chemical, thermal, and sometimes biological treatments that together are adequately protective of human health and the environment.

An example of a typical treatment sequence is illustrated by the Bridgeport Rental & Oil Services site in Connecticut. This 11-hectare site consisted of a lagoon containing 189 million liters of oil, oil-water emulsions, contaminated water, and sludge. The mixture was in three layers: an oily layer, an aqueous layer, and a sludge layer. It was contaminated with heavy metals, PCBs, and a variety of other toxic organic compounds such as benzene and methyl ethyl ketone. The immediate need was to lower the lagoon level for fear it would overflow during heavy rains. The initial treatment process was therefore designed to treat only the aqueous layer to decrease lagoon volume.

The treatment train consisted of an oil/waste separator

#### Steps for Evaluating and Selecting Alternative Technologies at Superfund Sites

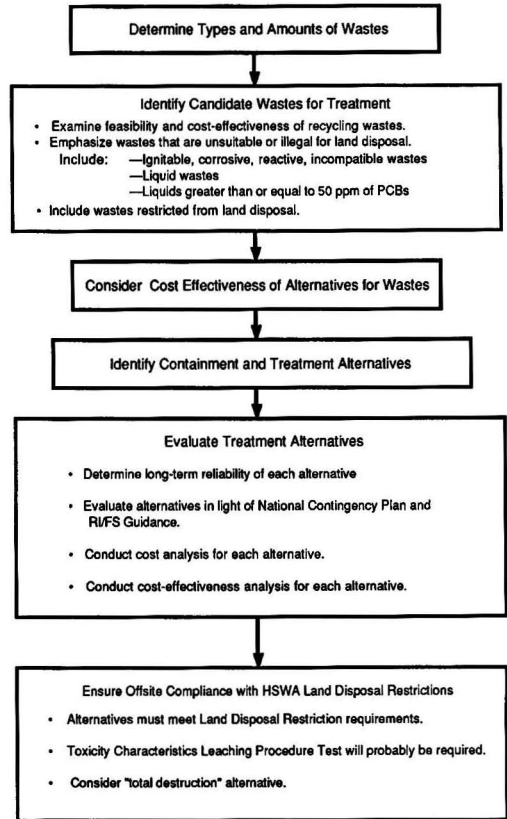


Figure 2. Steps for evaluating and selecting alternative technologies at Superfund sites.

to remove PCB-tainted oil, a flocculation basin and sand filter, and a mobile carbon adsorption unit. Carbon adsorption was chosen because of its low risk and relatively low cost. There was not much chance of high levels of pollution being discharged to the environment. The initial process used a portable carbon adsorption unit called the "Blue Magoo," though ultimately the project used a "package" treatment plant that since has been dismantled and removed.

#### *In Situ* Processes

One class of treatment that deserves additional special attention is "*in situ*" treatment—the treatment of wastes in place. So far *in situ* treatment has not been widely used, but there are many reasons why it may be desirable, even essential at certain sites.

*In situ* processes are needed where wastes are particularly hazardous to excavate, extremely high in volume, or physically inaccessible (such as lying under a building or river). In these situations, there may be no practical alternative to attempting to treat wastes in place. So far, no thermal-based processes have been proposed, but physical, chemical, and biological processes have already been tested in pilot and full scale.

*In situ* processes include soil vapor extraction in which vacuum wells can cause volatilization of organic com-

pounds by inducing a flow of air through the soil. Another *in situ* process is soil flushing wherein a solvent is passed through the soil and collected in extraction wells. Soils contaminated with PCBs can be treated chemically by application of alkaline polyethylene glycols (called "APEG"). Biological *in situ* processes include injection of microorganisms into the soil to metabolically destroy specialized classes of wastes.

There are a variety of problems with the use of *in situ* treatment, however, and some will be easier to overcome than others. Costs for this class of treatment are not well documented because the techniques are not in commercial use and are still largely experimental. Even when *in situ* treatment is more widely used, treatment costs will probably vary widely from site to site. Of greater concern will be controlling the amount and uniformity of treatment and of measuring "success" after application (it may be difficult to verify that a site is indeed clean after the treatment is finished). There may also be possibilities of migration of substances off site during or after a treatment. In some cases, *in situ* treatment may cause fugitive emissions because of uncontrolled underground factors (fractured rock, variable water tables, etc.). For these reasons, *in situ* treatment must be dealt with carefully in practical application.

**Mobile Technologies**

For various reasons, it is expected that mobile technologies will play an increasing role in the future. Many common and established technologies have been used in mobile format at CERCLA sites—i.e., they have been transported there on trucks for temporary use.

Mobile treatment is often less costly than fixed site treatment, especially in comparison to conventional treatment facilities built on site. They allow fast response to emergency situations and may therefore play an expanding role in removal actions as well as remedial programs. They obviate the need to transport wastes off site, thereby reducing the risks and the usually high costs of that transportation. Because of the inherent need to build "treatment trains" that link multiple technologies together, the mobile format also offers special advantages in flexibility: treatment can be more easily tailored to the needs of each site. Finally and less obviously, the mobile format may be particularly appropriate for some of the more experimental innovative and emerging technologies. Since innovative treatments are likely to be comparatively more costly on a per-ton basis, at least in the near term, the mobile format is economical because it permits a single mobile unit or series of units to be used at several sites over its useful life.

Many technologies are being tried in mobile format including physical, chemical, biological, and thermal processes. These include rotary and liquid injection kilns; mobile fixation techniques employing asphalt, cement, and lime-based technologies; chemical processes like neutralization, precipitation, band oxidation/reduction; physical processes such as activated carbon, air stripping, steam stripping, ion exchange, and distillation; and biological processes, including both anaerobic and aerobic treatments. More innovative processes are being tried in mobile form. These include fluidized bed incineration, infrared incineration, plasma arc pyrolysis, and wet air oxidation.

While mobile processes will play an increasing role in the Superfund program, much more research is needed to develop new and better processes. More importantly, incentives for developing and marketing mobile units need to be provided. In many cases, the necessary technology exists—it simply needs to be made available for use on site.

In order to nurture the development of necessary new treatment technologies, EPA and Congress are moving toward establishment of formal programs and procedures to support research, development, and demonstration of innovative and emerging technologies. Innovative technologies are those that are becoming available, but are not yet in common use at Superfund sites. Innovative technologies may include processes that are well-established but have not yet been tested on particular classes of Superfund wastes, or under Superfund field conditions. Emerging technologies include the less-developed and more speculative options. These are generally technologies still in the pilot or bench-test stage.

Current CERCLA reauthorization language illustrates Congress' concern for long-term support for development and testing of innovative and emerging technologies. Section 311(b) of the agreed-upon conference language calls for an alternative technology demonstration program to carry out a program of research, evaluation, testing, development, and demonstration of alternative or innovative treatment technologies. It authorizes EPA to enter into contracts, grants and cooperative agreements with public and private entities to conduct necessary demonstrations, requiring the Agency to initiate at least 10 field demonstration projects in each fiscal year. It sets aside up to \$20 million per year from the fund to cover these costs.

This conference language confirms commitments that EPA has already made through the initiation of the Superfund Innovative Technology Evaluation (SITE) Program. SITE has three objectives:

1. To overcome administrative, institutional, and technical impediments to the use of innovative and emerging treatment technologies,
2. To develop firm cost and performance data on these technologies, and
3. To support development of emerging technologies themselves through research, development, and demonstrations.

"Impediments" analysis and evaluation will include attention to such factors as liability insurance, public concern, availability of information to decision-makers, market development, permitting requirements, and other related issues. There may be a few instances where legal impediments against treatment may exist in Federal, State, or local law. To counter these, SITE will produce a series of policies and directives to enhance the use of treatment.

Technical programs under SITE will include general

TABLE 1. EXAMPLES OF INNOVATIVE AND EMERGING TECHNOLOGY UNDER DEVELOPMENT FOR USE AT SUPERFUND SITES

Treatment Category	Technology	Status
Thermal	Advanced Electric Reactor	Pilot Scale
	Circulating Bed Incineration	Pilot Scale
	Microwaves	Pilot Scale
	Plasma Arc Pyrolysis	Pilot Scale
	Pyrolyzing Rotary Kiln	Pilot Scale
Chemical	Wet Air Oxidation	Commercial Scale
	Catalytic Decomposition	Laboratory Scale
Physical	Metal Binding Compounds	Laboratory Scale
	In Situ Vitrification Generated Barriers	Laboratory Scale
	Bottom Isolation Barrier System	Laboratory Scale
Biological	Biochemical Processing	Commercial Scale
	Engineered Microorganisms	Laboratory Scale
	Soil Application of White Rot Fungus	Laboratory Scale

analysis of all innovative and emerging technologies and direct cooperative support for a series of demonstrations. One output of the program will be development of cost, performance, reliability, and cost-effectiveness data on each technology studied. Most demonstration programs from which this information is gathered will be undertaken at full operational scale at actual uncontrolled sites under realistic field conditions. Proposals are being solicited from the private sector and from routine response actions, though suggestions for other technologies and sites will also come from EPA's Office of Research and Development, from treatment programs at the Department of Defense and the Department of Energy, or even from suggestions raised at professional symposia and conferences.

Examples of innovative and emerging technologies that currently show promise and that may be tested under SITE are shown in Table 1.

## CONCLUSIONS

To summarize, the major lesson learned from the six years of Superfund's experience is that the program must emphasize permanent, long-term clean-up activities. Containment of wastes through land disposal is becoming the option of last resort; not only is it generally less reliable over the long term in protecting human health and the environment, it is rapidly losing its cost advantages.

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*The work described in this article has been reviewed by the Office of Emergency and Remedial Response, U.S. Environmental Protection Agency. The contents do not necessarily reflect the views and policies of the agency, nor does mention of trade names or commercial products constitute endorsement.*

The most effective technological approaches to managing hazardous waste from uncontrolled waste sites are treatment options that render Superfund wastes nonhazardous. The Superfund program must therefore place more emphasis on encouraging more rapid development of new treatment options and make better use of currently available technology. It is unlikely that we will ever discover any "perfect" technologies uniformly applicable to all sites. Multiple technologies must generally be used in "treatment trains" that take account of all aspects of the treatment process, especially the potential to inadvertently transfer pollution from one environmental medium to another. Treatment programs must continue to stress careful design of individualized treatment programs tailored to the needs of each site.

## LITERATURE CITED

1. Ruckelshaus, William D., "Controlling Hazardous Waste" *EPA Journal*, 10, No. 8 (October 1984).



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# Managing Hazardous Waste Risks Under the Massachusetts "Superfund" Law

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*Different options and strategies for managing hazardous waste risks are presented. Experience in Massachusetts under a state "Superfund" law (Chapter 21E) as applied to the selling, buying, and financing of real estate is drawn upon.*

*The sites in question are not "Superfund" sites. They are those commonly found in a state with a history of many old industries as well as with the expected number of gas stations with underground tanks. The approach discussed is that with a thorough site assessment involving historical research and if required, soil and ground water examination, the parties (sellers, buyers, and lenders) through use of a variety of special devices may successfully consummate real estate transactions. These devices include use of indemnification agreements, escrow funds, title insurance, and in some cases involve accomplishment of tank and contaminated soil removal before closing the real estate transaction.*

*Not following this course of action exposes some or all of the parties to the risk of liability for cleanup costs as well as for claims by other parties to the transaction.*

Drawing from his experience in Massachusetts, the writer explains how sellers, buyers and lenders manage the risks resulting from the presence of hazardous wastes in real estate. Following the passage in 1983 of Chapter 21E of the General Laws (establishing the "Massachusetts Superfund"), parties to commercial real estate transactions have discovered they cannot circumvent the problem. First, lenders fearful that a lien for cleanup costs will encumber the real estate serving as security for their loan — and one that takes priority over their first mortgage — require affirmative title insurance for protection.\* Title insurance companies in turn need assurances that the necessity for cleanup is remote. Second, anyone owning contaminated real estate, regardless of fault, faces liability for the entire cleanup. Therefore, sellers desire to pass such liability on to others and buyers do not want to assume same; or more realistically, the parties do not want to worsen their respective positions solely as a result of the sale (as contrasted to their own actions in handling and disposing of hazardous wastes).

The answer in both cases has been provided through so-called site assessments. They are prepared as part of virtually all commercial real estate transactions in Massachusetts. More effective than any regulatory enforcement effort, the privately administered site assessment process has transformed Massachusetts real estate practice.

\*Since writing this article, three title insurance companies have announced that commencing January 1, 1987 they will no longer issue such affirmative coverage in Massachusetts. If title insurance protection is no longer available in Massachusetts, it will mean that lenders will be assuming greater responsibility for risk assessment in this area.

Owners not only find out about the presence of hazardous waste but also learn more about past and present practices that have contributed to the hazardous waste problem. This leads to improved housekeeping and, when the contaminants are health threatening, cleanup. Thus, with the passage of Chapter 21E, owners of commercial real estate in Massachusetts have undertaken a largely self-enforced effort to clean up hazardous waste.

Serious cases may go beyond self-enforced solutions. This paper does not cover enforcement orders by the United States Environmental Protection Agency ("EPA") and the Massachusetts Department of Environmental Quality Engineering ("DEQE") and court actions directed at non-cooperating parties. And the sites discussed here are not Superfund sites, which are the most egregious hazardous waste sites. They are "garden variety" sites found in a state with a history of many old industries as well as the expected amount of gas stations with underground tanks, dry cleaning establishments, and the like.

After discussing the liability aspects, how the different actors in a commercial real estate transaction (seller, buyer and lender) control and limit this liability will be explained.

## LIABILITY

Liability under Chapter 21E is comprehensive: It reaches not only the involved party but also the passive owner; it covers the cost of containment or removal of all substances regulated under the Federal Comprehensive Environmental Response, Compensation and Liability Act of 1980 ("CERCLA") and more substances as well.



Parties liable under Chapter 21E include (a) those who arranged for the disposal as well as the transportation of the hazardous waste, (b) all past operators and owners of the land at the time the waste was stored or disposed of on the land, and (c) the present owner and operator of the land. Materials to be contained or removed include those covered under CERCLA as well as oil and any other materials dangerous to the public health or the environment. If such a covered material is released or threatened to be released, the liability for the cost of its cleanup is covered under Chapter 21E.

Liability is strict—meaning a party can be held liable regardless of fault. Further, the source of the particular hazardous waste found does not have to be traced, nor does the government enforcement agency have to prove injury.

Liability is joint and several—meaning the government can assess responsibility against a single owner or a single disposer for the entire cleanup cost, even though many others may have contributed to the problem. Moreover, liability does not stop with cost recovery. Liability of the responsible party may extend up to three times the cost of cleanup and can remain outstanding for long-term uncorrected problems.

There are few safe harbors open to the potentially liable person. Those that exist are difficult to qualify for and do not eliminate, but rather place a ceiling on, liability. Under Chapter 21E, Section 5, a party who is technically responsible under the Act but who is innocent of any release of hazardous substances on the property escapes liability for any amount in excess of the value of the property (after the cleanup). However, in order to gain this protection, the party in question has the burden of proving that the release resulted from an act of God, an act of war, or an act of an independent third party.

In light of joint and several liability, one may ask why there is interest by responsible parties in apportioning potential liability among themselves. If parties do not do this by agreement, the party who later undertakes or pays for the cost of cleanup (often the owner at the time of discovery of the problem) will make claim for contribution against the party who disposed of the waste or from the prior owner of the property (or such prior owner's successor in interest). The party seeking to recover the cost of cleanup may commence an action against the generators of the waste in environmental tort or under provisions in Chapter 21E and CERCLA requiring contributions by other liable parties. Against the prior owner, such party may recover the cost of cleanup (a) on grounds of misrepresentation made by the prior owner when such owner sold the property or (b) for breach of indemnity agreements made by the prior owner as part of the sale transaction. Likewise, in a government enforcement action against multiple defendants, once joint and several liability is determined, the defendants made subject to such liability will seek a judgment from the court allocating such liability among themselves.

Knowing that all responsible parties will be compelled to contribute to the cost of cleanup, parties to a sale (who themselves are responsible parties) recognize the value of allocating their respective responsibilities in advance. This is in the lender's best interest as well, for if the process breaks down and the government's lien for recovering cleanup costs enforced, the lender loses its first mortgage position.

#### **SITE ASSESSMENTS**

Site assessments are at two levels of detail. First, they screen for potential hazardous waste; and second, they involve chemical testing of soil and ground water. Screen-

ing entails several different investigations. Through a walk-over of the site, discolored soil, poor housekeeping practices, and other like conditions are identified. By study of the title abstract, building permits, old atlases, assessors' records and by talking with local residents and town officials, uses that formerly contributed hazardous waste to the site and surrounding area are identified. Through review of DEQE and EPA waste incident files, earlier spills are discovered. Finally, through review of permits and licenses issued by the fire department, board of selectmen, and other local boards and officials, existence and location of underground tanks are determined.

If old underground tanks, chemical dumping, or other problems are identified as part of the screening, testing for contaminants is undertaken. If found, the type and quantity of the contaminants is determined; and the relative health threatening characteristics established. This results in baseline data.

If warranted, the site assessment preparer will recommend specific cleanup actions. There are two kinds of response actions to a finding of hazardous waste: short-term and long-term. The first involves immediate cleanup and removal of the contamination; the second requires permanent sealing off of the contaminated area followed by regular monitoring.

Above all, it is important to develop complete data relevant to the problem at issue. If this is done, the responsible parties will be able to convince each other and DEQE of the nature of the problem and the appropriate remedy. This is most likely to lead to an agreement on how the cleanup will be planned and implemented.

#### **CONTROLLING RISK**

This will be examined from the perspective of the different parties to a real estate transaction: first the seller, second the buyer, and third the lender. The seller desires to convey the property without retaining responsibility for later removal of hazardous waste. However, if the seller knows about past spills of hazardous waste and does not disclose them the seller may be found guilty of misrepresentation. This follows on the basis of three different theories. First, because notice of such spills under Chapter 21C of the General Laws must be recorded in the registry of deeds, failure to record notice may constitute a misrepresentation. Second, because under most purchase and sale agreements sellers agree to deliver marketable title free of encumbrances, the potential application of the "superlien" by DEQE and EPA under Chapter 21E and CERCLA, respectively, for cleanup may violate this agreement. Third, because sales of commercial property fall under Chapter 93A of the General Laws (Unfair and Deceptive Trade Practices Act), the seller's failure to disclose known facts concerning the condition of the property may give rise to a cause of action under this statute.

Despite these principles, a seller may be tempted to "unload" the property and later escape future liability by selling assets remaining in the business of the seller to a third party. Ordinarily when one corporation sells its assets to another, the latter (the "successor business") does not assume the first corporation's liabilities. However, there are exceptions. If the successor business (1) implicitly agrees to assume liability, (2) has directors and officers similar to those of the transferring party, (3) continues the business of the transferor, or (4) acquired the assets as part of a fraudulent transfer entered into to escape liability, then the successor business may remain liable. Under these conditions (where liability survives), the current owner of the property faced with liability for cleanup will have recourse against successors in interest to other responsible parties.

It follows that the seller, by failure to disclose the existence of hazardous waste, runs the risk of a suit for damages by the buyer as a result of such sale. It also becomes difficult for the seller to realize value upon sale of the "non-contaminated" assets of the business. One way to define and limit such liability and erosion in asset value is for the seller to make disclosures to the buyer through a site assessment report.

A buyer, on the other hand, wants to be able to terminate its agreement to purchase if the buyer discovers a problem site. Or, if there is uncertainty about the site, buyers want sellers to make representations and warranties to narrow the area of uncertainty and to identify the parties responsible for potential losses. For example, sellers will be asked to represent that they have used due diligence in confirming that past operators handled and disposed of hazardous waste properly. Further, sellers will be asked to show that they have received no notices of any enforcement orders.

In addition, if buyers accept title to a site which may contain hazardous waste, they want the sellers to bear the cost of cleanup. This may be done (a) by establishing an escrow fund for that purpose, (b) by renegotiating the price downward to provide a "cushion" that will make up for the anticipated cleanup cost, or (c) by obtaining agreements of indemnification from the sellers. To accomplish any of these objectives, the parties require the data found in a site assessment report. A problem involving a short term remedy lends itself to this kind of settlement.

The seller's response to these demands by the buyer will be to cap the escrow fund and to limit the amount of the indemnification. In the latter case, the seller will also want a reasonable time limit during which the indemnification will be effective because the seller will argue that after a reasonable period the likelihood of any enforcement action will be negligible. Finally the sellers may see their liability increasing if housing uses or other "sensitive receptors" are instituted on the site. Therefore sellers may want to restrict the land so that such uses are prohibited.

Lenders have the same concerns and interests that buyers have but with the added comfort that they stand behind the first line of defense presented by the owner of the land. Until lenders foreclose and take possession of the land, they have no direct liability under Chapter 21E. Affirmative coverage in lender's title insurance policies offers protection to lenders as well. However, protection is limited. The title insurance only protects against loss resulting from DEQE's lien for cleanup costs gaining priority over the lender's mortgage. The amount of the protection is limited to the cost of cleanup of hazardous waste on the land as of the date of the policy.

Because lenders remain exposed to certain risks, they desire to make loans secured by real estate only when foreclosure is remote. Three different situations are presented. In the first, the lender looks to the buyer personally. Having obtained indemnity agreements, the lender may proceed against the buyer and avoid foreclosure altogether. In the second case the lender determines, as a result of the site assessment report, that either the likelihood of having to clean up hazardous material is minimal or if there is that likelihood, the cost of cleanup is small relative to the value of the land and improvements. A significantly contaminated site presents the third case. In these circumstances lenders are reluctant to make the loan. However, if the lender desires to do everything possible to insure the success of the transaction, the lender will support the parties' efforts to apportion responsibility in accordance with the site assessment, to establish escrow funds, and if necessary, to use a trust vehicle to insure response to any cleanup problem and thereby avoid the imposition of the "superlien."

## RELATIONSHIPS WITH SITE ASSESSMENT FIRMS AND DEQE

Often a single site assessment report will be prepared. Either the seller will provide it and the cost will be split or the buyer will obtain and pay for such report if none exists. Most often because the question of whether hazardous waste exists arises as a matter on which the buyer needs to satisfy buyer's title insurance company, the buyer often absorbs the cost of the investigation and preparation of the report.

In the case where a single report is obtained, the preparer of the report finds himself or herself in a conflict. The seller (often the party who originally engaged the engineering firm and in some cases the party who regularly employs such firm) wants the deal to close. The buyer, on the other hand, wants more and more tests and information to make certain that he or she is not making a mistake in buying the property. This conflict of interest, present when a firm represents "two masters" cannot help but affect, or give the appearance of affecting, the objectivity and thoroughness with which the firm undertakes the assignment.

The better practice is for each party to a sales transaction to order a separate report. Obviously data already obtained should be shared. However, the buyer's engineering firm should review such data, obtain additional data if required, and give advice and recommendations directly to the buyer.

Another practical issue the engineering firm and attorney face is whether DEQE should be informed of a finding of hazardous waste. Chapter 21E draws no limits — under the statute any spill or release should be reported. Some rule of reason must be established. If such reasonable threshold is exceeded and the client does not desire to report it, what is the obligation of the engineer and the attorney? As a matter of practice engineers and attorneys will advise their clients as to what to do and leave the ultimate decision to the client. If the public's health is immediately endangered, the professional has an obligation to contact the national response center and the appropriate state office.

The issue of reporting becomes more complicated in a sales transaction. Assuming the site has had no past involvement with DEQE or EPA, the seller is reluctant to open the door to investigation by one of those agencies. Nevertheless buyer and buyer's title insurance company often want the comfort of a letter from DEQE that no cleanup is warranted given the data developed in the site assessment report. Yet if the buyer does not go through with the purchase it is the seller, as owner of the property, who is left to contend with DEQE. If DEQE commences an investigation of the site, the seller alone (in a case where buyer has terminated the purchase and sale agreement) must satisfy DEQE that the apparent problem does not exist or that the substantial cleanup desired by the buyer is not warranted.

Knowing this likely scenario, the seller will attempt to limit in the negotiation of the purchase and sale agreement, the buyer's right to pass data on to DEQE or to ask for DEQE's "sign-off" on a site. However, this request runs the risk of "chilling" the sale. The mere making of the request enhances buyer's ability to obtain strong warranty language and indemnification agreements. In any event, if the seller in cases of significant hazardous waste, wants to consummate the sale, the buyer through buyer's site assessment firm must be allowed to contact DEQE.

## REACHING AGREEMENT ON REMEDIAL ACTION AND COST APPORTIONMENT

As discussed above, the site assessment serves as a baseline — a point of reference for allocating responsibility for cleanup. If cleanup is dictated as a condition to

sale, desired results may be measured in terms of lowering the levels of the contaminants by quantities specified in the agreement. If cleanup is a post-closing item, success in performing the cleanup will be similarly measured. Usually, the seller absorbs the pre or post-closing cleanup cost. In turn, the seller achieves the desired sale of the property as well as the termination of long term responsibility for the property.

If no cleanup is warranted either because the quantities of contaminants are below the levels DEQE and EPA consider to be critical or because (even though a significant quantity is found) no sensitive receptors exist, such as residential uses in the vicinity or ground water used for drinking purposes, the agreements to share costs of future cleanup could be apportioned in light of the site assessment. For example, the agreement could provide that (a) for contaminants found later during the period of buyer's ownership which differ from those found in the site assessment or (b) for contaminant levels which exceed those found in the site assessment, the buyer would be responsible. Other solutions could be presented by the engineering firm to the attorneys for the parties depending upon site conditions, the nature of past uses, and the uses proposed by the buyer.

The need to resolve issues through agreement in a purchase transaction emphasizes the importance of assembling clear and complete data in the site assessment process. To the extent this is done, seller, buyer, lender and, if involved, DEQE will be more likely to reach agreement on a cleanup solution thereby insuring that the ultimate sale will go through.

Often other complications arise in efforts to reach agreement over a site with suspected problems. First, parties other than the seller may be responsible for the presence of hazardous waste on the site. Sellers are unwilling to pay for cleanup problems caused by others. Second, while cost apportionments under a specific cleanup plan can oftentimes be reached, buyers are reluctant to assume longer term undefined responsibilities for cleanup.

One way to secure participation by a third party is to offer such party a full release at least as among responsible parties in return for a monetary contribution towards cleanup. Often third parties especially those who contributed relatively little of the total hazardous waste will be willing to pay a premium, i.e., more than their *pro rata* share as computed by the amount of waste they deposited compared to the total dumped on the site. For example, if a disposer was responsible for 2% of the waste dumped, such party could be asked, and might be willing, to pay 6% of the total cost of the cleanup in return for a release.

With respect to the buyer's fears of liability for undisclosed waste, several approaches should be considered. First, the seller could remain responsible under an indemnification agreement. This is practical when the seller is an established company with sufficient assets. Second, the buyer could attempt to limit its liability. For example, the buyer could establish a separate corporation to buy the property. If liability arises, the corporation's sole asset, the land with improvements, is at risk. However, one must be aware that once the hazardous waste is discovered, a stockholder/officer may be (a) guilty of tor-

tious conduct (subject to personal liability) if he or she does not use reasonable care in removing hazardous waste which presents an imminent and substantial danger to health or the environment, or (b) guilty of liability under Chapter 21E if he or she violates such Act or violates an order issued by DEQE under such Act.

The land could also be subdivided. In this manner the land with the suspected contamination could be separately owned and financed. Any of these approaches present difficulties and should be undertaken only with careful review and advice by one's attorney.

Finally, casualty insurance or a trust fund could be established. Insurance does not appear to be a practical alternative today. The trust approach requires only the consent of the parties. The advantage of the trust approach is that a single entity stands ready to respond to the problem. Parties will not be fighting among themselves as to who is responsible with the risk of precipitating a government enforcement action brought against all potentially responsible parties. In the case of a trust, the relative amount each party contributes, or agrees to contribute, to the trust fund can be based on a rational plan based on the findings in the site assessment report.

## CONCLUSION

Experience in Massachusetts demonstrates the value of parties to a transaction reaching agreement on hazardous waste problems as part of the purchase and sale negotiations and within the context of data developed in the site assessment process. In this way the parties terminate or consummate the sale without recourse to litigation. If they decide to go ahead, the parties as part of the transaction conduct the cleanup under an agreed-upon cost allocation formula. For future uncertain liabilities, the parties reach agreements for a rational plan of allocating responsibility. Use of special escrow funds or trust vehicles limit the risk of later litigation among the responsible parties who fear having disproportionate recoveries assessed against them.

When the technical data as part of the site assessment process is developed in the context of the parties' willingness to find solutions, and when both engineers and attorneys work to achieve these solutions, the risk of Chapter 21E liability becomes the stimulus for agreeing to cleanup and setting mechanisms in place to effect such cleanup — not for disrupting the real estate transaction itself.



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# Removal of Dissolved Organic Contaminants by Ozonation

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*This article focuses on the use of ozone for the elimination of dissolved organic pollutants from water and wastewaters. The physical and chemical phenomena prevailing during the contact of a polluted liquid stream with gaseous ozone-air or ozone-oxygen mixture in empty or packed columns is represented mathematically. The simulation procedure is based on defining the concentration profiles of ozone and the organic solutes in both liquid and gas phases by means of differential mass balances. Methods for the determination of necessary model parameters is outlined and the model is analyzed for its sensitivity to various process variables.*

## INTRODUCTION

The results of several laboratory and pilot plant studies have revealed that a large number of toxic compounds can be eliminated from water and wastewaters by ozonation. Full-scale application of ozone, for the removal of organic micropollutants, however, has been very limited. This reluctance might partly be due to the lack of a "well-defined" general representation of the physical and chemical phenomena prevailing during the contact of a polluted liquid stream with gaseous ozone-air or ozone-oxygen mixture.

It is the purpose of this paper to present a mathematical model portraying the removal of dissolved organic pollutants in empty or packed bed ozone contactors. The mathematical simulation is based on defining concentration profiles of ozone and organic solutes in both liquid and gas phases.

In addition to predicting the performance of given ozone contactors under known sets of inflow and operating conditions, the model can also be used to optimize the operational parameters for a given liquid stream and desired removal efficiency.

## BACKGROUND

### Consumption of Aqueous Ozone

Following its transfer from the gas phase, ozone initiates a chain of oxidation reactions in the bulk liquid phase. While a portion of molecular ozone is reacting directly with the available solutes, another part may decompose to form highly reactive secondary oxidants. Rather complex reaction mechanisms can be used to explain the kinetic behavior of ozone in "pure" waters and in the presence of various solutes [1, 2].

In "naturally-occurring" waters and in the presence of organic solutes, the rate of aqueous ozone consumption,  $r$ , can be lumped into a first-order expression [3, 4]:

$$r = w \cdot [O_3] \quad (1)$$

where  $[O_3]$  is the instantaneous bulk ozone concentration. The reaction rate constant, arbitrarily denoted as  $w$ , might be referred to as specific ozone utilization rate.

Theoretically, one can estimate  $w$  using available kinetic information in the proposed reaction mechanisms or similarly developed other schemes. However, ozone consumption is a strong function of the chemical composition and pH of the liquid phase, and it is not unusual to observe half-life variations of one order of magnitude even when the consumption rates in relatively clean surface or groundwaters are compared [3]. Since it is difficult to know the exact liquid-phase composition, specific ozone utilization rate for any water of interest should be determined experimentally. Recently, experiments have been conducted on synthetic water and waste samples, and the measured  $w$  values were correlated with the pH alkalinity and total organic carbon (TOC) content of the solution matrices [3]. In general, the half-life of ozone in natural water and wastewaters decreases with increasing pH and organic content and decreasing alkalinity, and may range anywhere from less than a minute to a couple of hours at ambient temperatures.

### Kinetics of Ozone Transfer

In order to predict the removal rate of an organic solute in an ozone contact column, it is necessary to quantify the amount of ozone transferred from gas into the liquid phase. The rate of ozone absorption,  $N$ , in a control volume can be expressed as follows:

$$N = K_{1a} \{ [O_3^*] - [O_3] \} \quad (2)$$

where  $K_{1a}$  is the volumetric mass transfer coefficient for ozone and  $[O_3^*]$  is the dissolved ozone concentration in equilibrium with the partial pressure of ozone at the gas-liquid interface.

Generally, the rate of gas absorption into a solution can be influenced by the solution composition and the chemical reactivity of the absorbing gas in the solution. Consid-



ering typical ozone utilization rates and organic concentrations encountered in water treatment applications it is concluded that the ozonation process mostly follows the "slow reaction regime." In other words, the process is essentially comprised of two distinct steps; physical absorption of ozone followed by the chemical oxidation in aqueous phase. There is appreciable amount of ozone in the bulk liquid phase, and no enhancement of mass transfer due to chemical reactions in the diffusive film. On the other hand, chemical composition of the liquid phase profoundly affects the absolute value of  $K_L a$  by changing the interfacial area available for mass transfer and the individual film coefficients [5].

Although an ample amount of literature is available on the semi-empirical estimation of  $K_L a$  in bubble columns and packed beds, the use of such relationships for the ozonation of water and wastewaters is limited due to the unpredictable effect of the complex matrices on mass transfer. Furthermore, in naturally-occurring and contaminated waters the reactive nature of ozone makes it impossible to physically separate the kinetics of chemical reactions from the kinetics of mass transfer and to measure the  $K_L a$  in the conventional sense. For such cases, however, the model equations developed in this study can be used for the prediction of  $K_L a$  values for both ozone and organic solutes in empty or packed bed ozone contactors [6].

#### Removal of Dissolved Organic Contaminants

Major mechanisms contributing to the removal of organic pollutants in ozone reactors can be identified as physical stripping (volatilization), oxidation by ozone molecules (direct oxidation) and oxidation by free radicals (indirect oxidation) [4].

The direct oxidation reactions conform to kinetic expressions that are first order with respect to both ozone and organic concentrations [7, 8]. Self-decomposition of ozone and its reactions with "initiating compounds" lead to the formation of the hydroxyl radical,  $OH\cdot$ , which is a strong, non-selective oxidant [1, 9]. Indirect oxidation with  $OH\cdot$  also follows second-order kinetics [9]. All organic and inorganic constituents of the liquid phase compete for  $OH\cdot$  and other radical species. Therefore, one can lump the direct and indirect oxidation rates into a "total oxidation rate" expression based on the fact that all radicals are immediately utilized upon their formation [4]:

$$r_i = k_T \cdot [S_i] \cdot [O_3] \quad (3)$$

where  $k_T$  is the total oxidation rate constant and  $[S_i]$  is the instantaneous bulk concentration of an arbitrarily selected organic pollutant  $i$ . Experimental measurement of  $k_T$  values as well as the relative extents of direct and indirect pathways for some organic compounds are discussed elsewhere [7, 10].

For volatile organics, physical stripping during the gas-liquid contact also becomes an important removal mechanism. Henry's law is generally used to express the equilibrium conditions for environmental applications involving sufficiently low pollutant concentrations. In natural or contaminated matrices, however, the absolute value of the Henry's law constants can significantly deviate from the pure-water values and has to be determined specifically [11].

#### MODEL EQUATIONS

The coordinate system used for this analysis is shown in Figure 1. The liquid stream to be ozonated enters the column at the top with a volumetric flowrate of  $Q_L$ . Gaseous ozone-air or ozone-oxygen mixture enters from the bottom with a volumetric flowrate of  $Q_G$ . In terms of nota-

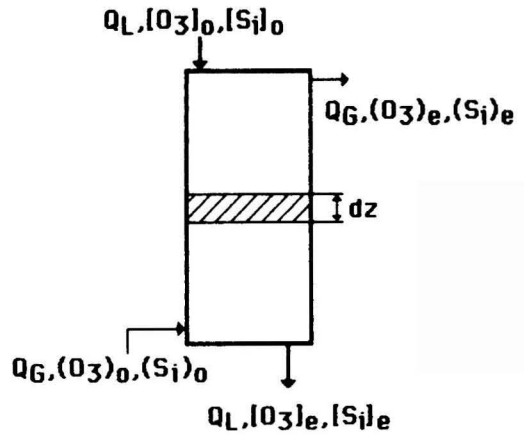


Figure 1. Process schematic for counter-current column.

tion, square and round brackets are for liquid and gas phase concentrations, respectively. The subscripts "o" and "e" stand for influent and effluent flows. Characteristics of empty and packed bed columns and other relevant definitions are given in the Appendix.

Assuming no gas-phase reaction and ideal plug flow in both phases, steady-state shell balances for ozone and a target organic pollutant  $i$  in the liquid and gas phases yield:

$$\frac{Q_L}{A} \frac{d[O_3]}{dz} = K_L a \cdot \{[O_3^*] - [O_3]\} - h_L \cdot w \cdot [O_3] \quad (4)$$

$$\frac{Q_G}{A} \frac{d(O_3)}{dz} = K_L a \cdot \{[O_3] - [O_3^*]\} \quad (5)$$

$$\frac{Q_L}{A} \frac{d[S_i]}{dz} = (K_L a)_i \cdot \{[S_i^*] - [S_i]\} - h_L \cdot k_T \cdot [S_i] \cdot [O_3] \quad (6)$$

$$\frac{Q_G}{A} \frac{d(S_i)}{dz} = (K_L a)_i \cdot \{[S_i] - [S_i^*]\} \quad (7)$$

where  $[S_i^*]$  is dissolved organic concentration in equilibrium with partial pressure of the contaminant at the gas-liquid interface.

The above equations imply constant values for  $h_L$  and the overall mass transfer coefficients throughout the column; which usually hold when the flow distributions and densities of the gas and liquid phases are uniform.

Numerical solution of this differential equation set requires as many initial conditions as the number of equations. However, in our case only 2 of the 4 initial conditions are known. That is,

@  $z = 0$ ;

$$[S_i] = [S_i]_e = \text{unknown}; \quad (S_i) = (S_i)_o = 0$$

$$(O_3) = (O_3)_o = \text{known}; \quad [O_3] = [O_3]_e = \text{unknown}$$

For a special case of given removal efficiency, i.e.,  $[S_i]_e$ , solution can be acquired by initially guessing  $[O_3]_e$  and then iterating until convergence. However, one can take advantage of the fact that all initial conditions are known at  $t = 0$ , and thus can map the spatial problem into the time domain to obtain a solution in terms of hydraulic retention time (HRT),  $t$ , for the liquid phase, which is defined as:

$$t = \frac{V_{EB}}{Q_L} = \frac{A \cdot z}{Q_L} \rightarrow dt = \frac{A}{Q_L} dz \quad (8)$$



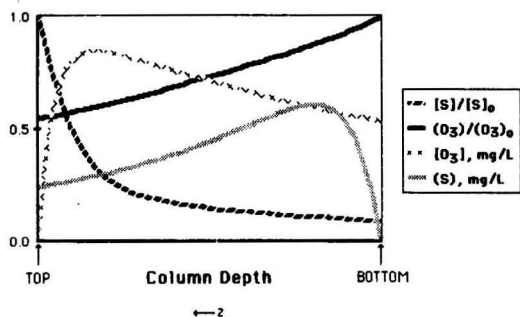


Figure 2. Sample concentration profiles for liquid and gas phase components.

The concentration profiles in the time domain are then obtained by substituting (8) into (4) through (7):

$$\frac{d[O_3]}{dt} = K_{L,a} \cdot \{[O_3^*] - [O_3]\} - h_L \cdot w \cdot [O_3] \quad (9)$$

$$\frac{d(O_3)}{dt} = K_{L,a} \cdot \{[O_3] - [O_3^*]\} \frac{Q_L}{Q_G} \quad (10)$$

$$\frac{d[S_i]}{dt} = (K_{L,a})_i \cdot \{[S_i^*] - [S_i]\} - h_L \cdot k_T \cdot [S_i] \cdot [O_3] \quad (11)$$

$$\frac{d(S_i)}{dt} = (K_{L,a})_i \cdot \{[S_i] - [S_i^*]\} \frac{Q_L}{Q_G} \quad (12)$$

with the initial conditions:

$$\begin{aligned} @ t = 0; [S_i] &= [S_i]_0 = \text{known}; (S_i) = (S_i)_0 = 0 \\ (O_3) &= (O_3)_0 = \text{known}; [O_3] = [O_3]_0 = 0 \end{aligned}$$

Furthermore, from Henry's Law:

$$[O_3^*] = \frac{(O_3)}{H}; [S_i^*] = \frac{(S_i)}{H_i} \quad (13)$$

where, H and  $H_i$  are the dimensionless Henry's Law constants for ozone and the target organic pollutant.

## RESULTS AND DISCUSSION

Equations (9) through (13) were solved numerically by a fourth-order explicit Runge-Kutta algorithm with a time increment of 0.25 seconds. For all practical purposes, the removal efficiency for the target compound was found to be invariant of  $[S_i]_0$ .

A detailed parametric sensitivity analysis is beyond the scope of this paper; instead sample cases are presented with arbitrary base values for the model parameters. Based on the works of several researchers, H is taken as 2.86 and  $(K_{L,a})$  is assumed to be 0.6 times  $K_{L,a}$  [4].

Shown in Figure 2 are the liquid and gas phase concentration profiles for ozone and the target organic compound

TABLE I. ARBITRARY BASE VALUES FOR THE MODEL PARAMETERS

Parameter	Base Value
w	0.05 s <sup>-1</sup>
$K_{L,a}$	0.03 s <sup>-1</sup>
$Q_G/Q_L$	3
$(O_3)_0$	0.135 mM
$h_L$	0.83
$k_T$	1000 L/mol · s
$H_i$	0.42
HRT	300 s

computed as a function of HRT and using the parameter values listed in Table I. The removal of the organic pollutant from the liquid phase can be determined from the  $[S]/[S]_0$  curve.

In Figure 3, the percent removal efficiency is presented as a function of  $H_i$  and  $k_T$ . For  $k_T$  values up to about 300 M<sup>-1</sup>s<sup>-1</sup>, the efficiency continues to increase with increasing volatility. Beyond this value, that is for more reactive compounds, the removal is relatively insensitive to  $H_i$ . These results indicate that the contribution of volatilization to the overall removal of the dissolved organic contaminants, in particular for the volatile ones that are not highly reactive toward ozone, can be of importance and has to be taken into account. Thus, the kinetic results of a batch ozonation study, where volatilization and oxidation are not separated properly, is inadequate for predicting the removal rates of volatile organics.

Model responses to operational parameters are shown in Figures 4-8. The plots were constructed by repeatedly executing the solution algorithm while varying one parameter at a time and keeping all the others fixed at their base values. However, due to potential interdependence of parameters, some responses might be over or under estimated. For instance, an increase in gas flow may result in an improvement of  $K_{L,a}$ , but may impair the liquid holdup. The analysis was carried out for 4 different groups of organic compounds:

- Group 1 highly reactive and non-volatile compounds, e.g., phenol and naphthalene ( $H_i = 0.02$  and  $k_T = 1000$  L/mol-s)
- Group 2 less reactive but volatile components, e.g., trichloroethylene ( $H_i = 0.42$  and  $k_T = 10$  L/mol-s)
- Group 3 moderately reactive but volatile compounds, e.g., o-xylene ( $H_i = 0.42$  and  $k_T = 100$  L/mol-s)
- Group 4 reactive but less volatile compounds, e.g., 1,2,4-trimethylbenzene ( $H_i = 0.24$  and  $k_T = 500$  L/mol-s)

The effect of gas-to-liquid ratio,  $(Q_G/Q_L)$ , on removal efficiency is plotted in Figure 4. The removal of reactive but less volatile organics is not affected by  $(Q_G/Q_L)$ . For more volatile and less reactive compounds, on the other hand, removal can be enhanced by increasing the ratio up to about 4. Other factors, such as maintainability of uniform flow and holdup, must also be considered when increasing the gas flow.

Figure 5 is a plot of removal efficiency versus ozone concentration in the inlet gas. Obviously, for non-reactive Group 2 compounds, an increase in the inlet ozone concentration has no effect on the removal. More reactive

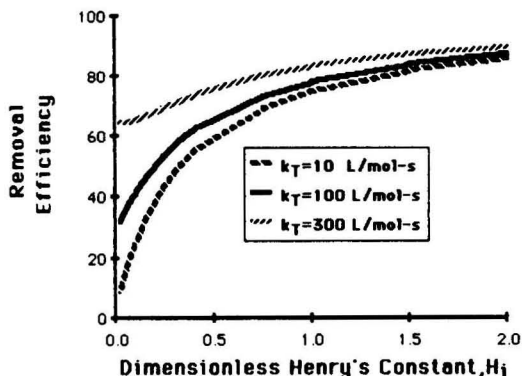


Figure 3. Percent removal efficiency as a function of  $k_T$  and  $H_i$ .

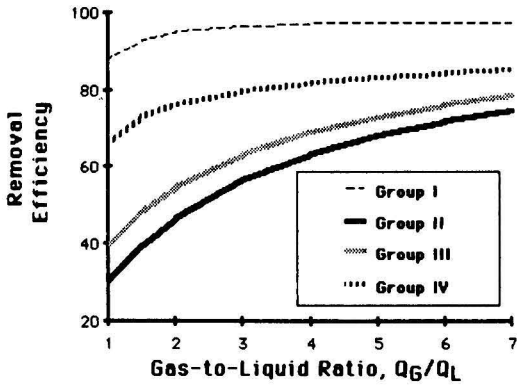


Figure 4. Effect of  $Q_G/Q_L$  on percent removal efficiency.

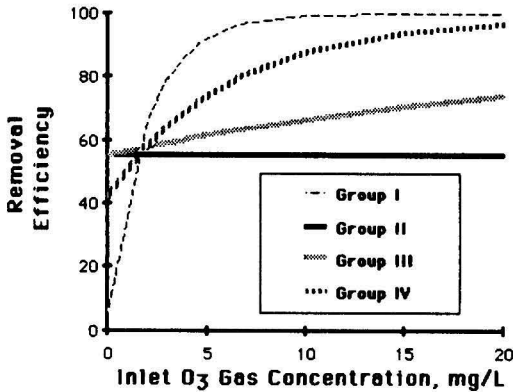


Figure 5. Effect of  $(O_3)_0$  on percent removal efficiency.

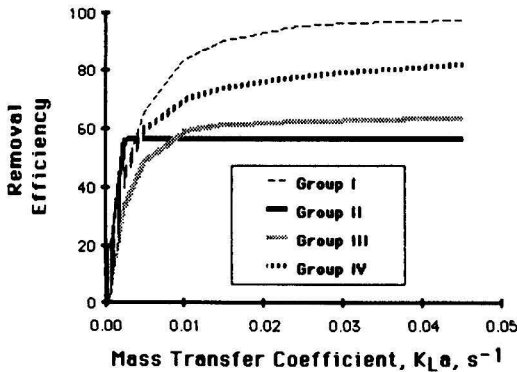


Figure 6. Effect of  $K_L a$  on percent removal efficiency.

compounds respond to increases in gas phase ozone concentration; the elimination of Group 3 and 4 continues to improve beyond gaseous ozone concentrations of 15 mg/L. Since, especially for highly reactive substances, the dependency on gaseous ozone levels off rather quickly, the selection of  $(O_3)_0$  should be made carefully to avoid waste of ozone in the exit gas.

Similarly, as it can be seen from Figure 6, higher  $K_L a$  values can not be of any advantage for the destruction of

less reactive solutes. It is also clear that efforts to increase  $K_L a$  beyond certain limits may not be beneficial at all. For the base values used in this study a value of approximately 0.015 per second corresponded to the maximum removals.

The effect of liquid-phase quality, as measured by  $w$ , is demonstrated in Figure 7. For groups 1, 3 and 4 removal efficiency deteriorates as  $w$  takes on larger values, i.e., as the water gets more polluted or alkaline. This is because of the fact that a lower aqueous ozone concentration can be sustained as  $w$  increases and less  $[O_3]$  becomes available for the reaction with the target compound. Since it is assumed that water quality does not affect  $H_L$  and  $K_L a$ , the removal of Group 2 compounds, which do not react with aqueous ozone, becomes insensitive to  $w$ . It is also interesting to note that Group 1 compounds, due to their high reactivity, are not as much affected from the early increases in  $w$  as the other two less reactive groups.

Finally, the response to the variation of liquid holdup is shown in Figure 8. At the selected levels of operational parameters, holdup does not appear to be a major factor. In general,  $K_L a$  is proportional to the gas holdup, and an increase in  $h_L$  should decrease the rate of mass transfer. On the other hand, an increase in  $h_L$  is advantageous for the removal of more reactive groups. In this study, since  $K_L a$  was assumed to be independent of  $h_L$ , the removal of reactive compounds was predicted to increase slightly as  $h_L$  approaches to unity.

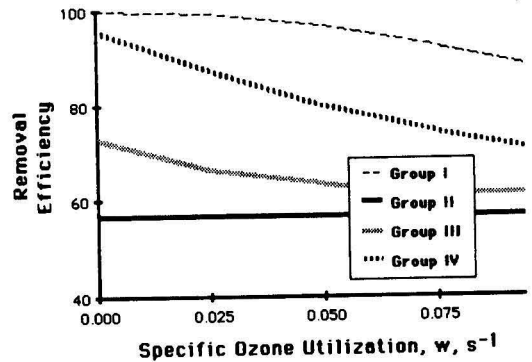


Figure 7. Effect of  $w$  on percent removal efficiency.

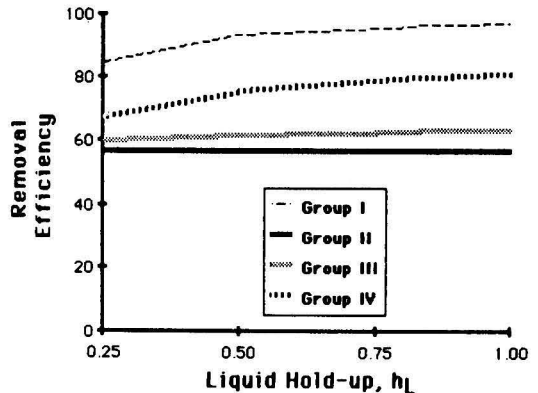


Figure 8. Effect of  $h_L$  on percent removal efficiency.

## CONCLUSION AND RECOMMENDATIONS

Major mechanisms contributing to the removal of organic pollutants in ozone reactors are stripping and total oxidation (direct plus indirect). The following factors influence the overall removal efficiency:

- (1) chemical reactivity of the organic compound, expressed as the total oxidation rate constant;
- (2) volatility of the organics, indicated by the Henry's Law constants;
- (3) contact opportunity between the phases as measured by the volumetric mass transfer coefficients;
- (4) gas-to-liquid ratio, which together with the bed characteristics, determines the contact time;
- (5) influent ozone concentration in the gas phase, which together with the chemical composition of water, quantified as  $w$ , and mass transfer properties, determines the available bulk ozone concentration at any given column section.

In light of the model predictions, any attempt to design an ozonation system should start with the characterization of the liquid stream, in terms of its  $w$  value. The values of  $k_T$  and  $H_1$  for the target pollutants must also be known. Then, a number of scenarios and reactor configurations can be tested with the model to optimize the operational conditions yielding the desired removal performance. Conversely, the efficiencies of existing reactors can also be predicted.

In addition to the removal of organic solutes from the liquid phase, the model also represents the gas-phase ozone and organic concentrations. This feature enables the evaluation of important concerns, such as safety precautions, and handling and/or recycling of the exit gas, ahead of time.

When used with the proper values of the operational parameters, the mathematical model presented in this paper, is applicable to both empty and packed bed ozone contact columns, in which axial and radial dispersion can be neglected. The model can easily be modified to handle co-current flows. Cases involving more than one target pollutant can be tackled by adding similar equations describing the rate of change for each organic compound.

This study can be considered as a forerunner on the way to developing reliable and yet practical design tools. Equipped with fundamental parameter determination techniques, such tools provide a more preferable alternative than the expensive and empirical pilot studies.

## ACKNOWLEDGEMENT

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## NOTATION

$H$	= Henry's Law constant, dimensionless
$K_{L,a}$	= volumetric mass transfer coefficient, $s^{-1}$
$k_T$	= total oxidation rate constant, $L/(\text{mole} \cdot s)$
$N$	= rate of ozone mass transfer, $\text{mole}/(L \cdot s)$
$Q_G$	= volumetric gas flow rate, $L/s$
$Q_L$	= volumetric liquid flow rate, $L/s$
$r$	= rate of ozone utilization, $\text{mole}/(L \cdot s)$
$r_1$	= rate of total oxidation, $\text{mole}/(L \cdot s)$
$S$	= organic contaminant

$t$	= hydraulic retention time (HRT), $s$
$w$	= specific ozone utilization rate, $s^{-1}$
$z$	= axial coordinate (column depth), $cm$
$(.)$	= gas-phase concentration, $\text{mole}/L$
$[.]$	= liquid-phase concentration, $\text{mole}/L$

## Subscripts

$i$	= counter for individual organic solutes
$e$	= effluent stream
$o$	= influent stream
$G$	= gas phase
$L$	= liquid phase

## Superscript

*	= concentration at the gas-liquid interface
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## APPENDIX

### Characteristics of Contact Columns and Related Definitions\*

Symbol	Definition	Remark
$z$	axial coordinate	
$A$	cross-sectional area	
$V_{EB}$	empty bed volume	$V_{EB} = A \cdot z$
$V_p$	packing volume	
$\phi$	packing fraction	$\phi = V_p/V_{EB}$ $\phi = 0$ ;(BC) $0 < \phi < 1$ ;(PB)
$V_L, V_G$	void volumes occupied by liquid and gas phases	$V_L + V_G = V_{EB}$ ;(BC) $= V_{EB}(1 - \phi)$ ;(PB)
$h_L, h_G$	liquid and gas phase holdups	$h_L = (V_L/V_{EB})$ $h_G = (V_G/V_{EB})$ $h_L + h_G = 1$ ;(BC) $= (1 - \phi)$ ;(PB)

\*BC = bubble column  
PB = packed bed

## LITERATURE CITED

1. Staehelin, J., and J. Hoigne, "Decomposition of Ozone in Water in the Presence of Organic Solutes Acting as Promoters and Inhibitors of Radical Chain Reactions," *Environ. Sci. Technol.*, **19**, 1206 (1985).
2. Gurol, M. D., and W. M. Bremen, "Kinetics and Mechanism of Ozonation of Free Cyanide Species in Water," *Environ. Sci. Technol.*, **19**, 804 (1985).
3. Yurteri, C., and M. D. Gurol, "Specific Ozone Utilization in Natural Waters: The Effects of Background Organic Matter, pH and Carbonate Species," submitted to *Ozone Sci., Eng.* (1987).
4. Gurol, M. D., "Factors Controlling the Removal of Organic Pollutants in Ozone Reactors," *Jour. AWWA*, **77**, 55 (1985).
5. Gurol, M. D., and S. Nekouinaini, "Effects of Organic Substances on Mass Transfer in Bubble Aeration," *Jour. WPCF*, **57**, 235 (1985).
6. Yurteri, C., and M. D. Gurol, "Microcomputer Applications in Environmental Engineering," *proceedings of the 4-th National Conference on Microcomputers in Civil Engineering*, Orlando, FLA., November 1986.
7. Hoigne, J., and H. Bader, "Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water," *Water. Res.*, **11**, 173 (1983).
8. Gurol, M. D., and S. Nekouinaini, "Kinetic Behavior of Ozone in Aqueous Solutions of Substituted Phenols," *Indus. & Chem. Engrg. Fundam.*, **23**, 54 (1984).

9. Hoigne, J., and H. Bader, "The Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous Solutions," *Water Res.*, **11**, 377 (1976).
10. Yurteri C., Kinetics and Mechanisms of Dissolved Organics Removal in Ozone Reactors, Ph.D. Dissertation, Drexel University, Philadelphia, Pa. (in progress).
11. Yurteri, C., D. F. Ryan, J. J. Callow, and M. D. Gurol, "The Effect of Water Composition on Henry's Law Constants," paper presented at the 59-th Annual WPCF Conference, Los Angeles, CA., October 1986.



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# Intermedia Transport of Organic Compounds in Biological Wastewater Treatment Processes

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*Organic compounds present in many industrial effluents are transported to varying extents to the gaseous or solid phase, in addition to potential biodegradation, during treatment. Knowledge of the fate of such compounds is critical for making valid policy and engineering decisions regarding issues such as the disposal of sludges, effluent toxicity, and emissions to the ambient air. To quantify the relative distribution of the fate of selected groups of compounds, a mathematical model is presented which describes the intermedia transport mechanisms including volatilization, solids sorption, and biodegradation. The extent of removal via each modeled pathway is a function of the physical properties of the specific compound and the process design and operational parameters of the system.*

## INTRODUCTION

When considering the treatment of conventional wastewater pollutants (BOD, TSS,  $\text{NH}_4$ ), it is recognized that a portion of the influent is not destructed in the process but rather is transferred to an alternative media (i.e. sludge) and removed from the system via wasting. The extent of transformation from the aqueous phase to the solid phase is governed by biological growth kinetics and the system operational conditions. Organic compounds present in effluents may be removed from the aqueous phase by various *non-biological* elimination mechanisms in addition to biodegradation. Consequently, both the overlying air mass above a treatment process and the solids removed from a treatment process must be considered as potential sinks of influent organic compounds in addition to the process aqueous effluent. This paper uses a mathematical model to describe the intermedia distribution of organic compounds as a function of (a) the physical properties of the compound and (b) the process design and operational parameters of the system.

The model developed for this study represents a synthesis of relationships observed or proposed by other investigators yielding an integrated model incorporating the three media (aqueous, solid, gaseous) of concern. The basis of the overall structure of the model draws from a USEPA funded program [1] which developed a similar form of model for the activated sludge process. However, significant differences exist between the EPA and NCASI models in the formulas defining removal rates and equilibrium conditions to allow for use of the model on a screening basis, i.e. without the need for extensive experimental data generation. Furthermore, the scope of the present model is expanded to include the aerated stabilization basin (ASB) process. The end product of this study

is a model which can be readily used by industry personnel.

The model is applied in this study to relate the distribution of organics to the three media during biological treatment. For example, the extent of transformation to the solid phase is presented as a function of the compound's octanol-water partition coefficient under an assumed set of design and operational conditions. Similarly, the relative stripping efficiency of surface aerators versus subsurface diffused aeration is simulated over a range of Henry's Law constant values. Finally, a series of model simulations tracing the removal pathways of four different types of compounds under various treatment configurations is presented.

## MODEL DESCRIPTION

Four elimination pathways are considered in the model; (a) air stripping associated with surface or subsurface aeration, (b) volatilization across nonturbulent surfaces, (c) adsorption onto biological solids, and (d) biodegradation. Volatilization is distinguished from forced stripping via aeration to investigate a previous report [2] that surface aerators play an insignificant role as chemical strippers in aerated stabilization basins.

In all cases, basin hydraulics are approximated as a single completely mixed reactor (CSTR) and steady-state conditions are assumed. The overall model equation has the form:

$$\frac{dC}{dt} Li = 0 = \frac{Q}{V} (C_{Li,i} - C_{Li}) - r_s - r_v - r_a - r_b \quad (1)$$



where,

- $C_{Li,i}, C_{Li}$  = influent and effluent concentration of compound i (mg/m<sup>3</sup>)
- $Q$  = volumetric liquid flow (m<sup>3</sup>/hr)
- $V$  = aeration basin volume (m<sup>3</sup>)
- $r_s$  = stripping removal rate (mg/m<sup>3</sup>/hr)
- $r_v$  = volatilization removal rate (mg/m<sup>3</sup>/hr)
- $r_a$  = adsorption removal rate (mg/m<sup>3</sup>/hr)
- $r_b$  = biodegradation removal rate (mg/m<sup>3</sup>/hr)

The model results are expressed in terms of percent removal by rearranging Equation 1 to the following form:

$$\frac{C_{Li,i} - C_{Li}}{C_{Li,i}} = \frac{r_s' + r_v' + r_a' + r_b'}{Q/V + r_s' + r_v' + r_a' + r_b'} \quad (2)$$

where,

$$r' = r/C_{Li}$$

### Stripping

Stripping is defined as the transfer of organics at dispersed gas/water interfaces such as the surface of water droplets forming the spray produced by a surface aerator or the surface of air bubbles produced by subsurface aeration devices. The rate of stripping is defined as:

$$r_s = K_L^s a (C_{Li}^* - C_{Li}) \quad (3)$$

where,

- $K_L^s a$  = overall mass transfer coefficient from the liquid phase (hr<sup>-1</sup>)
- $C_{Li}^*$  = liquid phase concentration of compound i in equilibrium with the gas phase

The ratio of the overall mass transfer coefficient of two volatile compounds has been shown to be independent of turbulence and temperature [3]. Because an estimate of the oxygen transfer for a given system can be made, oxygen is typically used as a reference for expressing the mass transfer of other volatile compounds:

$$K_L^s a_i = \Psi_i K_L a_{O_2} \quad (4)$$

where,

- $K_L^s a_i$  = overall mass transfer coefficient of compound i (hr<sup>-1</sup>)
- $\Psi_i$  = transfer rate proportionality coefficient (-)

The value of  $\Psi_i$  can either be measured directly or estimated from various relationships including the relative diffusivity in water of the compound and oxygen:

$$\Psi_i = \left( \frac{D_i}{D_{O_2}} \right)^n \quad (5)$$

For a highly mixed reactor, the film-penetration theory results in an exponent, n, value of 0.5. Reported measured values of n for two groups of compounds [4, 5] ranges from 0.61 to 0.66. However, in the latter study, the value of n is biased upwards by one of the six compounds (chloroform) analyzed which had an exponent value of 0.84. The average value of n for the remaining five compounds was 0.62. Chloroform had the lowest Henry's Law constant ( $5.3 \times 10^{-3}$  atm-m<sup>3</sup>/mol) of the six compounds included in that study.

According to the two-film mass transfer theory, the overall rate of stripping is the sum of the liquid and gas phase transfer resistances. The overall mass transfer coefficient is related to the liquid and gas phase transfer coefficients [5] by:

$$\frac{1}{K_L^s a} = \frac{1}{k_l^s a} + \frac{1}{H_c k_g^s a} \quad (6)$$

where,

- $k_l^s a$  = liquid phase mass transfer coefficient (hr<sup>-1</sup>)
- $k_g^s a$  = gas phase mass transfer coefficient (hr<sup>-1</sup>)
- $H_c$  = Henry's law constant (-)

The dimensionless form of the Henry's constant,  $H_c$ , is calculated from the model input Henry's Law constant (atm-m<sup>3</sup>/mol) according to [6]:

$$H_c = H/RT \quad (7)$$

where,

- $H$  = Henry's law constant (atm-m<sup>3</sup>/mol)
- $R$  = universal gas constant (atm-m<sup>3</sup>/mol<sup>o</sup>C)
- $T$  = absolute temperature (°K)

For highly volatile compounds, the gas phase resistance in Equation (6) becomes insignificant, thus the overall mass transfer rate is controlled by the liquid phase resistance:

$$K_L^s a = k_l^s a \quad (8)$$

Until recently, Equation (8) was felt to be appropriate for compounds with  $H_c$  greater than  $5 \times 10^{-3}$  atm-m<sup>3</sup>/mole [7]. This value, based on a ratio of  $k_g$  to  $k_l$  of 150, relates to 95 percent of the total resistance being associated with the liquid phase. A recent study [8] has demonstrated that the value of  $k_g/k_l$  for aeration basins may be significantly less than 150 and appears to be dependent on the mixing intensity of the basin. Based on this data, an assumption of complete liquid phase control (greater than 95%) in aeration basins is only valid at Henry's Law constants greater than  $2.4 \times 10^{-2}$  atm-m<sup>3</sup>/mole. Many organic compounds present in pulp and paper mill effluents have Henry's Law constants less than this value and therefore Equation (8) is not appropriate for use in this analysis, but rather Equation (6) must be applied.

The liquid phase transfer coefficient,  $k_l a$ , can be estimated by modifying Equation (4) and defining  $\Psi$  according to Equation (5):

$$k_l^s a_i = \Psi_i K_L a_{O_2} \quad (9)$$

This relationship appears to be valid based on the following observations; (a) gas phase resistance in oxygen transfer is not significant ( $H_{O_2} = 0.73$  atm-m<sup>3</sup>/mol), (b)  $\Psi$  is a function of the compound diffusivity in water only and not in air, and (c) stripping data for compounds controlled only by liquid phase resistance exhibit consistent values of n in Equation (5) whereas stripping data for chloroform, which is affected by both liquid and gas phase resistance, requires a larger value of n ( $\Psi$  is reduced). Therefore, in this study,  $\Psi_i$  is interpreted as the ratio of the liquid phase resistance of compound i and the total resistance (equivalent to the liquid phase resistance) of oxygen. Further, a single value of n (0.6) is assumed for all compounds.

Equations (5) and (9) provide an estimate of  $k_l a$  based on the oxygen transfer rate, the diffusivity of the compound in water, and an assumed value for n. In this study n is assigned a value of 0.6. An estimate of  $K_L a_{O_2}$  is made according to:

$$K_L a_{O_2} = \frac{0.454 N_o HP \alpha \theta^{T-20}}{C_s^* V} \quad (10)$$

where,

- $N_o$  = standard oxygen transfer rate (lbs. O<sub>2</sub>/HP/hr)
- HP = total aeration horsepower (HP)
- $\alpha, \theta$  = oxygen transfer correction factors (-)
- $C_s^*$  = dissolved oxygen saturation concentration at 20°C (mg/l)
- V = basin volume (10<sup>6</sup> liters)

The compound diffusivity in water is available for a limited number of compounds (9) or may be estimated by the Wilke and Chang relationship (10):

$$D_1 = 7.4 \times 10^{-8} \frac{(18x)^{1/2} T}{\eta V^{0.6}} \quad (11)$$

where,

- $D_1$  = diffusivity constant in water (cm<sup>2</sup>/sec)
- $x$  = association parameter for water
- $T$  = absolute temperature (°K)
- $\eta$  = viscosity of water (centipoise)
- $V$  = molar volume

Molar volumes are estimated by the LeBas method [11] and an association parameter value of 2.26 is used [12].

Munz and Roberts [8] have demonstrated that the ratio of  $k_g/k_l$  decreases with increasing basin turbulence. Their findings suggest that, for the hydraulic conditions representative of an activated sludge system, a value of  $k_g/k_l$  of 20 is more appropriate than the previously assumed value of 150 measured at natural water surfaces [13]. Inspection of data presented by Smith et al. [14] for intermediately volatile compounds appear to support Munz and Roberts' suggested value for  $k_g/k_l$ . Table 1 lists values of  $k_g/k_l$  calculated from the data of Smith et al. measured at oxygen transfer rates typical of activated sludge systems.

Throughout this study, the value of  $k_g/k_l$  suggested by Munz and Roberts is applied:

$$k_g^* a_1 = 20 k_l^* a_1 \quad (12)$$

**Surface Aeration:** For surface aeration,  $C_{1,*}$  is approximated as zero based on the assumption that sufficient atmospheric turbulence exists such that no appreciable buildup of the organic compound develops in the overlaying air mass. Although volatile compounds have been measured in a two meter layer above aerated stabilization basins treating pulp and paper effluents [2], the intended use of the model, in its present form as a screening model, does not warrant the development of an ambient air saturation module. Further, Roberts et al. [15] have estimated, using a simple atmospheric boundary layer model, that the fractional saturation of chloroform for a hypothetical activated sludge basin is on the order of five percent; well within the expected error margin of a screening model. Note that the assumption of no organic compound buildup in the overlaying air mass is valid only for basins which are not covered.

Assuming  $C_{L,*}$  to be zero reduces Equation (3) to:

$$r_s = -K_L^* a_1 C_{L1} \quad (13)$$

where  $K_L^* a_1$  is calculated by substituting Equations (9) and (12) into Equation (6).

The steady state equation for the removal of  $C_1$  from a CSTR aeration basin via surface aeration is written as:

$$C_{L1,i} - C_{L1} = V/Q K_L^* a_1 C_{L1} \quad (14)$$

where,

$C_{L1,i}$  = influent concentration of compound; (mg/m<sup>3</sup>)

TABLE 1. VALUES OF  $k_g/k_l$  FOR INTERMEDIATE VOLATILITY COMPOUNDS (DATA FROM REF. 14)

Compound	$K_L A_{O_2} (\text{hr}^{-1})$	$k_g/k_l$
Naphthalene	6.2	33
	10.9	60
	12.6	22
Anthracene	4.6	147
	5.0	33
	11.0	25

**Subsurface Aeration:** In subsurface aeration, transfer of the compound is into the rising bubble rather than directly to the atmosphere. Here, because of the small volume of the bubble, partial saturation of the bubble air can be expected to occur for intermediate to highly volatile compounds. The extent of saturation within the bubble [15] is calculated by:

$$\frac{C_{G,E}}{C_{L1} H_c} = (1 - e^{-\theta}) \quad (15)$$

where,

$$\theta = \frac{K_L^* a_1 V}{H_c Q_G}$$

- $C_{G,E}$  = concentration in exiting gas bubble
- $Q_G$  = gas flow rate (m<sup>3</sup>/hr)

The steady state equation for the removal of  $C_1$  from a CSTR aeration basin via subsurface aeration is written as:

$$C_{L1,i} - C_{L1} = \frac{Q_G}{Q_L} H_c C_{L1} (1 - e^{-\theta}) \quad (16)$$

#### Volatilization

Volatilization of organic compounds across basin surfaces may be modeled using the two-film model presented in the description of the model's stripping module (6). Liquid phase resistance of the compound is related to oxygen by the transfer proportionality constant  $\Psi$ . The rate of natural oxygen reaeration across the basin surface,  $K_L^* A_{O_2}$ , is estimated as 0.5 per day based at this time on values of  $K_a$  ( $k_2$ ) reported for rivers and streams [17]:

$$k_1^* a_1 = \Psi K_L^* a_{O_2} \quad (17)$$

where,

$k_1^* a$  = liquid phase mass transfer coefficient (hr<sup>-1</sup>)

Various methods are available to estimate the gas phase resistance across surfaces based on either the liquid phase resistance or environmental conditions. A ratio of  $k_g/k_l$  of 150, measured at the seawater-air interface [13], is often applied to estimate  $k_g$  from  $k_l$ . Other proposed relationships estimate  $k_g$  as a function of ambient velocities and the gas phase Schmit number of the compound [18, 19]. Mills [20] has related  $k_g$  to wind velocity, basin depth, and the compound's molecular weight according to:

$$k_g^* a = 700 \left( \frac{18}{MW} \right)^{1/4} V_w \frac{24}{100 Z} \quad (18)$$

where,

- $k_g^* a$  = gas phase mass transfer coefficient (hr<sup>-1</sup>)
- MW = compound molecular weight (gm/mole)
- $V_w$  = ambient wind velocity (m/sec)
- Z = basin depth (m)

Equation (18) is used in this study to estimate  $k_g$ .

Combining Equations (17) and (18) into the two-film mass transfer equation, Equation (6) yields the overall removal by surface volatilization.

$$r_v = \left( \frac{1}{\Psi K_L^* a_{O_2}} + \frac{1}{H_c 700 \left( \frac{18}{MW} \right)^{1/4} V_w \frac{24}{100 Z}} \right)^{-1} C_{L1} \quad (19)$$

#### Solids Adsorption

The rate of sorption of organic compounds onto biological solids has been demonstrated to be rapid. Blackburn

TABLE 2. MODEL INPUTS FOR SIMULATION OF ORGANIC COMPOUND REMOVAL PATHWAYS IN BIOLOGICAL WASTEWATER TREATMENT PROCESSES

	Activated Sludge	ASB
Flow (m <sup>3</sup> /sec)	0.44	0.44
Basin Volume (10 <sup>3</sup> m <sup>3</sup> )	9.5	303
Temperature (°C)	20	20
Surface Area (ha)	0.2	6.5
Mixed Liquid Vol. Suspended Solids (mg/l)	2000	150
Effluent Suspended Solids (kg/day)	1130	1130
Wasted Solids (kg/day)	3400	0
Oxygen Transfer Efficiency (kg O <sub>2</sub> /HP/hr)	1.14	1.14
Aeration Horsepower	700	450
Gas Flow* (m <sup>3</sup> /min)	240	155
Diffusivity (10 <sup>-5</sup> cm <sup>2</sup> /sec)	0.8	0.8
Molecular Weight (gm/M)	100	100
Ambient Wind Velocity (m/sec)	2	2
Surface Reaeration Coeff. (hr <sup>-1</sup> )	0.5	0.5
Biodegradation Rate (liter/mg-X/hr)	2 × 10 <sup>-4</sup>	2 × 10 <sup>-4</sup>

\*Subsurface aeration simulations only

et al. [1] found equilibrium times to be less than fifteen minutes for three test compounds while Pellizzari [21] observed that for two test compounds, all measurable adsorption occurred prior to the first sampling time of thirty minutes. Thus, an equilibrium condition between the aqueous and solid phases may be assumed in most wastewater treatment processes.

Various relationships are available to describe the tendency of a compound to adhere to solids including linear, Freundlich and Langmuir isotherms [22]. The linear isotherm is the simplest of the three, having the following form:

$$C_{si} = K_p C_{Li} \quad (20)$$

where,

- C<sub>si</sub> = equilibrium concentration on solids (mg/kg)
- K<sub>p</sub> = partition coefficient (liter/gm)

The Freundlich isotherm has a similar form:

$$C_{si} = K_f C_{Li}^{1/n} \quad (21)$$

A limited selection of partition coefficients for organic compounds onto activated sludge is available. Blackburn et al. [1] and Matter-Muller et al. [23] provide partition coefficients for three and six organic compounds, respectively, by fitting measured data to a linear isotherm model while Pellizzari [21] used the Freundlich isotherm to fit sorption data for six compounds. It is interesting to note that the values of *n*, determined for the six compounds by Pellizzari, are close to one (0.951 to 1.136), thus approximating the linear isotherm.

Where water-activated sludge partition coefficients are not available, various relationships have been proposed to approximate K<sub>p</sub> from the compound's octanol-water partition coefficient, K<sub>ow</sub> (1, 23). Octanol-water partition coefficients may be estimated from the water solubility of the compound [24]. Blackburn et al. [1] based their estimate of K<sub>p</sub> on the octanol-water partition coefficient and the lipid fraction in the biomass:

$$K_p = \frac{K_{ow} f_L}{\rho_L} \quad (22)$$

where,

- K<sub>ow</sub> = n-octanol/water partition coefficient (L/gm)
- f<sub>L</sub> = lipid weight fraction of biomass
- ρ<sub>L</sub> = density of lipids (gm/liter)

Matter-Muller et al. [23] provide a linear relationship between the logs of K<sub>p</sub> and K<sub>ow</sub> for activated sludge:

$$\log K_p = 0.67 \log K_{ow} - 2.61 \quad (23)$$

Equation (23) has been selected for estimating K<sub>p</sub> from K<sub>ow</sub> in this model because of its simplistic nature. Where measured values of K<sub>p</sub> are available, they may be entered directly into the model.

Matter-Muller et al. [23] have shown mathematically that the extent of removal can be expressed in terms of the partition coefficient and the rate of solids removed from the system:

$$r_a = \frac{SP K_p C_{Li}}{V} \quad (24)$$

where,

SP = rate of sludge removal (kg/hr)

The partition coefficient, K<sub>p</sub>, is generally assumed to be independent of the solids concentration. However, O'Connor and Connolly [25] have demonstrated an inverse relationship between solids concentration and the partition coefficient. Strongly hydrophobic compounds such as DDT (log K<sub>ow</sub> = 6) exhibited a ten-fold increase in partition coefficient for an order of magnitude decrease in total suspended solids obtained from river systems. Voice et al. [26] found an order of magnitude increase in K<sub>p</sub> for every two orders of magnitude decrease in solids concentration for four compounds with log K<sub>ow</sub> values ranging from one to five. The authors suggest the solids effect results from the presence of a liquid phase sorbing material not removed during the separation procedure prior to analysis. Furthermore, laboratory partition coefficients may not be directly applicable to real systems.

The significance of these findings regarding solids effects on K<sub>p</sub> to the present model is two-fold; (a) laboratory developed partition coefficients conducted at solids concentrations reflective of the treatment system may underestimate the extent of actual partitioning occurring in the treatment process and (b) extrapolating data developed at activated sludge concentrations to ASB solids concentrations may result in further underestimation of the actual partition coefficient. Further study of potential effects of solids concentration on partitioning in wastewater treatment processes is needed. In this study, the extent of solids partitioning is assumed to be independent of the solids concentration.

### Biodegradation

Biodegradability screening studies indicate that many of the priority pollutants are, to varying extents, biodegradable [27]. Thus, a biodegradation module is needed. Keeping within the screening nature of the present model, a simplistic biodegradation model is desired. Furthermore, because organic compounds in pulp and paper mill effluents are generally present at relatively low concentrations, the potential inhibitory effects of the compounds on biological activity do not need to be considered in the bio-kinetic relationships. For example, inhibitory concentrations of various priority organic pollutants range from 20 to 500 mg/l (28).

In anticipation of the model use for systems representing a wide range of biosolids concentrations (acti-

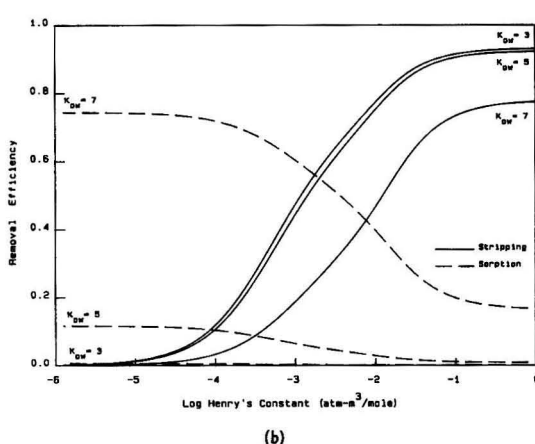
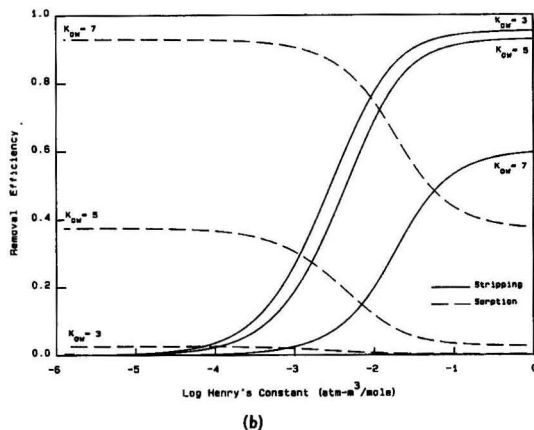
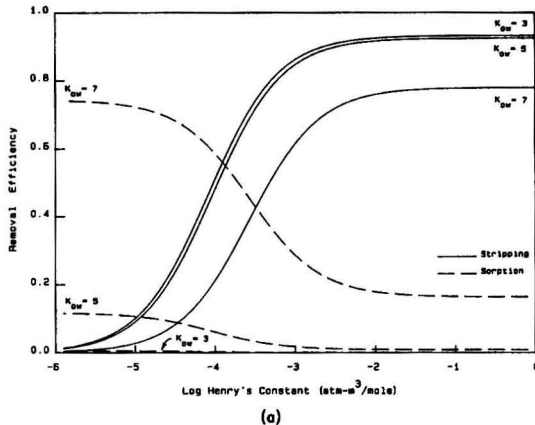
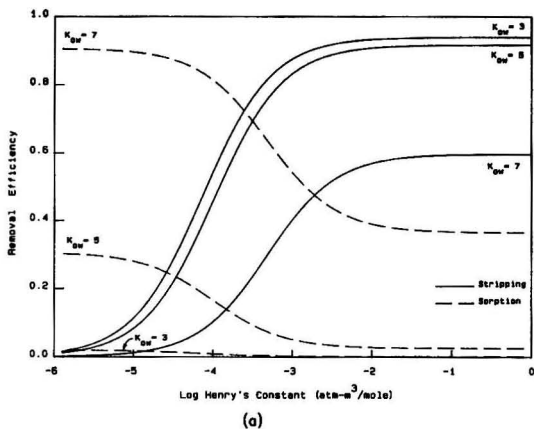


Figure 1. Stripping and sorption removal efficiencies for low biodegradable compounds—activated sludge: (a) surface aeration, (b) subsurface aeration.

Figure 2. Stripping and sorption removal efficiencies for low biodegradable compounds—ASB: (a) surface aeration, (b) subsurface aeration.

ivated sludge vs. ASB), it was deemed necessary to include the biosolids concentration in the biodegradation rate expression. Thus, a second order relationship is used:

$$r_b = k_2 \times C_{LI} \quad (25)$$

where,

$k_2$  = second order rate constant (liter/mg-X/hr)  
 $X$  = volatile suspended solids (mg/l)

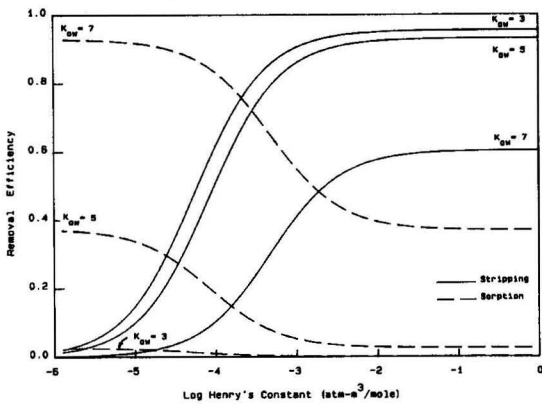
Sayler et al. (29) used a similar relationship for the prediction of the biodegradation fate of test compounds.

#### MODEL APPLICATION—GENERAL

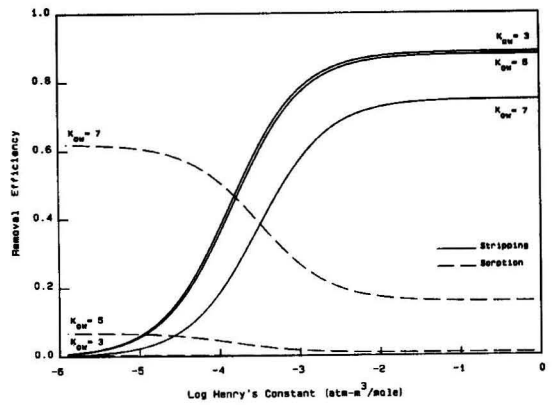
The model described in the preceding section is used to examine the relative distribution of the fate of influent organic compounds under various biological treatment process configurations including activated sludge and ASB processes equipped with surface or subsurface (diffused) aeration systems. Table 2 lists the input parameters used for these simulations. The results for each process configuration are presented over a range of Henry's constant from  $10^{-6}$  to  $10^0$  atm-m<sup>3</sup>/mole for octanol-water partition coefficients of 3, 5, and 7. Separate figures are provided for compounds categorized as exhibiting low and intermediate biodegradability.

Figure 1 displays the removal percentages associated with sorption to solids and the sum of forced stripping and volatilization in a hypothetical open activated sludge process. For the system simulated, at  $K_{ow}$  values less than 5, stripping is the dominant factor resulting in a significant transfer of compounds with  $H_c$  values greater than  $10^{-4}$  atm-m<sup>3</sup>/mole for surface aerators and greater than  $5 \times 10^{-3}$  for subsurface aeration devices. Subsurface aeration is a less efficient stripping mechanism because of the partial saturation of the rising air bubble. Sorption onto biological solids appears only to be significant for compounds with  $K_{ow}$  values greater than 5.

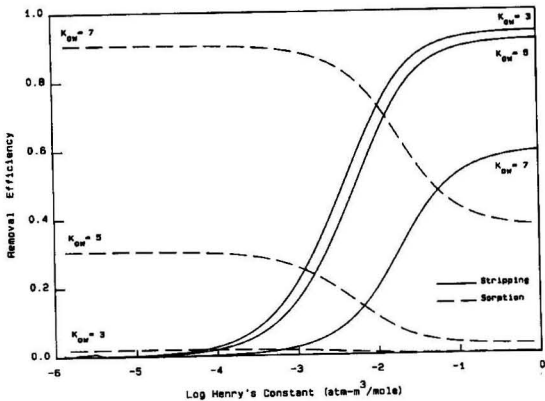
Simulation results for a hypothetical eight day resident time ASB are displayed in Figure 2. For surface aeration, similar removals to the activated sludge results are observed for compounds with  $K_{ow}$  values of 5 and less. However, removal efficiencies of compounds with  $K_{ow}$  equal to 7 are consistently fifteen percent less than those observed for the activated sludge process over the range of  $H_c$  values simulated. This is apparently associated with the lower solids production of the ASB process. A corresponding increase in stripping efficiency is observed as a result of more of the compound being available for stripping. This same phenomenon occurs to an even greater extent in the subsurface aeration ASB process. Another feature of the subsurface aeration results is that removal due to stripping plus volatilization exceeds that observed



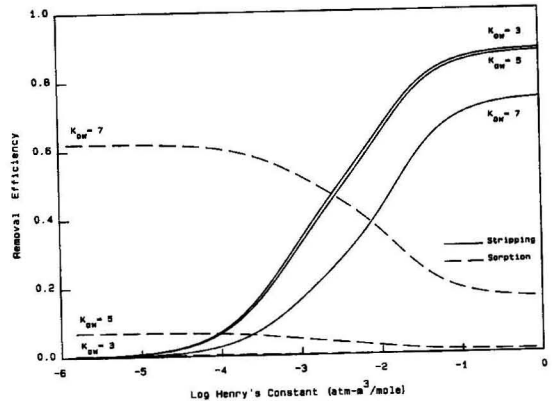
(a)



(a)



(b)



(b)

Figure 3. Stripping and sorption removal efficiencies for intermediate biodegradable compounds—activated sludge: (a) surface aeration, (b) subsurface aeration.

Figure 4. Stripping sorption removal efficiencies for intermediate biodegradable compounds—ASB: (a) surface aeration, (b) subsurface aeration.

for subsurface activated sludge process for compounds with  $H_c$  values ranging from  $10^{-4}$  to  $10^{-2}$  atm-m<sup>3</sup>/mole. As discussed below, this is primarily the result of volatilization across the nonturbulent basin surface.

Figures 3 and 4 display the model results for intermediate biodegradable compounds under the four treatment configurations simulated. Minor downward shifts in the sorption and stripping results (less than 5 percent) occur in the activated sludge simulation results while slightly larger downward shifts occur in the ASB simulations.

The maximum percent removal attributed to biodegradation for the simulations presented in Figures 3 and 4 occur at the smallest values for  $H_c$  and  $K_{ow}$  tested. In the activated sludge process, compounds categorized as exhibiting intermediate biodegradability realized a maximum biodegradability removal of thirty-two percent. A maximum value of fifty-four percent was determined for the ASB simulations.

A final set of simulations was run to investigate the contribution of natural volatilization to the total transfer of compounds to the atmosphere. Figure 5 displays the model results for an ASB system simulated with natural volatilization ( $K_1^{V_{aO_2}} = 0.5$ ) and without volatilization. Natural volatilization appears to play an insignificant role for systems employing surface aeration, apparently because of the high efficiency of the aerators themselves.

This observation conflicts with that made by Thibodeaux et al. [2] who concluded that, because of the greater natural surface area relative to the contact surface area resulting from surface aerators, natural volatilization dominates transfer to the atmosphere from ASB processes. The subsurface aeration results displayed in Figure 5 indicate that natural volatilization may account for as much as thirty-five percent of the total removal for compounds with  $H_c$  values ranging from  $10^{-4}$  to  $10^{-2}$ .

While the intended use of the model is to provide an estimate of the relative pathways of removal for a specific compound of known volatility, sorption and biodegradability, it is useful in this study to examine whole groups of compounds. Figure 6 displays the cumulative distribution of the Henry's constant for seventy non-metallic compounds presently listed by EPA as priority pollutants for which Henry's constants were available. For this group, the median  $H_c$  is approximately  $10^{-3}$  atm-m<sup>3</sup>/mole. Reference to Figures 1 and 2 indicates that either activated sludge or ASB processes utilizing surface aeration are capable of removing greater than 85 percent of at least fifty percent of the seventy priority pollutants from which Figure 6 was developed. For subsurface aeration systems, greater than 85 percent removal for at least fifteen percent of the seventy compounds can be expected.

Figure 7 displays  $K_{ow}$  values of 74 non-metallic priority



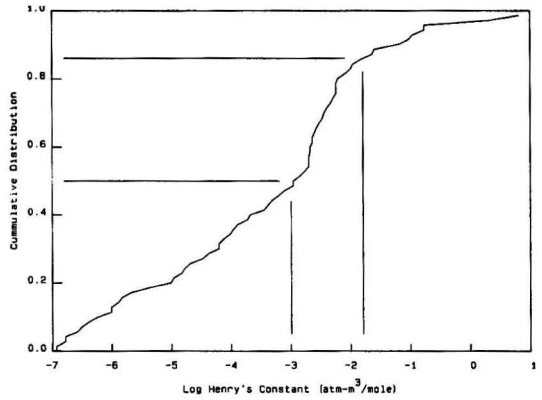
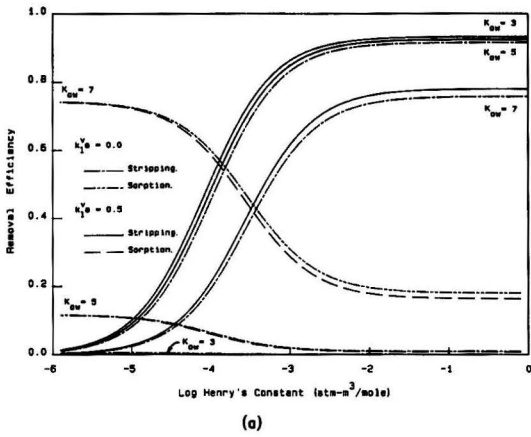


Figure 6. Cumulative distribution of Henry's Law constant for seventy non-metallic priority pollutants.

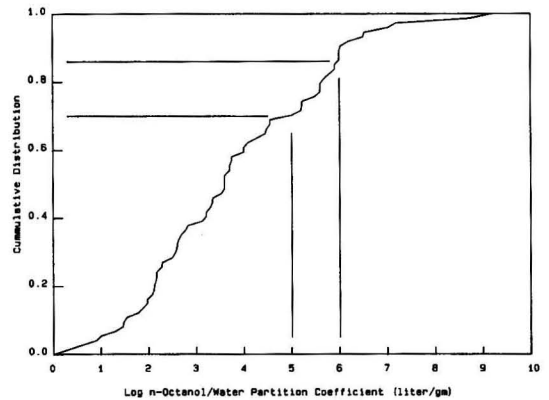
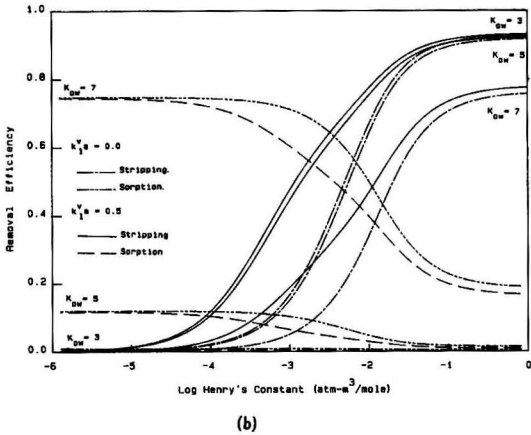


Figure 7. Cumulative distribution of n-octanol/water partition coefficients for seventy-four non-metallic priority pollutants.

Figure 5. Stripping and sorption removal efficiencies with and without natural surface reaeration for low biodegradable compounds—ASB: (a) surface aeration, (b) subsurface aeration.

pollutants. The median  $K_{ow}$  for this group is 3.7. It is interesting to note that only thirty percent of the compounds have  $K_{ow}$  values greater than 5.0 and only fifteen percent have  $K_{ow}$  values greater than 6.0. Referring once again to Figures 1 and 2 suggests that only a small subset of the priority pollutants will be transferred to the solids phase in significant quantities. Three of the seven compounds which (a) have  $K_{ow}$  greater or equal to 6.0, and (b) have  $H_c$  data available, were found to have potential for transfer to the gaseous phase as well as the solids phase. Henry's constant values were not available for four additional compounds displayed in Figure 7 with  $K_{ow}$  greater or equal to 6.0.

#### MODEL APPLICATION—PULP AND PAPER MILL EFFLUENTS

Removal pathways of four organic compounds potentially present in low concentrations in wastewaters from pulp and paper mills were screened using the model. The four treatment process configurations described in the preceding section were investigated. The compounds were selected to provide a range in volatility, sorbing tendency, and biodegradability as illustrated in Table 3. Table 4 lists the physical parameters of interest. Although these four compounds were selected in this study, this

does not infer that these compounds exist in all pulp and paper mill effluents. Indeed, hexachlorobenzene has only been reported present, in low concentrations, in one pulp mill effluent [34] and is generally not found in pulp mill effluents. It is included in this analysis only to provide an example of a strongly sorbing compound.

#### Activated Sludge Processes

Table 5 presents the model results for the hypothetical activated sludge process treating the four test compounds. As anticipated, phenol, and chloroform are removed from the aqueous phase via biodegradation, and stripping respectively. Hexachlorobenzene is removed via sorption and stripping where surface aeration is used.

TABLE 3. ANTICIPATED REMOVAL PATHWAY TENDENCIES OF FOUR TEST COMPOUNDS FOR MODEL SCREENING

Compound	Volatility	Sorption	Biodegradability
Phenol	Low	Low	High
Chloroform	High	Low	Medium
Tetrachloroguaiacol	Low	Medium	Low
Hexachlorobenzene	Medium	High	Low

TABLE 4. PROPERTIES OF TEST COMPOUNDS

Compound	Hc atm-m <sup>3</sup> /mol	Di <sup>(a)</sup> 10 <sup>-5</sup> cm <sup>2</sup> /s	MW gm/mol	log K <sub>ow</sub> L/gm	k <sub>s</sub> L/mg/hr
Phenol	2.7 × 10 <sup>-7</sup> (30)	0.86	94	1.46 (30)	2 × 10 <sup>-3</sup>
Chloroform	5.3 × 10 <sup>-3</sup> (5)	0.94	119	1.97 (24)	1 × 10 <sup>-3(b)</sup>
Tetrachloroguaiacol	1.0 × 10 <sup>-5</sup> (31)	0.55	262	4.5 (32)	1 × 10 <sup>-6(b)</sup>
Hexachlorobenzene	1.9 × 1.0 <sup>-4</sup> (20)	0.54	285	6.53 (33)	1 × 10 <sup>-6(b)</sup>

(a) Estimated by Wilkes and Chang method;  $\theta = 2.26$

(b) Estimated relative to phenol biodegradability

Numbers in parentheses indicate literature reference number.

Tetrachloroguaiacol is not removed in significant quantities by either of the aeration configurations.

Table 6 compares predicted effluent chloroform and tetrachloroguaiacol levels with actual activated sludge performance data collected during two NCASI sampling programs [35]. In the former sampling program, three 24-hour composite influent and effluent chloroform samples were collected for each mill. In the latter sampling program, five 24-hour composite influent and effluent samples were collected for each mill. Bear in mind that the comparisons involve predicted performance of a "typical" activated sludge process (described in Table 2) with a group of processes exhibiting a range of operating parameters such as horsepower intensity and aeration basins solids concentration. Thus, discrepancies between predicted and observed values may be partially due to differences between the assumed operating conditions and the actual conditions of the mills included in the sampling program.

Predicted overall chloroform removal of 96 percent for surface aeration activated sludge processes compares

well with average overall removals of 94 and 88 percent measured during the two sampling programs. Similarly, the predicted overall subsurface aeration removal of 72 percent compares well with measured average removals of 71 and 69 percent.

Tetrachloroguaiacol concentrations were measured in only one of the two sampling programs conducted. For each mill sampled, one 24-hour composite primary influent sample and five 24-hour composite secondary effluent samples were collected during two separate sampling periods. The average removal percentage for the seven surface aeration processes was thirteen percent. However, this removal percentage is potentially biased by the low tetrachloroguaiacol levels in the untreated mill effluent sample. Five of the seven mills exhibited influent tetrachloroguaiacol concentrations of less than 10 ppb. In one case, a -100 percent removal was found based on an influent concentration of 0.3 ppb and an effluent concentration of 0.6 ppb. Considering only mills with an untreated mill effluent level greater than 10 ppb (two mills), an average overall removal of 54 percent is calculated. The model prediction of 32 percent for surface aeration activated sludge processes falls between the average observed removals for all seven mills and for only mills with untreated effluents greater than 10 ppb. Additional process performance data is necessary to evaluate the model's accuracy for predicting tetrachloroguaiacol removal. The only subsurface aeration activated sludge process sampled had an average tetrachloroguaiacol removal efficiency of 58 percent compared to a predicted value of 23 percent.

The model results may also be compared with literature values. The modeled phenol removal is less than the 86 percent removal reported by Hannah et al. [36] and the 99 percent removal reported by Kincannon et al. [37]. The 72 percent removal of chloroform by the subsurface aeration system is in agreement with the 65 percent removal measured by Leuenberger et al. [31] for subsurface systems while the model prediction of low tetrachloroguaiacol removal efficiencies is consistent with that measured by Leuenberger (14 percent). The model agreement with literature values (and with the few measured values available from previous NCASI studies) is considered to be adequate, especially considering that the model was not calibrated to an actual system.

The impact of bubble saturation during stripping of volatile compounds is evident from the difference between modeled stripping efficiency for surface and subsurface aeration. For chloroform the difference is partially compensated for by an increased biodegradation removal resulting from higher chloroform concentrations available to the biological solids. For hexachlorobenzene, an increase in the removal via sorption is predicted for subsurface aeration systems.

TABLE 5. ESTIMATED PERCENT REMOVAL BY ALTERNATIVE PATHWAYS OF FOUR ORGANIC COMPOUNDS—ACTIVATED SLUDGE

Removal Pathway	Phenol	Surface Aeration		
		CHCl <sub>3</sub>	TCG <sup>1</sup>	HCB <sup>2</sup>
Forced Stripping	0	93	11	24
Natural Vol	0	0	0	0
Total to Atmos.	0	93	11	24
Sorption:				
Effluent Solids	0	0	5	16
Wasted Solids	0	0	16	50
Total Sorption	0	0	21	66
Biodegradation	50	2	0	0
Total Removal	50	96	32	90

(1) Tetrachloroguaiacol

(2) Hexachlorobenzene

Removal Pathway	Phenol	Subsurface Aeration		
		CHCl <sub>3</sub>	TCG <sup>1</sup>	HCB <sup>2</sup>
Forced Stripping	0	56	0	1
Natural Vol	0	2	0	0
Total to Atmos.	0	58	0	1
Sorption:				
Effluent Solids	0	0	6	22
Wasted Solids	0	0	17	65
Total Sorption	0	0	23	87
Biodegradation	50	14	0	0
Total Removal	50	72	23	88

(1) Tetrachloroguaiacol

(2) Hexachlorobenzene

TABLE 6. COMPARISON OF PREDICTED VERSUS MEASURED OVERALL REMOVAL PERCENT—ACTIVATED SLUDGE

Compound/Aeration	Predicted Avg (%)	NOB	Survey #1		Survey #2	
				Avg (%)	NOB	Avg (%)
Chloroform:						
Surface	96	3		94 (92-96) <sup>a</sup>	4	88 (86-90)
Subsurface	72	5		71 (14-96)	1	69
Tetrachloroguaiacol:						
Surface	32	7		13 (-100-68)	—	—
Subsurface	23	1		58	—	—

(a) Measured Range

**ASB Processes**

Table 7 presents the model results for the hypothetical aerated stabilization basin process. Two significant differences from the activated sludge results may be noted. First, the total removal of hexachlorobenzene is somewhat lower, apparently because of the lower rate of solids generation associated with the ASB process. Second, chloroform, the most volatile of the four compounds, is partially removed via the process of natural volatilization across the basin surface. As illustrated in Figure 3b, chloroform ( $H_e = 5.3 \times 10^{-3}$  atm-m<sup>3</sup>/mole) falls in the range of volatility most impacted by natural surface volatilization.

Table 8 compares predicted effluent chloroform and tetrachloroguaiacol levels with actual ASB performance data collected during the NCASI sampling programs just described. All sampling was performed at basins equipped with surface aerators. Predicted overall chloroform removal of 94 percent falls between the two average removals of 98 and 84 percent measured. Average tetrachloroguaiacol removal measured was 7 percent in the one sampling program where the analysis was made. The range of removal efficiencies, however, was very wide

(-169 to 84). Considering only mills with an average untreated effluent concentration of greater than 10 ppb (three mills), an average removal of 60 percent (30-84) is calculated. At these higher concentrations analytical precision plays a less significant role in the removal percentage calculation, thus data for these locations could be assumed to be more accurate than that for the other systems. None-the-less, because of the range of measured tetrachloroguaiacol removal efficiencies and the limited availability of data for basins with relatively high untreated effluent tetrachloroguaiacol levels, it is difficult to evaluate the accuracy of the predicted tetrachloroguaiacol removal efficiency until further data becomes available.

Comparing the model results to literature values, the predicted ASB phenol removal efficiency is greater than the thirty percent reported by Hannah et al. [36] for a bench-scale ASB process receiving a low strength influent phenol concentration (0.1 mg/l). The surface aeration chloroform removal is in good agreement with values of 92 and 94 percent removals reported by Voss [38] and Claeys et al. [39] for ASB processes. No data on ASB removal efficiencies for tetrachloroguaiacol or hexachlorobenzene, other than the NCASI data, are available.

**SUMMARY**

A model is presented to be used as a screening tool for the identification of the extent of intermedia transport of specific organic compounds in biological wastewater treatment processes. Four removal pathways are included in the model; forced air stripping, natural volatilization, solids sorption, and biodegradation. In this study, the model has been applied to examine the relationship between a compound's properties and the intermedia transport pathway most likely for the compound to undergo. The following observations may be made from this examination:

(1) In this model, transport to the solids phase is significant for compounds with octanol-water partition coefficients greater than 5 liter/gm. Transport to the gaseous phase via forced stripping, is significant for compounds with Henry's constants greater than  $1 \times 10^{-4}$  atm-m<sup>3</sup>/mole in processes employing surface aeration and greater than  $5 \times 10^{-3}$  atm-m<sup>3</sup>/mole in processes employing subsurface (bubble) aeration.

(2) In this model, biodegradation can be a significant removal pathway for some compounds with low octanol-water partition coefficients and low Henry's constants, such as phenol.

(3) In this model, natural volatilization across the surface of ASB processes is only significant for compounds with Henry's constants in the range of  $10^{-4}$  to  $10^{-2}$  atm-m<sup>3</sup>/mole where the basin is aerated with subsurface aeration devices. A maximum of 35 percent of the total removal was found to be attributable to natural volatilization in ASB processes equipped with subsurface aeration, whereas the maximum percent for surface aeration ASBs was only 10 percent.

TABLE 7. ESTIMATED PERCENT REMOVAL BY ALTERNATIVE PATHWAYS OF FOUR ORGANIC COMPOUNDS—AERATED STABILIZATION BASIN

Removal Pathway	Phenol	Surface Aeration		HCB <sup>2</sup>
		CHCl <sub>3</sub>	TCG <sup>1</sup>	
Forced Stripping	0	77	8	36
Natural Vol	0	10	1	4
Total to Atmos.	0	87	9	40
Sorption:				
Effluent Solids	0	0	6	38
Wasted Solids	0	0	0	0
Total Sorption	0	0	6	38
Biodegradation	70	7	0	0
Total Removal	70	94	16	78

(1) Tetrachloroguaiacol

(2) Hexachlorobenzene

Removal Pathway	Phenol	Subsurface Aeration		HCB <sup>2</sup>
		CHCl <sub>3</sub>	TCG <sup>1</sup>	
Forced Stripping	0	25	0	1
Natural Vol	0	33	1	7
Total to Atmos.	0	58	1	8
Sorption:				
Effluent Solids	0	0	7	58
Wasted Solids	0	0	0	0
Total Sorption	0	0	7	58
Biodegradation	71	23	0	0
Total Removal	71	81	8	66

(1) Tetrachloroguaiacol

(2) Hexachlorobenzene

TABLE 8. COMPARISON OF PREDICTED VERSUS MEASURED OVERALL REMOVAL PERCENT—ASB

Compound/Aeration	Predicted Avg (%)	NOB	Survey #1	Survey #2	
			Avg (%)	NOB	Avg (%)
Chloroform: Surface	94	7	98 (96-99) <sup>a</sup>	4	84 (82-86)
Tetrachloroguaiacol: Surface	16	10	7 (-169-84)	—	—

(a) Measured Range

(4) In this model, forced stripping via surface aeration can potentially provide greater than 85 percent removal of fifty percent of seventy priority pollutant compounds for which Henry's constants are available. For subsurface aeration the same removal efficiency via stripping can be expected for approximately fifteen percent of these seventy compounds.

(5) Based on the use of this model, between 15 and 30 percent of seventy-four priority pollutants for which octanol-water partition coefficients are available can be expected to be transferred in significant quantities to the solids phase via sorption during biological wastewater treatment.

(6) Organic compounds potentially present in pulp and paper industry effluents may be transferred to different media during treatment. The results of the model simulations suggest that the primary removal pathways are; biodegradation for phenol, forced stripping for chloroform, and a combination of forced stripping and solids sorption for hexachlorobenzene. The fourth compound modeled, tetrachloroguaiacol, was not estimated to be removed in significant quantities by ASB processes but the model estimated a maximum total of thirty-two percent removal by sorption and stripping in activated sludge processes.

(7) Comparison of predicted chloroform removal with measured removals in conventional activated sludge and ASB processes suggests that overall chloroform removal is accurately predicted by the model for these two types of processes under the conditions of comparison used here. The modeled removal mechanism is consistent with laboratory data which showed that a ten-fold increase in activated sludge solids content of 290 to 3100 ppm resulted in no significant biodegradation of chloroform and the loss was primarily due to stripping. Measured tetrachloroguaiacol removal efficiencies extend over a wide range, thus making evaluation of the model's accuracy difficult for this compound. Sludge, and possibly ambient air, measurements of tetrachloroguaiacol are needed in combination with influent and effluent values to examine (a) the cause of variability measured, and (b) the model's accuracy in predicting tetrachloroguaiacol removal.

(8) Although more data is needed to verify and refine the accuracy of this model, the model is recommended as a first-cut screening method for estimating the fate of particular organic compounds in biological treatment systems.

## LITERATURE CITED

- Blackburn, J. W. et al. "Organic Chemical Fate Prediction in Activated Sludge Treatment Processes," EPA-600/2-85/102 (1985).
- Thibodeaux, L. J., D. G. Parker, and H. H. Heck, "Measurement of Volatile Chemical Emissions From Wastewater Basins," EPA-600/2-82-095 (1982).
- Tsivoglou, E. C., et al., "Tracer Measurements of Atmospheric Reaeration — I. Laboratory Studies," *J. Water Pollution Control Federation*, **37**, (10), 1343 (1965).

- Smith, J. H., D. C. Bomberger, and D. L. Haynes, "Prediction of The Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies," *Environ. Sci. of Technol.*, **14**, (11), 1332 (1980).
- Roberts, P. V. and P. G. Dandliker, "Mass Transfer of Volatile Organic Contaminants from Aqueous Solution to the Atmosphere During Surface Aeration," *Environ. Sci. & Technol.*, **17**, (8), 484 (1983).
- Mackay, D. and A. W. Wolkoff, "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere," *Environ. Sci. & Technol.*, **7**, (7), 611 (1973).
- Mackay, D., W. Y. Shiu, and R. P. Sutherland, "Determination of Air-Water Henry's Law Constants for Hydrophobic Pollutants," *Environ. Sci. & Technol.*, **13**, (3), 333 (1979).
- Munz, C. and P. V. Roberts, "The Ratio of Gas-Phase to Liquid-Phase Mass Transfer Coefficients in Gas-Liquid Contacting Process," In: *Gas Transfer at Water Surfaces*, W. Brutsaert and G. H. Jirka (Eds.), D. Reidel Publishing Company, Boston (1984).
- Perry, R. H. and C. H. Chilton, *Chemical Engineers Handbook*, McGraw-Hill, New York (1973).
- Wilke, C. R. and P. Chang, "Correlation of Diffusion Coefficients in Dilute Solutions," *AIChE Journal*, **1**, (2), 264 (1955).
- Reid, R. C. and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York (1958).
- Hayduk, W. and H. Laudie, *AIChE Journal*, **20**, 611 (1974).
- Liss, P. S. and P. G. Slater, "Flux of Gases Across the Air-Sea Interface," *Nature*, **247**, 181 (1974).
- Smith, J. H., D. C. Bomberger, and D. L. Haynes, "Volatilization Rates of Intermediate and Low Volatility Chemicals From Water," *Chemosphere*, **10**, (3), 281 (1981).
- Roberts, P. V., C. Munz, and P. Dandliker, "Modeling Volatile Organic Solute Removal by Surface and Bubble Aeration," *J. Water Pollution Control Federation*, **56**, (2), 157 (1984).
- Matter-Muller, C. W. Gujjer, and W. Giger, "Transfer of Volatile Substances From Water to the Atmosphere," *Water Research*, **15**, 1271 (1981).
- Bowie, et al., "Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling," EPA-600/3-85/040 (1985).
- McKay, D. and A. Yeun, "Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water," *Environ. Sci. & Technol.*, **17**, (4), 211 (1983).
- Wolff, C. J. M. and H. B. van der Heijde, *Chemosphere*, **11**, 103 (1982).
- Mills, W. B. et al., "A Screening Procedure for Toxic and Conventional Pollutants in Surface and Groundwater — Part I," EPA-600/6-85/002a (1985).
- Pellizzari, E. D., "Volatile Organics in Aeration Gases at Municipal Treatment Plants," EPA-600/2-82-056 (1982).
- Voice, T. C. and W. J. Weber, "Sorption of Hydrophobic Compounds by Sediments, Soils and Suspended Solids—1," *Water Research*, **17**, (10), 1433 (1983).
- Matter-Muller, C. et al., "Non-Biological Elimination Mechanisms in a Biological Sewage Treatment Plant," *Progress in Water Technology*, **12**, 299 (1980).
- Chiou, C. T. et al., "Partition Coefficient and Bioaccumulation of Selected Organic Chemicals," *Environ. Sci. & Technol.*, **11**, (5), 475 (1977).
- O'Connor, D. J. and J. P. Connolly, "The Effect of Concentration of Adsorbing Solids on the Partition Coefficient," *Water Research*, **14**, 1517 (1980).
- Voice, T. C., C. P. Rice, and W. J. Weber, "Effect of Solids Concentration on the Sorptive, Partitioning of Hydrophobic

- Pollutants in Aquatic Systems," *Environ. Sci. & Technol.*, 17, (9), 513 (1983).
27. Tabak, H. H. et al., "Biodegradability Studies with Organic Priority Pollutant Compounds," *J. Water Pollution Control Federation*, 53, (10), 1503 (1981).
  28. Anthony, R. M. and L. H. Breinhurst, "Determining Maximum Influent Concentrations of Priority Pollutants for Treatment Plants," *J. Water Pollution Control Federation*, 53, (10), 1457 (1981).
  29. Sayler, G. S. et al., "Predictive Assessment of Priority Pollutant Bio-oxidation Kinetics in Activated Sludge," *Environmental Progress*, 3, (3), 153 (1984).
  30. Petrasek, A. C. et al., "Fate of Toxic Organic Compounds in Wastewater Treatment Plant," *J. Water Pollution Control Federation*, 55, (10), 1286 (1983).
  31. Leuenberger, C., "Persistent Chemicals in Pulp Mill Effluents-Occurrence and Behavior in an Activated Sludge Treatment Plant," *Water Research*, 19, (7), 885 (1985).
  32. Xie, T. M., B. Hulthe, and S. Folestad, "Determination of Partition Coefficients of Chlorinated Phenols, Guaiacols and Catechols by Shake-Flask GC and HPLC," *Chemosphere*, 13, (3), 445 (1984).
  33. Yalkowsky, S. H., S. C. Valvani and D. Mackay, "Estimation of the Aqueous Solubility of Some Aromatic Compounds," *Residue Reviews*, 85, 43 (1983).
  34. Bjorseth, A., G. E. Carlberg and M. Moller, "Determination of Halogenated Organic Compounds and Mutagenicity Testing of Spent Bleach Liquors," *Sci. Total Environ.*, 11, 197 ( ).
  35. "Supplemental Data Reflective of Available Technological Capability For Separation of Chlorinated Organics From Pulp and Paper Industry Wastewaters," NCASI Special Report No. 82-1 (1982).
  36. Hannah, S. A. et al., "Comparative Removal of Toxic Pollutants by Six Wastewater Treatment Processes," *J. Water Pollution Control Federation*, 58, (1), 27 (1986).
  37. Kincannon, D. F. et al., "Removal Mechanisms for Toxic Priority Pollutants," *J. Water Pollution Control Federation*, 55, (2), 157 (1983).
  38. Voss, R. M., "Chlorinated Neutral Organics in Biologically Treated Bleached Kraft Mill Effluents," *Environ. Sci. & Technol.*, 17, (9), 530 (1983).
  39. Claeys, R. R., L. E. LaFleur, and D. L. Borton, "Chlorinated Organics in Bleach Plant Effluents of Pulp and Paper Mills," NCASI Technical Bulletin No. 332 (1980).

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# A Comparison of the UCB Sulfur Recovery Process with Conventional Sulfur Recovery Technology for Treating Recycle Gas From a Crude Oil Residuum Hydrotreater

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*In this paper the University of California, Berkeley, Sulfur Recovery Process (UCBSRP) is compared to conventional technology for the case of the removal of H<sub>2</sub>S from the recycle gas of a high-pressure petroleum residuum hydrotreater. The conventional technology selected for this comparison consists of an absorber/stripper operation using diethanol amine as the absorbent, a Claus sulfur plant, and a SCOTT tail-gas treating unit. Flowsheets, stream flows and conditions, and the total purchased cost of the major items of equipment are presented for both processes. From this comparison it is estimated that the direct fixed capital (DFC) for the UCBSRP would be about 61% of that for the conventional technology. The utility costs for this application of the UCBSRP are estimated to be less than the credit for the high-pressure steam produced whereas the utility costs for the conventional process are substantially more.*

## INTRODUCTION

Hydrogen sulfide occurs as a contaminant in many different industrial gas streams. Examples of such streams include natural gas, refinery gases resulting from petroleum cracking and hydrodesulfurization, and the products of both high- and low-temperature coal gasification. The completeness with which the H<sub>2</sub>S must be removed depends on the use to which the gas stream must subsequently be put. In some cases the treated gas must contain less than 1 ppm H<sub>2</sub>S, in other cases much less stringent treatment is required. In all cases it is desirable to convert the recovered H<sub>2</sub>S to elemental sulfur with minimal escape of any sulfur compounds to the environment. When one considers that this industrial problem has been faced for at least as long as the use of synthetic or natural gas for domestic heating has been common, one is surprised by how many different commercial technologies are currently in use [2]. The purpose of this paper is to describe a new sulfur recovery process that is currently under development at the University of California, Berkeley. The project is being funded by the Coal Gasification Program of the U.S. Department of Energy through the Lawrence Berkeley Laboratory. Patent rights to this process are held by the University.

The UCB Sulfur Recovery Process (UCBSRP) is being developed as an alternative to conventional sulfur recovery technology for removing hydrogen sulfide from gas streams and converting it to elemental sulfur. In the

UCBSRP the hydrogen sulfide is absorbed by a physical solvent and the resulting solution of H<sub>2</sub>S is mixed with a stoichiometrically equivalent amount of sulfur dioxide dissolved in the same solvent. The reaction between the two sulfur compounds forms water, which is miscible with the solvent, and elemental sulfur, which crystallizes from solution when its solubility is exceeded. Part of the sulfur formed in the reaction is burned to make the SO<sub>2</sub> needed in the process, and the heat of combustion is recovered in a waste-heat boiler. The water content of the solvent is maintained at about 3 to 4 wt % by stripping the excess water from the side stream of solvent that is subsequently used to absorb the SO<sub>2</sub>. Sulfur is recovered by cooling the solution, settling the additional crystals that form, and centrifuging the slurry pumped from the bottom of the solvent surge tank.

The process configuration of the UCBSRP will vary with the partial pressure of H<sub>2</sub>S in the gas to be treated, the degree of H<sub>2</sub>S-removal required, with the selectivity for H<sub>2</sub>S desired, and with the nature of the other components in the gas to be treated. One configuration appears to be well suited for the treatment of gas streams in which the partial pressure of H<sub>2</sub>S is greater than 50 lbs/sq. in. absolute (psia) [340 kPa], a second is more advantageous when the H<sub>2</sub>S partial pressure lies between 5 and 50 psia [34 and 340 kPa], and a third would be used when the product of total pressure and inlet mole fraction of H<sub>2</sub>S is less than 5 psia. The first of these process configurations is the subject of this paper. The UCBSRP is normally

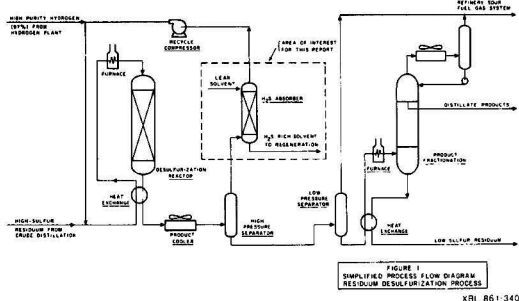


Figure 1. A simplified flow diagram for a crude oil residuum hydrodesulfurization process operating at a nominal pressure of 2000 psia (lbs/in<sup>2</sup> absolute) [14 MPa].

quite selective for H<sub>2</sub>S; COS should be hydrolyzed ahead of the primary absorber to insure its removal from the gas being treated. Small amounts of gases such as CO<sub>2</sub>, hydrocarbons, COS and mercaptans will be co-absorbed with the H<sub>2</sub>S; they are inert and will pass through the process unchanged without causing difficulties. Such gases may be recovered free of H<sub>2</sub>S but would require additional treatment to remove other sulfur compounds (if present). The gas treated in the primary absorber may be dried and its H<sub>2</sub>S content reduced to less than 1 part per million with little added process complexity or increase in operating cost.

### The Design Problem

It is common practice to include a recycle-gas scrubber in hydrotreating processes to remove the H<sub>2</sub>S formed in the process from the recycle loop. Figure 1 shows a simplified flow diagram for a crude oil residuum hydrodesulfurization process operating at a nominal pressure of 2000 psia (lbs/in<sup>2</sup> absolute) [14 MPa]. The absorber is designed for bulk removal of H<sub>2</sub>S. Complete H<sub>2</sub>S removal is not necessary since the gas is recycled to the reactor where H<sub>2</sub>S is generated by the hydrogenation of organic sulfur compounds. The operating rate chosen for this study was the recovery of 100 long tons [100 metric tons] per day of sulfur from 58.5 million standard cubic feet [1.56 standard cubic meters] per day of gas containing 5% H<sub>2</sub>S content is thereby reduced to above 0.5%. If the hydrotreater were to operate without the absorber, H<sub>2</sub>S would build up in the recycle gas to a much higher level. This would require operation at a still higher pressure to maintain the same hydrogen partial pressure in the reactor. It would also be necessary to provide additional hydrotreating catalyst since one effect of a high partial pressure of H<sub>2</sub>S is to suppress catalyst activity.

Conventional processing uses aqueous diethanol amine (DEA) to scrub H<sub>2</sub>S from recycle hydrogen. The absorber is placed in the process downstream of the product cooler and the high-pressure separator. After H<sub>2</sub>S removal, the hydrogen is compressed and recycled to the reactor preheaters. The DEA removes only H<sub>2</sub>S and a small amount of dissolved hydrogen. The solubility of hydrocarbons in the aqueous solution is small and there is relatively little hydrocarbon removal.

In this report the UCBSRP is compared to conventional technology for the case of the removal of H<sub>2</sub>S from the recycle gas of a high-pressure petroleum residuum hydrotreater. This application was chosen because it involves H<sub>2</sub>S removal with no co-absorption of CO<sub>2</sub> and minimal complication from the simultaneous removal of light hydrocarbons. Sulfur recovery is therefore empha-

sized. Table 1 summarizes the design bases.

The UCBSRP solvent absorbs some light hydrocarbons as well as hydrogen from the recycle gas. This will have very little effect on the hydrotreater material balance. The design for the UCBSRP includes facilities to deliver these hydrocarbons free of sulfur compounds to the refinery gas system. Recovered material is assumed to be utilized in facilities elsewhere in the refinery.

In the hydrotreating process some hydrogen sulfides leaves the recycle loop dissolved in the net hydrotreated product. This H<sub>2</sub>S ends up in a gas stream leaving the product separation section of the hydrotreater. No attempt has been made to treat this H<sub>2</sub>S in either case. In conventional processing this gas stream would be treated with aqueous DEA to remove H<sub>2</sub>S. This DEA solution would be regenerated in the same stripper as the DEA used for H<sub>2</sub>S removal from recycle gas. Similarly, the H<sub>2</sub>S (and propane and heavier hydrocarbons) can be recovered in the UCBSRP by feeding this gas stream to an enlarged version of the secondary absorber while using the same solvent regenerating equipment.

### PROCESS DESCRIPTION—UCB SULFUR RECOVERY PROCESS

#### Process Steps

**Primary Absorber:** The process flow diagram for the UCBSRP is shown in Figure 2. The component balances, temperatures and pressures for the numbered streams are given in Table 4. Sour recycle gas from the residuum hydrotreater is contacted with cool, lean solvent at a pres-

TABLE I. DESIGN BASIS FOR THE PROCESS COMPARISON UCB SULFUR RECOVERY PROCESS VS. CONVENTIONAL TECHNOLOGY

<b>Feed</b>		
<b>Residuum Desulfurization</b>		
Recycle Gas		
Pressure, psia (lbs/sq. in. abs.) [MPa]	2,000	[13.8]
Temperature, °C	35	
Rate, lb-mole/hr [kmol/hr]	6,412	[2,911]
Composition, mol%		
Hydrogen	79.35	
Methane	12.96	
Ethane	1.26	
Propane	0.89	
Butanes	0.39	
Pentane and Heavier	0.09	
Hydrogen Sulfide	5.00	
Water	0.05	
<b>Product Specifications</b>		
Treated Gas: H <sub>2</sub> S content, mol% (max.)	0.5	
Sulfur purity: wt% (min.)	99.98	
Waste Water:	Free of H <sub>2</sub> S or SO <sub>2</sub> contamination	
Stack Gas: SO <sub>2</sub> content, ppm (max.)	100	
Flash Gas to Refinery Fuel: H <sub>2</sub> S content, ppm (max.)	100	
<b>Utility Availability and Cost</b>		
Fuel Gas	\$/10 <sup>3</sup> std ft <sup>3</sup>	4.50
Electricity	\$/kW-hr	0.07
Steam: 615 psia [4.2 MPa] sat'd	\$/10 <sup>3</sup> lb	5.25
165 psia [1.14 MPa] sat'd	\$/10 <sup>3</sup> lb	4.50
75 psia [520 kPa] sat'd	\$/10 <sup>3</sup> lb	3.85
Cooling Water, 25°C	\$/10 <sup>3</sup> gal	0.10
Operating Rate:	Hours/year	8,000

Note: 10<sup>3</sup> std ft<sup>3</sup> = 0.027 std m<sup>3</sup>; 10<sup>3</sup> lb = 454 kg; 10<sup>3</sup> gal = 3.8 m<sup>3</sup>

sure of 2000 psia [13.8 MPa] in the primary absorber, T-1. The H<sub>2</sub>S level in the treated gas is reduced to about 0.5%. The heat of solution of the H<sub>2</sub>S raises the temperature of the solvent by about 30°C. The vapor-liquid equilibrium data for designing this column were obtained in this laboratory by S. F. Sciamanna [6].

**Reactor/Crystallizer:** The H<sub>2</sub>S-laden solution from the absorber is cooled and fed to the reactor/crystallizer, K-1, where the H<sub>2</sub>S reacts with SO<sub>2</sub> dissolved in a second liquid stream. The kinetics of this reaction, which is catalyzed by aromatic nitrogen compounds such as N,N-dimethyl aniline, was reported in a paper by Neumann and Lynn [4] and is the subject of further investigation in this laboratory [3]. The heat of reaction raises the temperature of the combined streams about 20°C. K-1 is operated at 130 psia [900 kPa], so flashing of dissolved gases also occurs. The crystallizer is operated as a fluidized bed of sulfur crystals. The crystal-size distribution produced in steady-state operation of the crystallizer is currently under study. Based on the results obtained in batch reactions the average crystal size is expected to exceed 100 micrometers. The two feed streams are introduced near the bottom of the vessel where they mix with the slurry of sulfur crystals near the bottom as reaction occurs.

**Secondary Absorber:** The flow the SO<sub>2</sub> solution entering K-1 is controlled so that a small excess of H<sub>2</sub>S is maintained after reaction is complete, as indicated by the H<sub>2</sub>S content of the vapor leaving K-1. About 1% of the H<sub>2</sub>S is left unreacted. Vapor from the crystallizer flows to secondary absorber T-2 where the residual H<sub>2</sub>S is absorbed by a solution of SO<sub>2</sub>. A study of the reactive absorption of H<sub>2</sub>S by a solution of SO<sub>2</sub> is currently underway. Calculations based on the kinetics data mentioned above indicate that the presence of the SO<sub>2</sub> should effectively enhance the rate of absorption of the H<sub>2</sub>S. Loss of SO<sub>2</sub> by stripping from this solution is prevented by scrubbing the vapor with lean solvent in the top of T-2. The sweet hydrocarbon vapor is then compressed for delivery to the plant fuel system.

Crystal-laden solvent from crystallizer K-1 is cooled to 35°C and flashed to atmospheric pressure in the solvent surge tank and settler, K-2. The vapor, hydrocarbons and residual H<sub>2</sub>S, leaving K-2 is compressed to 130 psia [900 kPa] in compressor C-1 and joins the vapor from K-1. K-2 is sized to permit gravity separation of sulfur crystals from the solvent. A liquid stream from the top of the vessel is fed back to the primary absorber, T-1, without further treatment. The water content of the solvent at this point in the process is 3 to 4 wt % H<sub>2</sub>O.

**Solvent Stripper:** The solvent stripper, T-4, receives feed preheated to 120°C (with some flashing of water and other vapors) from K-2. The column is reboiled with medium-pressure steam to reduce the water content of solvent to about 1 wt %. Residual H<sub>2</sub>S and hydrocarbons are also stripped from the solvent. The top bed of the solvent stripper is refluxed with water to minimize solvent loss to the net overhead stream. Overhead from the solvent stripper is condensed with cooling water. The column operates at atmospheric pressure. The hydrocarbon vapor and H<sub>2</sub>S in the stripper overhead are routed to compressor C-1 and sent to the secondary absorber T-2. Condensed water is stripped of H<sub>2</sub>S and used in the centrifuge and SO<sub>2</sub> scrubber are described later. Net water of reaction is sent to disposal.

The bottoms stream from the solvent stripper is cooled in exchange with incoming wet solvent. This stream becomes the cool, lean solvent used in the secondary absorber and in the SO<sub>2</sub> absorber, T-5. There is no SO<sub>2</sub> in this solvent because the crystallizer, surge tank and solvent stripper are maintained under slightly H<sub>2</sub>S-rich conditions. There is very little H<sub>2</sub>S in the solvent because of the flashing of hydrocarbons and water vapor at the inlet to T-4 and of the steam stripping within T-4.

**Sulfur Separation:** The crystallized sulfur product is removed from the bottom of the solvent settler and surge tank, K-2, as a slurry. It is fed to a pusher-type centrifuge. The centrifuge cake is washed with a rinse water stream and is then reslurried with solvent-free water. The solvent stream, combined with the rinse water is pumped from the centrifuge to solvent stripper. The sulfur-water slurry is heated under pressure above the melting point of sulfur and the two liquids are decanted in separator V-2. Water from this separation returns to the centrifuge. The net molten sulfur product is routed to a sulfur pit. This sulfur is substantially free of dissolved H<sub>2</sub>S since the sulfur crystals were washed with water before being melted.

**SO<sub>2</sub> Absorber:** A gas containing about 21% SO<sub>2</sub> is generated by combustion of part of the molten sulfur with air in a furnace and waste-heat boiler. Cool, lean solvent is

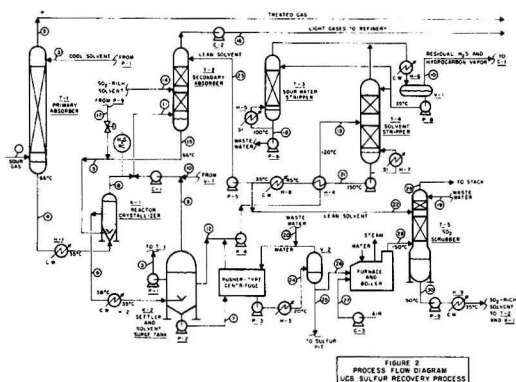
TABLE 2. COST SUMMARY  
UCB SULFUR RECOVERY PROCESS

Equipment Items	Purchased Cost	
Columns: T-1 to T-5		\$156,000
Vessels: K-1, K-2; V-1, V-2		57,500
Exchangers: H-1 to H-9		154,000
Furnace and Boiler:		135,000
Centrifuge:		50,000
Compressors: C-1 to C-3		114,000
Pumps: P-1 to P-9		128,000
Total cost of major equipment (1979)	*	\$795,000
Adjusted cost of major equipment	**	\$1,121,000
Estimated Direct Fixed Capital	***	\$5,605,000
Utilities	Rate of Use	Annual Cost
Electricity	490 kW	\$274,400
Steam Credit	<18,000 lbs/hr> <[8,200 kg/hr]>	<756,000>
Steam Consumption	9,900 lbs/hr [4,500 kg/hr]	357,800
Cooling Water	1,470 gal/min [333 m <sup>3</sup> /hr]	70,600
Total Annual Credit for Utilities		<\$53,200>

\* Based on cost data from Peters and Timmerhaus (1980), which are normalized to January, 1979, when the M & S Equipment Cost Index was 561.

\*\* Adjusted on the basis of the M & S Equipment Cost Index of 791 for October, 1985 (Chemical Engineering, Jan. 20, 1986).

\*\*\* Assumes D.F.C. equal to five times the total cost of items of major equipment.



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Figure 2. The process flow diagram for the UCSRP (University of California, Berkeley, Sulfur Recovery Process).

used to absorb this SO<sub>2</sub> in column T-5. Vapor-liquid equilibrium data obtained here [1] show the solubility of SO<sub>2</sub> in the solvent to be quite high, so the concentration of SO<sub>2</sub> in the gas leaving T-5 can readily be reduced to a few parts per million. A small water stream is fed to the top of the scrubber to minimize loss of solvent vapor. The bottom of the scrubber serves as a tank to provide an inventory of SO<sub>2</sub> solution to facilitate process control. Storage of SO<sub>2</sub> solution permits partial decoupling of the rate at which SO<sub>2</sub> is generated from the rate at which H<sub>2</sub>S is absorbed in T-1. The sulfur furnace can operate under steady conditions that need to be varied only occasionally in response to changes in the inventory of SO<sub>2</sub> solution in the bottom of T-5. The SO<sub>2</sub> solution is fed back to the process at K-1; part of it passes by way of the secondary absorber, T-2, where it enhances the absorption of H<sub>2</sub>S from the hydrocarbon stream leaving the process.

### Capital Costs and Utilities Requirements

Table 2 presents a summary of the equipment costs and the annual utilities requirements for the UCB Sulfur Recovery Process. The cost of each piece of major equipment was estimated from the cost data that are presented in Peters and Timmerhaus (1980). The detailed utilities use is given in Table 5.

### PROCESS DESCRIPTION—CONVENTIONAL TECHNOLOGY

#### Processing Subdivisions

The process flow diagram for the conventional technology chosen for this comparison is shown in Figure 3. Component flows, temperatures and pressures for the numbered streams are given in Table 4. Recycle gas from the residuum hydrotreating unit is contacted with aqueous diethanolamine (DEA) for H<sub>2</sub>S removal. Hydrogen sulfide is separated from DEA in a conventional DEA stripper, then fed to a three-stage Claus sulfur plant. About 96% of the sulfur is recovered as liquid in this plant. The balance leaves the Claus plant in the tail gas stream as H<sub>2</sub>S, SO<sub>2</sub>, the sulfur vapor. Other sulfur compounds may also be present.

Tail gas from the Claus plant is treated by the Shell Claus Off-gas Treatment (SCOT) process. This is a sulfur recovery process licensed from Shell Development Company of Houston, Texas. The process arrangement shown on the flow diagram is taken from open-literature descriptions of the process. Process conditions and flow rates are estimated. The Shell Development Company has not had

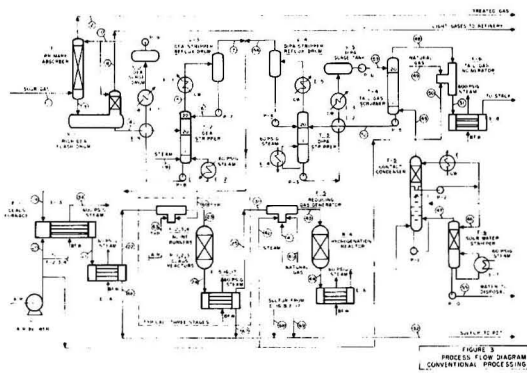


Figure 3. The process flow diagram for comparative conventional technology.

the opportunity to review or comment on these estimates. Any commercial application of this process requires a license from Shell.

**DEA Absorber/Stripper Operation:** DEA from the high pressure absorber, T-1, is flashed at 200 psia [1.4 MPa] for removal of dissolved and entrained hydrogen and hydrocarbons, then stripped at 25 psia [170 kPa] in a reboiled stripper. The lean DEA from the bottom of this stripper is cooled first by exchange with rich DEA, then by water cooling before it is fed back to the absorber. The acid gas is fed to the Claus plant.

**Claus Plant:** One-third of the H<sub>2</sub>S in the acid gas is oxidized to SO<sub>2</sub> with a controlled amount of air in furnace F-1, thereby forming a gas containing two moles of H<sub>2</sub>S per mole of SO<sub>2</sub>. At flame temperature the H<sub>2</sub>S and SO<sub>2</sub> are in chemical equilibrium with sulfur and water vapors. This gas mixture is cooled by generation of steam. Gas from the waste-heat boiler is further cooled to 168°C by generation of low pressure steam as most of the sulfur formed in the reaction furnace is condensed.

Gas from the first sulfur condenser is reheated to about 230°C and fed to a catalytic reactor, R-1, for further conversion to sulfur. The gas reheat is accomplished by the combustion of a small amount of the original acid gas feed in an inline burner, F-2. Products from the first converter are sent to a condenser to separate the sulfur made in the reactor. There follow two more stages, nearly identical to the first, consisting of reheat, reactor and condenser. Of the original H<sub>2</sub>S in the feed, about 56% reacts and is recovered as liquid sulfur in the first condenser E-14. The recovery in the condensers following the catalytic stages is 29%, 8%, and 3%, leaving about 4% in the form of unreacted H<sub>2</sub>S and SO<sub>2</sub> in the tail gas leaving the Claus plant.

**SCOT Process:** All sulfur compounds in the Claus plant tail gas are reduced to hydrogen sulfide in this part of the process. The tail gas is heated to about 345°C by an inline burner F-5. Substoichiometric operation of this burner provides a source of hydrogen and carbon monoxide for the reduction step that follows. The preheated mixture then flows to reactor R-4 and is passed over a hydrogena-

TABLE 3. COST SUMMARY  
CONVENTIONAL SULFUR RECOVERY TECHNOLOGY

Equipment Items		Purchased Cost
Columns: T-1 to T-6		\$241,000
Vessels: V-1 to V-5		78,000
Exchangers: E-1 to E-17		458,000
Furnaces, Boilers and Burners:		206,000
Reactors: R-1 to R-4		87,000
Compressors: C-1		100,000
Pumps: P-1 to P-10		132,000
Total cost of major equipment (1979)	*	\$1,302,000
Adjusted cost of major equipment	**	\$1,836,000
Estimated Direct Fixed Capital	***	\$9,179,000
Utilities	Rate of Use	Annual Cost
Fuel Consumption	29.6 lb-mol CH <sub>4</sub> /hr	\$405,000
Electricity	650 kW	362,700
Steam Credit	<23,300 lbs/hr>	<978,600>
Net Steam Consumption	13,000 lbs/hr	400,600
Cooling Water	1,645 gal/min	79,000
Total Annual Credit for Utilities		\$269,700

\* Based on cost data from Peters and Timmerhaus (1980), which are normalized to January, 1979, when the M & S Equipment Cost Index was 561.

\*\* Adjusted on the basis of the M & S Equipment Cost Index of 791 for October, 1985 (Chemical Engineering, Jan. 20, 1986).

\*\*\* Assumes D.F.C. equal to five times the total cost of items of major equipment. Note: 1000 lbs = 454 kg; 1000 gal = 3.8 m<sup>3</sup>

TABLE 4. STREAM FLOWS AND CONDITIONS FOR UCB SULFUR RECOVERY PROCESS

Stream:	11	12	13	14	15	16	17	18	19	20
H <sub>2</sub> lb-mol/hr	5088	5071	—	17	—	—	—	17	—	—
CH <sub>4</sub> lb-mol/hr	831	817	—	14	—	—	—	14	—	—
C <sub>2</sub> H <sub>6</sub> lb-mol/hr	8	74	1	8	—	5	—	3	2	2
C <sub>3</sub> H <sub>8</sub> lb-mol/hr	57	53	8	12	20	26	3	6	4	14
C <sub>4</sub> H <sub>10</sub> lb-mol/hr	25	23	8	10	23	30	3	3	8	14
C <sub>5</sub> <sup>+</sup> lb-mol/hr	6	6	4	4	7	11	2	—	—	7
H <sub>2</sub> S lb-mol/hr	321	29	1	293	—	2.9	0.4	0.1	0.1	1.8
SO <sub>2</sub> lb-mol/hr	—	—	—	—	145	—	—	—	—	—
H <sub>2</sub> O lb-mol/hr	3	—	261	264	127	681	104	—	—	—
S (dissolved) lb-mol/hr	—	—	12	12	23	73	5	—	—	—
S (solid or liquid) lb-mol/hr	—	—	—	—	—	397	438	—	—	—
Total lb-mol/hr	6412	6073	295	634	345	1225.9	555.4	43.1	14.1	38.8
Solvent Flow										
10 <sup>3</sup> lb/hr (gal/min)	—	—	125 (250)	125 (250)	201 (402)	326 (652)	50 (100)	—	—	—
Pressure (lbs/sq in abs)	2000	2000	2000	140	130	130	30	130	15	15
Temperature (deg C)	35	35	35	66	38	58	35	58	35	35
Stream:	11	12	13	14	15	16	17	18	19	20
H <sub>2</sub> lb-mol/hr	17	—	—	—	—	17	—	—	—	—
CH <sub>4</sub> lb-mol/hr	14	—	—	—	—	14	—	—	—	—
C <sub>2</sub> H <sub>6</sub> lb-mol/hr	7	2	2	—	—	7	—	—	—	—
C <sub>3</sub> H <sub>8</sub> lb-mol/hr	24	11	14	—	20	4	—	—	—	—
C <sub>4</sub> H <sub>10</sub> lb-mol/hr	25	11	14	—	23	2	—	—	—	—
C <sub>5</sub> <sup>+</sup> lb-mol/hr	7	5	7	—	7	—	—	—	—	—
H <sub>2</sub> S lb-mol/hr	2	1.4	1.8	—	—	—	—	—	—	—
SO <sub>2</sub> lb-mol/hr	—	—	—	7	6	—	139	—	—	—
H <sub>2</sub> O lb-mol/hr	—	316	470	6	8	—	119	370	50	50
S (dissolved) lb-mol/hr	—	15	20	1	4	—	19	—	—	—
S (solid or liquid) lb-mol/hr	—	—	—	—	—	—	—	—	—	—
Total lb-mol/hr	96	361.4	528.8	14	68	44	277	370	50	50
Solvent Flow										
10 <sup>3</sup> lb/hr (gal/min)	—	151 (302)	201 (402)	10 (20)	11 (22)	—	190 (380)	—	—	—
Pressure (lbs/sq in abs)	130	15	15	130	130	200	130	15	15	50
Temperature (deg C)	50	35	120	35	66	35	100	100	100	100
Stream:	21	22	23	24	25	26	27	28	29	30
N <sub>2</sub> lb-mol/hr	—	—	—	—	—	—	549	549	549	—
O <sub>2</sub> lb-mol/hr	—	—	—	—	—	—	146	—	—	—
SO <sub>2</sub> lb-mol/hr	—	—	—	—	—	—	—	146	0.001	146
H <sub>2</sub> O lb-mol/hr	100	100	—	1557	—	—	—	—	25	125
S (dissolved) lb-mol/hr	20	20	—	—	—	—	—	—	—	—
S (solid or liquid) lb-mol/hr	—	—	—	438	292	146	—	—	—	—
Total lb-mol/hr	120	120	—	1995	292	146	695	695	574	271
Solvent Flow										
10 <sup>3</sup> lb/hr (gal/min)	201 (402)	200 (400)	1 (2)	—	—	—	—	—	—	200 (400)
Pressure (lbs/sq in abs)	30	25	130	50	15	15	16	15.5	15	15
Temperature (deg C)	150	35	120	120	120	120	30	150	30	50

Note: 1000 lbs = 454 kg; 1 psia = 6.89 kPa; 1000 gal/min = 227 m<sup>3</sup>/hr

tion catalyst, typically a cobalt-molybdenum catalyst, where H<sub>2</sub> and CO reduce all sulfur compounds to H<sub>2</sub>S. The process is operated to maintain a hydrogen content of about 1% in the reactor effluent. Reactor effluent is first cooled by generation of low pressure steam in boiler E-6, is cooled further in a desuperheater that works by adia-

batic saturation of the gas, and is finally cooled to 50°C in a direct-contact condenser, T-5. The desuperheater provides a guard against misoperation that could leave residual SO<sub>2</sub> in the effluent gas from the reducing reactor, R-4. Any SO<sub>2</sub> present at this point will be absorbed in the circulating liquid, dramatically lowering the pH. A caustic



injection system is provided to neutralize the solution to a pH such that it absorbs substantially all of the SO<sub>2</sub> while passing most of the H<sub>2</sub>S. Water condensed in the contact condenser is routed to the H<sub>2</sub>S stripper, T-6, then cooled and sent to disposal. Overhead from the H<sub>2</sub>S stripper is returned to the desuperheater.

The H<sub>2</sub>S-containing gas from the contact condenser is scrubbed with an aqueous amine solution in column T-4. Either methyl-diethanol amine or di-isopropanol amine (DIPA) is used because of their selective absorption of H<sub>2</sub>S in the presence of CO<sub>2</sub>. A selective amine is required because the acid gas that is stripped subsequently from the amine solution is recycled to the front end of the Claus plant where H<sub>2</sub>S is recovered as sulfur. If the amine solution used in the SCOT process were not highly selective for H<sub>2</sub>S there would be a huge recycle stream of CO<sub>2</sub> as well, making the process impracticable. The selective amine permits H<sub>2</sub>S recycle with minimal buildup of CO<sub>2</sub>.

Tail gas from the H<sub>2</sub>S absorber is oxidized in incinerator F-6 to ensure that any sulfur compounds released from the process to the atmosphere have been converted to SO<sub>2</sub> and to recover the heating value of the residual hydrogen when the tail gas is cooled in boiler E-8.

### Capital Costs and Utilities Requirements

Table 3 presents a summary of the equipment costs and annual utilities requirements for recovering sulfur from the gas stream in question by this combination of conventional technologies. As before, the cost of each piece of major equipment was estimated from the cost data of Peters and Timmerhaus [5]. The detailed utilities consumption is given in Table 7.

## PROCESS COMPARISONS AND CONCLUSIONS

### Cost Comparisons

Tables 3 and 5 summarize the capital and utilities costs for the UCB Sulfur Recovery Process and for conventional sulfur recovery technology. The estimated total purchased equipment price for the UCBSRP is \$795,000 as of January 1979, when the M & S Equipment Cost Index [7] was 561. The value of this index at the end of the third quarter of 1985 was 791, making the current estimated purchase price of the equipment \$1,121,000. If one assumes a ratio of 5.0 between direct fixed capital (D.F.C) and the purchase price of the major equipment, the corresponding value of D.F.C. is \$5,605,000. The estimated total purchased equipment price for the conventional technology is \$1,302,000 as of 1979, which corresponds to \$1,836,000 in October, 1985, and an estimated D.F.C. of \$9,179,000. The cost of utilities for the UCBSRP is exceeded slightly by the credit for the high pressure steam produced, giving a net annual utility credit of \$53,000. The net cost of utilities for the conventional technology is about \$270,000 per year. The accuracy of absolute values of the capital estimates is probably no better than 30%. However, the accuracy of the value of the ratio of the two estimates should be considerably better since the processes are similar and the same estimating techniques were used for both. The D.F.C. for the UCBSRP is about 61% of that for conventional technology. The utilities cost figures depend, of course, on the unit costs assumed for electricity, steam and cooling water. The relative advantage shown for the UCBSRP would persist, however, for any reasonable set of unit costs because it is a net exporter of energy in the form of high pressure steam. The reasons for the cost advantages shown by the UCBSRP are discussed below.

### Equipment Requirements

**Process Similarities:** Equipment requirements for the UCBSRP are less than for conventional processing, primarily because the UCBSRP has fewer processing steps. The following pieces of equipment for the UCBSRP have the same or very similar counterparts in conventional processing:

- The H<sub>2</sub>S absorber is functionally the same for both processes, with nearly the same liquid flows and hence nearly the same pumping requirements. The H<sub>2</sub>S absorbers and absorbant feed pumps are major cost items for both processes.

- The sulfur furnace and boiler in the UCBSRP are similar in size and duty to the Claus furnace and boiler in the conventional process. The UCBSRP uses sulfur as a fuel, but there are no hydrocarbons present and control of the air flow can be less precise since the combustion mixture is maintained sulfur-rich to prevent SO<sub>3</sub> formation.

- The SO<sub>2</sub> absorber of the UCBSRP treats a flow of gas similar to the gas stream treated in the DIPA absorber in the SCOT process.

- The sour water strippers in the two processes are also similar in size and duty.

**Process Differences:** The major equipment differences between the two processes are:

- The UCBSRP has a crystallization and centrifuge operation that requires operation of liquid-solid handling equipment. However, this feature makes the production of sulfur crystals feasible and eliminates the presence of H<sub>2</sub>S and most other impurities in the sulfur product. In conventional processing sulfur is condensed as a liquid from a gas that contains H<sub>2</sub>S and other potentially soluble contaminants. The presence of H<sub>2</sub>S dissolved in liquid sulfur can be hazardous.

- Both processes require the same amount of air for H<sub>2</sub>S combustion. However, the SCOT process requires about 44% additional air for fuel oxidation. All of the air for the conventional process must be supplied at a pres-

TABLE 5. UTILITIES USE AND COSTS  
UCB SULFUR RECOVERY PROCESS

<b>Electric Power</b>		
Flash Gas Compressor, C-1	60	kW
Light Gas Compressor, C-2	9	
Air Blower, C-3	58	
Lean Solvent Pump, P-1	310	
Solvent Forwarding Pumps; P-4, P-7, P-9	48	
Small Pumps; P-2, P-3, P-5, P-6, P-8	5	
Total	490	kW
Annual* Cost @ \$0.07/kW-hr	\$274,400	kW
<b>Steam Produced, 615 psia</b>		
Waste heat boiler	<18,000>	lb/hr
Annual* Credit @ \$.25/10 <sup>3</sup> lb	<\$756,000>	
<b>Steam Consumed, 165 psia</b>		
Sulfur Melter, H-3	1100	lb/hr
Solvent Stripper Reboiler, H-7	8700	
Sour Water Stripper Reboiler, H-5	140	
Total steam consumed	9940	lb/hr
Annual* Cost @ \$4.50/10 <sup>3</sup> lb	\$357,800	
<b>Cooling Water</b>		
Solvent Coolers; H-1, H-2, H-8, H-9	1125	gal/min
Solvent Stripper Condenser, H-6	345	
Total cooling water usage	1470	gal/min
Annual* Cost @ \$0.10/10 <sup>3</sup> gal	\$70,600	
Total Net Annual* Credit for Utilities	<\$53,200>	

\* Annual costs based on an operating rate of 8,000 hrs/yr.

Note: 1000 lbs = 454 kg; 1 psia = 6.89 kPa; 1000 gal/min = 227 m<sup>3</sup>/hr

TABLE 6. STREAM FLOWS AND CONDITIONS FOR CONVENTIONAL PROCESSING

Stream:		DEA Absorber/Stripper									
		1	2	3	4	5	6	7	8	9	10
H <sub>2</sub>	lb-mol/hr	5088	5081	7	—	—	—	—	7	—	—
CH <sub>4</sub>	lb-mol/hr	831	831	—	—	—	—	—	—	—	—
C <sub>2</sub> H <sub>6</sub>	lb-mol/hr	81	81	—	—	—	—	—	—	—	—
C <sub>3</sub> H <sub>8</sub>	lb-mol/hr	57	56	1	—	—	—	—	1	—	—
C <sub>4</sub> H <sub>10</sub>	lb-mol/hr	25	24	1	—	—	—	—	1	—	—
C <sub>5</sub> <sup>+</sup>	lb-mol/hr	6	6	—	—	—	—	—	—	—	—
H <sub>2</sub> S	lb-mol/hr	321	29	295	295	292	—	292	—	—	3
H <sub>2</sub> O (vapor)	lb-mol/hr	3	3	—	—	254	233	21	—	21	—
Total	lb-mol/hr	6412	6111	304	295	546	233	313	9	21	3
Flow of 25% DEA											
10 <sup>3</sup> lb/hr		—	—	150	150	—	—	—	—	—	150
(gal/min)		—	—	(300)	(300)	—	—	—	—	—	(300)
Pressure		2000	2000	2000	200	30	30	25	200	35	2000
(lbs/sq in abs)											
Temperature		35	35	54	54	96	50	50	54	143	35
(deg C)											
Stream:		Claus Plant									
		19	20	21	22	23	24	25	26	27	28
N <sub>2</sub>	lb-mol/hr	—	509.4	509.4	509.4	529.7	529.7	529.7	550.0	550.0	550.0
O <sub>2</sub>	lb-mol/hr	—	135.4	—	—	—	—	—	—	—	—
H <sub>2</sub> S	lb-mol/hr	292.4	—	85.2	85.2	85.2	27.2	27.2	27.2	11.2	11.2
SO <sub>2</sub>	lb-mol/hr	—	—	31.8	31.8	35.4	6.4	6.4	10.0	2.0	2.0
H <sub>2</sub> O	lb-mol/hr	20.9	11.4	238.9	238.9	243.2	301.2	301.2	305.5	321.5	321.5
S (vapor or liquid)*	lb-mol/hr	—	—	175.4	3.1	3.1	90.1	3.1	3.1	27.1	3.2
Total	lb-mol/hr	313.3	656.2	1040.7	868.4	896.6	954.6	867.6	897.0	911.8	887.9
Temperature		50	25	315	168	228	325	168	226	255	168
(deg C)											
Stream		Clause Plant									
		29	30	31	32	33	34	35			
N <sub>2</sub>	lb-mol/hr	570.3	570.3	570.3	—	—	—	—			
O <sub>2</sub>	lb-mol/hr	—	—	—	—	—	—	—			
H <sub>2</sub> S	lb-mol/hr	11.2	5.2	5.2	—	—	—	—			
SO <sub>2</sub>	lb-mol/hr	5.6	2.6	2.6	—	—	—	—			
H <sub>2</sub> O	lb-mol/hr	325.8	331.8	332.6	—	1445	1045	400			
S (vapor or liquid)*	lb-mol/hr	3.6	12.6	3.5	292	—	—	—			
Total	lb-mol/hr	916.5	922.5	914.5	292	1445	1045	400			
Temperature		228	239	168	168	104	254	156			
(deg C)											
Stream:		SCOT Process									
		40	41	42	43	44	45	46	47		
H <sub>2</sub>	lb-mol/hr	—	—	—	24.2	19.2	19.2	—	—		
CH <sub>4</sub>	lb-mol/hr	17.6	—	—	—	—	—	—	—		
CO	lb-mol/hr	—	—	—	6.6	—	—	—	—		
CO <sub>2</sub>	lb-mol/hr	—	—	—	11.0	17.6	17.6	—	—		
N <sub>2</sub>	lb-mol/hr	—	—	74.5	644.8	644.8	644.8	—	—		
O <sub>2</sub>	lb-mol/hr	—	—	19.8	—	—	—	—	—		
H <sub>2</sub> S	lb-mol/hr	—	—	—	5.2	11.6	11.6	0.2	0.2		
SO <sub>2</sub>	lb-mol/hr	—	—	—	2.6	—	—	—	—		
H <sub>2</sub> O	lb-mol/hr	—	17.6	1.6	362.8	361.4	86.2	283.2	8.0		
S (vapor or liquid)	lb-mol/hr	—	—	—	3.8	—	—	—	—		
Total	lb-mol/hr	17.6	17.6	95.9	1061.0	1054.6	779.4	283.4	8.2		
Temperature		25	156	25	335	369	50	63	103		
(deg C)											

Table 6 continued

Stream:		SCOT Process									
		48	49	50	51	52	53	54	55		
H <sub>2</sub>	lb-mol/hr	19.2	—	—	—	—	—	—	—		
CH <sub>4</sub>	lb-mol/hr	—	12.0	—	—	—	—	—	—		
CO <sub>2</sub>	lb-mol/hr	17.6	—	—	29.6	—	—	—	—		
N <sub>2</sub>	lb-mol/hr	644.8	—	144.4	789.2	—	—	—	—		
O <sub>2</sub>	lb-mol/hr	—	—	38.4	4.8	—	—	—	—		
H <sub>2</sub> S	lb-mol/hr	—	—	—	—	11.6	—	—	11.6	—	
H <sub>2</sub> O	lb-mol/hr	3.2	—	3.2	49.6	—	—	—	0.8	275.0	
Total	lb-mol/hr	684.8	12.0	186.0	955.4	11.6	—	—	12.4	275.2	
Flow of 30% DIPA											
10 <sup>3</sup> lb/hr		—	—	—	—	62.1	62.1	—	—		
(gal/min)		—	—	—	—	(124.2)	(124.2)	—	—		
Temperature		50	25	25	538	50	50	50	50	104	
(deg C)											
Stream:		SCOT Process									
		60	61	62	63	64	65	66	67	68	69
N <sub>2</sub>	lb-mol/hr	—	—	—	20.3	20.3	20.3	—	—	—	—
O <sub>2</sub>	lb-mol/hr	—	—	—	5.4	5.4	5.4	—	—	—	—
H <sub>2</sub> S	lb-mol/hr	3.6	3.6	3.6	—	—	—	—	—	—	—
SO <sub>2</sub>	lb-mol/hr	—	—	—	—	—	—	—	—	—	—
H <sub>2</sub> O	lb-mol/hr	0.3	0.3	0.3	0.4	0.4	0.4	—	—	—	—
S (vapor or liquid)*		—	—	—	—	—	—	172	87	23.9	9.1
Total	lb-mol/hr	3.9	3.9	3.9	26.1	26.1	26.1	172	87	24	9
Temperature		50	50	50	25	25	25	168	168	168	168
(deg C)											

\* Sulfur molecules vary from S<sub>2</sub> to S<sub>8</sub>. Flows are given as equivalent S<sub>2</sub>.  
 Note: 1000 lbs = 454 kg; 1 psia = 6.89 kPa; 1000 gal/min = 227 m<sup>3</sup>/hr

sure substantially above that for the UCBSRP so that capital and operating costs for the air compressor are correspondingly greater.

- The solvent stripper for the UCBSRP is smaller than the DEA stripper in conventional processing. The H<sub>2</sub>S leaving the DEA stripper is accompanied by much more water vapor than the total amount of water that must be stripped from the solvent in the UCBSRP, so the steam requirement for the DEA stripper is about 66% greater. The UCBSRP solvent stripper is operated at near-atmospheric pressure, whereas the DEA stripper is at 25 psia [170 kPa], so the diameters are about the same. The height shown for the DEA stripper is almost twice that of the solvent stripper, reflecting the greater fractionation requirement for stripping H<sub>2</sub>S from a chemical solvent such as DEA.

- Conventional processing involves four different catalytic beds, all of which are subject to deactivation. The UCBSRP utilizes a catalyst that is part of the homogeneous liquid phase. No loss or deactivation of catalyst in the UCBSRP has been detected yet.

- Conventional processing drains liquid sulfur from four different condensers, whereas the UCBSRP has a single source of molten sulfur. As an additional option, the net sulfur product from the UCBSRP can be recovered as a coarse crystalline powder rather than as a liquid.

- Conventional processing has seven different heat exchangers that recover heat from hot gas streams, compared to a single such heat exchanger in the UCBSRP. The low heat-transfer coefficient typical of gas coolers requires considerable heat transfer area, which is reflected in the high costs for heat exchangers for this technology.

- Conventional processing has six different fired burners compared to a single flame in the UCBSRP.

- Conventional processing has a desuperheater, a direct-contact condenser, a second amine stripper, and an

H<sub>2</sub>S stripper that have no counterparts in the UCBSRP.

- The design basis chosen for this comparison requires removal of only 90% of the H<sub>2</sub>S from the gas passing through the primary absorber. To meet a much more stringent H<sub>2</sub>S specification, the UCBSRP would require a larger reactor-crystallizer, K-1, and a somewhat larger flow of solvent to the primary absorber, but no significant increase in steam consumption by the solvent stripper. To meet the same specification both the same of the DEA stripper for the conventional process and its steam consumption would need to be increased substantially.

- The design basis chosen for this comparison also calls for treating a gas containing 5% H<sub>2</sub>S at 2000 psi, which corresponds to a rather high partial pressure of H<sub>2</sub>S. If either the mole fraction of H<sub>2</sub>S or the total pressure were reduced while keeping the quantity of recovered sulfur constant, so that the volumetric gas flow in the primary absorber increased in inverse proportion to the partial pressure of the H<sub>2</sub>S, both processes would require some modification. In both processes the diameter of the primary absorber would increase. In the UCBSRP the liquid flow in the primary absorber would increase since this flow depends on the physical solubility of the H<sub>2</sub>S. The volumes of vessels K-1 and K-2 would also increase with the increased liquid flow. For the conventional technology the flow of DEA to the primary absorber would be nearly unchanged since it is a chemical solvent. However, the size and steam flow in the DEA stripper would need to increase in order to achieve the same H<sub>2</sub>S specification in the treated gas.

#### Utilities Requirements

The liquid flows to the H<sub>2</sub>S absorbers in the two processes are quite comparable and the electric power re-

TABLE 7. UTILITIES USE AND COSTS  
CONVENTIONAL SULFUR RECOVERY PROCESS

<b>Electric Power</b>		
Forwarding Pumps, P-5 to P-8, P-10	11.5	kW
Lean DEA Pump, P-9	372.0	
Air Blower, C-1	239.0	
Forwarding Pumps; P-1 to P-4	27.0	
Total electric power	649.5	kW
Annual* Cost @ \$0.07/kW-hr	\$363,700	per year
<b>Fuel Consumption (equivalent methane)</b>		
Reducing Gas Generator, F-5	17.6	lb mol/hr
Tail-Gas Incinerator, F-6	12.0	
Total fuel consumed	29.6	lb mol/hr
	(270,000 std cu ft/day)	
Annual* Cost @ \$4.50/10 <sup>3</sup> std ft <sup>3</sup>	\$405,000	
<b>Steam produced, 615 psia</b>		
Claus Furnace, E-13	<18,800>	lb/hr
Tail-Gas Boiler	<4,500>	
Total steam produced	<23,300>	lb/hr
Annual* Credit @ \$5.25/10 <sup>3</sup> lbs	<\$978,600>	
<b>Net Steam Consumed, 75 psia</b>		
DEA Reboiler, E-12	14,500	lb/hr
DEA Sparger, Stream 9	390	
Sulfur Condensers, E-15, 16, 17	<7,200>	
Low-Pressure Steam Generator, E-6	<2,900>	
DIPA Reboiler, E-4	7,400	
Sour Water Stripper Reboiler, E-7	500	
Reducing Gas Generator, Stream 41	320	
Net steam consumed	13,010	lb/hr
Annual* Cost @ \$3.85/10 <sup>3</sup> lbs	\$400,600	
<b>Cooling water</b>		
Condensers, E-5, E-11	340	gal/min
Amine Coolers, E-3, E-10	635	
Contact Condenser Cooler, E-1	670	
Total cooling water usage	1,645	gal/min
Annual* Cost @ \$0.10/10 <sup>3</sup> gal	\$79,000	
Net Annual* Utilities Cost	\$269,700	

\* Annual costs based on an operating rate of 8,000 hrs/yr.

Note: 1000 lbs = 454 kg; 1 psia = 6.89 kPa; 1000 gal/min = 227 m<sup>3</sup>/hr

quired by the two feed pumps is thus about the same. Because of the high pressure of the gas being treated this power exceeds 300 kW. The air blower for the conventional process requires substantially more power than that for the UCBSRP because, as noted above, additional air is needed for the SCOT process and all of the air must be supplied at a relatively high pressure. The high-pressure steam produced by burning sulfur in the waste-heat boiler in the UCBSRP is about the same as that from burning H<sub>2</sub>S in the Claus boiler. A small amount of additional steam is produced by the tail-gas boiler in the SCOT process. However, this additional steam is accompanied by a fuel cost that offsets about 40% of the high-pressure steam credit. No fuel is required by the UCBSRP. Low-pressure steam consumption and cooling-water usage do not differ greatly in the processes.

#### Development Status

The design of the UCB Sulfur Recovery Process is primarily based on experimental data obtained in this

laboratory (Demyanovich, 1984; Neumann, 1986; and Sciamanna, 1986), which are highly reproducible. The specification of carbon steel as a suitable material of construction is based on preliminary results from an ongoing corrosion study. A computer simulation of the whole process (Neumann, 1986) allows the expeditious consideration of design variations. The process configuration presented here is considered best for treating gases having a partial pressure of H<sub>2</sub>S exceeding 50 psia [340 kPa]. As noted in the Introduction, other configurations would be preferred for streams less concentrated in H<sub>2</sub>S and will be the subject of later reports. In general, the flow of solvent in the primary absorber increases inversely with the pressure of the gas being treated and is insensitive to the concentration of H<sub>2</sub>S in the gas. On the other hand, the sizes of the sulfur-handling facilities, the solvent stripper, the SO<sub>2</sub> absorber and the use of utilities are set almost entirely by the quantity of sulfur being recovered.

The designs of the crystallizer and of the secondary absorber are more speculative than those of the rest of the equipment because the experimental studies of these operations have just started. The uncertainties to be resolved by this research are the height required for the secondary absorber and the volume required for the crystallizer/reactor. Since these pieces of equipment do not represent a large fraction of the total equipment cost, the uncertainty in these costs is much smaller than the differential between the costs for the UCBSRP and those for conventional technology.

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#### LITERATURE CITED

1. Demyanovich, Robert J., Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley, February, 1984.
2. Kohl, Arthur, and Fred Riesenfeld, "Gas Purification," 3rd ED., Gulf Publ. Co., Houston, TX, 1979.
3. Neumann, Dan W., Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley, June, 1986.
4. Neumann, Dan W. and Scott Lynn, "The Kinetics of the Reaction of Hydrogen Sulfide and Sulfur Dioxide in Organic Solvents," *I&EC Process Design and Development*, 1986, 25, 248.
5. Peters, Max S., and Klaus D. Timmerhaus, "Plant Design and Economics for Chemical Engineers," 3rd Edition, McGraw-Hill, New York, 1980.
6. Sciamanna, Steven F., Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley, Spring, 1986.
7. "Economic Indicators," *Chemical Engineering* magazine, 86, No. 2, p. 7 (January 15, 1979).



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# Wet Gas Scrubbing: State of the Art in FCCU Emission Control

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*Particulates and SO<sub>2</sub> in Fluid Catalytic Cracking Unit (FCCU) flue gas can be controlled via wet gas scrubbing. Wet Gas Scrubbers (WGS) are compatible with the gaseous emission control devices such as CO boilers or High Temperature Regeneration (HTR) now in use on FCCU's and require no changes in FCCU operating procedures. Compared with a combination of particulate control with electrostatic precipitators and SO<sub>2</sub> control by FCCU feed desulfurization, WGS require less investment and have lower operating costs. Other advantages for WGS include higher service factor, smaller onsite plot space requirement, and simpler operation than electrostatic precipitators.*

*Purged scrubber liquid must be treated by conventional waste water treatment technology to reduce suspended solids and COD. Even after such treatment, the purge stream will still contain dissolved solids. However, at many locations, the disposal of the purge stream can be accommodated without adverse environmental problems.*

*Four commercial scrubbers, now in operation in Exxon Company, U.S.A. refineries, reduce particulate emissions to compliance levels with all pertinent regulations. SO<sub>2</sub> removals are in excess of 90%.*

*Currently, four licensee companies are also applying the Exxon scrubbing process. More are anticipated. These commercial units have accumulated over 64 years of combined operations (as of February 1, 1987).*

## INTRODUCTION

Within a modern refining complex, one of the major sources of potential atmospheric emissions is the Fluidized Catalytic Cracking Unit (FCCU). Potential emissions from an FCCU regenerator are of two general classifications, particulate and gaseous.

The dry particulate emissions pertain to the fine catalyst particles which have passed through the FCCU's cyclone system. The emitted catalyst is fine, in most cases, the majority of this material is in the sub-micron range. In the absence of moisture or sulfuric acid condensation, the normal cause of FCCU stack plume opacity is the presence of fine catalyst particles. Stack opacity is roughly proportional to exit catalyst loading, but is affected by other factors such as particle size distribution and stack diameter. As early as 1974, a New Source Performance Standard (NSPS) had been promulgated, regulating the amount of particulate which could be emitted from an FCCU.

With respect to the gaseous pollutants the two compounds requiring control are carbon monoxide (CO) and sulfur dioxide (SO<sub>2</sub>). The use of a CO boiler or HTR (High Temperature Regeneration) technology can effectively meet the CO regulations along with controlling other pollutants such as hydrocarbons and ammonia. A NSPS for CO emission was also promulgated in 1974. At the present time, however, the majority of SO<sub>2</sub> regulations are based on ground level concentration. Currently, the EPA is in the process of promulgating an NSPS which will regulate FCCU sulfur oxides emissions.

Concurrent with the passage of the initial Clean Air Act, Exxon began development work on a process to control atmospheric emissions of particulate and SO<sub>2</sub> from the FCCU. The resulting Wet Gas Scrubbing (WGS) process is a simple, effective and economic method of meeting current and proposed environmental regulations. Since startup of the first of these units in 1974, in excess of 64 years (as of February 1, 1987) of combined operations have been gained from eight operating units.

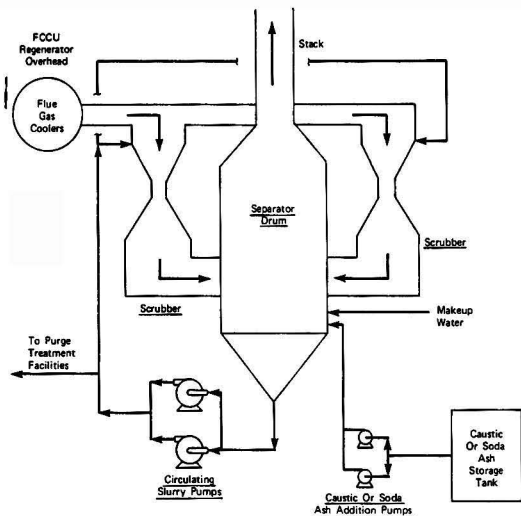


Figure 1. Schematic of scrubbing system.

### OPERATION

Figure 1 is a WGS flow plan. Tests have shown that the scrubbers can work equally well either upstream or downstream of a CO or waste heat boiler when the FCCU is combusting all of the carbon monoxide within the unit. However, if it is upstream of a CO boiler (i.e., FCCU flue gas contains greater than  $500 \text{ cm}^3/\text{m}^3$  (vppm) CO), the cooled saturated gas leaving the scrubber must be reheated to the high temperatures required for CO combustion. Primarily for this reason, and also to save on quench and ducting materials cost, it is recommended that the WGS be placed downstream of a CO or waste heat boiler.

The WGS removes particulate by washing it from the flue gas stream with droplets of a buffered scrubber liquid while  $\text{SO}_2$  is removed by reaction with the buffered solution. Thus, the WGS is designed to accomplish the following five functions:

- introduction of the flue gas and the scrubber liquid into the unit,
- intimate mixing of the flue gas and scrubber liquid to achieve particulate and  $\text{SO}_2$  removal,
- separation of the scrubber liquid from the clean flue gas,
- emission of the clean flue gas, and
- disposal of the liquid purge stream in an environmentally acceptable manner.

Depending on the configuration of the FCCU, whether it is a "grassroots" or retrofit application, and the local refinery circumstances, several options exist for carrying out these functions.

### FLUE GAS AND SCRUBBER LIQUID

Transporting the flue gas through the scrubber and mixing it with the scrubber liquid requires energy, which can be supplied as flue gas pressure drop. If the flue gas is available at the WGS inlet at approximately  $10.34 \text{ kPa}$  (1.5 psig), as would be the case in an FCCU operated under "full burn" conditions, then a high energy venturi scrubber can be used. Commercial experience has also shown that even if an energy recovery system (expander) has been installed in the FCCU flue gas circuit, a high energy venturi system can still be used due to its low back pressure requirement. A schematic of the high energy venturi is shown in Figure 2. In a high energy venturi scrubber, the pressure drop of the flue gas passing through the

throat of the venturi is used to atomize scrubber liquid, which is fed above the venturi throat at low pressures,  $6.89$  to  $34.47 \text{ kPa}$ , (1-5 psig) and low flow rates  $6.68 \times 10^{-4}$  to  $2.67 \times 10^{-3} \text{ m}^3/\text{m}^3$  (5-20 gal/kCF).

If the WGS is downstream of a CO boiler, where flue gas pressure is insufficient to use a high energy venturi, a jet ejector venturi can be used. The jet ejector venturi is shown schematically in Figure 3. Here, the scrubber liquid is atomized by pumping it through a spray nozzle. The draft induced by the high pressure,  $413.6$  to  $827.3 \text{ kPa}$  (60-120 psig), and high flow rate,  $6.68 \times 10^{-3}$  to  $1.34 \times 10^{-2} \text{ m}^3/\text{m}^3$  (50-100 gal/kCF), of the scrubber liquid moves the flue gas into and through the scrubber.

Because the high energy and the jet-ejector venturi systems have no moving parts in the flue gas stream, they are superior to conventional venturi scrubbers which use fans and must operate either in the hot, dusty environment upstream of the scrubber, or the cold, wet environment downstream of the scrubber. Both types of WGS systems have been successfully applied commercially.

### PARTICULATE AND $\text{SO}_2$ REMOVAL

With either the jet ejector or high energy venturi, particulate and  $\text{SO}_2$  removal takes place in the turbulent section of the venturi. Particulate scrubbing occurs by iner-

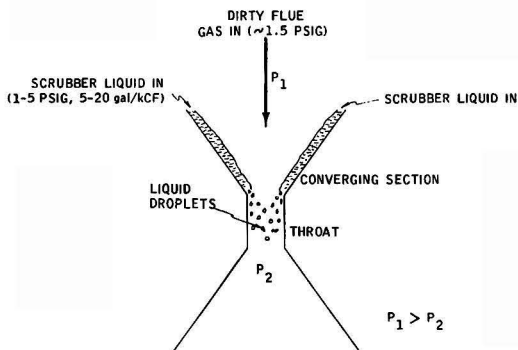


Figure 2. Liquid and gas introduction high energy venturi scrubbers.

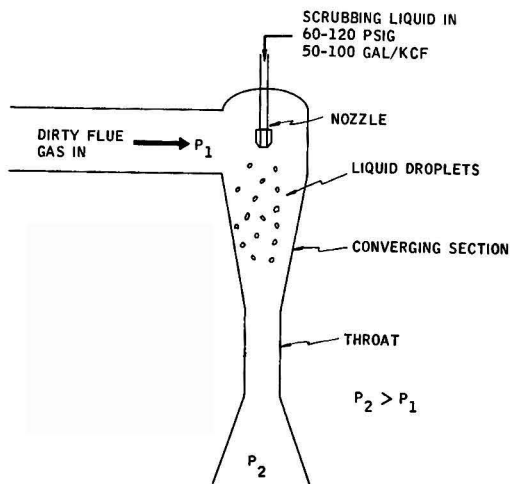


Figure 3. Liquid and gas introduction jet ejector venturi scrubbers.

tial impaction of the liquid droplets with the particles in the gas stream due to relative velocity differences. To restate this in simplified terms, particulate removal occurs in the same way a bullet strikes a target. In the high energy venturi, the bullets are the particles and the liquid droplets are the targets; while in the jet-ejector venturi the reverse is true. Operational factors which affect the degree of particulate removal include the throat velocity of the scrubber, the liquid-to-gas ratio, the inlet particle size distribution and the inlet loading of the particles.

Concurrent with the particulate removal, sulfur oxide removal also takes place. The high surface area presented by the liquid droplets and the intimate gas/liquid contacting provide ample opportunity for the reaction between the buffered scrubber liquid and the sulfur oxides to take place. Operating parameters which affect sulfur oxide removal include the inlet concentration of the sulfur oxides, the pH of the scrubbing liquid, the liquid-to-gas ratio of the scrubber, and the throat velocity of the gas.

Caustic or soda ash is added to the separated liquid to adjust its pH to the desired level and the vast majority is circulated back to the venturi's. However a small purge stream is removed to maintain an equilibrium level of suspended solids and dissolved salts.

#### SEPARATION OF THE SCRUBBER LIQUID FROM THE CLEAN FLUE GAS

Once the pollutants have been transferred from the flue gas to the liquid, the two phases must be separated in a disengaging drum or separator vessel and the cleaned gas emitted to the atmosphere. Separation of the liquid from the gas involves three steps, the first of which is the coalescence of the liquid droplets. Coalescence is the result of relative velocity differences between the various size droplets as the gas is decelerated from the scrubber throat. As a result of this phenomena, droplet growth occurs and few fine droplets enter the separator vessel. The absence of fine droplets permits the separation of the two phases by inertial forces and demisting devices.

Inertial forces, which are the result of a tangential entry design, begin to separate the two phases. However, this step produces only *minimal* separation since the inlet velocities are kept low to minimize erosion in this portion of the scrubbing system. A demisting device provides the final separation of the gas and liquid. The demisting device used is selected for its high efficiency, low plugging tendency, and low pressure drop.

#### CLEAN GAS EMISSION

The separated, clean gas is emitted to the atmosphere through a stack mounted atop the separator vessel. Since the gas is saturated with water, reheat can be added to reduce the length and frequency of the visible steam plume. The length and frequency of the visible steam plume can be estimated from data on WGS operation and local meteorological conditions. While reheat facilities were included in all of the initially installed WGS units, it is only periodically used at one northern location. Only one recent unit opted to install reheat facilities, but it has not operated these facilities since operation has shown that they are not required.

#### PURGE LIQUID RECEIVES TREATMENT

Removing pollutants from the air just to transform them into water pollutants provides little benefit from an environmental viewpoint. Therefore, the purge stream from the WGS system undergoes further treatment to insure that this stream is discharged in an environmentally acceptable manner. The primary pollutants dealt with are

the collected catalyst (suspended solids) and the Chemical Oxygen Demand (COD) associated with the presence of dissolved salts. These functions are carried out in the Purge Treatment Unit or PTU.

#### PTU DESIGNS

The design of the PTU is highly dependent on local circumstances such as the amount of plot space available, local water table, meteorological conditions, and owner preference. Thus, unlike the standardized designs for the WGS, the PTU designs have been varied. The design of a PTU is a trade off between real estate or plot space and investment. Nevertheless, all PTUs have been designed to produce an effluent which conforms to local environmental regulations.

The PTU for the original scrubber system consisted of a large pond. This pond was divided into three basins, one approximately 12.2 m by 12.2 m (40 ft. by 40 ft.), one approximately 1.2 ha (three acres) and one approximately 0.81 ha (two acres). Weirs were incorporated into each basin to allow for adjustment of holdup. The purge flowed into the smallest basin where most of the catalyst settled, then overflowed to the largest basin where there was sufficient retention time to insure almost complete separation of the catalyst from the liquid. Also within this basin a significant portion of the oxidation of the products of SO<sub>2</sub> removal took place. This was accomplished by natu-

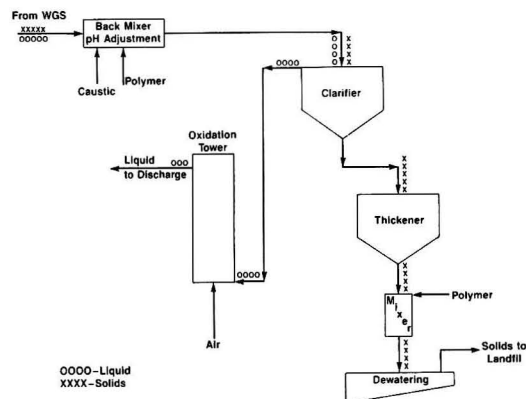


Figure 4. Flow plan for purge treatment unit.

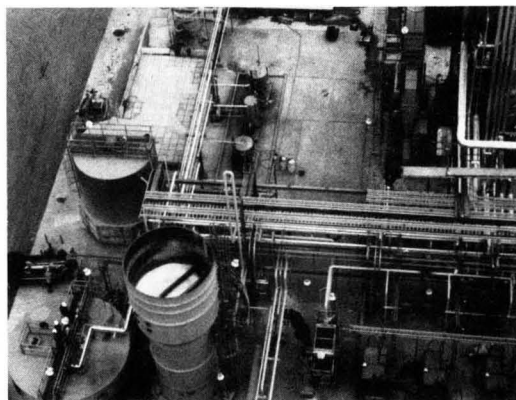


Figure 5. Typical commercial above ground PTU system.

TABLE 1. SUMMARY OF TYPICAL PERFORMANCE OF EXXON AND LICENSEE FCCU SCRUBBING SYSTEMS<sup>(5)</sup>

Unit	Pollutant <sup>(1)</sup>	Inlet Rate/ Concentration <sup>(2)</sup>	Outlet Rate/ Concentration	Regulation <sup>(4)</sup>	Collection Efficiency, %
Unit A	Part	NM	56.81 lb/hr	90.4 lb/hr	—
	SO <sub>2</sub>	915 vppm	37 vppm	N/A	95.6
Unit B	Part	NM	61.9 lb/hr	124.2 lb/hr	—
	SO <sub>2</sub>	1011 vppm	61.5 vppm	N/A	93.9
Unit C	Part	NM	63.0 lb/hr	190 lb/hr	—
	SO <sub>2</sub>	NM	5.3 vppm	N/A	—
Unit D	Part	560 lb/hr	24.8 lb/hr	30 lb/hr	95.6
	SO <sub>2</sub>	771 vppm	20 vppm	180 vppm	97.4
Unit E	Part	NM	0.16 lb/klb (6.2 lb/hr)	1 lb/klb <sup>(3)</sup>	—
	SO <sub>2</sub>	444 vppm	16.8 vppm	N/A	96.2
Unit F	Part	NM	0.26 lb/klb (5.0 lb/hr)	1.0 lb/klb <sup>(3)</sup>	—
	SO <sub>2</sub>	150 vppm	7.5 vppm	N/A	95.0
Unit G	Part	NM	0.82 lb/klb (17.6 lb/hr)	1.0 lb/klb <sup>(3)</sup>	—
	SO <sub>2</sub>	NM	4.7 vppm	245 vppm	—
Unit H	Part	NM		0.62 lb/klb	
	SO <sub>2</sub>	NM			

Notes:

- (1) Part = particulate (catalyst) emissions; SO<sub>2</sub> = sulfur dioxide emissions.
- (2) NM = not measured.
- (3) EPA New Source Performance Standards for FCCU, less than 1.0 pound catalyst emissions per 1000 pounds of coke burned equivalent to 1 kg of catalyst emissions per 1000 kg of coke burned.
- (4) N/A = no applicable source regulation, allowable emissions rate set by ground level concentration.
- (5) Conversions 1 lb/hr = 0.454 kg/hr  
 1 vppm = cm<sup>3</sup>/m<sup>3</sup>  
 1 lb/1000 lb = 1 kg/1000 kg.

ral oxygen uptake in the liquid. Finally the last basin was used to insure complete oxidation of the salts. In this design, no aids were used to assist with either the sedimentation or oxidation process. Due to extensive plot space requirements for this type of PTU design, no other PTU's have been designed in this manner, nor are any expected.

Obviously not all refineries could expend this amount of real estate on the PTU. Subsequent PTU's were ponds, but included the use of polymers to accelerate the sedimentation process. In addition, aeration devices such as surface and/or static tube aerators were also used to reduce the time and plot space required to complete the oxidation of the products of SO<sub>2</sub> removal. Of course, this reduction in plot space requirement was accompanied by an increase in investment.

In the latest generation of PTU's the emphasis has been on minimizing plot space requirements. This has

evolved because recent scrubber systems have been part of projects which are being incorporated into existing refineries. In addition, in several instances, a combination of high water tables and local government environmental requirements have restricted the use of ponding and thus the PTU had to be placed above ground. Thus, a combination of mechanical settling and oxidation devices are used which result in a compact unit. As has been previously stated the reduction in plot space is accompanied by an increase in investment. The following table shows the relative plot space and investment for a ponding (includes polymer injection and aeration devices) and an above ground PTU.

	Plot space	Investment
Ponding:	14 × base	Base
Above ground:	Base	1.8 × base

TABLE 2. EPA TESTING OF EXXON SCRUBBING SYSTEM

o SO <sub>2</sub> Removal	
by CEM tests (12 days)	93 percent average
by Method 8 (3 days)	95 percent average
o Particulate Removal	
by modified Method 5	85.2 percent average
o Emission Rates	
SO <sub>2</sub> inlet (Method 8)	396.8 vppm (average)
outlet (Method 8)	19.6 vppm (average)
Particulates	
inlet (Modified Method 5)	6.17 lb/1000 lb coke
outlet (Modified Method 5)	0.84 lb/1000 lb coke
NO <sub>x</sub> (Method 7)	93 vppm
Hydrocarbons	23 vppm

Notes:

- 1 vppm = 1 cm<sup>3</sup>/m<sup>3</sup>.
- 1 lb/1000 lb = 1 kg/1000 kg.

THE ABOVE GROUND PTU:  
THE LATEST GENERATION

A flow plan for an above ground PTU is shown in Figure 4. The purge from the scrubber system is first fed into a back mixing system where caustic and polymer are injected. Caustic is added to adjust the streams pH to prevent air stripping of the captured SO<sub>2</sub> in the subsequent oxidation step. Polymer is added to assist in the sedimentation process. After the back mix system, the purge is then fed into the reactor clarifier where the solids are separated from the process stream. Clarification was selected as the first treatment step since the catalyst is very erosive. Removal of the solids at this point allows for a downgrading of materials in the downstream equipment. Effluent from the clarifier contains typically less than 100 mg/kg (wppm) suspended solids which is sufficient to meet most discharge requirements.

Once the solids have been removed from the purge

TABLE 3. LISTING OF EXXON AND LICENSEE WET GAS SCRUBBING FACILITIES

Company	Type	Grassroots (GR)	Capacity	Startup Date
		or Retrofit (R)		
Exxon Company, U.S.A.	JEV	(R)	300,000 ACFM	March, 1974
Exxon Company, U.S.A.	JEV	(R)	455,000 ACFM	May, 1975
Exxon Company, U.S.A.	JEV	(R)	865,000 ACFM	January, 1976
Exxon Company, U.S.A.	JEV	(R)	730,000 ACFM	May, 1976
Licensee Unit No. 1	HEV	(GR)	200,000 ACFM	December, 1979
Licensee Unit No. 2	HEV	(GR)	110,000 ACFM	November, 1980
Licensee Unit No. 3	HEV	(GR)	110,000 ACFM	December, 1984
Licensee Unit No. 4	HEV	(R)	145,000 ACFM	April, 1985

**Note:**1 ft<sup>3</sup> = 0.0283 m<sup>3</sup>.

stream, it is pumped to the oxidation tower where it is mixed with compressed air. The type of tower selected has a high internal circulation rate which insures repeated, intimate mixing of the liquid and air streams. Upon leaving the oxidation tower, the water can be discharged since its COD (chemical oxygen demand) is less than 5 mg/l; however, some refineries have requested that the stream be cooled prior to its discharge in order to meet local requirements.

Meanwhile, the solids which have been collected and concentrated in the clarifier receive further treatment. There is periodic blowdown from the clarifier to the agitated clarifier sump. The solids collected in the sump are then pumped to the thickener where they are further concentrated prior to being stored in the bottom of the vessel with the liquid decanted back to the clarifier.

Periodically, a final processing step is performed upon the solids. Thickener bottoms pumps transfer a batch of the solids to a mixer where another polymer is added. The solids then go to a large granular bed vacuum filter where all free water is removed and returned back to the clarifier. The moist solids are then loaded into trucks for disposal in a sanitary landfill. Currently, landfill disposal of the solids is acceptable since several high pressure leachate tests have shown that the leachate contains substantially less than 100 times the drinking water standard for all priority pollutants.

Figure 5 is a view of a commercial installation of this type of PTU. Total plot space allocated for this unit is approximately 279 m<sup>2</sup> (3,000 ft<sup>2</sup>). The reactor clarifier is in the left foreground; the thickener is located directly above it; and granular bed filter is in the left background. Just to the right of the filter is the polymer storage area. The oxidation tower is in the center foreground and the air compressors are in the right foreground. Backmixing equipment is located just above the pipeway. This commercial installation has been in operation for approximately eighteen months and has had minimal operational problems.

**MEETING ENVIRONMENTAL GOALS**

Extensive testing has been conducted on all the WGS facilities by Exxon, its licensees, and various environmental control agencies. A summary of these results is shown in Table 1. It should be noted that as designed all of the WGS facilities are in compliance with their permitted values. In particular, all of the licensee units are in compliance with the current NSPS for FCCU's which requires that particulate emissions be reduced to less than 1 kg (lb, pound) of particulates per 1000 kg (lb, pounds) of coke burned. These units are required to meet this standard since they were constructed or modified after is-

suance of the NSPS. It should also be noted that these units would be in compliance with the proposed NSPS for SO<sub>2</sub> emissions.

**EPA TESTING**

Although one could explore the performance of any of the scrubbing systems in detail, the best choice would be to select the unit which was rigorously tested by the EPA as part of their current program on developing the sulfur oxides NSPS. EPA conducted a test program on an unit from May 4, 1981 through June 2, 1981. The primary purpose of these tests was to conduct continuous emission monitoring of sulfur oxides. However, during the course of this program, emissions of particulates, nitrogen oxides, and hydrocarbons were also conducted. It should be noted that during this entire program, neither Exxon personnel, who were not onsite, nor the refiner made any attempts to optimize WGS performance. Thus, the unit was

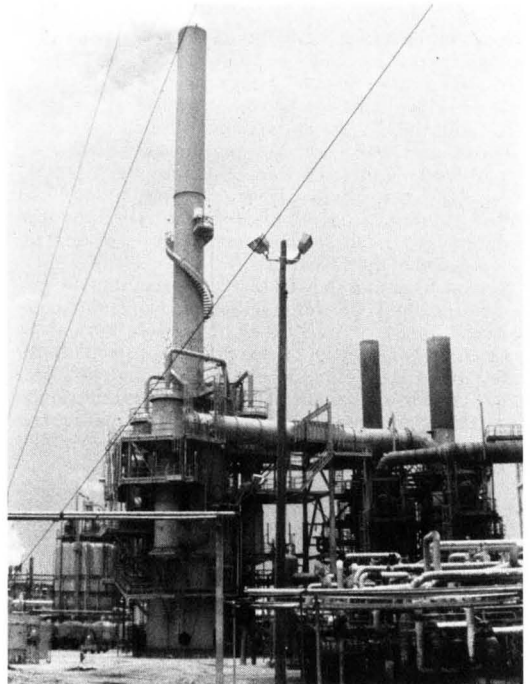


Figure 6. Typical jet-ejector venturi wet gas scrubber system.



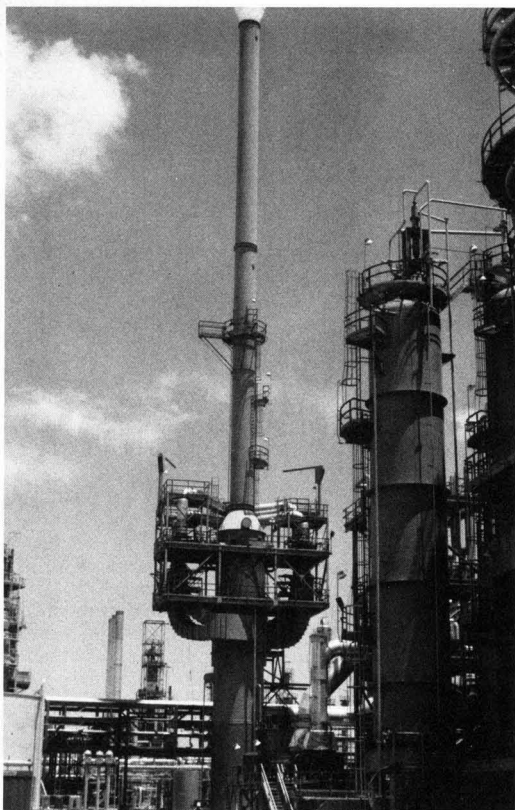


Figure 7. Typical high energy venturi wet gas scrubber system.

## ADVANTAGES

Based on our design and operation of the WGS systems, the following advantages have been confirmed.

- **Single Step Pollutant Removal:** The venturi is the only pollution control system which can remove both particulate and  $\text{SO}_2$  pollutants and achieve compliance with expected environmental regulations.

- **Flexible Performance:** Day to day operating changes (e.g., changes in flue gas rates, composition solids loading, temperature) can be readily handled, if necessary, by small changes in the WGS operating conditions. Even long term changes such as changes in FCCU catalyst type have been handled with little or no adjustment in WGS operation. In addition, the Exxon WGS system has experienced almost every upset that can occur in FCCU operation, including reverse flow, and has not required extensive attention during these upsets.

- **Compact System:** Typical onsite plot area requirements for the Exxon WGS system range from 93 to 465  $\text{m}^2$  (1,000 to 5,000  $\text{ft}^2$ ) for FCCU's ranging from 55.2 to 276.0  $\text{dm}^3/\text{s}$  (30 to 150  $\text{kb/D}$ ) feed rate. These low plot space requirements arise from the use of multiple, high capacity venturis mounted on a single separator, and the ability to locate supplemental equipment, such as the PTU, offsite. The lower onsite plot plan requirements relative to precipitators make scrubber retrofitting more practical. The lower onsite plot plan requirements also offer advantages with "grassroots" plants in that more space can be dedicated to process rather than pollution control units.

- **Reliability:** Based on Exxon's experience with various types of emission control facilities, it has been found that WGS system has higher service factors and lower maintenance costs than alternate emission control approaches. In fact, the WGS service factor is equal to or greater than the FCCU itself and no FCCU has been shutdown due to failure of the WGS system. Maintenance costs have proven to be lower than that for either electrostatic precipitators or conventional venturis.

- **Low Cost:** In most cases studied, the WGS system was more economical than a combination of feed desulfurization and electrostatic precipitators. Of course, the choice of an emission control system is dependent on feedstock quality, processing requirements, environmental regulations, and location. However, we believe that the attractiveness of FCCU WGS systems increases as either the sulfur content of the FCCU feed (such as adding atmospheric resid) or the severity of regulations increases.

For example, a study for a Gulf Coast "grass roots" 73.6  $\text{dm}^3/\text{s}$  (40  $\text{kb/SD}$ ) FCCU processing either virgin gas oil or a mixture of virgin and coker gas oils was recently considered. A WGS system, with a distillate hydrodesulfurization unit to maintain equivalent distillate quality, was compared to a combination of total feed desulfurization and electrostatic precipitators. All control equipment was designed to meet the current particulate NSPS and the proposed  $\text{SO}_2$  NSPS. For either case, the WGS system/distillate hydrodesulfurization combination showed an economic incentive of about six dollars per cubic meter (one dollar per barrel) even when credit was taken for FCCU yield improvements due to feed desulfurization.

## SUMMARY

The Exxon WGS system offers a unique combination of FCCU particulate and  $\text{SO}_2$  control capability with economic and operating advantages when compared to the combination of particulate control via electrostatic precipitators and  $\text{SO}_2$  control via feed desulfurization. The

tested without optimization. Results of these tests are shown in Table 2.

As can be seen from Table 2, twelve days of CEM testing showed that the scrubbing system averaged 93 percent sulfur dioxide removal. Subsequent manual testing using a modified EPA Method 8 test confirmed these results indicating 95 percent sulfur oxide removal across the scrubber (396.8  $\text{cm}^3/\text{m}^3$  (vppm) in and 19.9  $\text{cm}^3/\text{m}^3$  (vppm) out). Nitrogen oxide emissions averaged 93  $\text{cm}^3/\text{m}^3$  (vppm) and hydrocarbon emissions averaged 23  $\text{cm}^3/\text{m}^3$  (vppm). Since neither is controlled by the scrubbing system, these values are solely dependent on the operation of the FCCU.

Particulate testing showed that 85.2 percent of the solids entering the WGS were removed and an outlet emission rate of 0.84 kg (lb)/1000 kg (lb) of coke burned. In conducting these tests EPA's contractor substantially deviated from EPA Method 5 sampling and analytical procedures to provide specific developmental information to EPA. Based on these deviations, the outlet particulate loading is believed to be higher than would be expected if "standard" Method 5 practices were followed.

## WGS BACKGROUND

Exxon has designed and installed eight commercial WGS facilities. These are listed in Table 3. These systems were installed as part of "grass-roots" FCCU's or as retrofits on existing FCCU's. Scrubber type at each location depended on pressure availability. A typical jet-ejector WGS system is shown in Figure 6 while a typical high energy venturi is shown in Figure 7.

WGS system concept can be used with either of the gaseous emission control approaches now in use, CO boilers or high temperature regeneration. Eight commercial units, with over sixty-four years of combined operation, are now in service. The commercial units have demonstrated over 90% particulate removal and over 95% SO<sub>2</sub> removal.



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