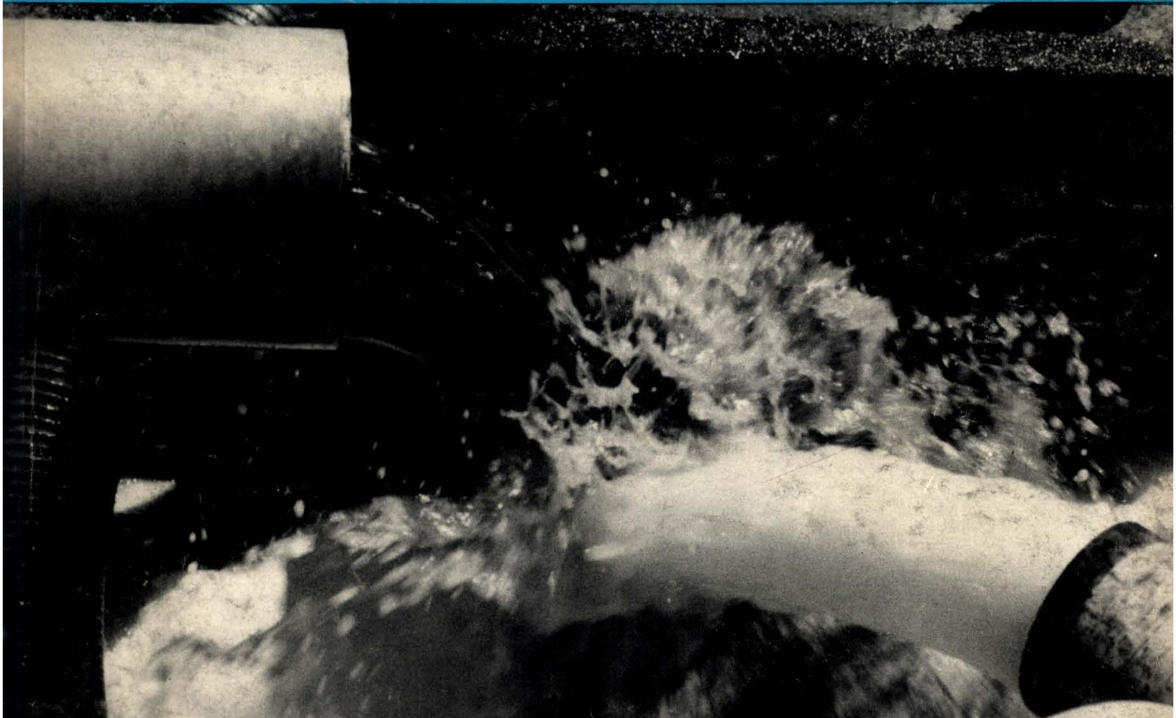
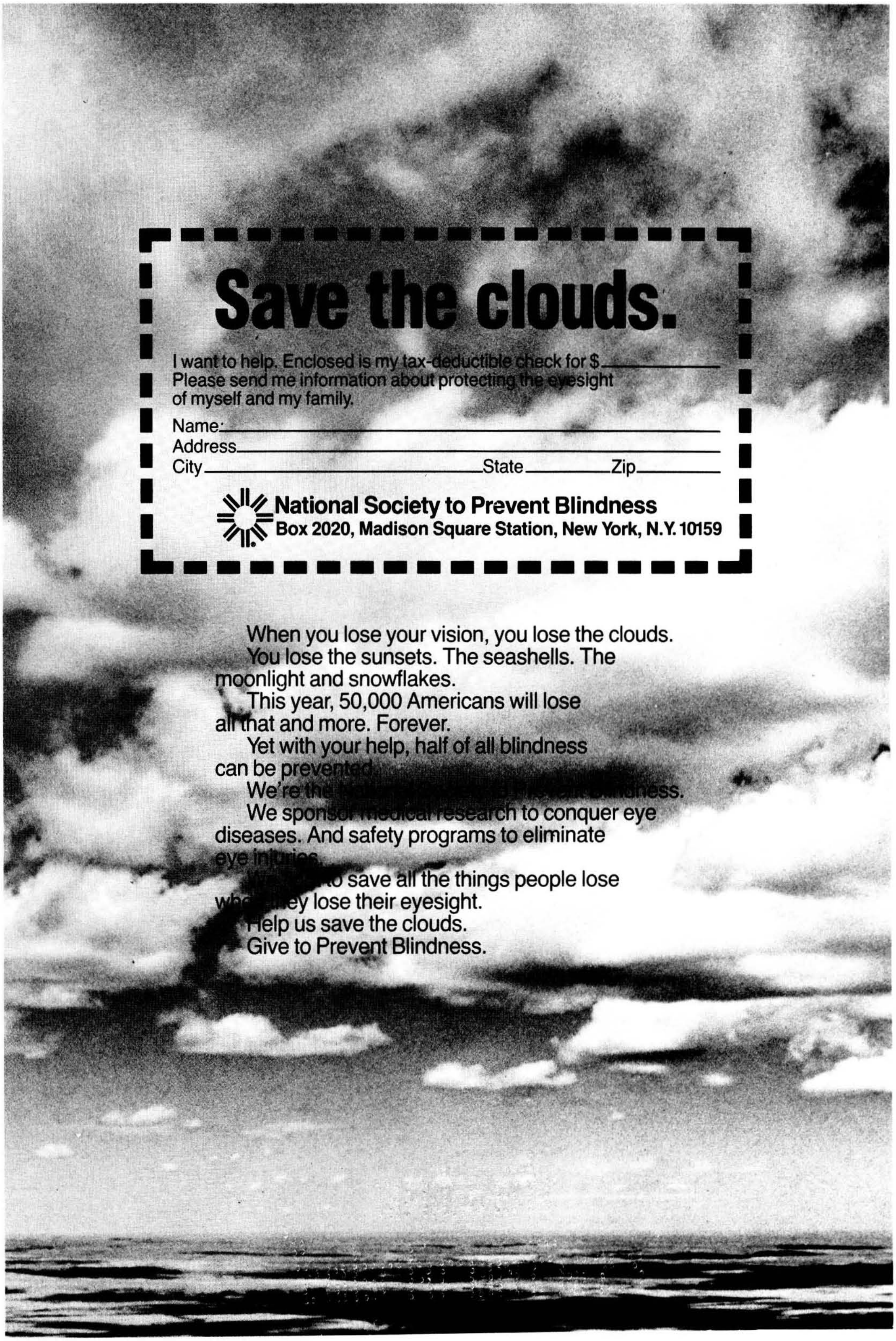
FEBRUARY, 1985

ENVIRONMENTAL PROGRESS





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ENVIRONMENTAL PROGRESS

February 1985 **Vol. 4, No. 1**

Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multi-faceted aspects of the pollution problem. It will provide thorough coverage of abatement, control, and containment of effluents and emissions within compliance standards. Papers will cover all aspects including water, air, liquid and solid wastes. Progress and technological advances vital to the environmental engineer will be reported.

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Cover: © 1985 Ronald F. Thomas/Taurus Photos. Wastewater treatment plant, Virginia Key, Florida. Construction water pumped from three wells to lower water table. Black water composed of hydrogen sulfide from pocket of organic matter.

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A Progress Report

by Louis R. Roberts

As many of you know, the Environmental Division has in the last year or so been developing a new organizational concept for the programs at our meetings. Historically, the programs for the Division have been aligned according to the primary concern in one of three environmental areas: air, water or solids. The new orientation proposed has to do with either fundamentals, process innovations, reuse, recovery and recycle, or treatment. The recent National AIChE meeting in Philadelphia was the first, I believe, in which a major block of papers was organized according to the new concept. I attended the meeting, and this is my reflection on the experience.

At the Philadelphia meeting, by my count, there were 29 sessions sponsored or co-sponsored by the Environmental Division. I chaired one session and attended at least part of four others. First of all, I was particularly impressed by the enthusiasm of the chairmen of the sessions. This was refreshing and something of a departure in my experience. I should point out that I am a frequent participant in the national meetings.

Second, I feel that the papers were generally of better than usual quality. Perhaps the new concept gives authors a fresh new and productive approach to public presentations dealing with environmental issues. I have no background in meeting statistics, but I thought that the sessions were well attended and that audience interest and participation was good. I can say for certain that the five papers presented in the session I chaired were all of good quality and well presented. I was pleased to be associated with that session.

It occurs to me that consideration of one's professional environmental concerns in the light of the new concept might provide for an added interest for chemical engineers. Instead of thinking that one has a problem in air or water pollution, one can think that one has a problem in the area of process improvement, or a challenge in the area of reuse or recycle of waste material. I suggest that the latter concept furnishes a much more professionally interesting approach, and is more compatible with good engineering practice.

I further suggest that the ever more stringent restrictions in the area of waste disposal give an even more emphatic incentive for chemical engineers to think along these lines of recycle and of process improvements and so on. Don't overlook the fact that emitting gaseous contaminants into the atmosphere is a form of waste disposal, just as are discharging liquid effluents to streams and burying solid materials.

It is certainly true that the historical alignment into air, water and solid areas is logical. My observation is that technologies peculiar to one area often do not transfer to another. However, I do not believe it follows that a practitioner in one area need not know much about the technologies in the others. As a matter of fact, I suggest that it is something less than professional to confine one's interest and knowledge to one narrow area. I further suggest that a professional organization such as the AIChE should provide both the incentive and the means for its members to expand their professional horizons. In my opinion, the new organizational concept works toward that goal.

For you "bottom-liners" out there, I offer what I consider to be the success of the Philadelphia meeting in the environmental area in support of the new organizational concept for the Environmental Division programs.

Louis R. Roberts holds a B.S. in Chemical Engineering from The University of Colorado: a M.A. in Physical Chemistry from Rice University and a Ph.D. in Chemical Engineering from the University of Texas. He has sixteen years industrial experience with Gulf Oil Corporation, Southwest Research Institute and Allied Chemical Corporation, plus thirteen years with the Texas Air Control Board.

Environmental Shorts. . .

Acid Rain on Building Materials Studied by Argonne National Labs

National artifacts, such as the Washington Monument, Jefferson Memorial, and other limestone and marble structures, may benefit from an acid rain study underway at the Department of Energy's Argonne National Laboratory.

This study is part of a long-range effort by several federal agencies to determine the effects of acid rain on building materials, such as various types of stone and metals.

Argonne obtained more than seven tons of Vermont marble and Indiana limestone from the National Bureau of Standards in Gaithersburg, Md., for the study. The uniform 50-lb. slabs will be precisely cut into sets of smaller, two-lb. briquettes and mounted on racks in various locations throughout the country. A total of four field testing locations have already been established in the eastern United States; additional sites are planned in the midwest and in Canada within the next two years.

Under the National Acid Deposition Assessment Program, the National Park Service is coordinating the study to find ways of preserving the country's historic monuments and buildings.

"Limestone and marble buildings and statues are especially susceptible to the effects of acid rain," said Arthur Youngdahl of Argonne's Materials Science and Technology Div., who is managing the stone exposure project.

Youngdahl and fellow Argonne scientists will study the disintegration effects of weathering by analyzing physical and chemical changes in the stone at various intervals during the study. Previously unexposed pieces of stone are being used for the study because scientists do not have enough historical data about air quality, rain chemistry, to deduce accurate measurements of past acid rain effects.

"One thing that research is proving is that there is time to understand acid rain better, as far as materials are concerned," Youngdahl said. "Our initial findings have shown that only a few microns of the surface of materials decompose each year."

Argonne will study samples from four field test locations: atop the West End Public Library in Washington, D.C., the Huntington Wildlife Forest in the Adirondack Mountains, near Newcomb, N.Y., Chester, N.J., near Newark; and the Research Triangle Park, near Raleigh-Durham, N.C.

The 10-year research project is under an Interagency Task Force on Acid Precipitation, established by Congress in 1980. Agencies include the U.S. Dept. of the Interior's National Park Service, U.S. Geological Survey, Bureau of Mines, Environmental Protection Agency, Argonne National Laboratory, and the National Bureau of Standards.

Hyacinths Used to Remove Heavy Metals from Polluted Waters

While some experts are recommending various physical changes to reduce metal-polluted water in northeastern Oklahoma's Tar and Lytle Creeks, Oklahoma State University researchers are putting Mother Nature to work on the problem.

Some research believe the solution to the problem lies in diverting the water to keep it from running into the mines and becoming contaminated with iron, lead, and zinc. Existing abandoned mine entrances and sink holes would be sealed with concrete.

OSU chemical engineering professors are evaluating the merits of growing water hyacinth plants *(Eichornis crassipes)* in the polluted water. These fast-growing plants have an affinity for absorbing heavy metals from the polluted water and storing them in the plant leaves, roots, and stems.

(Continued on next page)

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Once the metals are concentrated in the plants, the plants can be removed and replaced by fresh ones to continue the absorption process.

"We pursued the water hyacinth idea for removing heavy metals from polluted water after we saw the results of using the plants as an alternate water treatment media in animal waste water lagoons. Dr. Robert A. Willis, an OSU assistant professor of chemical engineering and director of the project by the school's University Center for Water Research, said.

Willis and his graduate assistants found the water hyacinth plants were extremely fast growing but could not withstand Oklahoma's low, winter temperatures. They needed a controlled environment where a usable population of plants would be available all year.

The Tar Creek water samples they collected contain 350 ppm iron, 88 ppm zinc, and less than 1 ppm lead. When they grew water hyacinths in this pure Tar Creek water, there was erratic uptake of the metals by the plants. Within 12 to 14 days, however, the plants died.

In the laboratory, the researchers found the ideal concentration for water hyacinth plant growth was a blending up to 50 per cent Tar Creek water. In this concentration, the plants remained viable beyond 30 days and exhibited new growth by sending out "runners" to form new plants.

To maintain the 50 per cent by volume concentration, the researchers have proposed a separate channel or tank located near the polluted water source with an upstream section to dilute the source water to 50 per cent.

As the water flows under the hyacinth plants, metals are absorbed. How low the concentration of metals might be is a function of contact area of the plant roots and flow rate of the water. The total metal concentration after 10 to 17 days in the 50 per cent test tanks was less than 2 ppm.

Part of the exit stream from the tank is returned to the creek or wherever it is needed. The remainder of the exit stream is remixed with the inlet stream to maintain the required 50 per cent concentration.

As new plants are formed, old plants with their higher concentrations of heavy metals will be removed, physically removing the metals from the water.

Critical to the success of the experiment is the need to maintain a population of water hyacinths throughout the year, especially during Oklahoma's cold, winter months. Designers are looking at several types of earth-house enclosures with the natural lighting of a greenhouse. They hope the subterranean feature will help keep the water temperature for the plants from falling too low or making large changes, all critical for maintaining the rapid growth of these plants.

For Waste Site Cleanup Joint Venture Formed

Chem-Technics, Inc., a specialty chemical company that markets chemical fixation and solidification (CFS) technology for the treatment of toxic and hazardous wastes, has formed CFS Systems of New Jersey, a joint venture with Paz Brothers, Inc., a heavy construction company. The new firm will undertake CFS treatment, excavation, transportation, and disposition of processed wastes in New Jersey.

Formed in 1957, Paz Brothers, Inc., has constructed waste treatment plants, secured landfills, and lagoons as well as provided industrial piping, pumping and transportation of hazardous wastes for leading industrial chemical companies.

George M. Fell, president of Chem-Technics said of the joint venture: "The combined skills of Chem-Technics and Paz Brothers offers industry, agencies and the public, technology, staff, and practical experience to provide safe, efficient, and long-term solutions to toxic and hazardous waste."

Environmental Publications Catalog Available

The American Society of Testing Materials has made available its Environmental Publications Catalog, which features four volumes of the *1984 Annual Books of ASTM Standards.* These volumes contain close to 400 ASTM standards for water and environmental technology; atmospheric analysis; occupational health and safety; pesticides; resource recovery; waste disposal; and hazardous substances and oil spill response.

Also described in the catalog are more than 30 ASTM Special Technical Publications (STPs) with the most current information on a variety of related subjects.

This catalog is available free of charge from: Sue Sweeney, ASTM, 1916 Race St., Philadelphia, Pa. 19103.

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Letters to the Editor

On "How the Super-Camel Got His Hump"

Environmental Progress 3, N2 (1984)

To the editor:

Mr. Super Camelico engineer Stacy Daniels attempts to make a case for the chemical industry and the bad rap they have taken with respect to hazardous wastes. As he sees it, the mismanagement was done by "a few unscrupulous or unknowing individuals" which resulted in "occasional failures."

I cannot imagine a more myopic, self-serving attitude towards the problem. What about the 22,000 abandoned hazardous waste sites now on the superfund list and the more than 50,000 sites identified? Are those the work of a few misguided souls? Dow's chemical injection problems at their Hemlock plant are well documented, as is their complicity in the Geneva Superfund site in Houston. Is this what Dr. Daniels considers "proper management?"

Dr. Daniels claims that the chemical industry played a major role in the development of incineration as a waste control technology. Yet he points out that only one percent of the hazardous waste generated is destroyed by incineration. Where is the follow through? If the chemical industry did such outstanding pioneering work, why aren't they using the fruits of invention?

Dr. Daniels concludes the article by stating "we must insure that hazardous wastes continue to be properly managed." The implication is that everything is under control, that self-management is working. However, despite the efforts of the chemical industry, RCRA has been toughened and CERLA will be strengthened. The attitude Mr. Daniels displays clearly illustrates why the problem is as bad as it is, and why efforts to do something are stonewalled and eroded. Denial of environmental problems has long afflicted the chemical industry; and his article is a manifestation of this large festering illness.

Jack V. Matson
Department of Civil Engineering
University of Houston
Houston, Texas 77004

Reply:

Dr. Matson takes exception to my recent SuperCamel editorial which was intended to provoke some reevaluation as well as provide some overall perspectives on hazardous waste management. The numbers used by Dr. Matson of thousands of abandoned sites are an example of the numbers game used by some to dramatize and sensationalize. As I point out in my remarks, one cannot always distinguish camels by numbers of "humps." Numbers of facilities must be tempered by quantities of wastes, as well as locations (onsite or offsite), facility types (storage, treatment, or disposal), and composition (concentrated or dilute; wet or dry; hazardous or non-hazardous; wastes, mixtures; or residues).

It is not enough to simply count "humps" and assume they are all the same. As emphasized in the 1983 OTA study, the greatest weakness is the inadequacy of databases to define the hazardous waste "problem." Good data are required to define the generation of waste, health and environmental effects, and adequacy of management facilities. Differences in the perceived types of quantities of wastes and the degrees to which they may pose hazards (risk assessment) are coupled with confusion as to the extent and focus of efforts to control them (risk management).

Rather than classify the universe of all solid wastes as equally hazardous, it is preferable to prioritize those sites posing the greatest risks for remedial actions, and then allocate resources as appropriate. Cases of mismanagement of solid wastes do exist, but I maintain they are the exception and not the rule. Solutions to the real problems associated with hazardous wastes will be realized only through cooperative actions by all concerned parties — industry, government, academia, and the public.

Stacy L. Daniels
H&ES Information Center
Dow Chemical USA
Midland, Michigan 48640

P. S. Dr. Matson also has made certain assertions regarding sites at Hemlock and Geneva. We do not have a plant at the former location and we are not one of the ten responsible parties issued notice letters for the latter.

Response to Article on Hazardous Waste Sites

To the editor:

This letter is prompted by the article, "Remedial Action at Uncontrolled Hazardous Waste Sites," by A. E. St. Clair and K. T. Ajmera [*Environmental Progress*, 3, 188 (1984)]. Our purpose is to call attention to what we consider are significant flaws in the format used by the agencies to select a mitigation alternative for the McColl site near Fullerton, California.

We agree with the article's statement calling for a thorough and systematic selection process in waste site mitigation. To this end, Shell Oil Company and other Potentially Responsible Parties have worked closely with the California Department of Health Services (DOHS), Region IX Environmental Protection Agency (EPA), and numerous other state, county and local agencies on the McColl site mitigation.

This cooperation yielded an extensive technical study costing in excess of $1MM to quantify the impact of the site and serve as a basis for selecting an appropriate mitigation plan. The study's primary conclusion was that the McColl site had minimal impact upon the adjacent community and environment. A DOHS health survey indicated periodic odor emissions affected only those closest to the site.

The evaluation of mitigation alternatives (subject of your article) to alleviate this problem was under the sole direction of the DOHS. While there is a disagreement between Shell and the agencies regarding their choice of mitigation alternatives at McColl, that is not the focus of this letter. Rather, it is Shell's concern that the format used by the agency to select a cost-effective alternative is flawed, and that steps taken by the state and its contractor in the detailed evaluation and cost-effectiveness phases significantly biased their study. We are also concerned that continued use of this format will introduce bias into future efforts at other sites and will yield additional recommendations that are not cost-effective. I have not listed *all* of our concerns with the process in this letter, but rather have focused on the more obvious and more critical items.

Very early in the detailed evaluation phase for the McColl site, the DOHS and their contractor significantly narrowed the scope of the containment alternative, resulting in an abnormally high cost estimate. While the authors of the previously-mentioned article stated that sensitivity evaluations are critical to a thorough technical analysis, such evaluations for containment at McColl were done only in the most superficial manner. Thus the impact of the agency's premises on the engineering design for containment was never clearly understood nor openly discussed.

Later, work by an independent contractor (Brown & Caldwell) clearly identified the impact of the agency's action:

☐ • A reinforced concrete wall was not necessary for seismic stability. Cribbing (commonly used in civil projects) with appropriate piling was determied to be more effective and significantly less costly.

☐ • The geohydrological data overwhelmingly indicated the absence of perched water at the site. With the water table at 200 feet, the 40-foot deep slurry wall surrounding the site was unnecessary.

These two items alone raised proposed containment costs by an estimated $8-10 million. Had the DOHS contractor made a sensitivity analysis similar to Brown & Caldwell's, the premises which influenced their selection of the more costly excavation alternative over containment could have been openly discussed and evaluated.

On the other hand, as stated in the article, detailed sensitivity studies were conducted for the excavation case. This yielded a clearer understanding of critical issues and a far broader range of costs. With their high cost estimate for containment, this yielded an unrealistically small differential cost and favored excavation in the later stages of the selection process.

An additional premise which further biased the selection was that the site chosen for waste excavated from McColl would pose no risk to human health or the environment. In light of EPA's recent concerns regarding leakage at many commercial RCRA sites selected for disposal of CERCLA wastes, the decision not to evaluate the proposed site is incongruous.

A final bias was introduced through the rating of excavation and containment alternatives (each of which met the DOHS criteria). A "multidisciplinary evaluation team" of contractor personnel, depending upon their *personal experience*, introduced *their* value judgments into the evaluation phase. While a sense of objectivity was gained by applying numerical values, in this instance it was an entirely *subjective* evaluation. In the early stages of technology screening, such a technique could have been used effectively to identify alternatives which met DOHS criteria. However, it is far too crude a tool in its present form to apply in the final selection between alternatives that otherwise met all criteria. It can be viewed in this instance merely as a format which allowed selection of a high cost alternative.

We understand that value judgments will necessarily enter into the final decision process to insure societal needs are met; however, they should come only after the technical evaluation itself is complete. Value judgments should be introduced by the controlling agency and *not* the contractor. In this way, the impact of the value judgement is clearly identified and understood, and is not shrouded in psuedo-technical requirements.

Many positive results have come from the McColl experience which will enhance society's future efforts to mitigate abandoned sites. However, an objective format for comparing alternatives and selecting a cost-effective mitigation method was not one of them. Instead, value judgments and individual prejudices were blended into and perceived as part of the technical evaluation.

In conclusion, we believe careful analysis of mitigation alternatives is required in order to select an appropriate response to each abandoned site being evaluated. The technical evaluation, with appropriate sensitivities, must be kept on a sound technical basis and free of value judgments. Then the proper decision makers can add the value judgments to insure the societal needs are met. While society may ultimately choose alternatives that are not cost-effective, it should do so openly and with a full understanding of the driving forces behind each decision.

W. J. Duchie, Manager
Environmental Programs
Health, Safety and Environment
Shell Oil Company
Houston, Texas 77210.

Reply:

We appreciate Mr. Duchie's comments concerning the methods used in selecting remedial action at the McColl site. His views reflect many of the concerns expressed both by regulators and by the regulated community as they have attempted to deal with the dynamic Superfund process. This program continues to evolve, however, and every case provides the opportunity for applying lessons learned to subsequent evaluations. Certainly, the McColl case will be no exception.

Hazardous waste issues involve the interface of science, politics, and society in solving serious and complex problems that may have very high stakes. Both value judgements and technical judgements must be made in order to integrate all of these considerations and the diverse perspectives of various parties; nowhere is this more evident than in the Superfund program.

In the McColl evaluation, judgements made by the regulatory agency, consistent with its view of its public mandate, established the framework within which the analysis of alternatives was performed. The responsibility of the contractor was to perform technical and cost analyses, to exercise professional judgement within the agency's framework, and then to provide the findings to the agency as input to its decision. Cost analyses were based upon the design criteria and evaluation framework specified by the agency. Evaluations of factors such as risks, impacts, and reliability of remedial action required that professional judgements be made. It is inherent in this process that the personal values and experiences of individuals, along with technical information, will affect these judgements. However, responsibilty for analysis of the contractor's recommendations, and for the final decision on remedial action at the McColl site, rested entirely within the agency. Subsequently, the agency's decision and the supporting analyses were further evaluated and approved by EPA regional staff and headquarters officials prior to issuance of funds under Superfund.

Individuals representing a broad spectrum of perspectives are concerned with the issue of how to select the most acceptable and cost-effective approaches to hazardous waste site mitigation. Open and constructive dialogue among all these parties is essential to achieving resolution of concerns such as those expressed by Mr. Duchie. To that end, we can all benefit from his comments and from any suggestions he may offer in the future as to alternate approaches.

Ann E. St. Clair
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Process Simulation of Flue-Gas Desulfurization Systems with Organic Solvents

A detailed study of the ability of three organic solvents to absorb sulfur dioxide contained in flue gas at low concentrations.

Paul M. Bever and George E. Klinzing, University of Pittsburgh, Pittsburgh, PA 15261

Oxides of sulfur and nitrogen are highly toxic gases [*1*]. Kaplan and Maxwell [2] pointed out that mortality and morbidity can be correlated to ambient levels of SO_2. Furthermore, SO_2 is the most harmful air pollutant to vegetation and to some building materials through an effect which has become known as acid rain. Sulfur dioxide is the precursor of the chemical that causes 40 to 60% of the acidity of precipitation.

The goal of this work is to optimize a flue gas absorption/stripping system, which produces concentrated SO_2 by regenerating the scrubbing liquid thermally. The streams leaving the scrubbing system are either pure enough to be emitted to the surroundings without causing any harm or may even be processed to give a salable product. Three possibilities suggest themselves for treating the concentrated stream produced:

1. Reduction to elemental sulfur by contacting it with H_2S (Claus Process).
2. Oxidation and subsequent hydration to give dilute sulfuric acid.
3. Drying and liquefaction.

To achieve the absorption/stripping goal a simulation program, which uses a tray to tray algorithm, is used. The results of this simulation are evaluated and compared in terms of utility costs. Figure 1 shows a schematic of the process studied.

SIMULATION PROGRAM AND STATEGY

The flue gas feed to the column was preset to a basis of 1 mole per unit time. Adaptation of energy requirements and flow rates to the purification of a flue gas stream of known size can be achieved by selecting an appropriate time unit. Consequently, the unit mole in the following denotes mole per mole flue gas and unit time. Similarly, calories are equivalent to calories per mole and unit time.

For all processes, removal efficiencies of 90% were considered as a sufficient design goal and a reasonable basis for process comparison [3].

Sulfur Dioxide Absorption

The composition of the flue gas was preset as follows: The concentration of the sulfur dioxide was selected as 1300 mole-ppm while the bulk of the gas stream was assumed to be inert towards absorption and was identified as nitrogen. In accordance with current practice we assumed that a Venturi scrubber is installed in front of the absorption unit to remove particulate matter. The flue gas is supposed to leave this scrubber at 50°C and to be water-saturated. Hence, the final composition of the flue gas entering the absorpton tower results in the following mole percentages:

— SO_2: 0.11%
— H_2O: 12.17%
— N_2: 87.71%

Three solvents as suggested by Sanza [*4*] were subjected to detailed studies:

- methyl pyrrolidone;
- a 1.0 M aqueous solution of citric acid, neutralized to a *p*H of 4.5,
- a 1.0 M aqueous solution of glycolic acid, neutralized to a *p*H of 4.5

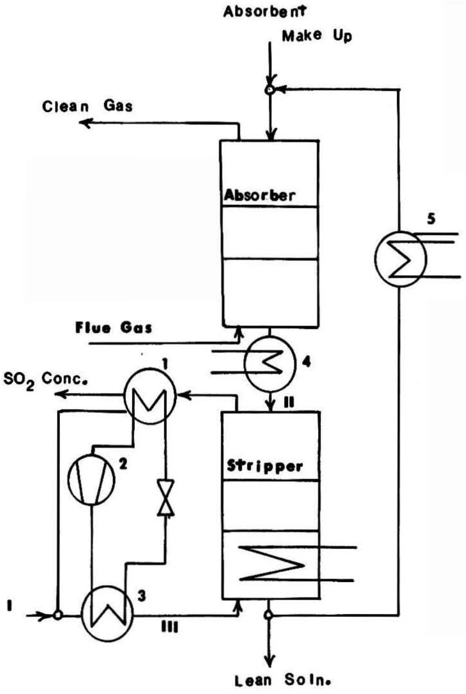

Figure 1. Generalized flow diagram of a flue gas desulfurization system: 1. Partial Condenser; 2. Compressor; 3. Stripping Steam Evaporator; 4. Preheater; 5. Cooler. I. Steam Make-up; II. Absorbent Solution; III. Stripping Steam.

The thermal regeneration of the absorbent was also simulated. As options for the energy supply, indirect heat transfer by heating steam was available as well as steam stripping of the solution. Cooling of the first stage, i.e., the top stage of the absorber, was necessary in the methyl pyrrolidone study. Both apparatuses, absorber and stripper, were assigned three stages. The solution leaving the stripper was either partly recycled directly to the absorber or processed mainly for the removal of water, which has been condensed out of the flue gas or the stripping steam. For the stripping steam a heat recovery system was designed based on a closed water cycle. The heat released during the condensation of the water is used by evaporating water at low pressure. This vapor is compressed and condensed on a higher temperature level, thereby vaporizing water to supply stripping steam.

The enthalpies for each component in both liquid and gas stream, were calculated separately and were assumed not to be subject to any interaction between different components. Accordingly, the specific enthalpies were weighted by the mole fraction of each component and added together to give the total specific enthalpy of a stream. Heat capacities were considered to be temperature independent. Pressure dependence of heat of vaporization and boiling temperature, however, were taken into account.

Equilibrium Data

Equilibrium data were expressed in terms of the *K*-value, i.e., the ratio of the mole fractions in gas and liquid phase.

The *K*-values for SO_2 were either obtained from an Antoine type of fugacity equations, which correlated the experimental data of Sanza and Walker [5], or were calculated from polynominals in temperature. The coefficients of these polynominals are functions of the SO_2 loading of the liquid phase. They were obtained by fitting a third order polynominals to Walker's data. Details are described in the work of Sanza [4]. The equilibrium subroutine and the data part of the program was adapted to the appropriate case.

The *K*-value for nitrogen was set to a very high number, thus accounting for the assumption that nitrogen is inert and does not go into solution. The *K*-values for water and methyl pyrrolidone were calculated from their pure-substance Antoine equation and the solid compounds of the buffer solution, citric acid, and glycolic acid, were considered to be basically nonvolatile.

Calculation Scheme

For the multicomponent system of components and trays the calculation procedures designed by Tierney [6] for distillation and extraction have been modified for absorption and stripping operations. For the material balance the following designations are employed:

v_i — vapor leaving stage *i*
l_i — liquid leaving stage *i*
a_{ij} — fraction of vapor leaving stage *j* and going to stage *i*
b_{ij} — fraction of liquid leaving stage *j* and going to stage *i*.
f_i — total feed to stage *i*

Using matrix notation the material balance can be written as

$$V + L = F + A'V + B'L \qquad (1)$$

where

$$V = (v_i \ldots V_n)^T$$
$$L = (l_i \ldots l_n)^T$$
$$F = (f_i \ldots f_n)^T$$

and A' = vapor distribution matrix
B' = liquid distribution matrix

Using X^j and Y^j as the j^{th} column of the composition matrix, the component material balance can be written as

$$A'VY^j + B'LX^j + F^j = VY^j + LX^j \qquad (2)$$

For the energy balance only enthalpy changes and heat transfer are considered. The enthalpy leaving the i^{th} stage is given as

$$v_i g_i + l_i h_i$$

where g_i = vapor enthalpy
h_i = liquid enthalpy

The enthalpy to the i^{th} stage is

$$k \sum_{\substack{k \neq l \\ k \neq i}}^{n} a_{ij}\, v_k g_k + \sum_{\substack{k \neq l \\ k \neq i}}^{n} b_{ik}\, l_k h_k + h_{fi}$$

If q_i is the recuperative heat exchange on stage *i*, the total energy balance for stage *i* is

$$\sum_{\substack{k \neq l \\ k \neq i}}^{n} a_{ik}\, v_k\, g_k + \sum_{\substack{k \neq l \\ k \neq i}}^{n} b_{ik}\, l_k\, h_k + f_i + q_i = v_i g_i + l_i h_i \qquad (3)$$

In order to solve the material and energy balances simultaneously, a correction of the iteration variables, temperature and liquid flow, is used to minimize the deviations from the laws of conservation of mass and energy. This method is basically the Newton-Raphson algorithm for two dimensions. The generalized correction equation is

$$\phi\, \Delta = \lambda \qquad (4)$$

where Δ is a vector of which the elements are n corrections for both variables, temperature and liquid flow rate.
ϕ is a matrix resulting from the selected numerical approach. In the case of the Newton-Raphson method, ϕ is the Jacobian matrix.
λ is a vector of which the elements are measures of the material and energy balance errors.

The calculation procedure has the following steps:

1. An initial temperature vector is assumed.
2. An initial liquid flow vector is assumed.
3. The vapor phase flow vector is calculated from the overall material balance.
4. The equilibrium ratio, *K*, is evaluated.
5. The liquid composition matrix is calculated from the component material balance.
6. The vapor composition matrix is calculated.
7. The Jacobian matrices are evaluated.
8. Two error vectors are calculated as

$$E^1 = \sum_{j=1}^{m} X^j - \sum_{j=1}^{m} Y^j \qquad (5)$$

$$E^2 = AVG + BLH + H_F + Q \qquad (6)$$

with their norm

$$\sigma = [\sum_{i=1}^{n} (E^i)^2]^{1/2} \qquad (7)$$

9. The error norms are calculated to ascertain termination of the routine.

Simulation Strategy

To achieve the desired result of a simulation, which in general was 90% removal efficiency of both absorber and stripper, a number of input variables were manipulated. After the reflux had been set in the flow distribution matrix for the liquid phase, the following entries were varied.

— The heat being exchanged on the first tray: This essentially corresponds to a heat exchanger on top of the absorption tower, if the heating coils could not be installed on the tray itself. The amount of heat was assigned negative numbers, which corresponds to cooling.
— The heat being exchanged on the sixth tray, which is the bottom tray of the stripper.
— The amount of stripping steam.
— The absorbent feed to the first tray.

In each simulation case it was observed that the interaction between the iteration variables liquid flow rates, temperatures, and the *K*-values was critical for the convergence of the solution and its behavior. The energy balance was of minor influence because its convergence criterion was less stringent than that of the material balance. Thus, a change in the heat-exchange vector did not directly alter the previous result in the desired direction.

RESULTS

Methyl Pyrrolidone

The absorption/stripping process was simulated using an loop scheme and recycling the liquid exiting the stripper to the entrance of the absorber at various recycle ratios. The recycle ratio *R* is defined by the liquid being returned to the absorber over the liquid leaving the stripper. Recycle ratios up to 0.95 were simulated. The results are presented in Table 1.

With increasing recycle ratio, cooling requirements and steam consumption increase, while the absorbent, which has to be added to the process as make up, lessens. The former effect, which increases the operating costs of the process, is due to an increasing liquid flow rate in the two columns. For the once through case, the liquid flow is 1.9 mole per time and mole flue gas, whereas, for $R = 0.95$, the liquid flow increases by almost one order of magnitude to 13 mole per unit time and mole flue gas. This is readily explained by the amount of water accumulating in the liquid phase, which almost reaches 95% for $R = 0.95$. In order to achieve the design goal of 90% SO_2 removal, high flow rates for increasing recycle ratios were necessary. The water in the liquid was introduced by the flue gas, which enters the column water saturated at 50°C, and by condensing steam.

Table 1 shows the energy requirements and the make up versus the recycle ratio. The energy requirements combine the energy for cooling and heating with the enthalpy of the stripping steam. It is evident that the required make up for a recycle ratio of 0.95 is smaller by more than factor 10 than the one for an open loop system. However, this decrease is linear, whereas the energy requirements stay almost constant for recycle ratios below 0.6, but increases drastically above $R = 0.8$.

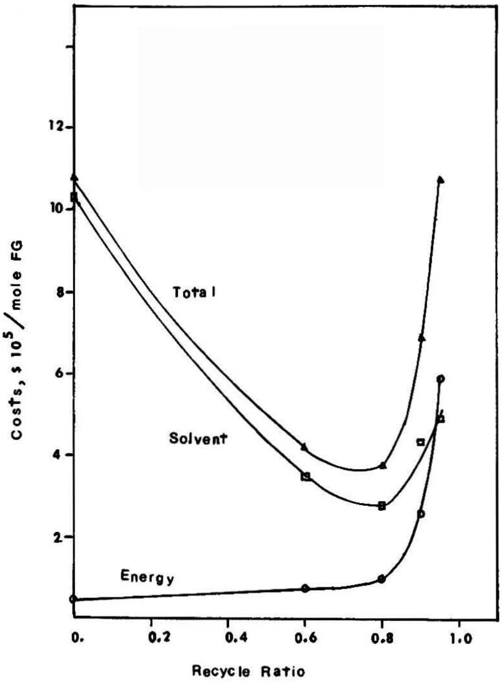

Figure 2. Operating costs vs. recycle ratio for methyl pyrrolidone.

This behavior suggest a minimum of operating costs at a recycle ratio between 0.6 and 0.95. To determine this minimum, a process scheme has been developed and the costs arising according to this scheme have been considered. The results are presented in Figure 2. Purification costs for the methyl pyrrolidone were analyzed. Whether distillation of the absorbent is less expensive than purchasing fresh pyrrolidone was also investigated. The result of this analysis shows a significant increase of purification costs with an increasing water content in the absorbent liquid from the stripping tower. The purification operating expenses, however, lie well below the costs of fresh pyrrolidone. Therefore, distillation costs rather than the costs for purchase of methyl pyrrolidone have been used for the estimation of the make-up costs.

Figure 2 shows that a minimum occurs at a recycle ratio of $R = 0.8$. At lower recycle ratios, the high make-up costs increase the overall operating costs. The variation of costs for energy are minor below $R = 0.6$ and do not compensate for the make-up costs. If the recycle ratio increases, SO_2 and water accumulate in the circulated liquid; this causes an increase of the internal liquid flow rate, which affects the energy requirements. In addition to this, the higher concentration of water in the bleed stream to the purification unit causes higher expenses for the water removal. Consequently, the make-up costs go through a minimum and increases for recycle ratios above $R = 0.8$.

TABLE 1. RESULTS OF ABSORBER/STRIPPER SIMULATION.
ABSORBENT: METHYL PYRROLIDONE

Recycle Ratio	Steam, indirect (cal)	Steam, direct (mol)	(cal)	Cooling (cal)	Total Energy Req (cal)	(% of max.)	Make-up (moles)	(% of max.)
0.0	0	0.37	3592	0	3592	12.6	0.42	100.0
0.6	0	0.37	3592	2400	5992	21.0	0.18	42.9
0.8	0	0.43	4174	3800	7974	27.9	0.08	19.0
0.9	2000	0.70	6795	7300	16095	56.3	0.06	14.3
0.95	7800	0.80	7766	13000	28565	100.0	0.038	9.0

Internal recycle.—Investigations were carried out to determine whether a partial clean up of the liquid leaving the absorber will decrease the operating costs for the whole scrubbing system. The idea was that only a part of the SO_2 rich solution is heated up for regeneration and is then cooled down subsequently when it is recyled. This strategy is expected to save utility costs for heat exchange, which is a major contributor to the total operation costs.

A study was performed at a recycle ratio of 0.8, which lies in the vicinity of the optimum case. The internal recycle, i.e., the amount of SO_2 rich solution which was returned to the top stage of the absorber without further processing the total liquid stream leaving the absorber, was set to 30%. The result of this study was compared to the case in which the total liquid stream is stripped. The process parameters of these two cases were equal, except for the heat exchange on the first stage, which was adjusted to obtain a comparable absorber efficiency for both cases. Table 2 shows the result of these two simulations. In both cases the feed of fresh absorbent was the same (0.08 mole) was well as the steam injected into the stripper (2 mole), while recuperative heat exchange in the stripper was not employed for either case.

Although the percentage of SO_2 removal from absorber and stripper did not differ significantly, the amount of cooling to the first tray was higher for the process with inner recycle. This can be explained in the following way.

The hold up of the SO_2 in the liquid phase is higher for the internal recycle case because a certain amount of SO_2 does not leave the system but is pumped back with the internal recycle. In order to obtain the necessary driving concentration difference, the SO_2 concentration in the liquid has to be decreased by increasing the total liquid flow in the column. In addition to this, the temperature can be lowered to decrease the K-value or, in other words, to increase the absorption capacity of the solution.

In fact, both these techniques have been used; see Table 2. The temperatures in the process with inner recycle are 7 to 9°C lower than those for the reference case. This would cause difficulties in a practical design case, because cooling to temperatures below 30°C with a cooling water tower is not possible throughout the year. In addition to this, the heat which has to be removed in the internal recycle case is more than 30% higher. The liquid which is circulated in the system increases from 2.3 to 4.1 mole per unit time. This large amount is necessary to dilute the sulfur dioxide from 366 ppm at the outlet of the absorber to 113 ppm at its entrance, see Figure 2.

TABLE 2. RESULTS OF THE INNER RECYCLE STUDY, COMPARED TO A SIMILAR CASE WITHOUT INNER RECYCLE

Internal Recycle	0.0	0.3
Feed of Methyl Pyrrolidone	0.08	0.08
Energy Supply		
Cooling on the first stage	3800 cal	5000 cal
Heating on the third stage	no	no
Percentage on SO_2 removal		
Absorber	92.77	92.61
Stripper	99.97	99.97
Process Variables		
Liquid flow in the absorber	2.3 mol	4.1 mol
Liquid flow in the stripper	2.7 mol	3.3 mol
Temperature range in absorber	31-46°C	24-37°C

This indicates that the possible advantage of an internal recycle is by far counterbalanced by the following disadvantages for processes with internal recycle:

- The temperatures in the absorber needs to be lowered. This elevates cooling requirements and might even require a refrigeration system.
- The liquid flow circulating in the system is higher, which means that costs for cooling water pumping increases.

Citric Acid

Simulation results were performed for recycle ratios varying between zero and 0.99; see Table 3. The utility costs are seen to decrease for increasing recycle ratios. This is not surprising in view of the fact that, in the once through study, the absorbent leaves the stripper with almost the same concentration as when it is introduced into the absorber, except for a certain amount of SO_2 which stays in solution. This amount, however, could be decreased by injecting more stripping steam.

The major cost factor for the process is the supply of citric acid. This cost contribution can be diminished by adding a purge treatment and reusing the processed buffer solution, thus avoiding to a certain degree the necessity to purchase new citric acid and sodium hydroxide. In fact, operation experiences [7] indicate that the need for new citric acid solution is negligible. Therefore, the costs of $\$8.18*10^{-5}$/mole flue gas can be considered an upper limit of the utility costs.

Internal recycle.—The internal recycle study similar to that for methyl pyrrolidone was performed. In this case, however, the process pictured in Figure 3 was simulated for internal recycle ratios varying between 0.1 and 0.9. The ratio R of external recycle from the bottom of the stripper to the entrance of the absorber was chosen to be 0.99 in accordance to the optimum for no internal recycle. The results are listed in Table 4.

The efficiencies of absorber and regenerator show an almost linear variation with the internal recycle ratio, however, in different directions. The efficiency of the absorber, i.e., the amount of SO_2 removed from the absorber referred to the amount coming in with the flue gas drops from a high of 90% at the reference case (no inner recycle) to a low of 61%, while the stripper efficiency increases from 90% to 99%.

The liquid flow rate from the first tray of the absorber to the second increases from a value of about 1 mole to 9.1

TABLE 3. SIMULATION RESULTS FOR CITRIC ACID; CHANGING RECYCLE RATIO

	Absorbent Feed		Stripping Steam		Steam Make-Up		Total
Recycle	(g-mil) $*10^3$	(\$) $*10^3$	(g-mol)	(\$) 10^6	(g-mol) $*10^2$	(\$) $*10^8$	(\$) $*10^3$
0.00	9.18	7.37	0.37	4.40	5.46	7.81	7.37
0.30	7.2	5.78	0.41	4.87	6.12	8.75	5.78
0.50	5.5	4.42	0.45	5.35	6.56	9.38	4.43
0.70	3.5	2.81	0.49	5.82	6.99	10.00	2.82
0.80	2.5	2.01	0.52	6.18	7.53	10.77	2.02
0.90	1.3	1.04	0.55	6.53	8.00	11.44	1.05
0.95	0.61	0.49	0.55	6.53	7.87	11.54	0.50
0.99	0.08	0.064	0.58	6.89	8.48	12.13	0.071
With 0.5 M Citric Acid							
0.99	0.09	0.072	0.80	9.50	9.00	12.7	0.082

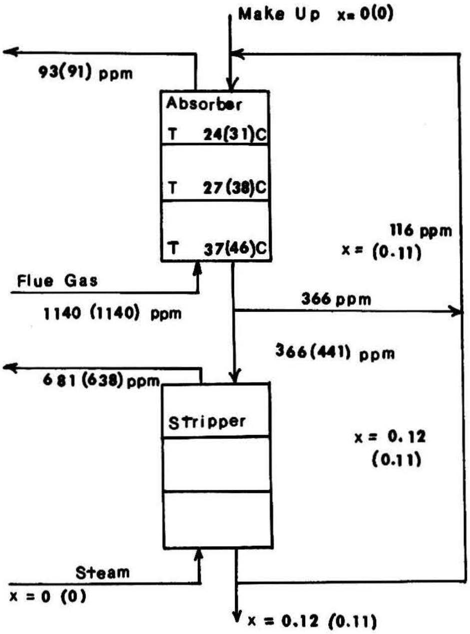

Figure 3. Process scheme for the internal recycle case.

moles/time. This behavior was also observed for the methyl pyrrolidone study.

Glycolic Acid

Glycolic acid was investigated in the same manner as citric acid. The results are listed in Table 5. The principal behavior is the same as the one in the citric acid case. The concentration of the water in the liquid phase does not vary considerably. The utility costs are decreasing with increasing recycle ratio with $R = 0.99$ again.

The cost determining factor was the make up material. As far as cost minimization by purge treatment goes, the remarks made in the last section hold.

It is worthwhile to point out that the costs for make up of the buffer solution are higher in the case of glycolic acid although it is less expensive than citric acid. This is due to higher liquid hold up in the absorber for glycolic acid; therefore, the required amount of make up is higher in the glycolic acid case. This increased hold up causes a larger steam input into the stripper. Therefore the selection of citric acid seems to be more favorable than glycolic acid regardless if the purge treatment is employed or not.

Variation of Absorber/Stripper Performance Data with the Number of Stages

A study was carried out to investigate the influence of the number of stages in each apparatus on the requirements for stripping steam and absorbent make-up. The number of stages in each column was increased from three to six in steps of one.

Table 6 contains the results of this study. As expected, the costs for stripping steam and feed make-up declined (42%). The savings in stripping steam are more pronounced (63%) than those for the absorbent feed reduction (39%), which in turn is more expensive. In general the incremental reduction of operating expenses per stage decreases for an increasing number of stages.

If the number of stages is increased, an impact between declining operating costs and increasing equipment costs is expected. A design of all absorber/stripper systems has been carried out for packed towers. The heights of the stripper and absorber columns have been calculated in order to meet mass transfer requirements. The cross sectional areas were selected to accommodate the fluid dynamics of the two phases within the packing. If consideration is given to the heat recovery system for the stripping steam, the total costs decrease because a smaller compressor is needed for the circulated steam.

As both operating costs and the costs for the purchased equipment decline with an increasing number of stages in the separation apparatus, nothing definite can be said about an optimum. However, as both cost items tend to level off, a flue gas desulfurization system with an absorber and stripper with six ideal stages seems to be most attractive.

TABLE 4. INNER RECYCLE STUDY FOR CITRIC ACID

Inner Recycle	Efficiencies Abs. (%)	Strip (&)	Liquid Flow Rate in the Absorber (mol)	Temperature in Abs. (°C)
0	90	90	1.0	51-59
0.1	87	91	1.03-1.04	51-59
0.3	81	93	1.32-1.34	51-59
0.4	78	94	1.54-1.56	51-59
0.5	74	95	1.84-1.87	51-59
0.6	71	96	2.30-2.33	52-59
0.7	67	97	3.06-3.09	52-29
0.8	64	98	4.56-4.61	53-59
0.9	61	99	9.03-9.09	55-59

TABLE 5. SIMULATION RESULTS FOR GLYCOLIC ACID; CHANGING RECYCLE RATIOS

Recycle	Absorbent Feed (g-mil) $*10^3$	($) $*10^3$	Stripping Steam (g-mol)	($) 10^6	Steam Make-Up (g-mol)	($) $*10^7$	Total ($) $*10^3$
0.00	15.40	10.6	0.39	4.63	0.086	1.23	10.6
0.50	9.35	6.45	0.485	5.76	0.104	1.49	6.45
0.75	5.40	3.73	0.57	6.77	0.121	1.73	3.74
0.90	2.35	1.62	0.65	7.72	0.134	1.92	1.63
0.99	0.17	1.17	0.70	8.32	0.142	2.03	1.25

Cost Consideration

Operating costs were determined to permit a comparison to be made between different solvents and the operating conditions so an optimum could be found. The operating and equipment costs have a degree of variability in them; however, they are meant to serve as a basis for comparison.

In order to get an idea about the cost range of the processes under consideration, the operating costs for the most favorable case have been referred to on an annual basis. The operational costs for citric acid in a process with twelve theoretical stages and at a recycle of 0.99 (see Table 6) are $4.78*10^{-5}$\$/mole flue gas. With a molelcular weight of the flue gas of 27 kg/kmol and a flow rate of 6890 kg/s, which is typical for a 500 MW power plant, [5], these costs are equivalent to

$$\$4.78*10^{-5}/\text{mol FG}*(3.048*10^{12}\text{mol FG/yr}) \quad (11)$$

$$= \$385*10^{6}/\text{yr}$$

If, however, no new buffer solution is necessary and everything can be recycled after being processed in a suitable purification unit, only the costs for stripping steam would arise. On an annual basis this scheme would give a cost of

$$3.56*10^{-6}\text{l/mol FG}*(8.048*10^{12}\text{mol FG/yr}) \quad (12)$$

$$= \$28.6*10^{6}/\text{yr}$$

or

$$= \$6.63*10^{-3}/\text{kWh} = 6.63 \text{ mils/kWh} \quad (13)$$

This is comparable to the annual costs for other flue gas desulfurization systems producing salable products, as listed in the EPA Utility Survey [8]. The annual costs range from 2.2 mils/kWh for the magnesium oxide process to 14.9 mils/kWh for the Wellman-Work process. Figure 4 gives a three dimensional plot showing the effect of temperature and pressure on this cost.

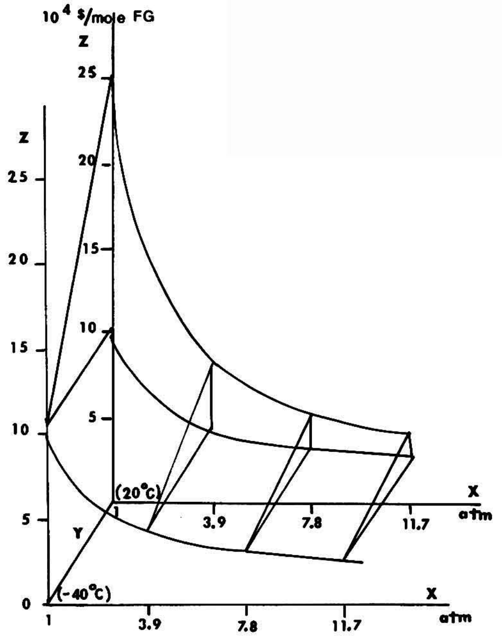

Figure 4. Interaction between temperatures and pressure in the absorber and operating costs for SO_2 absorption.

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TABLE 6. INFLUENCE OF NUMBER OF STAGES ON OPERATION COSTS

Recycle: 0.99
Absorbent: Citric Acid, 0.5M

Number of stages in each unit	Absorbent Feed, CA (mole)	Absorbent Feed, CA (10^{-5}\$)	Steam Feed (mole)	Steam Feed (10^{-6}\$)	Steam Make-Up (mole)	Steam Make-Up (10^{-8}\$)	Total (10^{-5}\$)
3	$9.0*10^{-5}$	7.23	0.8	9.5	0.09	12.7	8.18
4	$6.8*10^{-5}$	5.46	0.49	5.82	0.071	10.02	6.04
5	$6.0*10^{-5}$	4.82	0.37	4.40	6.4	9.03	5.26
6	$5.5*10^{-5}$	4.42	0.30	3.56	5.9	8.33	4.78

Improvements in Acetone Adsorption Efficiency

The use of a forced air-cooling cycle in a steam-regenerated carbon bed can lead to a significant increase in efficiency.

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Industrial process solvents are recovered by a variety of unit operations. Solvents in an air stream at low concentrations (10-30% LEL) are usually recovered via fixed carbon bed adsorption [*1-3*]. In fixed bed operations, after a carbon bed has adsorbed a working charge of solvent, the solvent is removed and collected so that the carbon can be reused. Multiple adsorbers are used in parallel to facilitate the regeneration process since a regenerating carbon bed is isolated from the solvent laden air (SLA).

Adsorbed solvent is usually removed from a carbon bed by using a steam purge to raise the temperature of the bed. As the temperature increases, the solvent load on the carbon decreases, and the desorbed solvent is carried out of the carbon bed by uncondensed steam. After the working charge has been removed, the adsorber is ready to collect more solvent from the SLA stream. However, the carbon bed is hot and saturated with water after steaming, and the adsorption process is more efficient if the adsorbent is relatively cool and dry. The objective of this study was to quantify the benefits and disadvantages of adding a cooling cycle to plant scale fixed bed adsorption equipment.

Cooling Cycles

Information in the literature and public opinion on cooling cycles varies from "cooling cycles are essential" to "cooling cycles are unsafe." Nonhebel [*1*] indicates the adsorption process is inefficient without a cooling cycle because the high water loadings, due to steam regeneration, reduce the capacity of the adsorbent to hold volatile organic compounds (VOCs). He also says that some adsorbed water is desirable so that solvent heats of adsorption can be negated by the desorbing water. Mantel [2] is neutral on the subject and suggests that cooling cycles may be unnecessary. He feels that the SLA dries and cools a carbon bed enough to prevent inefficiencies. Some process engineers feel that a relatively water-free carbon bed is dangerous, since dry carbon has a very high affinity for particular organic compounds and no means of dissipating the heats of adsorption. Hot spots form and may eventually develop into fires.

Parmele [3] offers a qualitative justification for cooling cycles by stating that high adsorption efficiencies are impossible without a cooling cycle, since hot and wet carbon beds work against the adsorption process in the beginning of the adsorption cycle. He also claims that the SLA will prevent heats of adsorption from raising the temperature of a carbon bed if solvent concentrations are low. Some activated carbon vendors state that corrosion problems are more severe in adsorption systems that do not cool and dry the carbon before introducing SLA. Evidently, solvent degradation reactions are more prevalent in a hot and wet carbon catalyst environment [*4*].

While Parmele's arguments are reasonable, retrofitting existing solvent recovery systems with cooling cycles cannot be justified based on qualitative engineering judgments. A computer model of plant scale adsorption equipment was needed to achieve the objective of this study. The formulation of the adsorption model was straightforward. However, obtaining the data that was required by the model and solving the set of equations that form the model were difficult.

Literature Review

To predict adequately the transient effect of the cooling cycle on a one-dimensional carbon bed adsorber, the mathematical model is, by necessity, complicated. The solutes carried by an incompressible carrier gas compete for space on the carbon particles and cannot be studied separately. The carbon bed is initially hot and wet (having been regenerated by steam) and is cooled by desorbing water into the air stream. The local equilibrium loading of the solutes is affected by the non-isothermal nature of the process. Finally, the slow approach of the actual loadings on the bed to the asymptotic equilibrium values infers significant resistance to mass transfer, which adds non-linear coupling effects to the problem. To meet these requirements, the governing set of coupled, non-linear partial differential equations (PDEs) were solved, as with most complicated problems of engineering interest, by numerical solution techniques. The model was limited to adsorption processes since desorption using steam involves different mechanisms. In the literature, only one paper was found that attempted to study a steam desorption model [*5*].

Rhee *et al.* [*6*] have reviewed the classical fixed-bed studies that used numerical solutions and Hlavacek *et al.* [*7*] have reviewed the general literature through 1979 for the various numerical techniques being used in adsorption modeling. Typical solution methods since 1979 continue to follow the same general trend. There are three basic computation methods: the Method of Characteristics [*8-12*], Orthogonal Collocation [*13-20*], and the Finite Difference Method [*15, 21-33*]. The basic equations to be solved are similar to those of Harwell, *et al.* [*8*], with the second-order diffusion and conductivity terms being added. No attempt is made to compare this continuous model to others, such as the cell model [*15, 21*].

Other researchers [*6, 7, 15*] have compared the various solution methods and concluded that particular problems are often best matched to a particular numerical technique. However, Finlayson [*34*] concludes that the Finite Difference Method (FDM) is probably best suited for the most general (and complicated) problems. As pointed out by Finlayson, two major drawbacks to FDM solutions of typical convection-diffusion equations are 1) the numerically generated oscillations that can occur for large Peclet numbers, and 2) the inaccuracies that can occur at sharp gradients over inadequate meshes. Two alternative ways to avoid these problems without an objectionably large number of spatial grid points are 1) to use higher-order differencing approximations [*35*], or 2) to use an adaptive (variable) mesh [*7, 15, 25, 36, 37*]. Thomson [*38*] recommends (in agreement with others [*39, 40*]) that using adaptive meshes with standard solution methods is preferable to higher-order-accurate schemes with uniform meshes. An adaptive mesh technique proposed by Eigenberger and Butt [*41*] was selected for use with a central differenced FDM scheme.

Limitations of Model

In recent work [*42*], several assumptions were made and limitations imposed to enable the known physical data to be incorporated into the mathematical model in a reasonable time frame. These are listed below.

1. Constant axial velocity.
2. No radial (transverse) variations.
3. Constant gas density.
4. For each component, the heat of adsorption is equal to the heat of vaporization.
5. For each component, the mass transfer coefficient is constant throughout a given simulation.
6. For any given cross-section, the gas and solid are in thermal equilibrium.
7. Multicomponent Langmuir equilibrium is assumed with no interaction on a bed between adsorbates.
8. No oxidation reactions.

The use of an ideal multicomponent, Langmuir-type equilibrium equation had a large impact on the results of the adsorption model. Several methods are available for modeling multicomponent adsorption equilibrium data [*43-46*]. The Langmuir model [*43*] is one of the oldest models that predicts multicomponent results from single component isotherms. The ideal adsorbed solution (IAS) model [*44*] is not better than the Langmuir model, since adsorbed component interactions are not considered by either. Costa *et al.* [*46*] have the best alternative found in the literature, short of obtaining multicomponent data, for predicting non-ideal interactions. They use liquid phase activity coefficients with the IAS model.

Acetone and water were the components of interest in this study. Acetone and water single-component equilibrium isotherms were available in proprietary literature [*47, 48*]. The acetone data, shown in Figure 1, were fit by regression analysis to Equation 9, which is the standard Langmuir equation. However, a problem developed when attempting to regress the S-shaped water data shown in Figure 2, which cannot be adequately represented by the Langmuir form. To circumvent the difficulty, water loadings on carbon at low gas-phase water concentrations were ignored, and the curves truncated along the dotted lines. The remaining curves were overlapped using the truncation/axis-intersection as a common origin, which produced curves similar to Figure 1. The regressed equations were then transposed horizontally by a coordinate transformation, back to their original location, resulting in Equation 10. The separately regressed single-component equations were combined in the final Langmuir form of the multicomponent equilibrium equation by summing the denominator terms. The loss of carbon activity with age was not considered. The errors created by assuming ideal multicomponent Langmuir adsorption were thought to be greater than those due to the assumption of new carbon.

Constant overall mass transfer coefficients (MTCs) in the rate equations also limit the model. While several methods are available for predicting MTCs, the data required by the methods severely restricts their use [*49*]. Effective diffusivity and particle geometry are used to calculate a MTC [*49, 50*]. In this study, the effective diffusivities of the adsorbing components, as they migrated to the interior of the carbon particles, were not known. Since pore and particle diffusion were considered to be the adsorption rate limiting steps, important mass transfer variables had to be approximated and assumed constant throughout a given simulation. Although the MTC for acetone was arbitrarily selected in this study, the ratio of the water MTC to that of acetone was kept at a constant 5.0 value. The ratio of air diffusivities for water and acetone is approximately 2.5 [*51*]. While this ratio is probably not applicable to effective particle diffusivities, the effective diffusivity for water is probably greater than that for acetone. Later, it will be shown the MTC for water had little effect on the results.

In actual plant operations the gas phase velocity may vary by as much as 25% because of temperature gradients in the carbon beds. Velocity has a large effect on system performance. Since temperature also affects the gas phase density, the constant density assumption may have influenced the outcome of this work. Assuming that the heats of adsorption were equal to the heats of vaporization for the adsorbates was a close approximation. According to Brunaer [*43*], the integral heat of adsorption for water is nearly equal to its heat of vaporization. While no data was found for acetone, Brunaer also states that the heats of adsorption for organic compounds are generally 1.5 times their respective heats of vaporization. However, a 50% increase in the heat of vaporization for acetone was not used and possible effects will be discussed later.

A final limitation that affected the results of this study was the condition of the carbon bed after the steaming cy-

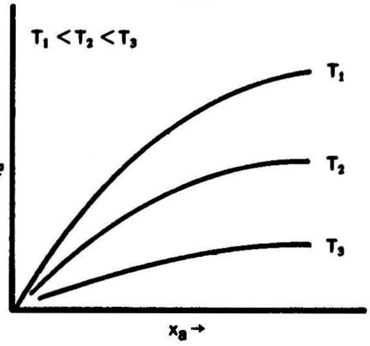

Figure 1. Acetone equilibrium loadings *vs.* concentration and temperature.

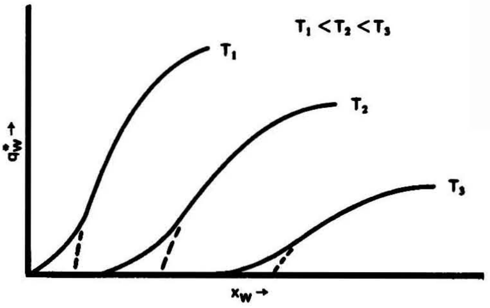

Figure 2. Water equilibrium loadings *vs.* concentration and temperature.

cle. The initial temperature and water concentration profiles were assumed to be flat and at equilibrium with steam at desorption conditions. Also, the bed did not contain acetone. In actual plant operations, an adsorbate heel is left on the carbon after the desorption cycle. Since the magnitude of the heel is unknown, the assumed initial conditions of the carbon bed probably had the same general effects on the model as the assumptions for the values of the equilibrium and mass transfer parameters. In other words, these three assumptions are closely related and changing any one affects the solvent adsorption rate. These effects will be discussed later along with details of how the MTCs were varied to duplicate operations in existing carbon beds.

Computer Model

For the two-component, non-equilibrium, non-isothermal, one-dimensional model of adsorption in a fixed bed, subject to the proceeding assumptions, the following equations apply. A glossary of notation is listed elsewhere.

$$\frac{\partial x_1}{\partial t} = D_1 \frac{\partial^2 x_1}{\partial z^2} - \frac{v}{\epsilon} \frac{\partial x_1}{\partial z} - \rho_b \frac{K_1}{\epsilon} (q_1^* - q_1) \tag{1}$$

$$\frac{\partial x_2}{\partial t} = D_2 \frac{\partial^2 x_2}{\partial z^2} - \frac{v}{\epsilon} \frac{\partial x_2}{\partial z} - \rho_b \frac{K_2}{\epsilon} (q_2^* - q_2) \tag{2}$$

$$\frac{\partial T}{\partial t} = \frac{(1 - \epsilon) K_T}{\overline{\rho c}} \frac{\partial^2 T}{\partial z^2} - \frac{v \rho_g c_{pg}}{\overline{\rho c}} \frac{\partial T}{\partial z} + \frac{K_w}{\overline{\rho c}} (T_s - T) + \frac{(\Delta H_1)}{\overline{\rho c}} \rho_b K_1 (q_1^* - q_1) + \frac{(\Delta H_2)}{\overline{\rho c}} \rho_b K_2 (q_2^* - q_2) \tag{3}$$

$$\frac{\partial q_1}{\partial t} = K_1 (q_1^* - q_1) \tag{4}$$

$$\frac{\partial q_2}{\partial t} = K_2 (q_2^* - q_2) \tag{5}$$

The first two equations are the mass balances for the two different solutes in an inert gas stream. The last term in each represents the rate of adsorption/desorption into the carbon bed. The third equation represents an energy balance of the combined gas/bed system. It includes heat transfer by conduction in the porous bed, convection in the gas, heat loss to the surroundings and heat addition/removal due to the adsorption/desorption rates of the solutes. The final two equations model the adsorbate loadings subject to a non-equilibrium linear driving force. Since the equilibrium loading q_i^* is typically a known (often regressed) function of the local concentrations and temperature, the first three equations are non-linear.

These five equations form a set of coupled, non-linear PDEs to be solved for two solute concentrations in the gas, an averaged gas/bed temperature, and two solute loadings on the bed. The five dependent variables are to be found in profile form down the length (depth) of the fixed bed for all times under consideration, subject to the specified boundary and initial conditions,

$$\left.\frac{\partial x_i}{\partial z}\right|_{x=0} = \frac{v}{D_i \epsilon} (x_i|_{z=0} - x_{iF}), \ i = 1, 2 \tag{6}$$

$$\left.\frac{\partial T}{\partial z}\right|_{z=0} = \frac{v \, \rho_g \, c_{pg}}{(1 - \epsilon) K_T} (T|_{z=0} - T_F) \tag{7}$$

$$\left.\frac{\partial x_1}{\partial z}\right|_{z=l} = \left.\frac{\partial x_2}{\partial z}\right|_{z=l} = \left.\frac{\partial T}{\partial z}\right|_{z=l} = 0 \tag{8}$$

for $0 < z < l$ (entrance at zero, exit at l), where $x_{iF} (i = 1, 2)$ and T_F are the feed values. The initial conditions are initial bed profiles for each of the dependent variables.

For this analysis, three point central difference approximations (for variable step-sizes) are employed for the spatial derivatives. Following Eigenberger and Butt [41], the differences are evaluated at the center of the "element," rather than at the center grid. Comparing the two approximations, centering the difference quotient at the element's center tended to be somewhat more stable when oscillations began to appear in the convectively dominated solutions. The three-point central differencing results in a non-symmetric tri-diagonal coefficient matrix, solvable by Thomas' algorithm [52].

The time derivative is evaluated as a two-point difference quotient with a fully implicit weighting of the right-hand side of the PDEs. For the non-linear source/sink terms, Quasilinearization [41, 53] is applied to form an orderly iteration procedure. The grid-adjuster routine [41] is basically a check of the smoothness of a parabolic curve-fitting over consecutive solution values. Through its addition (with interpolation) or deletion of grid points, the mesh adjuster gives the appearance of "moving" the grids so that the region of finer mesh can "follow" sharp gradients as they move through the bed in time. Due to the variability of the number and location of grid points, use of any varying time-step routines [54] becomes very cumbersome. Thus, only a constant time step was used in this numerical model.

The acetone equilibrium data (as depicted in Figure 1) were fit by regression analysis to the Langmuir-type equation

$$q_a^* = \frac{(A_1 + B_1 T + C_1 T^2) \, x_a}{1 + (A_2 + B_2 T + C_2 T^2) \, x_a} \tag{9}$$

using the Harwell Subroutine Library's VA05A. For water, the S-shaped equilibrium curves (shown in Figure 2) were modified, as discussed earlier, and fit by regression analysis to Equation (10).

$$q_w^* = \frac{(D_1 + E_1 T + F_1 T^2)[x_w - (G + HT + IT^2)]}{1 + (D_2 + E_2 T + F_2 T^2)[x_w - (G + HT + IT^2)]} \tag{10}$$

The computer program was written in standard double precision FORTRAN, and modeling a typical acetone/water-vapor/carbon-bed system for a complete adsorbing cycle, required 8 CPU minutes on an IBM 3033 (6500 integration steps). The number of grid points varied from 20 to 60, averaging 35 during a typical run. (Recall that five equations are solved at each grid). Also, the number of non-linear iterations changed due to the amount of variation in the solution between consecutive time-levels, which ranged to a maximum of 7 and averaged less than 2. The numerical results were easily plotted on printer paper (with reasonable resolution) by using a slightly modified form of IMSL routine USPLOT.

Matching Plant Data

The lack of key input parameters prevented the evaluation of cooling cycles solely with the computer model. However, operating data for existing plant-scale adsorbers were available, and the computer model duplicated plant operations after selecting appropriate values for the unknown input parameters: MTCs, equilibrium data, and initial carbon bed concentration and temperature profiles.

The shapes of the breakthrough curves were like those shown in Figure 3. The addition of a solvent heel to the initial bed profiles raised the left tail of the curve. Scaling the acetone equilibrium data, by multiplying Equation (9) by a constant, shifted the breakthrough curve on the time axis. The curve moved, intact, to the right when equilibrium loadings were increased and to the left if the loadings were decreased. The mass transfer coefficients affected the slope of the breakthrough curve, as shown in Figure 4. With this knowledge of the effects of the various input parameters, the computer model was used to rate several existing carbon bed operations.

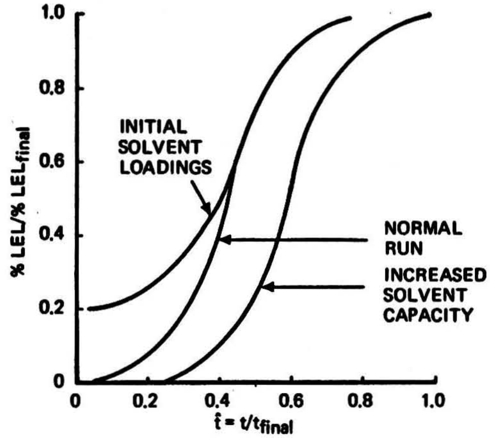

Figure 3. Exhaust acetone concentration vs. time for different bed conditions.

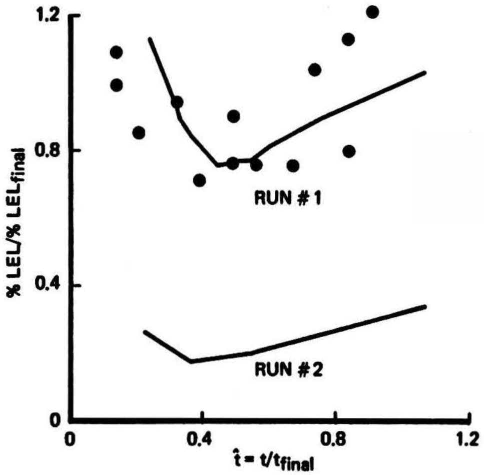

Figure 5. Exhaust acetone concentration vs. time compared to plant data (●).

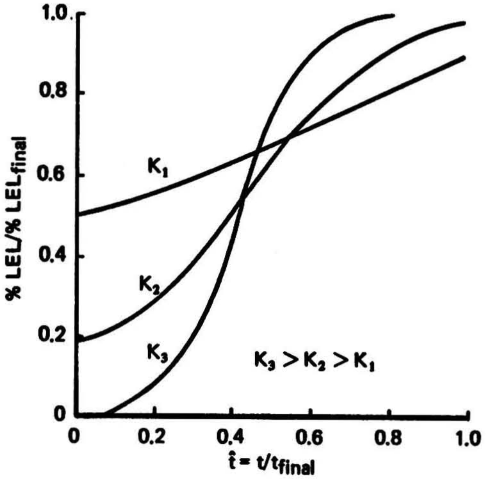

Figure 4. Exhaust acetone concentration vs. time for different acetone MTCs.

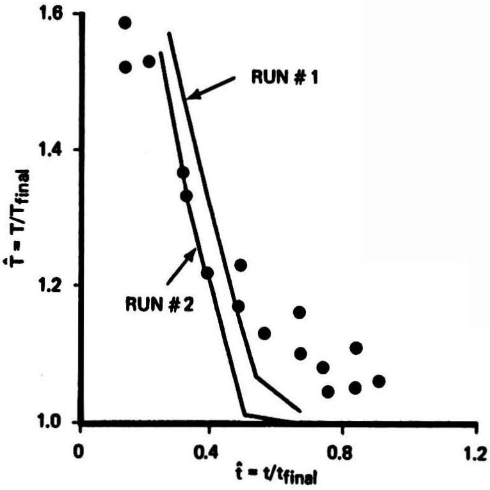

Figure 6. Exhaust air temperature vs. time compared to plant data (●).

Figure 5 shows plant data from a typical carbon bed, and the computer model predicted effluent concentrations using two values for the solvent MTC. To simplify the problem, the assumed equilibrium model and initial conditions were not varied. The time-averaged adsorption efficiencies for Run No. 1 and the plant data are the same. The solvent MTC in Run No. 2 was greater than that in Run No. 1. Figure 6 shows that the model does not fit the observed temperature data as well as it does effluent concentration data. Using a larger value for the heat of adsorption for acetone would improve the correlation substantially. The correlation was slightly improved after considering the heat capacity of the adsorbed water.

The MTCs that were used to model a carbon bed were also used in computer runs that simulated the addition of a cooling cycle prior to the adsorption cycle. The duration of the cooling cycle was limited to the time difference between the adsorption cycle and the steam cycle. The drying medium was an air stream equivalent to the SLA but without acetone.

Cooling Cycle Results

The effluent concentrations and temperatures in a carbon bed system retrofitted with a cooling cycle, as predicted by the computer model, are shown in Figure 7, 8, and 9. These results are compared to the effluent concentrations of the same system, but without a cooling cycle. Figures 10, 11 and 12 illustrate bed conditions during an adsorption cycle, and the only difference in the shape of the curves, between cooling and no cooling, was a shift in the time scale. For instance, the water loading curve in Figure 11 at $\hat{t} = .23$ became the water loading curve at $\hat{t} = 0$ with a cooling cycle. The primary effect of the cooling cycle was to purge the carbon bed of approximately 30% of its adsorbed water. The drying process had large cooling effect as illustrated in Figures 9 and 12. The SLA had the same effects, but as shown in Figure 7, with a major exception. While drying with solvent laden air, during the time interval $.23 < \hat{t} < .38$, acetone was being exhausted from the adsorber. Drying and cooling with pure air prior to the

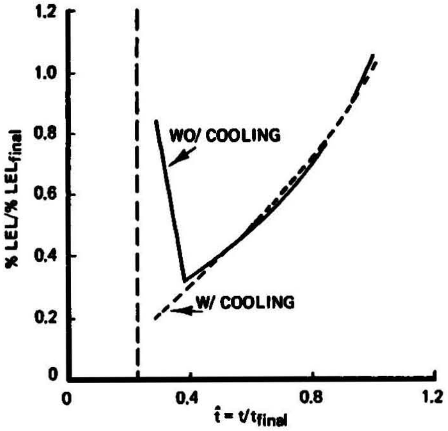

Figure 7. Exhaust acetone concentration vs. time (adsorption cycle begins at time = .23).

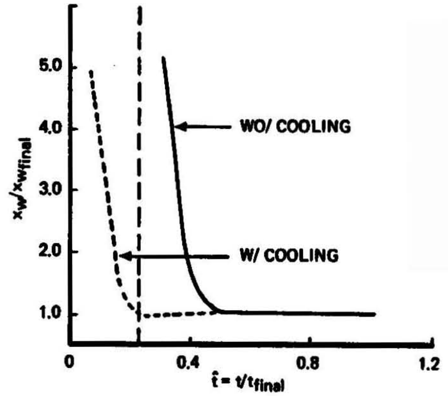

Figure 8. Exhaust water concentration vs. time (adsorption cycle begins at time = .23).

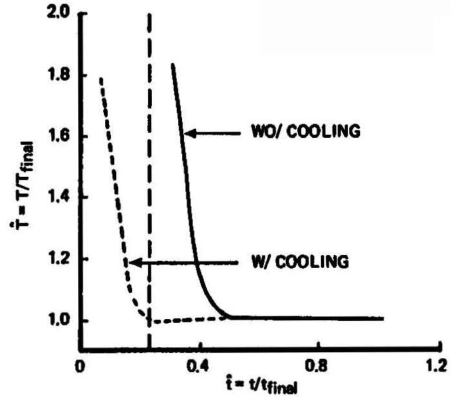

Figure 9. Exhaust air temperature vs. time (adsorption cycle begins at time = .23).

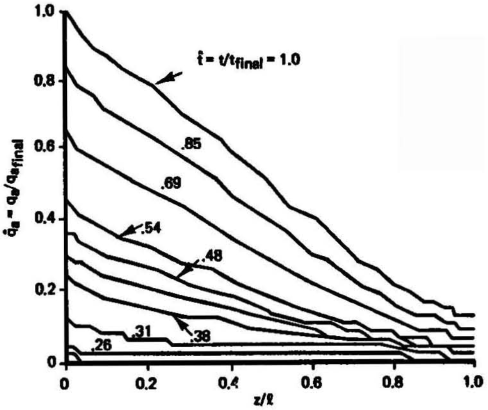

Figure 10. Acetone loading profiles at different times.

adsorption cycle increases adsorption efficiency by decreasing the initial acetone loss.

Most of the water left in the carbon bed after steaming remains in the carbon indefinitely. Figure 11 indicates that 65% to 85% of that water never leaves the system. The residual concentrations of water were slowly moving toward an equilibrium value that coincided with the inlet conditions of the solvent laden air, $\hat{q}^*_{w} = .51$. But, the rate of water mass transfer seemed to be slowed greatly by the lack of energy available to desorb the water. The only source of that energy, once the carbon bed temperatures had equilibrated at $\hat{T} \sim .40$, was the heat of adsorption for acetone. These phenomena explain the insensitivity of the model to the water mass transfer coefficient, the need for accurate heat of adsorption data, and the need for good multicomponent equilibrium data.

Unlike water, the major mass transfer limitations for acetone were its mass transfer coefficient and the adsorbed water. As discussed earlier, the simplifications in the equilibrium model and initial bed loadings were compensated by adjustment of the MTCs. The driving force for acetone mass transfer was reduced approximately 40% because of the adsorbed water. Also, it seems likely that the observed acetone mass transfer coefficient would increase in magnitude if the resistance provided by water could be eliminated.

The safety concerns about fires developing in carbon beds that use cooling cycles have not been completely addressed, but seem to be unsupported. The trends observed for low concentration acetone recovery indicate that a cooling cycle will not remove the water heat sink. The same amount of water removed by a cooling cycle is removed in normal carbon bed operations. The two processes have nearly identical final water loadings.

Economics

The engineering objective of this study was to evaluate the economics of retrofitting existing fixed carbon bed adsorbers with forced air cooling cycles. Safety concerns seem to be unsupported because of the residual water left on the bed. Also, the lower adsorption temperatures are are said to reduce corrosion problems by slowing solvent degradation reactions. While these are qualitative statements, they at least favor installing cooling cycles. However, the computer simulation predicted a 4% increase in adsorption efficiency via a cooling cycle, which was considered a significant improvement. The only disadvantages to installing a cooling cycle were the capital required and the increase in fan operating costs (the effluent air from one bed was assumed to be the cooling air for another bed). While the costs are relative, favorable economics indicated a substantial incentive for installing a cooling cycle.

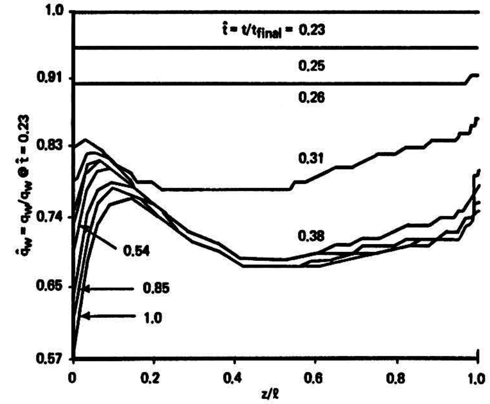

Figure 11. Water loading profiles at different times.

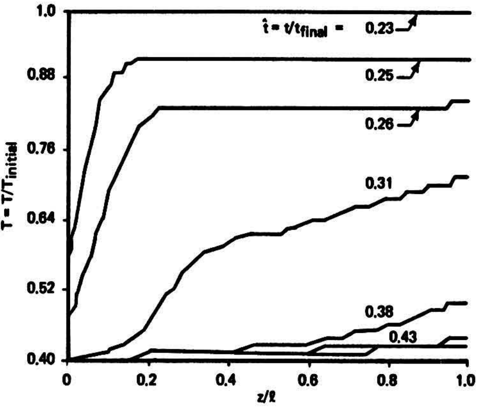

Figure 12. Bed temperature profiles at different times.

CONCLUSIONS

The adsorption of acetone and water from an air stream into a plant scale fixed carbon bed has been studied with and without a cooling cycle, after steam regeneration. The governing equations for a two-component, non-equilibrium, non-isothermal, one-dimensional carbon bed model form a set of coupled, non-linear partial differential equations. A computer program was developed to solve these equations numerically by a variable-grid finite-difference technique.

The computer simulations of the cooling cycle demonstrated that its primary effect was to purge a carbon bed of approximately 30% of the water adsorbed during the steam regeneration. This drying process also had a large cooling effect on the bed. Both of these effects enhanced the capability of the carbon bed to adsorb acetone once the bed was put back on stream. Without the cooling cycle, the solvent laden air stream also cooled and dried the bed, but, at least initially, acetone was being exhausted from the adsorber.

The projected 4% efficiency gain in the operation of the bed due to the addition of a cooling cycle was considered a significant improvement. The only disadvantages to installing a cooling cycle were the required capital and the increased operating costs of the fan. (The effluent air from one bed was assumed to be the cooling air for a parallel bed). While the above costs are relative, favorable economics indicated a substantial incentive for the installation.

NOMENCLATURE

c_{pb} = specific heat of bed, Btu/°F-lb bed (J/kg-°K)
c_{pg} = specific heat of gas, Btu/°F-lb gas (J/kg-°K)
$D_i(i = 1, 2)$ = diffusion coefficient for each component, ft²/min (m²/s)
ϵ = void fraction, ft³ void/ft³ bed (m³/m³)
$\Delta H_i(i = 1, 2)$ = heat of adsorption for each component, Btu/lb solute (J/kg)
$K_i(i = 1,2)$ = time parameter in the mass transfer rate equation for component (MTC), min^{-1} (sec^{-1})
K_T = thermal conductivity of bed, Btu/min-°F-ft (J/m-s-°K)
K_w = heat transfer coefficient to atmosphere, Btu/min-°F-ft² (J/m²-s-°K)
l = length, or depth of carbon bed, ft (m)
$q_i(i = 1, 2)$ = bed loading for each component, lb solute/lb bed (kg/kg)
$q_i^*(i = 1, 2)$ = equilibrium bed loading for each component, lb solute/lb bed (kg/kg)
ρ_b = bulk bed density, lb bed/ft³ bed (kg/m³)
ρ_g = gas density, lb solvent/ft³ bed (kg/m³)
$\overline{\rho c}$ = $\epsilon \rho_g c_{pg} + \rho_b c_{pb}$
t = time, min (sec)
T = combined gas/bad temperature, °F (°K)
T_F = feed temperature of inlet gas, °F (°K)
T_s = ambient temperature, °F (°K)
v = superficial gas velocity (uniform throughout bed), ft/min (m/s)
$x_i(i = 1, 2)$ = concentration of each component in gas, lbs solute/ft³ solvent (kg/m³)
$x_{iF}(i = 1, 2)$ = concentration of each component in inlet gas, lbs solute/ft³ solvent (kg/m³)
z = space dimension measured in direction of gas flow, ft (m)
$\hat{}$ = superscript refers to non-dimensional parameters as defined in the attached figures.

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Field Evaluation of Volatile Organic Compound Removal Efficiency for Full Scale Carbon Adsorption Systems.

Actual test data show that fixed-bed carbon adsorption systems can consistently operate at 95 percent VOC reduction or greater.

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The US Environmental Protection Agency (EPA) is currently evaluating the environmental and health impacts of volatile organic compound (VOC) emissions from a variety of industrial sources. As part of this effort, Radian Corporation has conducted a program (EPA Contract No. 68-03-3038) to evaluate the performance of full-scale vapor-phase carbon adsorption VOC control systems used for solvent recovery at industrial surface coating facilities. The program has focused on the field performance testing of several fixed-bed, steam-regenerated carbon adsorption systems used in the rubberized fabric, magnetic tape, and flexible packaging industries. The primary objective of the program was to assess the long-term VOC reduction performance of activated carbon adsorption systems.

This paper summarizes the technical results of the program. In particular, it discusses the testing methodology and analysis of the test results. Also, economic data for the full-scale carbon adsorption systems will be presented.

BACKGROUND

Surface coating involves the application of a material to a paper, plastic, metal, fabric, or wood substrate to form an intermediate or end-product with certain desired characteristics. Often the coating material is suspended or dissolved in an organic solvent and is applied to the substrate in a fluid state. Emissions of solvent vapors or volatile organic compounds (VOCs) occur during various processing steps, but primarily from the drying or curing of the wet coated substrate.

It has been estimated that the solvent emissions from the surface-coating industry account for approximately 10 percent of the 17,000,000 tons per year of man-made nonmethane VOC emissions in this country [*1*, *2*]. Therefore, surface coating ranks fourth as a VOC source behind fossil fuel handling and refining, solid waste disposal, and open sources (e.g., agricultural burning). It is estimated that over 80 percent of the VOC emissions from the surface coating industry are controllable [*1*]. Current available control technologies include coating process modifications, the use of low-solvent or solvent-free coatings, and the use of add-on control systems, such as carbon adsorption and incineration, either thermal or catalytic.

Regulatory Activity

The surface coating industry has become the subject of increasing regulatory activity because: 1) the industry contributes significantly to national and local VOC emission levels and 2) it has been determined that a significant portion of the VOC emissions can be controlled in an economically and environmentally acceptable manner.

Initial regulation of VOC emissions from surface coating facilities was imposed by local air pollution regulatory agencies, the most notable being Rule 66—Organic Solvent, adopted by the Los Angeles Air Pollution Control District. Rule 66 was a technology-forcing regulation which gave preferential treatment to users of so-called "non-photochemically reactive" solvents. Other local and state agencies adopted VOC regulations similar to Rule 66 on an as-needed basis.

The passing into law of the Clean Air Act and its 1977 amendments provided more systematic strategies for federal and state regulation of existing and new sources of VOC (and other) emissions [3]. For regulation of existing sources, the US EPA issued a series of documents referred to as Control Technique Guideline (CTG) reports. The CTG reports were designed to assist state agencies in the drafting of regulations, referred to as State Implementation Plans (SIP), most of which are now in place. For regulation of new sources, the federal EPA assumed the responsibility of drafting applicable regulations, referred to as New Source Performance Standards (NSPS) or, in the case of toxic materials, National Emission Standards for Hazardous Air Pollutants (NESHAP). NSPS regulations pertaining to new surface coating facilities that have been promulgated (finalized) include those for metal furniture, automobiles and light-duty trucks, graphic arts (publication rotogravure printing), large appliances, metal coil, pressure-sensitive tapes and labels, and beverage cans (3-10). NSPS are currently being considered or drafted for the magnetic tape, rubberized fabric, and flexible packaging coating industries. The NSPS which have been proposed and promulgated are generally based on the use of low-solvent or solvent-free type coatings or the use of add-on control technology.

Carbon Adsorption as a VOC Control Option

Add-on VOC control devices, such as carbon adsorption or incineration systems, have been widely used in the surface coating industry because they are readily available and generally do not adversely affect the coating process or product quality. In general, incineration of solvent vapors is selected for surface coating operations that are subject to VOC emission regulations but use a solvent formulation for which recovery is technically impractical. By comparison, the selection of carbon adsorption for VOC control is governed by economic, as well as regulatory, incentives. In particular, carbon adsorption/solvent recovery is suited for applications having a solvent formulation that is relatively expensive and/or easily recovered (i.e., either comprised of a single immiscible solvent or of several compounds that can be easily separated or reused as a mixture).

CARBON ADSORPTION THEORY AND APPLICATIONS

Over the past 50 years, significant research has been undertaken in academia and industry to achieve both fundamental and practical understanding of the adsorption of organic materials on active carbons. Several theories have been proposed to analytically predict activated carbon capacities [*11*]. Prominent among these is the Polanyi potential theory (with later revisions by Dubinin). With the potential theory, the adsorption capacity of a particular carbon-solvent pair can be used to predict the adsorption capacities of the particular carbon for numerous other organic compounds.

Most of the research to date has been for single organic components on a single virgin carbon. In actual application, most full-scale industrial systems use multicomponent solvents. However, theoretical derivations for multicomponent systems are complex and difficult to use. Although multicomponent theories have been developed, often based on concepts and data for single component theories, they are not as well developed or understood as the single component theories.

The design and application of full-scale carbon adsorption systems is a mature science. Designs are often based on theoretical predictions; however, a significant portion of design comes from "rule-of-thumb" factors and past operating experience. During adsorption, solvent-laden air (SLA) from the surface coating operation passes through the carbon bed at superficial velocities in the range of 0.15 to 0.50 meters per second (30 to 100 feet per minute). Bed depths range from 50 to 125 centimeters (20 to 50 inches). Usually, the inlet SLA temperature is less than 38°C (100°F) and the relative humidity is less than 50 percent. For regeneration of the carbon bed, low pressure steam is typically used to heat the bed and displace the adsorbed solvents. After steam regeneration, most designs provide for a cooling/drying period before the carbon bed is placed back in service.

SELECTION OF TEST SITES

Three criteria were used to select the test sites for the test program. These were: 1) selection of approximately two carbon adsorption systems in each of the rubberized fabric, magnetic tape, and flexible packaging industries; 2) selection of well-operated systems; and 3) selection of systems that processed a variety of solvents. These plants also had to be willing to cooperate during a two week test period and during a possible additional week of testing.

These criteria resulted in the initial identification and screening of almost 50 carbon adsorption systems. From the 50 systems, the final screening process resulted in the selection of six carbon adsorption system test sites. These sites were initially tested in 1982, with four of the six sites retested in 1983. The plant types and test dates are as follows:

- Plant 1—a rubberized fabric manufacturing facility using methyl ethyl ketone (MEK) solvent, tested in January 1982;
- Plant 2—a magnetic tape producer using a solvent mixture of toluene and tetrahydrofuran (THF), tested in February 1982 and retested in December 1983;
- Plant 3—a magnetic tape producer using a solvent formulation of toluene, THF, MEK, methyl isobutyl ketone (MIBK), and cyclohexanone, tested in March 1982;
- Plant 4—a flexible packager using hexane solvent, tested in June 1982 and retested in November 1983;
- Plant 5—a rubberized fabric manufacturer using toluene solvent, tested in July 1982 and retested in November 1983; and
- Plant 6—a flexible packager using a solvent formulation consisting primarily of toluene and isopropyl acetate (IPAC), tested in August 1982 and retested in November 1983.

The four retest sites were chosen because they did not experience major operating changes (primarily carbon replacement) since the original testing. The design of these systems and the results of testing are described in the next sections.

CARBON ADSORBER DESIGN PARAMETERS

The plants tested in this program represent a wide range of designs. For example, the adsorption systems at the rubberized fabric and flexible packaging plants feature horizontal carbon beds, although SLA flow direction through the beds differs (downward for the rubberized fabric plants and upward for the flexible packaging plants). Conversely, the magnetic tape plants feature adsorption systems with annular carbon beds although, again, SLA flow direction through the bed differs (inward for Plant 2 and outward for Plant 3). The number of carbon beds also varies considerably depending on plant size. The smallest system at Plant 1 (SLA capacity of 5.3 Nm^3/sec) has two beds, while the largest facility at Plant 6 (37.8 Nm^3/sec) features six beds.

The relative SLA flow rates, as compared to the bed carbon capacity, average approximately 0.0015 Nm^3/sec/kg carbon (1.5 scfm/lb carbon) for the six tested systems. Four of the plants have systems with relative SLA flow rates closely approximating this average value, but the designs for the adsorption systems at Plants 2 and 6 deviate significantly from the mean. The Plant 6 system design features a relatively conservative 0.00069 Nm^3/sec/kg carbon (0.65 scfm/lb carbon), whereas the Plant 2 design is characterized by a relatively high 0.0026 Nm^3/sec/kg (2.5 scfm/lb). Also, the horizontal bed systems generally feature average design superficial bed velocities of 0.45 m/sec (89 fpm), while the thin-bed designs of the annular bed systems feature lower velocities, nominally 0.33 m/sec (65 fpm).

Design solvent types vary considerably, although toluene is a major design component at five of the six plants. The lightest liquid molar volume solvent formulations are used at the magnetic tape plants and the heaviest solvents are used at the flexible packaging plants. The six designs are characterized by significant differences in inlet solvent loadings, with inlet concentrations ranging from less than 1000 ppmv to over 4000 ppmv. On a carbon basis, design solvent loadings vary over an order of magnitude, from 0.0066 to 0.097 kg solvent/kg carbon (0.0066 to 0.097 lb solvent/lb carbon).

Cost data were also developed for each of the tested facilities. In 1983 dollars, the total capital costs of the activated carbon systems range from $267,000 (Plant 5) to $2,685,000 (Plant 6). The capital cost normalized to the SLA flow rate ranges from $51,000 to $173,000 per Nm³/sec ($24 to $82 per scfm). The normalized annual costs range from 0.19 to 0.66 $/kg (0.09 to 0.30 $/lb) of recovered solvent.

SELECTION AND DEVELOPMENT OF TEST METHODS

Within the test program, the control efficiency of the carbon adsorption system at each individual test site was specified as the primary measurement effort. A continuous measurement system was chosen to accurately assess system performance as a function of changing process operating variables. These included changes in inlet solvent concentrations due to different surface coating conditions and changes in outlet solvent concentrations due to cyclic operation of the carbon adsorption systems. The VOC test method selected was very similar to the total hydrocarbon (THC) measurement technique described as EPA Reference Method 25A [*12*]. Significant development work centered on the design of a computerized data acquisition system for the THC analyzers.

Several other test methods were used on a periodic basis to complete the characterization of system performance. These included EPA reference methods (e.g., for volumetric gas flow rate measurement), ASTM methods (e.g., for determination of carbon properties), and other routine test methods (e.g., temperature and pressure measurements).

Table 1 presents a summary of the test parameters and test methods. Major test methods for the VOC concentration and carbon analysis are reviewed in the following subsections.

TABLE 1. TEST METHODS AND EQUIPMENT FOR PERFORMANCE EVALUATION

Test Parameter	Test Method/Equipment
Carbon Data	
—Type	Plant or vendor data
—Life/Makeup data	Plant or vendor data
—Particle size distribution	Sieve analysis
—Surface area	BET Method
—Moisture content	Xylene extraction
—Condition	CCl_4 activity test, retentivity test
—Amount per bed	Plant or vendor data
—Volatiles content	Thermal extraction
Solvent Composition	
—Type	Plant data
—Hydrocarbon content	GC
—H_2O content	Karl Fischer titration
Operation: General	
—Design	Plant or vendor data
—Operation and maintenance practices	Plant data
—Problem areas	Plant data
Operation: Adsorption Mode	
—Temperature (in/out)	Thermometer
—Duct pressure	Magnehelic® gauge, inclined manometer
—Relative humidity	In-duct psychrometer
—Bed depth/bed area	Direct measurement or from plant or design data
—Velocity/Volumetric flow rate	EPA Methods 1 and 2
—Length of mode (per bed)	Direct measurement with timer
—Gas-phase VOC analysis	Byron THC Analyzer, GC
—Electrical energy consumption	Plant data
—Temperature of streams to and from air cooler	Thermometer
—Type and flow rate of coolant to air cooler	Plant or design data
Operation: Regeneration Mode	
—Steam conditions	Pressure-plant gauge or data Temperature (in/out)—thermometer or steam tables Flow rate—plant data
—Length of mode (per bed)	Direct measurement with timer
—Temperature of streams to and from condenser	Thermometer
—Condenser coolant type and flow rate	Plant or design data
—Wastewater analysis (hydrocarbon dissolved in water)	GC
—Wastewater flow rate	Direct measurement
Operation: Cooling/Drying Mode	
—Medium/Method	Observation
—Temperature (in/out)	Thermometer
—Pressure	Magnehelic® gauge, inclined manometer
—Moisture content (in/out)	In-duct psychrometer
—Velocity/Volumetric flow rate	EPA Methods 1 and 2
—Length of mode (per bed)	Direct measurement with timer
—Gas-phase analysis	Byron THC Analyzer, GC

Solvent (VOC) Concentration Measurement

A continuous THC sampling/analytical system was used to measure solvent concentrations in the inlet and outlet gas streams of each carbon adsorber. A stainless steel rake-type sampling probe and inert TEFLON sampling lines were used to deliver continuous gas samples to inlet and outlet THC analyzers, as shown in Figure 1.

The THC analyzers operate on the flame ionization detection (FID) principle. By this method, the gas sample is introduced to an air/hydrogen flame with subsequent combustion of any organics in the gas sample. The resulting ionized combustion products establish an electrical current in the presence of oppositely charged electrodes. The strength of the current is directly proportional to the total amount (concentration) of organics present in the sample; therefore, the detector current output from a calibrated THC analyzer can be expressed as a total organic concentration.

A Byron Model 301 THC analyzer and a Byron Model 401 THC analyzer were used to measure THC concentrations of the adsorber inlet and outlet gas streams, respectively. The Model 301 provides a single THC reading every three minutes, while the 401 provides a THC measurement every minute. The analyzers were calibrated with multiple concentration levels of certified gas standards simulating the actual process streams to be analyzed, i.e., appropriate concentrations of solvent(s) in air. The analyzer calibration and process sampling data were automatically monitored, reduced, and stored by a microcomputer-based data acquisition system. Software for the acquisition system was developed as part of this program.

In addition to the THC measurement, a limited amount of gas-phase data was collected at selected plants using an FID-based gas chromatograph (GC) in a manner similar to EPA draft Method 18 [*13*]. The instrument used was a portable AID Model 511 GC. The GC technique was used to speciate the major organic components of the inlet and outlet gas streams. Speciation of the inlet SLA allowed confirmation of the plant-reported solvent composition. Speciation of the exhaust air showed the partitioning effect of activated carbon on various solvents.

Carbon Analysis

Samples of virgin and used carbon were collected for: 1) carbon tetrachloride (CCl_4) activity and retentivity testing, 2) surface area determination, 3) volatile content, 4) moisture content, and 5) particle size distribution analysis.

Carbon samples were subjected to CCl_4 activity testing according to ASTM D3467 [*14*]. CCl_4 activity is an indirect measure of the pore volume of an activated carbon and, therefore, the carbon's adsorption capacity. CCl_4 activity is defined as the ratio (in percent) of the weight of CCl_4 adsorbed by a carbon sample to the weight of the sample, when the carbon is saturated with CCl_4 under conditions listed in the method.

The CCl_4 retentivity testing determines the relative desorptive capability of activated carbons. In this test, dry air at specified conditions flows through a CCl_4-saturated carbon sample. The amount of CCl_4 remaining on the sample after a specified time period is compared to the weight of the virgin carbon to yield the retentivity value and, therefore, information about the relative ease of regeneration of the carbon.

The specific surface area of the fresh carbon used at each plant was determined by the Brunauer, Emmett, and Teller (BET) method, or ASTM C819 [*15*]. The surface area available for adsorption is directly related to a carbon's solvent removal efficiency. The method, which is based upon the adsorption of nitrogen at its boiling point, is a standard carbon analysis technique used for relative comparisons of carbon adsorption capacity.

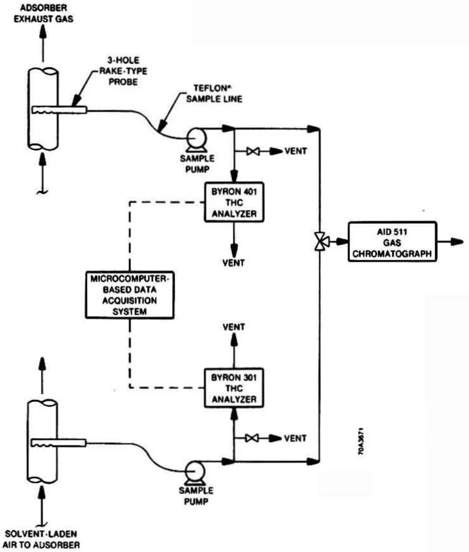

Figure 1. VOC sampling and analytical system.

Selected virgin and bed carbon samples were thermally desorbed at 600°C to determine the weight loss or volatile content of the carbon. The moisture portion of the volatilized matter was accounted for by the xylene extraction method of ASTM D2867 [*16*].

Determination of particle size distribution for virgin and used carbon from each plant was performed according to ASTM D2862 [*17*]. Carbon particle size distribution indicated the degree of attrition of the bed.

PROGRAM TEST RESULTS

Performance parameters for the six tested carbon adsorption systems are compared in Table 2. All six plants were originally tested in early 1982. During these tests, data were taken to characterize the VOC removal efficiency of the carbon bed systems and to characterize the conditions of the carbon. Four of the six plants were retested using the same methods approximately 18 to 22 months later. A comparison of the changes in performance was made in an attempt to define the effects of long-term carbon degradation. In general, the data in Table 2 indicate significant differences in performance from plant to plant and from test period to test period. However, these differences were not always attributable to carbon degradation.

The inlet VOC measurements for the six tested systems varied between plants and between test periods. Average inlet solvent concentrations ranged from nominally 1000 to 4000 ppmv. These solvent loadings correspond to approximately 5 to 20 percent of the lower explosive limits (LELs). Average adsorption times per bed for the six facilities showed significant variation, ranging from 64 to 560 minutes. Adsorption temperatures were generally less than 38°C (100°F) except for Plant 5. Steaming (desorption) periods ranged from 25 to 55 minutes, with the mean equal to approximately 30 minutes. Steam/recovered solvent ratios varied considerably, ranging from less than 1.0 kg/kg (1.0 lb/lb) at Plant 6 to 20 kg/kg (20 lb/lb) at Plant 1. Steam temperatures ranged from 110°C to 150°C (230°F to 300°F).

The average VOC control efficiency data presented in Table 2 indicate that, with the exception of the Plant 1 system, all tested adsorption systems were capable of achieving efficiencies of 95 percent or greater. (Mechanical problems at Plants 4 and 5 caused considerable decreases in the VOC control performance during the repeat testing.) Average removal efficiencies exceeding 99 percent were measured for two of the systems during the original testing.

The Plant 2 system showed VOC control performance degradation from 99+ percent (original testing) to 92 percent (repeat testing). Several operating factors may have contributed to this reduction in performance, including solvent formulation changes and changes in adsorption and desorption temperatures. However, these changes would not be expected to be the primary causes for the significant performance decrease measured. Rather, decreasing activity of the carbon appeared to be the primary cause. The deactivation of the carbon at Plant 2 was confirmed when the four-year-old carbon was replaced after the repeat test period. Subsequent plant measurements indicated VOC removal efficiencies exceeding 98 percent. These results suggest a useful carbon life for the Plant 2 system of approximately four years.

Plant 4 experienced significant mechanical malfunctions during the repeat test period, resulting in a very low overall VOC reduction performance. However, the low level of baseline emissions (i.e., the VOC emissions excluding excursions due to the mechanical valve malfunctions) indicated that the system was experiencing VOC removal performance similar to that of the original test period. This was verified by VOC analyses performed by the plant after the faulty valves were replaced (after the repeat test period), resulting in VOC removal levels similar to those measured during the original testing. With a carbon age of 4.5 years during the repeat test, the useful carbon life at Plant 4 was estimated to be relatively long (i.e., greater than 5 years).

For Plant 5, the degradation in VOC control efficiency was primarily due to mechanical problems, in particular, a leaking steam valve and channeling in Bed B (these were confirmed and repaired during a system shutdown several weeks after the repeat testing was completed). Variations in cycle timing, higher operating temperatures, lower inlet solvent concentrations, and increased carbon age appeared to account for a smaller portion of the performance decrease. The operating problems and other process variations prevent accurate comparison of the data sets. However, one major result is apparent; the useful carbon service life for the Plant 5 system is at least five years, based upon VOC removal levels of 98 percent measured during the original test period.

Plant 6 VOC control efficiencies were similar during both the original and repeat test periods, averaging almost 98 percent. Service time of the bed carbon was relatively short (0.2 to 1.6 years) compared to those of the other tested systems (2.0 to 6.5 years), and operating conditions were much more similar during the two test periods than for the other tested systems. Also, conservative design principles are incorporated into the Plant 6 carbon adsorption system. Because Plant 6 is a conservative design and has exhibited a lack of performance degradation between the two test periods, the useful life of the carbon is projected to be relatively long, perhaps in excess of five years.

CONCLUSIONS

The test data generated during this study show that fixed-bed carbon adsorption systems can consistently operate at 95 percent VOC reduction or greater, even after several years of operation. The VOC reduction performance, however, is greatly affected by system maintenance and operation. Corrosion may be a major factor in system malfunctions for several systems. General neglect of the

TABLE 2. COMPARISON OF TEST RESULTS — PLANTS 1-6

	Rubberized Fabric			Magnetic Tape			Flexible Packaging			
Plant	1	5		2		3	4		6	
	Original Test	Original Test	Repeat Test	Original Test	Repeat Test	Original Test	Original Test	Repeat Test	Original Test	Repeat Test
Solvent type	MEK	toluene	toluene	THF/ toluene[a]	THF/ toluene[a]	THF/ toluene/ MEK/ MIBK/ cyclohexanone	hexane	hexane	toluene/ IPAC	toluene/ IPAC
Adsorption mode length, min.	95[b]	150	200	64	65	47	120	90	470[b]	560[b]
SLA flow rate, Nm^3/sec (scfm)	5.4 (11,400)	4.3 (9,100)	3.7 (7,800)	4.6 (9,800)	4.5 (9,500)	9.4[c] (19,800)	8.3 (17,700)	10.7 (22,600)	15.8[d] (33,400)	16.0[d] (33,900)
Average inlet solvent concentration, ppmv	2,190	1,940	896	1,470	1,140	3,220	1,260[e]	940[e]	904	847
VOC control efficiency, %	84.9	97.6	80.5	99.7	95.2	94.7	99.0[e]	46.7[e,f]	97.5	97.9
Desorption mode length, min	55	50	40	32	32	35	25	25	30	30
Steam/recovered solvent, kg/kg (lb/lb)	20 (20)	8.2 (8.2)	15 (15)	5.2 (5.2)	6.5 (6.5)	6.0 (6.0)	4.6 (4.6)	11 (11)	1.0 (1.0)	0.8 (0.8)
Carbon age, years	0.4	5.0	6.5	2.0	3.8	0.4	3.0	4.5	0.2	1.6
Cost Information (1983 dollars)										
Total capital, $\$10^3$	622	267		650		1,800	1,334		2,685	
Relative capital cost, $\$10^3/Nm^3/sec$ (\$/scfm)	110 (56)	51 (24)		108 (51)		173 (82)	129 (61)		72 (34)	
Total annualized cost, $\$10^3$	262	125		325		1,430	494		839	
Relative annualized cost, \$/kg recovered solvent (\$/lb)	0.53 (0.24)	0.19 (0.09)		0.61 (0.28)		0.66 (0.30)	0.51 (0.23)		0.28 (0.13)	

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[a] Original THF/toluene percentages were 50/50; repeat test percentages were 75/25.

[b] Cycle timing controlled by exhaust gas (breakthrough) hydrocarbon analyzer.

[c] Flow rate measured when 4 of the 6 beds were in service (2 beds were on permanent standby).

[d] Process Train 1 conditions (total system capacity was twice that of Process Train 1).

[e] Measurements made at common inlet/common outlet.

[f] Removal efficiency is low due to steam valve leakage (99 percent efficiency was measured after repair of the valves).

system is also a prime contributor to poor performance.

Measurements of system performance and carbon properties indicate that the useful carbon life may be as short as a few months to as long as several years. Also, there are no known procedures to accurately predict useful carbon life. Currently used test methods, such as the CCl_4 activity test, do not appear to provide the data needed to measure adsorption capacity for used (degraded) carbons. Therefore, it is recommended that new test methods be developed to measure adsorption capacity (and other carbon properties such as retentivity and fouling) of used carbons, and that procedures be developed to use that data for estimating carbon life. Additional carbon life tests may include gas-phase testing of the SLA stream to determine the presence of possible contaminants which can foul the carbon bed. Measured levels of contaminants could possibly be related to useful carbon lives.

As part of the testing, an investigation of the mechanisms for carbon degradation is needed. Most degradation is believed to be caused by one or more of the following mechanisms: 1) adsorption or physical blockage of the micropore structure by contaminants, 2) obstruction of adsorption sites by by-products of organic polymerizations or reactions on the carbon surface, or 3) chemical reaction involving the carbon surface leading to a reduction in the availability of active sites. Information in the literature on these mechanisms is limited.

Also, methods to extend the useful carbon life should be investigated. In some applications, carbon life is acceptable under current conditions; however, in situations where carbon life is very short (i.e., less than one year), the extension of acceptable carbon performance through installation of a carbon bed protection device can be cost effective. Selection of an appropriate carbon bed protection device will be determined in large part by the mechanisms by which the bed becomes deactivated. Current methods for extending carbon life include pretreatment of the SLA stream with a fabric filter, a sacrificial guard bed, or a wet scrubber.

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DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendations for use.

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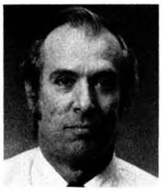

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Environmental Protection Agency's Risk Management Policy

A much needed clarification of the risk assessment and risk management procedures of the U.S. Environmental Protection Agency (EPA).

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The principal authority under the Clean Air Act (CAA) for control of toxic air pollutants is section 112, entitled National Emission Standards for Hazardous Air Pollutants. Section 112 defines "hazardous pollutant" as an "air pollutant to which no ambient air quality standard is applicable and which in the judgment of the Administrator causes, or contributes to, air pollution which may reasonably be anticipated to result in an increase in mortality or an increase in serious irreversible, or incapactitating reversible, illness." The Act provides that regulations under section 112 be established at a level to protect the public health with an "ample margin of safety."

To date, seven pollutants have been listed as hazardous under section 112. However, regulations that have been promulgated or proposed for these seven differ to some extent both in basis and in final level of control. This has resulted in part because of difficulty in interpreting the Clean Air Act. For example, what is an "ample margin of safety" for a pollutant, such as a carcinogen, with no proven threshold of effect? These differences also result from a number of basic scientific uncertainties, including defining the real extent of the air toxics problem and establishing toxicity to humans based on mathematical extrapolation from high-dose animal tests or occupational exposure to low-dose public exposure at ambient concentrations.

For several years, EPA had focused on technology solutions to these problems. In fact, that was the basis for proposed benzene regulations [*1*] in 1980 and 1981 and proposed arsenic regulations [2] last year. In those cases, the basis for control was best available technology, or BAT, with additional control applied if the risk remaining after application of BAT was judged to be unreasonable.

By BAT, EPA meant the best control available, considering economic, energy, and environmental impacts. BAT could be different for new and existing sources within a source category and could be equal to or more stringent than the best technology defined for New Source Performance Standards under section 111.

In that approach, the use of risk numbers generally was confined to areas of broad comparisons, e.g., in selecting source categories to evaluate and in assessing the incremental change in risk that results from application of various control options. The use of the absolute value of the risk numbers was avoided because of the many uncertainties.

There were legitimate concerns with this approach, particularly in the limited use of risk assessment for a health based statute and the use of technology and cost, which are not mentioned in section 112, as key factors in decision-making. While these concerns were being deliberated last summer, Administrator Ruckelshaus spoke before the National Academy of Sciences (NAS) [3] and issued a call for a more rational system for assessing and managing risks to the American public. He stated, among other things, that risk assessment should be improved, that risks should be weighed against the benefits of continued use and the risk of substitutes and environmental transfer, and that the public should be involved in the process to a greater extent. Risk assessment is defined as the scientific process where factual information on toxicology and exposure is used to estimate the health effects of exposure of individuals and populations to hazardous materials or situations. Risk management is the more judgmental process of weighing policy alternatives and selecting the most appropriate regulatory action, integrating the results of risk assessment with engineering data and with social, economic, and political concerns to reach a decision.

Risk Assessment

EPA's approach to risk assessment for suspected carcinogens may be divided into several steps. The first is a qualitative evaluation of the evidence to determine whether a substance should be considered a human carcinogen for regulatory purposes. The next stage is quantitative: how large is the risk of cancer at various levels of exposure? The result of this examination is a dose-response function which gives the lifetime risk per unit of exposure (or "potency"). The next stage is to estimate how many people are exposed to the substance, and at what levels. These exposure estimates then are combined with the dose-response function to obtain estimates of the public health risk caused by emissions of the pollutant into the environment.

All stages of the process are subject to uncertainties because of gaps in scientific knowledge and data limitations. One step that has great uncertainty is estimating the dose-response function. The fundamental problem is in extrapolating from data on the relatively high doses in the epidemiological or animal toxicological studies, to the far lower exposure levels found in the environment. In other words, it is necessary to extrapolate to doses often a thousand or more times lower than those at which increased cancer rates have been observed.

Scientists have proposed many different mathematical models for high dose to low dose extrapolation. EPA has in the past generally relied on the linear, non-threshold model. This model, also called the "one-hit model," rests on the assumption that cancer is initiated by a single hit on a cell.

Therefore, risk is proportional to dose. This model tends to predict the most conservative risk estimates at low doses; in fact, most other models predict much smaller risks at low doses. More recently, EPA has adopted the multi-stage model which has a linear component at low doses [4]. This model assumes that cancer is caused by a series of mutational steps, whose occurrence rest both on dose and potency. This model also results in a conservative estimate. Most scientists accept these models as giving plausible upper limit estimates for a chemical's potency at low levels of exposure. In other words, the potency of a substance is unlikely to be higher that estimated using the linear model, but could be substantially lower. Use of the linear non-threshold model reflects EPA's decision to err on the side of caution in the face of uncertainties. The final result of the linearized extrapolation is a "unit-risk factor," which gives the estimated upper limit lifetime risk per unit of exposure.

Exposure levels for each specific source category normally are derived using emissions estimates, dispersion modeling, and population data. For any given level of emissions, dispersion models can predict concentrations at different distances from the emission source. By combining these estimated concentrations with census data, the number of people exposed at different levels can be estimated. These models can vary in complexity depending upon the desired accuracy of the results. While exposure assessment focuses primarily on the media of direct concern to the analysis, all important routes of exposure will be evaluated and included.

The final public health risk estimates are the product of the exposure levels and the estimated unit-risk factor. Two summary measures are of particular interest: "maximum individual risk" and "total population impact." The former refers to the estimated increased lifetime risk from a source that is faced by the individual exposed to the predicted highest annual average concentration of the pollutant. Lifetime individual risk is expressed as a probability, e.g., one chance in ten thousand of getting cancer in the person's lifetime. For comparison, the average lifetime risk of contracting cancer for all causes in the United States is currently about 1 in 4. Estimates of maximum individual risk must be interpreted cautiously since very few people reside at the points of maximum concentration.

The second measure, "total population impact," takes account of people exposed at all concentrations, low as well as high. It is expressed in terms of estimated annual number of cancer cases, and provides a rough measure of the overall impact on public health. A total population impact of 0.05 per year, for example, means that the modeling predicts that emissions of the specific pollutant from the source category will cause one case of cancer every 20 years.

The two estimates taken together provide a better description of the magnitude and distribution of risk in a community than either number taken alone. "Maximum individual risk" tells us the worst risk, but not how many people are at risk. "Total population impact" describes the overall health impact on the entire exposed population, but not whether there are people at very high risk. Two chemicals or regulations could have similar population impacts, but very different maximum individual risks, or vice versa. Consequently, any sensible "risk management" system cannot rely on either measure alone; both are important.

Risk Management

Given the linear non-threshold assumption regarding risks from non-threshold pollutants at low doses, the only absolutely risk-free approach to setting standards for these pollutants would be to reduce exposures to zero. However, this would require extensive plant closure and we do not believe that Congress intended section 112 standards to cause that type of widespread disruption to the national economy. Thus, EPA has sought to establish an approach to risk management that allows for an appropriate control of emissions of hazardous air pollutants without an automatic closing of all sources of the pollutant.

The risk management approach that EPA has adopted for section 112 pollutants is as follows:

1. The agency should evaluate all source categories of the pollutant to determine which categories cause significant public health risks.
2. The source categories that are judged to cause significant risk are then evaluated. EPA examines the various options available to reduce emissions from these sources, including controls similar to those imposed under section 111 of the Clean Air Act (New Source Performance Standards) and closing the plant. Options are examined in terms of control efficiency, technical feasibility, and costs and reductions in risk that they achieve.

Using this risk management approach, regulatory decisions for arsenic and benzene as hazardous air pollutants under section 112 have been proposed or announced as intended. Important risk management information for these pollutants is summarized in Tables 1 and 2.

Summary

In summary, EPA has recently begun to articulate more clearly its position on risk assessment and risk management for toxic air pollutants. To this end, final decisions have been announced on benzene regulations and should be announced soon on radionuclides and arsenic. In addition, EPA has committed to decisions on whether or not to

TABLE 1. ARSENIC (PROPOSED JULY 20, 1983)

Source Category	No. of Plants	Total Emissions (Mt./yr)	Maximum Lifetime Risk		Aggregate Risk (Cases/yr)		Capital Cost 10^6\$	Annualized Cost 10^6\$	Price Increases %	Status*
			Current	After Best Control	Current	After Best Control				
Copper smelters										
High arsenic	1	282	9×10^{-2}	2.3×10^{-2}	4.4	0.85	3.5	1.5	0.5 -0.8	R
Low arsenic	14	738	1.7×10^{-2}	0.4×10^{-2}	0.4	0.16	35.3	9.5	0.1 -4.4	R
Glass manufacturing	15	37	25×10^{-4}	4×10^{-4}	0.29	0.05	27.4	4.9	0.04-3.1	R
Primary lead	5	43	1×10^{-4}	1×10^{-4}	0.03	0.03	—	—		N
Secondary lead	40	55	9×10^{-4}	9×10^{-4}	1.4	1.4	—	—		N
Zinc oxide	2	5	7×10^{-4}	7×10^{-4}	0.006	0.006	—	—		N
Cotton gins	320(?)	2	7×10^{-5}	7×10^{-5}	?	?	—	—		N
Primary zinc	5	0.3	6×10^{-6}	6×10^{-6}	0.002	0.002	—	—		N
Chemical	8	0.04	2×10^{-4}	2×10^{-4}	0.003	0.003	—	—		N

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* R - Proposed.
N - Proposed not to regulate.

Table 2. Benzene (Early 1984 Estimates)

Source Category	No. of Plants	Total Emissions (Mt./yr)	Maximum Lifetime Risk		Aggregate Risk (Cases/yr)		Capital Cost 10^6 $	Annualized Cost 10^6 $	Status*
			Current	After Best Control	Current	After Best Control			
Fugitives (Chem & Refining)	229	7900	2×10^{-3}	5×10^{-4}	0.45	0.14	5.5	0.4	R
Coke By-product	55	29000	8×10^{-3}	4×10^{-4}	2.6	0.23	30.9	(1.3)	R
Maleic Anhydride	3	960	8×10^{-5}	5×10^{-6}	0.03	0.02	6.4	2.8	N
Ethylbenzene Styrene	13	210	1×10^{-4}	9×10^{-6}	0.006	0.0006	2.7	1.0	N
Storage	126	620	4×10^{-5}	2.3×10^{-5}	0.04	0.03	7.3	1.3	U
Linear Alkylbenzene	5	260	1×10^{-4}	7×10^{-6}	0.025	0.004	1.6	0.6	U
Nitrobenzene	5	240	2×10^{-4}	2×10^{-5}	0.014	0.001	0.1	0.03	U
Chlorobenzene	4	110	1×10^{-4}	6×10^{-6}	0.017	0.0001	1.1	0.4	U
Ethylene	34	480	1×10^{-6}	3×10^{-8}	0.003	0.0002	13.3	4.2	U

* R - Intend to regulate.
N - Proposed not to regulate.
U - Undecided.

regulate 20-25 additional substances by the end of 1985 [5]. Those decisions will rely substantially on risk assessment.

The risk assessment/risk management process that is being used is not a Rosetta Stone with which we can completely decipher the problem of toxic air pollutants. We just are not knowledgeable enough yet to resolve many of the scientific and technical questions. It is, however, a framework for rational and responsible decision-making that allows the Administrator of EPA to make decisions appropriate to the needs of the public and the nation as a whole.

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Anaerobic Treatment of Concentrated Industrial Wastewater

Anaerobic digestion with the production of methane appears to be a possible treatment for industrial landfill leachate. Actual test results.

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Groundwater and surface water contamination can be due, in part, to infiltration of leachate from sanitary and industrial landfills. Typically, leachate contains a great diversity of organic and inorganic compounds; thus, an efficient treatment scheme must involve several process steps. A number of renovation techniques have been explored, including physical/chemical treatment and biological treatment. Biological treatment has been found to be applicable to leachate from recently constructed sanitary landfills [1]. These "new" leachates contain volatile acids and alcohols that are easily degraded microbiologically. Physical/chemical methods are best applied to biologically stabilized leachates. The application of biological treatment to industrial landfill leachate has not been considered until recently.

Biological treatment is considered to be the most cost-effective method for the reclamation of wastewater contaminated with organic materials. Often, it has the second advantage of complete assimilation of organic compounds and their removal from the environment. Incineration is the only alternative method that can accomplish this same end. Anaerobic treatment is particularly suited to the leachate used in this study because the major contaminants are precursors to anaerobic methane formation. These contaminants, short-chain, volatile fatty acids and alcohols, are most likely the products of the degradation of organic compounds in the landfill itself, and can be expected to be present in other industrial landfill residuals as well.

Microbial degradation that results in the formation of methane from soluble organics is carried out by three general groups of bacteria [2]. Hydrogen-producing bacteria hydrolyze, oxidize, and ferment complex organics to short-chain, volatile fatty acids, alcohols, and other neutral products. A second group, non-fermentative obligate proton reducers, oxidize volatile fatty acids greater than two carbon atoms and alcohols greater than one carbon atom in chain length to acetate and carbon dioxide. Methanogens form methane from acetate or hydrogen and carbon dioxide. At this point, the wastewater is considered stabilized.

Methane is formed from Reactions 1 and 2 listed in Table 1. Approximately 70% of the methane is formed from acetate, i.e., Reaction 2. If a wastewater contains sulfate or nitrate, competition for hydrogen occurs, leading to inhibition of methane production until the sulfate or nitrate is depleted. Sulfate reducing bacteria compete for acetate, also, and have growth rates on acetate and hydrogen that are slightly higher than the methanogens [5, 6]. The competition for hydrogen and acetate can be explained by the free energy values for the Reactions listed in Table 1. The thermodynamic feasibility of methane formation from acetate or hydrogen and carbon dioxide is less than for the sulfate reductions (ΔG is less negative); the sulfate reduction is less feasible than the nitrate reduction.

It is generally accepted that the methanogens obtain metabolic energy from the production of methane, although the mechanism is not completely understood. Methanogens have also been considered to be sensitive to certain chemicals, ions, and metals that are commonly found in leachates. However, recent studies have found methanogens to be tolerant of many such substances, when an adaptation period is allowed [7].

LEACHATE DESCRIPTION

The leachate used in this study originates from an industrial landfill and is supplied by the USEPA. Significant characteristics are summarized in Table 2. A high dissolved organic carbon (DOC) content is observed; acetic, propionic, and butyric acids account for approximately 40% of the organic solutes. High sulfate ion concentrations result from the pretreatment process employed to remove suspended matter and heavy metals that are inhibitory to biological processes. Pretreatment consists of lime coagulation followed by recarbonation and acidification with sulfuric acid.

The carbon-to-nitrogen ratio found in the leachate, 100:10, is acceptable for biological growth; the typical requirement is 100:6. However, the phosphorous level is low; phosphorous in the form of phosphate must be added. Sodium and calcium levels are high, but do not appear to cause toxicity.

CULTURE DEVELOPMENT

An anaerobic culture seed was obtained from the Berkeley Heights, N.J., sewage treatment plant and two cultures were developed. Two-liter reactors are mounted on magnetic stirrers. Water at 37°C is passed through a copper coil immersed in each reactor. Gas is collected over 1 N sulfuric acid solution.

TABLE 1

Reaction	$\Delta G^{o'}$ KJ/Reaction*
1. $H^+ + HCO_3^- + 4H_2 \rightarrow 3H_2O + CH_4$	−135.9
2. $CH_3COO^- + H_2O \rightarrow HCO_3^- + CH_4$	−31.0
3. $SO_4^= + H^+ + 4H_2 \rightarrow HS^- + 4H_2O$	−151.9
4. $SO_4^= + CH_3COO^- \rightarrow 2HCO_3 + HS^-$	−71.7
5. $NO_3^- + H_2 \rightarrow NO_2^- + H_2O$	−163.2
6. $2NO_2^- + 2H^+ + 3H_2 \rightarrow 2N_2 + 4H_2O$	−794.1

*$\Delta G^{o'}$ is the free energy evolved at standard conditions, 1 atm, 25°C and adjusted for the biological pH of 7. Calculated by Thauer, Ref. [4].

TABLE 2. LEACHATE CHARACTERISTICS

Parameter	Concentration, kg/m^3
COD	43.0
DOC	16.0
TKN	1.60
NH_4-N	1.12
Phosphorous	0.014
Acetic Acid	7.43
Propionic Acid	1.36
Butyric Acid	4.56
Dissolved Residue	17.0
Sulfate	3.4
Sulfide	Not Detected
Nitrate	0.011
Nitrite	0.002
Na^+, Ca^{++}	1.70-17.0

The initial culture (leachate culture) was adapted to a medium containing 50% leachate, 0.002 kg/m^3 yeast extract and 0.0016 kg/m^3 KH_2PO_4. This medium is added at a volume of 0.05 liter, every third day, to 1.5 liters of culture. Culture pH is about 7.4 and the gas composition is 80% methane, 18% carbon dioxide, and trace amounts of hydrogen sulfide. Hydrogen sulfide is also present in the reactor at about 0.10 kg/m^3. This culture has been maintained in the laboratory for nine months.

Because three components of the leachate constitute a large portion of the DOC and because these compounds are key intermediates in anaerobic digestion, it was deemed desirable to study the organisms that utilize these compounds. To accomplish this, a culture was selected for acetate-, propionate- and butyrate-utilizing organisms (VFA culture). A medium of acetic acid, 0.017 kg/m^3; propionic acid, 0.003 kg/m^3; butyric acid, 0.01 kg/m^3; NH_4HCO_3, 0.078 kg/m^3; KH_2PO_4, 0.0009 kg/m^3; and yeast extract, 0.002 kg/m^3 is added at 0.05 liter, every second day. The ratio of acids in this artificial leachate is similar to that found in the prototype leachate. This culture has been maintained in the laboratory for nine months. Gas composition is 71% methane and 29% carbon dioxide; culture pH is 7.3.

TOXICITY EXPERIMENT

The objective of this investigation is to compare the rates of utilization of acetate, propionate, and butyrate in leachate, containing possible toxicants, to a control using artificial leachate, with no toxicants. The experiment is performed using the culture selected for the volatile fatty acids (VFA culture) and the method developed by Miller for the cultivation of anaerobes [8].

A volume of 0.05 liter of culture is transferred to 0.1-liter serum bottles that are filled with a gas composition of 70% nitrogen and 30% carbon dioxide, capped with rubber stoppers and aluminum seals. Full strength leachate, 0.005 liter, with appropriate amounts of yeast extract and phosphorous, is injected into duplicate flasks. This corresponds to approximately a one-tenth dilution of leachate, six times higher than the dilution to which the leachate-digesting culture is adapted.

Gas volume is measured using a water-lubricated, calibrated glass syringe. Samples are taken twice daily and frozen for later analysis. Duplicate control flasks are dosed with an artificial medium composed of acetic, propionic, and butyric acids as found in the prototype leachate, with appropriate amounts of nitrogen, phosphorous, and yeast extract.

LEACHATE BATCH EXPERIMENTS

The objective of these experiments is to evaluate leachate dissolved organic carbon (DOC) removal and breakdown, or the appearance of specific compounds, to assess rate limiting kinetics.

Batch experiments using leachate are performed in duplicate 0.5 liter serum bottles capped with a rubber stopper containing a glass stopcock. A septum is held at the top of the stopcock; a hypodermic needle is inserted to remove samples and measure gas.

A medium containing (per liter) yeast extract, 0.002 kg, 0.02 liter of a 1 M phosphate buffer adjusted to pH 7; resazurin, 0.000001 kg; and 0.001 liter of a trace metal solution [9] is boiled to remove oxygen and cooled under nitrogen. After cooling, 0.065 liter of leachate, 0.002 kg $NaHCO_3$, 0.00025 kg cysteine hydrochloride and 0.00025 kg $Na_2S \cdot 9H_2O$ are added and the pH is adjusted to 7.1. The serum bottles, previously purged with nitrogen, are filled to 0.35 liter and 0.05 liter of either leachate culture or VFA culture are added as the innoculum.

ANALYTICAL METHODS

Volatile fatty acids and low molecular weight compounds are assayed using a Hewlett-Packard Model 5880A Gas Chromatograph equipped with a flame ionization detector. A three-foot, glass column (1/4 inch OD, 2 mm ID) packed with Supelco Carbopack C/0.3% Carbowax 20M/0.1% H_3PO_4 is used for separation of components.

Gas analysis is performed by gas chromatography using a thermal conductivity detector. A ten-foot, stainless steel, 1/8 inch OD column packed with Chromosorb 102 is used for separations.

DOC measurements are performed using the ampoule method and an Oceanography International Carbon Analyzer.

RESULTS AND DISCUSSION

Toxicity Experiment

The effects of diluted (one-tenth) prototype leachate on gas production, compared to a control receiving artificial leachate are shown in Figure 1. The control reactor produced a larger amount of gas; it received a higher dose of volatile fatty acids than the test reactor. However, the rates at which gas was produced were virtually the same, indicating that inhibition of methanogens is not a factor.

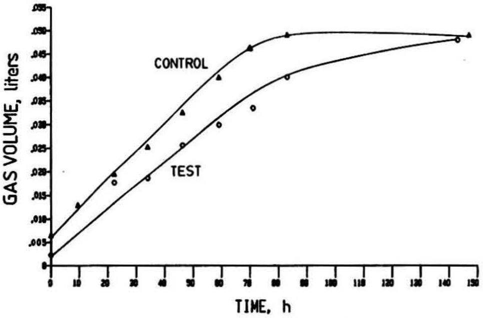

Figure 1. Gas production for control and test reactors during toxicity experiment.

Acetate, propionate, and butyrate levels are compared in Figures 2-4. Butyrate and propionate removals show a slight lag, about 20 hours, followed by a rapid decrease at rates comparable to the controls. The propionate control shows a lag or adaptation period of approximately 40 hours, possibly due to the relatively high concentration of propionate (0.225 kg/m³); a typical level in the master culture is 0.100 kg/m³. The rates of acetate removal are approximately the same, although the control shos a consistently higher concentration.

Batch Experiment #1 with One-Twentieth Dilution and Leachate Digesting Culture

Variations in the DOC of one of the duplicate reactors during the experimental period are described in Figure 5. The overall decrease from 1.097 kg/m³ to 0.423 kg/m³ is equivalent to 61% removal. The dip in DOC from 50-100 hours, followed by an increase, may be due to non-metabolic uptake and release of DOC, or rupture of cells with release of cell contents.

The rate of methane production, Figure 6, is very slow for the first 200 hours. This is most likely a result of sulfate-reducing bacteria competing for hydrogen and acetate. The extended lag period followed by rapid methane production cannot be attributed to cell growth, since methanogens are known for extremely slow growth. The volume of methane in m³ per kg of DOC removed is 1.22, compared to typical reported values of 0.91-0.93 [3].

The fate of the volatile fatty acids is described in Figure 7. The concentrations of these compounds provide clues to the degradation of leachate and rate-limiting steps. Ace-

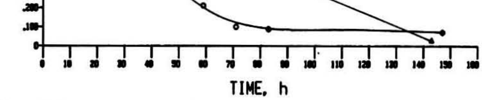

Figure 2. Acetate concentrations for control and test reactors during toxicity experiment.

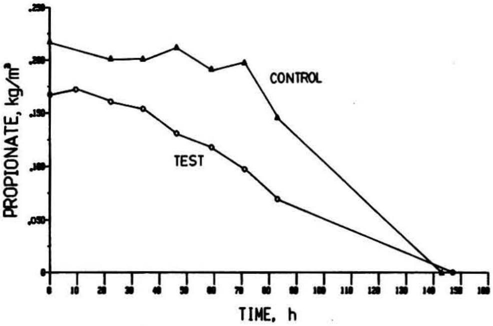

Figure 3. Propionate concentrations for control and test reactors during toxicity experiment.

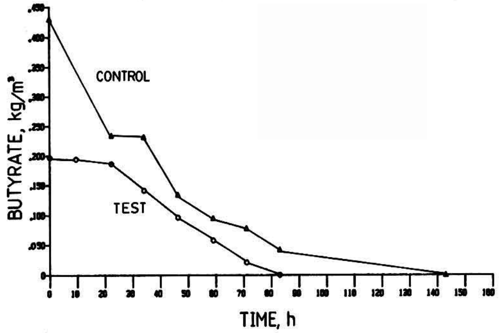

Figure 4. Butyrate concentrations for control and test reactors during toxicity experiment.

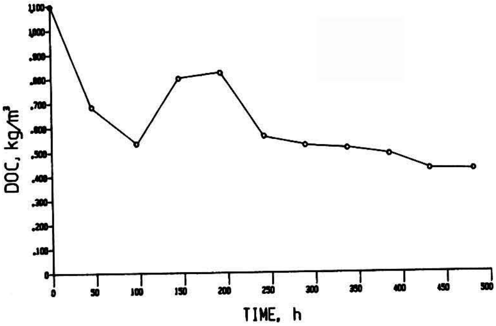

Figure 5. Dissolved organic carbon profile for Batch Experiment #1.

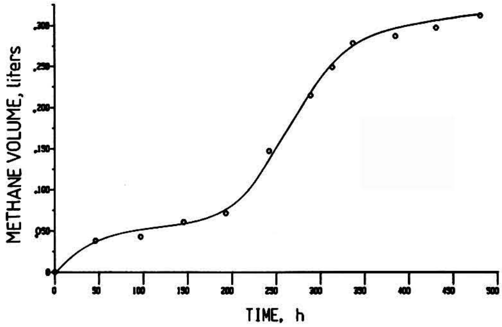

Figure 6. Methane production during Batch Experiment #1.

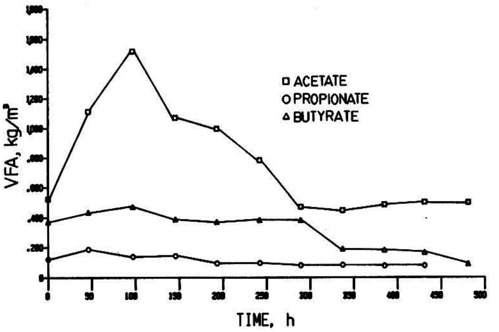

Figure 7. Volatile fatty acid profiles for Batch Experiment #1.

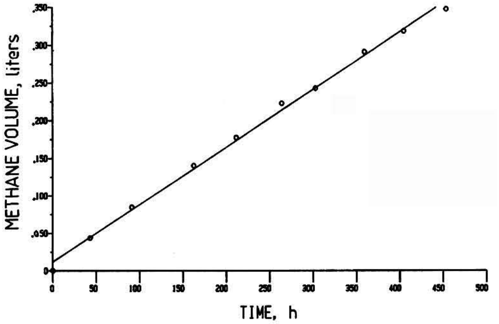

Figure 8. Methane production during Batch Experiment #2.

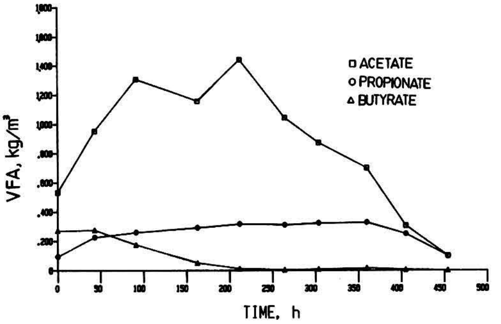

Figure 9. Volatile fatty acid profiles for Batch Experiment #2.

tate levels increase, followed by decreases, as expected. The formation of acetate is faster than the removal. Propionate and butyrate both increase, vary, and then decrease. This variability is indicative of the formation of propionate and butyrate from longer chain compounds. The formation of iso-butyrate is observed (not shown); separate experiments suggest it results from the metabolism of butyrate.

Batch Experiment #2 with One-Twentieth Leachate Dilution and VFA-Digesting Culture

The rate of methane formation during a batch experiment with a culture not adapted to leachate is shown in Figure 8. The rate is linear, with no inhibition observed, in contrast to the results from the leachate-digesting culture. The fate of the volatile fatty acids is described in Figure 9. Acetate increases and decreases; the rate of removal is slower than the rate of production. Propionate increases, remains fairly constant, then decreases. The formation of propionate may be the result of metabolism of other compounds in the leachate. Iso-butyrate (not shown) increases slightly and remains steady at a very low concentration (0.070 kg/m³). Butyrate decreases rapidly after a short lag period, in contrast to the results of the leachate-digesting culture.

SUMMARY AND CONCLUSIONS

Anaerobic digestion with the production of methane appears to be a possible treatment for industrial landfill leachate. The study of volatile fatty acids during batch experiments has provided several insights into the degradation of organic solutes in this complex wastewater. A one-tenth dilution of leachate led to a very slight lag period for the removal of acetate, propionate, and butyrate, with an unadapted culture of selected organisms. Leachate components do not affect the bacterial culture adversely, at a level fairly high concentration. However, the build-up of conservative or non-degradable compounds could affect the bacteria in a continuous process.

An overall DOC reduction of 61% was observed during a batch experiment using a leachate dilution of five per cent and a culture adapted to leachate. The build-up of butyrate indicates a breakdown of other, larger organic species in the leachate. This was not observed when a similar experiment was performed using a culture selected for volatile fatty acid degradation. Apparently, the organisms responsible for the formation of butyrate from higher compounds are not present in this culture.

Inhibition of methane occurs when the leachate adapted culture is dosed with leachate, presumably because of sulfate reducers. This problem could be eliminated by removing the sulfuric acid step from the pretreatment scheme or selecting a culture from a seed that does not contain sulfate reducers. The rate controlling step is probably acetate removal, hence the formation of methane. This is typical of anaerobic digestion systems [*1*]. Current research is using higher concentrations of leachate to study the effects on the microbial population. The degradation of other compounds in the leachate is being studied also.

ACKNOWEDGEMENTS

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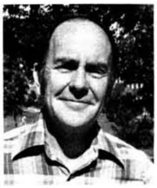

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Fate of Contaminants During Treatment of H-Coal Process Wastewaters

Details of a treatment train capable of significantly improving the quality of H-Coal process wastewaters, reducing contaminant concentrations to low levels.

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The ultimate fate of the components present in the process wastewaters produced by coal liquefaction and gasification facilities is of interest to those developing effective treatment strategies. Conversion processes generate wastewaters containing relatively high concentrations of phenol, ammonia, cyanide, and hydrogen sulfide, as well as other organic and inorganic compounds [*1*]. These components are not unique to coal conversion process wastewaters and are also found in various combinations in wastewaters of the petroleum, steel, and chemical process industries, among others. The bulk of the contaminants must be removed from the wastewater prior to reuse or discharge to the environment.

This paper reports the results of a treatability study of H-Coal liquefaction process wastewater. Previous investigations have demonstrated the applicability of conventional treatment technology in controlling the wastewater from gasification and liquefaction pilot plants [*2, 3, 4*]. It can be concluded from these earlier studies that no single treatment operation is capable of reducing all of the

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Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

wastewater contaminants to acceptable levels. With this in mind, a fully integrated treatment train and selected component unit operations, maintained and operated at the Pittsburgh Energy Technology Center, were employed to evaluate the treatment of recycle process water from the H-Coal Pilot Plant facility in Catlettsburg, Kentucky. Treatment operations included dissolved-gas stripping, solvent extraction, biochemical oxidation, activated-carbon adsorption, and wet-air oxidation. The effluents from the individual unit operations were analyzed for both gross characteristics and specific compounds. The specific compounds were determined in a more detailed analysis that employed high performance liquid chromatography, gas chromatography, and atomic absorption spectroscopy. To further elicit the fate of the contaminants, acute bioassays were performed on the treated and untreated effluents. The results of this study allow a determination of the degree of treatment required to meet plant-specific design criteria by comparison of water quality requirements with the detailed analysis of the wastewater after each step in the treatment train.

EXPERIMENTAL

Materials

The wastewater treated in this series of experiments was obtained from the 1.8 × 10^5 kg/day (200 ton/day) H-Coal pilot plant in Catlettsburg, Kentucky, during run Number 11. Kentucky Number 9 coal was the feedstock to the pilot plant during this run. The wastewater employed in these studies is combined liquefaction sour water originating from the separator and fractionation areas shown in Figure 1. The samples were collected under nitrogen from sample point 401 in twelve, 200-liter polyethylene-lined drums and shipped to the Pittsburgh Energy Technology Center. The wastewater was transferred to 830-liter stainless steel tanks and stored at 4°C under nitrogen until required for the investigation. The gross characteristics of the wastewater, as received, are reported in Table 1.

Operations and Equipment

The experimental wastewater treatment train employed in this investigation is shown in Figure 2. The main treatment train included 1) dissolved-gas stripping, 2) solvent extraction, 3) biochemical oxidation, and 4) activated-carbon adsorption. Alternative treatment configurations were also investigated. These included wet-air oxidation of the raw wastewater and biochemical oxidation of both diluted and undiluted dissolved-gas-stripped wastewater. The individual unit operations employed in this study are described below.

A 170-liter batch-stripping still equipped with a 3-meter, stainless steel, water-cooled reflux condenser was used to strip ammonia from the wastewater. The still was charged with raw sour water, heated to 90°C, and sparged with nitrogen. This operation was conducted in two steps. Free ammonia and hydrogen sulfide were removed from the wastewater at the pH of the wastewater. The stripping still was operated in this manner until no remaining sulfide species were detected. Lime [reagent-grade $Ca(OH)_2$] was then added to the contents of the stripping still to adjust the pH of the wastewater to between 10 and 11. Sparging with nitrogen at 90°C was then resumed to remove fixed ammonia from the wastewater. The dissolved-gas-stripping operation was continued at the elevated pH until the ammonia concentration decreased to less than 200 mg/L. After the stripping operation was completed, suspended particles of lime were removed by filtration through Whatman No. 3 filter paper. The wastewater was then neutralized with sulfuric acid. The noncondensed gases from the dissolved-gas-stripping operation were passed through Calgon type BPL activated carbon to remove hydrogen sulfide before they were vented to the atmosphere.

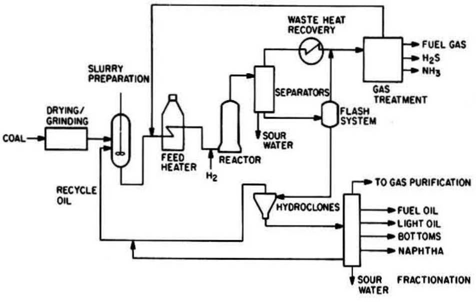

Figure 1. Schematic of the H-Coal Process.

TABLE 1. H-COAL COMBINED LIQUEFACTION SOUR WATER AS RECEIVED

	Values in mg/L except pH
pH	9.0
Total Organic Carbon (TOC)	11,030
Chemical Oxygen Demand (COD)	51,900
Phenols (4-aminoantipyrine method)	9,150
Total Dissolved Solids (TDS)	5,000
Alkalinity	12,000
Chloride	180
Biochemical Oxygen Demand (BOD)	15,900
Total Ammonia	5,500
Free Ammonia	4,850
Sulfide	3,900

Solvent extraction of the dissolved-gas-stripped wastewater was accomplished in a 36-stage, continuous, counter-current, liquid-liquid extraction column manufactured by the York Process Equipment Company (Model No. XB-3-36). The column is 1.22 m (48 inches) high, with an inside diameter of 7.6 cm (3 inches). It is constructed of Pyrex glass and employs a series of agitators on a central shaft, with horizontal annular baffles forming 36 stages. The column was operated at a solvent-to-water ratio of 0.10

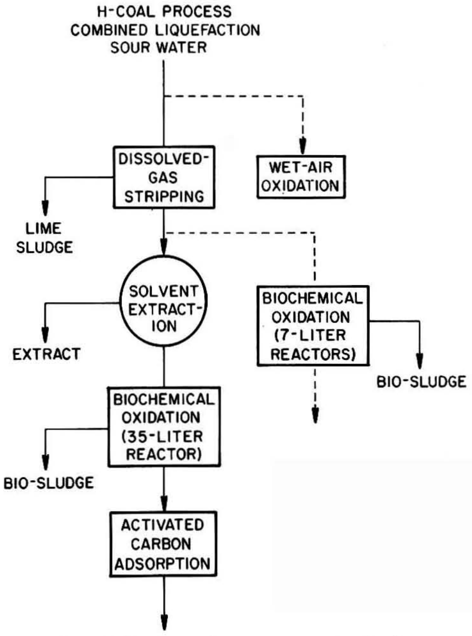

Figure 2. Experimental wastewater treatment train.

(by volume), with methyl isobutyl ketone as the dispersed phase. A wastewater flow rate of 0.4 L/min was fed to the column. Residual methyl isobutyl ketone was removed from the raffinate by sparging with nitrogen at 40°C until the methyl isobutyl ketone concentration was determined by liquid chromatograhy to be less than 100 mg/L.

All of the biochemical oxidation reactors contained an acclimated, mixed culture originally obtained from the biological treatment unit at the Clairton Coke Works of the U.S. Steel Corporation. The bacteria are mainly of the genus *Pseudomonas.* Vessels used in the biochemical oxidation kinetic model studies were 7-liter and 35-liter, complete-mix, aerobic activated-sludge reactors that have been described previously [2, 3]. These reactors were operated over a ten-month period to allow acclimation of the biomass, and data collection during steady-state performance. The 35-liter reactor was fed raffinate from the solvent extraction column and was the subject of detailed analysis. The 7-liter reactors were fed wastewater from the effluent of the dissolved-gas-stripping still for comparison. One reactor was fed undiluted, stripped H-Coal process wastewater, while two others were fed a solution containing H-Coal process wastewater diluted with tap water. Solutions of magnesium sulfate, ferric chloride, and a phosphate buffer were added to all of the wastewater fed to the biological reactors to provide the required nutrient concentrations. The feed rate of the reactors was controlled by precision positive-displacement pumps. The feed solutions were stored in stainless steel tanks at 4°C to minimize biological activity prior to introduction to the reactor. The aeration chambers were maintained at room temperature (approximately 24°C).

A continuous activated-carbon-adsorption column was operated as the final step of the treatment process. Effluent from the 35-liter biochemical oxidation reactor was allowed to flow through a sand bed, then through an acrylic column, with an inside diameter of 1.9 cm and a bed height of 0.78 m, that was charged with 100 g of Calgon Filtrasorb-400 granular activated carbon.

A 4-liter sample of untreated H-Coal process wastewater was provided to Zimpro, Inc., for laboratory wet-air oxidation tests. All oxidation experiments were performed in titanium laboratory autoclaves at temperatures of 250°C, 275°C, 300°C, and 320°C. The autoclaves were charged with 100 mL of raw wastewater and with air that supplied 120 percent of the oxygen equivalent of the sample chemical oxygen demand (COD). The charged autoclaves were then placed in a shaker mechanism, heated to the desired oxidation temperature, and held for one hour. Immediately after oxidation, the autoclaves were quenched with tap water. The characteristics of the wet-air oxidized wastewater, as determined by Zimpro, Inc., are given in Table 2. The results of additional characterization reported in this paper are for the sample oxidized at 275°C.

Bioassays

Short-term (acute) bioassays were employed using the fresh water invertebrate *Daphnia Magna* to determine median effective-concentration (48-h EC_{50}) values for the treated and untreated H-Coal process wastewaters. All tests were performed according to Standard Methods [5] and U.S. Environmental Protection Agency [6] procedures for acute assays, and were conducted in an environmentally controlled laboratory at 20 ± 0.5°C. Natural conditions were simulated via a 12-h light/dark lighting regime. Serial test dilutions were prepared for the untreated and treated wastewater on a volume percent basis with spring water. The spring water had a pH of 8.1; total alkalinity of 210 mg/L (as $CaCO_3$); and total hardness of 230 mg/L (as $CaCO_3$). Tests were started by inoculating ten neonate *D. magna* (less than 24-h old) in covered, 250-mL glass beakers containing replicate 100-mL volumes of each test dilution. A control beaker of spring water was also inoculated with an equal number of organisms and included with each test run.

TABLE 2. WET-AIR OXIDATION OF H-COAL PROCESS WASTEWATER

Oxidation Temperature, °C	250	275	300	320
Time at Temperature, min	60	60	60	60
Chemical Oxygen Demand,mg/L	8200	5300	4800	3300
Total Organic Carbon, mg/L	2210	1990	1560	1380
Total Kjeldahl Nitrogen, mg/L	4730	4650	4760	4760
Ammonia (reported as N), mg/L	4060	4450	4360	4350
Soluble Chloride, mg/L	125	124	138	118
Biochemical Oxygen Demand, mg/L	3530	3350	3110	2330
Total Sulfur, mg/L	4760	4880	4970	4960
Sulfate Sulfur, mg/L	4970	4980	4970	4970
pH	2.7	3.0	3.0	3.7

NOTE: Oxidation and analysis performed by Zimpro, Inc., Rothschild, Wisconsin.

Acute toxicity values and 95 percent confidence limits were determined for the wastewater samples using a computer program based on the Litchfield-Wilcoxon log-probit method. For the purpose of our study, the 48-h EC_{50} was defined as the percent concentration of wastewater that affects half of the test population over a two-day test period. Immobilization of the test organism was used as the bioassay endpoint.

Analytical Methods

The general characteristics of the wastewater—phenols (by the 4-aminoantipyrine method), cyanide, thiocyanate, total carbon, total inorganic carbon, total organic carbon, chemical oxygen demand, chloride, total ammonia, sulfide, and biochemical oxygen demand—were determined by the Analytical Chemistry Branch at the Pittsburgh Energy Technology Center using Standard Methods [5].

The organic components of the wastewater, the sludges formed, and the extract from solvent extraction were determined either by high-performance liquid chromatographic analyses or gas chromatographic analyses. High-performance liquid chromatographic analyses (LC) were carried out on a Hewlett-Packard model 1084B chromatograph. A Regis Hichrom C-18 reverse-phase column packed with 5 μm Spherisorb S5 ODS-II, which was protected by a Brownlee MPLC cartridge-type guard column with similar packing, was used for all LC analyses. Solvents were a pH 4 phosphate buffer prepared with J. T. Baker HPLC-grade water, and J. T. Baker HPLC-grade acetonitrile. Flow was 1.00 mL/min at a column temperature of 50°C, with detection at 220 nm and 273 nm, respectively, on duplicate sequential runs.

Gas chromatographic analyses (GC) were completed on a Hewlett-Packard model 5840A chromatograph equipped with a flame ionization detector and fitted with an Alpine West 30-m × 0.20-mm silica capillary coated with a 0.1-μm film of Superox 20M. Operating conditions, retention indices, and behavior of monohydric phenols on the Superox column are described in detail in the literature [7].

Liquid chromatographic analyses were carried out with external standards; GC analyses used p-*tert*-amylphenol as an internal standard. Before injection, samples for LC analysis were filtered through Acrodisc-CR disposable syringe filters with a 0.45-μm pore diameter. Gas chromatographic analysis was preceded by continuous extraction of a 10-mL aqueous sample with Baker Resi-Analyzed methylene chloride in Lab Glass microextractors. Volume adjustment of the extract to 5 mL resulted in a twofold increase in unknown concentrations in the extract. The extracts were dried before injection by passing down a short, disposable column packed with sintered anhydrous sodium sulfate.

Elemental analyses were conducted by two laboratories. Certain elements (magnesium, iron, cadmium, copper, and lead) were determined by the Analytical Chemistry Branch at the Pittsburgh Energy Technology Center using atomic absorption spectroscopy. Silicon, fluoride, and the remainder of the metals were determined by Huffman Laboratories, Wheatridge, Colorado.

RESULTS AND DISCUSSION

Discussion of results obtained during this investigation is divided into four sections: 1) the general characteristics of the wastewater, 2) the specific organic species identified, 3) the elements chosen for analysis, and 4) the aquatic toxicity of the wastewater.

General Characteristics

The general characteristics of the H-Coal process wastewater at each step in the treatment train are given in Table 3. This table includes values for specific contaminants, such as cyanide, thiocyanate, chloride, ammonia, and sulfide. It also includes parameters that encompass a wide range of contaminants in a single measurement, such as phenols determined by the 4-aminoantipyrine method (4-AAP Phenols), total organic carbon (TOC), chemical oxygen demand (COD), and biochemical oxygen demand (BOD).

Wet-air oxidation, at 275°C for 60 minutes, is seen to be capable of practically 90 percent reduction of the COD. The sulfide present in the wastewater is completely oxidized to sulfate, while approximately 77 percent of the TOC is removed from the wastewater. Wet-air oxidized wastewater would require further treatment to remove the remaining contaminants. Because of the small volume of wastewater oxidized by Zimpro, Inc., further treatability testing was not possible. The remaining BOD of 3350 mg/L suggests that the effluent from the wet-air oxidation of H-Coal process wastewater could be amenable to biochemical oxidation. This is in agreement with liquid chromatographic analysis of this sample, which shows the presence of a complex mixture of carboxylic acids.

The other columns in Table 3 describe the results of a sequence of treatment operations forming an integrated treatment process. Except for wet-air oxidation, the characteristics of the effluent from one treatment operation describe the influent to the successive treatment operation.

The untreated H-Coal process wastewater was first subjected to dissolved-gas stripping. In the free leg of this stripping process, most of the free ammonia and greater than 99 percent of the sulfide are removed at a pH of 9 or less. Approximately 97 percent of the inorganic carbon, mostly carbonates, is also removed. Most of the cyanide present in this wastewater is removed in this step, leaving 0.02 mg/L of cyanide in the wastewater.

Lime is added to the wastewater to allow further removal of ammonia by shifting the equilibrium between un-ionized and ionized ammonia. The dissolved-gas stripping operation was continued until 200 mg/L of ammonia remained in the wastewater, removing 96 percent of the ammonia in the untreated H-Coal process wastewater. Approximately 8 percent of the 4-AAP phenols were also stripped from the wastewater, potentially contaminating systems employed to recover sulfide and ammonia in a commercial-scale facility.

After dissolved-gas stripping, the wastewater was sent to a solvent extraction column. Contact with methyl isobutyl ketone in the extraction column removed the bulk of the 4-AAP phenols, leaving 40 mg/L requiring further processing. Approximately 93 percent of the TOC and 92 percent of the COD were also removed in this step. The organic compounds extracted by the methyl isobutyl ketone are primarily biodegradable. A BOD of 950 mg/L remained after solvent extraction.

After removal of residual solvent, the wastewater was subjected to biochemical oxidation. The 4-AAP phenols were removed to levels below the limit of detection, and essentially all of the BOD was removed from the wastewater. Biochemical oxidation removed 71 percent of the TOC and 75 percent of the COD. Effluent from the biochemical oxidation reactor could be considered for reuse in a facility in certain applications.

Biochemical oxidation effluent was subjected to activated-carbon adsorption as the last step in the treatment process. It is expected that the quality of water obtained from the activated-carbon column would be suitable for either reuse in the facility or discharge to the environment. This combination of wastewater treatment operations is capable of producing water with very low concentrations of 4-AAP phenols, TOC, COD, and BOD.

Organic Species

The distribution of organic compounds throughout the treatment train is of primary interest in this study. The concentrations of the organic compounds measured are given in Table 4. Attention was directed towards phenolic compounds, since liquid chromatographic determination of twelve specific phenols accounted for greater than 98 percent of the total organic carbon. It should be noted that the concentration of phenols determined by the 4-aminoanti-

TABLE 3. CHARACTERIZATION OF H-COAL PROCESS WASTEWATER DURING TREATMENT

			Dissolved-Gas Stripping				Activated-Carbon Column Effluent					
							Bed Volume[b]					
	Untreated H-Coal Wastewater	Wet-Air Oxidation at 275°C (Zimpro, Inc.)	Free-Leg (pH as received)	Fixed-Leg[a] (with lime) addition)	Solvent Extraction Raffinate Stripped of Residual Solvent	Biochemical Oxidation Effluent	2.61-6.45	6.68-11.18-	11.18-16.35	18.92-25.65	26.34-29.93	30.32-37.04
4-AAP Phenols	9150	—	8560	8390	40	≤1	0.21	≤1	0.03	≤1	0.02	≤1
Cyanide	0.12	—	0.02	0.02	0.02	0.01	—	—	—	0.02	—	0.02
Thiocyanate	15	—	10	≤5	≤5	≤5	—	≤5	—	≤5	—	≤ 5
Total Carbon	11400	2560	10400	9700	740	240	—	45	—	45	—	50
Total Inorganic Carbon	370	5	10	5	15	30	—	40	—	35	—	30
Total Organic Carbon	11030	2555	10390	9695	725	210	—	5	—	10	—	20
Chemical Oxygen Demand	51900	5300	34600	27000	2220	550	—	15	—	—	—	≤10
Chloride	180	125	80	150	90	90	—	90	—	110	—	100
Total Ammonia	5500	4450	1000	200	160	110	—	100	—	120	—	140
Sulfide	3900	—	≤10	≤10	≤10	≤10	—	≤10	—	≤ 10	—	≤10
Biochemical Oxygen Demand	15900	3350	—	—	950	5	—	—	—	5	—	10

NOTE: All concentrations given in mg/L.

[a] Values given are for the wastewater after removal of lime sludge and adjustment to pH = 7.0.

[b] One Bed Volume is defined as the total volume of the column occupied by the activated-carbon bed (221.2 cm^3).

TABLE 4. SPECIFIC ORGANIC COMPOUND ANALYSIS OF H-COAL PROCESS WASTEWATER DURING TREATMENT

	Untreated H-Coal Wastewater, mg/L	Wet-Air Oxidation at 275°C (Zimpro, Inc.), mg/L	Dissolved-Gas Stripping		Solvent Extraction		
			Effluent, mg/L	Lime Sludge,[a] g/kg (dry wt.)	Raffinate, mg/L	Raffinate Stripped of Residual Solvent, mg/L	Extract,[a] mg/L
Resorcinol	285	25	260	—	20	20	—
Catechol	145	≤0.5	50	—	3	≤0.5	—
2-Methylresorcinol	95	≤0.5	90	—	1	≤0.5	—
Phenol	9860	150	8930	370	75	65	52360
m- and p-Cresol	2300	40	1600	245	55	25	13310
o-Cresol	910	15	410	30	10	10	4685
3,4-Xylenol	125	1	105	15	2	3	300
2,3- and 3,5-Xylenol, and 4-Ethylphenol	125	1	90	50	2	4	1290
2,4- and 2,5-Xylenol	320	5	135	—	4	4	—
3-Ethylphenol	—	—	—	30	—	—	895
4-n-Propylphenol	—	—	—	2	—	—	120
4-Indanol	—	—	—	10	—	—	340
5-Indanol	—	—	—	15	—	—	245

NOTE: All concentrations determined by liquid chromatography except as noted.
[a] Organic compound concentrations determined by gas chromatography.

pyrine method is significantly lower than the concentration of phenols determined by LC (9150 and 14165 mg/L, respectively). There are several possible reasons for this discrepancy [8]. The 4-aminoantipyrine method does not determine para-substituted phenols in which the substituent is an alkyl, aryl, nitro, benzoyl, nitroso, or aldehyde group. An example of this would be para-cresol. And, because phenol itself is used as the standard for this colorimetric procedure, and ring substitution generally reduces the response in this method, concentrations reported for mixed phenols are low. In addition, steam distillation of phenols from the highly colored wastewater is required prior to their spectrophotometric determination with 4-aminoantipyrine. Incomplete steam distillation has been observed with these wastewaters, resulting in even lower values being reported.

The calculated stoichiometric carbon equivalents of the organic compounds identified in H-Coal process wastewater are given in Table 5. This table allows a comparison of the concentrations of specific compounds with the total organic carbon (TOC) concentration measured for the sample. This is done by multiplying the fraction of the molecular weight of the compound contributed by carbon by the concentration of the compound.

As can be seen in Table 4, phenols are generally depleted as they traverse the treatment train. Wet-air oxidation was not part of the integrated treatment and will be considered separately. Bioeffluent and carbon column effluent concentrations were below the detection limits (*ca.* 0.5 mg/L) for any of the components listed and are not presented. An item of note is the increase in unidentifiable TOC shown in Table 5, from about 190 mg/L in the raw water to about 770 mg/L in the dissolved-gas-stripping effluent. This was attributed to the formation of unidentified products during the stripping process, possibly by phenolic-coupling reactions. These reactions, which are oxidative in nature, were prevented from occurring in the raw water by the high hydrogen sulfide levels. The materials formed are not generally susceptible to extraction by methyl isobutyl ketone. After extraction, 627 mg/L unidentifiable TOC remains in the wastewater, which would be consistent with the phenolic-coupling postulate.

Further inspection of Table 4 shows that wet-air oxidation of the raw water for 60 minutes at 275°C depletes monohydric phenols to about 1 to 2 percent of their original values and essentially destroys catechol and 2-methylresorcinol. Resorcinol itself either is more resistant to wet-

TABLE 5. STOICHIOMETRIC CARBON EQUIVALENTS OF THE ORGANIC COMPOUNDS IDENTIFIED IN H-COAL PROCESS WASTEWATER

	Untreated H-Coal Wastewater		Wet-Air Oxidation at 275°C (Zimpro, Inc.)		Dissolved-Gas-Stripping Effluent		Solvent Extraction Raffinate Stripped of Residual Solvent	
	Carbon Equivalent, mg/L	Percent of Measured TOC	Carbon Equivalent, mg/L	Percent of Measured TOC	Carbon Equivalent, mg/L	Percent of Measured TOC	Carbon Equivalent, mg/L	Percent of Measured TOC
Resorcinol	187	1.7	16	0.6	170	1.8	13	1.8
Catechol	95	0.9	0	0	33	0.3	0	0
2-Methylresorcinol	64	0.6	0	0	61	0.6	0	0
Phenol	7550	68.4	115	4.5	6838	70.5	50	6.9
m- and p-Cresol	1788	16.2	31	1.2	1244	12.8	19	2.6
o-Cresol	708	6.4	12	0.5	319	3.3	8	1.1
3,4-Xylenol	98	0.9	1	0	83	0.9	2	0.3
2,3- and 3,5-Xylenol, and 4-Ethylphenol	98	0.9	1	0	71	0.7	3	0.4
2,4- and 2,5-Xylenol	252	2.3	4	0.2	106	1.1	3	0.4
Calculated Total Organic Carbon Equivalent	10840	98.3	180	7.0	8925	92.0	98	13.5
Measured Total Organic Carbon	11030	—	2555	—	9695	—	725	—
Unidentified Organic Carbon	190	1.7	2375	93.0	770	8.0	627	86.5

air oxidation than any of the other phenols or is being formed from the oxidation of phenol. This latter postulate must be rejected on the grounds that in known oxidations of phenol with oxygen or ozone, resorcinol is not a product. Only 7 percent of the TOC of the wet-air oxidized sample was identified as phenols. Liquid chromatographic analysis of this sample showed the presence of a complex mixture of carboxylic acids, the expected products for this type of reaction.

Elements

Elemental distribution during operation of the treatment train was also of interest, especially distribution of those elements affecting reuse and disposal. As can be seen in Table 6, the metals tend to concentrate in the lime and bio-sludge. This is not unexpected, as the increased pH of the lime slurry should precipitate heavy metals, and the bio-sludge is an effective chelating surface for most of the same metals. Calcium from lime addition during dissolved-gas stripping is also accumulated in the bio-sludge. Fluoride ion is concentrated in both the lime sludge, presumably as CaF_2, and the bio-sludge. Values for silicon, present as SiO_2, are somewhat erratic, but Table 6 makes it apparent that the source for silicon is the lime added in the fixed-leg-stripping operation. This is also the case for selenium, lead, and barium, and is most noticeable with barium, where the aqueous concentration increased from ≤0.10 to 8.2 mg/L. It should be noted that the lime used in this study was reagent-grade calcium hydroxide.

The calcium and barium values reported for the activated-carbon column effluent in Bed Volumes 6.68-11.18, 18.92-25.65, and 30.32-37.04 are much higher than expected and appear to be the result of contamination of the samples. Analyses of additional samples (Bed Volumes: 2.61-6.45, 11.18-16.35, and 26.34-29.93) showed calcium and barium concentrations consistent with those reported for preceding treatment operations.

Aquatic Toxicology

Acute toxicity tests were performed on the untreated H-Coal process wastewater and on samples taken after each treatment operation. Bioassay and chemical characterization results are shown in Table 7. A progressive reduction in acute toxicity followed each unit operation of the integrated treatment train. Acute toxicity removal was also recorded after wet-air oxidation. The complete treatment sequence resulted in a 99.9 percent decrease in acute toxicity, from a 48-h EC_{50} of 0.03 percent for the untreated wastewater to 64.0 percent for the activated-carbon-column effluent (Bed Volume: 6.68-11.18). The decrease in acute toxicity after treatment accompanied significant reductions in the inorganic and organic components of the wastewater.

The histogram of the relative toxicity of each of the unit operations' effluents to the untreated wastewater, shown in Figure 3, demonstrates the effectiveness of each of these unit operations. The initial step of the integrated treatment train involved dissolved-gas stripping to reduce the high concentration of ammonia present in the wastewater. This unit operation removed over 96 percent of the total ammonia, reducing the toxicity of the wastewater by 75 percent. The addition of calcium hydroxide in the fixed leg of the dissolved-gas-stripping process may account for the slight increase in toxicity observed for this sample in comparison to the free leg of the dissolved-gas-stripping process.

The largest reductions in acute toxicity occurred after solvent extraction of the wastewater with methyl isobutyl

TABLE 6. ELEMENTAL ANALYSIS OF H-COAL PROCESS WASTEWATER DURING TREATMENT

	Untreated H-Coal Wastewater	Dissolved-Gas Stripping				Solvent Extraction Raffinate Stripped of Residual Solvent	Biochemical Oxidation Effluent	Biosludge	Activated-Carbon Column Effluent					
		Free-Leg (pH as received)	Fixed-Leg[a] (with lime addition)	Lime[b]	Lime Sludge				Bed Volume[c] 2.61-6.45	6.68-11.18	11.18-16.35	18.92-25.65	26.34-29.93	30.32-37.04
Magnesium	0.7	0.9	0.7	—	—	2.0	10	≤10	—	10	—	10	—	8
Calcium	3	20	800	—	—	700	600	118400	400	1500	500	1900	700	1900
Copper	0.1	0.1	0.1	≤0.5	3.7	0.1	0.1	100	—	≤0.1	—	≤0.1	—	≤0.1
Lead	≤0.1	≤0.1	≤0.1	≤0.5	≤0.5	0.2	0.2	—	—	≤0.1	—	≤0.1	—	0.2
Iron	1.0	1.0	0.8	200	250	0.2	0.1	1400	—	≤0.1	—	≤0.1	—	≤0.1
Cadmium	≤0.01	—	—	≤0.2	≤0.5	≤0.005	≤0.005	3.4	—	≤0.01	—	—	—	—
Mercury	≤0.002	—	—	≤0.1	6.7	≤0.002	≤0.002	≤0.1	—	≤0.001	—	—	—	—
Barium	≤0.1	—	—	600	200	8.2	7.6	200	0.3	370	0.4	—	0.7	—
Arsenic	0.12	—	—	1.6	4.3	0.06	0.03	64	—	0.04	—	—	—	—
Selenium	0.02	—	—	1.2	36	0.05	0.01	12	—	0.03	—	—	—	—
Beryllium	≤0.01	—	—	0.49	0.24	≤0.01	≤0.01	0.25	—	≤0.01	—	—	—	—
Silicon	≤2.0	—	—	17900	27600	4.6	3.3	13200	—	2.0	—	—	—	—
Fluoride	4	—	—	≤200	300	0.2	0.2	200	—	0.5	—	—	—	—

Note: All concentrations given in mg/L (except lime, lime sludge, and biosludge concentrations which are based on the dry weight of the sample and given in mg/kg).
[a] Values given are for the wastewater after removal of lime sludge and adjustment to pH = 7.0.
[b] Lime denotes the reagent-grade calcium hydroxide ($Ca(OH)_2$) added to the wastewater to raise pH during dissolved-gas stripping.
[c] One Bed Volume is defined as the total volume of the column occupied by the activated bed (221.2 cm^3).

TABLE 7. ACUTE TOXICITY AND CHEMICAL CHARACTERIZATION OF TREATED AND UNTREATED H-COAL LIQUEFACTION WASTEWATERS

	48-h EC_{50} (%)	4-AAP Phenols (mg/L)	TOC (mg/L)	COD (mg/L)	Total NH_3 (mg/L)	Sulfide (mg/L)
Untreated Wastewater	0.03	9150	11030	51900	5500	3900
Dissolved-Gas Stripping						
free-leg	0.15	8560	10390	34600	1000	≤10
fixed-leg	0.12	9100	10100	34600	200	≤10
Solvent Extraction	2.55	50	890	2580	180	≤10
Biochemical Oxidation	53.0	≤1	140	340	110	≤10
Activated-Carbon Adsorption (Bed Volume: 6.68-11.18)	64.0	≤1	5	15	100	≤10
Wet-Air Oxidation	0.32	—	2555	5300	4450	—

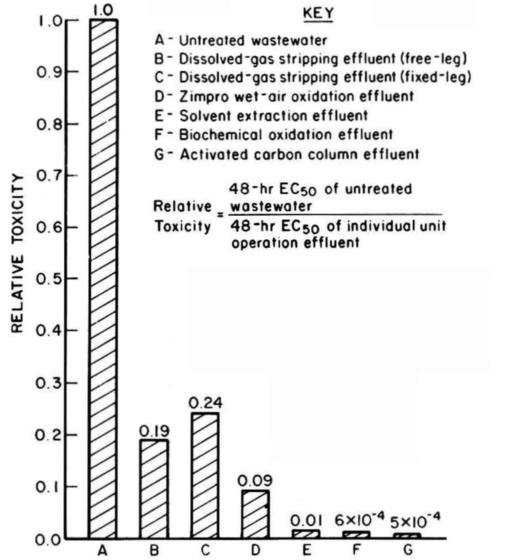

Figure 3. Relative toxicities of treated and untreated H-Coal wastewater.

ketone and after biochemical oxidation. The effluents from the solvent extraction column and the biochemical oxidation reactor were over 20 times less toxic than their respective influents.

Activated-carbon adsorption (Bed Volumes 6.68 to 11.18) was responsible for the lowest observed toxicity, a 48-h EC_{50} of 64.0 percent. Analysis of the activated-carbon-column effluent revealed phenol, TOC, COD, and total ammonia concentrations of ≤ 1 mg/L, 5 mg/L, 15 mg/L, and 100 mg/L, respectively. However, this effluent contained 1500 mg/L calcium. This high calcium concentration may contribute, in part, to the acute toxicity remaining after activated-carbon treatment. These high calcium values were unexpected. Analyses of other composite samples from the activated-carbon column showed calcium concentrations between 400 mg/L and 700 mg/L, as reported in Table 6, suggesting that the composite samples chosen for the acute toxicity assays were contaminated with lime. The barium concentration for Bed Volumes 6.68 to 11.18 is also much higher than for the other samples analyzed, with a concentration of 370 mg/L. Because of the possible contamination of the samples tested, the aquatic toxicity of the uncontaminated samples may be lower than that reported.

A sample of the untreated wastewater also underwent laboratory wet-air oxidation at 275°C for 60 minutes. Due to the high acidity (a pH of 3.0) of the wet-air oxidized sample, the test dilutions were adjusted to pH 7.8 with reagent-grade calcium hydroxide prior to assaying. At this pH, the 48-h EC_{50} of the effluent was 0.32 percent. Although this represents an 11-fold decrease in acute toxicity, it is comparatively small when viewed in light of the overall acute toxicity reduction and probably reflects the high total ammonia concentration remaining in the wastewater. The calcium added to this sample for neutralization might also contribute to the residual acute toxicity.

SUMMARY

The treatment train investigated is capable of significantly improving the quality of H-Coal process wastewater, reducing contaminant concentrations to low levels. The detailed characterization of the effluents from each of the unit operations in the treatment sequence allows a determination of the degree of treatment required for specific applications for reuse in the facility or for discharge to the environment. The observed aquatic toxicity of the wastewater was drastically decreased over the treatment train employed, indicating that any contaminants remaining in the wastewater (whether identified or not) do not contribute significantly to its aquatic toxicity.

Measurements of the constituents in the sludges formed during treatment indicate that certain elements could accumulate in the lime sludge and the bio-sludge, requiring proper disposal. The concentration of various organic constituents measured in the extract from solvent extraction can be used to determine the value of the crude phenolic stream that could be recovered as a by-product.

The sequence and choice of unit operations used in this treatability study are not intended to suggest an optimal or preferred treatment system. Alternate arrangements and other combinations of wastewater treatment unit operations and processes should be considered in the design of a coal liquefaction facility. Removal of phenols, by solvent extraction of the wastewater, before dissolved-gas stripping would reduce organic compound contamination in the processes used to recover ammonia and sulfur from the sour gas produced during dissolved-gas stripping. However, more careful consideration of the solvent used in phenol extraction would be necessary because of potential interaction with the high concentration of sulfide present in the wastewater. Solvent extraction also benefits biochemical oxidation of this wastewater. Dilution is a potential alternative to solvent extraction but requires a greater volume of wastewater under aeration. Wet-air oxidation could be used in place of both dissolved-gas stripping and solvent extraction. The use of activated-carbon adsorption in the treatment of this wastewater would depend on the quality of water required. Activated carbon removes color and residual organic contaminants, producing a high-quality water.

Treatment operations not included in the scope of this study might also be required in a system treating H-Coal process wastewater. If ammonia concentrations less than 100 mg/L are required for a particular reuse application or for discharge to the environment, the use of biological nitrification or other processes could be necessary.

Environmentally acceptable coal liquefaction facilities can be constructed if these factors are carefully considered and thoughtfully incorporated into their design.

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Gasifier Wastewater Treatment: Phase I Cooling Tower Assessment

Details of an advanced study of the treatability of wastewaters from the fixed-bed gasification of lignite.

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The Great Plains Gasification Associates (GPGA) plant at Beulah, North Dakota, and many other gasification plants in the future will be generating millions of liters of wastewater per day. Due to the limited number of gasifiers operating in this country, there is a need to develop environmental data concerning the wastewaters produced from the various gasification processes. The University of North Dakota Energy Research Center (UNDERC) has been operating a pilot-scale oxygen blown fixed-bed gasifier with lignite to provide wastewaters for subsequent characterization, and treatment and reuse studies. UNDERC also has a pilot-scale wastewater treatment system designed according to proposed commercial applications. These capabilities have led to the development of an extensive wastewater treatment/reuse program at UNDERC.

The principal goal of the gasification research at UNDERC is to develop environmental data on the treatability of wastewaters from the fixed-bed gasification of lignite. The extent of treatment is dictated by end use, or ultimate disposal options available at a given location. In water deficient regions such as the western United States, the reuse of wastewaters as makeup for an evaporative cooling tower will be a key factor in minimizing plant water requirements and the volume of water requiring ultimate disposal. Research activities at UNDERC are focused around the cooling tower, where the reuse of treated gasification wastewaters has not been demonstrated in this country. The extent of treatment needed to produce a makeup to the cooling tower which minimizes the environmental and economic risks is unknown. The most cost-effective approach is to provide minimal treatment. Fixed-bed gasification wastewaters are represented by solvent extraction for reduction of organic contaminants (e.g., phenols) and steam stripping for reduction of ammonia and acid gas (e.g., hydrogen cyanide and sulfide). However, this wastewater still contains several thousand mg/liter of COD and significant quantities of ammonia. The behavior of these contaminants in a cooling tower with respect to drift loss, biological activity, and associated fouling of heat transfer and other surfaces, system corrosion, and the solubility of dissolved solids is unknown.

TEST PROGRAM OBJECTIVES

The objective of Phase I cooling tower testing was to evaluate the effectiveness of using minimally treated wastewater (solvent extracted and steam stripped—referred to as stripped gas liquor) as makeup to a cooling tower. This level of treatment was chosen as it corresponds to the current GPGA design for wastewater treatment. Wastewater generated in the slagging fixed-bed gasifier (SFBG) was pretreated in the UNDERC treatment train to produce wastewater with phenol and ammonia concentrations which correspond to those published for the GPGA design [1]. The UNDERC cooling tower and associated test equipment was designed to simulate heat duties and tube velocities reported for the GPGA design. This equipment was used as part of the two-month test of the environmental and operating problems associated with the use of stripped gas liquor as cooling tower makeup.

PREPARATION OF STRIPPED GAS LIQUOR

Wastewater for use in the Phase I cooling tower assessment was produced from slagging fixed-bed gasification of lignite. The lignite chosen for wastewater production came from the Indian Head mine near Mercer, North Dakota. In addition to having favorable ash properties for slagging operations, this lignite was from the same seam, and in fact, within a few miles of the mine to supply the GPGA plant. Thus, the choice of the coal was made to lessen possible differences with respect to GPGA in the nature of organics in wastewater, which are thought to be coal specific.

The UNDERC gasifier, which has been previously described [2, 3, 4], is a pilot-scale slagging version of the commercial dry-ash, fixed-bed process. Wastewaters are collected in a quenching vessel (spray cooler) where the product gases and devolatilization products from the gasifier are cooled by contacting with a cooled recirculating stream of gas liquor. Water vapors, tars, and oils are condensed, and soluble gases such as NH_3, CO_2, HCN, and H_2S are scrubbed from the overhead gases. Wastewater is separated from tars and oils by gravity in a tar/oil/water separator.

Pretreatment Of Gasification Wastewater

Pretreatment of the gas liquor consists of filtration through coarse gravel to remove residual suspended tars, solvent extraction for reduction of phenolic compounds, and stripping of dissolved gases such as ammonia, hydrogen sulfide, and hydrogen cyanide. The solvent extraction is performed in a 0.15 m-diameter by 3.0 m high York-Scheibel agitated packed glass column. Diisopropyl ether is used at a solvent-to-wastewater ratio of 1:11 to reduce phenol concentrations to approximately 150 mg/liter. The solvent and final phenol concentration were chosen to simulate the proposed operations at GPGA using the Phenosolvan Process [1].

The solvent-extracted gas liquor is steam stripped in a 0.20 m diameter by 3.5 m high packed column. A steam rate of approximately 0.23 mg/liter (1.9 lb/gal) SGL produces a final effluent with an ammonia level of 500 mg/liter. This level of stripping is performed to match published GPGA design data, and does not represent the total removal of the free ammonia. Wastewater from the steam stripper is referred to as stripped gas liquor (SGL). Table 1 presents steady-state concentrations of the wastewater as it is processed through the pretreatment train.

TABLE 1. STEADY-STATE WASTEWATER CONCENTRATIONS AFTER SUCCESSIVE PRETREATMENT STEPS

	Filtered (mg/liter)	Extracted (mg/liter)	Stripped (mg/liter)
Methanol	1450	1440	230
Acetone	40	50	10
Acetonitrile	420	370	2
Isopropyl ether	0	3410	0
Propionitrile	85	38	0
Phenol	4560	210	160
Cresol	2480	33	30
Dimethyl Hydantoin	2280	2340	2140
Ethyl-methyl Hydantoin	510	520	490
Acetate	NA	NA	180
ph	8.3	8.5	8.9
Alkalinity	23200	23100	1500
Ammonia	7890	7980	565
Sulfide	370	300	8
Cyanide	75	63	39
Thiocyanate	230	200	210
COD	27900	16200	5700

Comparison Of Stripped Gas Liquor

UNDERC analysis of SGL indicates that some differences exist in the organic contaminants in the SFBG wastewater versus design analysis for Great Plains [1]. A typical analysis of the stripped gas liquor is compared with the analysis of SGL anticipated as feed to the cooling tower by GPGA in Table 2.

The reported analyses for the SGL and for the GPGA design were generated at SASOL in 1974 from operation on 1.1 × 10^7 kg of North Dakota lignite [1]. The major differences are the concentration of fatty acids, the presence of significant amounts of hydantoins, and higher COD in the UNDERC wastewaters. The differences are the result of higher operating temperatures in the UNDERC slagging gasifier as compared to the Lurgi.

TEST EQUIPMENT DESCRIPTION

A schematic of the cooling tower test loop is presented in Figure 1. The system consists primarily of a cooling tower and instrumented test heat transfer equipment. The design operating conditions for major equipment items are presented in Table 3. This equipment is described in detail by Willson *et al.* [5].

Cooling Tower

The test cooling tower is a packaged Baltimore Aircoil Company, Model VXT-20WC with a forced draft fan and operated in a counterflow configuration. The cross sectional area of this tower is 0.46 square meters which allowed a liquid/gas ratio simulating that proposed by GPGA. A forced draft fan equipped with dampers controls air flow through the tower to maintain a constant cooling water sump temperature of 28°C. The cooling tower exhaust duct is equipped with ports for sampling equipment and velocity and temperature (wet and dry bulb) measurements.

As indicated previously, the major objective of the UNDERC Phase I cooling tower test was to investigate the proposed use of minimally treated process wastewater as cooling tower makeup. To make this investigation as meaningful as possible, efforts were made to design and

TABLE 2. COMPARISON OF STRIPPED GAS LIQUOR (MG/LITER)

	GPGA	UNDERC
Methanol	—[a]	230
Fatty Acids	1600	290
Phenol	150	160
Hydantoins	—[a]	2600
NH_3	500	570
COD	2900	5700

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[a] No analysis of these compounds available.

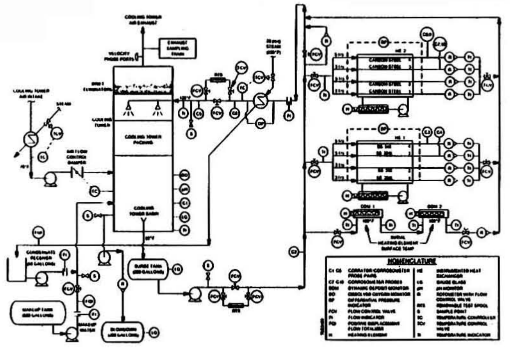

Figure 1. Schematic of UNDERC pilot cooling tower system.

operate the UNDERC pilot cooling tower in a manner which closely simulated the operating plants for the GPGA cooling tower. The UNDERC tower uses a more dense packing than the GPGA tower but uses less packing depth to compensate. The key points are a high degee of similarity in the water circulation rate (in terms of liters per min per meter squared of packing surface, (1.19 versus 1.22 (liter/min)/m^2)), air flow rate (0.89 versus 0.77 (m^3/min)/(liter/min)), identical circulating water temperatures, and system turnover time (15 versus 20 min) between the GPGA and UNDERC towers respectively [6]. Because of these important similarities, the UNDERC pilot cooling tower should produce a realistic simulation of the operating conditions in a commercial cooling tower.

Test Heat Exchangers

The cooling water leaving the cooling tower was pumped through two instrumented shell-in-tube test heat exchangers operating in parallel. The flow rates and metallurgy for each tube are given in Table 3. Each tube has its own flow controller, inlet and outlet thermistors, and differential pressure gauge for monitoring heat transfer and fouling buildup.

Dynamic Deposit Monitors

In addition to the test heat exchangers, two Calgon Dynamic Deposit Monitors (DDM) were operated in parallel with the test heat exchangers. In the DDM, the cooling water flows across a heating element. As fouling occurs, the skin temperature of the heating element increases to maintain a constant heat flux into the cooling water. The change in these data can be correlated to determine the rate of degradation of the performance of heat transfer equipment. Cooling water flow through the DDM's was set at a linear velocity of 0.31 m/sec across the heating element as per the manufacturer's recommendation to accelerate fouling and corrosion.

RESULTS AND DISCUSSION

Process Performance

The operability and performance of the test cooling tower system is important in evaluating the results obtained from the test program. The process performance is based on the operating conditions achieved during the test run and the factors which affected performance. Discussions of the issues of biofouling, corrosion, and inorganic/organic fouling are presented in later sections. A detailed presentation of the material discussed in this paper has been prepared [5].

A significant problem associated with the cooling tower involved excessive foaming of the circulating water. This problem occurred immediately after startup of the system using stripped gas liquor. Three antifoam agents were tested, all of which successfully controlled foaming. Initially, a glycol-based antifoaming agent was used at a dosage rate of 5 ml every 2 hours (equal to a "shock treatment"

TABLE 3. DESIGN OPERATING CONDITIONS

Parameter	Design/ Typical Value	
Cooling Tower		
Recirculating Water Rate, liter/min	34	
Makeup Water Rate, liter/min	0.95	
Cycles of Concentration	10	
Air Rate, m^3/min	25	
Inlet Water Temperature, °C	49	
Outlet (Basin) Water Temperature, °C	28	
	Heat Exchanger 1 (HE-1)	Heat Exchanger 2 (HE-2)
Tube Type/Velocity (m/sec)		
Tube #1	304L SS/0.91	carbon steel/0.91
Tube #2	316 SS/0.91	carbon steel/1.52
Tube #3	304L SS/1.52	carbon steel/0.91
Tube #4	316 SS/1.52	carbon steel/1.52
Shell-side Water Temperature, °C	88	50
Tube Wall Temperature, °C	60	38
Dynamic Deposit Monitor	DDM-1	DDM-2
Cooling Water Velocity, m/sec	0.31	0.31
Heat Flux, W/m^2	8000	27000
Initial Skin Temperature, °C	38	65

of approximately 10 mg/liter). Two silicon-based antifoam agents (Calgon CL37 and Union Carbide UC #3882) were used at dosages of 5 ml every 1 to 2 hours (shock treatment of 10 to 20 mg/liter).

Comparison of the cooling tower blowdown with the makeup concentrations are presented in Table 4. The average cycles of concentration, as measured by the chloride ion, was 9.6. Most of the inorganic constituents cycled up from 8 to 9 times in the cooling tower. Notable deviations from this pattern are ammonia and alkalinity which cycled up less than two times, as well as all organic compounds except hydantoins. The reason for this phenomenon can be attributed to a combination of stripping, biological activity, and fouling mechanisms. These mechanisms are discussed in more detail in subsequent sections.

Biofouling

Biofouling is a detrimental phenomenon which can occur in recirculating cooling water systems. Microbial fouling is primarily caused by bacterial growth. Such growths interfere with cooling water flow and ultimately reduce the heat transfer efficiency of the system and may cause reduction in processing capacity or unscheduled shutdown [7]. These biofilms also enhance corrosion processes by several mechanisms and are detrimental to all iron based and many other alloys [8, 9]. The cooling water at the UNDERC test facility contains a vast array of organic and inorganic compounds, many of which provide an ideal environment for microbial growth suspended in the water and on the heat exchanger surfaces. Therefore, related biological problems were expected and special attention was given to the identification of any such problems.

The UNDERC cooling tower was seeded to ensure microbial access during the 50-day test run. Seed consisted of acclimated activated sludge and a phosphate-buffered soil extract. The microbial testing conducted on water samples, test coupons, and cooling tower deposits included total aerobic heterotrophic bacterial and fungal counts, microbe identification, testing for nitrifying bacteria, iron oxidizers, and sulfur oxidizers.

The total heterotrophic aerobic bacterial count (THAC) was used to monitor the level of biological activity in the cooling tower. The total counts quadrupled within 14 days after the tower was seeded and leveled off at around 4 × 10^6 counts/ml. Little variation was noted in counts taken at various points in the system.

TABLE 4. COOLING TOWER MAKEUP AND BLOWDOWN STREAM CHARACTERIZATION

Chemical/Physical Constituent	Makeup (mg/liter)	Blowdown (mg/liter)
Total Suspended Solids	37	890
Total Dissolved Solids	3500	30,000
BOD	1600	5,900
TOC	2500	17,000
COD	6300	45,000
Dissolved Oxygen	0.52	6.4
Phenol	140	150
Cresol	30	19
5,5-Dimethyl Hydantoin	1800	15,000
5-Ethyl-5 Methyl Hydantoin	460	3,900
Acetone	18	20
Methanol	190	57
Acetate	180	1100
pH, Units	9.1	8.0
Conductivity, μmho/cm	2700	8100
Alkalinity as $CaCO_3$	1500	2600
Ammonia	550	1200
Sulfate	19	170
Chloride	25	220
Total Cyanide	31	280
Thiocyanate	200	1700
Calcium	2.3	27
Sodium	180	1600
Silicon	3.9	25
Iron	15	130

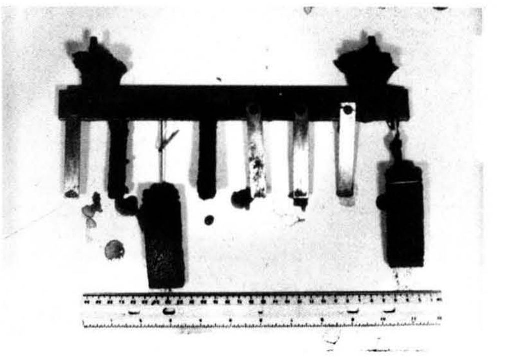

Figure 2. Test coupons removed from the UNDERC tower basin after completion of Phase I testing. (From left: concrete, 304L stainless steel, 304L stainless steel, 316 stainless steel, carbon steel, concrete, carbon steel, 316 stainless steel).

Test coupons were examined after the run for signs of corrosion and biofouling. Deposits on the stainless steel and carbon steel coupons are essentially the same as those observed on the test heat exchanger tubes (see Figure 2): 1) a thin black layer of deposit with no corrosion evident on stainless steel, and 2) on carbon steel, deposits were very thick, under which heavy pitting and corrosion were apparent. The moderate to high THAC per cm^2 (6.2×10^5 to 2.0×10^9) measured on these coupons demonstrates that these coupons were biofouled and indicate that corrosion of the carbon steel was biologically enhanced.

Throughout the cooling tower test program, all of the heat exchanger tubes experienced some degree of fouling. Data collected from test heat exchanger HE-1 indicated very little, if any, decline in the heat transfer coefficients for the stainless steel tubes and no difference between the types of stainless. The low velocity tubes showed a loss of less than 10% in heat transfer coefficient while no long-term effects were noted in the high velocity tubes.

All four carbon steel tubes in HE-2 experienced rapid increases in pressure drop accompanied by corresponding decreases in the heat transfer coefficient. Figure 3 shows trends typical of the carbon steel tubes. In the low velocity tubes, the heat transfer coefficient decreased by 30% to 60%. A 10% to 25% loss of heat transfer was noted in the high velocity tubes.

Data from the Dynamic Deposit Monitors also indicate that, at low velocities, the use of SGL as makeup water will have a severe effect on heat transfer. In DDM-1, operated at a skin temperature of 38°C, a 44% reduction in heat

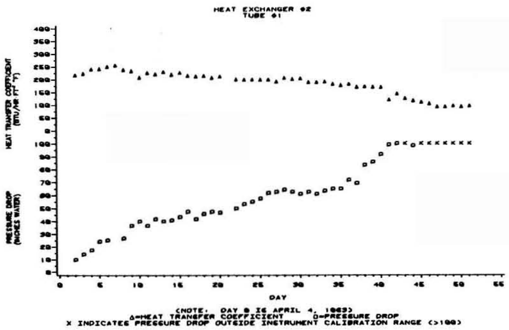

Figure 3. Typical data for heat transfer coefficient and pressure drop for carbon steel heat exchanger tubes aged in Phase I testing.

transfer was noted over a 41 day period. In DDM-2, operated with an initial skin temperature of 65°C, the heat transfer loss was 31% over the same period of time.

Fouling deposits from each tube were dried and weighed after the test. The stainless steel tubes in both heat exchangers accumulated deposits that amounted to less than 40 g/m² tube surface area. The accumulation of fouling was significant in the carbon steel tubes—up to 750 g/m² for tube #1, the most heavily fouled tube. A comparison of the deposit accumulation in tubes with different velocities indicates a much greater accumulation in the low velocity tubes than in the high velocity tubes.

Analysis of attached growth coupons showed that *Pseudomonas spp.* are the major cause of biofouling. They are likely to be enhancing corrosion, or harboring anaerobic bacteria such as sulfate reducers, which more aggressively increase metal loss and pitting. Biofouling of the heat transfer surfaces had a major impact in the terms of heat transfer reduction and an increase in pressure drop across heat exchanger equipment. The control of these organisms would be absolutely essential in a full scale industrial system.

Corrosion

The corrosive effects of using SGL as a cooling tower makeup were evaluated during this test using several different methods. Corrosion rates were determined for carbon steel, 304L and 316 stainless steel using weight loss coupons and Rhorback Corrosometer and Corrator probes. Metallurgical examination of the heat exchanger tubes was also used to determine the implications of the corrosiveness of the SGL.

The corrosion rates measured during this test are shown in Table 5. The carbon steel coupon analysis indicated that corrosion rates of 12.5 to 24.2 mils/year can be expected in an uninhibited cooling tower system using SGL as makeup. The carbon steel coupons showed heavy accumulations of biofouling and corrosion products on the coupon surfaces. Results from the stainless steel coupons and corrosion measuring probes indicate very little corrosion for 304L stainless steel (<0.08 mpy).

After the run, heat exchanger tubes were removed and sectioned for detailed analysis. Tube sections were examined for pitting and changes in metal structure using an electron microscope. Fouling deposits consisted mainly of black and red rust tubercles covered with biofouling deposits. Cleaned carbon steel sections showed evidence of pitting over the entire surface.

A photomicrograph of Tube #3 is shown in Figure 4. The outside of each tube was exposed to distilled water at a temperature of 50°C. The inside surface of the tubes were exposed to the concentrated gas liquor. Severe pitting with pits ranging between 2.5 to 6 mils deep was noted on the carbon steel tubes as a result of exposure to the SGL. Table 6 summarizes the electron microscope analysis of all carbon steel tube sections. Should localized pitting occur at the maximum rates indicated by the test results (6 mils per 50 days), pitting failures could occur within a few years after system startup. Photomicrographs of the stainless steel tube sections indicated that exposure to the concentrated gas liquor in the cooling tower had a negligible effect on the stainless steel tubes.

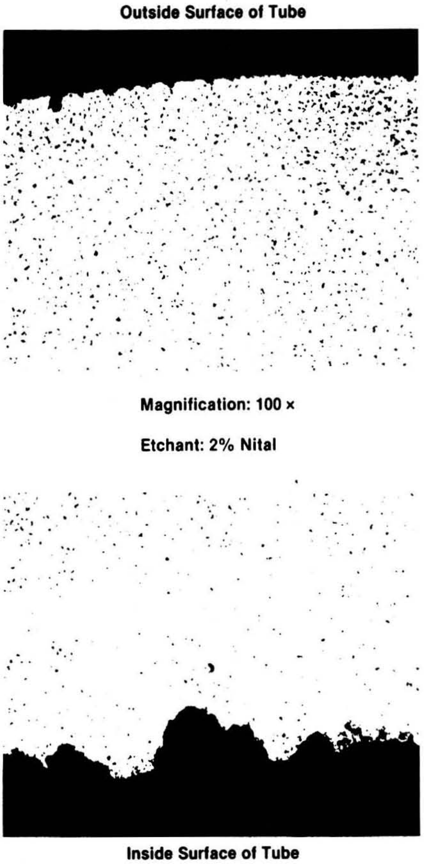

Figure 4. Photomicrograph of carbon steel heat exchanger tube surface (Tube #3 from heat exchanger 2).

During the cooling tower test, Type V concrete test coupons were exposed at three locations in the cooling tower. Observation of the concrete coupons that were exposed to the flow of cooling air (above the spray nozzles, and between the packing and basin water) indicated that, although the cementing material appeared to be intact, approximately 2 mm of the aggregates had dissolved as a result of reactions with acids in the system.

The coupon that had been submerged in the basin water was noticeably stained and the surface of the coupons appeared to be quite friable when brushed with a steel brush. The aggregates in the basin coupon were loose and could be readily dislodged. The basin coupon also had several very fine fractures randomly distributed throughout the matrix.

TABLE 5. CORROSION RATES FOR SGL FED COOLING TOWER

Monitoring Location	Velocity (m/sec)	Temp (°C)	Corrosion Rates (mpy) Carbon Steel	 304 Stainless
Cooling Tower Basin	<0.03	28	12.5	0.02
DDM Inlet	0.58	28	24.2	—
Heat Exchanger Outlet	0.12	36	14.3	0.03
Cooling Tower Inlet	0.58	49	22.6	0.08

TABLE 6. ELECTRON MICROSCOPE ANALYSIS OF CARBON STEEL SECTIONS

Tube Number	Exposure Time, Days	Fluid Velocity in Tube, m/sec	Pits Depths mils	 mils/year[a]
1	50	0.91	4	24
2	12	1.52	3-5	75-125
2A	38	1.52	2.5	20
3	44	0.91	6	41

[a] Based on 300 days of service at the observed pitting rate.

Data collected during this test indicated that corrosion will be a major concern for cooling systems using SGL as makeup. The carbon steel data indicate that general corrosion rates are in the 12.5 to 24 mils/year range. Pitting corrosion will also be a critical problem in a SGL fed cooling system. These data indicate that carbon steel should be used selectively with a large corrosion allowance if the bare metal is to be exposed to the cooling water. The use of lined pipe or other piping material (FRP or stainless) and/or corrosion inhibitors, biocides and dispersants should be considered.

Atmospheric Emissions

During Phase I testing, three independent sampling campaigns to determine the atmospheric emissions from the cooling tower were conducted. Measured exhaust air concentrations for the major species are presented in Table 7. Component material balances on the UNDERC cooling tower indicated that an average of 91% of the phenol in the makeup to the cooling tower was stripped during the cooling cycle. Eighty-one percent of the ammonia and 25% of the methanol were also stripped. Material balances also indicate that approximately 75% of the methanol was biodegraded, while only a small portion of the phenol was available for consumption by the microorganims.

A comparison of exhaust air concentrations to OSHA/NIOSH maximum exposure limits indicated that, although exposure limits are not exceeded by any of the constituents in the exhaust air, the measured exhaust air phenol concentration (8000 $\mu g/m^3$) far exceeds the reported phenol odor threshold of 165 $\mu g/m^3$. These results are discussed in detail elsewhere [*10, 11*].

CONCLUSIONS

A vast amount of data was collected and evaluated during this test. The major results have been presented with the more important conclusions concerning the use of SGL as cooling tower makeup summarized here.

Ammonia, alkalinity, phenol, and other non-hydantoin organics were removed from the cooling water by stripping and/or biological degradation with the phenol concentration in the exhaust air exceeding the odor threshold.

Foaming of the circulating water will be a problem using SGL as makeup, and foaming control will be required. Both glycol and silicon based agents were used successfully to control foaming during this test.

The SGL feed cooling system supported a high level of biological activity (1 to 10 million/ml), predominantly *Pseudomonas aeruginosa*. This high level of activity led to severe biofouling of all carbon steel surfaces. Biofouling control will be a key factor in maintaining clean heat transfer surfaces in an industrial system using similar wastewater. Fouling of stainless steel was not a major problem.

TABLE 7. COOLING TOWER EXHAUST AIR CHARACTERISTICS

Parameter	04/29/83	05/03/83	05/11/83
Ammonia	31,100	NA	22,600
Phenol	9,920	6,100	7,920
Methanol	2,960	NA	1,950
Cresol	2,400	3,570	880
Acetone	440	NA	480
Acetonitrile	ND	NA	125
5,5-Dimethylhydantoin	ND	ND	100

Note: All Values are reported in $\mu g/m^3$
ND - Not Detected
NA - Not Analyzed.

General corrosion rates of 12.5 to 24 mils/year were measured for carbon steel in various parts of the system. Corrosion rates increased with increasing temperature and velocity. Under deposit pitting penetration rates of 20 to 125 mils/year were measured. These rates indicate that carbon steel will not provide an adequate service life if used as thin walled heat exchanger tubing without the use of corrosion inhibitors and biocides. Both 304L and 316 stainless steel heat exchanger tubes showed no significant metal loss from either general or pitting corrosion. Hydration of Type V concrete occurred after exposure to the SGL cooling water, resulting in increased friability and loosening of the bonding between the concrete and the aggregate.

Results from this study indicate that the use of stripped gas liquor similar to that produced by the UNDERC pilot gasifier as cooling tower makeup is limited by a number of potentially serious operating problems. This water could be used for cooling tower makeup only after additional treatment or possibly with the use of biocides, corrosion inhibitors, and other control methods.

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The authors of this paper would like to acknowledge several groups of people who have contributed to the success of this project. Assistance in planning the operation and choosing operating conditions that will simulate those used in a commercial gasification plant was afforded to us by Fred Kuhn and his associates of ANG Coal Gasification Company, sponsors of the GPGA project.

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Wastewater Treatment Systems for Synthetic Fuels Plants Based on Peat and Oil Shale

An up-to-date review of the sources and treatment of wastewaters from synthetic-fuels plants based on peat and oil shale.

Irwin Frankel and Marvin Drabkin, U.S. Synthetic Fuels Corp., Washington, D.C.

This paper briefly describes the wastewater treatment systems being used or proposed for use in synthetic fuel projects which were based on peat and oil shale, and which were under consideration by the United States Synthetic Fuels Corporation (SFC) as of January 1984. The spectrum of projects under consideration by the SFC at this date is, as expected, somewhat varied.

The wastewater technologies utilized are functions of three major factors:

- Nature of the fossil fuel raw material.
- Nature of the fuel conversion process.
- Site-Specific considerations, i.e., zero discharge of wastewater.

As a result of the above factors, plus the individual choices of each project for wastewater technology, one finds little commonality in approach. In order to acquaint the reader with some essentials of the two peat and the five oil shale projects under consideration, reference is made to Tables 1 and 2.

Source material for this paper, unless otherwise noted, was derived from internal files and from proposed information submitted to the SFC. All material was reviewed with sponsors prior to this presentation.

NORTHERN PEAT ENERGY

A combined anaerobic/aerobic process is proposed for wastewater treatment. It consists of a mesophilic anaerobic contact reactor followed by an aerobic sludge tank. The excess sludge from the aerobic stage is returned to the anaerobic stage and digested there (Figure 1).

Extensive pilot plant tests have been made by Sorigoma AB in Sweden with wastewater from the wet-carbonizing of peat. In these tests, BOD reduction was greater than 95% and COD, 75%. About 60% of the COD entering the anaerobic reactor was converted to a gas composed of 70% (vol.) of methane and 30% of CO_2. This gas will be collected and utilized in the Northern Peat project. Nitrogen concentration in the wastewater is high, but some phosphorus (as phosphoric acid) is required for microbial nutrition.

TABLE 1. PEAT AND OIL SHALE PROJECTS UNDER CONSIDERATION BY THE SFC (AS OF JANUARY 1985)

Project	Feed Stock	Basic Process	Principal Product
Northern Peat Energy	Maine Peat	Wet Carbonization	Solid fuel pellets
Peat Methanol Associates (PMA)	North Carolina Peat	KBW Entrained-bed gasification	Methanol
Seep Ridge	Utah Oil Shale	True In-situ retorting	Raw shale oil
Means	Kentucky Oil Shale	Dravo Circular Grate retorting	Shale oil syncrude
Paraho-Ute	Utah Oil Shale	Paraho retorting	Shale oil syncrude
Cathedral Bluffs	Colorado Oil Shale	Union Oil above-ground retorting plus modified *in-situ* retorting	Shale oil syncrude
Union	Colorado Oil Shale	Union Oil above-ground retorting	Shale oil syncrude

TABLE 2. TABULATION OF PROCESS WASTEWATER SOURCES AND TREATMENT TECHNOLOGIES

Project	Source of Process Wastewater	Basic Approach	Principal Wastewater Treatment Technologies
Northern Peat Energy	Wet "carbonization" of peat	Treat and discharge via NPDES permit	Sorigoma (Swedish) technology
PMA	Raw syngas cleanup; Methanol synthesis	Treat and discharge via NPDES permit	SWS*, Alkaline chlorination, and bio-aeration and other treatments
Seep Ridge	Retort water and off gas condensate	Zero discharge	Thermosludge boiler commercial disposal of sludge
Means	Retort water and off gas condensate	Zero discharge	SWS, commercially available technologies including wet air oxidation
Paraho-Ute	Retort water and off gas condensate	Zero discharge	SWS, proprietary biological treatment
Cathedral Bluffs	Above ground retort water and off gas condensate, and MIS retort water and off gas condensate	Zero discharge	SWS, codisposal w/spent shale
Union	Retort water and off gas condensate	Zero discharge	SWS, codisposal w/spent shale

*SWS—Sour Water Stripping

Typical wastewater from Finnish peat analyzes for a BOD5 of about 7,000 mg/liter, COD of 17,000 mg/liter, TSS of about 20 mg/liter, and pH of 4-5. The BOD and COD values for Maine peat are reported to be somewhat lower. Treated wastewater will be discharged to the nearby Penobscot River, returned to the peat bogs, or a combination of both.

PEAT METHANOL ASSOCIATES (PMA) PEAT GASIFICATION PROJECT—WASTEWATER TREATMENT

The basic approach to wastewater treatment in the PMA project is to treat process and non-process wastewater separately, followed by discharge of the combined treated effluent to surface waters under an NPDES permit.
The project wastewater treatment system consists of six main areas:

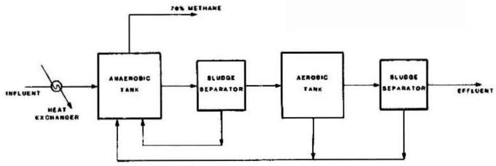

Figure 1. Northern Peat Energy wastewater treatment system.

1. Inorganic Treatment
2. Biological Treatment
3. Coagulation/Flocculation Treatment
4. Polishing Pond Treatment
5. Sludge Treatment
6. Stormwater Treatment

The various treatment systems are given in schematic form in Figure 2. The inorganic treatment system consists of a combined NH_3 and cyanide still where pH adjustment and steam stripping are used to remove free NH_3 and cya-

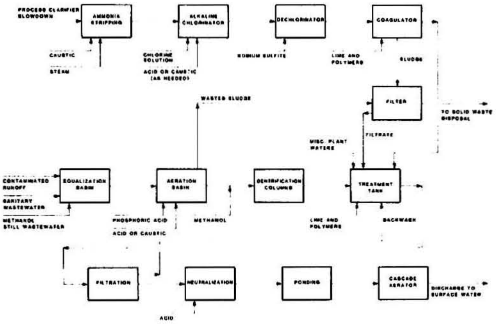

Figure 2. PMA wastewater treatment scheme.

nide. Stripped off-gases are incinerated. Remaining fixed cyanide and NH_3 are removed from the wastewater by alkaline and breakpoint chlorination, and metals precipitated by lime addition. Treatment is in the order given.

Organic pollutants are primarily removed by the biological treatment system which consists of activated sludge biological treatment (with the addition of suitable nutrients), to achieve nitrification, followed by denitrification.

Combined wastewater treatment streams from the inorganic treatment system, the biological treatment system and the sludge treatment system (along with various process area blowdown streams) are treated by lime softening, followed by coagulation/flocculation/settling and filtration prior to discharge to polishing ponds. It should be noted that the combined stream has very low levels of organic contaminants prior to this treatment sequence.

Two ponds in series are designed to retain the total wastewater flow for approximately 30 days each following the lime softening/filtration and neutralization treatment processes. Natural degradation processes serve to polish the wastewater before micro-screening, reaeration, and final discharge to surface waters.

Sludge generated in the wastewater treatment plant is first held in a sludge-receiving tank where gravity thickening is achieved. Supernatant liquor overflows the thickening tank and is routed back to the lime softener. The thickened sludge is pumped at a controlled rate to a belt press filter where the sludge is dewatered by compression to a high solids cake for disposal.

All of the major treatment steps described above have been verified in laboratory-scale treatment studies using simulated wastewater.

SEEP RIDGE

Crude shale oil is presently being recovered as an oil/water emulsion from the retorts. Water and oil are separated in a heater/treater unit followed by an API separator for the oily water. This water is then stream stripped for removal of ammonia and other gases, is combined with lesser quantities of wastewater from other sources, and is pumped with water treatment chemicals (mostly soda ash) to the KTI Thermosludge boiler. The water is largely converted to steam in this unique unit, leaving behind a pumpable sludge which is commercially disposed of. Sanitary wastes are handled by a separate system (Figure 3).

MEANS

During normal operations, the wastewater treatment system will operate automatically by level control instrumentation and require only periodic operator monitoring. In the event of hydraulic or contaminated surges, the off-specification wastestream can be diverted to an emergency diversion basin.

Plant-generated wastewaters (which contain high concentrations of dissolved organics, inorganics, and ammonia) are primarily utilized as dust suppressant spray water or for moistening spent shale following suitable treatment. This stream is initially subjected to wet air oxidation (at elevated temperature and pressure), where the COD is reduced by about 90%. After pressure let-down and gas separation, the ammonia is steam-stripped to about 50 mg/liter to permit treatment of this wastestream by bio-oxidation. In a roughly parallel subsystem (see Figure 4), the process sewer water, plus non-process wastewaters such as contaminated storm water and water from the emergency diversion basin, pass through a primary separation (a corrugated plate interceptor), where any suspended solids and oil are concentrated and then pumped to the equalization mixer tank along with the wet oxidation effluent just upstream from the bio-oxidation step.

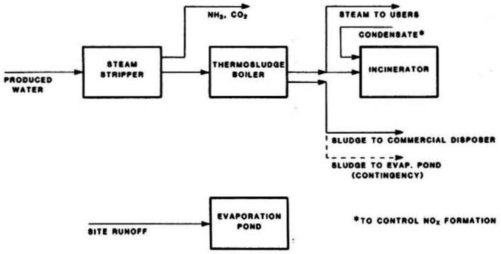

Figure 3. SEEP Ridge wastewater treatment system.

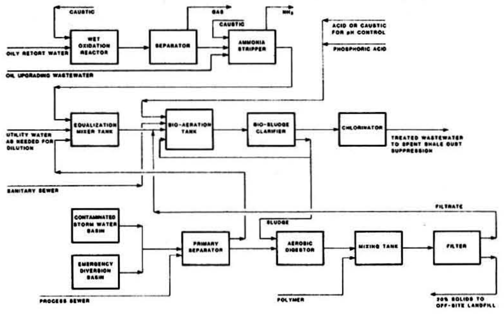

Figure 4. Means Oil Shale wastewater treatment system.

The equalized organics-contaminated stream is combined with sanitary wastewater and pumped to the bio-oxidizer to reduce COD and BOD, and its effluent passes to a clarifier. Overflow from this clarifier is then chlorinated, and the disinfected effluent is then used as dust suppressant on spent shale. Underflow from the bio-sludge clarifier is combined with underflow from the primary separator, and both are introduced into an aerobic digestor which is mechanically (mixer) aerated. At regular intervals the aerator is turned off, the digested sludge is allowed to settle and then pumped to a polymer mixing tank, followed by mechanical dewatering. The 20% solid sludge cake is trucked off-site to an authorized landfill, and filtrate is recycled to the bio-aeration tank.

PARAHO-UTE PROJECT

This oil shale project (as is the case with all Western oil shale projects) is based on zero discharge with reuse of all wastewaters (after suitable treatment), principally for spent shale moisturization. Three types of wastewaters will be associated with the proposed commercial facility:

1. Organic-laden wastewaters from process facilities
2. Inorganic-laden wastewater from water treatment units and boiler and cooling tower blowdown
3. Sanitary wastewaters

The wastewater treatment systems consist of essentially three treatment schemes, each designed to treat one of the three types of wastewater listed above. These treatment schemes are shown in schematic form in Figure 5.

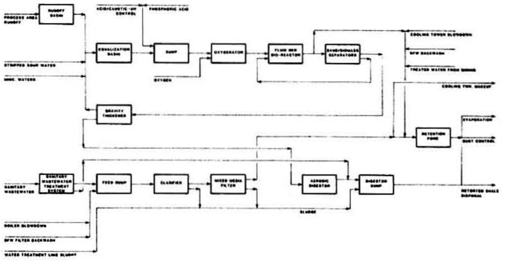

Figure 5. Paraho-UTE wastewater treatment.

Organic wastewaters include stripped water from sour water treatment (the major effluent to wastewater treatment), condensate from steam users, retort service wastewater, and process area runoff. These are combined in a equalization basin provided with oil skimming facilities.

Equalized wastewater is combined with recycle from biological treatment units, oxygenated with a stream of pure oxygen from an on-site cryogenic oxygen plant, and processed in a biological treatment system consisting of proprietary-design fluidized bed reactors. Effluent exiting the biological treatment system is stored in a retention pond (along with other effluent streams) from which water is used in retorted shale disposal operations.

Table 3 compares some of the anticipated characteristics of influent to the wastewater treatment system (sour water treatment effluent), and retention pond water.

Biomass exiting the biological treatment system is separated from the fluidized bed reactor growth media (sand), with the growth media then returned to the reactors and the resultant sludge thickened in gravity thickeners. Supernatant from the thickeners is returned to the equalization basin and the underflow is stabilized in aerobic digesters using oxygen. Stabilized sludge from this system together with sanitary sludge and water treatment lime sludge are combined and used in retorted shale wetting operations.

Inorganic wastewaters including boiler feedwater treatment backwash and cooling tower blowdown, are stored in the wastewater retention pond and used for retorted shale wetting.

Water treatment filter backwash, boiler blowdown, and treated sanitary wastewater are combined, clarified, filtered, and reused as cooling tower makeup.

Package wastewater treatment systems are used for sanitary wastewater and mine water treatment. Sludges from both of these systems are used for retorted shale wetting.

The principal process wastewater treatment step (biological treatment of stripped sour waters from the oil shale retorting process in fluidized bed reactors) has been verified in pilot scale tests.

CATHEDRAL BLUFFS

Although interconnected, the process and the non-process wastewater treatment systems are sufficiently complex that these systems are shown on separate flow sheets (Figures 6 and 7, respectively). It should be noted that biological processes are not used on any wastewater emanating from any of the Above Ground Retorts (AGR), the Modified In-Site (MIS) retorts, or the Oil Upgrading (OUG) areas. Some waters are stream-stripped, and oily waters pass through an API separator. All process wastewaters are subsequently recycled to the extent possible, but are principally used to cool and moisturize spent shale, or recycled to any MIS retorts which are in a quenching mode.

The principal source of input water into the treatment system is the mine water. After pH adjustment, flocculent treating, and sand filtration, the partially treated mine water is directed to a number of users (see Figure 7). Principal users are the cooling water system, potable water users, boiler feedwater preparation, service water systems, vegetation, and the AGR area. Excess mine water is reinjected into the earth or is discharged to the Piceance Creek.

TABLE 3. PARAHO-UTE PROJECT COMPARISONS OF ORGANIC WASTEWATER INFLUENT AND RETENTION POND TREATED WATER

Parameter	Anticipated Value Stripped Wastewater	Wastewater Retention Pond
COD, mg/liter	18,000	1,000
BODs, mg/liter	9,000	63
TSS, mg/liter	50	95
pH	8-9	6.5-8

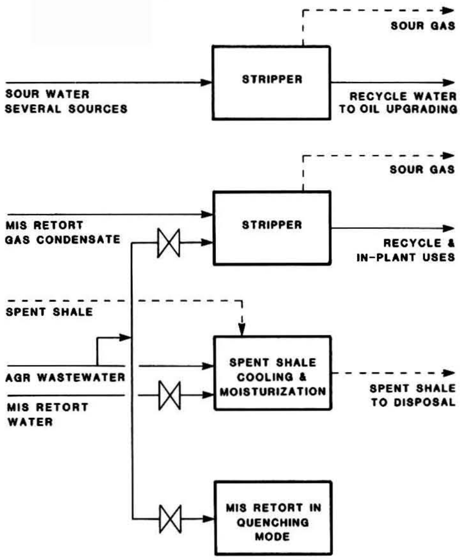

Figure 6. Cathedral Bluffs Process wastewater treatment system.

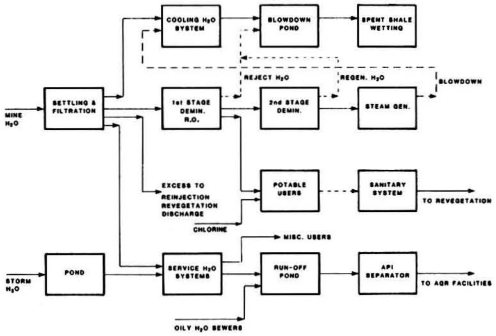

Figure 7. Cathedral Bluffs non-process wastewater treatment system.

Treated mine water that is used for potable and boiler feedwater (BFW) purposes is further treated in a first stage demineralization (reverse osmosis). The reject water from R.O. is pumped to the cooling water system blowdown pond, where it is stored for eventual usage in spent shale wetting. The R.O. product water is divided into a potable water source and as a feed to the second stage demineralization, which is the required next step for an adequate quality BWF.

Sewage from the mine support area and the surface facilities is gravity fed to a collection sump, then pumped to a packaged biological treatment system. The treated wastewater is chlorinated and held in a chlorine contact chamber for 30 minutes before discharge. This water is used for spent shale revegetation, but any excess is discharged to the Piceance Creek.

MIS wastewaters have been characterized at Occidental's Logan Wash test site. EPA has studied various treatment methods for MIS gas condensate using freshly generated wastewater [*1*]. Treatment of stripped MIS wastewaters by reinjection into the spent MIS retorts was evacuated by Oxy during the recent Retort 7 and 8 runs at Logan Wash and appears to be a viable approach in terms of organics reduction [2].

UNION OIL PARACHUTE OIL SHALE PROJECT (PHASE I AND II) WASTEWATER TREATMENT

The Union Oil Parachute oil shale project will feature zero discharge of wastewaters (both process and non-process). All wastewaters generated in both the Phase I and Phase II projects will be used in cooling and wetting the retorted shale prior to placement on a spent shale pile in the valley of the East Fork Parachute Creek. The process wastewaters will be first stripped to remove H_2S and NH_3 prior to reuse for spent shale moisturization. Table 4 summarizes the major sources and treatment of the various wastewater streams prior to reuse. The treatment of process wastewater is shown in Figure 8 in schematic form.

TABLE 4. TREATMENT OF UNION OIL PARACHUTE SHALE PLANT WASTEWATER

Description	Treatment
Mine/Retort	
Mine Inflow	None required
Retort Condensate	Stream stripping & oil water separation
Ammonia Scrubber Water	Stream stripping & oily water separation
Deasher Water	Direct to shale cooling
Demineralizer Regenerant and Rinse	None required
Boiler Blowdown	None required
Cooling Tower Blowdown	None required
Fractionation Condensate	Stream stripping & oily water separation
Sanitary Sewage	Aeration
Storm Runoff Within Process Area	Oil/water separation
Raw Shale Oil Upgrading Plant	
Hydrotreater Wash Water	Stripping
Cooling Tower Blowdown	None required
Demineralizer Regenerant and Rinse	None required
Boiler Blowdown	None required
Sanitary Sewage	Aeration
Storm Runoff	Oil/water separation

Source: Union Oil Parachute Phase II Project Permit Amendment to the Colorado Mined Land Reclamation Division, 1983

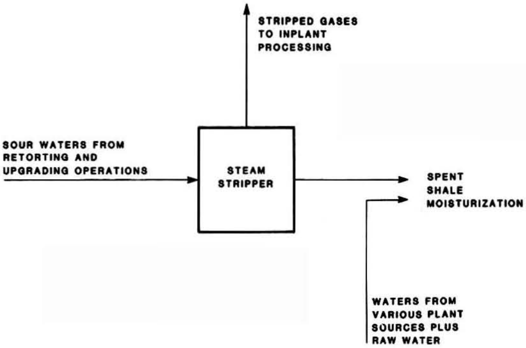

Figure 8. Union Parachute Phase Process wastewater treatment.

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Secondary Utilization of Trace Halogenated Organic Compounds in Biofilms

It is shown that, under proper conditions, many potentially hazardous halogenated organic compounds present at very low concentrations can be biotransformed by fixed film reactors plus a growth-sustaining substrate.

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The movement and fate of trace and toxic organic compounds has become of increasing concern because of the potentially harmful effects such materials can have to humans and to the environment. Some trace organic compounds are biodegradable when present in millimolar concentrations and might be expected to be degraded when discharged to the environment. The potential for degradation of trace organic compounds is generally enhanced when bacteria are attached as biofilms to solid surfaces in natural water bodies, soils, aquifers, or engineered treatment systems, such as trickling filters, rotating biological contactors, and activated-carbon columns. The substrate concentration and electron acceptor are factors that affect biotransformation of organic micropollutants. This paper presents results of experimental evaluation of the concept of secondary utilization by biofilms, which allows trace concentrations of organic contaminants to be biotransformed to still lower levels.

A steady-state biofilm model that incorporated many of the factors affecting the biofilm kinetics for a single growth-rate-limiting substrate was developed and evaluated by Rittmann and McCarty [*1, 2*]. Their model solution yielded both the steady-state flux of substrate into a biofilm and biofilm thickness using independently determined rate parameters. Their research indicated both theoretically and experimentally [3] that, for a single trace organic compound under steady-state conditions, at least a minimum concentration (S_{min}) is necessary to support a sufficient bacterial population to decompose the compound because microorganisms require energy to maintain themselves. This limiting value is given by the relationship

$$S_{min} = K_s \frac{b}{Yk - b} \qquad (1)$$

S_{min} is the minimum-substrate concentration for existence of a steady-state biofilm, K_s is the Monod half-maximum-rate concentration, b is the first-order decay coefficient, k is the maximum specific rate of substrate utilization by the bacteria, and Y is the cell yield. At concentrations below S_{min}, the entire biofilm would be in net decay and would eventually cease to exist. Hence, in order to sustain a biofilm reaction for the long term, the rate-limiting substrate must be present at a concentration greater than S_{min}. Values of S_{min} may be on the order of a fraction of a mg/L to several mg/L depending on substrate, electron acceptor, and organism.

Many organic micropollutants are present at concentrations below S_{min} and would aparently go unutilized. However, simultaneous utilization of many different substrates is possible. An organic compound which is at a concentration below S_{min} may be biodegradable by secondary utilization. In secondary utilization, the organic compound, which does not provide significant energy or carbon for bacterial growth, can be utilized as a secondary substrate by a biofilm that is grown and sustained through utilization of a primary substrate, which is present at a concentration greater than its S_{min}. A primary substrate provides the organism energy and carbon for cell synthesis, whereas secondary substrates may or may not contribute either to cell growth. A secondary substrate need not share enzymatic pathways with the primary substrate, although the bacteria must be capable of transforming both compounds.

Laboratory Evaluation of Secondary Utilization

The concept of secondary utilization was evaluated through basic continuous-flow column studies for periods longer than a year with mixed bacterial cultures, using aerobic and methanogenic conditions [*4, 5, 6*]. Glass beads were used as the support media for the biofilms in order to minimize adsorptive effects, and acetate was used as the primary substrate to sustain bacterial growth. A group of priority pollutants was selected as secondary substrates at concentrations between 10 and 30 μg/L. These studies included inorganic nutrients and buffers.

Trace concentrations of chlorinated benzenes were degraded by biofilm bacteria sustained with acetate as the primary substrate under aerobic conditions, but these same compounds persisted under methanogenic conditions (Table 1). Between 10 days and 5 months were required for acclimation of the biofilm culture to the chlorinated aromatics. The number and position of chlorine atoms on the benzene ring affected the initial acclimation

TABLE 1. AVERAGE UTILIZATION OF SUBSTRATES FED CONTINUOUSLY TO AEROBIC AND METHANOGENIC BIOFILM REACTORS

	Aerobic Biofilm Column* (20-min detention time)		Methanogenic Biofilm Column* (2-day detention time)	
Substrate	Influent Conc. μg/L	% Removal	Influent Conc. μg/L	% Removal
Primary				
Acetate	1 mg/L	98 ± 2	100 mg/L	99 ± 1
Secondary				
Chlorinated Aromatics:				
chlorobenzene	11.3 ± 2.5	91 ± 3	22 ± 5	0 ± 15
	1.57 ± 0.3	85 ± 6	—	—
1,2-dichlorobenzene	9.6 ± 2.4	97 ± 1	15 ± 3	0 ± 15
1,3-dichlorobenzene	9.8 ± 1.8	71 ± 8	10 ± 3	0 ± 15
1,4-dichlorobenzene	10.8 ± 1.8	99 ± 1	10 ± 3	0 ± 15
1,2,4-trichlorobenzene	9.2 ± 1.6	95 ± 3	11 ± 3	0 ± 15
Nonchlorinated Aromatics:				
ethylbenzene	9.1 ± 2	99 ± 1	12.0 ± 4	7 ± 26
styrene	7.6 ± 1.5	> 99	7.9 ± 2	8 ± 26
naphthalene	13.8 ± 3.5	99 ± 1	28.8 ± 7	−2 ± 29
Halogenated Aliphatics:				
chloroform	28.5 ± 4.2	−2 ± 20	28 ± 7	99 ± 1
carbon tetrachloride	†	—	17 ± 1	> 99
1,2-dichloroethane	†	—	22 ± 3	−1 ± 20
1,1,1-trichloroethane	15.9 ± 3.3	5 ± 27	18 ± 2	97 ± 3
1,1,2,2-tetrachloroethane	†	—	27 ± 1	97 ± 3
tetrachloroethylene	9.8 ± 3.7	2 ± 40	15 ± 4	76 ± 10
bromodichloromethane	†	—	26 ± 3	> 99
dibromochloromethane	†	—	25 ± 2	> 99
bromoform	†	—	26 ± 2	> 99
1,2-dibromoethane	†	—	27 ± 2	> 99

*One standard deviation of the mean values are given.

†Compound not included in feed to aerobic column. These compounds were not degraded in aerobic batch cultures.

period and the extent of transformation. Chlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene were oxidized to CO_2 without detectable intermediates in the presence of bacteria, confirming removal by biooxidation [5].

The low-molecular-weight halogenated aliphatic compounds studied were not degraded by the aerobic biofilm, but evidence for secondary utilization of these compounds was obtained under methanogenic conditions (Table 1). Degradation of the brominated aliphatics to below detection limit occurred with almost no acclimation period required, while significant removals of the chlorinated aliphatics did not occur until after a 10 to 15 week lag period. Nearly complete oxidation of some of the chlorinated aliphatics to CO_2 under methanogenic conditions confirmed removal by biooxidation [6]. Both biological and chemical processes appeared to be acting to transform the brominated compounds. A few of the halogenated aliphatics were transformed in the presence of active denitrifying bacteria.

Secondary Utilization Rates

Modeling of secondary utilization is based on the relationship between the primary and secondary substrate. Since the primary substrate is the rate-limiting organic electron donor which contributes energy and carbon to the long-term growth and maintenance of the biofilm, the utilization of the primary substrate and growth of the biofilm are described by the steady-state biofilm model of Rittmann and McCarty [*1*]. Steady-state utilization of secondary substrates is described by coupling the biofilm thickness, which is controlled from degradation of the primary substrate, with individually determined rate parameters for each secondary substrate.

For secondary substrates, the Monod-type expression used to model substrate utilization reduces to first order ($S_f << K_s$)

$$\frac{dS_f}{dt} = -\frac{kX_fS_f}{K_s} \qquad (2)$$

Here, S_f is the concentration of substrate at a point within the biofilm and X_f is the active cell density. Consequently, for trace substrates, there will be a linear relationship between substrate flux into the biofilm and substrate concentration, and the fractional removal in a fixed-film reactor should be nearly constant for any concentration in the feed. This was observed for chlorobenzene utilization under aerobic conditions (Table 1). When the influent concentration of chlorobenzene was decreased from 11.3 to 1.57 μg/L, this resulted in a corresponding decrease in effluent concentration, resulting in 85 percent removal or about the same as that obtained previously.

Once acclimation has occurred, then rate of degradation of secondary substrates appears to be a function of active organism concentration and the ratio of k to K_s. Modeling the rate of acetate (primary substrate), chlorobenzene, and 1,4-dichlorobenzene (secondary substrates) utilization in the aerobic biofilm reactor results in apparent k to K_s ratios for the substrates of 3.8, 2.5, and 11 L mg^{-1} day^{-1}, respectively [7]. The ratio of k to K_S for acetate and chloroform biotransformation in the methanogenic biofilm reactor was 0.63 and 0.85 L mg^{-1} day^{-1}, respectively [7]. Although the utilization kinetics for each substrate appeared to be unique, the ratio of k to K_s for each secondary substrate was similar to the value for the primary substrate. The k/K_s ratios were within the range expected for aerobic and methanogenic heterotrophic bacterial growth under low substrate concentrations [*8*].

A simple batch model using first-order decomposition kinetics may be adequate to describe biotransformation for large-scale subsurface contamination with low numbers of active organisms and slow groundwater movement. Here, biotransformation rates will be slow and limited by the reaction rate rather than mass transport. Degradation half-lives under aerobic and methanogenic conditions resulting from typical subsurface organism concentrations [9] and rate constants derived from the biofilm column modeling studies are shown in Table 2. These calculations show that, even at extremely low organism concentrations in the ground, significant biotransformation rates of organic micropollutants can occur.

Summary

Secondary utilization is a means by which bacteria are able to degrade very low concentrations of organic compounds, even those which are lower in concentration than the S_{min} concentration for the primary substrate. The laboratory results clearly indicated that, under proper conditions, many potentially hazardous halogenated organic compounds present at very low concentrations can be biotransformed by fixed-film bacteria provided with an additional growth-sustaining substrate. Secondary utilization is a promising concept for explaining and modeling biotransformation of organic micropollutants in the environment. Kinetic concepts developed for primary substrates appear to be applicable to secondary substrates.

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TABLE 2. HALF-LIVES OF BIOTRANSFORMATION MODELED WITH FIRST-ORDER KINETICS AS A FUNCTION OF ACTIVE ORGANISM CONCENTRATION

Organism Concentration		Degradation Half-Life, days	
mg/L	No./mL*	Aerobic Respiration†	Methanogenesis§
10	10^7	0.014	0.14
1	10^6	0.14	1.39
0.1	10^5	1.39	13.9
0.01	10^4	13.9	139
0.001	10^3	139	1,390

*Organism dry weight taken as 10^{-12} g/cell. †Assumed k/K_s = 5 L/mg cells-day.
§Assumed k/K_s = 0.5 L/mg cells-day.

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Oxidation of Cyanides in Industrial Wastewaters by Ozone

Fundamental kinetic and mechanistic data for the reactions of ozone with cyanide provide a solid basis for practical applications.

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Various industrial processes such as metal finishing, photographic bleaching, and iron and steel manufacturing produce substantial amounts of wastewaters which may contain as much as 30,000 mg/L of free cyanide and metal complexes of cyanide. Chlorination at high pH is the standard treatment process for cyanide containing wastewaters. However, chlorine must be used in considerable excess to destroy cyanogenchloride, the toxic intermediate product of the chlorine-cyanide reaction. The addition of excess chlorine increases the total solids content of water, making it undesirable for recycling and reuse purposes, and leaves high chlorine residual which is toxic to aquatic life. In addition, various chlorinated organics may be produced if the wastewater contains organic substances.

Ozone is an alternative process for oxidation of cyanides. However, the lack of information on the chemical kinetics and the mechanism of the ozonation reactions of cyanide compounds has limited the widespread application of ozone by preventing engineers from making reliable design decisions and cost estimations. Previous researchers [*1-8*], investigating the ozonation of cyanides in semi-batch or continuous-flow reactors, have generated rate equations of lumped parameters which combine the kinetics of chemical reactions and the kinetics of ozone absorption, and are therefore empirical and system-specific. Furthermore, there is disagreement in the literature as to the effects of metal complexation of cyanide on the reaction kinetics [*3, 4, 6*].

The objectives of this study are to generate fundamental kinetic and mechanistic data for the reactions of ozone with cyanide by distinguishing between the mass transfer of ozone and the oxidation and decomposition reactions of ozone, and to understand the effects of complexation of cyanide with copper and iron.

The kinetics of the fast chemical reactions of ozone with free cyanide were studied by using a stopped-flow spectrophotometer. The stoichiometric relations among the reactants and the products, and the effect of complexation were investigated by an ozone bubble reactor under dynamic conditions, as reported earlier for phenolic compounds [*9, 10*].

EXPERIMENTAL METHODS

Ozone was produced from oxygen by a Welsbach, Model T-408 ozone generator. The experimental set-up is shown in Figure 1. The percentage of ozone produced in the oxygen gas was controlled by changing the power input to the generator. The gas flow meter was calibrated before and after the experimental runs by using a soap-film column connected to the downstream of the reactor and the KI traps.

The reactor was a 500-mL gas washing bottle with a sintered-glass dispersion tube to deliver ozone gas to the bottom of the reactor. To keep the temperature of the contents of the reactor constant at 20°C, water was continuously circulated by a water pump from a 20°C water bath through a water jacket around the reactor. Excess ozone gas passed out through the top of the reactor into a gas washing bottle containing KI solution. The concentration of ozone in the effluent gas, $(O_3)_{eff}$, was measured by taking samples from the KI trap during each experimental run and titrating the iodine in the samples with $Na_2S_2O_3$ according to *Standard Methods* [*11*]. Two gas washing bottles containing KI solution were connected to the system in parallel to the reactor to determine the quantity of ozone applied to the reactor, $(O_3)_{inf}$. Before each experimental run, the ozone-oxygen mixture was diverted around the reactor into these traps for a constant period of time. Samples taken from the traps were titrated as explained above.

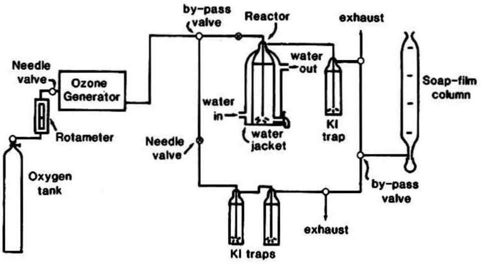

Figure 1. Experimental set-up

Kinetic studies were performed using a Durrum, Model 110 Stopped-Flow Spectrophotometer in which solutions of cyanide and ozone were mixed in a 20-mm light path, 0.063-mL cuvette with a deadtime of less than 2 milliseconds. The reaction temperature was maintained constant at 20°C. The concentration of ozone was monitored by measurement of the absorption of UV light at 260 nm. Absorption by cyanide and the buffer salts at this wavelength was negligible. The data of absorption *vs.* time were recorded by a Tektronix, Model 5115 Storage Oscilloscope, and then were either traced manually on graph paper, or photographed by a Polaroid camera attached to the oscilloscope screen. The experiments were repeated several times, usually using different time scales, to insure reproducibility.

TEST SOLUTIONS AND ANALYTICAL METHODS

All solutions were prepared from deionized and glass-distilled water. The pH of ozone solution was adjusted to 2.5 with dilute sulfuric acid in order to minimize ozone loss by decomposition. Ozone gas was bubbled through this solution in the bubble reactor until equilibration. Ozone solution was kept as stock (20-30 mg/L ozone) for subsequent use in the stopped-flow spectrophotometer. Free cyanide solutions were prepared by dissolving NaCN in phosphate buffers. The pH of the cyanide solutions was adjusted by sodium hydroxide or sulfuric acid to a value predetermined by mixing ozone solutions at pH 2.5 with an equal volume of cyanide solution to obtain the desired pH in the mixture. This procedure simulated the equal-volume mixing in the stopped flow spectrophotometer.

Copper complexes of cyanide were prepared by dissolving NaCN and CuCN in phosphate buffer. Since the original ratio of cyanide to copper was 4:1, the predominant species in solutions before ozonation was $Cu(CN)_4^{-3}$. Solutions of iron-cyanide complexes were prepared by dissolving $K_3Fe(CN)_6$ in buffer solutions; hence $Fe(CN)_6^{-3}$ was the predominant species in the unozonated solutions.

The concentration of ozone in stock solution and in the gas phase was measured by the KI method [*11*]. In ozonated cyanide solutions ozone was measured by both the KI and the Indigo methods [*12*], which yielded similar results, indicating the absence of any interferences by the reaction products. Free cyanide and cyanate were measured, respectively, by titration with silver nitrate [*11*] and by acid hydrolysis [*11*]. Solutions of copper-cyanide complexes were treated with EDTA under acidic conditions at 50°C for decomplexation of cyanide [*13*]; the concentration of cyanide was measured colorimetrically after it reacted with chloramine-T at neutral pH [*11*]. The concentration of cyanide in solutions of iron-cyanide complexes was measured by monitoring the light absorbance of $Fe(CN)_6^{-3}$ at 410 nm [*14*]. However, when copper was added to iron-cyanide solutions, it interfered with the absorption at this wavelength. Therefore, these solutions were exposed to UV radiation at acidic pH in the presence of sodium sulfide for decomplexation [*15*]. After the addition of bismuth nitrate and pH adjustment to 11.5, cyanide ion was measured by an Orion cyanide electrode.

KINETIC ANALYSIS

For a batch system the general rate expression for the reaction of ozone with cyanide can be expressed as

$$-d\,[O_3]/dt = k\,[CN_T]^n\,[O_3]^m \qquad (1)$$

where $[O_3]$ and $[CN_T]$ are the concentrations of ozone and the total cyanide, and k is the reaction rate constant.

Kinetic studies were performed with the stopped-flow spectrophotometer in at least 5-fold and up to 1300-fold stoichiometric excess of total cyanide. Under such conditions, Equation 1 becomes

$$-d\,[O_3]/[O_3]^m = k_{obs} \qquad (2)$$

where

$$k_{obs} = k\,[CN_T]^n \qquad (3)$$

As will be shown later, the order of the reaction with respect to ozone is 1.0. Hence, the integrated form of Equation 2 becomes

$$\ln\,(A/Ao) = k_{obs} \cdot t \qquad (4)$$

Where A and Ao are the absorption at time t and zero, respectively, and are directly proportional to the concentration of ozone in water. The function in (A/Ao) was plotted as a function of time, according to Equation 4; the psuedo-first order rate constant, k_{obs}, was determined from the slope of the straight-line drawn by using a linear regression model.

The reaction order with respect to total cyanide, n, was determined by plotting $\log k_{obs}$ *vs.* $\log [CN_T]$, according to the following equation for various pH values.

$$\log k_{obs} = \log k + n \log\,[CN_T] \qquad (5)$$

The reaction rate constant, k, was obtained from the intercept of the linear regression lines.

The rate of self-decomposition of ozone at several pH values was determined by a similar procedure. For this case, the cyanide solution was replaced by a buffer solution.

Kinetic experiments were performed for initial cyanide concentrations of 1.9×10^{-4}-0.46 M (5-12,000 mg/L), and ozone concentrations of 1.0×10^{-4}-3.1×10^{-4} M (5-15 mg/L) in the pH range of 2.5 to 12.0. The reactions were observed to be very fast. For example, in the presence of 3.8×10^{-3} M cyanide, the reaction was completed within 12 milliseconds, following a pseudo-first order reaction kinetics with a rate constant of 118 sec^{-1}, as shown in Figure 2. On the other hand, it took 4.5 seconds for ozone to disappear by self-decomposition, yielding a decomposition rate constant of 0.88 sec^{-1}. Assuming that the decomposition is initiated by a reaction step which is first-order with respect to both ozone and the hydroxide ion [*16, 17*], the second-order rate constant for the decomposition of ozone is calculated as 560 L/mole-sec, which is consistent with the rate constant reported by Forni *et al.* [*17*] as 540 ± 20 L/mole-sec. This and similar results at other pH values indicated that the rate of hydroxide-ion-initiated decomposition of ozone is negligible compared to the rate of the reaction of ozone with cyanide ion.

The pseudo-first order rate constants observed in the presence of different concentrations of excess cyanide,

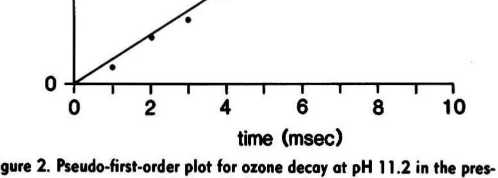

Figure 2. Pseudo-first-order plot for ozone decay at pH 11.2 in the presence of 3.8 × 10^{-3} M total cyanide.

k_{obs}, were plotted in Figure 3 as a function of total cyanide concentration, $[CN_T]$, according to Equation 5, for pH values 11.2, 9.5 and 7.0. For equal concentrations of $[CN_T]$, k_{obs} increased with increasing pH, reaching a value of approximately 1000 sec^{-1} at pH 11.2 for a $[CN_T]$ value of 0.25 M. This rate, which corresponds to a half-life of 0.7 milliseconds, is about the maximum which can be observed by the stopped-flow instrument used in this study.

According to Figure 3, the dependence of k_{obs} on $[CN_T]$ seems to vary with pH. An statistical analysis for a 95 percent confidence interval ($p = 0.95$) yields the following rate expressions for pH values of 11.2, 9.5, and 7.0, respectively.

$$d\,[O_3]/dt = (2600 \pm 700)\,[CN_T]^{0.55\pm0.06}\,[O_3] \qquad (6)$$

$$d\,[O_3]/dt = (2700 \pm 850)\,[CN_T]^{0.83\pm0.14}\,[O_3] \qquad (7)$$

$$d\,[O_3]/dt = (550 \pm 200)\,[CN_T]^{1.06\pm0.10}\,[O_3] \qquad (8)$$

Similar experiments conducted at pH 2.5, where decomposition of ozone is negligible [8], and cyanide is primarily in the form of HCN, showed that the reaction of molecular ozone with HCN is very slow. On the other hand, when k_{obs} was plotted as a function of cyanide ion concentration, $[CN^-]$, for the experiments conducted between pH 2.5 and 12.0, all the data points fit reasonably well to a single straight-line (correlation coefficient = 0.9557), as shown in Figure 4, indicating that ozone reacts primarily with the cyanide ion.

Hence, the overall rate expression can be represented by Equation 9 which describes the line in Figure 4 for p = 0.95.

$$d\,[O_3]/dt = (3300 \pm 1500)\,[CN^-]^{0.63\sim\pm0.04}\,[O_3] \qquad (9)$$

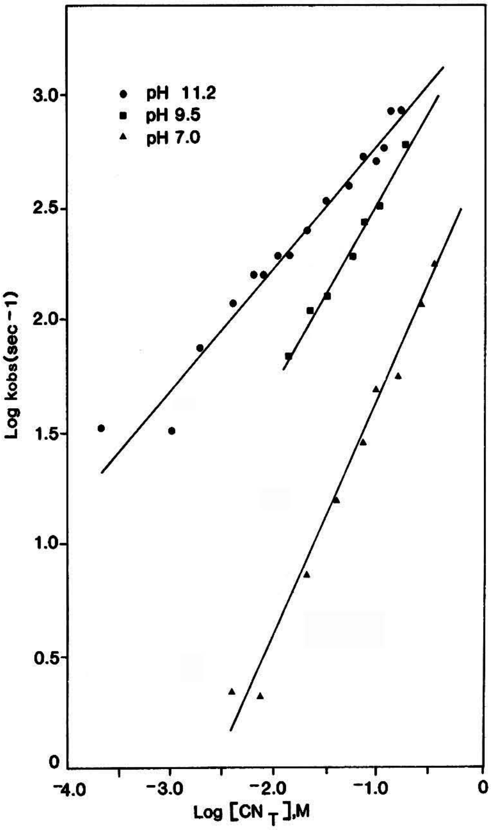

Figure 3. Observed pseudo-first-order rate constant for ozone decay vs. concentration of total cyanide.

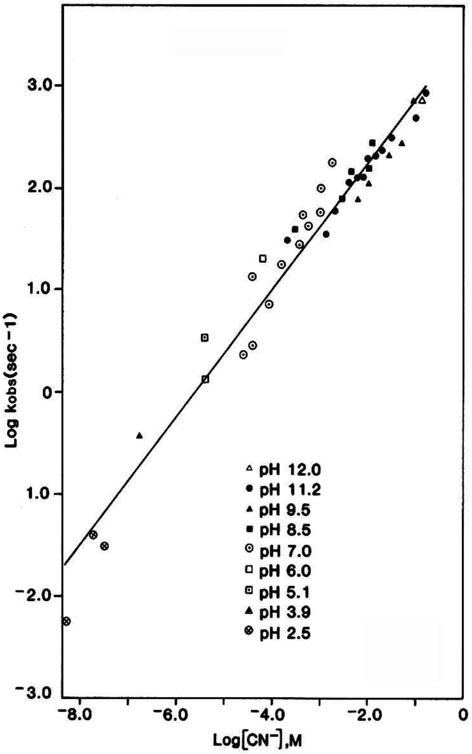

Figure 4. Observed pseudo-first-order rate constant for ozone decay vs. concentration of cyanide ion.

The reaction of ozone with cyanide does not appear to be a simple bimolecular reaction, since the rate of disappearance of ozone (Equation 9) is not first order with respect to cyanide ion as would be expected from an elementary direct reaction of ozone.

EXPERIMENTS IN BUBBLE REACTOR

Free Cyanide

Experiments were performed with free cyanide in the bubble reactor for a gas flow rate of 0.5 L/min. The applied ozone dosage was 19 mg/min. In Figure 5, the observed concentration of total cyanide, cyanate, and ozone residual versus time of ozonation in the bubble column are shown for the pH values of 11.2, 7.0, and 2.5.

At pH 11.2, the removal rate of cyanide was mass-transfer limited because of its very high oxidation rate with ozone, as indicated by the zero-order behavior of the cya-

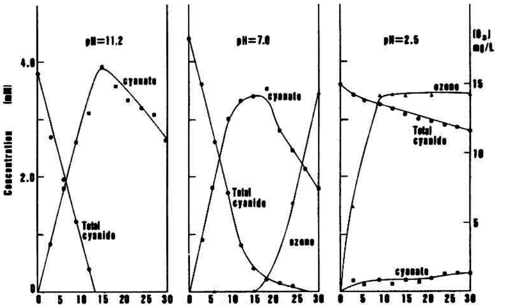

Figure 5. Profiles of total cyanide, cyanate, and ozone residual in the bubble reactor for pH 11.2, 7.0 and 2.5.

nide profile. Cyanate appeared in the solution at a rate which was equal to the rate of removal of cyanide, indicating a one-to-one stoichiometric relation between cyanide and cyanate. After cyanide was oxidized completely, cyanate started to react with ozone at a much slower rate. During the course of the experiment at this pH, ozone did not appear in the solution because of its rapid consumption by the oxidation and the decomposition reactions.

The removal rate of cyanide at pH 7.0 was equal to the rate at pH 11.2, and was mass-transfer limited for the first twelve minutes of ozonation under the experimental conditions of this study. However, after the total cyanide concentration was reduced to about 0.8 mM, the oxidation reaction became the rate-limiting step. Ozone appeared in solution as soon as the system became reaction-rate limited, and accumulated until reaching a plateau at about 14 mg/L. Cyanate was produced at an equal rate the cyanide was oxidized, however oxidation of cyanate started while cyanide still existed in the solution.

At pH 2.5, volatilization of HCN contributed more to the removal of cyanide than its oxidation by ozone, as demonstrated by independent experimentations with pure oxygen. Nevertheless, oxidation of cyanide produced equal moles of cyanate. Due to slow oxidation and decomposition of ozone at this pH, ozone appeared in solution instantaneously, and stabilized at a saturation value of about 14 mg/L.

These results of the experiments with the bubble reactor imply an economic advantage for the high-pH oxidation process, in addition to confirming the results of the batch experiments with the stopped-flow spectrophotometer.

Copper-Complexed Cyanide

In Figure 6, the concentration of cyanide as a function of time of ozonation is shown for free cyanide and copper complexes of cyanide under the same experimental conditions. The disappearance of free cyanide again followed a straight-line, revealing the mass-transfer limited nature of the oxidation process. The presence of copper significantly increased the rate of cyanide disappearance by enhancing the rate of mass transfer of ozone from the gas phase to the solution. The comparison of the initial rates for cyanide disappearance indicates a 5-fold enhancement in the presence of 0.96 mM copper. The increase in the rate of ozone absorption in the presence of copper was observed by monitoring the ozone concentration in the effluent gas, as shown in Figure 6. During the oxidation of free cyanide, ozone was detected in the effluent gas immediately. Ozone concentration increased quickly and reached a steady-state value of about 24 mg/L when 35 percent of the cyanide was oxidized. On the other hand, in the presence of copper, no ozone was detected in the effluent gas for the first three minutes of reaction. The breakthrough occurred after about 85 percent of cyanide was oxidized. Ozone concentration increased quickly and stabilized at about 26 mg/L. The molar ratio of ozone consumed per mole of cyanide oxidized was determined to be 1.2 ∓ 0.2 from mass balance calculations for both free cyanide and cyanide complexed with copper.

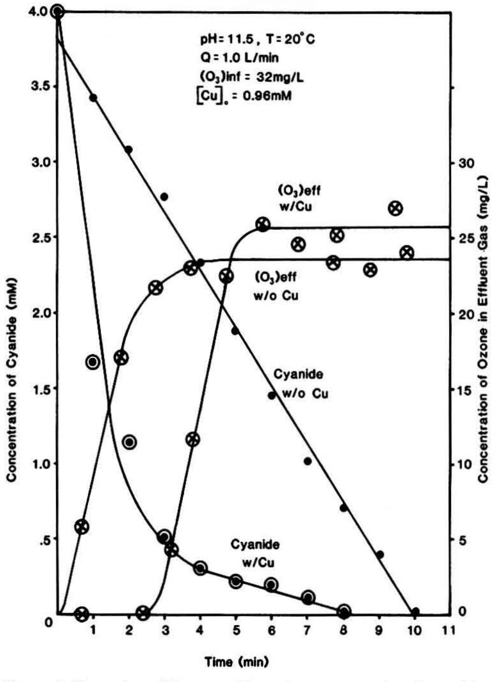

Figure 6. Ozonation of free cyanide and copper-complexed cyanide.

During the oxidation of cyanide in the presence of copper, copper released from cyanide complexes formed various precipitates. Precipitation became extensive after the third minute of ozonation which corresponded to the change in the oxidation rate of cyanide. Additionally, the speciation of soluble copper is expected to change with time as cyanide is removed from the solution, and Cu(I) is oxidized to Cu(II). Hence, the reduction in the concentration of soluble copper as well as the formation of different complexes of cyanide might be responsible for the significant decrease in the oxidation rate.

One mole of cyanate, CNO^-, was produced for each mole of cyanide oxidized in both the absence and presence of copper, as shown in Figure 7. In the absence of ozone, the hydrolysis of cyanate to carbonate and ammonia, as suggested by Selm [2], did not occur at pH 11.5 over a time period of practical importance. However, cyanate was oxidized further by ozone. Bremen [19] observed that the rate constant for the reaction of ozone with cyanate is about two orders-of-magnitude smaller than the rate constant of cyanide oxidation. Consequently, cyanate concentration continued to increase until cyanide was oxidized completely.

Iron-Complexed Cyanide

Figure 8 presents evidence that the complexation of cyanide to iron hinders the oxidation of cyanide by ozone to a great extent. This supports the earlier reports by Mauk *et al.* [20] and Streebin *et al.* [21]. Increasing the ozone concentration in the applied gas did not affect the oxidation rate of iron-complexed cyanide. After 90 minutes of ozonation, about 25 percent of cyanide was oxidized. However, chemical analysis throughout this time period showed no buildup of cyanate in the solution. Independent experiments proved that iron did not interfere with cyanate analysis.

During the oxidation process, no ozone residual could be detected in the solution phase since ozone decomposed completely at this pH of 11.5. Under the experimental conditions, the absorption of more than 30 moles of ozone was required for the oxidation of each mole of iron-complexed cyanide. These observations support an indirect reaction mechanism in which the hydroxyl radicals generated upon decomposition of ozone operate as the predominant oxidizing agents. Hence, it could be concluded that cyanate reacts with the hydroxyl radicals as soon as it is formed from cyanide, since these radicals are known to be nonselective oxidants. Alternatively, oxidation of cyanide in iron complexes may not proceed through cyanate.

Solutions of iron-cyanide complexes were ozonated in the presence of various amounts of copper ($CuSO_4$) in order to determine whether copper can also increase the re-

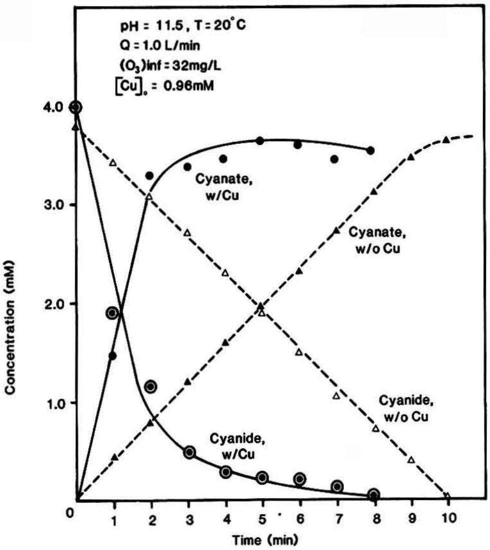

Figure 7. Oxidation of cyanide to cyanate by ozone.

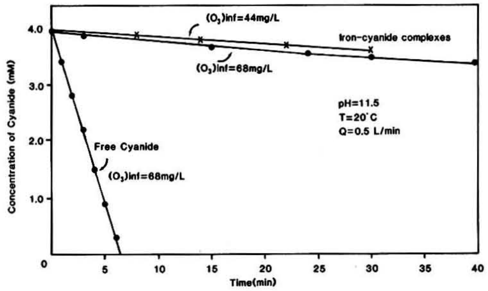

Figure 8. Ozonation of free cyanide and iron-complexed cyanide.

moval rate of cyanide in iron complexes. In Figure 9, the cyanide profiles for the Cu/CN ratio of zero, ¼ and ½ are shown under the same experimental conditions. The amount of cyanide which is removed during the first 15 minutes of ozonation increased by a factor of 4 in the presence of 0.96 mM copper, and by a factor of 8 in the presence of 1.92 mM copper. Consequently, the ozone requirement for the oxidation of one mole of cyanide was lowered proportionately. The rate of removal slowed down after the first 15 minutes, again probably because of the precipitation of copper from the solution. During the reaction period, no buildup of cyanate was observed.

These experimental observations indicate that the iron-cyanide complexes in metal plating wastewaters may not be oxidized by ozone within a reasonable period of time. However, if copper is present in a wastewater, e.g., copper plating wastewater, ozone treatment may still be an economically feasible alternative.

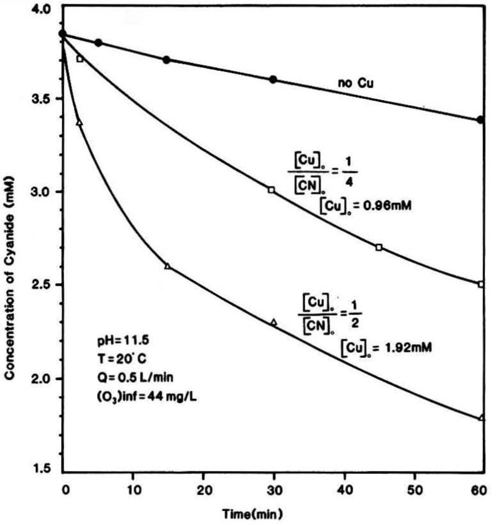

Figure 9. The effect of copper on removal rate of iron-complexed cyanide.

MECHANISM OF COPPER-CATALYSIS

Cu(II) is believed to be unstable in the presence of cyanide. Reports by Cotton and Wilkinson [22] and Barton *et al.* [23] suggest that the catalytic effect of copper which was observed in the present study is due to an independent oxidation/reduction reaction between Cu(II) and cyanide. In order to test this hypothesis, $CuSO_4$ was added to cyanide solutions in various amounts at pH 11.5 in the absence of ozone. After one hour of stirring, the samples were analyzed for cyanide and cyanate. The results are summarized in Table 1.

Cyanide in free form and in complexes with Cu(I) was oxidized with approximately one-to-one ratio to cyanate by Cu(II), as postulated above. However, in iron-cyanide solutions, no cyanate formation was detected in spite of the removal of significant amounts of cyanide. Since the presence of neither iron nor copper has any observable interference on the analytical technique for cyanate, it can be assumed that no cyanate is produced in this reaction.

In view of the presented experimental evidence, the following net reaction can be presented to explain the catalytic effect of copper on the oxidation of cyanide by ozone:

$$2\,Cu^{+} + 11\,CN^{-} + 3\,O_3 \rightarrow 2\,Cu(CN)_4^{-3} + 3\,CNO^{-} + 3\,O_2 \qquad (10)$$

The complexation of cyanide with iron is much stronger than with copper (K_{eq} is 10^{47} for $Fe(CN)_6^{-3}$; $10^{30.3}$ for $Cu(CN)_4^{-3}$; and 10^{25} for $Cu(CN)_4^{-2}$)[24,25]. Therefore, the effect of copper on the oxidation rate of iron-complexed cyanide cannot be explained by an exchange mechanism between copper and iron. Additionally, the absence of cyanate in the reaction mixture eliminates the applicability of the above reaction for iron-cyanide complexes.

TABLE 1. OXIDATION OF CYANIDE BY COPPER

$\frac{[Cu]_o}{[CN]_o}$	Free Cyanide		Copper-Cyanide		Iron-Cyanide	
	Cyanide mM	Cyanate mM	Cyanide mM	Cyanate mM	Cyanide mM	Cyanate
0	3.84	0	3.84	0	3.84	0
1/4	3.05	0.46	3.22	0.41	3.84	not detected
1/2	2.71	0.78	3.27	0.43	3.47	not detected
1/1	2.88	1.00	2.06	0.61	2.04	not detected
2/1	2.80	0.99	3.18	0.58	0.87	not detected

CONCLUSIONS

In the absence of any metals, ozone reacts primarily with the cyanide ion with a very fast rate; its reaction with hydrogen cyanide is negligible. The reaction is first order with respect to ozone and fractional order with respect to cyanide ion. This fractional order is an indication that the reaction is not a simple, bimolecular elementary reaction, but involves the formation and reaction of free radicals.

Upon oxidation of each mole of cyanide, one mole of ozone is consumed, and one mole of cyanate is produced as the intermediate product of the reaction. Oxidation of cyanate by ozone is a slow reaction; therefore, cyanate accumulates in the solution until cyanide is oxidized completely. The oxidation of cyanide at high pH is expected to be mass-transfer limited under the operating conditions of most experimental and full-scale ozone contactors. The kinetic regime for operations at neutral pH should depend upon the mass-transfer characteristics of the ozone contactors as well as the concentration of cyanide in water.

The presence of copper causes a significant increase in the oxidation rate of cyanide, but does not affect the stoichiometric relations. The mechanism of copper-catalysis involves an oxidation-reduction reaction between Cu(II) and cyanide ion.

The complexation of cyanide with iron hinders the oxidation of cyanide significantly. Cyanate is not detected as an intermediate product.

ACKNOWLEDGEMENT

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Hazardous Waste and the Common Law Theories of Liability

A primer for chemical engineers, based on actual examples of cases involving hazardous waste and environmental pollution.

Charleston C. K. Wang, Groeber & Wang, Cincinnati, Ohio 45219

THE COMMON LAW TORT: A PRIMER

(a) The Common Law Tradition

The American common law tradition derives from the laws and legal practices of England. English common law is that body of legal principles which have accumulated and become established through custom and usage in the courts of law over the course of English history. It is that body of judge-made decisions which has been used as precedents by subsequent courts. The cornerstone of the common law is the doctrine of *stare decisis,* which literally means "to abide by or adhere to decided cases." In practice, it imposes upon the courts of law the duty to recognize and follow the authority of previous court decisions or precedents in cases where the facts are similar.

In American jurisprudence, the phrase refers to the portion of the common law of England (including acts of Parliament where applicable) which has been adopted and in force at the time of the Revolution, and the subsequent common law decisions of American courts. The courts in each state and other political entities (e.g., District of Columbia and U.S. possessions) are each a separate jurisdiction in their own right and, as such, make common law for that jurisdiction. Therefore, the common law is prolific and there are as many common law systems as there are political entities in the United States. However, do not despair, as courts yield to and follow the most logical path in most cases, and there are more similarities in the common law among the various jurisdictions than there are differences, although it is important to know the differences as well.

On another matter which may cause concern to engineers and scientists, it is interesting to note that, while the doctrine of *stare decisis* is accorded great deference by judges, it is not an absolute rule, for the courts, including the United States Supreme Court, recognize that there are instances when past decisions have to be modified in part or even in whole. This is an extremely important recognition in the area of disputes arising from technological factors which wind up in our courts for resolution because technology means change and innovation and as such, the common law often must necessarily change in order to keep up with and be responsive to new problems associated with everchanging technology.

Nevertheless, on many occasions, the argument has been raised that our common law courts grounded in *stare decisis* are too backward looking (i.e. dependent on precedents) to be effective in resolving novel technological problems. Indeed, as an alternative, interested parties have resorted to another fountainhead of law, the legislature, for answers in the form of legislative or statutory law.

(b) Legislative/Statutory Law

The legislature is one of the other branches of American government and, under current practice, is actually the major source of new law. In the area of hazardous waste, the most relevant and powerful legislature is, of course, the United States Congress. In addition, there are the various state and local legislatures which add to the proliferation of legislative or codified law. As the popular legislature is not a technical or scientific body, the usual practice is to enact very broad statements of social policy, with the details to be filled in by rulemaking by the various "expert" administrative or regulatory agencies. In the end, we are governed by a corpus of statutory laws <u>and</u> detailed rules and regulations which have the force of law.

One important difference which can be observed between legislative law and common law in the area of hazardous waste is that the common law usually comes into play only after the fact of injury or damage has occurred, whereas legislative law often seeks to implement the public policy goal of prevention (e.g., toxic testing, proper record or manifest keeping, hazard monitoring, etc.), in addition to defining financial and criminal liability. On the subject of criminal liability, note that the common law has been totally superceded by statutory criminal codes in all American jurisdictions. The common law crime no longer exists in the United States. This means that one can be convicted criminally and run the risk of a jail term only if one is shown to have violated a specific provision of the jurisdiction's criminal code.

As the topic of this paper is liability for hazardous waste under the common law, the above observations on legislative law will have to suffice. We will leave the discussion on legislative law with the note that legislative law is at least as important in defining liability and must be reckoned with along with the requirements of the common law in hazardous waste matters. I am sure that engineering and technical practitioners in the area of hazardous waste are already more familiar with the codified requirements than the more esoteric common law and I hope that the rest of the paper can serve as valuable material for my colleagues' use. The other item to remember about statutory provisions is that many of the acts permit "private attorney general" actions by members of the public injured by activities covered by the acts.

(c) The Common Law Tort

In the area of hazardous waste, the most relevant subset of the common law is the law of torts. A tort (from Latin torquere meaning to twist, and hence the English, torture, distort, contort, etc.) is simply a private or civil wrong committed by one party upon another by way of a breach of duty expected of the wrongdoer, independent of any duty arising from contract on agreement between the two parties, for which the law will require compensation by the wrongdoer towards the victim of the wrong. In other words, it is a violation by the wrongdoer of his or her duty owing to the victim and the duty arises by operation of law and not by contract. The three elements of a tort are (1) existence of a legal duty from the defendant to the plaintiff, (2) the breach of that duty by the defendant, and (3) injury or damages as a result of which the law recognizes a remedy.

Torts are usually further subdivided into three types: (i) intentional torts, (ii) negligent torts, and (iii) strict torts.

(i) Intentional Torts—Examples of intentional torts are assault, battery, libel, slander, and false arrest. As can be seen from its name and examples, this tort requires a certain mental state or *scienter* (hence, the English conscience). There must be intent or an appreciation of the substantial certainty of outcome by the intentional tortfeasor. Liability is thus based on a voluntary act by which the tortfeasor knows with substantial certainty that some expected result will follow. For example, if A were to aim a loaded gun at B and pull the trigger, A knows with substantial certainty that B will be killed or injured. Another example is that if A were to put sodium cyanide in B's dinner, A knows with substantial certainty that B will die upon eating the dinner.

In the area of hazardous waste, liability may arise via an intentional tort, the most apparent example being that of intentional trespass to another's land (either private or public) by midnight dampers. The intent present in midnight dumping is so strong and repugnant to public policy that in most states, midnight dumping of hazardous waste has been defined in the statutory code as criminal offenses against the state. Trespass will be discussed in detail later in the paper under its own subheading.

(ii) Negligence—Negligence is probably the most common tort action today. In contrast to the intentional tort which requires the commission of a deliberate act, negligence arises from the failure to exercise the level of reasonable care which the law expects of a reasonable person under similar circumstances. Negligence is personal carelessness or fault which injures another. Please note that the standard or level of reasonable care is not fixed but changes with the defendant and the circumstances. For example, a surgeon is held to the standard of care of his or her profession while the passer-by/good samaritan who stops to apply cardio-pulmonary resusitation to a heart attack victim is held to another standard. Along with the concept of reasonable care, negligence is based on the concept of a foreseeable injury. Normally a negligence claim is not available for a unforeseeable injury. Negligence is further classified as simple, and as willful and wanton. An example of a simple negligence is the act of causing a traffic accident by failing to come to a full stop at a stop sign before a busy intersection, while the act of causing a traffic accident by participating in an all out drag race along a residential road (with no actual intent to collide with another person or vehicle) may be classified as willful and wanton negligence. Wanton and reckless conduct are grounds for imposing punitive or exemplary damages. Like the intentional tort, but unlike strict liability below, negligence is based upon the defendant's conduct (either commission or omission) rather than a condition.

Examples of negligence in the hazardous waste area will be discussed in detail under its own subheading.

(iii) Strict or Absolute Liability—As the name suggests, strict liability is liability without fault. It is the defendant's nightmare, for under the doctrine the defendant can be shackled with liability regardless of the existence or absence of care or of negligence, good faith or bad faith, knowledge or ignorance. It is really an extension of public policy which compels a party to be insurer of the safety of its product or activity and to pay for any damages resulting from that product or activity whenever injury occurs. Liability is imposed upon the proof of physical causation by the defendant. The defendant may have exercised all available care and prudence known at that time but, under the pure form of strict liability, that will not save the defendant. Hence, the physical condition which results from the defendant's pursuits determines liability, and not the actual conduct.

Historically, strict or absolute liability grew out of injuries caused by ultrahazardous activities such as blasting with dynamite which can cause injury despite the use of all available precautions. The current and notorious application of this legal doctrine is, of course, in the area of products liability, whereby the manufacturer is made the unwitting insurer of the safety of its product. The rationale is that the manufacturer has the best control over the design, manufacture, and pricing of the product, and is thus best able to control the safety of the product and, failing that, is in the best position to pay for the damage and then distribute this cost among the other consumers of the product through appropriate pricing adjustments.

Because of the inherent nature of hazardous waste, there is a probability that many of the jurisdictions may in due course adopt this doctrine in one form or another when adjudicating liability for injuries caused by hazardous wastes. In view of this possibility, a detailed discussion will be presented later in this paper under its own subheading.

THE SHIELD OF STATUTE OF LIMITATIONS

(a) Definition

A statute of limitations is a legislated law which sets forth the legal time limit within which suit may be brought in a court of law after the accrual of the legal right to sue and, if exceeded, will serve as a bar to the bringing of the claim before the court. It is thus a technical defense which is used by the defendant to prevent stale suits from being heard in the courts, thereby extinguishing their legal efficacy. Most courts take the position that the wrong is still present except that no redress can be sought from the court because suit had not been brought within the time period required by the statute of limitations.

The actual time period prescribed will actually vary according to the type of action and to the jurisdiction. The time period is usually longer for contracts than for torts, the written contracts enjoying a longer period than oral contracts, while the intentional torts are restricted by a shorter period than negligent torts.

(b) Application to Hazardous Waste Litigation

As the health problems arising from hazardous waste are basically chemical exposure injuries with long latency periods, the statute of limitations applicable to these injuries assume critical importance. While acute injuries like burns and acute poisoning may manifest themselves in a matter of hours or days, latency periods for carcinogenesis, teratogenesis, and mutagenesis can be as long as twenty years or more after initial exposure. As most hazardous waste litigation involves tort claims, the shorter statute of limitations usually applies. For example, in Ohio, the statute of limitations for intentional torts is one year and for negligence, it is two years.

If the statute begins to run from the date of initial exposure, many potential plaintiffs are barred from bringing suit even before the manifestation of injury. This is one example of the entanglement between the laws of justice with the laws of science. In view of the contradiction, at least thirty nine states have adopted a "discovery rule" in one form or another. As its name suggests, the "discovery rule" means that a prescribed period only begins to run after the plaintiff has discovered or, applying reasonable care, would have discovered a certain triggering event. In recognition of the fact that many potential plaintiffs may not even be aware of exposure to a toxic substance or who may not connect observed symptoms with exposure to an etiologic agent, even with professional medical help some of the "discovery rule" jurisdictions have defined the triggering event as the discovery of the causal connection between a manifested injury and the exposure to a certain chemical. Some jurisdictions go even farther in defining the triggering event as the discovery by the injured of the fact that a legal cause of action is available.

Then there are the states which reject the "discovery rule," wherein the statute of limitations remains an effective barrier to a lawsuit based on chronic disease. Therefore, in those jurisdictions which reject the "discovery rule," a plaintiff can be time barred from bringing suit even before the manifestion of the injury and the realization of a causal connection between injury and exposure.

Since the statute of limitations determine whether a claim can be entertained in court at all, it is the first item of consideration for both the plaintiff and the defendant. The defendant can use the statute of limitations as a powerful, inpenetrable shield if the law so allows, and the statute can be anathema to the plaintiff. See *Tyson v. Johns Manville Sales Corp.*, 399 So. 2d 263 (Ala. 1981). As substantial rights and economic interests hang in the balance, this is an ever changing area which requires due diligence in research and analysis before proceeding.

HAZARDOUS WASTE AND THE COMMON LAW

(a) Negligence

As mentioned earlier, negligence is probably the most frequent action brought in tort claims. It does not require proof by the plaintiff of the defendant's intent, which is subjective and difficult to prove, but it requires the showing of the defendant's failure to exercise the level of reasonable care required of him or her by law and custom, thereby exposing the plaintiff to an unreasonable risk of harm.

In the area of hazardous wastes, a lawsuit based on the negligence theory can conceivably be brought for injuries resulting from:

(i) the faulty or improper storage of wastes, (ii) the faulty or improper transportation of wastes, (iii) the faulty or improper disposal of wastes, and (iv) the faulty treatment of wastes.

Fault is derived from a relative breach of the duty of care against a standard or benchmark which the court accepts for comparing the level of care possible and the actual level of care used. It is therefore apparent that, as long as the state of the art technology at the time of the conduct was not used, there exists a possibility of liability under the theory of negligence. The further away one strays from the state of the art technology, the greater the risk of liability. The plaintiff has the burden of first establishing the standard of care existing at the time, as well as the control by the defendant and the subsequent breach of that standard. This is shown by the use of testimony from expert witnesses. Likewise, the defendant must refute the opinions of the plaintiff's expert witnesses through the testimony of his or her own expert witnesses. Very often negligence trails end up as a battle of the expert witnesses.

A duty of reasonable care or reasonable standard of conduct may also be imposed by legislative or administrative regulation, in which case a breach of which could constitute *negligence per se*. The trial court usually exercises discretion whether to accept the legislative standard in a private civil suit. In so doing, the court looks at the legislative intent behind the enactment to decide whether the legislative standard is appropriate for the civil action. Thus, where the legislative intent is to protect the particular class of persons to which the plaintiff belongs, or where the claim is against a violation of an interest which the statute is intended to protect or where the harm or injury is the type against which the statute is intended to prevent, then the applicability of the statute is clear and the court usually goes no further in its inquiry and the standard is adopted. When this happens, the remaining issue of fact is that of the breach and of the physical causal connection between the breach and plaintiff's injury.

Examples of cases based on negligence are *Knabe v. National Supply Division of Armco Steel*, 592 F. 2d 841 (5th Cir. 1979) (failure to secure or to take prompt remedial action over discharge of hazardous substances from a waste holding pond); *Pine v. Rizzo*, 186 Okla. 35, 96 P. 2d 17 (1939) (negligent contamination of subsurface waters); *Cities Services Gas Co. v. Eggers*, 186 Okla. 466, 96 P. 2d 1114 (1940) (negligent discharge of saltwater onto plaintiff's land from the oil drilling activities on defendant's property); and *Defeo v. People's Gas Co. of New Jersey*, 6 N.J. Misc. 790, 142 A. 756 (1928) (negligent discharge of natural gas).

From the hazardous waste plaintiff's position, one weakness in using negligence is that the improper conduct with the hazardous waste may have occurred many years ago and evidence of both the standard or care and of the acts constituting the breach of standard may be difficult to produce. For this and other reasons, plaintiffs rarely rely solely on negligence in their suits for exposure to hazardous waste.

(b) Trespass

Trespass is the intentional or, to a lesser degree, the negligent entry or intrusion onto the plaintiff's land by the defendant's person or by an object within defendant's control. Trespass only protects the plaintiff's possessionary interest in his or her land; therefore, a plaintiff cannot sue in trespass if he or she is not in possession of the land, i.e., not physically present on the land. Trespass is an ancient common law action deriving from the times of feudal lords and people like Robin Hood and his team of professional poachers. Thus, historically, trespass required a physical entry onto the land like walking on it or, in the minimum, intrusion by a tangible object like a speeding bullet or large chunks of rock. This requirement has brought grief to many an aspiring plaintiff complaining of pollution. To this day, this ancient *sine qua non* persists, at least in concept and in argument although, like the Oregon Supreme Court, it has been converted to a requirement for instrusion "by visible or invisible pieces of matter or by energy which can be measured only by the mathematical language of the physicist." *Martin v. Reynolds Metals Co.*, 221 Ore. 86, 94, 342 P. 2d 790, 794 (1959) (court was referring to fluoride particulates from defendant's smelter falling onto plaintiff's land); *see also Borland v. Sanders Lead Company*, 369 So. 2d 523 (Ala. 1979); but *compare Born v. Exxon Corp.*, 338 So. 2d 933 (Ala. 1980).

Trespass actions over environmental pollution have tended to be merged with the other theories like negligence, nuisance, and strict liability, although it may enjoy a resurgence in efficacy and popularity in the area of percolating liquid wastes. With respect to nuisance (discussed next), liability in trespass attaches upon the showing of the intrusion or entry from the faulty or improper activities of the defendant without the explicit balancing of the gravity of the harm against the social utility of defendant's conduct, something which is required in a nuisance action.

(c) Nuisance

(i) Private Nuisance—A private nuisance is defined as the unlawful interference with another's use and enjoyment of land. It is an equitable action for which an injunction or court order commanding the defendant to do or stop doing certain things (further details on remedies are given later). In addition to equitable remedies, monetary damages may also be obtained subsequently. As mentioned earlier, nuisance today may become merged with the action of trespass, especially when the distinction between visible entry and invisible entry (e.g., noise, gases, and radiation) becomes blurred. Nuisance may also become merged with strict liability (see discussion of strict liability below).

Being an equitable action, the judicial resolution of a nuisance action mandates a balancing of equities or fairness. Specifically, the court will weigh the nature and extent of plaintiff's injuries with the social and economic utility of the defendant's activities which constitute the nuisance. Thus, a nuisance claim may become difficult to win for the plaintiff, especially when an industry has great overall social utility. It is interesting to note that there exists a defense known as "coming to the nuisance" where the activities of the defendant preceded the plaintiff. Like everything else in the law, there is a split among common law jurisdictions as to the viability of this defense.

Private nusiance actions can be brought for interference of the use and enjoyment of land by noise, air pollution, water pollution, and underground water pollution. It is interesting to note that the fact that a hazardous waste facility has a government permit (as today most, if not all facilities must have permits) may not be a valid defense to a nuisance action.

(ii) Public Nuisance—A public nuisance is defined as a violation of a public law which characterizes certain offensive activity and thus proscribes it. Being an encroachment upon a public right, it can be redressed only by the public prosecutor unless otherwise provided by legislation. Statutes may define nuisance broadly: public nuisance need not be based upon an unreasonable interference with the use and enjoyment of land.

(d) Strict Liability

(i) Rylands v. Fletcher: Strict Liability imposed for a "non-natural" use of land—Rylands v. Fletcher [*Fletcher v. Rylands*, 1865, 3 H. & C. 774, 159 Eng. Rep. 737, rev. in *Fletcher v. Rylands*, 1866, L.R. 1 Ex. 265, aff'd in *Rylands v. Fletcher*, 1868, L.R. 3 H.L. 330] is an English case decided in 1868 which has been accepted and applied by the majority of American jurisdictions in some form. The defendants were mill owners who hired independent contractors to build a reservoir on their land. The water in the reservoir broke through into the disused shaft of an abandoned coal mine, flowed along the connecting passages and flooded plaintiff's adjoining mine. The case, as decided by the House of Lords, stands for the proposition that strict liability will be imposed for the "non-natural" use of defendant's land, as distinguished from "any purpose for which it might in the ordinary course of the enjoyment of land be used." The English courts, and the American courts which follow the rule will inquire into (1) the character of the condition or activity, and (2) the place and manner in which it existed and its relation to its surroundings. Thus, the customs of the community, and the natural fitness or adaptation of the land for the condition or activity are important factors. Thus, it is apparent that *Rylands v. Fletcher* is not a pure strict liability doctrine, but, more like the theory of nuisance, calls for the balancing of a number of parameters.

(ii) Other Modern Cases of Strict Liability—American Courts have tended to follow rather than reject *Rylands v. Fletcher*. But it is interesting to review some of the judicial definitions of "non-natural" and other balancing efforts.

In *Cities Service Co. v. Florida*, 312 S0. 2d 799 (Fl. Ct. App. 1945) the Florida Court determined the "non-natural" character of phosphate slime storage by assessing the size of the risk.

A Texas case, *Turner v. Big Lake Oil Co.*, 128 Tex. 155, 96 S.W. 2d 221 (1936), involved a suit for damages as a result of the escape of salt water from ponds associated with oil well operations. The salt water escaped onto the plaintiffs grasslands, killing vegetation and poisoning livestock watering holes. The court found that the storage of salt water was an absolute necessity for the Texas oil industry and it insisted that the plaintiff prove negligence before recovering.

In *Fritz v. E.I. DuPont deNemours & Co.*, 45 Del. 427, 75 A. 2d 301 (1950), plaintiff was injured by chlorine gas escaping from defendant's plant. The plaintiff filed suit, claiming that "such a hazardous activity that DuPont could have reasonably foreseen that certain harm would result to any person within the area of operation in the event the chlorine should escape." The court weighed the inherent hazard of escaping chlorine gas with the state's policy not to "strangle corporate and industrial enterprise." On the basis of evidence presented, the court determined that the use of chlorine gas at the plant was not "unusual" and was not "dangerous *per se* in the light of recognized industrial use." In a later case, *Catholic Welfare Guild v. Brodney Corp.*, 58 Del. 246, 208 A 2d 301 (1964) the Delaware Supreme Court found for strict liability for injuries from a blasting operation. The Court reconciled this case from *Fritz* by making the distinction that the plant in *Fritz* was located in a rural area whereas the blasting occurred in the City of Wilmington.

Despite the diverse interpretations of the above examples which were decided in the last thirty years, under current public opinion, sentiment, and perceptions, the operation of hazardous waste facilities would appear to be more "non-natural" than "natural." This is especially so if the case went before a jury. Therefore, there is a good probability that strict liability will apply to toxic injury and hazardous waste suits.

As mentioned previously, the most infamous applications of the concept of strict/absolute liability are in products liability. However, in most hornbooks, legal treatises, and texts, the subject of products liability is treated separately in its own right. See e.g. Prosser's *Law of Torts*. The strict liability doctrine as applied to defective products are a purer of "stricter" form of strict liability than the doctrine under *Rylands v. Fletcher*. Products liability evolved as a result of the perceived public policy need to shift the burden of risk, costs, and loss to the industry which benefits from marketing the product. In economics language, strict products liability attempts to internalize the risks within the industry. Strong reasons exist for the imposition of strict liability in hazardous waste situations. It is rather ironical that, while hazardous waste, being a "waste" is not a "product," in the sense that it is a valuable, marketable product, it nevertheless is part of the process or chain of production of valuable, marketable products. A number of legal commentators have emphasized the similarities between injuries from defective products and from hazardous wastes.

Significantly, the judiciary has been impressed by the similarities. The New Jersey Superior Court in *City of Bridgetown v. B. P. Oil, Inc.*, 146 N. J. Super., 169, at 177-178, 369 A. 2d 49 (1976), and in *Dept. of Transportation v. PSC Resources, Inc.*, 159 N. J. Super. 154 (1978) have analogized strict products liability to liability from the improper storage of hazardous substances and the pollution of a lake:

> While in New Jersey the concept of strict liability regardless of negligence has been developed in

products liability cases, see *Herbstman v. Eastman Kodak Co.*, 68 N.J. 1, 342 A. 2d 181 (1968), it has not yet been extended to tort cases such as the one at bar. As can be seen, however, there is a varying standard of care required in negligence cases, depending on the amount of danger involved in the activity engaged in. In the case at bar, the activity, storage of oil, created a substantial risk, and the defendant therefore had a high standard of care established by statute with the requirement for high standard because of the inherent dangers involved in the storage, defendant must be required to exercise an extremely high burden. As has been discussed, strict liability has been applied to products liability cases. In view of our developing insight into the impact of pollution upon the environment because of the nature of this activity, and the statutory prohibition against pollution, this is the proper time to extend the concept of strict liability in this state to those who store ultrahazardous or pollutant substances. This means that a defendant becomes liable for damages caused to a proper plaintiff.

This rule is really neither real or novel. For generations it has been the common law rule that an owner of realty is required to refrain from injury to the land of his neighbor. "*Sic utere tuo ut alienum non laedas*" [use your property in such a manner as not to injure that of another] is older than "when in the course of human events. . ." 9 *Coke* 59, 1 Blackstones, Commentaries 306; Harper and James, Law of Torts, Section 142 at 71 (1965).

DAMAGES AND REMEDIES

Remedies are the means by which a legal right to enforced, or the violation of a right is prevented, redressed, or compensated. There are basically two kinds of judicial tort remedies:

(1) Remedies at Law
(2) Remedies at Equity

For our purposes, it is sufficient to say that the traditional common law remedy is limited to the award of monetary damages to compensate for a tort injury, and the equitable remedy entails the judicial injunction which is a court order commanding the defendant to do or stop doing a certain thing. Thus it is apparent that in the area of hazardous waste, the injunction is the more powerful and efficacious remedy as it has preventative characteristics whereas the traditional common law remedy of damages is limited to after-the-fact compensation.

CONCLUSIONS

The law is often said to be "a seemless web." This paper has attempted to cut into this seemless web from the direction of hazardous wastes. As this area if a technologically complex one, it is expected that the common law courts will render diverse and sometimes conflicting or even confusing decisions. As a observer or student in this area, the objective is not to be overwhelmed by the diversity and contradictions but to remember that the common law is as complex as the subject matter and the society over which it governs. The common law, along with statutory law, has and will continue to have great impact in the operation of hazardous waste facilities. Given the explosive expansion of public awareness and scrutiny in this area, the application of the common law to problems involving hazardous waste will increase, especially in the area of victim compensation. It therefore behooves the chemical engineer working in this area to have a basic appreciation of the impact of the common law to hazardous wastes. However, as the area is an ever changing one, competent professional assistance is invaluable in the face of concrete problems or cases.

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New Sludge Destruction Process

Demonstration and operating results from application of the Vertech Treatment System to an actual municipal waste in Longmont, Colorado.

Gerald C. Rappe, Vertech Treatment Systems, Westminster, Colorado 80234

VerTech Treatment Systems is a new entity that was formed in September 1983 by Bow Valley when they exercised their option for this innovative waste destruction technology. Bow Valley is a diversified international company engaged in natural resource development and energy industry services. It specializes in exploration and production, drilling equipment, coal mining, and resource services.

Elements of VerTech's Technology (Figure 1)

The most important elements of this technology are:

- Wet air oxidation
- Drilling
- Reactor design and construction
- Scale control
- Materials selection
- Instrumentation and control

The principles of wet air oxidation are well established [*1*, *2*, *3*], but high capital and operating/maintenance costs have limited the application of the technology.

The present unique patented system [*4*] utilizes conventional oilfield drilling technology to provide a drilled, cased, and cemented well about a mile (1.6 km) deep.

Reactor design is based on hydrodynamic models for two-phase flow, predominantly in a Taylor bubble or slug flow regime [*5*]. These models have been validated with data from VerTech's commercial installation at Longmont.

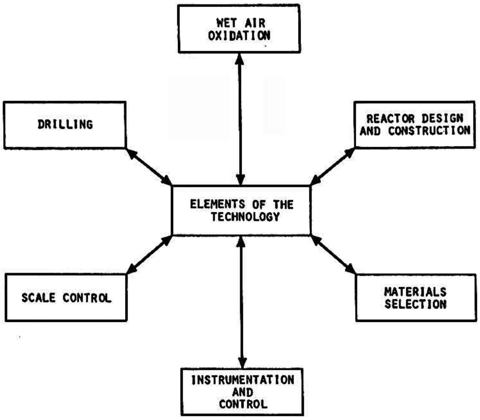


Figure 1. Elements of VerTech technology.

Reactor design and installation must interact successfully to provide sustained continuous operation with sufficient instrumentation to allow easy operator control and meet all system performance objectives.

Many wastes, particularly those high in solids, may produce a scale at elevated temperatures in the reactor. Effective scale-inhibition and control systems are necessary for sustained operation. VerTech has developed and successfully demonstrated these high temperature scale inhibitors at Longmont.

Materials selection is important to sustain a 20-year reactor life. Duplex stainless steels combine high strength and excellent corrosion resistance, both of which are necessary to provide a cost-effective reactor design. These materials are resistant to stress corrosion cracking with chloride concentrations up to 1000 ppm. Above this limit corrosion tests are recommended.

VerTech vs. Conventional Wet Air Oxidation

A comparison of this below-ground technology with conventional wet air oxidation is provided in Table 1. VerTech's process is sludge destruction and the solid end-product is an inert ash which may be used as a filler for bricks.

Conventional wet air oxidation is predominantly sludge conditioning. This improves subsequent dewatering but, for the case of biological sludge, one must still face disposal or further processing of a concentrated biological sludge.

There are significant differences in the reactor configurations. In the vertical tube reactor, the aqueous waste stream flows co-currently with air in an annular space 5200 ft (1.6 km) deep and is subjected to an increasing temperature profile to a maximum of about 550°F (288°C). The reactor system is essentially plug flow with an L/D ratio greater than 30,000.

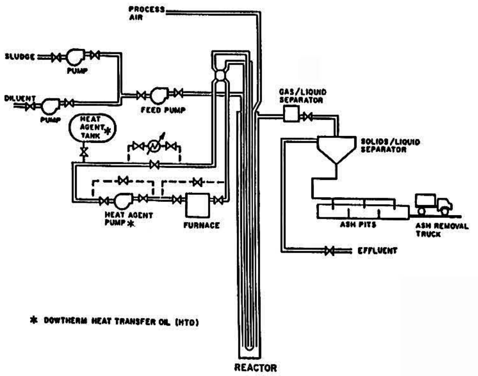
TABLE 1. WET AIR OXIDATION

	VERTECH	CONVENTIONAL W.A.O.
Process	Sludge Destruction	Sludge Conditioning
Solids	Inert Ash	Improve Sludges Dewatering Sludge to be disposed
Reactor Temperature	70°F to 520°F (20°C to 277°C)	375°F to 400°F (190°C to 205°C)
Reactor Mixing	Plug Flow	Back-mixed Reactors in Series
L/D Ratio	Greater than 30,000	10
COD Reduction	up to 80%	10-30%
Liquid Effluent	2000 mg/L COD Easy to recycle	30,000-50,000 mg/L (COD) Causes Odor Problems

By contrast, conventional surface wet oxidation is at a constant temperature between 375°-400°F (190°-205°C) in a series of reactor vessels with a 4 ft diameter and typically with a L/D ratio of 10. Thus, the reactors are back-mixed.

Process Flow Diagram

A simplified process flow diagram is shown in Figure 2 and a schematic of the reactor cross-section is shown in Figure 3. To put the reactor in an overall "process perspective," we take concentrated wastes such as a waste activated sludge and typically dilute to about 10,000 mg/L of COD. The diluted waste is combined with air and flows co-currently down through the downcomer and up through the upcomer. A significant advantage of this



PROCESS FLOW DIAGRAM

Figure 2. Process flow diagram.

VERTICAL TUBE REACTOR

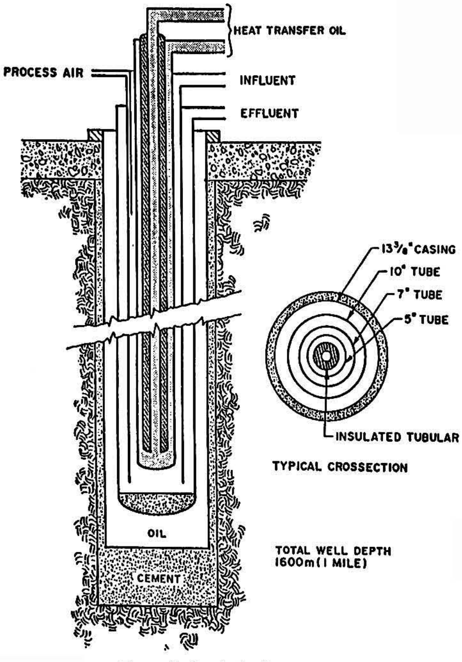


Figure 3. Vertical-tube reactor.

below-ground configuration is that one needs only to pump and compress to 400 psi (2.76 MPa) at surface to obtain 1400 psi (9.65 MPa) at the bottom of the well. Reaction begins to take place at the point where the temperature exceeds 350°F (177°C), typically about 800 ft (240 m). The rest of the reactor, from 800 ft (240 m) to 5200 ft (1.6 km), is an effective reaction zone.

Downstream of the reactor the effluent flows to a gas/liquid separator. There is no air pollution problem, no oxides of nitrogen are formed, and no organics are present in the gas phase. The dilute slurry flows to a lamella separator for clarification and thickening. The overflow can then be returned to the wastewater treatment plant; the lamella underflow which contains the concentrated inert ash solids then is dewatered prior to final solids disposal.

A circulating hot oil system brings the reactants up to temperature and establishes the temperature profile within the reactor. When steady-state temperatures are achieved in the surrounding rock formation, the heat input requirements can be substantially reduced. At higher COD influent concentrations, sufficient energy can be generated by oxidation to permit energy to be extracted from the system.

Longmont, a city of 50,000 people, generates 8 million gallons of wastewater and produces about 5 dry tons of biological sludge daily. The VerTech system consisting of a reactor 10 in. (0.25 m) diameter by a mile (1.6 km) deep is now processing all of Longmont's sludge.

Reactor Installation

The installation process is critical to successful reactor operation. A hole is drilled according to the best oilfield practices. This includes drilling the hole to meet straightness specifications, followed by casing and then cementing the casing in place. Additional casing strings may also be required to prevent contamination of sub-surface aquifers.

After the casing is cemented, installation of the reactor and internal strings of pipe begins. The reactor wall is installed first and is then followed by the upcomer, the downcomer, and the heat exchanger strings of pipe.

The installation process for each string is quite similar. The pipe is installed in 40-foot sections. Each section is first lifted to a vertical position; the threaded connections are cleaned, and power tongs are used to tighten each joint. Then each connection is tested to assure leak-tight operation; the pipe is lowered and the process is repeated until the last pipe in the series is in place. Then a hanger is placed on top of the last section of pipe and the hanger is set into a spoolpiece which forms part of the wellhead. In essence, each string of pipe is ultimately supported at the surface by the outer casing. The wellhead consists of a conventional bolted construction and is the method to convert influent and effluent reactor flows to annular spaces within the reactor.

Technology Development

Significant events in the development of the VerTech technology are shown in the VTR Chronogram (Figure 4). Experiments were started in a laboratory batch reactor (LBR) in 1973 [6]. This led to a 2-inch (5.1 cm) diameter reactor 1500 ft (460 m) deep, which was installed at Lowry Bombing Range in 1977. Successful pilot plant results led to design and construction of the Longmont, Colorado, demonstration plant in 1982-83. Start-up was in the summer of 1983. After a two-and-a-half month operating period, the reactor was shut down. Modifications and improvements to the reactor design were engineered late in 1983. The reactor was then retrofitted in early 1984, and start-up began again in May 1984. Effective July 1, 1984, an EPA grant to the city of Longmont was initiated for assessing the performance of the VerTech Treatment System.

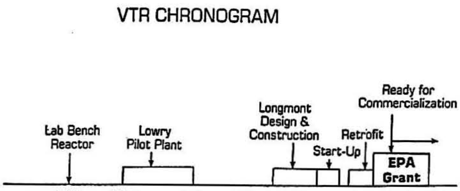


Figure 4. VTR chronogram.

Status of Longmont Demonstration Unit

A retrofit of the Longmont demonstration plant was completed in May 1984 and included replacing reactor inner tubing strings, installing a conventional wellhead with bolted construction with double metal seals, and the addition of improved instrumentation and data acquisition systems. The May start-up began with air/water tests to verify hydrodynamic models. This was followed by a reactor heat-up leading to aerated flow tests at elevated temperatures.

VerTech began to process sludge from the Longmont wastewater treatment plant in June. We have now had more than eight months of continuous 24-hour per day, 7-day per week successful operation. We are operating well above 500°F (260°C) and the reactor runs smoothly and reliably. As part of the EPA grant to the City of Longmont, parametric tests are in progress which will last about 12 weeks to be followed by reliability testing at a specific set of conditions. The EPA grant will continue until May 1985.

VerTech Treatment Systems: A Demonstrated Technology

Some of our accomplishments to date: we have utilized conventional oil field technology wherever appropriate, and changed from welded connections to threaded pipe. Threaded connections are easier and faster to install and make the reactor more serviceable. We have adapted conventional wellhead construction and used proven oilfield installation techniques.

We are utilizing an insulated tubular heat exchanger which is capable of extended performance at 700°F (370°C). There has been no degradation in performance of the heat exchanger or degradation of the heat transfer oil. We have operated the reactor as high as 530°F (277°C) and maintained 490°F (255°C) for 3-week periods between acid washes. We have achieved smooth and stable reactor operation (see Figure 5) with an effective reactor zone that starts about 800 ft (240 m) and extends to the bottom of the reactor 5200 ft (1.6 km).

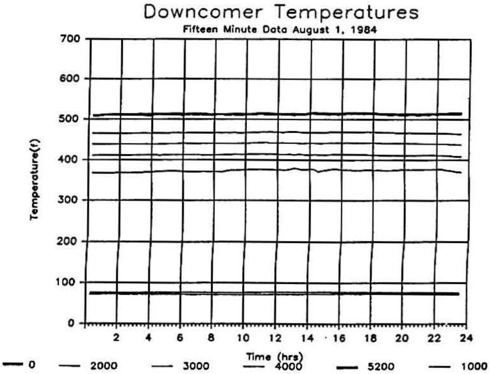


Figure 5. Downcomer temperatures.

We have demonstrated that our instrumentation provides for safe and reliable operation. The system is easily controlled and the operators are at all times fully aware of how the system is operating. The data acquisition system has been an extremely useful diagnostic tool which is used for trend analysis. We have been able to establish a strong engineering data base and currently are accumulating and storing about 6000 data points a day.

The hydrodynamic model accurately predicts two-phase flow. We can predict the pressure profile to within 25 psi (0.17 MPa) for liquid flow and within 100 psi (0.69 MPa) for two-phase flow (see Figures 6 and 7).

For scale control, we have demonstrated scale inhibitors that will perform effectively at temperatures above 500°F. Less than 10% of the calcium passing through the reactor is retained, thus reducing the formation of calcium sulfate anhydrite scale. Periodically, nitric acid is used to remove the scale. We have been able to demonstrate that all reactor scale has been removed by means of flow tests subsequent to descaling.

For COD reduction, the tests at Longmont are in excellent agreement with laboratory batch reactor results using actual temperature profile data from Longmont. COD reduction depends on a number of variables: maximum temperature, the temperature profile, the effective reactor residence time and influent COD concentration. Some recent data are shown in Figure 8. COD reduction increases with increasing inlet COD concentration and temperature.

Technology is Ready for Commercialization

Below-ground waste destruction technology has now reached the point where it is ready for commercialization. As previously mentioned, we have eight months of sustained operation of our demonstration unit at Longmont. Some of the possible applications are municipal sludges, pulp and paper industry wastes, tar sand tailings, petrochemical wastes, and hazardous and toxic wastes. Some selective results are shown in Figures 9-11 based on LBR test results for municipal sludge, pulp and paperboard mill waste, and tar sand tailings.

Most of our efforts have been spent in processing municipal sludge, and, at Longmont we are processing a mixture of both municipal and industrial sludge. As shown in Figure 9, for an East Coast municipal sludge, with an influent of about 10,000 mg/L of chemical oxygen demand, the effluent was about 2800 mg/L. This represents a 72% COD reduction. Similar results have been achieved with sludge at Longmont.

In the pulp and paper industry we have used the laboratory batch reactor on pulp and paper board wastes. The

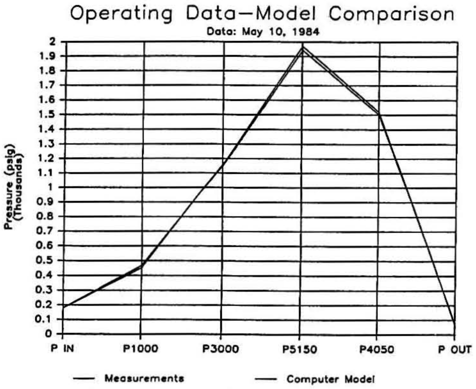


Figure 6. Operating data—model comparison.

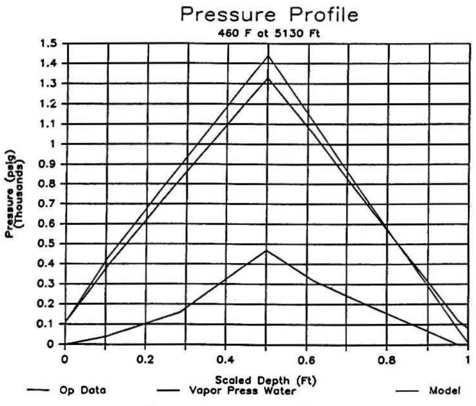


Figure 7. Pressure profile.

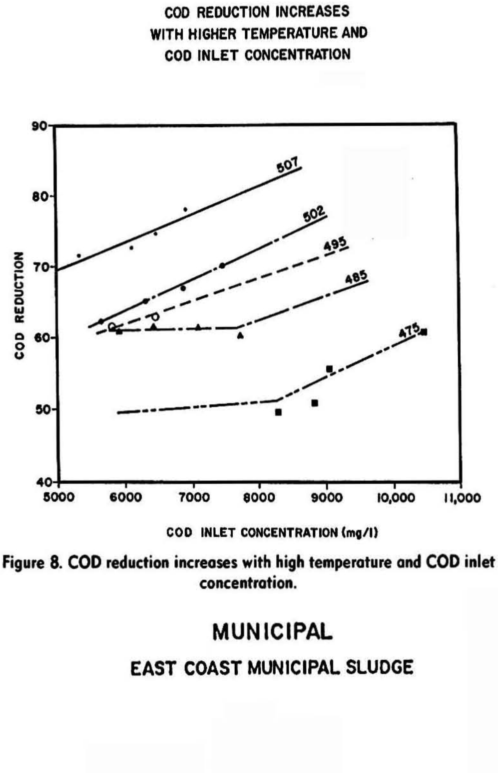


Figure 8. COD reduction increases with high temperature and COD inlet concentration.

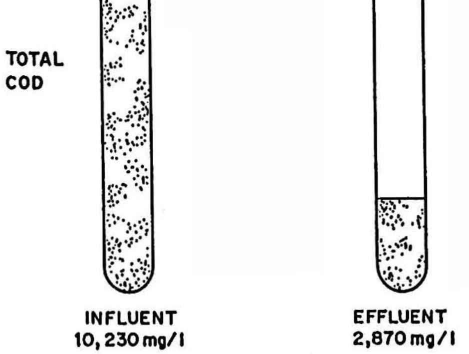


Figure 9. Municipal. East Coast municipal sludge.

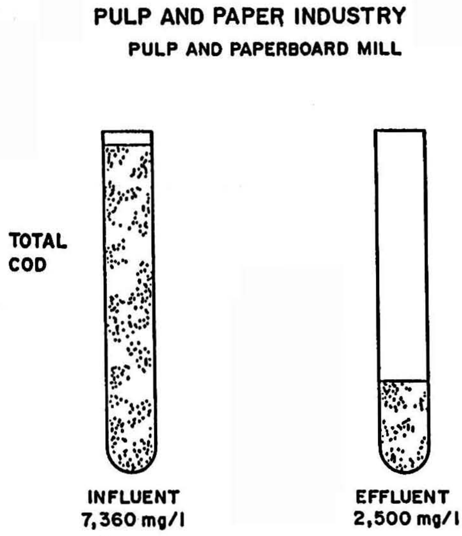


Figure 10. Pulp and paper industry. Pulp and paperboard mill.

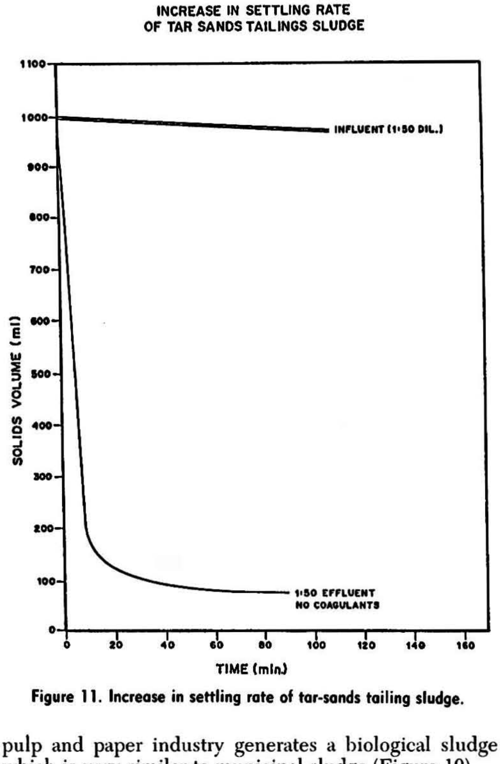


Figure 11. Increase in settling rate of tar-sands tailing sludge.

pulp and paper industry generates a biological sludge which is very similar to municipal sludge (Figure 10).

We have also processed waste from tar sands tailings. The settling rate is very slow, even when tailings pond sludge is diluted by a factor of 50. However, by passing the material through a vertical tube reactor and oxidizing the oils at the surface of the sand particles, the settling rate improves dramatically, as shown in Figure 11.

Improvements at Demonstration Plant

There are some planned improvements we plan to make at Longmont over the next 3 to 6 months.

- In the influent system currently we are relating air flow to total solids, whereas chemical oxygen demand is the right variable to determine the amount of oxygen that is needed for oxidation.
- In the hot oil system we will be increasing the burner capacity and replacing two thermocouples which failed. Due to a flexible reactor design we do not have to pull any of the reactor's internal strings of pipe to remove the thermocouples or install new ones.
- The effluent system will be designed for both erosion and corrosion.
- We plan to improve the performance of the gas/liquid separator and the lamella separator by increasing capacity and reducing vibration, respectively.
- Bench scale bioreactors have been placed in operation to establish effluent treatability.
- We plan to carry out tests at Longmont with oxygen-enriched air which has the potential for significantly increasing reactor capacity. The economics are favorable and we expect installation by the end of September 1984.

Summary

The VerTech Treatment System is very flexible; the technology is multidisciplinary and highly interactive. It is a synergistic combination of wet oxidation and conventional oil-drilling technology. The Longmont unit is successfully demonstrating this technology. It combines two-phase flow with effective heat transfer. Our hydrodynamic models have been validated. We have demonstrated a high COD reduction, steady and reliable system operation, and have shown that both scale and corrosion are under control. Therefore, we believe that the technology is ready for commercialization.

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Gerald C. Rappe is Vice President of Engineering at VerTech Treatment Systems. He holds a Doctor of Science degree in Chemical Engineering from the Massachusetts Institute of Technology. He has fifteen years experience in petroleum refining and chemical process technology developed. He has also authored several publications and has had four patents issued.

Effects of Waste Oil Contamination

Experimental documentation indicates that the practice of treating roads with waste oil for dust suppression can deteriorate the environment. Health risks are still being debated.

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The objective of this study was to evaluate the potential for harm to human health or to the environment presented by the use of waste oil as a dust suppressant. This study is one of three funded by the U.S. Environmental Protection Agency, Office of Solid Waste, to assess the environmental impact of common waste oil practices. The practices covered in the other two studies are waste oil storage and use of waste oil as a fuel.

USE OF WASTE OIL AS A DUST SUPPRESSANT

A state-by-state survey was conducted to determine the extent of road oiling in the United States. Based on results of this survey and on other unpublished data, an estimated 30 to 50 million gallons (113 to 189 thousand cubic meters) of waste oil per year is used in commercial road oiling activity in the United States. If road oiling by self-generators* is included, an estimated 50 to 80 million gallons (189 to 303 thousand cubic meters) of waste oil per year is used for this purpose. Road oiling is most common in the northern Rocky Mountain states, the extreme Southwest, and the Southeast. A moderate amount is also practiced in the Northwest and in northern New England.

The concentrations of potentially hazardous constituents in waste oil used for road oiling vary greatly from sample to sample. Several descriptive statistical methods have been used to summarize the concentrations of metals, chlorinated solvents, and other organics found in waste oil. The data presented in Table 1 clearly indicate that waste oil used as a road oil may contain high levels of potentially hazardous materials.

ENVIRONMENTAL FATE OF WASTE OIL COMPONENTS

Dispersion models were applied to the movement of waste oil from road surfaces in an effort to quantify the extent of possible contamination of air and surface waters. Evaporation, seepage, and dust transport typically occur simultaneously, but at different rates, depending on environmental conditions. Rainfall runoff, which is of a more intermittent nature, is restricted to periods of heavy rainfall. A reasonable worst-case scenario approach was cho-

TABLE 1. SUMMARY OF RESULTS OF ANALYSES FOR POTENTIALLY HAZARDOUS CONSTITUENTS FOUND IN WASTE OIL[a]

	Samples Detecting Contaminant (percent)	Concentration at 90th Percentile[b] (mg/kg)	Concentration Range (mg/kg)	
			Low	High
Metals				
Arsenic	100	16	0.4	45
Barium	79	485	0	3,906
Cadmium	46	28	0	36
Chromium	81	28	0.1	537
Lead	93.8	1,000	0	3,500
Zinc	98	1,500	0.7	5,000
Chlorinated Solvents				
Dichlorodifluoromethane	68	860	0	2,200
Trichlorotrifluoroethane	57	130	0	550,000
1,1,1-Trichloroethane	85	1,300	0	110,000
Trichloroethylene	76	1,049	0	330,000
Tetrachloroethylene	89	1,200	1	3,900
Total Chlorine	100	6,150	40	459,000
Other Organics				
Benzene	70	160	0	280
Toluene	83	1,300	0	5,100
Xylene	79	570	0	139,000
Benz(a)anthracene	82	35	5	660
Benzo(a)pyrene	58	33	3.2	405
PCBs	33	50	0.4	3,150
Naphthalene	100	580	110	790

[a] The development of these statistical summaries is described in a 1983 report by Bider *et al.* (Reference [*1*]).
[b] Ninety percent of the analyzed waste-oil samples had contaminant concentrations below the given value.

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*Self-generators are defined as waste oil generators who use the oil as a dust suppressant in their own property. Some examples are mining and logging companies.

sen to describe the conditions that would result in the worst levels of environmental contamination. In some cases, sensitivity analyses were also conducted.

Evaporation

The worst-case scenario for evaporation assumes a hot, dry environment under which the rate of evaporation of waste oil components is very rapid. The calculated evaporation rate was then used to predict the concentration of each of the major waste oil components in the air above and downwind of the roadway. Calculations were completed based on the 90th percentile levels shown in Table 1. Airborne concentrations depend on the contaminant concentration in the waste oil and the rate of evaporation.

Surface evaporation rates were calculated by using the model developed by Mackay [2] (Equations 1 and 2).

$$q = KP_i/RT_s \qquad (1)$$

The evaporation rate, q (mol/m^2-h) is dependent on P_i, the partial vapor pressure (atm), R, the ideal gas constant (m^3 atm/mol K), and T_s, the soil surface temperature (K). The mass transfer coefficient, K (m/h), was calculated from:

$$K = 0.0292\, V^{0.78} W^{-0.11} Sc^{-0.67} \qquad (2)$$

The wind velocity, V, is measured at a height of 10 m (m/h), W is the road width (m), and Sc is the Schmidt number (unitless).

The mathematical model used to estimate airborne concentrations resulting from this road oiling scenario is a single-compartment dilution model. The average concentration of each contaminant in the plume is calculated by the following equations:

$$C = \frac{G}{Q}(1 - e^{-nt}) \qquad (3)$$

where C equals the average concentration in the plume (m^3/m^3), G is the generation rate (m^3/min), Q is the air flow rate (m^3/min), n is the number of air changes per minute, and t represents the duration of exposure (min). The generation rate is determined from:

$$G = qA \qquad (4)$$

where q is the evaporation rate (m^3/m^2-min), calculated from Equation 1 and expressed as minutes, and A is the unit area of evaporation (m^2), which is equal to 5.5 m^2 for the typical oiled road. The flow rate (Q) is determined from:

$$Q = WP \qquad (5)$$

where W is the wind speed (m/min) and P is the average cross-sectional area of the plume (m^2), which is equal to one-half the unit height of the plume (m^2). The number of air changes per minute, n, is calculated from:

$$n = \frac{Q}{V} \qquad (6)$$

where V is the volume of the plume which is equal to the cross-sectional area of the plume (P) multiplied by the plume length (L).

Figure 1 illustrates the plume configuration, assuming the wind blows perpendicular to the roadway. Plume height (X), and plume length (L) are given in Table 2, which can be used by first determining the plume length from:

$$L = TW/60 \qquad (7)$$

where T is the time for complete evaporation from Table 3 and W is the wind speed (m/min).

The results of the calculations for evaporation rate, generation rate, and the eight hour airborne concentrations of selected waste oil contaminants are shown in Table 3.

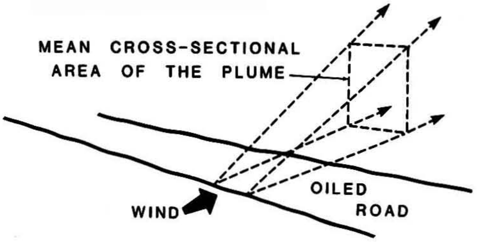

Figure 1. Hypothetical plume from an unpaved oiled road.

Contaminated Dust

Calculations of the maximum 30-day average ambient air concentrations of toxic (threshold) and carcinogenic waste oil contaminants were based on an assumed set of worst-case conditions that include low evaporation and rainfall runoff of waste oil components from the road surface. Conditions typical of the arid Southwest were used in all models.

Initial dust suppression has been observed to be 75 percent effective [3, 4]. For the purposes of this study, dust suppression is assumed to be 75 percent effective on Day 1 and to decrease in a straight line to zero percent control 30 days later. Contaminant concentration is highest immediately after the waste oil is applied. This concentration decreases over time as a result of evaporation and removal by rainfall. Worst-case conditions for contaminant concentrations on dust particles are zero rainfall and low temperatures (during which evaporation is minimal).

Metals Concentrations on Soil Particles

Any metals in the waste oil applied to the road are assumed to remain adsorbed to dust particles. The potential metal concentration on dust emissions is determined primarily by the original concentration of metal in the waste oil applied to the road and the type of road surface. Most metals will adsorb (either reversibly or irreversibly) to the surface of soil particles. Worst-case conditions assume irreversible adsorption; however, in the worst-case situation modeled in this report, zero rainfall is assumed, which eliminates the possibility of desorption of metals into rainfall. The concentration of metal on soil particles, C_s (g/g), is determined by multiplying the original metal concentration, C_i (g/liter), in the waste oil times the waste oil application rate, A (liters/m^2), and then dividing by depth of penetration of oil into the road surface, d (cm), and the average soil density, ρ (2.65 g/cm^3).

$$C_s = \frac{C_i A}{10{,}000\, d\, \rho} \qquad (8)$$

Depth of oil penetration into the road surface depends on the road surface type and the oil application rate and varies from 0.65 to 7.36 centimeters.

Organic Chemical Concentration on Soil Particles

Concentration of organic chemicals on soil particles at any given moment in time depends on the amount of evaporation of the chemical that has occurred. Evaporation is

TABLE 2. DOWNWIND DISTANCES AND RELATED PLUME HEIGHT (meters)

Downwind Distance (L)	Plume Height (X)
0-10	5
10-100	20
100-1,000	90
1,000-10,000	140
10,000-100,000	330

Source: Based on meteorological mixing heights for a D stability class.

TABLE 3. EVAPORATIVE EMISSIONS OF SELECTED WASTE OIL CONTAMINANTS

Waste Oil Contaminant	Evaporation Rate[a] (m^3/m^2 per hour)	Generation Rate (m^3/min)	Estimated Time for Complete Evaporation[b] (min)	Eight-Hour Airborne Concentration $\mu g/m^3$
Aroclor 1248 (PCB)	—	—	5×10^8	—
Benzene	0.0015	1.4×10^{-4}	255	198
Dichlorodifluoromethane	0.0096	8.8×10^{-4}	23	3,598
Tetrachloroethylene	0.0011	1.0×10^{-4}	161	345
Toluene	0.0033	3.0×10^{-4}	96	602
Trichloroethane	0.0092	8.4×10^{-4}	24	3,804
Trichloroethylene	0.0047	4.3×10^{-4}	47	1,231
Trichlorotrifluoroethane	0.0266	2.44×10^{-3}	5	15,450
Xylene	0.0008	7×10^{-5}	343	127

[a] Based on 90th percentile concentrations (Table 1).

[b] Assumes evaporation rate remains constant during the evaporation period.

affected by numerous variables, but it depends most strongly on the temperature of the road surface, the vapor pressure of the organic chemical component, and whether or not the oil is still on the surface of the road or has penetrated into the road subsurface. Evaporation will proceed more rapidly from the road surface than after it penetrates the soil. This analysis assumes rapid soil penetration and moderately low temperature as part of worst-case conditions.

The concentration of organic chemical contaminants on soils was calculated by using subsurface evaporation rates and assumes that all of the waste oil has penetrated the road within 5 minutes after its application to the road surface. Calculations assume that evaporation occurs on the surface during the first 5 minutes. Subsequent evaporation rates are based on subsurface evaporation models by Thibodeaux (Equations 9 through 11) [5, 6].

$$q_s = \left(0.5 \times \frac{D_s C_a C_5 A}{10{,}000\ td}\right)^{1/2} \tag{9}$$

The subsurface evaporation rate, q_s (g/cm^2-s), is calculated from D_s, the soil diffusion rate (m^2/s), C_a, the vapor concentration in soil pore spaces (g/cm^3), C_5, the concentration in oil after 5 minutes of surface evaporation (g/liter), A, the oil application rate (liters/m^2), t, the time since oil application(s) and d, the depth of oil penetration (cm).

Soil diffusion, D_s, is dependent on the air diffusion constant, D_a (cm^2/s), and the soil porosity, n.

$$D_s = D_a n^{3/4} \tag{10}$$

The vapor concentration in soil pore spaces, C_a (g/cm^3) can be calculated from the partial vapor pressure of the oil component i, P_i (in atmospheres) the ideal gas constant, R (cm^3-atm/mol-K), the soil subsurface temperature, T (K), and the molecular weight, M_w, of the oil component.

$$C_a = M_w P_i / RT \tag{11}$$

Once the subsurface evaporation rate for a particular oil component has been calculated, the concentration of components remaining in the soil can be calculated by simply subtracting the amount that has evaporated from the initial concentration. Concentrations of organic chemicals for various road surface types were calculated for a 30-day period following road oil application.

Ambient Dust Concentrations

Ambient concentrations of waste-oil contaminants on dust particles were determined using a modified HIWAY-2 Model [7], based on contaminated soil concentrations and climatic conditions. This model gives 1-hour concentrations of contaminant emissions from a finite length of roadway. These 1-hour HIWAY-2 concentrations were converted (via statistical techniques) [8] to a maximum 30-day average. Results are given in Table 4.

TABLE 4. AMBIENT AIR CONCENTRATIONS DUE TO CONTAMINATED DUST FROM HEAVILY USED ROADS ($\mu g/m^3$)

	Distance from Roadway			
Waste-Oil Contaminant	10 m Low	10 m High	100 m Low	100 m High
Barium	0.0086	0.1209	0.0006	0.0087
Chromium	0.0005	0.0070	<0.0001	0.0005
Lead	0.0185	0.2534	0.0013	0.0183
Zinc	0.0209	0.2866	0.0015	0.0207
Toluene	<0.0001	0.0099	<0.0001	0.0007
Xylene	0.0010	0.0160	<0.0001	0.0011
Naphthalene	0.0003	0.1224	<0.0001	0.0088
Arsenic	0.0003	0.0040	<0.0001	0.0003
Cadmium	<0.0001	0.0010	<0.0001	<0.0001
Benzene	<0.0001	0.0005	<0.0001	<0.0001
PCBs	0.0009	0.0125	<0.0001	0.0009
Trichloroethane	0.0001	0.0958	<0.0001	0.0069
Tetrachloroethylene	0.0023	0.0177	0.0002	0.0013
Trichloroethylene	<0.0001	0.1203	<0.0001	0.0087

Runoff

The calculation of the concentration of waste oil components in road surface runoff, C_r (mg/liter), is a simple one in which the initial oil-component concentration, C_i (mg/liter), is multiplied by the application rate, A (liters/m^2), and then divided by the volume of rain that falls on the road surface (Equation 12), which can be determined by multiplying rainfall intensity, I (in/hr) times rainfall duration, t (min).

$$C_r = 2.36\ C_i A / It \tag{12}$$

Calculations of worst-case stream concentrations are based on the assumption that roads are placed at one-mile intervals and that all of the roads in a watershed are oiled. This means that each one mile of road has an individual watershed of 0.5 square mile or 320 acres (1.3 square kilometers). Runoff from the road surface is diluted by runoff from 0.5 square mile (1.3 square kilometers) of watershed (Figure 2). Field runoff, however, is less than the volume of rain that falls on the field surface because of infiltration. Runoff coefficients for fields are reported to vary from 0.5 to 0.35 [9], which means that only 5 to 35 percent of the rain that falls on a field leaves as runoff. Because the concern was high rainfall intensities that result in high runoff, 35 percent rainfall runoff was used in the modeling. Once runoff volume from the field was known, worst-case stream concentrations were calculated.

A sensitivity analysis was conducted to determine stream concentrations when less than 100 percent of the oil is washed from the road surface (Table 5). A typical-case situation was also evaluated in which 5 percent and 0.5 percent of the oil is washed from the road. The conditions

Figure 2. Rainfall runoff patterns for an oiled road.

closely approximate those observed by GCA in runoff experiments [*10*]. Soluble and adsorbed contaminants are included in the 5 percent runoff, whereas the 0.5 percent value represents only those contaminants that are soluble when they reach the stream.

SIGNIFICANCE OF MODEL RESULTS

Environmental limits have not been set for most of the waste oil contaminants, but all of the contaminants studied are known to be either toxic or carcinogenic. The health risks associated with waste oil contamination of the environment are still being debated. However, it is apparent that deterioration of the environment can occur due to the use of waste oil as a dust suppressant.

ACKNOWLEDGEMENTS

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TABLE 5. SENSITIVITY ANALYSIS OF A STREAM ADJACENT TO AN OILED SAND ROAD BASED ON 90TH PERCENTILE CONTAMINANT LEVELS[a]

	100% Oil Runoff		90% Oil Runoff		75% Oil Runoff		50% Oil Runoff		25% Oil Runoff		5% Oil Runoff		0.5% Oil Runoff	
	High[b]	Low[c]	High[b]	Low[c]	High[b]	Low[c]	High[b]	Low[c]	High[b]	Low[c]	High[b]	Low[c]	High[b]	Low[c]
Metals														
Arsenic	0.36	0.01	0.32	9.00×10^{-3}	0.27	7.50×10^{-3}	0.18	5.00×10^{-3}	9.00×10^{-2}	2.50×10^{-3}	1.80×10^{-2}	5.00×10^{-4}	1.8×10^{-3}	5.00×10^{-5}
Barium	10.95	0.32	9.86	0.29	8.21	0.24	5.48	0.16	2.75	8.0×10^{-2}	0.55	1.60×10^{-2}	5.48×10^{-2}	1.60×10^{-3}
Cadmium	0.09	2.65×10^{-3}	8.1×10^{-2}	2.39×10^{-3}	6.8×10^{-2}	1.99×10^{-3}	4.5×10^{-2}	1.33×10^{-3}	2.3×10^{-2}	6.63×10^{-3}	4.5×10^{-3}	1.33×10^{-4}	4.50×10^{-4}	1.33×10^{-5}
Chromium	0.63	1.85×10^{-2}	5.70×10^{-2}	1.67×10^{-2}	4.7×10^{-2}	1.39×10^{-2}	3.1×10^{-2}	9.25×10^{-3}	1.6×10^{-2}	4.63×10^{-3}	3.20×10^{-3}	9.25×10^{-4}	3.20×10^{-4}	9.25×10^{-5}
Lead	22.6	0.66	20.3	0.59	17.0	0.50	11.3	0.33	5.75	0.17	1.13	3.30×10^{-2}	0.11	3.30×10^{-3}
Zinc	26.0	0.76	23.4	0.68	19.5	0.57	13.0	0.38	6.50	0.19	1.30	3.80×10^{-2}	0.13	3.80×10^{-3}
Chlorinated Organics														
Dichlorodifluoromethane	19.4	0.57	17.5	0.51	14.6	0.43	9.70	0.28	4.85	0.14	0.97	2.85×10^{-2}	9.70×10^{-2}	2.85×10^{-3}
Trichlorotrifluoroethane	2.93	0.09	2.64	8.10×10^{-2}	2.20	6.75×10^{-2}	1.47	4.5×10^{-2}	0.73	2.25×10^{-2}	0.15	4.50×10^{-3}	1.47×10^{-2}	4.50×10^{-4}
Trichloroethane	29.4	0.86	26.5	0.77	22.1	0.65	14.7	0.43	7.35	0.22	1.47	4.30×10^{-2}	0.15	4.30×10^{-3}
Trichloroethylene	23.7	0.69	21.3	0.62	17.8	0.52	11.8	0.35	5.93	0.17	1.18	3.45×10^{-2}	0.12	3.45×10^{-3}
Tetrachloroethylene	27.1	0.79	24.4	0.71	20.3	0.59	13.6	0.40	6.78	0.20	1.36	3.95×10^{-2}	0.14	3.95×10^{-3}
Other Organics														
Benzene	3.61	0.11	3.25	9.90×10^{-2}	2.71	8.25×10^{-2}	1.81	5.5×10^{-2}	0.90	2.75×10^{-2}	0.18	5.50×10^{-3}	1.81×10^{-2}	5.50×10^{-4}
Toluene	27.1	0.79	24.4	0.71	20.3	0.59	13.6	0.40	6.78	0.20	1.36	3.95×10^{-2}	0.14	3.95×10^{-3}
Xylene	12.9	0.38	11.6	0.34	9.68	0.29	6.45	0.19	3.23	9.50×10^{-2}	0.65	1.90×10^{-2}	6.45×10^{-2}	1.90×10^{-3}
Benzo(a)anthracene	0.79	2.31×10^{-2}	0.71	2.08×10^{-2}	0.59	1.73×10^{-2}	0.40	1.16×10^{-2}	0.20	5.78×10^{-3}	4.00×10^{-2}	1.16×10^{-3}	4.00×10^{-3}	1.16×10^{-4}
Benzo(a)pyrene	0.75	0.02	0.68	1.80×10^{-2}	0.56	1.50×10^{-2}	0.38	1.00×10^{-2}	0.19	5.00×10^{-3}	3.80×10^{-2}	1.00×10^{-3}	3.80×10^{-3}	1.00×10^{-4}
Naphthalene	13.1	0.38	11.8	0.34	9.83	0.29	6.55	0.19	3.28	9.5×10^{-2}	0.66	1.90×10^{-2}	6.55×10^{-2}	1.90×10^{-3}
PCBs	1.13	0.03	1.02	2.70×10^{-2}	0.85	2.25×10^{-2}	0.57	1.50×10^{-2}	0.28	7.50×10^{-3}	5.70×10^{-2}	1.50×10^{-3}	5.70×10^{-3}	1.50×10^{-4}

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[a] Assumes roads placed at one-mile intervals and watershed for each mile of oiled road is therefore 0.5 square mile or 320 acres.
[b] Based on a heavily oiled road and a heavy Nevada rainfall.
[c] Based on a lightly oiled road and a heavy Florida rainfall.

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Designing a Synthetic Fuel Plant for Low Sulfur Emissions

The North Alabama Coal-to-Methanol Plant is designed for 99.7 percent sulfur removal. Here's how it's done.

Ira Silverberg, Tennessee Valley Authority, Knoxville, Tenn. 37902

The North Alabama Coal-to-Methanol (NACM) plant is designed to produce approximately 2,000 metric tons per day of Federal Grade AA methanol by indirect coal liquefaction of approximately 3,100 metric tons per day of eastern bituminous coal using Texaco gasifiers. Sour gas and air streams produced in the gasification, water handling, shift, and acid gas removal units are treated in a Claus-SCOT sulfur recovery unit. H_2S emissions from molten sulfur storage tanks are controlled by a caustic scrubber. During normal plant operation there are three gaseous emissions points that contain sulfur compounds: a CO_2 vent gas from acid gas removal, an incinerated tail gas stream from sulfur recovery, and the scrubber vent from the molten sulfur storage tanks. These streams combined contain about 0.3 percent of the sulfur in the coal feed to the gasifiers, resulting in an overall plant sulfur removal efficiency of about 99.7 percent.

PROJECT STATUS

In 1979, the Tennessee Valley Authority (TVA) initiated the design of a commercial-scale coal gasification plant. It was anticipated that the successful completion of this plant would encourage development of a synfuels industry, which could ultimately lead to energy independence for the United States. The subsequent fall in oil prices has slowed development of a synfuels industry, even though the need for energy independence as a matter of national security remains. In 1980, Congress created the United States Synthetic Fuels Corporation (SFC) to aid private industry in the development of synfuels projects. In 1981, TVA began to turn its project over to private industry. This led to the formation of the NACM Consortium which will ultimately own the project. The Consortium is actively seeking financial assistance from the SFC.

The present paper describes the process steps that produce sour gas and air streams, and the sulfur removal and recovery processes that have been proposed for use at the NACM plant.

PLANT DESCRIPTION

The plant will be located in northeast Alabama at Murphy Hill, on the Tennessee River, near Guntersville, Alabama (northeast of Birmingham). The plant is scheduled to begin commercial operation in 1989. Approximately 3,100 metric tons (3,400 short tons per day), as received basis, of eastern bituminous coal will be gasified to produce approximately 2,000 metric tons per day (2,207 short tons per day) of Federal Grade AA methanol. Up to 114 metric tons per day (112 long tons per day) of molten sulfur will be produced as a by-product. A typical coal analysis is shown in Table 1. The design coal sulfur range is 3.25 to 3.94 weight percent total sulfur on a dry basis.

TABLE 1. TYPICAL COAL ANALYSIS, ILLINOIS NO. 6

Ultimate Analysis	Dry Basis, Weight Percent
Carbon	69.93
Hydrogen	4.90
Nitrogen	1.21
Chlorine	0.14
Sulfur	3.58
Ash	11.30
Oxygen	8.94
	100.00

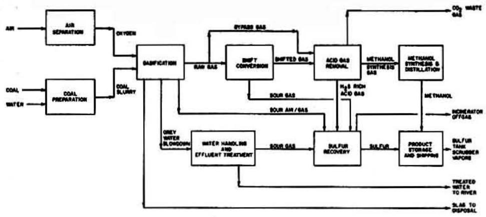

Figure 1. Block flow diagram.

Figure 1 is a block flow diagram which shows the major processing steps. Texaco gasifiers are used to produce a raw gas consisting mostly of CO, H_2, and CO_2. Most sulfur compounds in the coal appear as H_2S and COS in the raw gas. The ratio of H_2S to COS is approximately 17 to 1. The remaining uncombusted sulfur appears in the slag. A typical raw gas analysis is shown in Table 2. The raw gas is processed through a series of steps which include gas cooling and particulate removal, CO shift conversion, acid gas removal, and methanol synthesis and distillation.

CONTROL OF SULFUR EMISSIONS

Gasification Unit (Figure 2)—Raw gas is quenched in the bottom of the gasifier. Slag captured by the quench water falls into a lock-hopper and from there into the slag sump. Trace amounts of H_2S and COS are released by the quench water in the sump. Therefore, the sump is covered and the sour air is routed to the sulfur recovery unit.

Black water containing char (high carbon ash) overflows from the quench chamber and is flashed prior to entering a clarifier. The sour flash gas, which contains sulfur compounds plus ammonia and HCN, is routed to the sulfur recovery unit. The overflow from the clarifier (called greywater), is recycled to the particulate scrubber. A portion of the grey water is purged to the water handling unit in order to control the level of chlorides and dissolved solids in the scrubber recycle water loop.

Water Handling Unit (Figure 3)—In this unit acid gases and ammonia are removed from wastewater streams. The unit receives the grey-water purge from gasification, cold condensate from the shift process, and the aqueous blowdown from an ammonia scrubber located in the shift unit. The three wastewater streams are combined and the dissolved gases are stripped in two stages by the CYAM process, licensed by USS Engineers and Consultants, Inc. (UEC), a subsidiary of U.S. Steel Corporation. Stripped gases from CYAM process are treated in the PHOSAM-W process, also licensed by UEC, to recover ammonia as a liquid anhydrous by-product. The effluent from the CYAM process is sent to the effluent treatment unit for further processing before discharge. The PHOSAM-W process accomplishes the recovery of ammonia from the gaseous discharge of the CYAM process through selective absorption of ammonia with ammonium phosphate solution followed by regeneration of absorption solution by desorption of ammonia. The desorbed ammonia is refined to an anhydrous product. The sour gas stream leaving the PHOSAM-W process, containing mostly H_2S, COS, and CO_2 with small amounts of HCN and NH_3, is sent to the sulfur recovery unit.

TABLE 2. TYPICAL RAW GAS ANALYSIS

Component	Dry Basis, Volume Percent
CO + H_2	80.2
CO_2	17.9
H_2S + COS	1.2
Inerts	0.7
NH_3 + HCN	Trace
	100.0

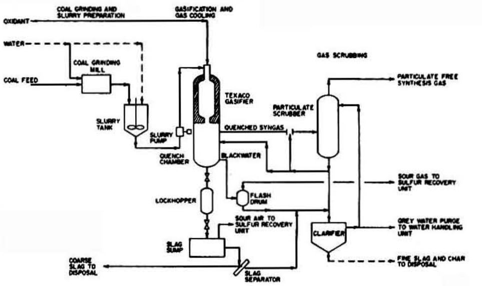

Figure 2. Texaco coal gasification process—direct quench mode.

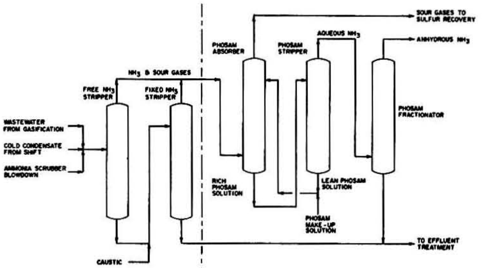

Figure 3. Water handling unit.

Shift Unit (Figure 4)—In the shift unit the hydrogen to carbon monoxide ratio of the particulate free raw gas is adjusted to the correct ratio for methanol synthesis by the reaction of carbon monoxide with steam to form carbon dioxide and hydrogen. The reaction takes place over sulfur tolerant catalyst. The shift catalyst also catalyzes the hydrolysis of COS in the raw gas to H_2S. To achieve the correct hydrogen to carbon monoxide ratio part of the raw gas is passed through the shift reactor and part of the raw gas is bypassed. Both the stream leaving the shift reactor and the bypass stream are cooled in a series of heat exchangers. The condensate recovered from these gas streams is flashed. The sour flash gas is sent to the sulfur recovery unit. The bypass gas stream passes through a water scrubber to remove the last traces of ammonia from the gas. The blowdown from this scrubber is routed to the water handling unit. Both the shifted and bypass gas streams are routed to the acid gas removal unit.

Acid Gas Removal Unit (Figure 5)—The Rectisol process, physical absorption with cold methanol, has been selected for acid gas removal. This process is licensed jointly by Linde and Lurgi, AG. There is considerable commercial experience with Rectisol acid gas removal at coal gasification plants, including a recently commissioned

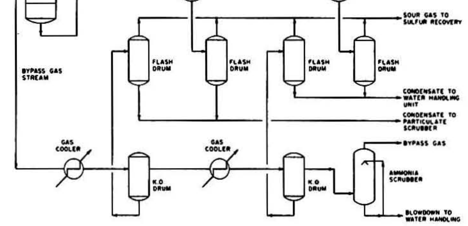

Figure 4. Shift unit.

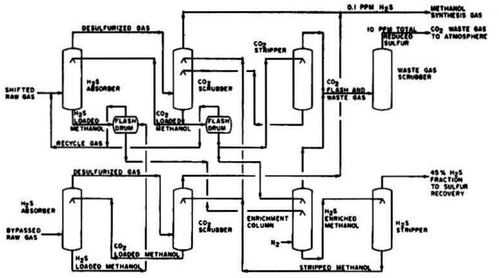

Figure 5. Acid gas removal unit—Rectisol process.

unit at Tennessee Eastman's coal gasification plant in Kingsport, Tennessee [1]. Two important features that led to the selection of the Rectisol process are its ability to remove both H_2S and COS down to very low levels in the methanol synthesis gas and its ability to selectively remove sulfur compounds over CO_2 in order to produce a suitable Claus feed. The Rectisol unit at the NACM plant is designed to produce a methanol synthesis gas with 0.1 ppmv total reduced sulfur. This level allows direct feed to the methanol synthesis reactor without further treatment. The Rectisol unit also produces an H_2S rich acid gas feed to the Claus unit with 45 percent minimum H_2S content and a CO_2 waste gas stream with 10 ppmv maximum total reduced sulfur. This CO_2 waste gas stream will be vented to the atmosphere.

In the Rectisol unit the shifted and bypass gas streams are first contacted with CO_2 loaded methanol in separate H_2S absorbers. The desulfurized gas continues on to separate CO_2 absorbers and from there to methanol synthesis. The H_2S and CO_2 loaded methanol from the H_2S absorbers is flashed to recover H_2 and CO. The flash gas is recycled to the shifted gas H_2S absorber. The methanol is sent to an enrichment column. In the bottom half of the enrichment column, nitrogen is used to strip CO_2 from the loaded methanol. In the process some H_2S and COS is also stripped. In the top half of the column fresh CO_2 loaded methanol is introduced to reabsorb the H_2S and COS. In this way the enrichment column produces an H_2S and CO_2 ratio in the loaded methanol leaving the bottom of the enrichment column, which corresponds to a 45 percent H_2S concentration in the Claus unit feed. In addition a CO_2 waste gas leaves the top of the enrichment column, combines with another CO_2 waste stream from the CO_2 stripper, and is released to the atmosphere. The methanol leaving the bottom of the enrichment column is fed to an H_2S stripper which produces the H_2S rich acid gas feed to the Claus unit and a regenerated methanol stream which is circulated back to the CO_2 absorbers.

Sulfur Recovery Unit (Figure 6)—The sulfur recovery unit uses the Claus and SCOT processes. The Claus unit consists of a thermal reactor and three catalytic reactors in series, with sulfur condensers and reheaters between each reactor. The Claus thermal reactor is divided into two zones. The three sour gas streams (from gasification, water handling, and shift) which contain traces of ammonia and HCN are fed into the first zone along with a portion of the H_2S rich acid gas. In the first zone, ammonia and HCN are destroyed at high temperature. Destruction of ammonia and HCN is necessary to prevent pluggage, corrosion, and catalyst deactivation problems [2, 3, 4]. The remainder of the H_2S rich acid gas is fed into the second lower temperature zone. The sour air stream from gasification is used to provide part of the air requirement for the thermal reactor. Overall, in the thermal reactor, one-third of the H_2S is converted to SO_2. The H_2S and SO_2 then react to form sulfur vapor and water in both the thermal and catalytic reactors. About 95 percent of the sulfur in the feed is removed by one pass through the Claus unit.

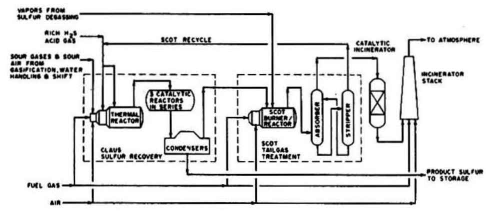

Figure 6. Sulfur recovery.

The molten sulfur produced in the Claus condensers flows into a sulfur sump. The molten sulfur contains the equivalent of about 250 ppmw H_2S, as H_2S and hydrogen polysulfide [5, 6]. In the sump the sulfur will be degassed to 10 ppmw. Three technologies currently under consideration for this project are the Exxon, Shell, and Societe Nationale Elf Aquitaine (SNEA) sulfur degasification processes. These processes use catalyst or agitation to degas the molten sulfur. The H_2S that evolves during degassing is fed to the SCOT unit. The major feed stream to the SCOT unit is Claus tail gas. SO_2, COS, and sulfur vapor in the SCOT feed streams are catalytically converted to H_2S in the SCOT reactor. Following the SCOT reactor the gas passes through a waste heat boiler, a quench tower, and an absorber. Methyldiethanol amine (MDEA) is circulated in the absorber to remove H_2S. The SCOT tail gas is catalytically incinerated, producing a tail gas with about 400 ppmv SO_2 on a dry oxygen-free basis. The gas exits from a 65 meter stack. This is the deminimus, or minimum, stack height that requires no special justification under present EPA rules of good engineering practice. The overall sulfur removal of the Claus and SCOT units is projected to be 99.75 percent, which should represent Best Available Control Technology (BACT) for these units. This will be confirmed during detailed design. The sulfur removal efficiency is limited mainly by the COS content of the gas entering the SCOT absorber, which in turn is dependent upon the equilibrium of CO_2, H_2S, COS, and water in the SCOT reactor.

Product Storage and Shipping Unit—Molten sulfur from the sulfur sump is pumped to 60-day capacity storage tanks to await shipment from the plant by barge. After degassing in the sulfur sump the molten sulfur still contains 10 ppmw H_2S. Modeling was performed to determine the potential for odors outside the plant battery limits. With the close proximity of the sulfur storage tanks to the Tennessee River, the modeling showed a potential odor

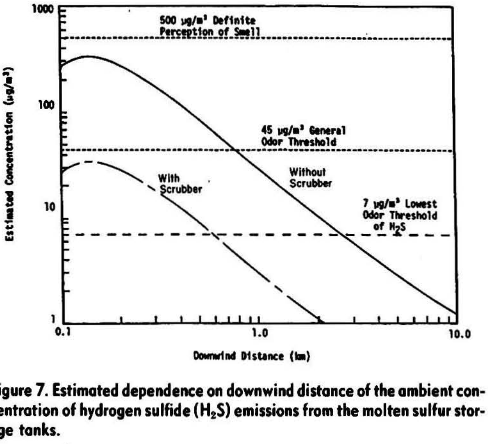

Figure 7. Estimated dependence on downwind distance of the ambient concentration of hydrogen sulfide (H_2S) emissions from the molten sulfur storage tanks.

TABLE 3. OVERALL SULFUR BALANCE*

	Stream Name	Quantity	Percent of Total	Percent of Total Emissions
		(Metric Tons/Day)		
Sulfur In	Sulfur to acid gas removal	109.0	95.6	—
	Sulfur in sour gas and sour air streams	5.0	4.4	
	Total	114.0	100.0	
Sulfur Out	Molten sulfur	113.69	99.727	—
	Incinerated sulfur recovery unit tail gas	0.28	0.246	90.1
	CO_2 waste gas	0.03	0.026	9.5
	Sulfur tank scrubber vent	0.001	0.001	0.4
	Total	114.001	100.000	100.0

*Based on highest sulfur coal.

problem within 0.7 km of the tanks if all of H_2S contained in the sulfur were to evolve (see Figure 7) [7]. To control this potential odor problem a caustic scrubber is used to remove H_2S from gas leaving the tank vents. The scrubber efficiency is about 90 percent. This results in an estimated ambient H_2S concentration below the general odor threshold.

An overall sulfur balance for the plant is shown in Table 3. This table shows that a significant fraction of the plant sulfur input (4.4 percent) is recovered by treating the sour gas and air streams produced in the gasification, water handling, and shift units. The table also shows that the major sulfur emission point is the sulfur recovery unit tail gas (90.1 percent of total emissions). The CO_2 waste gas stream contributes an additional 9.5 percent and the sulfur tank scrubber vent contributes the remaining 0.4 percent.

CONCLUSIONS

The NACM plant is designed for high sulfur removal efficiency. This will be achieved by designing the acid gas removal unit to supply a concentrated H_2S rich feed to the sulfur recovery unit, while producing a low sulfur CO_2 waste gas; by routing the various sour gas streams in the plant to the sulfur recovery unit for treatment; and by control of sulfur storage tank emissions.

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Ira Silverberg is a senior chemical engineer with 13 years experience in coal gasification, utility flue gas desulfurization systems and air pollution control engineering. Before joining TVA he worked for the New York City Department of Air Resources. He holds a Bachelor of Engineering degree from the City College of New York.

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It shall (a) further the application of chemical engineering in the environmental field; (b) provide, in cooperation with the national Program Commitee, suitable programs on environmental topics of current interest; (c) provide a communication medium for chemical engineers and other individuals to exchange nonconfidential information concerning all facets of environmental activity; (d) promote publication of papers of interest to chemical engineers in environmental activities; (e) coordinate the Institute's activities with other societies active in the environmental field; (f) act as a source of information for chemical engineers who are not actively engaged in the environmental field to bring to their attention the importance of concern for the environment, the need for its consideration in the design and operation of process plants, and opportunities in research and design of equipment and processes to solve environmental problems; (g) encourage chemical engineering educators to place suitable emphasis on protecting our environment and encourage excellence in courses in environmental engineering.

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1. Combined SO_2/NO_x Flue Gas Cleanup. I
2. Combined SO_2/NO_x Flue Gas Cleanup. II
3. Hazardous Waste Site Cleanup/Hindsite Analysis
4. Refinery Processing as Related to the Greenhouse Effect and Acid Rain*
5. Impact of Ash on Coal Utilization*
6. Dealing with Sulfur by the Gulf Coast Petrochemical Industry*
7. Safe Handling of Hazardous Particulates (Safety and Health Division)
8. Air Permitting: The Process and Its Problems.*

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* Programmed jointly with the Fuels and Petrochemical Division.

Conferences

The International Association on Water Pollution Research and Control announces four specialized conferences and workshops that are to be held during 1985:

Instrumentation and Control of Water and Wastewater Treatment and Transport Systems. Houston and Denver, USA; 27 April-4 May 1985; *Contact:* Prof. J. F. Andrews, Department of Civil Engineering, Rice University, Houston, Texas 77251.

Environmental Risk Assessment of Chemicals—Fate and Effects of Chemicals in The Environment. Tokyo, Japan; 28-30 May 1985; *Contact:* Prof. S. Matsui, Faculty of Engineering, Kanazawa University, 2-40-20 Kodatsuno, Kanazawa 920, Japan.

Acid Precipitation: Water Quality Control and Human Health. Uppsala, Sweden; 14-15 August 1985; *Contact:* Dr. B. Hultman, VAV, Regeringsgatan 86, S-111 39, Stockholm, Sweden.

Modeling of Biological Wastewater Treatment. Copenhagen, Denmark; 28-30 August 1985; *Contact:* Prof. M. Henze, Department of Environmental Engineering, Building 115C, Technical University of Denmark, DK-2800, Lyngby, Denmark.

Hazardous Materials Control Research Institute (HMCRI) announces the National Conference & Exhibition on Hazardous Waste and Environmental Emergencies (HWEE), May 13-15, 1985 in Cincinnati, Ohio. Sponsoring groups include: HMCRI, U.S. E.P.A., Federal Emergency Management Agency, Department of Defense, University of Toledo, Association of State and Territorial Solid Waste Management Officials, National Association of Local Governments on Hazardous Waste, Centers for Disease Control, Portland Cement Association, and the National Environmental Health Association.

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The ASME/EPRI/APCA Third Symposium on "Integrated Environmental Controls for Fossil Fuel Power Plants" will be held September 17-19, 1985 at the Pittsburgh Hilton Hotel, Pittsburgh, PA. Abstracts and papers are invited for the following session topics:

- Control Technologies for New Pulverized Coal-Fired Power Plants
- Alternate Coal-Fired Power Plants
- Planning and Siting for New and Expanded Fossil Fuel Power Plants
- Retrofit and Life Extension Control Technologies and Costs for Existing Fossil Fuel Power Plants
- Operation and Maintenance of Retrofit Controls
- Resource Sharing

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AIChE Publications—1985

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