ENVIRONMENTAL PROGRESS

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Flue gas desulfurization system supplied by Peabody Process Systems to Seminole Electric Co-op included five absorbers 30 ft. in diameter and 80 ft. high.

How the Super-Camel Got His Hump

by Stacy L. Daniels

The Camel's hump is an ugly lump
Which well you may see at the Zoo,
But uglier yet is the hump we get
From having too little to do.

—Rudyard Kipling, How the Camel Got
His Hump, (Just So Stories, 1902)

In his *Just So Stories*, Kipling told how the camel got his hump by being "most 'scruciating idle," and when spoken to, saying, "Humph," just "Humph," and no more. By having too little to do, and by not helping the other animals in their work for Man, the camel made more work. Just so, by mismanaging some hazardous wastes, a few unscrupulous or unknowing individuals have made more work for others who bear the brunt of public criticisms, regulatory actions, and cleanup costs.

We are hearing too many "Humphs" about these occasional failures, and not enough "Hurrahs" about the many successes. Hazardous waste management is a general societal concern and not the sole province of any particular industry. The chemical industry, however, must continue in its leadership role and recognize its responsibility to tell the truth often enough and loud enough to encourage proper management of hazardous wastes by all involved.

Regulation of hazardous *wastes* and hazardous *materials* has created a veritable menagerie. First there was the "Elephant" of the Resource Conservation and Recovery Act. (RCRA) [1]. Now there's the "SuperCamel" of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), i.e. "Superfund." Reauthorization of both will have major impacts upon future costs and waste management practices.

On first sight, camels appear to be supercilious creations with smug, disdainful expressions. They are often unfairly characterized as bad tempered, irritable, and obstinate. Seemingly placid, they are keen enough to resent ill-treatment, and if loaded too heavily, they grumble and

often lie down and refuse to budge. These minor quirks, however, are overridden by the immense usefulness of the camel to man over thousands of years. Similarly, there are a number of false impressions of the nature of the SuperCamel. The chemical industry is unfairly perceived by some to have mismanaged hazardous wastes. Its significant contributions to food production, medicine, housing, waste treatment, and improved living standards are forgotten.

The SuperCamel has got his humps! It's not from having too little to do, but rather from doing too little to inform the public that in the chemical industry.

(i) most hazardous wastes have been properly managed on the sites of their original generation, and

(ii) most on-site facilities are still active and still under the direct and responsible control of the original generators.

The chemical industry, in fact, has pioneered much of the analytical and toxicological methodology for detecting trace chemicals in the environment and for determining their hazards. It has also played a major role in developing waste control technologies, such as incineration.

WHAT'S HAZARDOUS?

There are several misleading and even fantastic beliefs about the mating habits of camels. It has been said, for example, that wild camels require human assistance to breed! There is nothing unusual about the mating of the camel. Just so, there have been unreliable and uninformed assessments of the wastes of the SuperCamel.

There is nothing unusual about chemical waste management. Sufficient technology already exists for control of hazardous wastes. Government, industry, and the public must work together, however, toward development of reasonable guidelines and regulations, and establishment of equitable means for funding proper hazardous waste management.

When does an Elephant turn into a SuperCamel? It is hard for a chemical engineer to explain to a layperson just when a *raw material* becomes a *process intermediate* becomes a *final product* becomes a *waste* [2]. It is harder to differentiate between *recovery* of energy and material values from *undiscarded* materials, and *treatment and disposal* of wastes from *discarded* materials. Nevertheless, these are important differences that the chemical engineer must explain if the issues are to be discussed rationally.

Where does RCRA stop and CERCLA begin? It all depends on what's a waste and what's not, and who's doing what, with which. The Elephant and the SuperCamel both need prodigious memories to track everything from cradle to grave. As originally conceived, RCRA was to deal with *existing and new facilities* for management of *hazardous wastes* of known and responsible ownership; CERCLA was to deal with *abandoned sites* having no responsible owners and posing imminent hazards requiring remedial actions. Unfortunately, the well-intentioned differences between waste and *non*waste, hazard and *non*hazard, and science and *non*science have been blurred in the layperson's eye.

Does the SuperCamel have one hump, or two, or more? Interpretations of survey data [3] must be done with caution. One must distinguish *numbers* of waste generators from *numbers* of management facilities from *quantities* of waste; *onsite* from *offsite* facilities; *storage* from *treatment* from *disposal* facilities; *concentrated dry* wastes from *dilute wet* wastes; *hazardous* from *nonhazardous* wastes; or *wastes* from *mixtures* from *residues*.

Just so:

* 264 million metric tons (wet wt) or 71 billion gallons of hazardous wastes produced by 14,098 generators.
* 95% produced by 5% generators.
* 96% managed onsite; 4% managed offsite.
* 97% dilute wastewaters with <0.1% hazardous constituents.
* 68% wastes and 25% facilities in chemical industry.
* 67% treated; 51% stored; 20% disposed; and/or 4% recycled. (*)
* 6% disposed waste is landfilled.
* 1% treated waste is incinerated.

Chemical engineers should not be surprised by these facts. The public, the government, and the media are often astounded. No wonder it is commonplace to assume incorrectly that "most wastes are solids that are landfilled offsite." The problems lie more in the *uncertainties* of definitions of the *real* hazards [4], and in the *perceptions of potential* hazards [5]. Just as Elephants come in shades of grey, just so do SuperCamels come in shades of brown. Risk assessment considers: how much, where and when, does what, to whom? Risk management considers: what extent demands what response?

(*) More than one management technique can be applied, hence >100%.

HOW CLEAN IS CLEAN?

The camel can endure extreme privation in widely varying climates—ideal qualities in a beast of burden. It is well adapted for life in regions ranging from broiling deserts to freezing mountains. Just so, the SuperCamel must also have stamina to traipse the shifting sands of public opinion. Just as the camel husbands his water, it is prudent for the SuperCamel to practice resource conservation. Energy and material values can be recovered at the source. Liquid wastes can be restricted from landfills if they are amenable to wastewater treatment or high-temperature incineration. Where possible, it is preferable to reduce waste volumes and to destroy hazardous constituents, and not subject them to perpetual care in landfills.

WHO PAYS FOR WHAT?

To the camel driver, the camel is an absolute necessity, providing transportation, milk, meat, clothing, and companionship. The camel stoically carries its burden across trackless wastes for long hours without complaint. Just so, the SuperCamel provides sustenance to many—the environmentalist, with emerging issues to consider; the regulator, with regulations to promulgate; the contractor, with sites to clean up; the journalist, with stories to tell; and the chemical engineer, with problems to solve. It is imperative, however, that issues be well-founded; regulations well-conceived; remedial actions well-planned; technologies well-developed; and monies well-spent at a reasoned pace.

Should the camel be valued on the food it eats, the load it carries, the sustenance it provides, or the droppings it leaves behind? The same value judgements can be applied to "head-end" vs. "tail-end" taxes imposed on our SuperCamel. Unlike the camel, quantities of raw materials consumed, process intermediates handled, products made, and wastes generated are not directly related. Nevertheless, the "head" and not the "tail" wags our SuperCamel! Taxes are applied entirely on the quantities of chemical feedstocks consumed. This is highly inequitable for two reasons.

First, about 70% of $1.6 billion is collected from only 12 companies, which do not dispose of wastes in proportion to materials used! Second, a major disincentive is created which strongly precludes practicing the most environmentally preferable alternatives! No credits are given for recycling to minimize wastes *before* they are generated, or for treatment to reduce wastes *after* they are generated. Practioners of energy/material recovery or waste treatment are penalized even as they minimize wastes requiring ultimate disposal on land. Are the intended "resource conservation and recovery" aspects of RCRA and the "comprehensive environmental response and compensation" aspects of CERLA to be mere hollow concepts?

A much more equitable basis for the Superfund would be a "waste-end" tax directly applied to dry-weight quantities of wastes *disposed* of "on and in the land," and not on materials *used*. Twenty states have variations of a "waste-end" tax with generally favorable results. A federal "waste-end" tax indeed could be simply administered. The chemical industry supports reauthorization of the Superfund assuming a more equitable funding mechanism is incorporated.

EPILOGUE

In 1855, Congress appropriated $30,000 in an unsuccessful attempt to introduce camels into the American Southwest. Most, eventually, were turned loose where they menaced crops and stampeded horses. Laws were passed prohibiting camels at large. Wild camels were shot on sight. So ended the greatest attempt at acclimating foreign animals ever made in the United States. Just so, $1,800,000,000 is being applied to continue the greatest attempt to corral hazardous wastes. Hopefully, the SuperCamel will not become extinct and proper hazardous waste management will continue.

Has the last straw been placed on the SuperCamel; has the last knot been tied in its tail? It behooves the SuperCamel and the SuperCamel drivers to work together to solve the real problems facing the chemical industry. We must act, as individual citizens, as chemical engineers, as spokespersons of the chemical industry, and as members of the American Institute of Chemical Engineers (AIChE) [6]. We can not sit still! We cannot frowst around a fire with a good book. We must insure that hazardous wastes continue to be properly managed. We must not be afraid to "dig" until we perspire from our efforts.

The cure for this ill is not to sit still,
Or frowst with a book by the fire,
But to take a large hoe and a shovel also,
And dig til you gently perspire.

—Rudyard Kipling, *How the Camel Got His Hump*

Just so!

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Environmental Shorts. . .

Method to Detect Leaks in Lined Impoundments Developed

Southwest Research Institute geophysicists have developed a new way to locate leaks in lined liquid waste surface impoundments which could help reduce or prevent the contamination of water resources by hazardous materials.

Because toxic waste materials are commonly stored as liquids in man-made ponds that depend on low permeability underliners of plastic designed to minimize seepage into adjacent soil, the liners can be damaged by the waste handling and emplacement process. Moreover, defects can occur in the liner material itself, with resultant leakage going unnoticed until ground water tests reveal its presence.

The Southwest Research Institute developed-method depends on a geophysical technique known as earth resistivity. This involved injecting an electric current across or through material being tested and measuring the resultant potential distribution to detect anomalies or sources of resistance.

With this new method, a survey system using electrical resistance measurements is established in the impoundment area, and leaks are located in the liner by the systematic measurement and mapping of surface potentials, caused by electrical current flow through penetrations in the liner.

Project leader David W. Shultz of the Institute's Geoscience's Dept. reports that irregularities in the surface equipotential contours reveal areas of high current density within lined impoundment, and hence, designate the concentrated current paths associated with leaks in the liner.

In tests at a 1.5 million gal, 50,000 sq ft lined impoundment built on the Institute grounds to support the research, Shultz and his coworkers have shown that their system will detect a one in. hole in the liner and can pinpoint it within one ft of the actual location.

"New or existing storage facility liner systems can be surveyed without damaging the liner and remedial repairs made possible to halt contamination of surrounding water resources," Shultz said.

During operation of the survey system, a voltage applied between a current source electrode within the lined impoundment and a remote current return electrode, causes an electrical current to flow through any penetrations in the liner. The resulting potential distribution on the surface of the water is affected by the current flow through the leak and can be used to locate the leak. These surface potentials are measuring using two electrodes, one floating and one stationary. The floating electrode is moved across the surface of the water in a designated scanning grid pattern. Measurements are recorded and processed by computer.

Research for the program was funded by the EPA.

Microwave Unit Developed To Remove Coal's Pollutants

Because "cooking" coal with microwaves may be a way of freeing nearly all of the sulfur and other potential pollutants locked in coal's complex chemical structure, the U.S. Dept. of Energy has selected TRW, Inc. to design and construct a continuous feed microwave processing unit.

The TRW researchers will base their design on the ability of microwave radiation to heat specific points in coal where impurities reside. Tuned to the proper frequency, microwaves will pass relatively undisturbed through most of the coal, but on striking sulfur and other mineral matter, the radiation is stopped and its energy converted to heat.

Within one-to-two minutes, very high temperatures are created at points deep within coal's molecular structure, causing the impurities to break their chemical bonds and form water soluble substances that can be washed out of the coal. The coal, itself, remains relatively unaffected.

Working out of their Redondo Beach, Calif., facilities, the TRW researchers will employ this concept in a microwave unit capable of processing 20 lbs/h coal in a continuous manner. Previously, tests had been limited to a unit processing separate, one lb quantities of coal.

If the continuous feed unit proves successful, the next step would be to link the complete sequence of process steps—mixing with sodium hydroxide, drying, microwave, irradiation, water wash, acid wash, and chemical regeneration. The goal is to develop a process that can produce coals that meet or exceed federal environmental standards for sulfur dioxide emissions with no additional clean-up as well as removing more than 95 per cent of the ash in coal.

This project will be managed by the DOE's Pittsburgh Energy Technology Center.

Laser Herbicides Kill Undesirable Plants

Scientists from the Univ. of Illinois have discovered a potential class of environmentally safe plant killing substances, called "laser" herbicides, whose destructive force is unleashed by sunlight.

Tests of the laser herbicides, which are made of readily available chemicals, show that the herbicides destroy many weeds troublesome to farmers while leaving crops such as corn, wheat, barley, and oats unharmed. According to scientists working on the project, which was funded by the National Science Foundation's Metabolic Biology Program and the Univ. of Illinois' Agricultural Research Station, these herbicides work by causing a plant to stockpile light-sensitive chemicals whose chain reaction of destruction and death is triggered by the rising sun.

"The plants literally commit suicide," Dr. Constantin A. Rebeiz, a plant physiologist and leader of the research group, reported. "This is a breakthrough in herbicide design, both conceptually and from an environmental impact standpoint.

"Our research has been aimed at the design of herbicides that would kill undesirable plants via a predetermined and novel mode of action, based on sound biochemical principles."

The prime ingredient of the laser herbicides tested by the Illinois researchers is delta-aminolevulnic acid, or ALA. An amino acid found in all plant and animal cells, ALA is a natural building block in the chemical construction of chlorophyll.

Specifically, ALA is used by plants to make tetrapyrroles, a group of extremely light-sensitive chemicals that form chlorophyll in the presence of sunlight. Amounts and kinds of tetrapyrroles formed and accumulated depend on the species of the plant. The differences among plants in their capacity to destroy or convert the excess tetrapyrroles into harmless substances determines which plants would be affected.

The ALA-based laser herbicide is sprayed just before nightfall and absorbed by the plants. Spurred on in the darkness by a chemical activator in the herbicide, new tetrapyrroles are formed quickly from the added ALA. Since no light is present at night, the tetrapyrroles are not processed into chlorophyll, and they build up into a vast reservoir of light-sensitive chemicals.

Rebeiz likens the situation to a keg of explosive black powder being filled a little at a time, when sunlight can be thought of as a match.

"If you let these biochemical precursors accumulate slowly and 'burn' them a little at a time as they accumulate, as in daylight, then you won't have a problem—only a steady fizzle. But if you allow them to build up in large amounts and ignite them all at once with sunlight, then the whole thing is going to 'explode.'"

What happens in the first few hours after the sun rises is nothing short of an escalating chain reaction of destruction, Rebeiz reports. When sunlight hits the light-sensitive stockpile of tetrapyrroles, a rapid chemical reaction is set in motion that leads to the formation of free radicals. The free radicals destroy the tissue structure in the plant's cells by creating more and more free radicals and more damage until cell membranes leak. Dehydration and death follow.

Ethyl Vice Chairman Charges EPA Misrepresents Data

Lawrence E. Blanchard, Jr., the vice chairman of Ethyl Corp. told an Environmental Protection Agency hearing in late August that the agency has "misused and misrepresented" health data on lead antiknocks in gasoline.

In spite of "overwhelming information to the contrary, EPA continues to allege adverse effects of low-level lead exposure on neurobehavior. It is grossly unfair to charge people who can't afford a new car billions of dollars a year because of the illegal actions of certain owners of new cars."

Instead, Blanchard argued, proper enforcement of auto inspection and maintenance programs under the Clean Air Act "could sharply reduce misfueling and tampering at little or no extra cost." He also said that the EPA should "stop surveying and fiddle-faddling with this program and get on with enforcing effective inspection and maintenance programs."

The EPA had estimated that the cost of extending inspection and maintenance programs to cover all vehicles requiring unleaded gasoline would be approximately $650 million per year.

Blanchard claims that is "chicken feed compared to the $3 billion a year that this rule will cost the owners of old cars. This proposal is patently ridiculous. Only the EPA could come up with such a solution.'"

He also charged that "this proposal is just another chapter in a long and sordid novel written by the EPA to try to make lead in gasoline the scapegoat for other environmental programs." He said that they "will continue to succeed until and unless the press begins to examine the material put out by the EPA with the same critical approach they apply to the material put out by other government agencies."

Blanchard warned that by drastically reducing the lead content in gasoline, EPA would create a larger threat to public health in a 55 per cent increase in polynuclear aromatic hydrocarbon emissions. "Some of these emissions are known carcinogens and other are eye irritants and contributors to photochemical smog."

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Three Mile Island Cleanup

Experiences, Waste Disposal, And Environmental Impact

Lester J. King and James H. Opelka, Editors

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

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

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

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

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Design of Steam-Stripping Processes

A new method for scale-up of stripping columns is based on the use of a harmonic-mean vapor-to-liquid rate.

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When volatile components are present in wastewater, stream stripping is sometimes a cost-effective treatment technology. Steam stripping is a multicomponent separation in a distillation column. A feed containing components to be removed flows down a column countercurrent to steam, which removes (strips) the volatiles and carries them out the top. For many specific compounds a data base and computer-program library exist that make column design possible without experiments. However, in wastewater treatment it may not always be possible or economical to identify all the compounds present; thus, column operation cannot be simulated. In this case, experiments to gather performance data are required.

As part of a program to develop a design for a steam stripper to remove the volatile gases ammonia, carbon dioxide, and hydrogen sulfide from an industrial wastewater, both laboratory-scale experiments on real wastewater and computer simulations of full-scale stripper performance were used. The laboratory experiments were designed to demonstrate the usefulness of stripping and to find the approximate number of equilibrium stages and steam rates required for effective treatment. The computer simulations were designed to guide and supplement the experimental results and to show that such simulations could be used to develop an optimum design in terms of capital and energy costs.

Stripping column performance is often reported in terms of the number of trays, plates, or equilibrium stages in the column and the steam rate used [1, 2]. Steam rates are expressed in terms of vapor flows in a particular part of the column relative to the feed rate, often in units of lb/gal or, alternatively, in dimensionless units of weight of steam per weight of wastewater feed. The total steam rate refers to the amount of vapor leaving the reboiler (neglecting the presence of other components), and the stripping steam rate refers to the vapor leaving the feed tray (again neglecting the presence of other components).

When the laboratory results were compared to simulations in terms of equilibrium stages and total or stripping steam rates, they did not match well. For examples, a laboratory column with 10 equilibrium stages and a 0.5 lb/gal (0.06 kg/kg) stripping steam rate showed practically 100% ammonia removal, whereas a simulation showed only 50% removal. Even though great care was used in designing the laboratory apparatus to minimize heat losses, we found that high heat losses, condensation, and unexpected additional equilibrium stages were present and that they all were important. Dealing with these factors forced us to abandon stripping steam rates or total steam rates as appropriate parameters for comparing column performance. When experimental data were reanalyzed to include both the unexpected heat losses and the extra equilibrium stages and, even more important, when the experimental and simulated results were compared on the basis of a harmonic mean vapor rate, their performances matched. The

harmonic mean steam rate and the number of equilibrium stages determined from laboratory-scale experiments can thus be used to design full-scale equipment.

Experimental Apparatus

The laboratory apparatus used is illustrated in Figure 1. It contained an electrically heated reboiler, with a hydraulic level control to regulate bottoms withdrawal. The reboiler was filled with glass beads to minimize hold up. The bottoms were cooled before collection and could easily be kept under an inert atmosphere before analysis when sulfides or other readily oxidized species were present. The stripping column itself was designed so that the number of equilibrium stages in it could be easily identified and controlled. It consisted of several vacuum-jacketed Oldershaw column sections that fit together so that the number of equilibrium stages could be easily varied. The Oldershaw column sections contained sieve trays 1 inch in diameter. For hydrocarbon solvents the col-
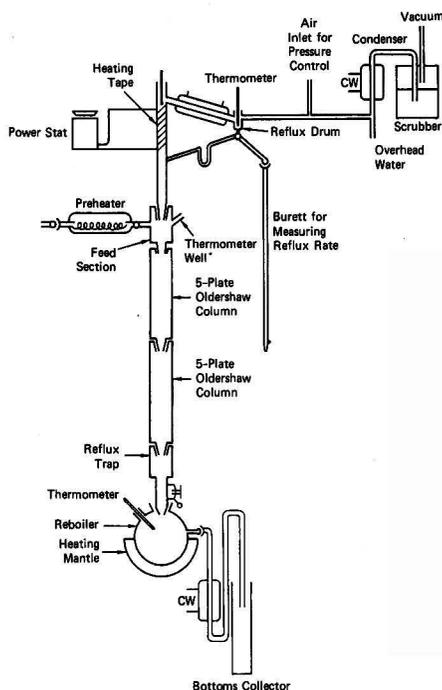
Figure 1. Schematic of experimental stripping apparatus.

umns appear to have a tray efficiency of 60% [3] over a broad range of flow rates, but our experience suggests an 80% efficiency should be assumed for wastewaters.

The feed was introduced by a peristaltic pump through a preheat exchanger that was heated by a recirculating oil bath. This allowed good regulation of the feed flow rate and temperature. The condenser section was rather novel, in that it was designed to avoid any counter-current flows of liquid and vapor. Heating tape prevented any condensation in the vapor riser until enough height had been gained to reach a down-flow condenser that was cooled by a recirculating oil bath. This arrangement assured that only one equilibium stage was present in the reflux condenser, but did not affect the liquid and vapor flows in the column or the energy balance. The reflux could be collected or returned to the column through a small vapor trap (which was heated to minimize any unmeasurable impacts on the column energy balance). Uncondensed vapors were collected and cooled so that the overhead water rate could be quantified for determining the mass balance. Noncondensibles were collected in a scrubber so that they could be included in the mass balance if required.

Between the reboiler and the Oldershaw column sections was a specialized piece of glassware called a "reflux trap." It contained a vacuum-jacketed reservoir that could intercept all liquid flowing down the column when a diversion valve was turned. The reservoir had a calibrated volume so that the liquid flow rate at the column bottom could be determined by diverting the flow and measuring the time required to fill the reservoir. This diversion did not affect liquid and vapor flows in the column sections, but did cause the liquid level in the reboiler to fall as liquid was retained in the reservoir. The diversion valve and a 6-inch glass stem connecting the trap to the reboiler were not vacuum-jacketed and were responsible for the unexpected portion of the high heat losses in the laboratory system. The cooling and counter-current liquid and vapor flows in the reflux trap apparently introduced two extra equilibrium stages into the apparatus.

The major liquid and vapor flows in the column are identified in Figure 2. V_T, the overhead water, and L_T, the reflux, could be measured at the column top. L_2 (so named because, in the standard notation that starts numbering stages up from the reboiler as number 1, it would be the liquid leaving the second equilibrium stage) could be measured at the column bottom using the reflux trap (not shown) between the column bottom and the reboiler. L_B could be measured by timing the collecting of bottoms. Once the total heat losses (which are the sum of the individual q_1 shown on Figure 2) had been determined, all other important flows could be determined by mass and energy balances. How the measurements were made is summarized in Table 1. On the assumption that the individual q_i's in the overall heat loss were the same on each tray, individual liquid and vapor flows between the sieve trays or equilibrium stages could be estimated.

After it was determined that heat losses were important, the heat lost in the uninsulated section of the reflux trap was determined by making a series of measurements of L_2 with and without enclosing the section with fiberglass insulation. The results, illustrated in Figure 3, showed that the losses were equivalent to approximately 0.85 g/min of steam. The heat loss Σq_i was between 0.5 and 0.7 g/min of steam, depending on which column sections were being used. It is important to note that even the vacuum jacketed column sections had heat losses large enough to seriously affect the performance of the stripping column. Because heating rates, Q_B, of from 2 to 4 g/min of steam were used when stripping wastewater fed at 7 to 20 cm³/min, the total heat losses (including both the Oldershaw column losses and the reflux trap losses) varied between 40% and 70%. These losses were far larger than would be found in a full-scale column, where 1% or 2% would be expected.
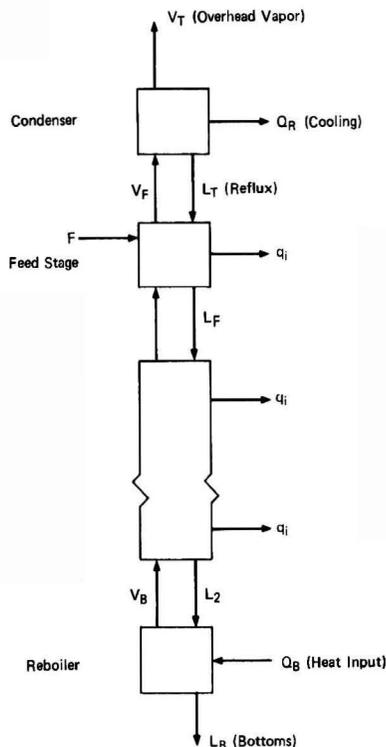
Figure 2. Important mass and energy flows in stripping column.

Review of Stripping Fundamentals

The performance of a simple stripper of N equilibrium stages with no heat losses and no reflux can be approximated by the expression [4]:

$$f_N = \frac{1 - S}{1 - S^{N+1}} \qquad (1)$$

where f_N is the fraction of a component in the feed that remains in the bottoms. S is the stripping factor $K(V/L)$ where V is the (~ constant) vapor rate, L is the (~ constant) liquid rate in the columns, and K is the effective average vapor-liquid partition coefficient for the component being considered. The stripping performance is obviously a strong function of S. For a stripper with N stages and a reflux condenser, the appropriate formulas for column performance are:

TABLE 1. MEASUREMENT OF MATERIAL AND ENERGY FLOWS IN LABORATORY COLUMN

Material and Energy Flow Rates	Measured Quantity	Comments
V_T - Overhead vapor	V_T (feed off)	—
V_b - Total steam	L_2 (feed off)	Measured with condenser at 20°C so that V_T is practically zero.
V_F - Stripping steam	L_T (feed on)	$L_T << F$ so that diversion of L_T to measure flow rate does not change energy balance significantly.
Σq_i - Heat loss	V_B - L_T (feed off)	Heat-loss rate can also be confirmed by energy balance.
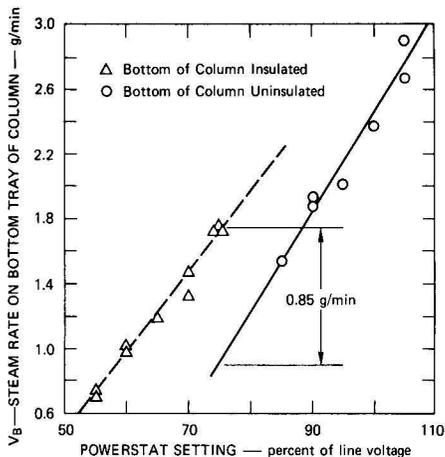
Figure 3. Determination of heat losses in uninsulated reflux trap.

$$f_{N+C} = f_N \left[1 - \frac{(1 - f_N)}{(1 + S_C)} \right]^{-1} \qquad (2)$$

and

$$S_C = K_C (V_F/L_T) \qquad (3)$$

where K_C is the vapor-liquid partition coefficient in the condenser. Even though the reflux condenser affects the performance of the column, f_{N+C} is still a strong function of S or $K(V/L)$.

In a column with a temperature profile and changing liquid and vapor rates caused by heat losses and enthalpy effects, S could be different on each stage and some average must be used to describe column performance. For stripping of volatile components from wastewaters, there are several factors that govern the choice of the most appropriate average.

First, wastewater is mostly water, which means that any contaminants are present at low concentrations and concentration effects on K should be minor. Second, because the contaminants are at low concentrations, the liquid composition would not change much, which means that temperature changes from tray to tray would be small. For both these reasons, K should be relatively constant throughout most of the column. The only exception is the reflux condenser, which would be cooler than the rest of the column and would contain a liquid phase with high concentrations of contaminants. Because the effect of reflux is treated separately [Equation (2)], this exception is not significant.

If noncondensable gases such as ammonia, carbon dioxide, and hydrogen sulfide are present, K would still be almost constant, but the reason is more complicated. Ammonia is a weak base, and carbon dioxide and hydrogen sulfide are weak acids. They are sparingly soluble by themselves; however, if present together, the base and the acid neutralize each other and solubilities can be high. When both base and acid are present, the K factor for each is a stong function of the amount of the other present. The solution pH serves as an intermediate parameter for this effect.

Bomberger [2] showed, for a refinery sour water where ammonia was the base and hydrogen sulfide was the acid, that the K factors of the two behaved as is shown in Figure 4, which was developed for a column at 100°C. At low pH, such as would occur if ammonia were absent or present at low concentration, hydrogen sulfide would be present as H_2S, which is highly volatile and sparingly soluble. K_S, which describes its volatility, is large. Ammonia, if it were present, would be present as NH_4^+ and would not be vola-

tile at all. At high pH, such as would occur if hydrogen sulfide were absent or present at low concentrations, ammonia would be present as NH_3, which is more volatile than water. Its K factor, identified as K_N, is approximately 10. Sulfide would not be volatile.

The result of the pH behavior of K_S and K_N can be illustrated by considering first a stripper feed rich in sulfide and then one rich in ammonia. A feed containing a molar excess of sulfide would start out acidic. Under this condition of $K_S > K_N$, the feed would lose a higher percentage of its sulfide than its ammonia on each stripping stage. As the feed progressed down the stripping column, it would become more basic until it approached a pH of about 9, where $K_S = K_N$, and it would then lose the same percentage of both components on each stripping stage below this point in the column. This equal percentage loss would keep the concentration ratios, and thus pH and K, constant during the rest of the feed's passage through the stripper.

A feed that starts with an excess of ammonia would initially lose ammonia more rapidly than sulfide and would approach a constant pH of 9 from the basic side. In cases where steam rates are high, excess sulfide or ammonia might be lost quite rapidly, so that, for most of the stripper, $K_S = K_N$ = constant. Similar behavior would be expected if ammonia and carbon dioxide were the base/acid pair. A detailed examination of stage concentrations and K factors in some of our computer simulations confirmed this effect. Those simulations used detailed mass and energy balances on each equilibrium stage, not the simplified expression for f_N. The K factors differed from the value of 10 shown in Figure 4, because the simulations were for a different temperature.

Most Appropriate Type of Mean to Use for V/L

With K approximately constant for volatile components, column performance is mainly determined by the V/L profile in the column, and the overall performance should correlate well with the number of equilibrium stages and some appropriate average V/L. Two different columns with similar temperature profiles and with the same number of stages and the same effective mean V/L should perform similarly.

The question as to the most appropriate type of mean to employ for correlating the column V/L profile versus the
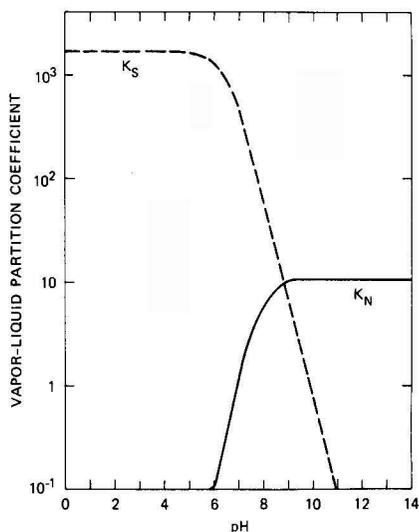
Figure 4. Vapor-liquid partition coefficients for ammonia and sulfide as a function of pH at 1 atmosphere and 100°C.

stripping performance is difficult to answer by rigorous mathematical derivation from stripping theory. However, at least one crucial property that an appropriate type of mean must exhibit is suggested by Equation (1): if the V/L ratio on even one (or more) of the column stages is zero, then the appropriate mean V/L for the entire column must be zero. This is qualitatively quite evident because, if no vapor leaves one of the stages, no stripping can occur. Note that the arithmetic mean would not satisfy the above criterion. Neither would the root-mean-square (RMS) mean satisfy it.

A generalized expression for a "mean," covering many of the most commonly used types, is as follows:

$$\text{Mean}_c\,(V/L) = \left[\frac{1}{N}\sum_{i=1}^{N}(V/L)^c_i\right]^{1/c} \qquad (4)$$

where the individual types are distinguished by different values of the constant, c, as follows:

c	Type of $\text{Mean}_c\,(V/L)$
1	Arithmetic
2	RMS
−1	Harmonic
$0 \pm \epsilon$	Geometric (where ϵ is an infinitesimal)
~1/3	Logarithmic

Both the harmonic mean and the geometric mean do satisfy the criterion that they are zero if any single component is zero. Empirically, it was observed that, of these two types, the harmonic mean V/L ratio exhibited a slightly better correlation with stripping performance. Accordingly, the harmonic mean V/L was adopted as our standard correlating parameter.

In evaluating the harmonic mean, the vapor flow leaving a stage was used for V and the liquid flow into a stage was used for L. Thus, for the reboiler, $V_i = V_B$ and $L_i = L_2$. The harmonic mean V/L ratio was then expressed as a "stripping steam rate" and "total steam rate", which are also stream flow ratios.

Refluxed Strippers

Examples of the data analyses applied to the experimental and simulation results, respectively, are shown in Tables 2 and 3. Table 2 was derived from an experimental column setup that included only a single five-tray Oldershaw section, a reboiler, and an overhead condenser. The assumed 4.8 equilibrium stages in the Oldershaw section was reported as 5 to simplify presentation. Because of the high heat losses, the V/L profile was highly pyramidal, with larger vapor flows near the column bottom and small flows near the top. The significant change in vapor flow at the feed tray resulted from heating the feed to column temperature.

Table 3 was derived from a simulation run that at-

TABLE 2. CALCULATIONS OF HARMONIC MEAN V/L FOR A FIVE-TRAY LABORATORY COLUMN WITH A REBOILER AND HIGH HEAT LOSSES

Equilibrium Stage	V/L (kg/kg)	Comments
6 (feed)	0.06	Measure as F/V_F since $L_T << F$
5	0.09	An average value reflecting
4	0.09	heat losses in vacuum-jacketed
3	0.09	section of column
2	0.11	
	0.12	Extra equilibrium stages due
	0.14	to condensation in uninsulated section above reboiler
1 (reboiler)	0.15	
Total column	$(V/L)_{hm}$ = 0.10 kg/kg (0.83 lb/gal)	

TABLE 3. CALCULATIONS OF HARMONIC MEAN V/L FOR A FIVE-EQUILIBRIUM-STAGE SIMULATED COLUMN WITH A REBOILER AND HIGH HEAT LOSSES

Equilibrium Stage	V/L (kg/kg)	Comments
6 (feed)	0.05	Large decrease in vapor rate
5	0.10	at column top due to heating
4	0.12	feed to column temperature
3	0.13	
2	0.14	
1 (reboiler)	0.16	
Total column	$(V/L)_{hm}$ = 0.10 kg/kg (0.83 lb/gal)	

tempted to mimic the heat losses in the experimental column. Even though the overall V/L profile was different from the one in the experimental column, it had virtually the same harmonic mean V/L. In both of these analyses, the presence of the reflux condenser was ignored. The reflux did not have a significant impact on the energy balance because it was small relative to the feed. Therefore, the V/L profile was, by and large, independent of the reflux. As was shown previously, the reflux condenser does affect the overall performance of the column; however, we felt that the effect would be approximately the same in the experimental and simulated columns and thus did not need to be included explicitly in this comparison. (It was also convenient to ignore the condenser because the stripping factor, S_c, in the condenser of the experimental column was not known because of the significant concentration effects on K there.)

The total, the harmonic mean, and the stripping steam rates calculated for five-tray and ten-tray experimental setups are summarized in Table 4. (Data from some seven-tray experiments were similar but are not shown.) At low steam rates, the difference between the harmonic-mean steam rate and the stripping steam rate was quite significant. At higher rates, the difference was not so large. The total steam rate was always quite different from the other two.

Both the experimental ammonia removal for the three column configurations and three simulated results (that were chosen because they had the appropriate number of equilibrium stages) are shown in Figure 5. A similar figure could be prepared for the acid gases (carbon diox-

TABLE 4. COMPARISON OF STRIPPING STEAM RATES AND HARMONIC MEAN STEAM RATES IN A LABORATORY COLUMN WITH LARGE HEAT LOSSES[a]

	Total Steam Rate (lb/gal)[d]	Harmonic Mean Steam Rate (lb/gal)[d]	Stripping Steam Rate, F/V_F (lb/gal)[d]
10-Tray column[b]	2.15	0.60	0.21
	2.18	0.72	0.30
	2.53	1.07	0.60
	3.32	1.88	1.39
5-Tray column[c]	1.42	0.83	0.50
	1.59	1.00	0.66
	2.62	1.27	0.73
	3.19	1.81	1.24

[a] Total heat lost was approximately 40 to 70% of the heat applied.

[b] 10 trays × 80% efficiency = 8 equilibrium stages
Equilibrium stages above reboiler = 2
Reboiler = 1
Total = 11

[c] 5 trays × 80% efficiency ≅ 5 equilibrium stages
Equilibrium stages above reboiler = 2
Reboiler = 1
Total = 8

[d] 1 lb/gal = 0.12 kg/kg.
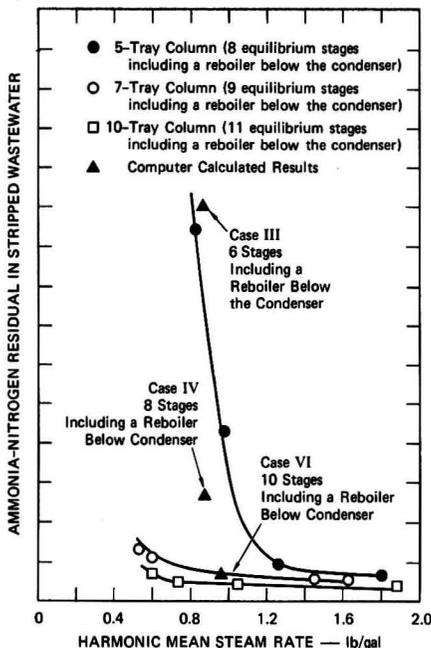
Figure 5. Comparison of experimental and simulated stripping in a column with reflux (1 lb/gal ≈ 0.12 kg/kg).

TABLE 5. CALCULATED STRIPPING STEAM RATES AND HARMONIC MEAN STEAM RATES IN A FULL-SIZED COLUMN WITH TYPICAL HEAT LOSSES[a]

Total Steam Rate (lb/gal)[b]	Harmonic Mean Steam Rate (lb/gal)[b]	Stripping Steam Rate (lb/gal)[b]
0.80	0.70	0.42
1.20	1.11	0.85
1.60	1.53	1.26

[a] Total heat lost is less than 1% of the heat applied.
[b] 1 lb/gal = 0.12 kg/kg.

ide and hydrogen sulfide). The experimental results fell nicely into the pattern one might expect. At high steam rates all the experimental columns were quite effective removing ammonia: they achieved well over 90% removal, and it is hard to make distinctions between results. At the lower steam rates, the columns with more stages performed the best. The Case III simulation, which was based on six equilibrium stages, was very close to the experimental curve derived from experiments with an eight-equilibrium-stage column. It lay above the curve, as would be expected. Case IV, which was an eight-equilibrium-stage simulation, was also close to the eight-stage experimental column. Case VI, which was a ten-stage simulation, fell (as it should) between the nine- and eleven-stage experimental curves. The results did not agree perfectly, in part because the wastewater contained some fixed ammonia that was held in solution by unidentified organic or inorganic acids. The computer simulation was unable to include the effects of ammonia fixation and always predicted more complete stripping than could be obtained with the real feed, regardless of steam rates or number of equilibrium stages. Also, the plot ignores the effects of reflux. It is important to note that, if the results shown in Figure 5 were plotted on the basis of total stream rates or stripping steam rates, the simulation results would be nowhere near the experimental curves because the details of the V/L profiles in the experimental and simulated columns were so different.

Nonrefluxed Strippers

The apparent success in comparing columns with different V/L profiles, using harmonic mean steam rates (as illustrated in Figure 5) could be viewed as somewhat artificial because this correlation technique was developed using those data. In addition, the simulated full-scale columns contained artificially high heat losses in an attempt to match their V/L profiles to the ones in the experimental columns. However, a second set of experiments

and simulations was available to test the concept of correlating by means of harmonic mean steam rates. A second sample of wastewater had been stripped in a seven-tray column with a reboiler but without reflux (an assumed total of nine equilibrium stage.) The sample was treated with caustic to eliminate fixed ammonia, so at high steam rates ammonia residuals in the stripped bottoms were practically zero. A set of simulations were run based on seven equilibrium stages and no reflux. In the simulations, no artificially high heat losses were assumed, but rather only those that would be expected for a well-insulated, full-size column. The various steam rates that resulted in the simulated column are shown in Table 5. The total and the harmonic-mean steam rates were very close, because a detailed examination of the V/L profile showed that it was almost constant up to the feed tray. At the feed tray some condensation occurred to heat the feed, and the stripping steam rate was therefore lower. The results for the experimental column, which are not shown, were quite different. The V/L profile was pyramidal, and the total steam rate, the harmonic steam rate, and the stripping steam rate were all significantly different.

The simulated and experimental results are compared in Figure 6. The results are gratifying. The performance curves are close to each other (as is required) and the experimental results (which are based on more equilibrium stages) are to the left, where they belong. The experimental column could achieve better performance with less steam because it contained more equilibrium stages.
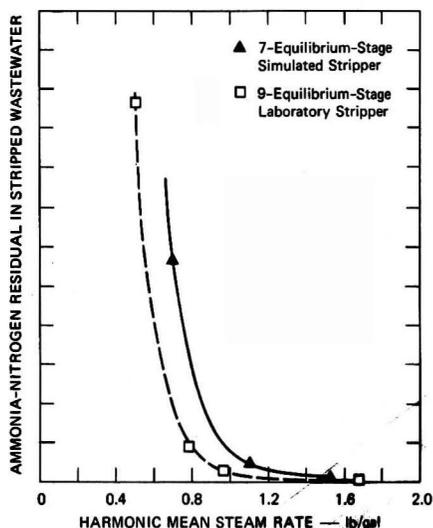
Figure 6. Comparison of experimental and simulated stripping column without reflux (1 lb/gal ≈ 0.12 kg/kg).

Conclusions

A good correlation has been demonstrated of the stripping of a particular component in terms of two fundamental parameters: 1) the number of equilibrium stages, and 2) the harmonic mean steam rate. Columns with widely differing V/L profiles but the same number of stages and harmonic mean steam rates yielded equivalent stripping effectiveness when they were operated at the same general temperature. The harmonic-mean steam rate method has been demonstrated for a wastewater containing the volatile gases ammonia, carbon dioxide, and hydrogen sulfide, but should also work well for any other system where a component has a relatively constant K factor throughout most of the column. The method should be useful for designing full-scale columns using laboratory stripping data when it is impossible to use computer simulations for the full-scale column design. It should be particularly useful for wastewater streams where it is not possible or economical to identify all the components present.

Acknowledgment

Laboratory stripping experiments were conducted by Robert L. Boughton and Duane Chirolo. Chemical analyses were conducted by David Ingersoll and Daniel Combs. Their contributions were important factors in the success of the study.

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Anaerobic Treatment of Fermentation Wastewaters

A case history from Puerto Rico on the technology and economics of a new anaerobic-treatment filtration process.

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The production of methane from organic waste matter has been practiced for well over a century. Anaerobic fermentation, until recently, has been generally practiced to reduce the volume of solid waste requiring disposal and to improve the handling characteristics of the waste. A good example is the anaerobic digestion of municipal sewage sludge. The steadily increasing cost of energy has made anaerobic treatment attractive for high and even medium strength wastewaters as demonstrated by the recent proliferation of commercially available anaerobic processes (Stafford, Hawks, Horton) [1].

The requirement to significantly reduce the total biochemical oxygen demand (BOD) discharged by its rum distillery prompted Bacardi Corporation to carefully investigate the treatment and disposal technologies available. Anaerobic treatment of rum slops, which contain over 90% of the BOD discharged by the distillery, was first studied in 1974 by Schea et al. in laboratory and pilot scale units, at the Bacardi Corporation distillery, (Schea,

Dorion, Rodríquez, Ramos) [2]. These and later studies begun in 1980 demonstrated that anaerobic fermentation was the most cost effective process available for the treatment of rum slops. The laboratory and pilot plant studies which led to the development of the patented Bacardi Corporation Anaerobic Treatment Technology are described in a previous paper (Szendrey) [3, 4].

The seed material for the laboratory and pilot studies begun in 1980 was obtained from fresh cow manure. A period of several months was required for this seed to become well acclimated to the strong effluent characteristic of a rum distillery. The composition of this effluent, which is also known as mosto, vinasse, and rum slops, can be variable, depending on the source of the cane molasses and the fermentation process used.

As the construction of the first phase of the full scale anaerobic treatment plant progressed, the question of the seeding and startup of the 3.5 million gallon (1.32475E07 L) anaerobic filter became more and more pressing.

TABLE 1. RUM SLOPS COMPOSITION

Parameter	Unit	Range
BOD$_5$	mg/liter	36,000 - 42,000
COD	mg/liter	80,000 - 105,000
TSS*	mg/liter	3,000 - 8,000
TS	%	7.5 - 11.0
N (Kjeldahl)	mg/liter	790 - 1,450
P (ortho)	mg/liter	50 - 100
pH	SU	4.2 - 5.0
Alkalinity (CaCO$_3$)	mg/liter	600 - 1,700
Vol. Acids (CH$_3$CO$_2$H)	mg/liter	4,000 - 7,000
Specific Gravity	—	1.02 - 1.05
Color	APHA	75,000 - 100,000
Sulfates	mg/liter	4,000 - 10,000

*With molasses clarification and yeast recycle

The two options available for seeding were: (1) To use cow manure, of which an unlimited supply was close at hand but who's organisms were not acclimated to the rum slops and would constitute a serious handling problem, and (2) to use the well acclimated seed available from the 3,000 gal (1.1355E05 L) pilot anaerobic plant, in operation since mid 1980, of which only a relatively small supply was readily available. The use of either of the available seed materials left us facing the possibility of a long startup period for the 3.5 million gal (1.32475E07 L) anaerobic filter; therefore, it was decided to attempt to cultivate a large volume of seed organisms using the pilot unit effluent to reduce the time required for startup.

A total of ca. 500,000 gal (1.8925E06 L) of seed solution was prepared and used to seed the anaerobic filter. The anaerobic filter developed rapidly. Four months after startup, the biogas being produced was contributing to the fuel being consumed in the steam boilers. By the end of 1982, the anaerobic filter was consistently producing over 1.5 million ft^3 of biogas per day (4.24752705E04 m^3/day). The capability of shutting down the anaerobic filter during periods when the distillery is shutdown for maintenance or repairs, and rapidly restarting the filter once slops flow from the distillery resumes, was demonstrated and refined during the first year of operation (Szendrey) [4].

The installed capital cost for the anaerobic-treatment plant, exclusive of additional equipment such as boiler retrofit, etc., was $7.6 million, or approximately $53.50 per lb of BOD applied per day. The operating and maintenance cost during the first year of operation averaged $.0183 per pound of BOD removed, while the benefit from the biogas produced averaged $3,000 per day for the last 6 months of 1982. These treatment costs are lower than those associated with aerobic treatment, even without taking the methane credit into consideration. As the price of fuel oil and gas increase, the Bacardi Corporation process has the potential of providing a reasonable payback period. Industries charged according to the BOD discharged to municipal treatment plants would benefit from lower charges as well as energy credits.

The Bacardi Corporation process is amenable to many other wastewaters and substrates. Samples from a variety of industries have already been evaluated and found to be amenable to treatment using this anaerobic treatment technology.

SEEDING

After careful consideration, we decided that a faster startup of the anaerobic filter could be achieved with seed from the pilot unit. Once the decision was made, plans to grow a sufficient seed volume for the startup of the 3.5 million gal (1,32475E07 L) anaerobic filter were begun. In essence, the plan called for utilizing successively larger

tanks to first collect and then incubate the 300-400 gal of effluent from the pilot plant until a sufficiently large seed volume was developed. The tankage being installed in the anaerobic treatment plant was evaluated for this application.

The first phase of the full scale anaerobic plant designed by Black & Veatch of Kansas City, Mo., consists of a 750,000 gal (2.83875E06 L) holding tank, a cooling system, a 3.5 million gal (1.32475E07 L) submerged downflow anaerobic filter and effluent pumps for the slops; two 18,000 gal (6.813E04 L) fiberglass caustic storage tanks for pH control, a nutrient feed system and a gas storage and handling system composed of high and low pressure compressors, a gas storage sphere and an emergency flare.

The major components of the system are illustrated in Figure 1 and the anaerobic filter in Figure 2.

Given the slow doubling time of mesophylic methanogens (Clausen, Ford, Shah)[5], a fairly long time would be required to develop the estimated 500,000 gal of seed for the startup of the anaerobic filter from the 300 to 400 gal/day (1.1355E03-1.514E03 L/day) of effluent available from the pilot plant.

A check on the status of the tanks and equipment at the construction site for the full scale anaerobic treatment plant, which was within 7 months of completion, revealed that the 18,000 gal (6.813E04 L) fiberglass caustic storage tanks were ready to be installed and that the construction schedule could be adjusted so that the 750,000 gal (2.83875E06 L) rum slops holding tank and the emergency flare could be completed two months prior to the scheduled startup of the anaerobic filter. Based on the equipment available, a plan to develop the seed required for the startup and the actual startup of the anaerobic filter was prepared. The plan consisted of the following major steps.

- Seed collection and storage.
- Preparation of seed propagation tank.
- Seed propagation
- Preparation of anaerobic filter for seeding.
- Seeding and startup of anaerobic filter.
- Development of immobilized cell layer on plastic media in anaerobic filter.

The plan called for the collection and storage of effluent from the pilot anaerobic unit until a large enough volume to seed the 750,000 gal (2.83875E06 L) slops holding tank,
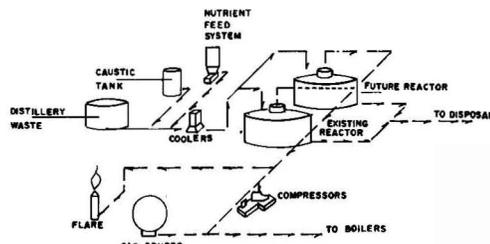
Figure 1. Major components of system.
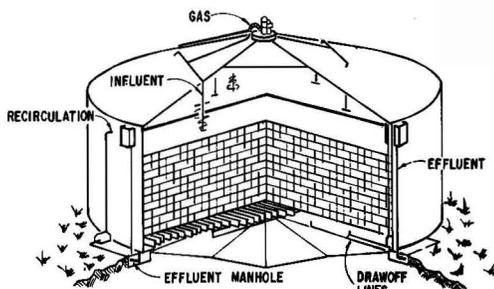
Figure 2. Modified anaerobic filter.

which would serve as the propagation tank, was obtained. Seed would be propagated in the rum slops holding tank for seeding the anaerobic filter. The schedule of events required careful planning so that the anaerobic filter was ready for seeding. Delays in propagation or filter construction would result in a lower seed volume or seed degradation, respectively. The seeding procedure is shown schematically in Figure 3.

Seed Collection and Storage

Both laboratory and pilot tests have demonstrated that anaerobic seed material in the form of a sludge or liquid could be stored, under anaerobic conditions for extended periods of time without significantly decreasing the activity of the seed. A sample of sludge from one of our laboratory units was once stored for six months in an open steel pail and was found to be active when used as seed for a laboratory test.

For seed collection and storage, we decided to use one of our 18,000 gal (6.813E04 L) fiberglass caustic storage tanks. The tank was fitted with a recirculation pump, associated piping and a water seal to prevent air from entering. The air in the tank was displaced with carbon dioxide until the oxygen content in the tank was less than 1%. The effluent from our pilot anaerobic plant was collected in a closed 700 gal (2.6495E03 L) stainless steel portable tank and transferred to the caustic storage tank daily. Although this step was not carried out under strict anaerobic conditions, the seed material was protected from the air as much as possible. The seed material being collected in the caustic storage tank was monitored for pH and COD and the gas produced was also monitored to assure that air was not entering the tank. The pH was maintained close to 7.5 and the COD was kept at 25,000 to 30,000 mg/liter by adding caustic and raw rum slops as required. After six weeks, a total of 13,000 gal (4.9205E04 L) of seed material had been collected. A slow evolution of methane rich gas during the collection period suggested that the seed was active.

Preparation of Seed Propagation Tank

Concurrent with the collection of the pilot plant effluent in the caustic storage tank, the 750,000 gal (2.83875E06 L) rum slops holding tank was sealed and a gas line with flame arrestor was connected from the top of the tank to the emegency flare. The tank was also fitted with a liquid level gauge and a manometer to monitor volume and pressure. Finally, the tank was fitted with a recirculation pump and piping, and the suction side of the piping tied into the rum slops outfall. Nutrients and caustics could be added through a connection in the recirculation line. Since the slops holding tank was not a pressure vessel, care was taken to provide a means of rapidly venting the vessel. This precaution proved most useful on a number of occasions.

Seed Propagation

Before transferring the seed material collected in the caustic storage tank, 150,000 gal of water were added to the tank and the tank was purged with approximately 25,000
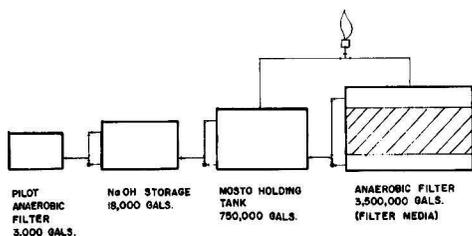
lbs (1.133981E04 kg) of carbon dioxide to lower the oxygen content to below 1.0%. The pH of the water was raised to 9.0 S.U. with caustic and carbon dioxide was added until the pH dropped to 7.5 S.U. This procedure produced a well buffered aqueous solution. The seed from the caustic storage tank was now transferred to the slops holding tank, followed by 20,000 gal (7.57E04 L) of rum slops. The pH in the tank was carefully monitored and maintained at *ca.* 7.5 using caustic. Nutrients in the form of urea and ammonium phosphate were added after the seeding and the tank was fed 16,000 gal (6.056E04 L) of slops per day to propagate seed. The temperature in the slops holding tank slowly rose to 95°F (308.15°K) from the addition of the hot rum slops. The rate of rum slops addition near the end of the seed propagation stage was controlled by the rate of radiative heat loss in the holding tank as no direct means of cooling was available. The contents of the tank were monitored for pH, nutrients, temperature, COD, BOD, TSS, and gas composition. The gas produced was burned in the emergency flare prior to discharge to the atmosphere. By the time the construction of the anaerobic filter was complete, 600,000 gal (2.271E06 L) of active seed material having a TSS of 17,000-20,000 mg/l had been produced. The copious amount of methane rich gas produced during propagation again suggested that an active seed had been produced.

Preparation of Anaerobic Filter for Seeding

Normally, all influents to the anaerobic filter would enter through the top; therefore, temporary provisions to introduce water and rum slops through the bottoms were made to avoid introducing material through the top until the plastic medium was completely submerged. Means of introducing carbon dioxide and a temporary liquid level gauge were also provided.

Seeding and Startup of Anaerobic Filter

A volume of 1.8 million gal (6.813E06 L) of water was added to the anaerobic filter and the pH was adjusted to 9.0, using caustic. The tank was then purged with 45,000 lbs (2.0412E03 kg) of CO₂ to displace the air and reduce the oxygen content below 1.0%. The pH was next adjusted to 7.5 using caustic, as it had fallen to below 7.0 during the carbon dioxide addition. Next, 600,000 gal of rum slops cooled to 120°F (322.040 K) and 3,000 gal of caustic were added in preparation for introducing the seed. The seed propagated in the rum slops holding tank was then slowly transferred to the anaerobic filter and recirculation in the anaerobic filter was begun.

Development of Immobilized Cell Film on Plastic Medium

After seeding, the anaerobic filter liquid volume was at *ca.* 3.0 million gal (1.1355E07 L). An additional 500,000 gal (1.8925E06 L) of rum slops were slowly added over the next week and the contents were recirculated for the next five weeks without further additions of rum slops. During this period, the initial film of immobilized microbes was deposited on the plastic medium in the anaerobic filter. After five weeks of recirculation, daily rum slops feed was begun at the rate of 40,000 gal per day (28 gpm) (105.98L/min). The temperature of the anaerobic filter was raised to and maintained at 98°F (309.82°K) by controlling the temperature of the rum slops being fed. The rate of rum slops addition from this point on was determined by the ability of the anaerobic filter to remove the BOD present in rum slops and the concentration of volatile acids present. Actually, COD, a more rapid and precise analysis, was used to calculate the BOD removal

Figure 3. Flow diagram for propagation of seed and startup of anaerobic filter.

efficiencies being attained. By May, 1982, three months after regular rum slops feeding was initiated, the slops feed rate was over 230,000 gal per day (8.7055E05 L/day) and sufficient quantities of biogas were being produced to be burned in our boiler and provide a meaningful percentage of the distillery's fuel requirement. The BOD removal efficiency and gas production rate of the anaerobic filter continued to improve through 1982. Table 2 summarizes the monthly performance of the anaerobic filter in 1982.

Table 2 clearly demonstrates that the capacity of the anaerobic filter was continually improving throughout 1982. This fact agrees with observations made by others studying anaerobic processes. The anaerobic filter received no feed during the distillery shutdowns in July and October of 1982 (Dague)[6].

The ability of the anaerobic filter to remain active for extended periods without receiving an influent is a very important feature of the Bacardi Corporation anaerobic filter and is discussed in more detail in the next section.

OPERATION OF ANAEROBIC FILTER

Our goal for 1983 was to study the characteristics of the anaerobic filter and to also determine its optimum and maximum loading rates. After the annual maintenance shutdown of the rum distillery, from Dec. 13, 1982 to January 21, 1983, rum slops feed to the anaerobic filter was resumed. The feed rate to the anaerobic filter was controlled by the rate of rum slops production in the distillery until February of 1983. A summary of the first six months of operation for this year is given in Table 3.

Based on our studies of the operation of our anaerobic filter it appears that the highest loading the anaerobic filter is currently capable of sustaining over an extended period of time is 0.9 lbs of COD per ft^3 of medium (14.42 kg/m^3). A loading 0.8 lbs of COD per ft^3 of medium (12.82 kg/m^3) was found to be the optimum. These values compare favorably with those reported by Dague in 1982 (Dague) [6]. The lower gas production and BOD removal rates listed in Table 2 are a result of overloading during studies aimed at defining the maximum sustained load the anaerobic filter was capable of treating. The pH in the anaerobic filter under normal operating conditions falls between 7.2 and 7.4. No caustic additions to the anaerobic filter or the rum slops fed are required under normal operating conditions. The rum slops are naturally rich in most nutrients; therefore, no nutrients are currently being added on a regular bases. We have tested the result of adding additional nitrogen, phosphorus, iron, nickel, and cobalt to the system and have not observed significant improvements in filter efficiency. Studies of other micronutrients are being conducted in lab.-scale units (Kelly, 1983; Diekert and et al. 1981, Murray and Van den Berg, 1981) [7, 8, 9, 10]. There is more than sufficient hydrogen sulfide present, as rum slops may contain up to 1% sulfate, (Scherer, Sahm) [11]. It is interesting to note that the system has acclimated to hydrogen sulfide levels that have been reported as inhibitory and even fatal to anaerobic systems (Lawrence and McCarty, 1966) [12, 13]. The operating temperature of our anaerobic filter is 100 ± 2°F (310.93°K), although excursions up to 106°F (353.54°K) have occurred without any noticeable effect on the efficiency. The volatile acids concentration is our most important operating parameter and averages between 3,000 and 4,000 mg/liter while concentrations above 5,000 mg/liter become inhibitory (McCarthy, 1964) [14]. The al-

TABLE 2

Month	Influent Gal/Day × 10³	BOD in Lbs/Day × 10³	BOD Out Lbs/day × 10³	% Removed	Biogas Ft³/day × 10³
Jan*	23.8	6.92	.99	85.7	100.0
Feb	24.6	7.26	1.1	84.8	102.7
Mar	37.9	11.28	1.56	86.2	158.1
Apr	130.1	31.88	5.88	81.5	500.0
May	233.1	64.78	10.03	84.5	967.7
Jun	286.1	87.61	16.36	81.3	1073.8
Jul**	233.4	66.75	10.33	84.5	—
Aug	264.0	72.89	10.86	85.1	1052.4
Sep	339.1	102.23	14.04	86.3	1323.6
Oct ***	355.5	94.10	16.98	82.0	1053.3
Nov	392.4	115.07	30.08	73.9	1582.2
Dec	413.8	127.96	26.38	79.4	2087.9

* Anaerobic filter feeding begun on January 25, 1982.
** Distillery shutdown for 3 weeks
*** Distillery shutdown for 2 weeks
Conversion Factors to SI for Table 2
Gal/Day - 3.7854118E-03 m³/day
Lbs/Day - 4.535924E-01 kg/day
Ft³/Day - 2.8316847E-02 m³/day

TABLE 3

Month	Influent Gal/Day × 10³	BOD in Lbs/Day × 10³	BOD Out Lbs/Day × 10³	% Removed	Biogas Ft³/Day × 10³
Jan	432.1	105.3	18.2	82.7	1006.3
Feb	448.1	102.3	24.7	75.9	1656.6
Mar*	432.9	117.5	46.4	60.53	1297.3
Apr	430.4	127.1	39.6	68.86	1427.2
May	414.0	111.9	35.7	68.12	1307.9
June	375.8	100.4	29.9	70.17	1376.8

* The anaerobic filter was overloaded.
Conversion Factors to SI for Table 3
Gal/Day - 3.7854118E-03 m³/Day
Lbs/Day - 4.535924E-01 kg/Day
Ft³/Day - 2.8316847E-02 m³/Day

kalinity is controlled by the characteristic of the rum slops fed and while there is considerable variation, no inhibitory effects have been noted (Li$_3$ and Sutton, 1983) [15]. Biogas production has averaged 8.5 ft^3 per pound of COD removed (0.53 m^3/kg) both in the pilot and the full scale plant. This value is in the range predicted for this wastewater (McCarthy, 1964) [16].

The methane content of the gas is sensitive to the pH and the volatile acids concentration. The optimum and maximum operating values determined thus far for our anaerobic filter are presented in Table 4.

Since distilleries, like many other industries, must shut down for periodic maintenance, we tested the effects of interrupting the rum slops feed to the pilot and now, the full scale anaerobic filter. As of now, we have interrupted the rum slops feed to the anaerobic filter on four occasions, the longest being our annual year-end maintenance shutdown, which lasted seven weeks. As proven in our pilot studies, we can interrupt the feed to the anaerobic filter for extended periods of time and re-establish design feed rates within 24 to 48 hours after the distillery startup. One 3,000 gal (1.1355E04 L) pilot plant was not fed for an 8 month period and design feed rates were re-established in one week. We believe that this capability of the Bacardi Corporation system is unique and essential for the successful application of anaerobic technology in a wide variety of industries.

The BOD removal rates achieved by the anaerobic digestion of rum slops approached 90% in the laboratory and led us to suspect that a small proportion of the organic constituents present were biodegradable by aerobic but not by anaerobic organisms. To test our suspicions, we set up a 500 ml contact anaerobic digester in the laboratory and periodically analyzed samples for BOD and COD for a two-month period. The results confirmed our suspicions, as the BOD and COD values remained constant after 14 days of digestion.

Other industrial effluents were tested using this procedure and were found to contain a lower proportion of non-anaerobically digestable BOD. For example, over 98% of the BOD in the slops from a distillery using sugar beet molasses was found to be anaerobically digestable by this method.

Although it is accepted that anaerobic digestion is an exothermic process, I have not found examples where a temperature rise has been observed and/or quantified for an industrial wastewater. We have observed an 8°F (259.82°K) temperature rise in our 3.5 million gallon anaerobic filter when the loading is 0.8 lbs of COD per ft^3 of plastic medium (12.82 kg/m^3). Heat loss from the anaerobic filter is minimal, and is calculated to be between 1/4 and 1/2°F per day at our operating temperatures.

We have tested a number of diverse industrial wastewaters using the novel Bacardi Corporation anaerobic process. Up to now we have had the opportunity to test:

Pharmaceutical antibiotic fermentation wastewater.
Citric acid fermentation wastewater.
Pulp paper mill wastewater.
Cheese whey.
Yeast production wastewater.
Beet molasses distillery slops.
Beer brewery wastewater.
Organic chemical manufacturing wastewater.
Winery wastewaters.

All of the above were found to be amenable to treatment using the Bacardi Corporation process. The anaerobic filter loadings attainable are different for each wastewater but most were found to be more biodegradable than rum slops (Van den Berg, Kennedy and Hamoda, 1981) [17]. In general, most wastewaters having a BOD greater than 500 mg/liter and a TSS content of below 15,000 mg/liter can be treated by the Bacardi Corporation Anaerobic Process if they are biodegradable.

CAPITAL AND OPERATING COST

The total cost of the first phase of the Bacardi Corporation anaerobic treatment plant, including boiler retrofitting, a new water tank, a new electrical substation, and some equipment for the second phase, was $8.34 million. Obviously, the plant was installed to meet our specific needs and the cost may vary for other sites. Based on what we have learned during construction and operation of the plant, we believe that a plant of equal capacity could be installed at a significantly lower cost. Some of the factors affecting the cost of our treatment plant were:

- The treatment plant was installed under severe time constraints to meet environmental regulations as well as to serve as a source of energy.
- The novel Bacardi Corporation Anaerobic System is the first of a kind and, at the same time, the world's largest anaerobic plant. To assure the success of the process, the plant was conservatively designed and contains features found not be essential to the process.
- The currently installed plant was designed to treat approximately 50% of the effluent from the distillery, however, much of the equipment installed was sized and installed to accommodate the total effluent.

The operating and maintenance costs of the Bacardi Corporation System have been calculated for 1982. The figures include startup costs and credit for biogas received for less than seven months. The total 1982

TABLE 4

Parameter	Units	Optimum Value	Maximum or Minimum Sustainable value
Loading	lbs COD/ft^3	0.80	0.9
pH	S.U.	7.3	7.0
Temp.	°F	98-102	1.06
Vol. Acids	mg/liter	3,500	5,000
Sulfates	%	0.5	1%
Alkalinity	mg/liter	4,000-6,000	—

* Conversion Factors to SI for Table 4
tk = (t$_f$ + 459.67)/1.8

$$\frac{ft^3}{lb} = 6.243E\text{-}02$$

$$\frac{lb\ COD}{ft^3} = 1.6018E01$$
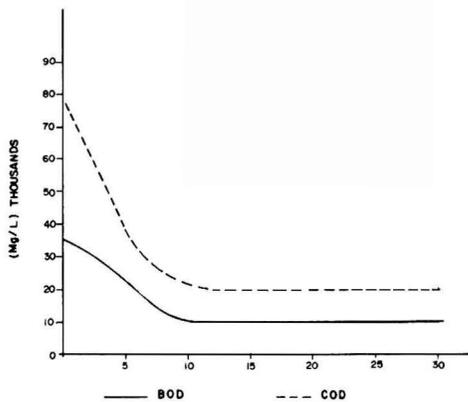
Figure 4. Ultimate anaerobic BOD and COD.

BOD
COD

Figure 6. Effect of oil-price changes on benefits from generation of methane.

operating and maintenance costs for the anaerobic plant were $275,000, of which over $100,000 was for electricity for the gas compressors (electricity rates spent in Puerto Rico are about $0.10/KWH). Less than $25,000 was spent on caustic. The cost per pound of BOD removed was $0.0183 per pound, while the cost per million BTU's generated as biogas was $2.68. We expect that this year the cost per pound of BOD removed will be close to $0.01 and the cost per million BTU's produced will be reduced to approximately $1.50. The biogas generated in 1982 was equivalent to 685,550 gal of fuel oil. We expect to produce the equivalent of 1,400,000 gal of fuel oil in 1983.

Based on the capital and operating cost data currently available, an attempt has been made to determine the point at which the plant is capable of paying off its investment. The value of the fuel oil replaced has been chosen as the yardstick with which to measure the economics of the process. Figure 5 shows that an anaerobic treatment plant whose methane is used to replace fuel oil will become economical when the cost of fuel oil exceeds $33 per barrel. However, if this same anaerobic-treatment plant reduces the pounds of BOD discharged to a municipal plant that charges a fee for the BOD it receives, the economics improve significantly. Since we discharge without a fee for BOD, our economic performance is measured solely by the value of the fuel oil replaced. We have found a few industries where the pay-back for the installation of our anaerobic technology is below three years because of the high fees paid for BOD discharges to municipal treatment plants. In countries where energy is expensive, the payback period, based on the value of energy recovered alone, is favorable.
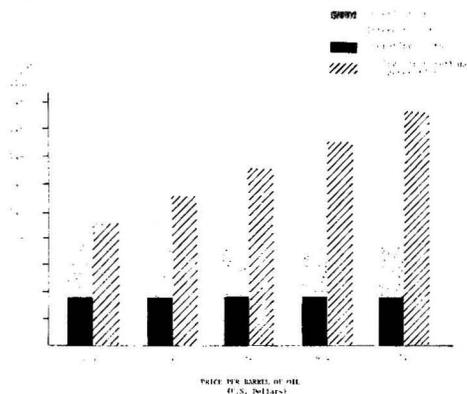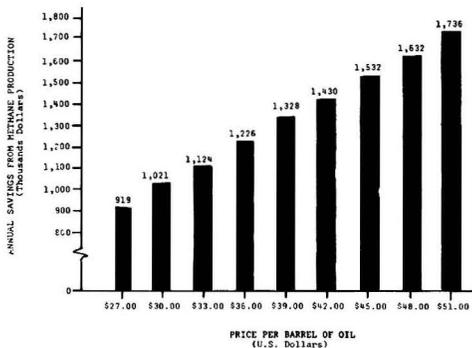
SUMMARY AND CONCLUSIONS

The Bacardi Corporation Anaerobic System has been shown to be an efficient and versatile method for significantly reducing the organic discharge from a molasses based distillery as well as a source of a significant fraction of the energy required for distillation. The most significant features demonstrated thus far are:

- Flexibility—The system can handle large variations in loading.
- Stop, re-start capability—Shutdowns of 3 to 7 weeks will not adversely affect the system.
- Low energy requirements—The 3.5 million (1.32475E07 L) anaerobic filter requires only 12 (8.948398E01 watts) horsepower for mixing. A comparable contact digester would require well over 800 (5.96559896E03 watts) horsepower.
- Net energy producer—The system produces more energy than it consumes.
- High loading rates—The system has been operated at a loading rate of 0.9 lbs of COD/ft³ medium (14.42 kg/m³).
- Payback opportunity—Depending on the volume of wastewater treated, fuel costs and sewer use fees, the system has the potential to pay for itself.
- Highly buffered system—Wastewater at a pH of 4.2-4.7 can be fed without neutralization. Caustic is only required for startups.
- Produces a clean readily usable fuel. The methane produced can be burned in boilers to produce steam, drive a gas turbine to produce electricity, or fuel an internal-combustion engine.

The Bacardi Corporation Anaerobic System is applicable to many wastewater streams containing organic material. To date wastewaters from other distilleries using different substrates have been evaluated in our laboratory and shown to be treatable using our system. Many other waste streams in the food, beverage, chemical, and other industries can also utilize this system.

Figure 5. Savings from methane generation and other costs of a waste-treatment plant at different oil prices.

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Polishing Treatment of Coal Liquefaction Wastewaters

Detailed description of a mobile wastewater-treatment pilot plant with application to actual coal-liquefaction wastewaters.

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Many options for regulation of the coal conversion industry, ranging from regulated discharge to zero discharge of aqueous wastes to the environment, have to be considered. Under either scenario, advanced control technologies may be necessary to produce a suitable treated wastewater.

During the mid-1970s, environmental control technology assessments performed at ORNL and elsewhere highlighted a number of unit operations that appeared to hold promise for application to future coal conversion facilities [1]. Beyond such primary treatment sequences as solvent extraction, steam stripping, and biodegradation of the residual organics polishing processes such as softening, demineralization via reverse osmosis and electrodialysis, and ozonation and carbon adsorption for removal of trace organics can be combined to upgrade the wastewater to the point where it can be reused internally or discharged as an environmentally benign waste. For various reasons, only a limited amount of advanced control technology was included in the coal conversion pilot plants constructed in the mid-1970s. As a result, ORNL was asked by the Assistant Secretary for Environment, U.S. Department of Energy, to develop comprehensive environmental and health plans to study the H-Coal Direct Liquefaction Pilot Plant (H-Coal) being constructed at Carlettsburg, Kentucky. As part of the comprehensive program, a process development unit (PDU) for studying advanced wastewater treatment polishing processes was built and operated at H-Coal by Oak Ridge National Laboratory (ORNL). A detailed design and documentation of the R&D capabilities of the PDU are given elsewhere [2].

The PDU was operated at H-Coal during fiscal year 1982. Results from these tests are summarized in [3] and detailed in [4]. On conclusion of the tests, the PDU was transported to the Advanced Coal Liquefaction R&D Facility (ACLF) in Wilsonville, Alabama. Treatment studies were performed at the ACFL during fiscal year 1983, the results of which are the primary subject of this paper.

DESCRIPTION OF PDU

Each of the units in the PDU was designed for a nominal throughput of 60 mL/s (1 gpm). The units were constructed as skid-mounted, self-contained modules that included the vessels, piping, pumps, and instrumentation for each unit. A mixed-media roughing filter was used to prefilter the incoming wastewater stream before it entered the 2.65-m³ (700-gal) mix/surge tanks associated with each unit. The subassemblies were installed in two 12.4-m- (40-ft)-long van trailers for use at the Catlettsburg site. As shown in Figure 1, the three processing units were located in one trailer, while the tanks, roughing filter, and reagent storage vessels were placed in the other. All of the components that contacted the process water were constructed of either 304 or 316 stainless steel. The polishing processes could be interconnected (if desired) to produce a series of various processing strategies, or they could be operated individually. Each unit included a 2.65-m³ (700-gal) mix/surge tank at the front end to permit mixing of any necessary reagents with the process water and to provide surge capacity between the units during series operation. Each tank was equipped with a circulation pump which
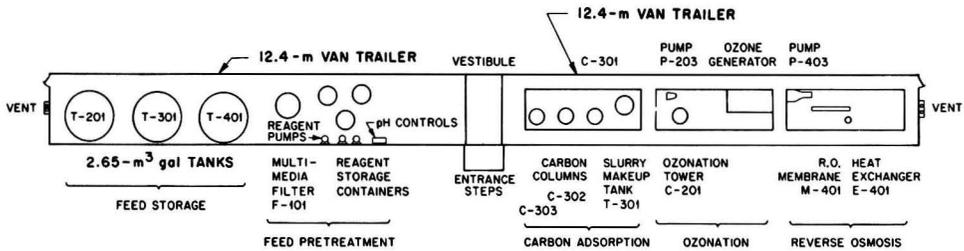
Figure 1. Layout of polishing train in two 12.4-m- (40 ft)-long van trailers as designed by ORNL.

maintained agitation in the tank and provided the head necessary to supply water to the process unit. A pH probe was included in each circulation loop to monitor and regulate the pH in the tank.

Ozonation Unit

A diagram of the ozonation system is shown in Figure 2(a). Ozone was contacted in counterflow with influent water in an open vertical column (26.5 cm diam. by 1.5 m high). The liquid level in the column was controlled in such a manner that the liquid residence time in the column could be varied independently of the liquid flow rate through the column. Four sample ports were positioned along the length of the column and also on the inlet and outlet streams. The maximum gas flow is 85 L/min (3.0 scfm). The gas phase was dispersed into the column by a 20-cm-diam. porous ceramic disk located in the conical bottom section; the nominal bubble size is 3 mm. Column pressure could be controlled at levels up to 0.3 MPa (30 psig). Before entering the column, the influent stream was filtered to remove suspended solids that could exert an additional ozone demand.

Carbon Adsorption Unit

The carbon adsorption system, shown schematically in Figure 2 (b), consisted of from one to three equally sized columns (26.5 cm diam. by 1.5 m high) filled with granular activated carbon. If the adsorption wavefront could be contained in two columns, then these columns could be operated in series at one time, while the third was being emptied of spent carbon and refilled with a fresh carbon charge. Thus, the first bed in the series became completely contaminant-saturated before it was taken out of service for reloading. The piping network would allow any one of the columns to be first in the treatment sequence. This arrangment provided for the continuous processing of water without interruption of flow during the column unloading-reloading operation. Each column had four sample ports along its length, as well as inlet and outlet sample ports. The column samples were withdrawn from the center of the bed. The influent stream was filtered to lower the suspended solids loading, thus decreasing the rate at which the carbon beds blind. The liquid flow rate to the column was regulated by a flow control loop. Carbon slurry was transported to and from the columns by pneumatic overpressure. Water-flush lines function both in the cleaning of the carbon slurry transport lines and in backflushing the column underdrains. Over-pressure protection was provided by rupture disks on each column.

Reverse Osmosis Unit

The reverse osmosis system [Figure 2(c)] consisted primarily of a high-pressure positive displacement feed pump [440 mL/s at 7.0 MPa (7 gpm at 1000 psi)], a pressure control system for maintaining the desired feed pressure to the membrane, and a membrane assembly. A concentrate

recycle loop was included for high-recovery studies. With recirculation of the concentrate stream, high liquid velocities across the membrane could be maintained concurrent with high permeate recovery. The system could also be operated in the one-pass mode, which eliminated the concentrate recycle; thus, the concentrate stream made one pass through the membrane and then exited the system via the permeate and concentrate discharge lines. In either mode of operation, liquid throughput was set by the combination of membrane permeability and concentrate flow rate (the latter was set by a flow controller). A heat exchanger was included for temperature control since most membranes are temperature sensitive. At high recycle rates, the heat exchanger could be used to remove excess heat generated by pump power dissipation, or it could be used to supply heating for elevated-temperature tests. The influent

(a) FLOW DIAGRAM OF OZONATION UNIT

(b) FLOW DIAGRAM OF CARBON ADSORPTION UNIT

(c) FLOW DIAGRAM OF REVERSE OSMOSIS UNIT
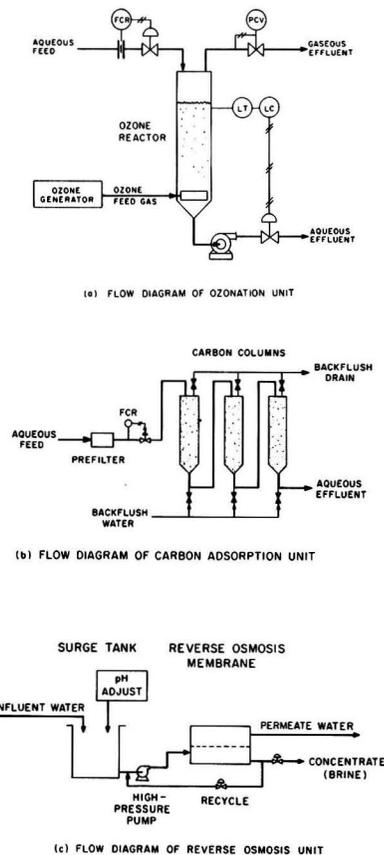
Figure 2. PDU flow schematics: (a) ozonation unit, (b) carbon adsorption system, and (c) reverse osmosis unit.

stream was filtered (typically to 5 μm) to remove suspended solids that could blind the membrane surface. The conductivities of the feed, concentrate, and permeate streams were monitored continuously to provide an on-line measurement of separation effectiveness; sample ports were also included on these three streams.

Analytical Support Laboratory

In addition to the two process unit trailers, a third trailer was outfitted to function as an analytical support laboratory to the PDU. Analyses performed in the laboratory were standard tests necessary to monitor daily operation of the process units. These tests included chemical oxygen demand (COD), total organic carbon (TOC), phenol, total dissolved and suspended solids (TDS, TSS), calcium, magnesium, sulfate, alkalinity, color, and pH. All analytical procedures were performed by the methods given in *Standard Methods for the Examination of Water and Wastewater* [5], with a few minor deviations and exceptions. This trailer also functioned as a site for sample preservation so that more sophisticated analyses could be performed upon return to ORNL.

ADVANCED COAL LIQUEFACTION R&D FACILITY

The ACLF consists of units for performing dissolution-type coal liquefaction (originally via SRC-I technology), a Kerr-McGee Critical Solvent Deashing unit, and a hydrotreater. A detailed description of the system is given by Sapp [6].

A flow diagram of the wastewater treatment plant at Wilsonville is shown in Figure 3. The major components of the facility are: (1) the pretreatment tanks used to reduce levels of sulfide and organic compounds via catalyzed air oxidation and occasional oxidation by hydrogen peroxide, (2) an equalization basin, (3) two activated sludge units operated in series with clarifiers after each, and (4) a sand filter for final suspended solids removal prior to discharge of the water to Yellowleaf Creek. A more detailed accounting of the design and operation of this plant is given by Sapp [6]. Takeoff points for the ORNL PDU were the equalization storage tank and the clarified effluent from the settler downstream of the first stage bioreactor. Typical analyses of these two streams and the clarified effluent from the second stage bioreactor are given in

Table 1. The two source terms for the wastewater plant are (1) a high-strength waste system, which is protected from rainwater runoff (termed the caustic waste system); and (2) a low-strength waste, which originates from rainwater and process area runoff, boiler blowdown, and cooling-water blowdown (termed the liquid waste stream). The ORNL PDU was sited adjacent to the wastewater treatment plant. Water was pumped to the PDU from the two source points via a submersible sump pump.

TREATABILITY STUDIES

Two treatability tests were made with the PDU at the ACFL, the first (W-1) in February 1983 and the second (W-2) in May 1983. During W-1 and W-2, feedwater for performance of a carbon adsorption bed-depth/service-time study was obtained from the equalization basin. The carbon adsorption effluent was saved during W-1 and used as feed to the reverse osmosis (RO) unit; the RO feed for the W-2 study was obtained from the A-clarifier overflow stream after first-stage biotreatment. Ozonation studies were performed with equalization basin water (W-1 and W-2) and A-clarifier effluent (W-2 only). A summary of test results, by unit process, is given below. A detailed accounting of these studies is given elsewhere [7].

Carbon Adsorption

During both W-1 and W-2 campaigns, the carbon adsorption unit was operated on equalization basin feedwater to obtain bed-depth/service-time data using a regenerated Darco activated carbon which was supplied by Envirotrol, Inc. The carbon was obtained from the pool used at H-Coal to treat the low strength wastewater. Prior to system startup, the activated carbon was degassed at ~90°C for ≥6 h in the presence of water. This process was performed batchwise with each batch corresponding to one column volume. Following the degassing operation, the carbon was transferred to the appropriate column and back-flushed with tap water for ≥1 h. The resulting total bed depth was ~4.5 m (15 ft). Feedwater to the system was passed through the multimedia filter, diluted with the appropriate volume of tap water (campaign W-2 only) to produce a TOC concentration of ~150 mg/L, and then stored in the carbon unit feed tank. The pH of the tank contents was controlled by the addition of H_2SO_4. From the feed
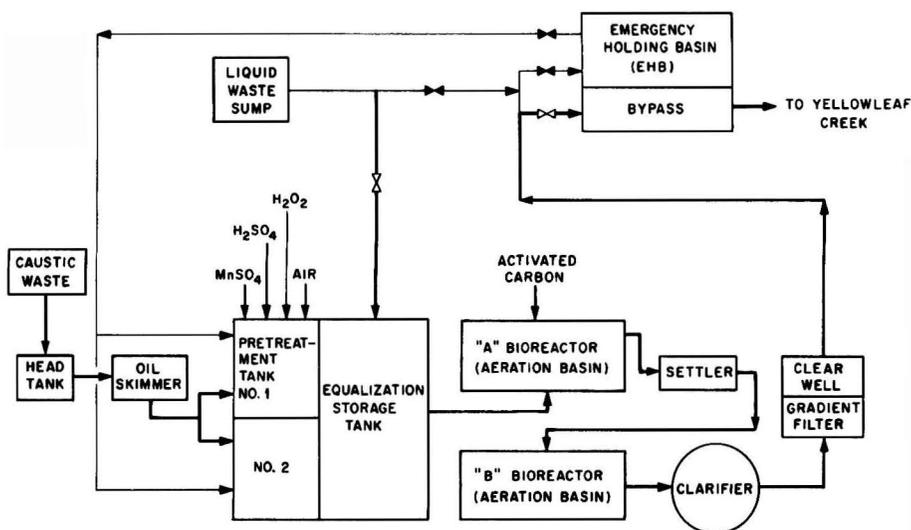
Figure 3. Wilsonville wastewater treatment system

| Origin | pH | COD (mg/L) | | TSS (mg/L) | Alkalinity[a] (mg/L) | TDS (mg/L) | Color (c.u.)[b] | TOC (mg/L) |
		Unfiltered	Filtered					
Bioreactor feed	9.9	1660	1510	67	1965	6840	2100	387
First-stage bioreactor effluent	8.2	183	77	93	133	7840	560	32
Second-stage bioreactor effluent	7.9	104	72	53	80	7300	424	27

[a] As CaCO₃.
[b] Standard color units.

tank the water was passed sequentially through 30-μm and 10-μm wound-polypropylene filters, then fed at a constant flow rate to the carbon unit. The operating conditions and feed characteristics for each test are summarized in Table 2. Each test was terminated when the pressure drop through the system exceeded available pumping head, indicating a blockage in one or more of the columns. Evidence from inspection of the adsorption carbon after the W-1 campaign indicated that biomass accumulation was probably the plug-causing agent [8]. The large swings in pH (from ~7 to 13 to 7) that occurred during W-2 caused precipitation of a gelatinous organic material on the carbon and subsequent plugging. The variation in pH was due to the mal-function of the pH control system on the system feed tank.

Concentration data obtained as a function of bed depth and time during each test were analyzed by the bed-depth/service-time method (BDST) [9], which results in values for the height and rate of movement of the adsorption wavefront (HMTZ and RMTZ, respectively). A typical set of BDST data is given in Figure 4. These data were obtained during run period 2 of campaign W-2. For a given fractional removal of color (1 — C/Co), Figure 4 enables the potential service time before breakthrough (ordinate) to be determined for a given bed depth (abscissa). The reciprocal slope of the BDST curve is the RMTZ, and the intercept of the curve with the abscissa is the HMTZ.

The BDST data are summarized in Table 3 for all monitored components. Comparison of the W-1 data with the W-2 data shows that the values calculated for HMTZ and RMTZ in campaign W-1 are less for all components that those obtained during W-2. This situation is due to the substantially lower contaminant concentrations encountered during W-1, yielding, as would be expected, lower bed ex-

haustion rates (RMTZ) and required bed depths (HMTZ). In assessing the W-2 data, it is apparent that the difference in pH between runs 1 and 2 (7.4 vs. 10.2) resulted in only minor variation in RMTZ but caused substantial increases in HMTZ. A value of maximum removal is given in Table 3 for each component. This value is the lowest C/Co obtained (generally early in a test) and is indicative of the ultimate cleanup potential by granular activated carbon (GAC). These data indicate a non-adsorbable fraction for each component except phenol, which is nearly completely removed. The low removal of COD is indicative of a high fraction of inorganic COD, and the maximal values of 60 to 80% for TOC and color indicate a significant amount of nonadsorbable organic material.

To assess the removal of organic compounds by GAC, samples were taken and analyzed by a method developed by Maskarinec et al. [10]. The results of these analyses are shown in Figure 5, where gas chromatographic (GC) scans of the GAC aqueous feed and effluent are compared with those for a standard sample containing a wide variety of organic compounds. Each compound in the standard is present at a concentration of ~20 mg/L. The wastewater samples were concentrated by a factor of ~250 before injection in the gas chromatograph. The TOC of the feed is 37 mg/L and consists primarily of compounds between tetrahydronaphthalene and tetrachlorobiphenyl [as shown in Figure 5(a)]. As shown in Figure 5 (c), the effluent contains essentially no compounds that show up on a GC scan. The residual TOC is 6 mg/L, which indicates that some compounds incapable of being chromatographed and/or some nonadsorbable organic species are present, possibly organic acids, many of which are not readily adsorbed [11].

TABLE 2. NOMINAL OPERATING CONDITIONS FOR EACH CARBON
ADSORPTION TEST

| Parameter | Campaign W-1 | Campaign W-2 | |
		Period 1	Period 2
Aqueous flow rate, mL/s	63	62	66
Aqueous temperature, °C	22	26	27
Feed parameters:[a]			
TOC, mg/L	50	130	155
pH	7.2	7.4	10.2
COD, mg/L	380	810	805
Color[a]	345	580	950
Phenol, mg/L	7	32	31
TSS, mg/L	27	34	35

[a] Values given in standard color units (c.u.).

Figure 4. Bed-depth/service-time plot for color derived from data obtained during campaign W-2 run period 2.

TABLE 3. SUMMARY OF CARBON ADSORPTION BDST PARAMETERS

Parameter	Maximum removal (%)	C/Co	RMTZ[1] (cm/h)			HMTZ (cm)		
			Campaign W-1	Campaign W-2		Campaign W-1	Campaign W-2	
				Run 1	Run 2		Run 1	Run 2
COD	30	0.7	0.9	2.3	3.8	>35	130	250
Color	65-85[b]	0.5	0.6	3.4	1.3	50	65	191
Phenol	>95	0.1	0.34	1.8	1.8	48	64	54
TOC	60-70	0.5	1.5	2.4	1.9	28	65	131

[a] Average values.
[b] pH dependent.

OZONATION

Four different types of ozonation tests were performed at the ACFL to assess application of this treatment technique to the coal-liquefaction waste. Each of these tests is summarized below.

Purgeable Organics Test

This test was performed to evaluate the potential for simple air-stripping of contaminants from the wastewater. The ozone reactor was filled to the 50% level (~42 L) with equalization basin wastewater which was diluted 1:1 with process water. Ozone-free air was supplied by the ozone generator to the reactor at a gas flow rate of 28.4 std L/min. The reactor pressure was 135 kPa (5 psig).

Organic removal was measured in terms of TOC and COD. Initial values of these parameters were 150 and 760 mg/L, respectively. A linear decrease with time was mea-

sured in each case. After 30 min of sparging, the TOC was 130 mg/L (14% reduction) and the COD was 740 mg/L (3% reduction). GC scans before and after sparging indicated a 17% reduction in TOC, thus corroborating the TOC data.

Batch Ozonation Test

This test was performed to determine the amount of ozone required to completely remove or reduce contaminant concentrations to a steady-state value. TOC, COD, color, and phenol reductions were monitored during this test.

The ozone reactor was initially operated in the continuous-flow mode to allow the ozone generator to stabilize. A 1:1 dilution of equalization basin wastewater with process water was continuously fed to the reactor at 4.2 L/min, corresponding to a hydraulic residence time of ~10 min. The gas feed rate was 30 std L/min and had an

Figure 5. Trace-organic analysis of carbon adsorption feed (b) and effluent (c) as compared with a standard (a).

ozone (O_3) concentration of 9.8 mg/L. After three hydraulic residence times, the aqueous feed was stopped and the reactor was operated in the batch mode (hydraulically) with continuous gas feed. The initial values of TOC, COD, phenol, and color were 116 mg/L, 586 mg/L, 10 mg/L, and 745 c.u./L, respectively. Phenol and color were reduced to levels below the detection limits in less than 60 min and followed simple first-order kinetics. TOC and COD were reduced to steady values of 50 and 75 mg/L, respectively, in ~180 min. The COD and TOC reductions were found to take place via two first-order reaction regimes: an initial rapid-rate regime (first-order rate constant, k_1, ≈0.01 min^{-1} for TOC); and a second, much slower, regime (k_2 ≈0.002 min^{-1} for TOC). A representative first-order plot of TOC concentration reduction is given in Figure 6. A summary of the measured rate constant(s) for each constituent is given in Table 4. Neufeld et al. [12] reported similar behavior occurring during the ozonation of gasification wastewaters. The explanation for this behavior can be postulated as follows: The easily oxidized organics will be degraded rapidly, thereby exhibiting the inital fast reaction regime, while the refractory organics that were either formed during ozonation or were initially present in the wastewater will exhibit the slower reaction regime.

A second possible explanation for the two-regime behavior is that the initial high-rate regime is due to combined volatiles stripping and chemical reaction, while the second low rate regime is due to chemical reaction alone. The TOC removal rate for simple stripping is 0.7 mg/L min. The initial TOC removal rate in the reacting system, therefore, appears to be due partially (~65%) to stripping and partially (~35%) to chemical reaction. We hypothesize that, once all of the strippable material is removed, the subsequent removal is by chemical reaction alone—hence the reduced rate.

During the batch test, the ozone utilization efficiency decreased from ~75% during the first 30 min to ~10% after 240 min of operation. The TOC removal efficiency (cumulative TOC removed ÷ cumulative O_3 absorbed) was maximal at 70 min with a value of 0.2 g TOC/g O_3 absorbed, indicating that this is the point of maximum efficiency for the process. After 300 min, the TOC efficiency was 0.06 g per gram of O_3 absorbed.

Ozonation Matrix Test

A series of continuous-flow ozonation tests were performed to measure the effect of ozone dose rate (D_{oz}), pH, and hydraulic residence time (τ) on contaminant concentration reduction. A Box-Behnken [13] fractional factorial design was followed to perform these experiments,
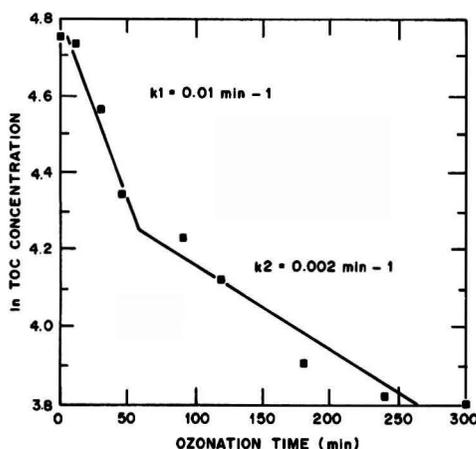
Figure 6. First-order kinetic plot of TOC concentration vs. ozonation time.

TABLE 4. SUMMARY OF KINETIC PARAMETERS FOR OZONATION OF ACLF WASTEWATER

Parameter	First order rate constant[a] (min^{-1})	
	k_1	k_2
Total organic carbon (TOC)	0.01	0.002
Chemical oxygen demand (COD)	0.02	0.004
Phenol	0.07	
Color	0.06	

[a] k_1 refers to the initial high-rate period, k_2 refers to the secondary low-rate period.

thereby reducing the required number of tests from 27 (full factorial) to 15. The range of variables tested is given in Table 5. The waste-water for these tests was taken from the "A" clarifier downstream of the first activated-sludge unit. The feed and effluent concentration ranges for the various constituents are given in Table 6.

A fractional removal of TOC in the range of 0.5 to 0.74 was measured at pH 3.4. At higher pH values, the fractional removal was substantially lower (0.18 to 0.35). Substantial color removal (85 to 100%) was attained at all except one set of conditions (pH = 7.3, D_{oz} = 3.3 mg/L min, τ = 10 min) where ~78% color reduction was measured. COD reduction tended to be greatest at low pH; however, a large amount of scatter in the data due to low concentrations prevented accurate analysis.

The TOC reaction rate surface is depicted in Figure 7. As shown, the reaction rate increases with decreased pH and τ. Over the range studied, D_{oz} had minimal effect since ozone was always present in excess. The surface shown in Figure 7 was generated from a second-order polynomial in pH and τ. The response surface for color has similar features. Actual maximum reaction rates were measured to be 1.3 mg/L min and 25 c.u./L min for TOC and color, respectively. The increase in reaction rate at low residence time is likely due to the predominance of the rapid initial reaction and stripping phemonena discussed in the previous section. For the color causing constituents the effect of reaction with ozone is likely to be more pronounced than the stripping effect. The color molecules are normally high molecular weight organics with low volatility.

TABLE 5. RANGE OF VARIABLES TESTED IN THE OZONATION MATRIX TEST

Variable	Value		
	Low	Medium	High
pH[a]	3.4	7.3	9.6
D_{oz}[b]	3.3	5.8	8.2
τ[c]	10	30	50

[a] Aqueous-phase pH.
[b] Ozone dose rate (mg/L · min).
[c] Hydraulic residence time (min).

TABLE 6. FEED AND EFFLUENT CHARACTERISTICS DURING THE MATRIX TEST

Characteristic	Range of concentration (mg/L)	
	Feed	Effluent
TOC	20-40	10-25
Color	200-270[a]	0-70[a]
COD[b]	10-100	0-38
Phenol	<1	<1

[a] Standard color units (c.u.).
[b] Values lower than 100 are subject to large analytical error.
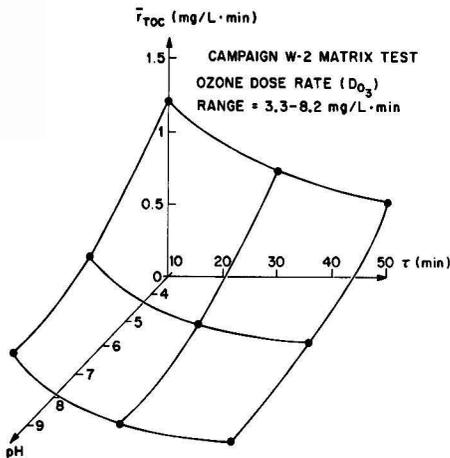
Figure 7. Ozonation reaction-rate response surface for total organic carbon.

TOC and color removal efficiencies (mass of contaminant removed divided by mass of O_3 input) were enhanced at low residence time and low pH. Ozone absorption efficiency tended to be greatest at low residence time and dose rate and high pH. As noted above, TOC removal efficiency was greatest at low pH. Ozone decomposes at significant rates at high pH ($t_{1/2} = 0.5$ min at pH 10.4, $t_{1/2} = 41$ min at pH 7.6) [13]. The apparently higher efficiency at high pH may primarily be the result of ozone decomposition rate being greater than the ozone/TOC reaction rate.

Effect of Ozonation on Adsorption Efficiency

Samples of ozonation feed and effluent were taken during the ozonation matrix test and subjected to carbon adsorption in batch isotherm tests using Darco regenerated carbon. A sample volume of 50 mL was added to a flask containing 4.4 to 118 mg of activated carbon. The flasks were then shaken in a shaker bath that was maintained at 25°C for 3 h. The amount adsorbed was calculated by analyzing the liquid phase before and after adsorption.

The unozonated feed TOC was reduced from ~40 mg/L to ~20 mg/L by adsorption. The ozonated sample contained ~20 mg/L TOC and was unaffected by adsorption. Evidently, the adsorbable constituents present in the feed were removed by ozonation.

REVERSE OSMOSIS TESTING

The objectives of the RO testing program were to demonstrate the capability for processing coal conversion wastewater through commercially available RO units, to measure process performance, and to identify potential operating problems.

Two different RO membranes were successfully tested: a spiral-wound cellulose acetate unit manufactured by Osmonics, Inc. (model 192T-97CA), and a hollow-fiber module sold by Dow Chemical Co. (XFS 43260.00 LP). The design specifications for the Osmonics membrane are 97% Na^+ rejection at 1000 mg/L NaCl in the feed, 25°C, 2.76 MPa (400 psig) membrane pressure, and 10% recovery; the permeate rate is 9.2 mL/s at the stated conditions. The Dowex XFS 43260.00 membrane module is designed to operate at a feed pressure of 1.72 MPa (250 psig). The design specifications for the module are a 197-mL/s (3.1 gpm) permeate flow rate with 92% Na^+ rejection when operated at standard test conditions of 1.72 MPa, 1500 mg/L NaCl, 25°C, and 75% feed recovery. The Osmonics unit was tested on equalization basin water before (test 3) and

after (test 1) carbon adsorption treatment and on water from clarifier A downstream of the first biotreater (test 4). The Dow unit was tested solely on carbon-adsorption-treated equalization basin wastewater (test 2).

Water pretreatment during each test consisted of the following steps:
1. Feedwater was collected in one of the 2.65-m³ (700-gal) storage tanks and the pH as controlled at ~5.5 via automatic addition of sulfuric acid.
2. Antiscalent (Pfizer Co. Flocon-100) was added to the feed tank at ~10 mg/L to help prevent formation of scale on the RO membrane.
3. The water was pumped from the feed tank sequentially through 10-μm and 5-μm cartidge filters for the reduction of suspended solids.

The test procedure consisted of baseline operation successively on water and wastewater, followed by operation on tap water at conditions identical to the first tap-water period. This procedure enabled identification of any decay in membrane performance.

A summary of feed water characteristics for each test is given in Table 7. The water for tests 1 and 2, obtained as carbon adsorption effluent, is very similar to the test 4 feedwater which is the effluent from the first biotreater. The major difference is TOC concentration, which is lower for the carbon unit effluent. The feed for test 3, obtained from the equalization basin, is more contaminated in terms of organic constituents (TOC and phenol) but is essentially the same for the inorganics as the test 1, 2, and 4 feed material. Data for the four test periods are summarized in Table 8.

The data from test 1 indicate stable operation at up to 75% feed recovery. Pre- and post-test tap water permeate flow rates were identical (8.8 mL/s), which compares favorably with the manufacturer's specification of 9.2 mL/s at 10% recovery and indicates no short-term fouling of the membrane. Measurements of TDS rejection at various recovery values indicate a decrease in rejection from 97% at 50% recovery to 84% at 74% recovery. This result is expected because of the increase in trans-membrane TDS diffusion rate due to the increased driving force afforded by the higher recovery. The TDS rejection value of 97% compares favorably with the manufacturer's value of 97% Na^+ rejection at 10% recovery.

Operation of the Dow module during test 2 indicates performance similar to the Osmonics unit in terms of component rejection. This module gave lower sulfate rejection (71 vs. 100%). In terms of organic rejection, ~70% of both TOC and color were rejected. After ~60 h of operation, the

TABLE 7. CHARACTERISTICS OF REVERSE OSMOSIS FEED AFTER PRETREATMENT

Component	Test number			
	1[a]	2[b]	3[c]	4[d]
pH	5.4	5.9	5.5	5.2
TOC, mg/L	7	11	50	24
COD, mg/L	—	—	382	56
Phenol, mg/L	—	—	20	0.8
Alkalinity,[e] mg/L	23	26	52	25
Calcium,[e] mg/L	72	54	60	62
Hardness,[e] mg/L	110	164	108	104
Sulfate, mg/L	315	2550	1705	1940
Conductivity, μS/cm	7750	1260	5930	4475
TDS, mg/L	5430	5220	3940	3125
SDI$_{15}$	—	5.8	—	—
Temperature, °C	17.5	22	25	28

[a] Osmonics unit operated on carbon adsorption effluent as feed.
[b] Dow module operated on carbon adsorption effluent as feed.
[c] Osmonics unit operated on equalization basin feed.
[d] Osmonics unit operated on A clarifier feed.
[e] As CaCO₃ equivalents.

TABLE 8. SUMMARY OF REVERSE OSMOSIS OPERATING DATA

Parameter	Test number			
	1	2	3	4
Operating time, h	71	96[a]	38	236
Membrane feed pressure, MPa (psia)	2.2-2.9 (315-415)	0.72-1.8 (105- 265)	2.9 (415)	2.9 (415)
Recovery, %	53-75	60-75	46	47-70[b]
Permeate flow rate,[c] mL/s				
Initial	8.8	74	10.7	12.1
Final	8.8	67[d]	e	10.1
		Recovery[g] (%)		
Rejection,[f] %	64	68	46	60
Conductivity	77	76	93	89
Total dissolved solids	92	91	97	95
Total hardness[h]	—	—	—	94
Alkalinity	57	51	88	71
Sulfate	100	71	—	94
TOC	86	72	67	86
Color	—	69	58	95
Phenol	—	—	52	76
COD	—	—	86	—

[a] At ~60 h, 0.95 L (1 quart) of motor oil from the feed pump introduced to the system.
[b] Most of test performed at 50-60% recovery.
[c] Tap water permeate flow rate; identical conditions for initial and final data acquisition.
[d] After cleaning with phosphoric acid cleaner; 51 mL/s before cleaning.
[e] No final tap water test due to equipment failure; permeate flow during test indicates stability.
[f] Rejection = (mass rate of contaminant in brine) ÷ (mass rate of contaminant in feed) × 100. Values in table refer to rejection of each component at the specified recovery.
[g] Recovery = (permeate flow rate ÷ feed flowrate) × 100.
[h] As CaCO₃ equivalent.

RO feed pump seals failed, dumping ~0.95 L (1 quart) of motor oil into the RO system. The immediate result was a decrease in permeate flow rate from ~70 mL/s to ~50 mL/s, indicating significant blockage of the membrane surface. Cleaning of the unit with phosphoric acid-based cleaner returned the permeate flow to 67 mL/s, giving a net decrease of 9.5% in permeate flow during the run. It is impossible to determine what fraction of this flow decline is due to oil vs. wastewater contamination. Trace-metal analyses of samples of the feed, permeate, and brine taken during operation indicate barium, iron, magnesium, and manganese as possible scale-causing agents, due to nonclosure of the individual element mass balances.

Test 3, which used the Osmonics module and equalization basin feedwater, was cut short because of a component failure in the RO unit. Operation was maintained for a ~38-h period, during which the data reported in Table 8 were taken. These data indicate higher inorganic component rejection than was measured in test 1. Rejection of TOC is slightly lower (67 vs. 86%) but at a significantly higher concentration (50 vs. 7 mg/L). The rejection of phenol, 52%, indicated that the phenol present is not simple monohydric phenol with a molecular weight of 92. The molecular weight cutoff for this membrane is ~200. Operational problems prevented the final tap-water test from being performed; therefore, a direct assessment of membrane performance could not be made. Inspection of the permeate flow rate-vs-time data indicates stable performance with no short term flux decline.

The final RO test was performed with an Osmonics membrane and utilized feedwater obtained from clarifier A. Following an initial run with tap water, the unit was placed on-line and operated for ~22 h at 50% recovery; at this time, the feed recovery was increased to 70%. After ~79 h of operation, a blockage occurred in the concentrate flow-control system which subjected the membrane to recovery values near 100%. The high-recovery period resulted in a decrease in productivity. After the membrane

had been cleaned with both phosphoric acid and iodoform cleaners, a tap-water permeate rate of 10.8 mL/s, or ~90% of the initial value, was obtained. Following cleaning, the unit was operated for the remainder of the test at ~60% feed recovery. Inspection of the data in Table 8 for test 4 indicates values of rejection for both organic and inorganic species nearly the same, or greater than, those measured in the previous tests. Trend plots of constituent rejection during the test showed no decrease in membrane efficiency. Membrane productivity declined by 16.5% during the test as indicated in Figure 8, where tap water permeate flow rate is presented as a function of time. About half of this decrease could be attributed to membrane compaction [14], leaving a decrease of ~8% due probably to contaminants adhering to the membrane. The data point at 121 h in Figure 8 was taken after the membrane had been cleaned.

The cleaning solutions were analyzed for metals before and after use to identify contaminants on the membrane. The resulting data, presented in Table 9, indicate that substantial levels of Al, Ba, Fe, K, Mn, Na, Cr, Cu, and Zn were present on the membrane. Visual inspection of the membrane showed a thin layer of brown solids deposited on the surface. Scanning electron microscope (SEM) analysis of a piece of the membrane resulted in the scans presented in Figure 9, which suggest significant increases of Al, Si, S, Cl, Ca, Cr, Fe, Cu, and Zn on the membrane surface. These data, in conjunction with the cleaning solution results in Table 9, tend to support each other and give a fairly detailed description of the metals present in the membrane deposits. In addition, they indicate the complex nature of the chemistry that one must deal with in treating coal conversion wastewaters via reverse osmosis.

CONCLUSIONS

Treatability studies were performed on the ACFL wastewater streams using the unit processes of carbon adsorption, ozonation, and reverse osmosis which were contained in the transportable ORNL wastewater treatment PDU.

Carbon adsorption treatment of the equalization basin wastewater was performed using regenerated Darco activated carbon. HMTZ and RMTZ data were obtained for low- and high-strength wastewater at pH~7 and for high strength wastewater at pH 10. Constituents monitored were TOC, color, phenol, and COD. Both HMTZ and RMTZ were found to increase with wastewater strength at pH 7. With the high-strength waste, variation in pH from 7
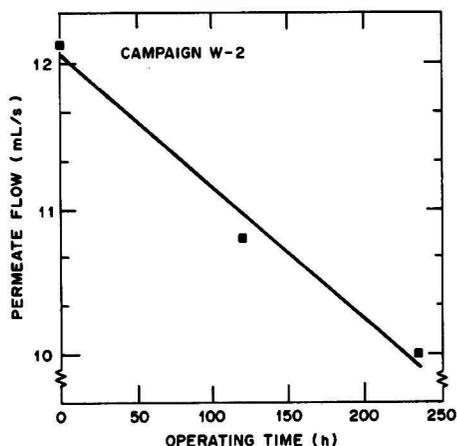
Figure 8. Membrane productivity decrease during RO testing in campaign W-2.

Metal	Contaminant concentration raw cleaning solution (mg/L)		Concentration increase (%)	
	CS cleaner	I2D cleaner	CS cleaner	I2D cleaner
Al	0.06	0.09	130	120
Ba	<0.005	<0.005	>118	>110
Fe	0.05	0.37	4450	1270
K	10.8	9.7	22	—
Mn	0.005	<0.001	5115	>4780
Na	9.3	6.5	270	20
Cr	0.13	<0.02	—	>50
Cu	<0.03	0.6	—	790
Zn	0.39	0.19	—	220

to 10 caused only minor changes in RMTZ but substantial increases in HMTZ. Maximum possible removals using GAC were found to vary from 30% for COD to >95% for phenol. A chromatograph of GAC effluent shows essentially no measurable components; yet ~6 ppm TOC (near the detection limit) remains, which is nonadsorbable and incapable of being chromatographed. This residual TOC could consist of organic acids that are known to be weakly adsorbed. Column plugging was encountered from two probable sources; biomass accumulation and chemical precipitation or organic material.

Results of ozonation tests indicate that 14% of TOC and 3% of COD can be removed from the equalization basin water by air-stripping in 30 min. A batch reaction test using ozone revealed a two regime first-order removal process for TOC and COD consisting of a rapid first step followed by a much slower second step. This is thought to be due to a combination of air-stripping and the presence of a range of organic compounds which have varied reactivities to ozone. During the batch test, color and phenol were reduced to below detection limits, via single-regime first-order kientics, in less than 60 min. In addition, TOC and COD were reduced to stable values of 50 and 75 mg/L, respectively, in 180 min. A continuous ozonation matrix test was performed to investigate the effects of pH, hydraulic residence time, and ozone dose rate. Substantial reductions in color were measured (85 to 100%) at nearly all conditions tested. TOC and color removal were found to be enhanced at low pH and hydraulic residence time and were relatively insensitive to ozone dose rate. Ozone ab-

sorption efficiency was enhanced at high pH; however, the ozone decomposition rate was also highest at high pH levels. The net effect was higher TOC removal at low pH. Carbon adsorption of pre- and post-ozonized samples indicated that ozone treatment removed the adsorbable TOC.

A spiral wound cellulose acetate RO membrane was tested on equalization basin water both before and after carbon adsorption treatment and on water from clarifier A. A hollow-fiber cellulose acetate module was tested on carbon adsorption treated equalization-basin wastewater.

Operation of both units on carbon adsorption effluent was satisfactory at feed recoveries up to 75%, with a total dissolved solids rejection of ~92%, and a TOC rejection of 72 (hollow-fiber) to 86% (spiral wound). Throughout the duration of the test, no degradation in productivity was measured for the spiral-wound module; however, a 9.5% decrease was measured for the hollow-fiber unit.

Operation of the spiral-wound unit on equalization basin water indicated no short-term decline in productivity and rejections of TDS and TOC of 97 and 67%, respectively.

The final test of the spiral-wound unit on clarifier A overflow was made over a period of 236 h. As before, component rejections showed no measurable decline during the test. Productivity declined by ~17% and was unaffected by cleaning with phosphoric acid or iodoform cleaners. Chemical analysis of the cleaning solutions and SEM inspection of the membrane surface indicate that a wide variety of inorganic constituents deposited on the membrane. These materials were either present in the feed as colloidal material or were precipitated during RO concentration.

Time constraints of the project allowed 236 h to be the maximum length of the RO test. Although this test length provides more information on membrane performance than shorter tests do, it would be necessary to make a much longer test (~6 mo) for accurate performance definition. At this time it is not known if the trend shown in Figure 8 continues or if the membrane productivity would stabilize after further operation.

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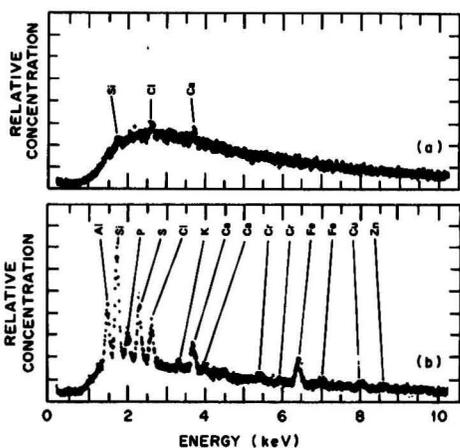
Figure 9. Scanning electron microscope analysis of Osmonics reverse omosis membrane: (a) clean and (b) contaminated.

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Bench-Scale Treatment of Lurgi Gasifier and H-Coal Wastewaters by the PACT System

A revealing progress report on the continuing effort to develop a cost-effective process for the production of synfuels by the coal-gasification route.

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Synfuel production wastewaters originate from condensate streams, washwaters, and runoff, and contain a variety of pollutants which pose a significant treatment challenge. For facilities where wastewaters are treated for discharge, a wastewater treatment process which can economically and reliably produce an acceptable effluent quality is required. Where wastewater reuse is desirable, the wastewater treatment system becomes an integral part of the overall production facility and must be selected to provide high reliability and sufficient removal of total organics to allow such reuse.

Due to the waste constituents present in most synfuels wastewaters and the need to provide effective wastewater treatment prior to reuse or discharge, much attention has been focused on the PACT wastewater treatment system [1, 2, 3, 4, 5, 6]. The PACT system employs the addition of powdered activated carbon to the aeration basin of the activated sludge process (Figure 1). Powdered activated carbon addition enhances removals of adsorbable organics and toxics, permitting improved biological oxidation and nitrification of these wastewaters. Improved treatment stability is obtained by the adsorption of shock organic loads. When carbon regeneration is used in conjunction with the PACT system, secondary biological sludge disposal is eliminated and spent powdered carbon is regenerated for reuse.

Evaluations by Castaldi and Ford [3] have shown the PACT system and Wet Air Regeneration combination to be cost-effective for treatment of Lurgi gasifier wastewaters compared to activated sludge systems employing waste sludge incineration or land disposal of waste sludges. Other studies have shown that reliable treatment is obtained with PACT and Wet Air Regeneration combination [6, 7].
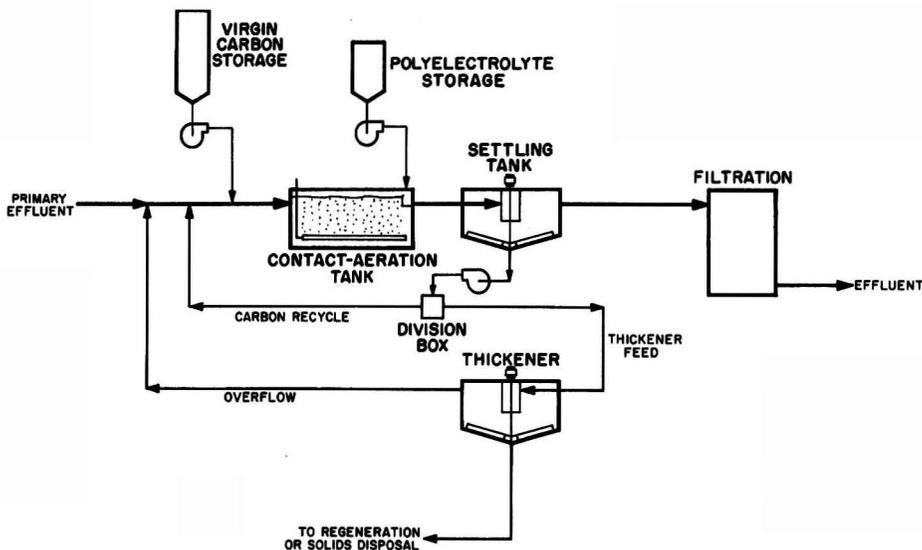
Figure 1. PACT wastewater treatment system. General process diagram.

This paper discusses the results of PACT and Wet Air Regeneration treatability studies performed on wastewaters from two synthetic fuel production processes: the Lurgi/Mobil M Process and the H-Coal Process.

The Lurgi Pressure Gasification process is used to produce synthesis gas which is further processed into chemical feedstock and liquid fuels including gasoline. The wastewater contains ammonia, phenols, organic acids, and a variety of other organics. Laboratory treatability studies were performed on a mixture of Lurgi gasifier wastewater obtained from SASOL in South Africa and a synthesized Mobil M process (methanol-to-gasoline) wastewater. The Lurgi wastewater had been phenol extracted and ammonia stripped prior to treatment studies.

The H-Coal coal liquefaction process is one of several promising synthetic fuels production technologies currently under development. The H-Coal process converts coal catalytically to hydrocarbon liquids such as gasoline and fuel oil. The process wastewater contains ammonia, phenols, and other organics. The H-Coal process wastewater used in this study was obtained from the H-Coal liquefaction pilot facility in Catlettsburg, Ky, and was phenol extracted and ammonia stripped prior to treatment studies.

EXPERIMENTAL

Equipment

Bench-scale treatment was performed using 2- to 4-liter circular acrylic aeration chambers with external clarifiers (Figure 2). The clarifiers were acrylic Imhoff cones with open bottoms. Humidified air was introduced at the bottom of the aeration chambers and was used for both aeration and mixing. Supplement mixing was provided by mechanical mixers. Peristaltic pumps provided waste feeding, clarifier underflow recycle, and pH control (when automatic pH controllers were used). Sludge recycle rates were about 200 percent of the feed flow to minimize the amount and residence time of sludge in the clarifier. Clarified effluent overflowed from an effluent port and was collected in 9-liter glass bottles.

Feed Preparation

The Lurgi/Mobil M feed consisted of a mixture of 8 parts of phenol extracted, ammonia stripped gas liquor from a Lurgi gasifier and 3 parts of a synthesized Mobil M

(methanol-to-gasoline) wastewater. This composition duplicated the waste from a proposed production facility. The Lurgi wastewater was collected at SASOL in South Africa in nitrogen-blanketed drums, shipped by air freight to Rothschild, Wis., composited, and rebarreled for cold storage prior to use in the laboratory and pilot testing.

The Mobil M wastewater was synthesized according to the coal to be processed in the production facility. The major components of the Mobil M waste were organic acids (acetic, propionic, butyric, and valeric acid), methanol, ethanol, acetaldehyde, acetone, methyl ethyl ketone, other aldehydes and ketones, and unleaded gasoline.

Two batches of Lurgi gasifier wastewater were used during the study. Analyses are given in Table 1 for each batch and for the 8:3 Lurgi/Mobil M mixtures. The second batch of Lurgi wastewater was supplemented with additional organic acids (896 mg/liter acetic, 230 mg/liter propionic, 128 mg/liter n-butyric, and 26 mg/liter n-valeric acids) to maintain the target concentration of 1600 mg/liter organic acids in the stripped liquor.

H-Coal process wastewater was collected during an H-Coal pilot plant production run at approximately 220 tons/day of Kentucky #9 and Illinois #6 coals and normal washwater and steam rates. To accomplish NH_3-N removal, NaOH was added to the H-Coal pilot plant ammonia steam stripper during the wastewater collection period. The raw wastewater was subsequently phenol
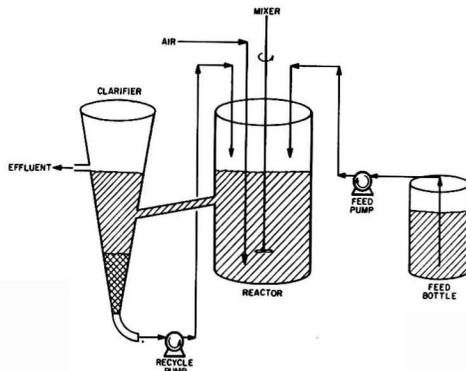
Figure 2. Bench-scale PACT system.

TABLE 1. ANALYSES OF LURGI/MOBIL M FEED SAMPLES

Sample	Phase I Waste		Phase 2 Waste	
	Lurgi	Lurgi/Mobil M	Lurgi	Lurgi/Mobil M*
COD, mg/liter	1090	1560	722	2270
BOD$_5$, mg/liter	269	708	132	1344
Soluble Organic Carbon, mg/liter	356	296	181	—
Total Solids, mg/liter	1000	1400	360	—
Total Ash, mg/liter	600	200	360	—
Total Volatile Solids, mg/liter	400	1200	0	—
Suspended Solids, mg/liter	28	70	17	—
Suspended Ash, mg/liter	<5	30	<5	—
Volatile Suspended Solids, mg/liter	>23	40	>12	—
TKN, mg/liter	229	152	107	98.9
NH$_3$-N, mg/liter	137.8	103	98.7	69.8
NO$_3$-N, mg/liter	<1.0	<1.0	4.6	<1.0
NO$_2$-N, mg/liter	<1.0	<1.0	<1.0	<1.0
CN-N, mg/liter	15.8	10.8	10.5	7.5
SCN-N, mg/liter	18.8	10.0	11.7	7.9
Total Phenols, mg/liter	7.63	6.7	3.76	2.6
Volatile Acids, mg/liter	330	400	320	1600
True Color, APHA Units	1822	1150	2615	367
pH	7.6	4.8	7.5	4.0

* Spiked with Volatile Acids.

solvent extracted by Chem-Pro Inc. The waste was transported to Rothschild, Wis. by refrigerated trailer and, upon receipt, was maintained in refrigerated storage throughout the treatment study.

The individual drums of ammonia stripped, dephenolated waste were individually run through the PACT systems. Variation in the wastewater characteristics (COD, BOD$_5$, DOC) were observed during the studies due to differences in the waste from drum to drum. The analysis of H-Coal wastewater from an individual drum is reported in Table 2.

The ammonia nitrogen concentration in the stripped, dephenolated H-Coal wastewater was 3.47 mg/liter NH$_3$-N. Since one goal of the study was to demonstrate nitrification, the feed was spiked with ammonium chloride to obtain 150 mg/liter NH$_3$-N. The feed pH was adjusted to 8.0 to minimize ammonia volatilization. pH controllers with 2.2 M KHCO$_3$/NaOH buffer were used to maintain mixed liquor pH values in the 8 to 8.5 range.

Both Lurgi/Mobil M and H-Coal wastewaters were analyzed for macro and micro-nutrients. Nutrients which were deficient, based on values cited in the literature [8, 9, 10], were: Mn, Cu, Zn, Mo, Mg, Co, Ca, K, Fe, and P.

Operation

Units were operated at 20 + 2°C either by use of immersion heaters or by housing in a constant temperature cabinet. Control of mixed liquor pH to a range of 6.5 to 8.5 was accomplished through either acid or base addition.

Prepared feed was kept mixed using magnetic mixers. Hydraulic detention times (HDT) were maintained by adjusting feed pump flow rates. In most cases the feed and sludge recycle pumping was intermittent and was controlled by interval timers. This allowed the use of relatively high flow rates which minimized plugging in tubing.

Reactor operation was initiated using seed mixed liquor from a local municipal activated sludge system. For the Lurgi/Mobil M study, feed pumping was started at the full design pumping rate with few acclimation problems noted. In the H-Coal study, the reactors were seeded with municipal activated sludge, mixed liquor from a previous PACT system synfuels treatment study, and mixed liquor from an activated sludge system to which H-Coal pilot plant waste was being fed. Acclimation in the H-Coal study was accomplished over a three-week period by

TABLE 2. NH$_3$ STRIPPED AND PHENOL EXTRACTED H-COAL WASTEWATER CHARACTERIZATION

Parameter	Result	Parameter	Result
pH	10.3	CN, mg/liter	2.2
COD, mg/liter	1945	SCN, mg/liter	29.0
BOD, mg/liter	834	SO$_4$-S, mg/liter	19.5
DOC, mg/liter	521.6	S Total, mg/liter	2.2
Phenol (C$_6$H$_5$OH), mg/liter	175	Alkalinity (as CaCO$_3$), mg/liter	600.6
Phenol, Total, mg/liter	259	Soluble K, mg/liter	1.90
Total Solids, mg/liter	2650	Soluble Na, mg/liter	797.2
Total Ash, mg/liter	1980	Total Ca, mg/liter	1.8
Suspended Solids, mg/liter	1.9	Soluble Ca, mg/liter	0.8
Suspended Ash, mg/liter	<0.9	Total Mg, mg/liter	0.4
Color, APHA	9014	Soluble Mg, mg/liter	0.25
TKN, mg/liter	39.4	Total Fe, mg/liter	3.42
NH$_3$-N, mg/liter	3.47	Soluble Fe, mg/liter	2.70
NO$_3$-N, mg/liter	<1.0	Soluble Mn, mg/liter	0.18
NO$_2$-N, mg/liter	<1.0	Soluble Cu, mg/liter	0.03
P Total, mg/liter	1.78	Soluble Zn, mg/liter	0.22
Soluble Chloride, mg/liter	697	Soluble Mo, mg/liter	<1.0
		Soluble Co, mg/liter	0.01

steadily increasing the proportion of H-Coal wastewater in domestic primary effluent until 100 percent H-Coal wastewater was achieved.

Units operated in the Lurgi/Mobil M study included a conventional activated sludge system, a single stage PACT system, and a two-stage PACT system. In the H-Coal study, single stage and two-stage PACT systems were operated. For the two stage studies, settled effluent from the first stage unit was used as feed to the second stage.

Daily operation of the biological reactors included measurement of effluent volume, mixed liquor pH, dissolved oxygen, and oxygen uptake rates. Sludge was wasted daily from the aeration basin to maintain the target solids residence time. This resulted in a slightly shorter SRT value than desired since solids were also lost from the system via the effluent and mixed liquor sampling. Reported SRT's account for these losses.

Mixed liquor wasted from the PACT system pilot units was regenerated daily in 316 stainless steel laboratory autoclaves at 230 to 240°C for 60 minutes. The wet air regenerated carbon slurry was sampled for volatile suspended solids—assumed equivalent to the volatile activated carbon—and returned to the aeration basin. This analysis was used to calculate the amount of carbon returned to the biological system and the weight of virgin makeup carbon (Hydrodarco H) needed to maintain the desired carbon dose.

Analyses

The analytical routine for the pilot plants involved daily sampling of the mixed liquor and regenerated carbon for volatile suspended solids and three mixed liquor samples per week for determination of biomass and activated carbon concentrations using the nitric acid digestion technique. Effluent samples were analyzed daily for suspended solids and ash. Three samples of feed and effluent per week were analyzed for the following parameters:

COD	Total Ash
BOD₅	Phenols
TKN	Total CN⁻
NH₃-N	SCN⁻
NO₃-N	SO₄-S
NO₂-N	pH
Total Solids	Color

Effluent samples were 24-hour composites. Feed analyses were performed on unfiltered samples while effluent analyses, except for suspended solids and ash, were performed after filtration through 0.45-μm membrane filters to simulate effluent filtration. In addition, feed and effluent dissolved organic carbon (DOC) was measured in the H-Coal study.

All analytical procedures used were according to Standard Methods [11], or the EPA Methods for Chemical Analysis of Water and Wastes [12]. Some minor procedural modifications were made to eliminate interferences or provide for the use of automated analytical equipment. Biomass and carbon concentrations were determined by a nitric acid digestion technique developed by Zimpro Inc. Priority pollutants were analyzed by EPA Method 624 and 625 using GC/MS [13].

Hydantoins

To investigate the fate of hydantoins, wet air oxidation of a Lurgi-type gasification wastewater was conducted using 500-ml titanium autoclaves. 5,5-Dimethylhydantoin was quantified by reverse-phase liquid chromatography using a variable wavelength u.v. detector at 220 nm. The mobile phase was 100% water at 1.2 ml/min and 1300 psig. Two 10-μ Spherisorb ODS columns (4.6 mm × 250 mm) con-

nected in series gave a k value of 2.65 for 5,5-dimethylhydantoin. Sample size was 10 μl.

A PACT system isotherm was performed by contacting the gasification wastewater (diluted 1:5) with varying doses of virgin Hydrodarco H powdered activated carbon plus concentrated biomass from a municipal activated sludge system. Sample slurries were mixed and aerated for two hours, then vacuum filtered. The filtrates were analyzed for 5,5-dimethylhydantoin.

RESULTS AND DISCUSSION

Lurgi/Mobil M Wastewater Treatment

Four bench-scale pilot plants were operated on the Lurgi/Mobil M wastewater. One unit was operated as a conventional activated sludge system without waste solids handling. Two pilot plants were operated as single stage PACT systems and a fourth pilot plant provided two-stage PACT treatment. Two study phases were evaluated. During Phase 1—a screening test only—the Lurgi/Mobil M waste contained a low volatile acids concentration and a BOD/COD ratio of 0.45. SRT values were comparable for all units (Table 3) but the hydraulic detention times for the PACT systems were less than half the activated sludge unit.

Only limited performance data was collected for Phase 1 (Table 4). Comparison of COD removals indicate a significant improvment in performance with PACT treatment. Color actually increased across the activated sludge system. Excellent color removal was demonstrated with the PACT systems. As indicated by the nitrogen data, partial nitrification was achieved in the PACT units during

TABLE 3. PILOT SYSTEM OPERATING CONDITIONS LURGI/MOBIL M WASTEWATER TREATMENT

Unit	Single Stage		Two Stage PACT	
	Activated Sludge	PACT	Stage 1	Stage 2
Phase 1				
HDT, hrs.	53	24	26	24
SRT, days	16.7	19.5	18.8	17.1
Mixed Liquor Volatile Carbon g/liter	0	13.7	5.1	2.5
Biomass, g/liter	1.6	2.3	3.6	0.7
Phase 2				
HDT, hrs.		24	7	24
SRT, days		36.3	7.6	29.0
Mixed Liquor Volatile Carbon g/liter		18.3	6.2	11.8
Biomass, g/liter		6.8	8.0	1.1

TABLE 4. PERFORMANCE SUMMARY—PHASE 1 LURGI/MOBIL M WASTEWATER TREATMENT

Unit	Single Stage		Two Stage PACT*
	Activated Sludge	PACT	
COD, mg/liter			
Feed	1560	1580	1560
Effluent	256	110	94
% Removal	83.6	93.0	94.0
Color, APHA			
Feed	1150	1012	1150
Effluent	1786	117	153
% Removal	—	88.4	86.7
NH₃-N, mg/liter			
Feed	103	104	103
Effluent	105	87.8	92.8
% Removal	—	15.6%	9.9%

* % Removals for overall two-stage treatment.

Phase 1 while little nitrification occurred in the activated sludge unit.

During Phase 2, detailed pilot studies of the PACT system were conducted on a second quantity of gasifier wastewater. The activated sludge pilot system was not operated due to the high effluent COD levels. This waste was less concentrated than the first gasification waste (Table 1). During Phase 2, the gasification wastewater was spiked to 1600 mg/liter volatile acids to simulate the expected gasification liquor characteristics on the production run coal. This resulted in a higher feed COD than in Phase 1. The detention time and the SRT's for the single stage PACT system and second stage PACT system were increased to 36.3, and 29.0 days, respectively (Table 4). The HDT and SRT of the first stage of the two stage PACT unit were shortened to 7.4 hours and 7.6 days, respectively. The mixed liquor carbon levels were increased in the Phase 2 studies.

Since the treatment objectives during Phase 2 were to nitrify and produced a low effluent soluble COD concentration, increased SRT's were appropriate for the nitrification stages and higher carbon dose rates were examined.

Phase 2 performance data (Table 5) shows effective COD and color removals, and phenol, cyanide, and thiocyanate reductions with the PACT systems. Essentially complete ammonia removals were observed in the single stage and two stage PACT systems. In the two stage PACT system, the bulk of the organic removal occurred in the first stage while nitrification occurred in the second stage. Substantial denitrification was also apparent.

Hydantoin Removal   Hydantoins are heterocyclic compounds, believed to be formed by reaction of ketones or aldehydes with ammonia, carbonate, and cyanide [14] (Equation 1):

$$R_2C=O + NH_3 + HCN \rightarrow R_2C\stackrel{NH_2}{\underset{CN}{}} + CO_2 \rightarrow$$

(1)
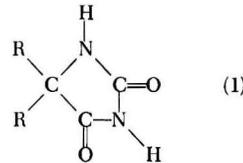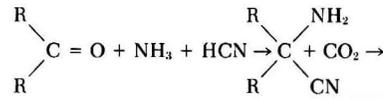
This class of compound is characterized by high water solubility and resistance to biodegradation. 5,5-Dimethylhydantoin ($R=CH_3$) was reported as the major hydantoin constituent in a Lurgi gasifier wastewater [14]. Hydantoins were not specifically analyzed during this Lurgi/Mobil M study. However, a small sample of a gasification liquor obtained from another source contained approximately 2600 mg/liter hydantoins.

The destruction of hydantoins at wet air regeneration conditions was investigated using 5,5-dimethylhydantoin analyzed by liquid chromatography. The results (Table 7) show that wet oxidation of the wastewater at 240°C for 60 min. results in nearly 95% destruction of 5,5-dimethylhydantoin. In addition, the oxidized waste BOD_5 was markedly increased and the BOD_5/COD ratio, a measure of biodegradability, also increased.

A PACT system isotherm, using Hydrodarco H powdered activated carbon plus concentrated biomass, was also performed on a 1:5 dilution of the gasification liquor to simulate treatment by PACT. The isotherm plot of 5,5-dimethylhydantoin (Figure 3) shows this compound to be adsorbable. Higher molecular weight hydantoins, with layer alkyl groups, should be more efficiently adsorbed compared to the dimethyl compound.

TABLE 6. WET AIR OXIDATION OF A GASIFICATION LIQUOR[1]

	Feed	Oxidation Product
5,5-Dimethylhydantoin, mg/liter	2254	127
5,5-Dimethylhydantoin Removal, %	—	94.4
COD, g/liter	6.26	4.80
COD Removal, %	—	23.3
BOD_5, g/liter	0.789	2.38
BOD_5/COD	0.126	0.496

[1] Oxidation at 240° for 60 minutes.

TABLE 5. PERFORMANCE SUMMARY—PHASE 2 LURGI/MOBIL M WASTEWATER TREATMENT

Unit	Single Stage PACT	Two Stage PACT*
COD, mg/liter		
Feed	2270	2270
Effluent	45.6	53
% Removal	98.0	97.7
BOD_5, mg/liter		
Feed	1344	1344
Effluent	<6	<4
% Removal	>99.6	>99.7
Phenols, mg/liter		
Feed	2.6	2.6
Effluent	<0.1	<1.0
% Removal	>96.1	>96.2
Color, APHA		
Feed	367	367
Effluent	39	69
% Removal	89.4	81.2
CN-N, mg/liter		
Feed	7.5	7.7
Effluent	0.08	0.11
% Removal	99.0	98.5
SCN-N, mg/liter		
Feed	7.89	7.89
Effluent	<0.48	0.50
% Removal	>93.9	93.7
TKN, mg/liter		
Feed	98.9	98.9
Effluent	5.5	5.7
NH_3-N, mg/liter		
Feed	69.8	69.8
Effluent	<1.1	<1.0
NO_3-N, mg/liter		
Feed	<1.0	<1.0
Effluent	21.8	44.4
NO_2-N, mg/liter		
Feed	<1.0	<1.0
Effluent	<1.0	<1.4

*% Removals are for overall two-stage treatment.

TABLE 7.
PACT SYSTEM OPERATING CONDITIONS H-COAL WASTEWATER TREATMENT

Single Stage

Phase	1	2	3
HDT, hrs.	24	25	24
SRT, days	23.3	25.1	23.3
Mixed Liquor Volatile Carbon, g/liter	13.4	16.7	21.8
Biomass, g/liter	6.1	5.2	8.2

Two Stage

Phase	1		2	
Unit	Stage 1	Stage 2	Stage 1	Stage 2
HDT, hrs/.	9	24	9	23
SRT, days	4.5	21.2	4.3	22.8
Mixed Liquor Volatile Carbon, g/liter	8.2	15.1	11.5	7.7
Biomass, g/liter	4.4	1.2	5.4	1.6
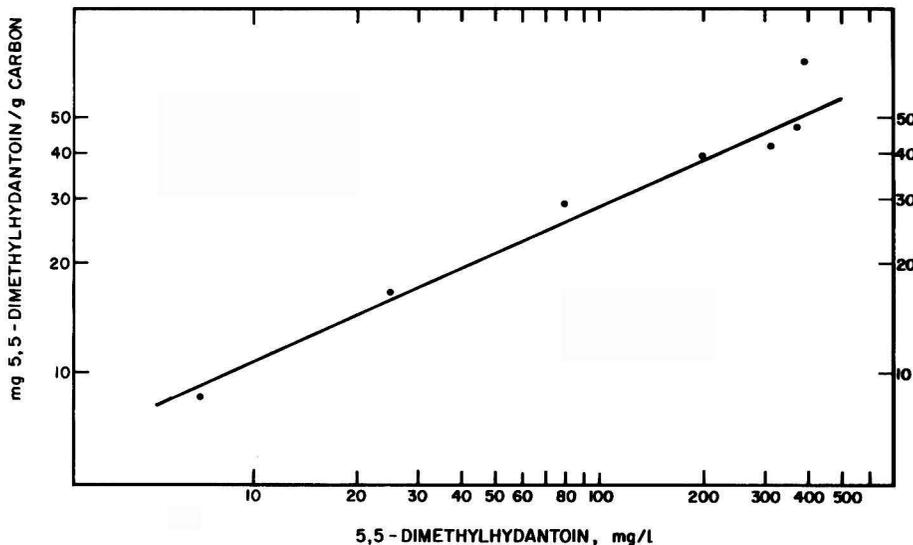
Figure 3. Lurgi-type wastewater diluted 1:5. Isotherm of 5,5-dimethylhydantoin.

H-Coal Wastewater Treatment

Single and two-stage bench-scale H-Coal PACT systems were operated at the conditions listed in Table 8. Only the mixed liquor volatile carbon levels varied in the three phases of single stage PACT system operation. A two-stage PACT system was operated for two phases at different carbon concentrations. In Phase 1, the second stage mixed liquor volatile carbon concentration was much higher than the first stage while in Phase 2, the first stage carbon concentration was higher than the second stage.

Performance data for the single stage PACT system is reported in Table 9. Performance was similar for all three phases, suggesting that the optimum mixed liquor carbon level was at or below the ranges tested. Phenol removal greater than 99 percent was observed for all three single stage pilot tests. Essentially complete nitrification was observed for all three of the single stage PACT system pilot plants.

Two-stage PACT system treatment of the H-Coal wastewater (Table 10) was more effective than single stage treatment. The two stage system net hydraulic detention time was longer and two stages of carbon contact were provided. The second stage provided polishing for organics removal and nitrification. Significantly improved color removals were also observed for two-stage treatment.

In terms of organic removal (COD, BOD, DOC, phenol, color), it appeared that the Phase 1 condition, with a lower carbon level in the first stage and a high carbon level in the second, provided better performance than Phase 2, in which the carbon levels were essentially reversed. As with single stage PACT system treatment, nitrification was essentially complete in the two-stage system and occurred primarily in the second stage. SRT and HDT values for the first stage were too short for nitrification.

Priority pollutants were analyzed on a sample of the H-Coal wastewater feed and on a composite sample of the bench-scale two-stage effluent. Only phenol and 2,4-dimethylphenol were found in the H-Coal feed (Table 11). Effluent levels were below detection limits (10 μg/liter). Phthalates were found in both the feed and effluent, probably resulting from plastics used in handling the wastes during the study. A comparison of the GC/MS ion chromatograms for the base/neutral and acid fractions of the feed and effluent (Figures 4 and 5) show significantly fewer compounds present in the effluent.

Stress Tests

Stress tests were performed on the H-Coal bench-scale treatment units to simulate changes in raw wastewater feed characteristics based on possible upstream production process failures. The stress tests simulated an ammonia stripper failure, an ammonia stripper caustic addition failure, and a phenol extraction failure, and are described in Table 11.

Ammonia Stripper Failure Stress Test   Stripper failure would result in sour-water ammonia nitrogen and sulfide levels of 750 and 100 mg/liter and cyanide and thiocyanate levels of 50 and 100 mg/liter. Normal steady state feed concentrations of the NH_3-N, H_2S, CN-N, and SCN-N through the H-Coal study averaged about 145, <10, 1, and 6 mg/liter, respectively. To monitor PACT system response, effluent samples were collected every three hours during the stress test and daily for several days afterwards.

A plot of nitrogen data versus time for the single stage effluent (Figure 6) shows a steady increase in effluent NH_3-N to a maximum near 300 mg/liter. Following the stress test, NO_3-N levels decreased and NO_2-N increased markedly until nitrite was the dominant nitrogen form. The sum of NO_3-N and NO_2-N remained fairly constant. The single stage PACT system returned to normal effluent ammonia levels in 6 to 7 days following the stress condition.

The single stage system effluent BOD_5 and total phenol concentration remained constant through the test period. However, the effluent COD and DOC levels did increase—likely resulting from analytical interferences due to the high nitrite levels. Low effluent COD and DOC concentrations were obtained in a few days. Increased effluent total cyanide and thiocyanate concentrations were observed, perhaps due to nitrite toxicity.

The two stage PACT system showed delayed and less pronounced response to the ammonia stripper failure than the single stage system. The effluent ammonia showed a gradual increase through the test with the NO_2-N concentration increased to a maximum of approximately 100 mg/liter. The peak NO_2-N level occurred 4 days after the stress test (Figure 7).

In the 4 to 6 days following the stress test, the effluent ammonia concentration returned to a low level (<1 mg/liter as N). The effluent NO_3-N and NO_2-N concentra-

TABLE 8. Single Stage PACT System Performance H-Coal Wastewater Treatment

Phase	1	2	3
COD, mg/liter			
Feed	1731	1780	1876
Effluent	376	303	300
% Removal	78.3	83.0	84.0
BOD$_5$, mg/liter			
Feed	724	708	706
Effluent	9	<7	12
% Removal	98.7	>99.0	98.4
DOC, mg/liter			
Feed	498	519	493
Effluent	119	76	90
% Removal	76.1	85.3	81.7
Phenols, mg/liter			
Feed	241	227	268
Effluent	2	0.9	1.7
% Removal	99.2	99.6	99.4
Color, APHA			
Feed	9443	10360	8488
Effluent	3799	2710	2844
% Removal	59.8	73.8	66.5
TKN, mg/liter			
Feed	173	186	203
Effluent	11.9	9.8	11.0
% Removal	93.1	94.7	94.6
NH$_3$-N, mg/liter			
Feed	134.4	149	149.4
Effluent	<1.1	<2.4	<1.5
% Removal	>99.2	>98.4	>99.0
CN-N, mg/liter			
Feed	1.18	1.06	1.08
Effluent	0.11	0.39	0.18
% Removal	90.9	63.2	83.5
SCN-N, mg/liter*			
Feed	6.78	5.0	8.19
Effluent	1.18	0.93	1.75
% Removal	82.6	81.4	78.7
NO$_3$-N, mg/liter			
Feed	<1.0	<1.1	<1.2
Effluent	152.2	187	179.1
NO$_2$-N, mg/liter			
Feed	<1.0	<1.0	<1.0
Effluent	<1.4	<1.0	<1.1

* SCN data suspect due to analytical interference.

TABLE 9. Two Stage PACT System Performance H-Coal Wastewater Treatment*

	Phase 1	Phase 2
COD, mg/liter		
Feed	1780	1792
Effluent	186	219
% Removal	89.6	87.8
BOD$_5$, mg/liter		
Feed	708	716
Effluent	<6	<6
% Removal	>99.2	>99.2
DOC, mg/liter		
Feed	519	496
Effluent	43.2	49.7
% Removal	91.7	90.0
Phenols, mg/liter		
Feed	227	254
Effluent	0.61	1.05
% Removal	99.7	99.6
Color, APHA		
Feed	10360	9008
Effluent	881	1349
% Removal	91.5	85.0
TKN, mg/liter		
Feed	186	185
Effluent	5.0	6.7
% Removal	97.3	96.4
NH$_3$-N, mg/liter		
Feed	149	140.7
Effluent	<1.4	<1.4
% Removal	>99.1	>90.0
CN-N, mg/liter		
Feed	1.06	1.14
Effluent	0.20	0.15
% Removal	81.1	86.8
SCN-N, mg/liter**		
Feed	5.0	7.4
Effluent	0.6	1.4
% Removal	88.0	87.8
NO$_3$-N, mg/liter		
Feed	<1.1	<1.1
Effluent	175	163.5
NO$_2$-N, mg/liter		
Feed	<1.0	<1.0
Effluent	<18.5	1.0

*% Removals are for overall two-stage treatment.
** SCN data suspect due to analytical interference.

tions required a somewhat longer period (6 to 7 days) to return to normal levels, as did effluent cyanide and thiocyanate. The effluent total phenols showed no significant change during this stress test. The effluent COD and DOC concentrations increased during the two stage stress test, again, possibly due to nitrite interference. No increase in effluent BOD was observed. The effluent DOC level returned to normal levels within about 3 days.

Ammonia Stripper Caustic Failure The second stress test on the bench scale PACT system pilot units treating H-Coal waste simulated a loss of caustic feed to the ammonia stripper. The test objective was to increase the PACT system feed ammonia concentration to 750 mg/liter and maintain biological nitrification. Increases in feed ammonia concentrations of 25 percent every 2 or 3 days were planned over a period of several weeks.

The single stage PACT system effluent NH$_3$-N concentration remained at a lower level throughout the ammonia stripper caustic failure stress test (Figure 8). Conversion of ammonia nitrogen was not inhibited at feed NH$_3$-N levels of up to 570 mg/liter; however, the ammonia was converted in large part to NO$_2$-N and not to NO$_3$-N. The test was terminated at 570 mg/liter in the single stage system to begin the subsequent phenol stress test.

Single stage effluent COD levels increased as feed ammonia levels increased, due possibly to inhibition of the organisms responsible for carbonaceous COD reduction,

TABLE 10. H-Coal Wastewater Treatment Priority Pollutants—Two Stage PACT Treatment—Phase 1 (All Values in µg/L)

Compound	Feed	Pact Effluent
Phenol	185,000	<10
2,4-dimethylphenol	51	<10

TABLE 11. Stress Tests H-Coal Process Waste Single and Two Stage PACT Systems

Stress Test	NH$_3$ Stripper Failure	NH$_3$Stripper Caustic Failure	Phenol Extraction Failure
Time to Reach Maximum	8 hrs.	25% increase every 3 days	8 hrs.
Duration	10 hrs.	20 days with NH$_3$-N > 550 mg/liter	10 hrs.
Time to Decrease	8 hrs.	—	8 hrs.
NH$_3$-N, mg/liter	750	750	150
H$_2$S, mg/liter	100	5	5
Phenolics, mg/liter	230	230	2660
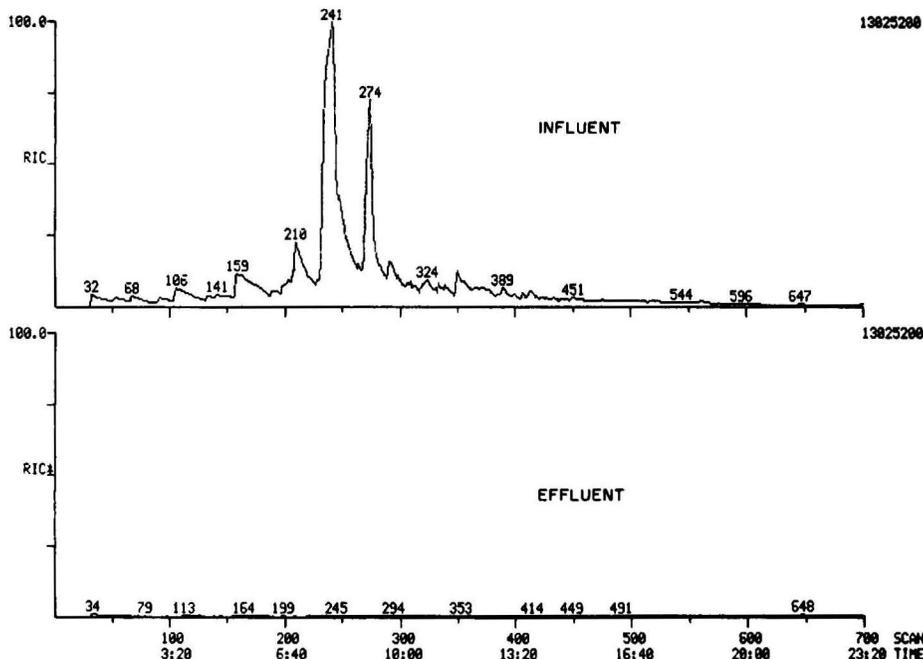
Figure 4. PACT/wet-air regeneration performance. Synfuels wastewater—GC/MS acid fraction profile.

or oxygen demand from the high effluent nitrite nitrogen concentrations. The COD method used did not include protection against nitrite oxygen demand.

The effluent BOD_5 levels did not increase during the stress test. A BOD_5 increase due to nitrite would not be expected since the BOD method used inhibits nitrification. The effluent DOC level did not show significant variation except that a higher DOC level was observed over a

one-week period. Variations of this magnitude had been observed during steady state operation; thus a definite correlation between the caustic failure and effluent DOC could not be made.

A small increase in the single stage PACT unit effluent total phenols concentration from less than 2.5 mg/liter to a maximum of 6.3 mg/liter was observed during the ammonia-stripper caustic failure test. The relationship be-
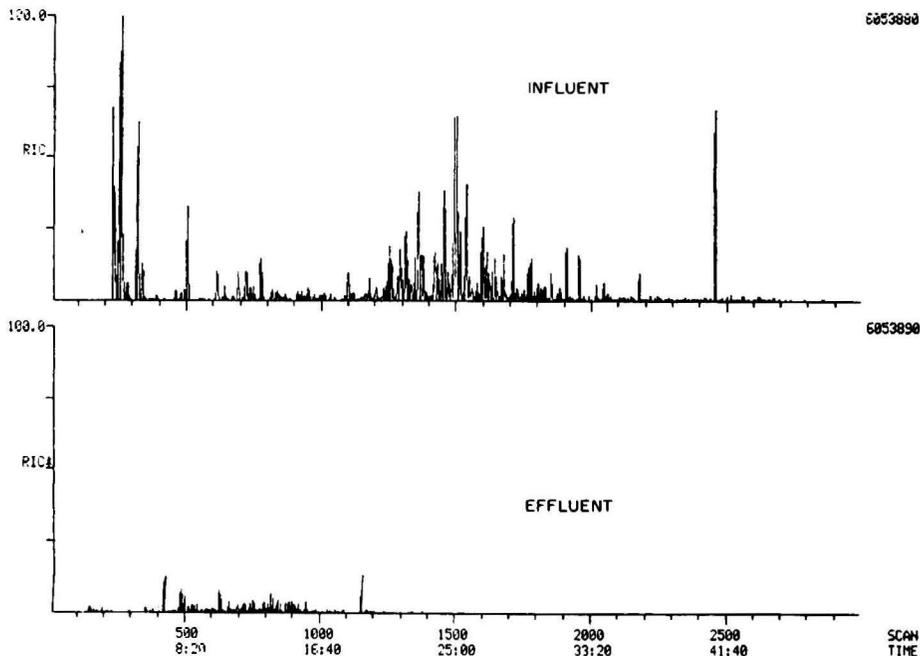
Figure 5. PACT/wet-air regeneration performance. Synfuels wastewater—GC/MS base/neutral fraction profile.
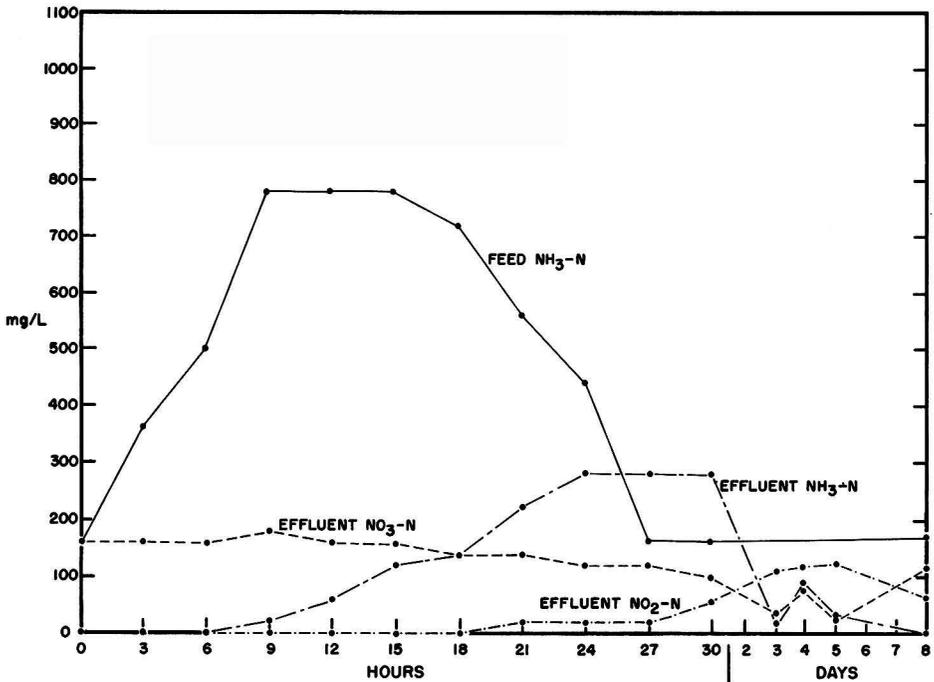
Figure 6. Stress test: ammonia-stripper failure. Single-stage PACT. H-coal process waste.

tween spike ammonia concentrations and increased effluent phenols has been observed in other studies and has not been fully explained.

The performance of the two stage PACT system was similar to that of the single stage PACT system during the

caustic failure test. For most of the test period, the effluent NH₃-N level was at a low concentration with complete conversion to NO₃-N. As the feed wastewater NH₃-N concentration approached 600 mg/liter, increased effluent NH₃-N was observed. At this point the feed NH₃-N con-
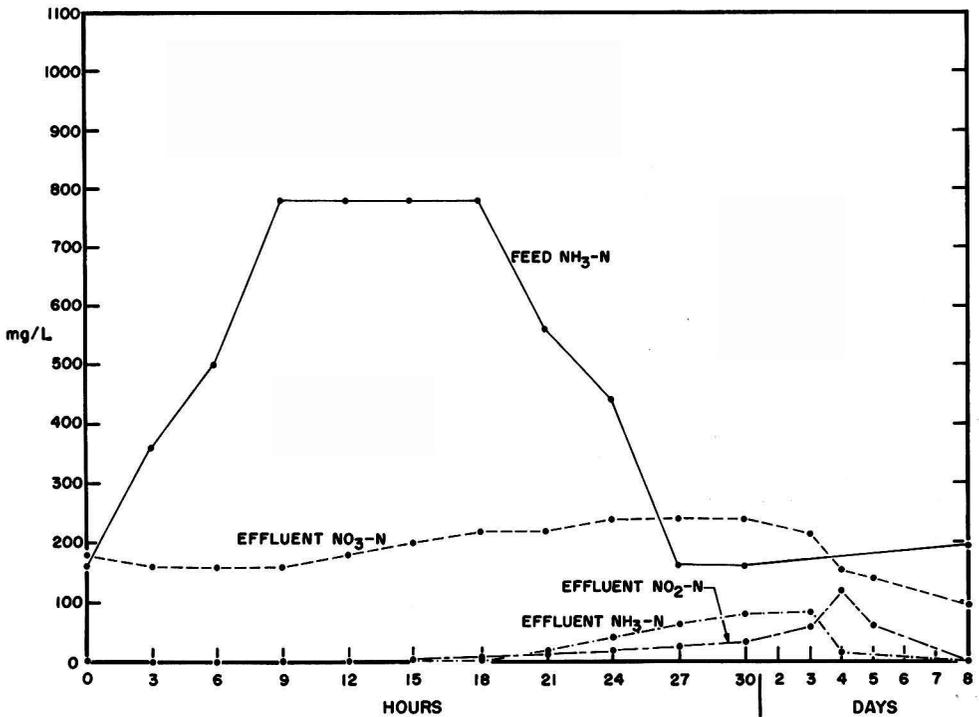
Figure 7. Stress test: ammonia-stripper failure. Two-stage PACT. H-coal process waste.
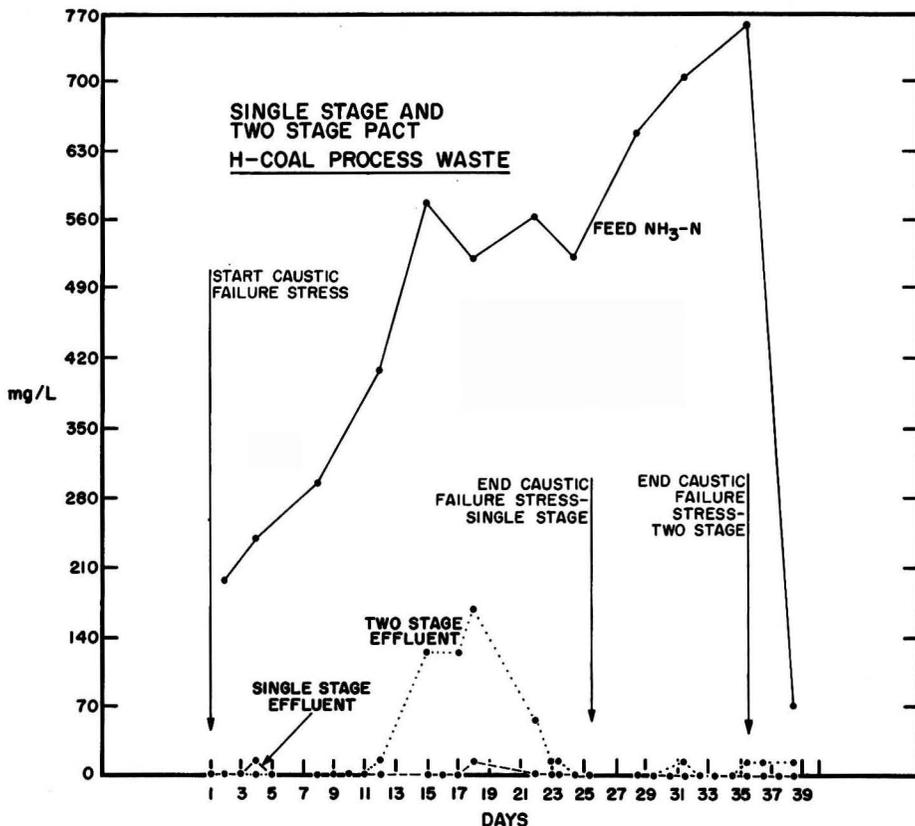
Figure 8. Stress test: ammonia-stripper caustic failure. Single-stage and two-stage PACT. H-coal process waste.

centration was held constant to allow acclimation. Complete ammonia reduction was again established and the stress test was continued.

For the remainder of the stress test, nitrite was the dominant second stage effluent nitrogen form. The predominance of nitrite in both the single-stage effluents during the caustic failure stress test, and to some extent in the stripper failure stress test, suggests inhibition of the second step—nitrite to nitrate—in the nitrification process by ammonia or by the nitrite formed in the first step of the nitrification process.

The two stage PACT system effluent BOD_5 and DOC levels were not affected by the stress test. However, second stage effluent COD concentrations higher than the first stage effluent were noted, confirming COD interferences by the increased nitrite concentration.

Second stage effluent phenols increased to as high as 7.7 mg/liter during the second half of the stress test compared to an average of 1.05 mg/liter during steady state treatment. The fact that this increase appeared only after high levels of nitrite were also present again suggests that nitrite may be involved in the slight inhibition of phenol removal observed.

Upon termination of the caustic failure stress tests the single and two stage PACT systems returned to typical treatment performance.

Phenol Extraction Failure   Two stress tests were performed to evaluate the PACT system response to failure of the sour water phenol extraction process. In the first stress test, feed containing 1440 mg/liter phenol was feed to the single-stage PACT unit. In the second test, wastewater feed containing 2660 mg/liter phenol was fed to both the single stage and two stage PACT systems. Effluent

samples were taken every three hours during the stress tests and daily for several days afterwards to gauge system response.

The stress test at 1440 mg/liter phenols to the single stage PACT system showed virtually no effect on the effluent phenol levels or effluent BOD_5, COD, or DOC concentrations. The subsequent stress test in the single and two stage PACT units at 2660 mg/liter phenol also indicated no adverse effect on effluent phenol levels (see Figure 9). Decreases in total effluent nitrogen and increases in oxygen uptake rates were observed for both systems during this stress test. The decrease in effluent nitrogen was attributed to nutrient uptake. These data indicate that the PACT systems were capable of quickly assimilating large increases in feed phenol levels in the H-Coal sour water by carbon adsorption of the phenol, followed by biological degradation of the adsorbed phenol.

CONCLUSIONS

As a result of the bench-scale studies, larger scale pilot tests of the PACT system and Wet Air Regeneration were conducted to develop design data for Lurgi gasifier/Mobil M and the H-Coal process wastewaters [15]. The PACT systems consistently nitrified these wastes in both single and two stage flow schemes, providing effluent NH_3-N concentrations less than 1.0 mg/liter. The two stage PACT systems demonstrated the best overall removal of total organics (COD, DOC) and should be considered where total organics removal is required for wastewater reuse.

Stress testing performed on the H-Coal sour water verified that treatment with the PACT system provides continuous, reliable treatment resistant to synfuels pro-
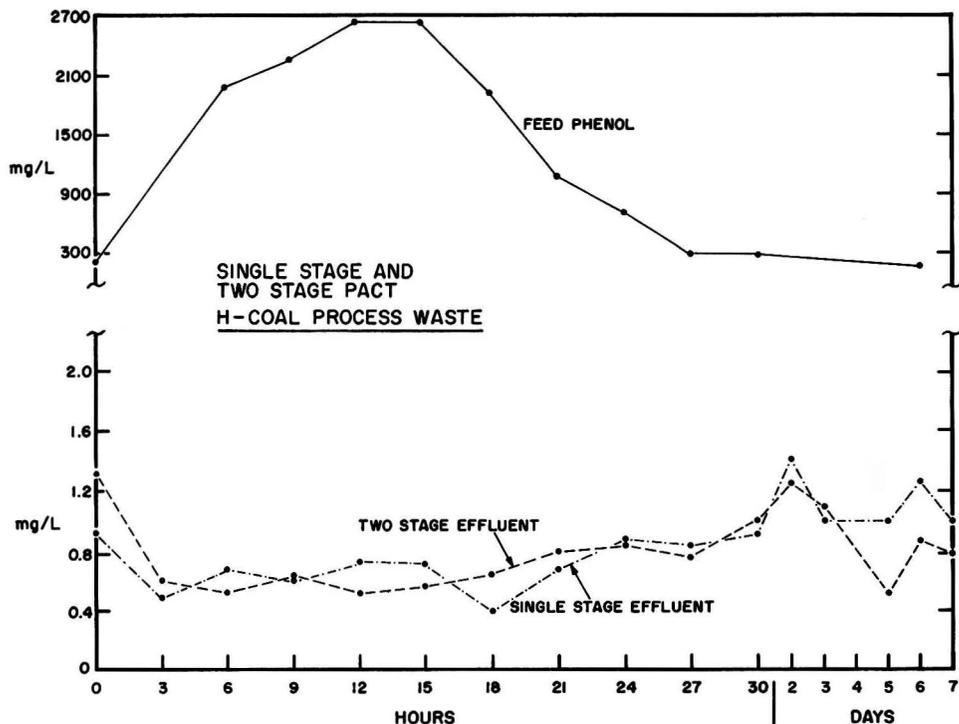
Figure 9. Stress test: Phenol-extraction failure. Single-stage and two- stage PACT. H-coal process waste.

duction facility upset or process failure. Following each stress test, the PACT system returned to optimum treatment within 2 to 4 days.

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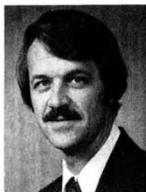
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Biooxidation of Coal Gasification Wastewaters

Fixed-film, fluidized-bed bioreactors have been used successfully to treat dilute synthetic and actual wastewaters for long periods of time.

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

The major portion of the dissolved organics can be removed by using conventional biooxidation processes such as activated sludge [2] or trickle filters. However, these conventional processes require relatively large capital investments and large land areas, are subject to environmental stress (temperature, rainfall), and may produce environmental stress (aerosols, odors).

An alternative technology for biooxidation of dissolved organics is the fixed-film, fluidized-bed bioreactor. This technology, which is currently under development at Oak Ridge National Laboratory [3-6](ORNL), offers several advantages relative to conventional biooxidation technologies. Lower capital costs are projected since the high density of retained cells enables high organic removal rates at low hydraulic retention times and thus permits smaller reactors. The fixed films are expected to provide improved resistance to shock and toxins relative to suspended growth systems, as evidenced by work done at ORNL with similar fixed-film systems. Health and environmental effects associated with open-air systems are minimized by the use of closed-reactor systems with off-gas control.

Process development work is being carried out to demonstrate the technical feasibility of this process for coal gasification wastewaters. Two laboratory-scale bioreactors have been constructed and successfully operated for more than 1 year to treat synthetic wastewaters. Dilute actual wastewaters have been treated continuously for approximately 9 months. Bioreactor performance, batch kinetic studies, and development, characterization, and preservation of the microbial culture are described in this report.

EXPERIMENTAL PROCEDURES

Bioreactor Design

The laboratory-scale bioreactor, shown in Figure 1, is a glass column 5 cm ID and 1.5 m tall with a water jacket for temperature control. There is a solids disengaging zone at the top, with an angled effluent discharge arm to allow solids to return to the main column. Recycle of solids or liquid is possible if desired. Two reactor systems of this type have been operated.

The solid support particles chosen for the initial process development work are 30-60 mesh anthracite coal. The wastewater treatment industry has historically used coal for fixed-film processes, and considerable earlier work at ORNL with other biological fluidized-bed applications indicated that anthracite coal is especially effective for retaining stable fixed films. Coal is less dense than sand (another common support), which allows fluidization at a lower liquid velocity and hence permits a smaller reactor for a given contact time.

A minimum liquid flow rate of 0.021-0.024 m^3/h is necessary to fluidize the bed and to allow adequate gas flow without slugging. This corresponds to a superficial linear velocity of ~13 m/h. Pure oxygen gas is introduced at the bottom of the bioreactor through a metal frit at a flow rate of typically 0.012 m^3/h, or about 50% of the liquid flow rate. This flow rate is sufficient to maintain ~0.005 kg/m^3 of dissolved oxygen in the liquid phase above the bed. The reactor is equipped with a dissolved oxygen probe and a pH probe.
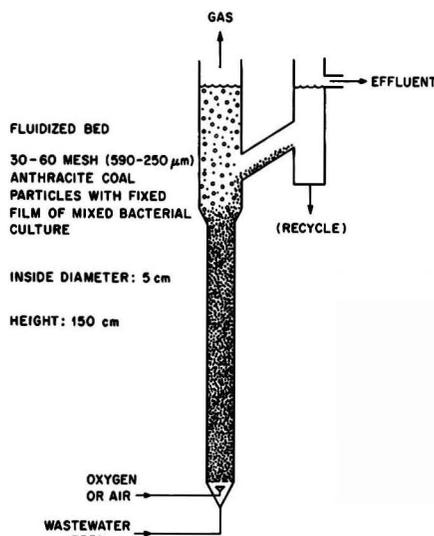
Fig. 1. Fixed-film, fluidized-bed bioreactor

Phenobac® (Polybac Corporation, Berlin, N.J.) was selected as the inoculum for initial studies. Earlier work at ORNL had shown this culture to be effective for phenol degradation in a fixed-film mode [5]. A mixture of BICHEM® 1001 and 1002 (Sybron/Biochemical, Salem, Va.) also has been evaluated. Once fixed films are established on coal particles, samples of the cultures are readily preserved by lyophilization.

Analytical Techniques

Five-milliliter samples of influent and effluent were collected and filtered immediately through a 0.45-μm filter (Millipore). Analyses were ususally done immediately; however, freezing and storage of the samples for several days had no effect on the phenol assay. Phenol was determined colorimetrically using the 4-aminoantipyrine (4-AAP) method [7]. Chemical oxygen demand (COD) was determined using the Hach procedure [8]. Total organic carbon (TOC) was determined using a Beckman 915A TOC analyzer with a Beckman 865 infrared analyzer. Thiocyanate was determined by a modified form of the method described in *Standard Methods* [9]. Polyhydric phenols were determined periodically by high pressure liquid chromatography (HPLC) [10].

Bioreactor Start-up

The start-up procedure, which is quite straightforward, is based on experience at ORNL and consultations with vendors such as Sybron. First, the bioreactor is filled with clean coal plus a synthetic phenol feed solution [11] containing ~0.2% whey and 0.2% dibasic sodium phosphate, and an inoculum of the culture is added. The bioreactor is then operated at total recycle at ~0.024 m³/h. Phenol is added periodically to maintain a concentration of 0.05-0.10 kg/m³. After approximately 4 days at 30°C, films can be seen on the coal with the aid of a microscope. At this point, a gradual change from total recycle to zero recycle is effected over a several-day period while maintaining a constant flow rate of ~0.024 m³/h through the bed. The growth of the films continues for 1-2 weeks, at which time a durable film is achieved. Excess cell mass is shed naturally due to the mechanical shearing action; in addition, it is quite practical to shear excess films from the coal in a separate device if necessary [6]. This start-up procedure has also been successfully demonstrated using coal-biomass inocula that were removed from the operating reactor several months earlier and stored as lyophilized preparations.

Batch Kinetic Studies

Batch kinetic studies were carried out in 500-ml Erlenmeyer flasks that were baffled at the base to promote mixing. Biomass-laden coal was removed from an operating bioreactor and washed three to five times with the basic mineral salts medium. Five to twenty milliliters (settled volume) of the washed biomass-coal particles was combined with mineral salts medium to a volume of 90-95 ml in the flasks and agitated at 165 rpm in a temperature-controlled water bath. Air or O₂ (~0.005 m³/h) was intro-duced through a tube extended below the liquid level. After temperature equilibration (300-600 s), phenol was added to initiate the reaction. The concentration and the volume of the added phenol solution were adjusted to give the desired initial phenol concentration and a total reaction volume of 100 ml. Aliquots were removed from the reaction flasks at intervals, briefly centrifuged to remove particulates, and analyzed for residual phenol using the 4-aminoantipyrine assay.

Coal Gasification Wastewaters

Raw wastewaters were obtained from the Holston Army Ammunition Plant in Kingsport, Tennessee, and from the Morgantown Energy Technology Center (METC). The wastewaters were stored at 4°C without further treatment. Characteristics of these raw wastewaters are shown in Table 1. The METC water contained a significant quantity of oil (~2%) which was removed with a cartridge fiber media filter prior to use. The raw water was diluted 1X to 5X to form a feed concentrate, to which salts and micronutrients were added [11]. This concentrate was further diluted with process water as it was fed continuously to the bioreactor. Relatively dilute wastewaters containing 0.01-0.02 kg/m³ of phenols were used initially to minimize stress on the culture. The concentration of phenols was increased gradually over ~3 weeks by reducing the process water diluent. Maximum concentrations of phenolics in the bioreactor were 0.01-0.2 kg/m³. The higher value corresponds to a feed stream of ~5% METC wastewater with 80% effluent recycle.

RESULTS

Bioreactor Performance

Typical operating data with Holston and METC wastewaters are shown in Table 2. The Polybac-initiated bioreactor has been operated successfully for more than 1 year with no significant problems. After short-term downtimes (leaks, holidays, minor repairs, etc.) the system recovers within several days to original performance levels. Effluents with phenol concentrations of <0.001 kg/m³ have been obtained in this reactor with influent phenol in the 0.030-kg/m³ range and a hydraulic retention time in the bed of ~240 s. This result and the data obtained in the kinetic batch studies described below indicate that higher phenol concentrations could probably be reduced to <0.001 kg/m³ by using a longer residence time. The volumetric removal rate for phenol is defined as the difference between the influent and the effluent concentrations, multiplied by the liquid volumetric flow rate and divided by the settled bed volume in the bioreactor. Performance of a similar Sybron-initiated bioreactor has been comparable to that of the Polybac-initiated bioreactor.

Several campaigns were carried out with a synthetic wastewater in which the liquid flow rate was increased from 0.024 m³/h to ~0.060 m³/h in 0.012-m³/h increments. Typical results (Table 3) show that the degradation rate increases substantially with flow, which suggests a liquid-solid mass transfer effect. This is reasonable in view of the typical correlation of mass transfer coefficient with particle Reynolds number, N_{Re_p}, such as

TABLE 1. CHARACTERISTICS OF RAW WASTEWATERS

	COD (kg/m³)	TOC (kg/m³)	Phenols (kg/m³)		pH
			HPLC[a]	4-AAP[a]	
Holston	23.6	6.8	3.1	2.33	7.86
METC	50.0	6.7	8.8	6.0	8.5

[a]See text.

Holston wastewater[a]

Phenols (4-AAP)			Thiocyanate		
Concentration (kg/m³ × 10³)		Degradation rate (kg/m³ bed · d)	Concentration (kg/m³ × 10³)		Degradation rate (kg/m³ bed · d)
Influent	Effluent		Influent	Effluent	
20	2	9.9			
33	4	16.3	22	13	5.0
32	13	12.7	23	20	2.2
66	23	15.8	43	31	6.2
83	39	16.6	49	41	2.9
95	58	17.3			

METC wastewater[b]

Phenols (4-AAP)

Concentration (kg/m³ × 10³)		Degradation rate (kg/m³ bed · d)	Liquid flowrate (m³/h × 10³)	Effluent recycle (%)
Influent	Effluent			
25	3	13.2	35	75
40	8	17.0	38	41
38	12	22.5	47	61
39	19	13.0	35	56
52	25	16.1	40	33
66	35	14.3	31	41
65	41	14.8	37	79
147	129	10.9	37	79
202	180	16.4	43	80

[a]Bed volume 1.7-2.8 × 10⁻³m³; temperature, 30°C; flow rate, 45-51 × 10⁻³m³/h; no effluent recycle.
[b]Bed volume, 1.3-1.7 × 10⁻³m³; temperature, 30°C.

$$N_{Sh} = 2.0 + 1.5 \, (N_{Sc})^{1/3} \, [(1 - \epsilon) \, N_{Re_p}]^{1/2},$$

where N_{Sh} is the dimensionless mass transfer coefficient, N_{Sc} is the Schmidt number, and ϵ is the liquid void fraction in the bed. Although ϵ increases with liquid velocity, the dependence is approximately to the <0.3 power [12]. The rate of oxygen transfer from the liquid to the organisms on the particle surface, as calculated using this correlation for the mass transfer coefficient, is of the same magnitude as the observed phenol degradation rates when the molar O_2:phenol stoichiometric ratio of of 7:1 is considered. This ratio of 7:1 applies to complete conversion of the carbon, hydrogen, and oxygen in phenol to carbon dioxide and water. Thus, it seems likely that the performance of the bioreactor is limited by transfer of dissolved oxygen to the particle surface.

The effect of O_2 in the gas phase on the phenol degradation rate was examined using synthetic wastewater. A brief summary of the results is presented in Table 4. The gas flow rates were increased for the air + O_2 and air only tests in order to increase the gas-liquid mass transfer coefficient. However, the decreased oxygen concentration in the gas decreases the driving force for mass transfer which more than offsets the increased $K_L a$. Note that, for the 50:50 air: O_2 mixture, the gas flow rate was increased by ~40% relative to the pure O_2 case while the O_2 concentration is decreased by ~40%. Thus, the total oxygen throughput was the same in both cases. The net result of decreasing the oxgen concentration in the influent gas is a decrease in phenol degradation rate (i.e., the bioreactor is oyxgen-limited).

A dissolved oxygen probe placed in the liquid above the bed generally indicates substantial dissolved oxygen in the reactor effluent. In the experiments above, the measured effluent dissolved oxygen decreased with decreasing O_2 concentrations in the influent gas.

TABLE 3. EFFECT OF LIQUID FLOW RATE ON BIOREACTOR PERFORMANCE[a]

Volumetric flow rate (m³/h × 10³)	Phenol concentration (kg/m³ × 10³)		Volumetric phenol removal rate (kg/m³ bed · d)
	Influent	Effluent	
23	44	16	7.6
29	85	52	11.4
36	138	107	13.8
43	108	76	16.4
52	52	24	18.0
54	66	39	18.0
59	70	48	23.2
60	63	36	20.0
64	63	35	21.9

[a]Bed volume, ~2 × 10⁻³m³; temperature, 30°C; Polybac bioreactor.

TABLE 4. EFFECT OF FEED GAS OXYGEN CONTENT AND FLOWRATE ON PHENOL DEGRADATION RATE WITH SYNTHETIC WASTEWATER[a]

Oxygen content of gas (% by volume)	Gas flowrate (m³/h × 10³)	Average degradation rate (kg/m³ bed · d)
100	3.3	15.0
~60.5	4.5	10.9
21	8.7	5.3

[a]Liquid flowrate, ~30 × 10⁻³ m³/h; influent phenol concentration, 0.05-0.07 kg/m³.

TABLE 5. BATCH KINETICS OF PHENOL DEGRADATION

Condition[a]	Initial phenol degradation rate (kg/m³ coal-biomass · d)
Air sparged	
5×10^{-6}m³ coal-biomass	59
10×10^{-6}m³ coal-biomass	32
20×10^{-6}m³ coal-biomass	19
Oxygen sparged	
5×10^{-6}m³ coal-biomass	69
10×10^{-6}m³ coal-biomass	62
20×10^{-6}m³ coal-biomass	53

[a]Initial phenol, ~0.1 kg/m³; total volume, 1 × 10⁻⁴m³; gas flow, ~5.4 × 10⁻³m³/h; agitation, ~165 rpm; baffled flasks; temperature, 25°C; coal-biomass from Sybron bioreactor.

Reaction Kinetics

An experimental program has been carried out to develop a kinetic model for the biooxidation reaction. Typical results from shake-flask experiments are shown in Figure 2 and Tables 5 and 6. Experiments were done at several oxygen concentrations. The reaction rate appears to be zero order in both phenol and oxygen concentrations down to ~0.01 kg/m³ phenol and ~0.002 kg/m³ oxygen. For a Michaelis-Menten kinetic scheme, the K_M for phenol appears to be 0.001-0.005 kg/m³. The stronger dependence of the phenol degradation rate on the quantity of coal-biomass in the air-sparged flasks (Table 5) is believed to be due to mass transfer limitations for oxygen associated with liquid-to-particle transfer (the diffusional driving force is less than that with pure oxygen) plus the relatively poorer solids mixing at higher solids quantities. An approximate first-order dependence on quantity of fixed

Figure 2. Kinetics of phenol degradation in batch reactors. Baffled flasks; total liquid volume, 1 × 10⁻⁴m³; oxygen flow, ~5.4 × 10⁻³m³/h; agitation, ~165 rpm; cultures from Sybron bioreactor; 5 × 10⁻⁶m³ of coal-biomass. Note: mg/L = 1 × 10⁻³kg/m³; min = 60s; mg/L coal-biomass · min = 1.44 kg/m coal-biomass · d.

films was observed in other experiments not reported in detail here; however, accurate determination of this dependence was hampered by the lack of a suitable efficient assay for the quantity of fixed films attached to coal. Progress is being made on this assay problem. The rates in Figure 2 suggest an activation energy of ~42 J/kmol, which is a reasonable value for this type of reaction. A weaker temperature dependence has been seen in the continuous bioreactors and is probably attributable to mass transfer limitations at low liquid flow rates. The rates obtained in the continuous bioreactors are somewhat less than those in the batch experiments, probably because of mass transfer limitations discussed earlier. There appear to be opportunities for improvement of degradation rates in the continuous bioreactor.

Microbial Characterization of Fixed-Film Cultures

A number of species were isolated from the bioreactors and identified, as shown in Table 7. Since the compositions of the commercial microbial preparations are unknown, it is not known if species in the original inocula have been maintained. However, it is interesting to note the variety of pseudomonads in both bioreactors and the diversity of species in general. The Sybron/BICHEM bioreactor had been maintained on monohydric phenol plus micronutrients, whereas the Polybac bioreactor was maintained on a more complex feed [13] for 11 months before the culture was sampled for these characterization studies. The species listed in Table 7 are consistent with those found in another wastewater treatment plant [14].

CONCLUSIONS

Fixed-film, fluidized-bed bioreactors have been used successfully to treat dilute synthetic wastewaters on a continuous basis for more than 1 year and dilute actual wastewaters for 9 months. The bioreactors have exhibited stable biological activity, and no difficult operating problems have been encountered. Effluent phenol concentra-

	Time (s)	4-AAP phenols concentration $(kg/m^3 \times 10^3)$	Estimated degradation rate $(kg/m^3 \text{ coal-biomass} \cdot d)$
Monohydric phenol	0	108.6	
	600	94.6	
	1200	77.2	37
	1800	54.2	
	2400	30.4	
	4200	0	
Monohydric phenol	0	82.8	
(0.035 kg/m³)	600	66.9	
+ METC wastewater	1200	49.9	36
(~0.5% v/v)	1800	29.8	
	2400	7.6	
	4200	1.6	
METC wastewater	0	55.5	
(~1% v/v)	600	42.5	
	1200	26.6	30
	1800	11.8	
	2400	3.8	
	4200	2.3	

[a]7 × 10⁻⁶m³ coal-biomass; total volume, 75 × 10⁻⁶m³ in 250 × 10⁻⁶m³ baffled flasks; air; 30°C.

tions of $\leq 0.001 \text{ kg/m}^3$ are readily achievable in laboratory-scale bioreactors with a synthetic wastewater containing 0.03-0.04 kg/m³ of phenol at a hydraulic residence time of approximately 240 s in the bed. Dilute actual wastewaters have been treated successfully. Volumetric reaction rates in the reactors are substantially higher than those in suspended growth systems (e.g., activated sludge) due to the high concentration of retained cells on the support particles. Laboratory-scale activated-sludge systems with sludge recycle may exhibit volumetric phenol removal rates of 5-6 kg/m³ · d [1, 15], whereas current studies have shown potential for tenfold higher rates in fixed-film fluidized-bed bioreactors under favorable operating conditions.

ACKNOWLEDGMENT

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TABLE 7. CHARACTERIZATION OF MICROBIAL CULTURES

Source of culture	Organisms tentatively identified
Bioreactor initiated with Sybron/BICHEM® 1001 and 1002	*Pseudomonas aeruginosa* *Pseudomonas putida* *Pseudomonas mendocina* *Pseudomonas chichorii* *Pseudomonas stutzeri* *Pseudomonas fluorescens* Unidentified yeast
Bioreactor initiated with Polybac Phenobac®	*Pseudomonas fluorescens* *Pseudomonas mendocina* *Pseudomonas stutzeri* *Pseudomonas alcaligenes* *Pseudomonas* sp. *Alcaligenes* sp. (two isolates) *Flavobacterium ferrugineum* *Arthrobacter globiformis* *Endomycopsis* sp. Four unidentified bacteria

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The Nature of the CO₂ Problem: Certainties and Uncertainties

An authoritative look at the whole question of CO_2 emissions to the atmosphere. How serious is the problem and what present action can or should be taken?

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The small quantity (0.03 of one percent) of CO_2 in the atmosphere is an important regulator of the Earth's average temperature and the global climate. Radiant energy from the sun is balanced by outgoing long-wave energy from the Earth, but carbon dioxide molecules, which absorb some of the long-wave energy but not the incoming solar energy, cause the Earth's surface to have a temperature higher than it would have if the atmosphere had no carbon dioxide. The reason for this result is illustrated in Figure 1. The lower portion of the figure shows the absorption of energy by many of the atmospheric gases. The upper portion of the figure shows the energy spectrum of the thermal radiation of both the Sun and the Earth. Our concern results

from absorption of infrared radiation by the CO_2 molecules, particularly at wave lengths near 15×10^{-6} meters, corresponding to the band of maximum power in the infrared spectrum of the Earth's radiation. This results in a warming of the lower layers of the atmosphere and consequently the Earth's surface. Thus, the thermal balance of the planet, the atmospheric circulation, and the global climate are dependent on the amount of carbon dioxide in the atmosphere.

The atmosphere exchanges carbon dioxide with other large reservoirs, especially the terrestrial biosphere and the oceans (Baes *et al.*, 1977) [2]. In the natural, unperturbed system, the net exchange of CO_2 between the
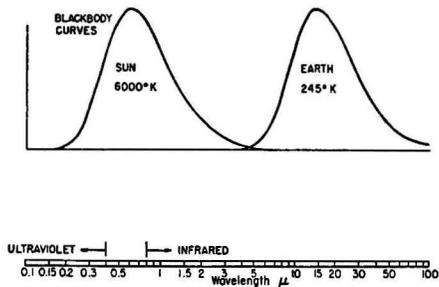
Figure 1. Radiant energy spectra and absorption bands of atmospheric gases.

Figure 2. Monthly average atmospheric CO_2 concentrations observed at Mauna Loa Observatory, Hawaii.

atmosphere and the global biosphere is near zero. If carbon dioxide in the atmosphere is increased, the rate of carbon fixation by photosynthesis will increase, but so will the rate of return to the atmosphere through respiration and decay. With enhanced CO_2 in the atmosphere the amount by which the fixation rate exceeds the return rate will work to counter the effect of whatever phenomenon caused the increase. At present the net rate of uptake is insufficient to balance CO_2 produced by the fossil fuel combustion and as a result the atmospheric CO_2 concentration is increasing.

The exchanges of carbon dioxide between the atmosphere and the oceans occur in amounts much larger than that added to the atmosphere by fossil fuel combustion. For the unperturbed system, the amount absorbed by one part of the ocean is balanced by that released by another part. Just as in the case of the biosphere, with an atmospheric CO_2 increase the net amount taken up by the ocean should increase, but this increase has not been sufficient to keep the atmosphere from retaining some of the CO_2 from fossil fuels.

If global society continues its heavy use of fossil fuel resources, the CO_2 concentration will not only continue to rise, but will exist for a long time even after fossil fuel use is curtailed or eliminated. Climate changes resulting from enhanced atmospheric CO_2 will occur gradually over a period of several decades or even centuries. This may make adaptation easier, but because the changes will persist for such a long time the potential problem should not be taken lightly.

We now ask where the scientific community stands on the issue: what is certain and what involves what levels of uncertainty.

CERTAINTIES

The first thing of which we are certain is that atmospheric CO_2 has been increasing. The seasonal cycle resulting from exchanges of CO_2 between the atmosphere and the biosphere is evident as well as the year-to-year increases in observations at Mauna Loa Observatory and other locations around the world. Data of Keeling et al. (1982) [7] plotted in Figure 2, show the seasonal cycle and the longer-term increases at Mauna Loa, and measurements from all over the world are now sufficient to assure that the annual increases are global: the Mauna Loa data are representative of the full global atmosphere in this respect.
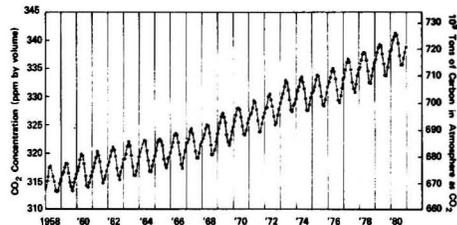
We also know that, on a global scale, the annual rate of CO_2 emissions from fossil fuel combustion has been increasing. The most recent demonstration of this is in Marland and Rotty (1983) [8]. (See Figure 3). Although the growth rate in the use of oil and gas has been reduced since 1973, the total annual CO_2 emissions have continued to increase (except for the 1979-82 period when energy use and annual CO_2 emissions were reduced slightly as a result of the worldwide economic recession). The annual emission rates from fossil fuels grew at a steady 4.5 percent per year from 1950 until 1973. Following 1973 the emission rates show a pattern of slower growth: about half of the pre-1973 rate. The changes in fuel use that occurred in 1973 resulted in sharp discontinuities in the case of oil and gas. It is clear from the data that annual rates of CO_2 emission from fossil fuels have grown by a factor greater than 3 during the past thirty years and strongly suggests that, in the absence of world economic stagnation, growth will almost certainly continue.

The atmospheric increase can account for only part of the CO_2 released through fossil fuel combustion. Therefore the system does not behave in a single cause/single effect relationship. Some of the fossil fuel CO_2 has been distributed to other reservoirs in the carbon cycle, and it is also possible that other sources, i.e., forest clearing, are providing additional sources of CO_2. Although the size of the total source (fossil fuel plus forests) is uncertain, there can be no doubt that CO_2 produced by fossil fuel combustion is a major contributor to the observed increase in the atmosphere.

A look at the global carbon cycle, shown in Figure 4 (Bolin et al., 1979 [3]; Bolin, 1981 [4]; Emanuel et al. [5],
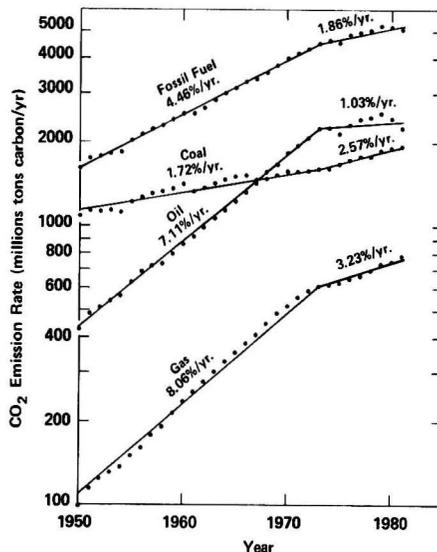
Figure 3. Global annual emission rates of CO_2 from fossil fuel combustion.

ATMOSPHERE
720 (+ 2-3/yr)

Slow
39
14
480
Rapid
74
43
5
80
25
31
90
90
Surface 580
25
31
31
Intermediate 6600
900
140
Deep 31800
4300+
(Recoverable)
1500 Older Soils Inactive

SEDIMENTS
organic C: 7,000,000
limestone: 30,000,000

FOSSIL FUEL   **TERRESTRIAL BIOSPHERE**   **OCEAN**
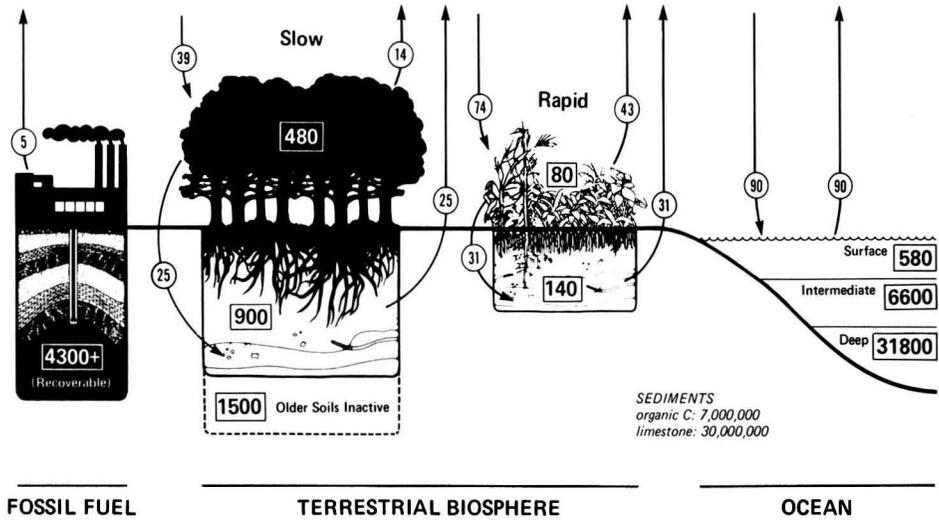
Figure 4. The global carbon cycle (pool sizes, □, in 10^9 tons; fluxes, ○, in 10^9 tons per year).

1981), enables us to put the fossil fuel perturbation in perspective. The 5000 million tons of carbon being released to the atmosphere by fossil fuel combustion each year is about 1/20 of that exchanged between the atmosphere and the oceans or between the atmosphere and the terrestrial biosphere.

Clearly, the observed increase of CO_2 in the atmosphere since 1958 has been small in comparison to the size of the reservoirs in the carbon cycle. Although we don't know how much carbon will be ultimately released by fossil fuel consumption, data suggest that somewhere in the neighborhood of 4100 billion tons of carbon are stored in the recoverable conventional fossil fuel resources. For example, values in Table 1 are from Rotty and Marland (1980) [10]. Recoverable conventional oil and gas together do not contain sufficient carbon to cause a doubling of the CO_2 content of the atmosphere, but use of even a small part of the world's abundant coal resources can easily result in doubled CO_2 concentrations. Although there is some uncertainty in the resource numbers we do know that there are sufficient resources that their future exploitation could easily release sufficient CO_2 to cause a significant increase in the 725×10^9 tons of carbon now in the atmosphere.

We also know that use of fossil fuels will continue. Not only has the annual rate of global CO_2 emissions from fossil fuels more than tripled during the interval 1950-1980 (from 1.6 million tons C to nearly 5.2 million tons C), but the fraction of the total that was released from North America and Western Europe has dropped markedly (Rotty and Marland, 1983) [11]. Figure 5 shows the distribution of the CO_2 emissions among the six major geopolitical segments of the world for 1950, 1965, and 1980. The areas of the circles are proportional to the total CO_2 emissions for that year. The developing world and the Asian countries with centrally planned economies have been growing most rapidly in CO_2 emissions. The numbers on the line segments of Figure 6 indicate the growth rate. Countries with centrally planned economies do not show steady growth with a possible adjustment (e.g., North America in 1973), but rather a slowly decreasing rate of growth. Growth rates in poorer parts of the world have been much greater than those in more industrialized nations. Within some regions individual countries show emission growth patterns much different from nearby neighbors. In spite of the differences, fossil fuel use on the global scale will continue to increase even if the highly industrial countries level off or grow more slowly.

TABLE 1. ENERGY AND CARBON CONTAINED IN FOSSIL FUEL RESERVOIRS

	Energy Content Best Estimate (10^8 joules)	Best Current* Estimates (10^9 tons C)	Upper Limit* Speculations (10^9 tons C)	Historic Consumption up to 1978 (10^9 tons C)
Ultimately recoverable conventional petroleum products	13,240	230	380	35
Ultimately recoverable conventional natural gas	10,440	143	230	15
Ultimately recoverable conventional coal	147,900	3,510	6,315	100
Shale oil	9,870	173**	9,530**	
Tar sands and heavy oil	4,290	75	200	
Total	185,750	4,131	16,655	150

*Not including that produced prior to 1978.
**Not including CO_2 driven off from carbonate rock in retorting.

1618 million tons C
1950

3126 million tons C
1965

5170 million tons C
1980
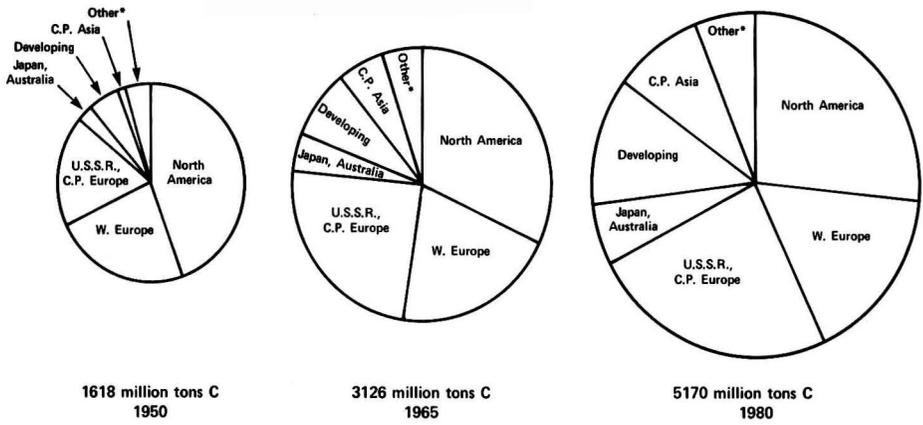
*Includes Worldwide Gas Flaring; Fuel in Bunkers;
Oxidation of Non-Fuel Petroleum Products.

Figure 5. The changing pattern of fossil fuel CO_2 emissions.
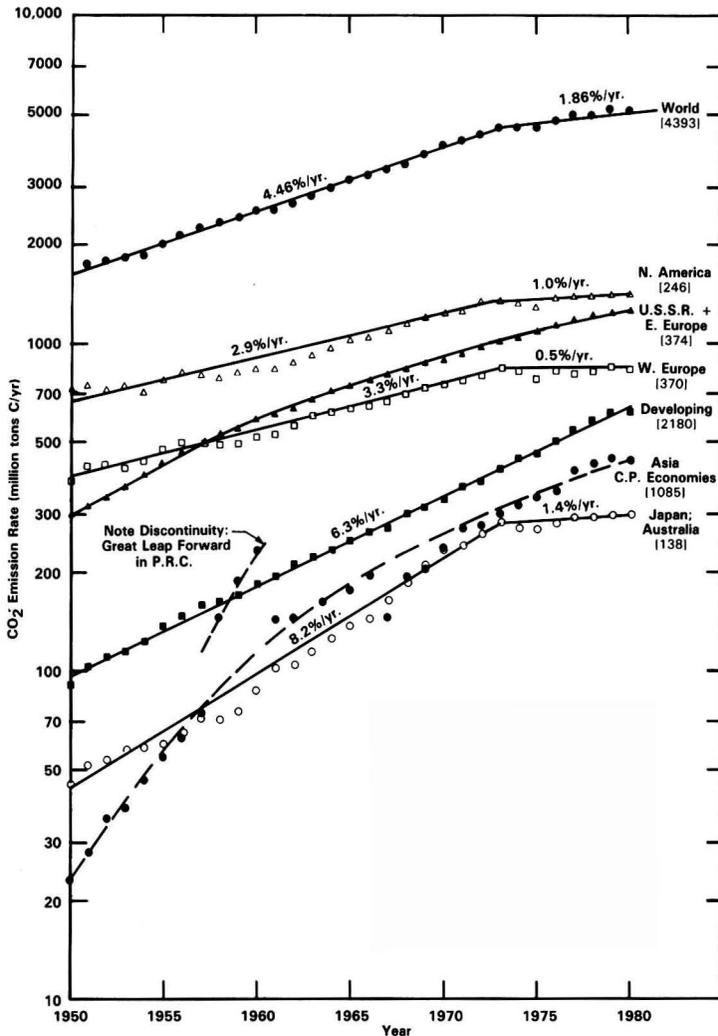
Figure 6. CO_2 emissions by world segment.

QUALIFIED UNCERTAINTIES

Although we know that CO_2 molecules absorb infrared radiation, how this absorption and reradiation of energy by elements of the atmosphere will change the climate must be deduced from our understanding of atmospheric physics. The physics becomes very complex when the changes in the radiative balance resulting from enhanced CO_2 is applied to a moving fluid heated and cooled by the condensation and evaporation of water. To obtain a general idea of how this can affect global climate, very large computer models have been developed and exercised under a variety of conditions. The model experiments with increased CO_2 show that warming at the surface occurs and is greatest at high latitudes and in the winter season. Although a National Research Council panel of experts (NRC, 1979) has concluded ". . . the equilibrium global surface warming from a doubling of CO_2 [is] near 3°C with a possible error of ± 1.5°C," we must remember that this is dependent on model experiments. It is probably safe to say that increased atmospheric CO_2 will cause a global warming but the exact amount of warming associated with a given CO_2 increase and the details of the resulting climate change remain uncertain.

Although we know that fossil fuel use is bound to increase and we strongly suspect it will increase at rates sufficient to cause CO_2 concern, the rate at which the use will occur is dependent on many factors. Among the most critical factors are population growth, economic growth, and technological development. The future is, of course, unknowable, but based on "mid-range" assumptions of population, economics, and technology, a sample projection of fossil fuel use shown in Figure 7 (AAES, 1983) [1] was used to deduce the resulting atmospheric CO_2 concentration (also indicated in the figure). The atmospheric CO_2 concentrations for this example are computed by a carbon-cycle model which attempts to systematically increment the reservoirs in the global carbon cycle on a year-by-year basis. In this example the rate of emission grows from the present 5×10^9 tons carbon per year to about 13.5×10^9 tons carbon per year around 2065 and declines thereafter. By 2065 the atmospheric CO_2 concentration will have approximately doubled and will be growing at a rate of about 4 ppm/yr. Even though fossil fuel use and therefore CO_2 emissions decline after 2065 in this example, the atmo-

spheric CO_2 continues to rise for another 225 years reaching a peak of about 950 ppm around 2290. The effect of fossil fuel use will be observed centuries after fossil fuel has begun to be phased out.

With substantially reduced dependence on fossil fuels (i.e., the annual CO_2 emissions growing slowly), it could be possible for the emissions to reach a peak of only 6.75 billion tons of carbon per year around 2065 and decline gradually thereafter. This example is shown in Figure 8. With these assumptions of reduced use of fossil fuels, the atmospheric CO_2 concentration will have risen to only 444 ppm by 2065 but will continue to rise until reaching a peak value of 717 ppm in the middle years of the 25th century—four centuries after fossil fuel use has started to decline. With low fossil fuel use scenarios, the lag between the peak of fossil fuel use and the peak in the atmospheric CO_2 concentration is longer because more fossil fuel remains to be used after the peak is reached. It is difficult to envisage a fossil fuel use pattern for the future in which the atmospheric CO_2 concentrations will not continue to rise. Drastic measures, beyond what is likely, would be required, so we strongly suspect that CO_2 concentrations will continue to rise throughout the next century.

OTHER UNCERTAINTIES

Although atmospheric CO_2 has definitely increased during the past several decades, no clearly identifiable climate change has resulted. Does this prove that the climate theory and model results are incorrect? The magnitude of the increase in CO_2 during the past century is only large enough to give a climate change about the same size as the "natural" variability in climate. If the theory is correct, within the next two decades the signal of the CO_2 effect on climate should become quite clear. The climate effects of several factors have been separated in attempting to reconstruct the course of annual average temperature fluctuation during the past century. An outstanding example of this type of work is that of Hansen et al. (1981) [6]. Hansen and his colleagues considered the combined effects of CO_2 concentration, volcanic activity, and solar variability on the global average temperature and compared the result with the temperature record for the past century. Figure 9 shows their results on the left with a time lag introduced by considering the thermal inertia of only 100m
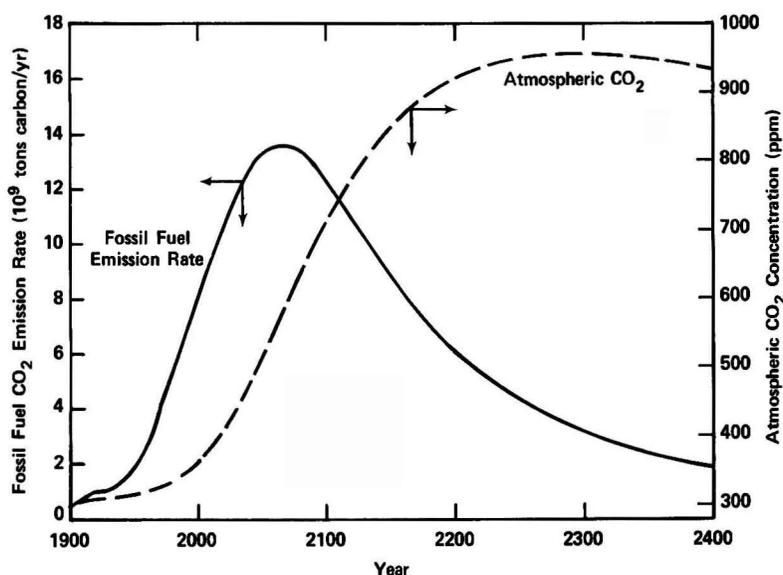
Figure 7. Sample scenario of fossil fuel emissions and resulting atmospheric CO_2 concentrations.
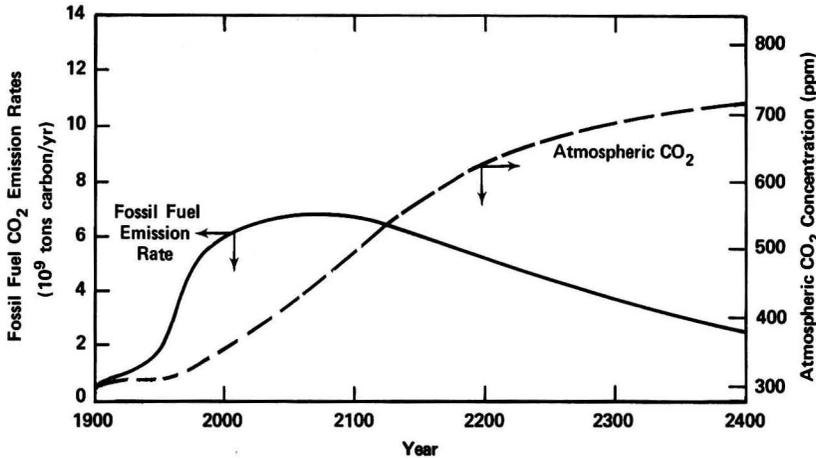
Figure 8. Emissions scenario with reduced dependence on fossil fuels and resulting atmospheric CO_2 concentrations.

mixed-layer ocean and on the right with heat diffusion to 1000 m. Such efforts have been unable to prove irrefutably that we have had a CO_2 warming, but demonstrate that climate changes that may have occurred are not inconsistent with a CO_2 effect. Uncertainty remains about both the rate of temperature rise and the amount of climate change that can result from a specified increase in atmospheric CO_2.

Our lack of knowledge about "how fast?" and "how much?" is even more evident in the consideration of detailed climatic changes that may occur over critical regions of the globe. At present even the most detailed and most sophisticated models offer little in quantitative details of "where?" and "how much more or less?"

If the world encounters a climatic change of the magnitude suggested by the climate models for a CO_2 doubling during the next century, what will be the effect on people? Human society has adapted to the present climate through evolutionary processes that have taken many centuries. The global ecological systems have also evolved over very long periods of time. We do not know the capacity of global society to adapt to climatic changes of different magnitudes. Usually there are costs in adapting to a new situation, but when these costs are spread over a human generation or more they may be quite tolerable. To state that the present climate is the best climate for the world's people is to imply that we have evolved to the most desirable state of being. We have very limited ability to imagine what would have developed if the world had had a different climatic pattern in the past as a result of being slightly warmer or cooler. We don't know that the present state is the best
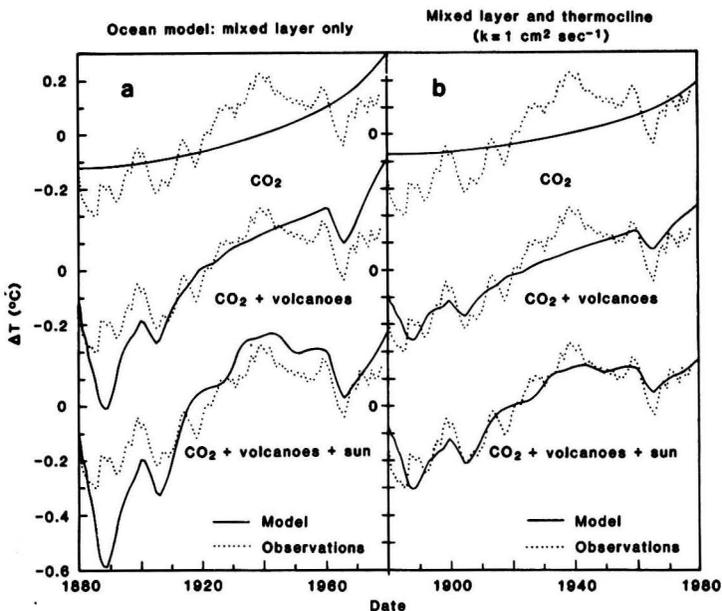
Global temperature trend obtained from climate model with sensitivity 2.8°C for doubled CO_2. The results in (a) are based on a 100-m mixed-layer ocean for heat capacity; those in (b) include diffusion of heat into the thermocline to 1000 m. The forcings by CO_2, volcanoes, and the sun are based on Broecker (25), Lamb (27), and Hoyt (48). Mean ΔT is zero for observations and model.

Figure 9. Global temperature trends from climate models.

state, but we know that there are usually costs associated with change. It remains for us to learn how to evaluate the costs as well as evaluating the long-term results of the changes.

CONCLUSIONS

Although there are large uncertainties and unknowns, the magnitude of the potential consequences is so immense that we would be irresponsible to ignore the problem.

While maintaining growth and hopes for a better life among all peoples of the world, we can take some actions to assure a tolerable future. Foremost among these is the meeting of future global energy demand with technologies that release as little carbon dioxide as possible, at least until more is known about the potential climatic changes. Because the recoverable resources of fossil fuels are so large (and relatively inexpensive), it will be very difficult to reduce fossil fuel use in the global energy system in the near future. Nonfossil energy supplies, i.e., solar and nuclear, produce no carbon dioxide, but costs and reliability of these alternatives will continue to encourage large use of the fossil resources.

In my opinion the biggest single factor that will determine the magnitude of the CO_2 problem in the future is the amount of fossil fuels—oil, gas, and coal—that is used in the next 50 years. An obvious solution is the development of nonfossil energy sources and employing them where and when this can be done without disrupting the world economy now so heavily dependent on fossil fuels.

Especially in developing nations of the world, where growth in energy demand is so great, there is an unusual opportunity to take advantage of alternative energy supplies before a larger energy system based on fossil fuels becomes firmly fixed. By emphasizing decentralized solar energy, biomass, and wind energy technologies where these can appropriately substitute for fossil fuels in the rural and poorer areas, and more sophisticated solar and nuclear energy where the technological development permits, we can at least slow the atmospheric CO_2 increases and gain time to better understand all of the aspects of the problem.

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Management of Industrial Hazardous Wastes

An organized hierarchy brings out techniques which will truly solve the problems of long-term storage of hazardous wastes.

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A variety of approaches to the management of hazardous industrial wastes exist in many developed and developing countries. These techniques, in general terms, are depicted in Figure 1. There are basically three general options: 1) elimination or reuse of the hazardous waste, 2) conversion of the hazardous waste into nonhazardous or less hazardous material, and 3) perpetual storage. These general options differ substantially in terms of philosophy, time-frame, technique, and economics. At present, perpetual storage methods are the most prevalent and, hence, are often the focus of attention for both regulatory and industrial personnel. This general description was modified and developed from a hierarchy for hazardous-waste management (Overcash, 1981) as a result of the work of a National Academy of Sciences Committee on Hazardous Waste Disposal [1]. Funding for this committee was equally provided by the American Institute of Chemical Engineers (with assistance of the Environmental Division) and the U.S. Environmental Protection Agency.

Optimum, successive utilization of the three general options would result in a decreasing flow of hazardous wastes, Figure 1. Only the most inert and smallest volume of materials should be considered for perpetual storage. The hierarchy identified in Figure 1 should be followed in the management of hazardous wastes by the following decision or planning process: 1) in-plant alternatives should be used to reduce the volume and toxicity of generated hazardous wastes, 2) remaining wastes that are generated should be converted to less hazardous forms and should be reduced in volume, and 3) any residues and wastes that still remain and are hazardous should be stored in a manner that minimizes risks to the environment and the public.

Identification and understanding of this hierarchy leads to rational decisions, lowest risk solutions, and better public understanding of the issues. The management approaches outlined in Figure 1 also stress prevention and reduction rather than treatment and storage and aim to reduce the risk to the environment and public. Thus, the emphasis is on positive rather than negative management options. In the following discussion, reference is made to the Resource Conservation and Recovery Act (RCRA), a United States law relating to hazardous waste. Similar laws exist in other countries and so the international reader may have to interpret the reference to RCRA accordingly.

In-Plant Options

In-plant options are probably the most powerful and cost-effective means of managing hazardous wastes. These options represent approaches that generally minimize impact on public health and the environment. Prevention is substituted for end-of-pipe management. These options include:

1. Process modifications to eliminate or minimize specific hazardous wastes. These involve altering the chemistry or the chemical engineering operations to achieve the desired waste elimination within the constraint of acceptable and economical product manufacturing.
2. Recycle and reuse processes to prevent materials from exiting the plant as waste. These techniques recognize that the hazardous components of wastes may be usable reactant materials in other production processes or may be converted to less hazardous by-products by repeated recycling.

The technologies of wastes elimination cannot realistically be used to prevent generation of all hazardous wastes. The achievement of zero discharge by process modification or by recycle and reuse is not always the most cost-effective means of managing hazardous waste, nor is it always theoretically possible. Process modification options generally cannot make the resultant industrial waste or sludge nonhazardous, but they can significantly reduce the volume of hazardous material. In fact, the potential of process modification and recycle/reuse in reducing the volume of hazardous waste is so significant that these options should be strongly emphasized and encouraged.

As the costs of the waste treatment and disposal increase, direct payback through the use of chemicals removed prior to waste disposal does not need to just offset the cost of chemical removal. The value of reclaimed chemicals plus the savings in ultimate waste disposition can match or exceed the cost of alternative options. An example may be cited from the leather and tanning industry:
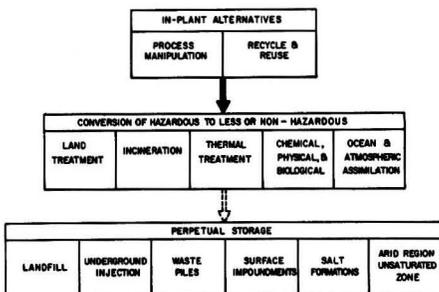
Figure 1. Hazardous waste management alternatives-hierarchy of options.

Chromium removal from wastes has been well demonstrated, but the net gains from recovery and sale on the commercial chromium market have been marginal. However, the substantially increased costs of secure landfill or even the lower cost of land treatment under pending RCRA regulations indicate that it will probably become cost-effective to remove the chromium from such wastes (Overcash 1980).

Conversion Technologies

Technologies that convert hazardous wastes into less hazardous or nonhazardous wastes fall into two classes:
1. Incineration, thermal treatment, chemical, physical, and biological processes that convert wastes from a hazardous to a less hazardous or nonhazardous state. These processes produce a residue (either as a by-product or as a waste stream) that may or may not have an adverse environmental impact and that must be discharged to the environment or stored in an environmentally sound manner.
2. Land treatment that converts the hazardous wastes but also provides the ultimate disposal site.

Perpetual Storage

Perpetual storage is the most prevalent existing hazardous-waste management practice. Each perpetual-storage technology attempts to place the waste material in a highly condensed or concentrated configuration in which the hazardous constituents do not move. Generally little or no conversion from a toxic and hazardous state occurs, and, hence, care, monitoring, and migration prevention are required for an indefinite period. Spans of at least 500-1000 years are realistic as a period of concern for hazardous wastes in landfills and perpetual storage options. Regulations under RCRA establishing the period of concern for landfills as 30 years are considered unrealistic but typical of governmental policy. Such short control periods do not diminish the probability of containment system failure after 30 years; rather, they only mask the likelihood of adverse impacts and the true economics of perpetual care. The storage technologies clearly involve a long-term obligation because, with time, particularly at a closed site, most of the changes that can occur are adverse (e.g., eventual penetration of a surface cover, gas diffusion and leakage to atmosphere, and leakage of mobile constituents to groundwater). Experience with nuclear waste repositories provides an example of unsuccessful results with long-term storage. These have a proven record of leakage to the environment despite the best intentions during a period of even less than 50 years.

The central questions to be addressed with regard to perpetual storage concern the technology and the procedures for implementation. Perpetual-storage technologies have had some of the most careful thinking and evaluation of all hazardous-waste management options. The question still not being widely addressed is how to accommodate these sites over their greater than 500 year life. It is indeed possible that hazardous waste problems and consequences are merely being postponed and will have to be dealt with by future generations. If this could be justified convincingly (or even addressed), then a realistic consideration of the direction for hazardous-waste management can be undertaken.

It is desirable to select the perpetual-storage alternatives that are the most stable and provide the greatest true isolation from the rest of the environment. Thus, the environment advantages of salt domes and arid-region unsaturated zones are superior to salt beds, membrane- or clay-lined secure landfills, and deep wells and are greatly superior to surface impoundments and waste piles.

TIME-FRAMES

The options noted in Figure 1 have different liabilities and time-frames associated with them. The production process alternatives relate to very short time-frames (hours to days), with effects limited to those of short duration (i.e., those resulting from extreme process operating conditions).

The environmental and societal effects of conversion technologies involve an expanded time-frame (minutes to years). Short- and long-term effects on air and groundwater quality must be addressed. Dispersion occurs in a current time-frame and is taken into account as part of the design and monitoring approach. The effects must not violate acceptable air, drinking water, and land-use standards. Thus, the effects of these conversion technologies are essentially short-term. The liability is with and the impact is on those who generate or treat the waste, and not typically on future generations.

For the storage category, the time-frame is much longer (decades to centuries). The ultimate environmental impact occurs in all media and is largely unaddressed in present regulations. The liability is therefore shifted from those who generate or store the waste (the present generation) to future generations. These technologies clearly provide a potentially adverse environmental legacy.

Figure 2 was developed to display this progression of time-frames and to provide a perspective on the impact of various management alternatives. The shorter the lifetime of the hazardous-waste technology, the better the control and the lower the dispersion potential generally associated with that technology. Lifetimes in excess of human life expectancy create much larger unknowns and much less opportunity for management and control.

ZERO RISK AND ZERO DISCHARGE

These concepts are interwoven explicitly and implicitly into most environmental discussions. That one cannot achieve zero risk or zero discharge is clear. The laws of thermodynamics and probability assure that zero risk or zero discharge cannot be achieved. Although the authors cannot attempt to assign quantitative values to acceptable risk, it should be recognized that there is a critical need for a reasonable level of risk assessment to be developed and put into practice in the very near future.

It has been argued that zero risk and zero discharge serve as valuable goals for society, even though they may be unachievable. Regulations have often accepted that philosophy. However, this impossible target has become a liability in achieving real progress. Statements and indirect bases of judgment related to zero risk and zero discharge frequently cause an irrational response by those being regulated and reduce the credibility of any national effort to solve hazardous-waste management problems. Goals of zero risk and zero discharge initially were effective in overcoming the inertia to solving environmental problems; but have since become an impediment to progress in hazardous-waste management. Thus, the technical and political community must continually reject the criteria of zero risk or zero discharge in evaluating the acceptability of technologies for hazardous-waste management. To the extent that the public maintains a belief in zero risk and zero discharge, there will be major difficulties in managing hazardous wastes.

The alternative to a requirement of zero risk and zero discharge is an acceptance of some level of risk and some level of discharge. This is a far more complex approach than that involving zero risk or zero discharge, but it cannot be avoided just because it is complex. It can be concluded that the bulk of all risk and discharge must be assumed in a present-day time-frame and not deferred to future generations. This is an apparently more expensive

approach than deferment, particularly if future deferment costs are neglected, as is presently the case. Reducing future liability by treating or eliminating hazardous waste, however, is socially more desirable.

In the area of risk acceptance, risk quantification is urgently needed. Most activities of daily life pose some risk of injury, sickness, or death. Similarly, there is some risk associated with hazardous-waste management, and some alternatives have higher risks than others. It is essential that some level of risk assessment be put into practical use. This could occur through a combination of scientific and judicial review and opinion, regulatory practice, professional society standards, and public awareness and acceptance. A pragmatic method of establishing an acceptable level of risk would be to quantify the risks currently in place in the daily life of society.

The U.S. Office of Technology Assessment (OTA) (1981) approached this problem in terms of a degree-of-hazard concept applied to regulatory policies. This is a limited approach and focuses on criteria for defining hazard. The broad and more important problem is the level of acceptable risk. That some technologies, when applied to hazardous industrial wastes, will have higher risk factors than other technologies must be considered in decisions regarding such wastes (including the final management and/or disposal).

SPECIFIC TECHNOLOGY NEEDS

In a detailed review of the major hazardous-waste conversion/treatment and perpetual storage options, the National Academy of Sciences Committee developed important informational needs that would then permit more wide-spread usage of a number of hazardous-waste alternatives. These are listed below. It is important to note that any organization or country can and should consider undertaking the efforts necessary for these research and development programs as the problems are so large, widespread, and site-specific that no one set of answers will emerge for all countries.

Chemical and Physical Techniques:

1. Attention is needed for metal removal and/or recovery particularly at low levels in complex wastes;
2. Chemical reaction and separation processes must be designed for waste elimination as well as in the treatment of hazardous wastes.

Biological Techniques:

1. Mechanistic studies are needed to assess the decomposition and improvements possible for toxic organic compounds in biological processes;

2. Genetic engineering and traditional biochemical selection must be continually used to develop more rapid and versatile biological treatment processes.

Land Treatment:

1. Expansion of the data base and economic evaluations are important for this under-utilized but economically attractive alternative. This is especially true in developing countries with land availability;
2. Specific demonstration systems are needed to increase the use of land treatment (Overcash, 1979).

Ocean Assimilation:

1. The effects of past ocean dumping should be investigated to quantify the assimilative capacity limits of the ocean environment;
2. Monitoring and pilot-scale testing systems are needed to permit adequate design.

Incineration:

1. Rates, operating conditions, and residence time for combustion of specific compounds, often in a complex mixture must be developed to permit compliance with atmospheric emission standards;
2. Emission control and off-shore systems need to be further improved.

Thermal Methods:

1. Molten salt, fluidized bed, wet air oxidation, and pyrolysis systems must be evaluated regarding scale-up design in order to better develop these alternatives;
2. Improved materials of construction and realization of economies-to-scale are important needs for thermal techniques.

Landfills:

1. The long-term (greater than 500 years) behavior and economics must be evaluated to put this technology in perspective;
2. Methods for modeling and corrective action related to landfills will become imperative in the future.

Permanent Storage:

1. Inventories of salt formations, arid-region zones, and stable, deep geologic formations are necessary to begin consideration of alternatives to landfills;
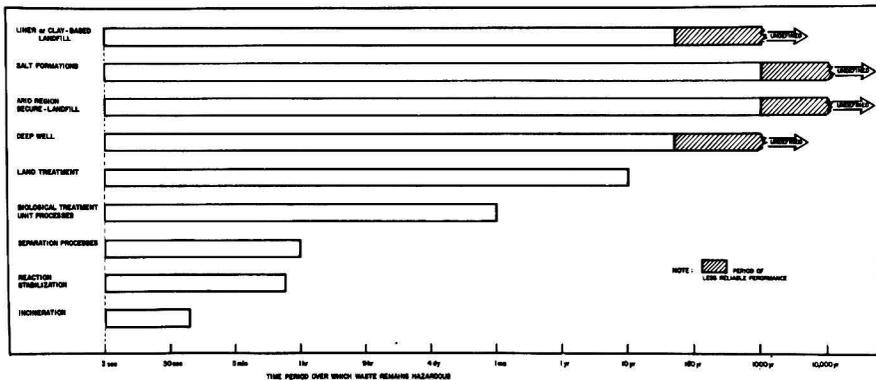
Figure 2. Time frame of concern for hazardous-waste management alternatives.

2. The economics of long-term storage must be developed for the existing design criteria to demonstrate the suitability of these perpetual-storage operations.

SUMMARY

The management of hazardous wastes is becoming better understood as the old simple-minded solutions (such as landfills) are evaluated carefully and improved methods are developed. It is important to put various alternative approaches in an organized hierarchy for emphasis on those techniques which truly solve the problems of hazardous waste, Figure 1. Because of the volumes of information available, no paper or report can do justice to all. The results of the National Academy of Sciences Committee are related to improvements that will be necessary to expand the use of a whole variety of hazardous-waste management options. The reader should consult the entire committee report for further details (NMAB 1983). As a general conclusion, it is clear that substantial short-term as well as long-term improvement is needed and is possible for the technologies used to manage hazardous wastes.

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Adsorption Systems for Air Pollution Control

A state-of-the-art review of recent advances in the use of Pressure Swing Adsorption (PSA) systems for air-pollution control.

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Significant advances have occurred within the last decade in the use of Pressure Swing Adsorption (PSA) systems for air-pollution control. The traditional heat-regenerated adsorption systems suffer from poor thermodynamic efficiency, due primarily to the need to heat the adsorbent, and heat losses to the surroundings. The evolution of improved adsorbents and the development of predictive calculation techniques which eliminate the need for extensive pilot testing to determine performance have provided a valuable new PSA tool to the chemical engineer for air-pollution control.

The following discussion covers applications involving hydrocarbon emission control using PSA which were popular in the last decade and reviews some of the emerging PSA technologies which are likely to impact this decade. The adsorbent most discussed is activated carbon. This adsorbent has seen the widest application in hydrocarbon emission control and has also seen major changes which allow it to function effectively as a PSA adsorbent.

Applications which have recently been developed for hydrogen sulfide processing are also discussed.

THE USE OF ACTIVATED CARBON IN PSA SYSTEMS

Activated carbon has been widely applied for several years in both air and water pollution control involving the removal of organics. The traditional system involved ambient temperature adsorption and heat (usually steam) regeneration. The activated carbons were chosen because of their ability to remove organics down to a few ppm and retain the organics very strongly. This strong retention characteristic is reflected in the large amounts of energy required to regenerate the carbon. However, the very characteristics which made activated carbons excellent adsorbents for organics in heat-regenerated systems made them poor adsorbents for PSA systems. PSA systems accomplish bulk separation of organics and need to be easily regenerated without heat. Some differences between

heat-regenerated and vacuum-regenerated carbons are shown in Figure 1.

The carbon which might be used to remove trace organics from water would:

A. Be highly regenerated in its normal working condition.
B. Have a steep slope at high values of adsorption potential.
C. Not be required to have a high saturation capacity.
   The carbon which would accomplish bulk PSA separation of organics would:
A. Be nearly totally saturated in its normal working condition.
B. Have a very steep slope at low values of adsorption potential.
C. Be required to have a high saturation capacity.

The initial market demand which generated a large need for PSA carbons came from the automotive industry, where PSA is used to control hydrocarbon emissions from the automobile fuel tank. Regeneration is accomplished by a combination of vacuum and stripping air purge by flowing a small volume of air across the adsorbent cannister to the intake manifold while the engine is running. The result is a reduction of hydrocarbon emissions down to about 3,000 ppm of vented air. While this is considered "bulk" separation where adsorbents are concerned, it represents highly efficient separation when compared to other separation techniques such as absorption or refrigeration.

The transition from PSA system applications in automobiles to applications in major processing plants came via first applying the technology to gasoline-vapor recovery in loading and storage, then vent processing in polymer plants and has now evolved to include several applications in petroleum production and natural gas processing. The following discussion of applications traces that evolution of the use of the new PSA activated carbons.

GASOLINE VAPOR RECOVERY

The first successful installation of PSA technology is an industrial application of gasoline-vapor recovery was in 1976 when an Adsorption Absorption Vapor Recovery Process was installed at a small truck-loading facility in Hackensack, New Jersey. The process (Figure 2) had the unique design feature of controlling the absorber recycle

Figure 1. Comparison of activated carbons.
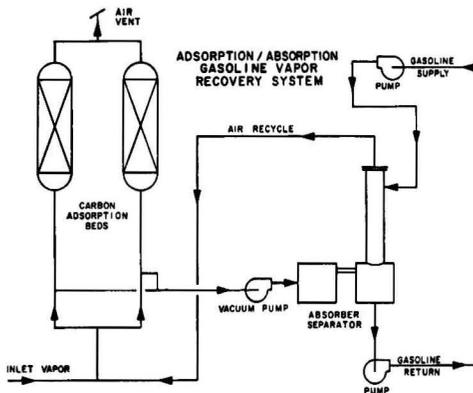
Figure 2. Standard gasoline vapor recovery flow sheet.

to prevent excessive adsorber loading. The concept represented a breakthrough and over 500 systems have been installed worldwide since the initial unit. Applications have primarily been for hydrocarbon emission control at loading and storage facilities for fuels and installations exist at most major refining and terminal operations in the United States.

The process involves adsorption of hydrocarbons from air displaced from storage tanks or vehicles being filled. Regeneration of the off-stream bed is accomplished by application of vacuum to the adsorbent. The hydrocarbons are removed in chromatographic succession and absorbed in an absorber whose overhead recycles to the on-stream bed. The critical design of the absorber is based on accepting the widely varying feed (both flow and composition) and producing a controlled recycle to the on-stream bed.

The advantages of the Adsorption Absorption Vapor Recovery System over previous technologies were:

A. Ability to accept extremely wide variations in vapor inlet flows and compositions while maintaining nearly constant atmospheric emissions (normally 3,000 ppm vol).
B. Low energy consumption. The work is applied only to the hydrocarbons with air being rejected to the atmosphere.
C. Simplicity and ease of operation.

OTHER APPLICATIONS OF PSA TECHNOLOGY IN VAPOR RECOVERY

Several other applications of PSA technology in vapor recovery from loading and storage applications have been done such as the Benzene Vapor Recovery System at a barge-loading facility shown in Figure 3.

Marine loading facilities represent a more complex design problem for vapor recovery due to the size of the systems, variety of materials being loaded, and the Coast Guard safety restrictions. Adsorption, oil absorption, refrigeration, vapor incineration, and combinations of these technologies are all applicable to marine systems. PSA-base recovery unit designs will normally apply when limited varieties of materials are loaded.

These systems point out some of the limitations of the technology.

Applications are generally limited to recovery of mixtures of relatively light hydrocarbons. Although some high-boiling compounds exist in gasoline, the vapor reaching a recovery unit is primarily composed of materials lighter than 100 molecular weight. Other technologies are usually superior when vapor recovery of high-boiling materials is done. For example, if an application involves
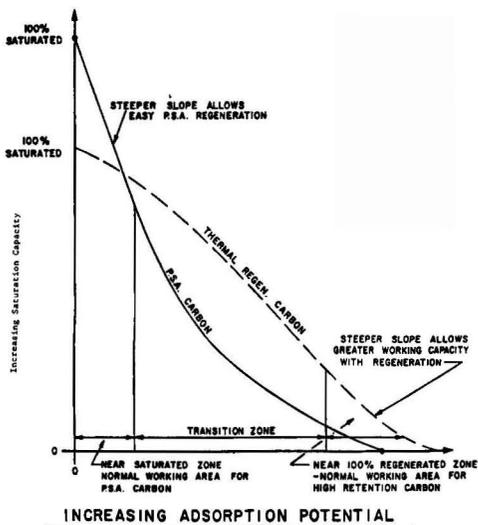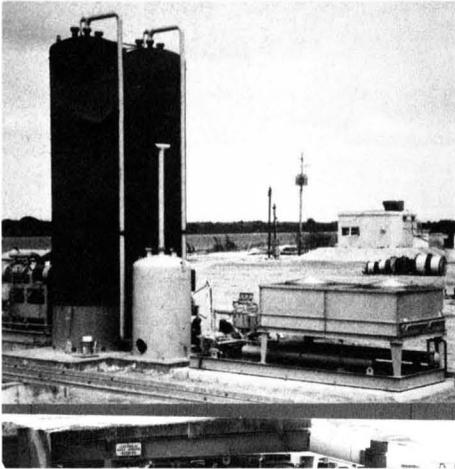
Figure 3. Barge-loading facility.

Figure 5. Mixed hydrocarbons recovery unit.

recovery of a vapor whose lightest compound is 100 MW, simple refrigeration would probably be more efficient. Activated carbon would remove the hydrocarbons down to a few ppm but regeneration by pressure swing would be difficult.

Another concern in vapor-recovery applications involves oxidation reactions. Some compounds such as ketones will oxidize when exposed to air. The exothermic reaction releases heat and accelerates with temperature. Thus, special care is required in the design of systems where air feed to recovery units contains materials which are readily oxidized. The surface of the carbon represents an excellent reaction site. Problems can include:

A. Temperature build-up in idle beds from oxidation of certain classes of chemicals such as ketones, aldehydes, peroxides, oxides, and some acids.
B. Fouling of the beds due to solids formation such as sulfur deposition caused by hydrogen sulfide oxida-

tion. This reaction prevents the use of adsorption for vapor recovery from sour crude oils if the vapor feed includes oxygen.

ADSORPTION PROCESSING IN POLYMER PLANT VENTS

Considerable amounts of expensive monomer are lost through vents to the atmosphere and flare systems in polymer production plants. The first major application of PSA technology to the solution of the monomer loss problem came in the 1978 installation of a mixed hydrocarbon recovery unit which separated stripping nitrogen from hydrocarbons (mostly butanes) at a polyethylene plant. This installation, shown in Figures 4 through 6, won Vaaler Award Honors recognition.

Additional applications of PSA technology in the polymer industry include hydrocarbon removal from reactor purge streams. These purge streams are normally vented to the flare to control the build-up of inerts in the reaction loop. Unfortunately, the purged inerts carry considerable valuable monomer to the flare as well. PSA technology in
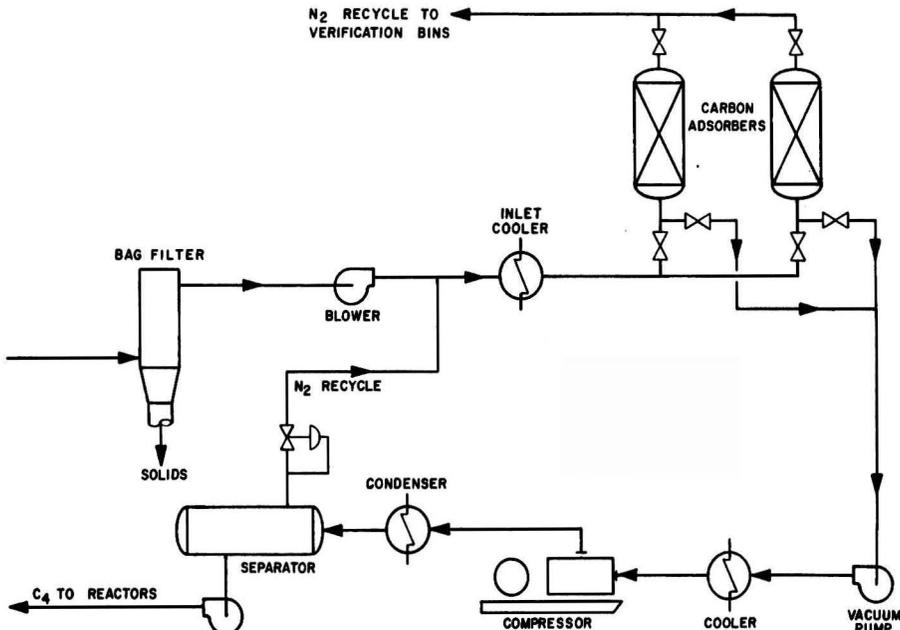
Figure 4. Adsorption unit for polyethylene vent control.
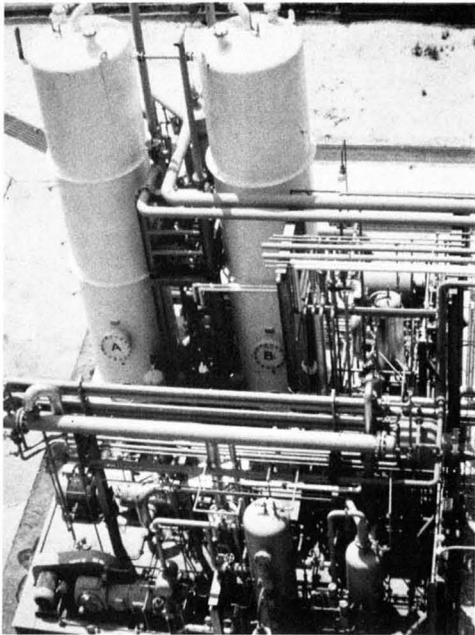
Figure 6. Mixed hydrocarbons recovery unit.

Figure 8. Pressure Swing Adsorption. Fuel conditioning unit.

these applications often involves adsorption at an elevated pressure (source of purge) and desorption at a reduced positive pressure.

Another fundamental limit of PSA technology is highlighted in processing polymer plant vents. A widely recognized pollution problem involves discharge of large volumes of air (or nitrogen) to the atmosphere which contains a very low concentration of hydrocarbons. Examples are ethylene vents in polyethylene plant pneumatic-transfer systems and vents from dry houses in the rubber industry. PSA will enrich the hydrocarbons in a feed stream by re-jecting air (or nitrogen) to the atmosphere. In order to be most effective, the enrichment should be to such a point that liquefaction can readily occur. For most light hydrocarbons, a minimum feed concentration of between 1% and 10% by volume is required to have an efficient PSA system.

FUEL PROCESSING VIA PSA

A recent application of PSA technology involves fuel purification. The Fuel Conditioning Unit is shown in Figures 7 and 8. The application involves fuel purification for field compressor drivers and use of the compressor pressure differential to regenerate the adsorbent. Reduction in engine exhaust emissions of hydrocarbons, NO_x, and SO_x are achieved with this technology and the improved engine performance makes it attractive in places where high quality fuel is unavailable such as offshore and remote onshore producing areas. This same technology can be effectively used in process plants for the removal of hydrogen sulfide (and heavy hydrocarbons) from potential sources of fuel. Hydrogen sulfide removal can be classified into two categories:
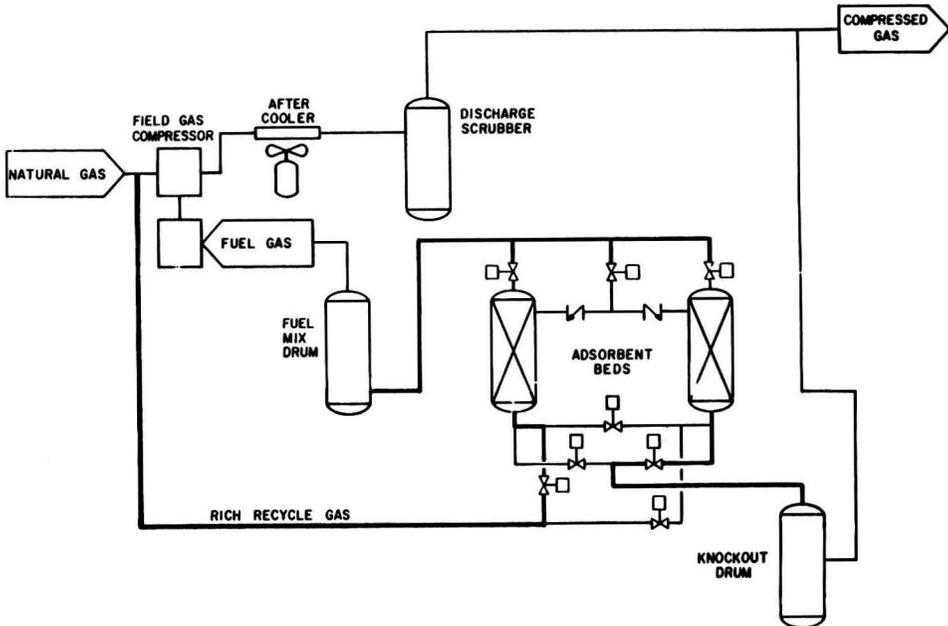
Figure 7. Pressure Swing Adsorption. Fuel conditioning unit.
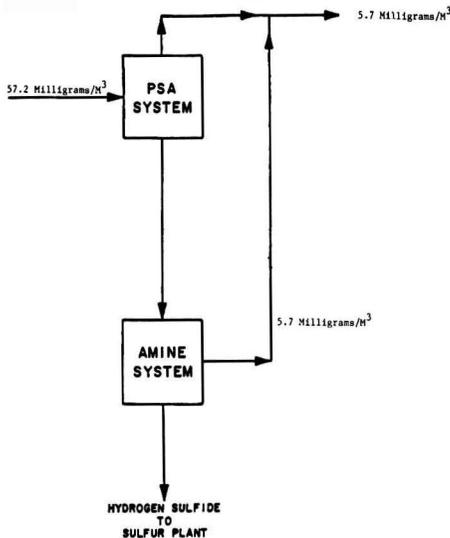
Figure 9. Combination PSA system.

B. Enrichment—Fuel which contains small amounts of hydrogen sulfide cannot be effectively processed in systems which are otherwise effective and inexpensive. PSA systems can be used (sometimes in combination with heat) to reduce hydrogen-sulfide concentrations to very low levels and produce a small volume of hydrogen sulfide-enriched gas for processing in conventional treatment systems. These systems may involve more sophisticated adsorbents than conventional activated carbon. An example is shown in Figure 9.

SUMMARY

The development of improved adsorbents has opened the doors to the use of PSA technology in several applications of air-pollution control. From a beginning in the last half of the seventies, over 500 installations have been made, which represent only a few applications. Most of these applications have been discussed herein and involved hydrocarbon emission reduction. The author anticipates many more applications and many hundreds more installations in the decade of the eighties as this technology becomes better known in the petroleum and petrochemical industry.

A. Bulk Removal—Examples of bulk removal are hydrogen sulfide-separation to make acceptable engine and heater fuel. For example, a standard petroleum production Fuel Conditioning Unit will reduce the hydrogen-sulfide content from as high as 3% (vol) to less than 0.3% (vol). The hydrogen sulfide is reduced so that the gas may be used directly as fuel or may pass through secondary treatment (such as iron sponge) with significant load reduction on the secondary treatment.

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SO₂ Removal By Limestone Dual Alkali

The DA process has the advantages of clear solution scrubbing, high SO₂ removal efficiency, low liquid to gas ratio and reliability.

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The sodium based dual alkali (DA) process is one of the second generation flue gas desulfurization (FGD) technologies currently utilized in the United States [1]. The DA process has the advantages of clear solution scrubbing, high SO₂ removal efficiency, low liquid to gas (L/G) ratio, and high reliability, [2]. All existing commercial-scale DA systems use lime to react with spent scrubber effluent and regenerate the sodium sulfite scrubbing solution. Since lime is produced from limestone by an energy intensive calcination process, the direct use of limestone is increasingly more attractive with the rising cost of energy. In recent years, unit weight lime cost has been as much as 5 to 10 times the cost of limestone. It is estimated that a significant cost savings could be realized by converting a DA FGD system from lime to limestone [3].

In order to promote the more advanced and more economical limestone DA air pollution control technology, EPA's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina (IERL-RTP, NC) has sponsored a series of research projects. Factors influencing limestone reactivity and system chemistry were identified by early laboratory work. Limestone regenerations of simulated scrubbing solutions were studied by bench-scale tests with promising results [4, 5]. The technical feasibility of the limestone DA process was evaluated by conducting prototype testing with the 20 MW facility at Gulf Power Company's Scholz Steam Plant [6]. Excellent SO₂ removal efficiencies in excess of 95 percent were achieved; limestone utilizations were also high, over 97 percent. However, the soda ash consumption of 0.29 moles of Na₂CO₃/mole of SO₂ removed far exceeded con-

ventional consumption of 0.05 in a lime DA system [7]. Solids content in the filter cake ranged between 35 and 45 percent, which was below the anticipated 50 to 55 percent. The continuous operation was also limited by the intermittent production of very fine, needle-shaped crystalline solids with poor settleability. These fine solids did not settle in the thickener and caused interruption of system operation or system upset, when they were carried over from the thickener overflow to the absorber.

In order to support future full-scale operation and to promote system feasibility, a pilot-scale dual alkali system was established by IERL-RTP, and testing started in 1979. The pilot plant successfully simulated the prototype-scale testing at Scholz steam plant and later demonstrated the long term operability of limestone dual alkali processes [3]. Additional pilot plant tests were conducted to study factors affecting filter cake quality and soda ash consumption rate. This paper reports on the results of testing during the period February 1982 through March 1983. This recent pilot plant testing showed that significant improvement in soda ash consumption and filter cake quality could be achieved with proper system control. The causes of system upset by non-settleable solids were also identified and demonstrated in tests. The objectives of this paper are to present the highlights of recent pilot plant testing and to discuss, generally, limestone dual alkali processes.

TEST FACILITY

The absorber is a 23 cm (9 inch) diameter tray tower designed for 8 m³/min flue gas capacity (0.1 MW). The overall process flow diagram is shown in Figure 1. Flue gas from an oil/gas-fired boiler is drawn through the absorption tower by an induced draft fan located immediately upstream from the stack. Gaseous SO₂ from cylinders is fed into the ducting before the absorber to spike the flue gas to predetermined concentrations of SO₂. The oxygen content of the flue gas is controlled by adjusting the boiler excess air. The absorber contains a spray section (quench) followed by three trays in series for gas/liquid contacting. The trays are sieve-type with 4.8 mm (3/16-inch) holes on a 9.5 mm (3/8-inch) triangular spacing. Design pressure drop
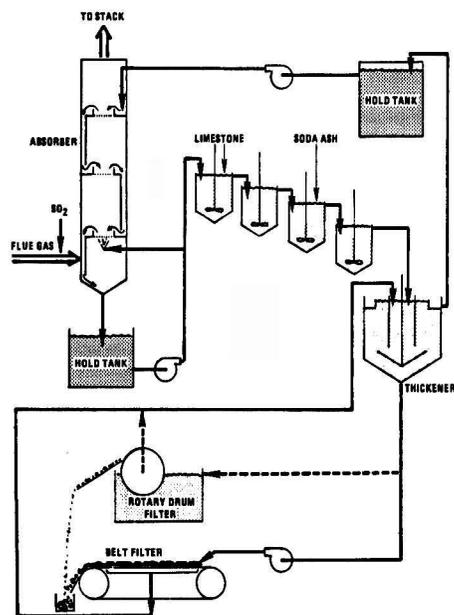
Figure 1. Flow diagram of IERL-RTP dual alkali pilot plant.

across the trays is 20 cm (8 inches) of water. Regenerated scrubbing liquor from the thickener hold tank is fed to the top tray and overflows a 1.3 cm (1/2-inch) weir into a collection box and then to successive trays via internal downcomers and weirs countercurrent to the flue gas flow. To prevent short-circuiting of gas around the trays, liquor from the bottom tray is collected in a weir box and overflows to the hold tank through a standpipe.

Spent scrubbing solution from the hold tank is pumped to the reactor system based on liquid level control. Slurry flows through the four reactors in series by gravity overflow. Limestone is fed to the first reactor as 40% slurry. The feedrate is manually set as required for either pH or reactant stoichiometry control. Soda ash is added to the second or the third reactor as a dry powder (for ease of operation in a small pilot unit).

Reactor effluent slurry flows by gravity to the thickener centerwell. Clarified liquor overflows from the thickener to the forward feed hold tank from which it is pumped to the absorber.

Two dewatering systems, a rotary drum filter and a belt filter, were used to evaluate the filterability of the thickener underflow slurry. The drum filter is equipped with a single stage cake washing device and the belt filter with a three-stage countercurrent washing system.

PROCESS CHEMISTRY

The overall main reaction in a limestone regenerated DA process may be represented by:

$$CaCO_{3(s)} + SO_{2(g)} \xrightarrow{H_2O} CaSO_{3(s)} + CO_{2(g)} \quad [1]$$
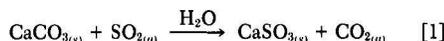
One mole of limestone reacts with 1 mole of SO₂ to produce 1 mole of calcium sulfite and 1 mole of carbon dioxide, according to this equation.

Reactions in the Absorber

The major chemical reactions that occur in the absorber include:

Absorption

$$SO_{2(g)} \rightarrow SO_{2(aq)} \quad (2)$$

$$O_{2(g)} \rightarrow O_{2(aq)} \quad (3)$$

Desorption

$$H_2CO_{3(aq)} \rightarrow CO_{2(aq)} + H_2O_{(l)} \quad (4)$$

Neutralization

$$SO_3^{--}{}_{(aq)} + SO_{2(aq)} + H_2O_{(l)} \rightarrow 2HSO_3^-{}_{(aq)} \quad (5)$$

$$HCO_3^-{}_{(aq)} + SO_{2(aq)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)} + HSO_3^-{}_{(aq)} \quad (6)$$

Oxidation

$$HSO_3^-{}_{(aq)} + 1/2\ O_{2(aq)} \rightarrow SO_4^{--}{}_{(aq)} + H^+{}_{(aq)} \quad (7)$$

$$SO_3^{--}{}_{(aq)} + 1/2\ O_{2(aq)} \rightarrow SO_4^{--}{}_{(aq)} \quad (8)$$
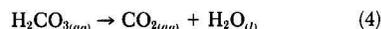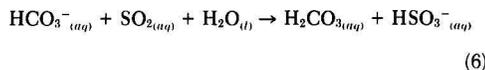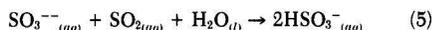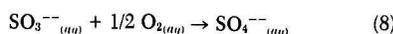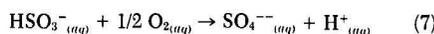
Absorption of SO₂ and desorption of CO₂ are governed by gas-liquid mass transfer and equilibria between the SO₂ and CO₂ in the flue gas and in the recirculated scrubbing liquor. If the alkaline species in the scrubbing liquor (e.g., SO₃⁻⁻), were reduced by low pH due to insufficient limestone stoichiometry, a drop of SO₂ absorption rate will re-

sult. On the other hand, higher L/G ratio and liquid holdup in the absorber can increase the SO_2 removal efficiency.

Neutralization of the absorbed SO_2 by aqueous alkaline species is dominated by the essentially instantaneous reaction between SO_3^{--} and hydrated SO_2. Oxidation of the sulfate species to sulfate ion is accompanied by the absorption of oxygen in the flue gas. The oxidation reaction occurs predominantly in the absorber. However, any contact between oxygen (from air or flue gas) and aqueous sulfite or bisulfite will result in oxidation.

Reactions in the Reactors

The primary chemical reactions that occur in the reactors include:

Dissolution and Desorption

$$CaCO_{3(s)} + HSO_3^-{}_{(aq)} \rightarrow Ca^{++}{}_{(aq)} + SO_3^{--}{}_{(aq)} + HCO_3^-{}_{(aq)} \tag{9}$$

$$HCO_3^-{}_{(aq)} + HSO_3^-{}_{(aq)} \rightarrow H_2CO_{3(aq)} + SO_3^{--}{}_{(aq)} \tag{10}$$

$$H_2CO_{3(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} \tag{11}$$

Precipitation

$$Ca^{++}{}_{(aq)} + (1-x)SO_3^{--}{}_{(aq)} + xSO_4^{--}{}_{(aq)} + yH_2O_{(l)} \rightarrow$$
$$Ca(SO_3)_{1-x}(SO_4)_x \cdot yH_2O_{(s)} \tag{12}$$
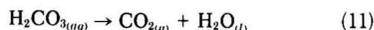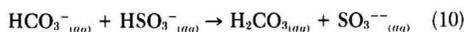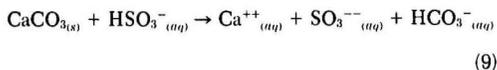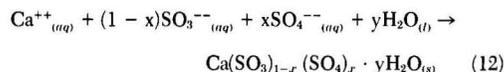
Limestone is dissolved in the reactors to replenish the aqueous alkaline species which are consumed by the neutralization reaction in the absorber. Most of the carbon dioxide resulting from limestone dissolution evolves into the atmosphere from the reactor surface. The system product is a solid solution, $Ca(SO_3)_{1-x}(SO_4)_x \cdot yH_2O$, where x is proportional to the oxidation level and ranges up to about 0.2. Limestone utilization is defined as:

$$\text{Percent utilization} = 100 \times TS/TCa$$
$$= 100/\text{stoichiometric ratio} \tag{13}$$

where TS: total sulfur in the product solids, moles
TCa: total calcium in the product solids, moles

Precipitation of solids occurs in accordance with the solubility product, K_{sp}, which is taken here to be equal to (8).

$$K_{sp} = a_{Ca^{++}} \cdot a_{SO_3^{++}} = 4.5 \times 10^{-7} \text{ (mole/liter)}^{-2} \text{ at } 50°C \tag{14}$$

where $a_{Ca^{++}}$ and $a_{SO_3^{--}}$ are calcium and sulfite ion activities, respectively.

Since the sulfite ion concentration in the scrubbing liquor is usually maintained in the range of 0.1 to 0.5 M, the calcium ion concentration is extremely low; i.e., sodium is the dominant cation in the scrubbing liquor. Due to the low solubility, most of the carbon dioxide produced by the dissolution of limestone evolves almost immediately into the atmosphere. The concentration of carbonate species (<0.05M) in the absorbent liquor is usually orders of magnitude lower than that of sulfite species.

The process chemical conditions can be reflected by two important concentration ratios, sulfite to bisulfite and sulfate to sulfite. The sulfite to bisulfite molar ratio and the pH are interdependent and can be adjusted by limestone stoichiometry. The sulfate to sulfite molar ratio is determined by the balance of oxidation and coprecipitation rates. The absolute concentration of all species is reflected by the total sodium concentration, which is controlled by Na_2CO_3 addition.

RESULTS AND DISCUSSION

Pilot plant tests have been performed over a wide range of operating conditions. The results demonstrate that solids with reasonably good dewatering properties can be produced over a range of simulated utility boiler operating conditions. Soda ash consumption rate substantially lower than that in previous test programs can be achieved by improved filter cake washing. System upset simulation tests were conducted to identify the causes of system upset. It was demonstrated that system upset could be avoided by proper design and control of the processes. The pilot plant has been operated successfully for more than 10 months over the wide range of operating conditions without any system upset. The various aspects of system performance are discussed below.

SO₂ Removal

Over 92% SO_2 removal efficiency was readily achieved at 3000 ppm flue gas SO_2 concentration. The two SO_2 monitoring techniques, ultraviolet and wet gas analysis, were in good agreement. The SO_2 removal efficiency was a function of system pH, sulfite ion concentration, and absorber internals. Material balance indicated that the absorber "make-per-pass" (moles of SO_2 absorbed per liter of absorbent flowing in the absorber) was in the range of 0.1 to 0.13 mole of SO_2 per liter of scrubbing solution, which was an order of magnitude higher than that of slurry scrubbing processes. The high make-per-pass of the pilot limestone dual alkali absorber was reflected by the low L/G ratios (0.8-1.2 l/m³ or 6-9 gal/1000 acf utilized), as shown in Table 2, compared with the high L/G (5.3-9.3 l/m³ or 40-70 gal/1000 acf, usually) of slurry scrubbing processes (9).

Limestone Utilization

High calcium, fine grind Fredonia limestone was utilized to regenerate the scrubbing liquor in all testing described herein. In previous testing, simulating conditions at the Gulf Power Scholz plant, Sylacauga limestone was also tested in certain runs and proved to be acceptable.

As shown by Equation 9, bisulfite ion is the predominant acidic species which reacts with the limestone and dissolves it. Figure 2 illustrates the effect of acidity concentration on limestone utilization obtained from the pilot plant tests with the pH of regenerated liquor between 6.4 and 6.5. (Acidity in a DA system is defined as the concentration of all acid species determined by titrating a quantity of solution with standard base to the thymolphthalein end point of pH 10.6). A minimum concentration of acidity at 0.2 M was needed to attain 90% limestone utilization. When the acidity concentration was above 0.4 M, 95-100% limestone utilization could be achieved. Since the acidity concentration of a concentrated mode DA process is usually higher than 0.2 M, it was concluded that high limestone utilization (greater than 90%) could be obtained in the DA process under normal operating conditions.

Oxidation and Sulfate Balance

Two effects of oxidation were observed during the pilot plant tests, sulfate ion accumulation and solids quality deterioration. The latter will be discussed in the next section. The level of sulfate ion accumulation is determined by the oxidation rate and sulfate removal rate. Sulfate ion can leave the system either in liquids, wetting the waste product as sodium sulfate, or in solids as calcium sulfite/sulfate crystals. The latter is more desirable because sodium is not lost, and the waste cake will contain less soluble salts which can be leached into the ground water near a disposal site. Calcium sulfate is coprecipitated with calcium
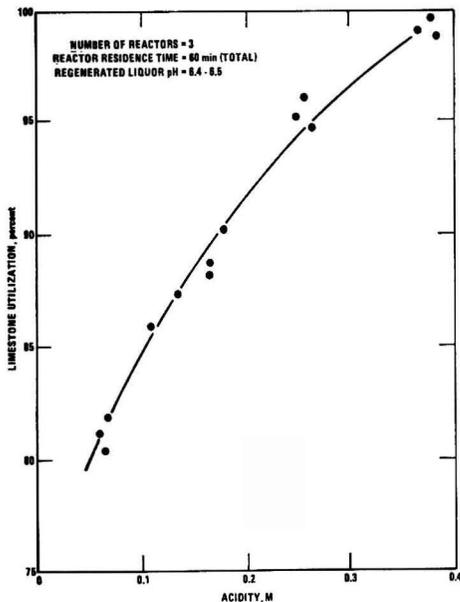
Figure 2. Effect of (thymolphthalein) acidity on limestone utilization.

sulfite in the reactors to form a "solid solution" as indicated by Equation 12. (The liquid phase calcium and sulfate concentrations never exceed the gypsum solubility product, and no pure gypsum phase forms.) The relationship between sulfate/sulfite molar ratio in the liquid and in the precipitated solids is shown in Figure 3. Overall, the pilot plant sulfate balance showed that the DA system was capable of keeping up with oxidation rates up to 20% of the SO_2 removed—oxidation rates higher than those anticipated for most medium- and high-sulfur coal applications. (An oxidation rate of 20% is equivalent to a SO_4^{--}/SO_3^{--} molar ratio of 0.25 in the solids.) In other words, sulfate balance can be accomplished by calcium sulfite/sulfate coprecipitation with closed-loop operation for the medium- to high-sulfur coal applications other limestone DA processes.

Oxidation is an important but undesirable side reaction in DA processes since high oxidation could convert the useful total oxidizable sulfur (TOS, moles of sulfite ion plus bisulfite ion per liter of solution) species to inert sulfate ion and deteriorate solids qualities. Efforts have been made to characterize the oxidation reaction and to minimize its rate.
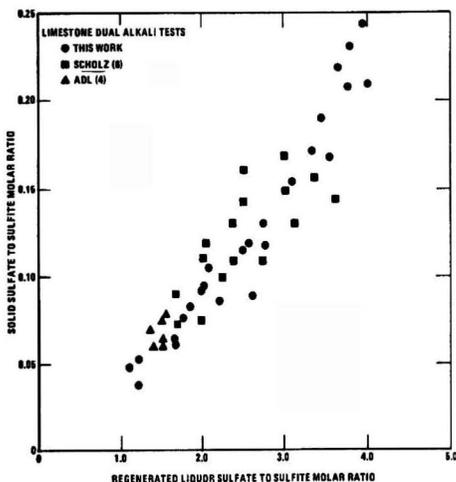
Short term (8 to 12 hours each run) pilot plant tests were performed by recirculating $Na_2SO_3/NaHSO_3$ solution around the absorber which was isolated from the rest of the system. Oxidation tests were conducted at 3.5, 5.5, 8.5% flue gas oxygen concentrations. The initial TOS concentration was set at 0.3 to 0.4 M and the solution pH at about 6.7. The oxidation rate increased from 2.35 to 3.08 gmole/hr as the oxygen concentration was raised from 3.5 to 5.5%. Oxidation rate at 3.77 gmole/hr was obtained with 8.5% flue gas oxygen. It was concluded that the oxidation rate in the DA absorber is a function of flue gas oxygen concentration.

The effectiveness of sodium thiosulfate as an oxidation inhibitor was also evaluated by pilot plant testing. It was suggested that the thiosulfate ion might act as a radical scavenger to deactivate the radicals that promoted the oxidation of sulfite and/or bisulfite ions. Results shown in Figure 4 indicate that the concentration ratio of thiosulfate ion to TOS was an important factor determining the effectiveness of sodium thiosulfate as an oxidation inhibitor. Insignificant effect was observed when the thiosulfate to TOS ratio was below 0.1. If 50% reduction of the oxidation rate is desirable, the thiosulfate to TOS ratio must be maintained at 0.5 or above, under conditions tested. In general, the action of thiosulfate as an oxidation inhibitor may be dependent upon the ratio of thiosulfate to TOS as shown in Figure 4. Since the TOS concentrations in DA systems are orders of magnitude higher than in limestone slurry scrubbing systems, a much higher concentration of thiosulfate may be required in DA systems. In limestone slurry scrubbing only a few hundred ppm of thiosulfate was reported to be effective for oxidation inhibition. However, for a concentrated sodium based limestone DA process, the TOS concentration is expected to be in the range of 0.7 to 1.0 M. Therefore, a significant amount of sodium thiosulfate would be required to cut the oxidation rate by 50%. The feasibility of using sodium thiosulfate as an oxidation inhibitor will be determined by economic trade-offs and other site specific factors.

Filter Cake Quality

Probably the most significant impact of oxidation on system performance observed during the pilot plant tests was the change in filter cake quality. As shown in Figure

Figure 3. Ratio of sulfate to sulfite in solids as a function of sulfate to sulfite ratio in regenerated liquor.
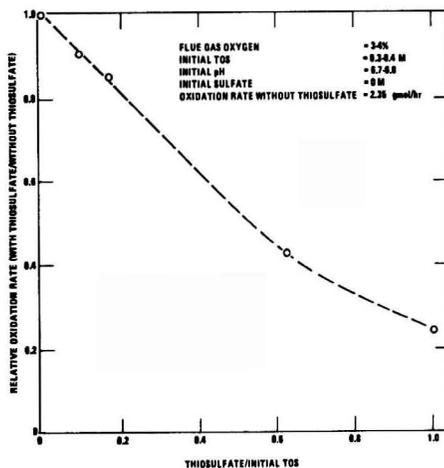
Figure 4. Effectiveness of sodium thiosulfate as an oxidation inhibitor.

5, the % insoluble solids in the filter cake dropped with the increase of oxidation rate reflected by the sulfate to sulfite molar ratio in the regenerated liquor. When the sulfate to sulfite molar ratio was below 1.5, filter cake % insoluble solids reached 60%. The % insoluble solids in the filter cake varied inversely with the sulfate to sulfite molar ratio, reaching about 35% at a sulfate to sulfite molar ratio of 4. Operation under these conditions was considered to be undesirable because of the poor physical properties of the waste and the high losses of sodium compounds.

Coulter counter analyses were conducted to measure the particle size distribution in the reactor effluent at various sulfate to sulfite molar ratios. However, no significant changes in particle size distribution were obtained, and the mean particle diameter remained at about 20 μm even though the filter cake % insoluble solids content dropped from 60 to 35 percent. The product solids were further examined under a scanning electron microscope (SEM) to observe the detailed morphology of the individual solid particles. The photomicrographs showed that the solid "particles" were actually clusters composed of agglomerates of crystals. The "particles" which gave 60% solids filter cake were composed of thicker, larger, and better defined crystals or platelets. However, the 35% filter cake "particles" were agglomerates of thinner, smaller, more needle-like crystals. In addition to thin platelets or needles, crystal fractures (which might be caused by the collision of agitator blades) were also observed with 35% filter cake particles generated at high sulfate to sulfite molar ratio. It may also be postulated that the coprecipitated sulfate ion acts as an impurity which inhibits crystal growth and causes crystal defects.

High Active Sodium vs. Low Active Sodium*

In order to evaluate the effects of operating conditions on system performances such as oxidation rate and filter cake % insoluble solids, long term demonstration tests were performed at high (1.2 M) and low (0.48 M) active sodium concentrations. Results summarized in Table 1 indicate that at high active sodium the sulfate to sulfite molar

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*Active sodium is defined as $2[SO_3^{--}] + 2[CO_3^{--}] + [HCO_3^-] + [HSO_3^-]$ expressed as Na^+ concentration. Active sodium is actually a misnomer since Na^+ does not participate in any of the dual alkali reactions but is used for convenience.
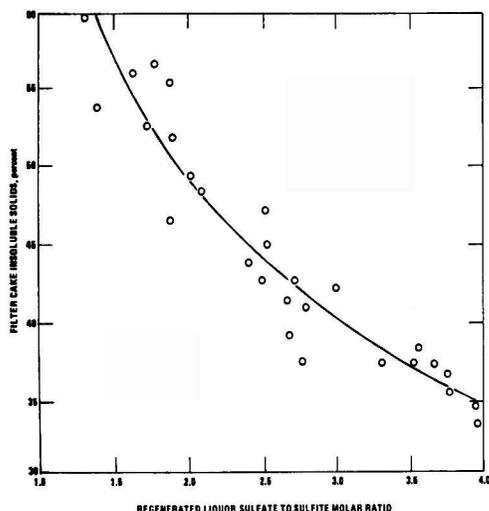
TABLE 1. THE EFFECTS OF ACTIVE SODIUM AND IONIC STRENGTH ON OXIDATION AND RESULTING FILTER CAKE QUALITY AT THE IERL-RTP DUAL ALKALI PILOT PLANT

	High Active Sodium Mode	Low Active Sodium Mode
Active sodium, M	1.2	0.48
Total sodium, M	3.0	1.5
Ionic strength, M	4.5	2.25
Sulfate/sulfite molar ratio[a]	1.9	3.9
Oxidation rate[b], %	8	18
Filter cake insoluble Solids, %	52	35
Flue Gas O$_2$, %	7.1	7.0

(a) in regenerated liquor
(b) based on filter cake analyses

ratio was 1.9 which was considerably lower than the 3.9 obtained from low active sodium test. Filter cake analyses also indicate that the 8% oxidation level at high active sodium was considerably lower than the 18% observed at low active sodium. The lower sulfate to sulfite molar ratio and oxidation rate at high active sodium are reflected by the higher filter cake % insoluble solids as shown in Table 1. The decrease of oxidation rate with the increase of active sodium concentration is probably due to the ionic strength effect. As shown in Table 1, the high active sodium mode was operated with 4.5 M ionic strength which is 100% higher than that of low active sodium. Data in the literature indicate that both the solubility and diffusivity of oxygen in aqueous solutions can be reduced by higher ionic strength through the change of liquid viscosity. As a result, the mass transfer rate of oxygen from flue gas to scrubbing solution is reduced, and the liquid-phase oxidation rate is also decreased.

Soda Ash Consumption

With a properly designed and operated system, the majority of the sodium loss should occur with the liquor entrained in the filter cake. Sodium ion concentration in the scrubbing liquor, filter cake % insoluble solids, and filter cake wash efficiency are the three major factors determining the rate of sodium consumption. The typical sodium ion concentration of a limestone DA process is expected to be in the range of 2 to 3 M. As shown in Figure 6, the soda ash consumption will be significant if there is no filter cake washing to recover the sodium species, especially when the filter cake % insoluble solids is below 50%. However, the soda ash consumption can be reduced substantially by filter cake washing with a reasonable wash efficiency. The filter cake wash efficiency was defined as:

washing efficiency

$$= \left(1 - \frac{\text{sodium content after washing}}{\text{sodium content before washing}}\right) \times 100\% \quad (15)$$

A rotary drum filter with single stage washing was first used to evaluate the washability of sodium compounds from the filter cake. Only 10 to 20% wash efficiency was obtained. The poor wash efficiency was attributed to filter cloth blinding or poor filter design. Most of the wash water did not penetrate the cake and just flowed down off the filter cake surface.

In an effort to reduce sodium losses by improving wash efficiency, a belt filter with three stages of countercurrent washing was installed and then evaluated. Three sets of filter cake washing tests were conducted. The results, compared with wash efficiencies predicted by a wash model, are shown in Figure 7. The wash efficiency, assuming countercurrent washing with complete mixing of

Figure 5. Percent filter cake solids as a function of sulfate to sulfite ratio in the regenerated scrubbing liquor.
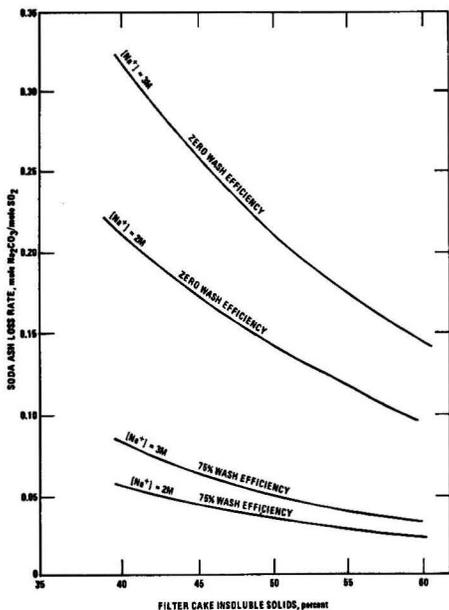
Figure 6. Soda ash loss rate through unwashed filter cake as a function of filter cake insoluble solids and scrubbing liquor sodium concentrations.

wash water and occluded liquor at each stage, can be calculated by this model as follows:

$$\text{wash efficiency} = \left(1 - \frac{R - 1}{R^{n+1} - 1}\right) \times 100\% \text{ where } R > 1$$

(16)

where R is the number of filter cake water displacements, and n is the number of washing stages.

Figure 7 shows that wash efficiencies lower than those predicted by the model were obtained from the pilot plant. With two filter cake water displacements and three washing stages, approximately 75% wash efficiency was observed, which is 18.3 percentage points lower than the predicted 93.3% wash efficiency. There are two reasons for the difference. First, the wash model assumes that all sodium species are washable. However, data indicated that some sodium species are not washable. However, data indicated that
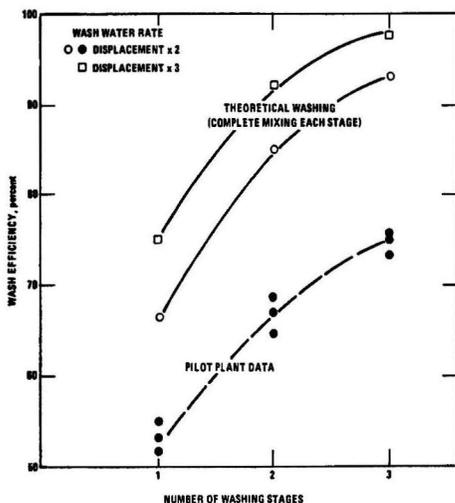
about 10 to 15% of the sodium species are not washable. Coprecipitation and crystal occlusion might explain why some of the sodium species contained in the filter cake cannot be washed out. Secondly, the model assumes an even distribution and complete mixing of wash water with the entrained cake liquor. However, cake cracking causes some bypassing or channeling of wash water and results in less than ideal mixing conditions.

The model indicates that the filter cake washing efficiency could be maximized by further increasing the quantity of wash water and/or the number of washing stages. Two displacements of wash water were used in these tests since that was the volume of wash water permitted by material balance when limestone was added to the DA reactors at 40% slurry (limestone in fresh water). Material balance indicates that if limestone is fed as a dry powder, the wash rate can be increased to three displacements, corresponding to an ideal wash efficiency of 97.5%.

Pilot plant data indicated that the average filter cake insoluble solids was about 52% at 3M total sodium concentration (Table 1). Figure 6 indicated that the soda ash requirement to replenish the sodium loss with unwashed filter cake should be about 0.2 mole Na_2CO_3 per mole of SO_2 absorbed. If 75% filter cake wash efficiency is achieved, the soda ash consumption rate is predicted to be as low as 0.05 mole Na_2CO_3 per mole of SO_2 absorbed.

Simulation of System Upsets

System upsets are characterized by non-settling finely divided solids suspended throughout the liquid in the system. The thickener cannot produce clear regenerated liquor overflow to feed the absorber, and the system ceases to function as a dual alkali process.

Pilot plant testing indicated that system upsets may be caused either mechanically or chemically. Mechanical attrition of crystals produced poor quality, non-settleable solids (3, 10). System upset was also observed to be purely a function of chemistry; specifically, it would occur with sulfate to sulfite molar ratios above about 4.

A mechanically caused upset was demonstrated by using the reactor design shown in Figure 8a, which included long baffles and the agitators pumping downward. This design produced a quiescent zone between the baffles and the wall of the tank. Large crystals tended to settle in the quiescent zone and accumulate in the reactors. As crystals were accumulating, the reactor solids concentration increased and the filter cake quality deteriorated. It was suspected that the increase of solids concentration favored crystal attrition, and the attrition produced extremely fine particles. Eventually, the overload of fine solids overflowed to the thickener and produced a system upset. Solids quality was improved by using the continuous stirred tank reactors with agitators pumping upward as shown in Figure 8b. When the reactor solids concentration was 3% or below, the solids settling rate reached 1.5 to 2 cm/min vs. the 0.1 cm/min during upset conditions.

A chemical upset was produced by decreasing the soda ash make-up rate to zero to let the sulfate to sulfite molar ratio increase. The solids qualities, including solids settling rate and filter cake % insoluble solids, deteriorated with the increase of sulfate to sulfite molar ratio. System upset occurred when sulfate to sulfite molar ratio reached 4.3. Heavy doses of soda ash were then added to the reactors in an attempt to reduce the sulfate to sulfite molar ratio and to reverse the system upset. The sulfate to sulfite molar ratio decreased gradually with associated improvement in solids qualities. When the sulfate to sulfite molar ratio decreased below 1.5, the solids settling rate reached 2.5 cm/min, and filter cake insoluble solids content reached 60%. This indicated that the chemical upset was reversible by adjusting the system chemistry.

Figure 7. Performance of belt filter with countercurrent washing.
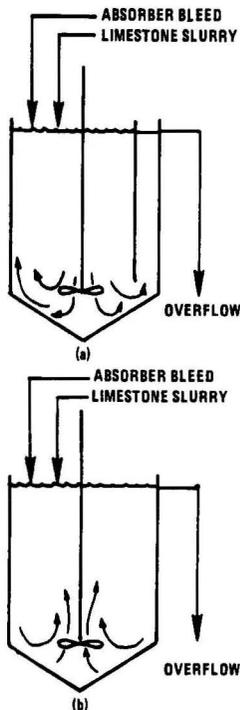
Figure 8. Reactor flow patterns utilized for system upset simulation tests.

CONCLUSIONS

The following conclusions were drawn from the pilot plant studies:

1. The results confirmed that limestone dual alkali processes can provide the advantages of clear solution scrubbing with high SO_2 removal efficiency at low L/G and high limestone utilization.

2. The level of oxidation can be reduced by increasing the ionic strength in scrubbing solutions. The removal of the oxidation product, sulfate ion, can be accomplished by calcium sulfite/sulfate coprecipitation as solid solution with closed-loop operation and filter cake washing for medium- and high-sulfur coal applications.

3. The filter cake quality was affected by levels of oxidation or liquid phase sulfate to sulfite molar ratios. Pilot plant tests demonstrated that filter cake % insoluble solids can be improved from 35% to 52% by increasing the active sodium concentration from 0.48 M to 1.2 M to reduce the oxidation level and sulfate to sulfite molar ratio.

4. The soda ash consumption rate was influenced by scrubbing solution sodium concentration, filter cake quality, and cake wash efficiency. Pilot results achieved cake wash efficiency of 75% using three stages of countercurrent washing. Material balance projected that a soda ash consumption of 0.05 mole Na_2CO_3 per mole SO_2 removed should be attainable with closed-loop operation and 75% cake wash efficiency.

5. System upsets assumed to be caused by mechanical crystal attrition may be avoided by better design and operation of reactors, agitators, and pumps. Chemically induced system upset caused by high sulfate to sulfite molar ratio is reversible and can be avoided by controlling the system chemistry in medium- and high- sulfur coal applications with normal levels of oxygen in the flue gas.

Recent Test Results and Future Direction

Recent test results have shown a vast improvement in the performance of the limestone regenerated dual alkali process. The improved performance was primarily attributed to the use of highly reactive limestone (aragonite). It was also found that finer grinds and lower magnesium content in the limestone contributed to improved performance.

Aragonite, which is very reactive due to its porous surface structure was tested in a high active sodium mode with 8.5% flue gas O_2 concentration. Ninety-four percent SO_2 removal efficiency was obtained with 95% limestone utilization. It should be noted that higher removal efficiency would be expected in a properly engineered large scale absorber, since the pilot unit is not optimally designed for SO_2 absorption. More significantly, filter cake insoluble solids reached as high as 75%, with typical values in the 60 to 70% range. While using aragonite, foaming in the reactors, possibly caused by impurities in the limestone, was observed and caused a minor problem. The problem was quickly alleviated through the use of an anti-foaming agent (ester in high molecular weight alcohol) in small quantities. The quantity used was only 125 g/metric ton of limestone; and this consumption rate was estimated to be equivalent to increasing the cost of limestone by about 2%.

Test results with Aragonite demonstrate that appropriate limestone selection and specification is essential in optimizing limestone dual alkali process performance. A series of pilot plant tests are proceeding to evaluate the scrubber performance with respect to various limestone types and grinds. Techniques which have the potential of characterizing limestone reactivities applicable to dual alkali processes are also being developed.

LITERATURE CITED

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AIChE ENVIRONMENTAL DIVISION DIVISION NEWSLETTER

Environmental Division (1970)

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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Environmental Sessions at San Francisco

At the 1984 Annual AIChE Meeting in San Francisco, the Environmental Division will present the following technical sessions:

	Chairman	Time of Presentation
Chemical Engineering Fundamentals Applied to the Environment	M. R. Overcash	November 29, morning
Membrane Processes in Pollution Control	D. Bhattacharyya	November 29, afternoon
Emerging Techniques for Heavy Metal Removal and Organics Destruction	B. M. Kim	November 30, morning

Continuing Education

The following courses will be offered at the 1984 AIChE Annual Meeting in San Francisco:

Noise Control in the Process Industries	November 24-25
Atmospheric Diffusion Modeling	November 28-29
Air Pollution Control	November 25-27
Industrial Water Conditioning	November 26-27
Water Quality Engineering for Industry	November 28-29
Advanced Waste Water Treatment	November 30-December 1

Awards at Philadelphia Dinner

During the 1984 Summer National Meeting of AIChE, the Larry K. Cecil Environmental Division Award Dinner was held at the Palace Hotel in Philadelphia on the evening of August 21. Demand for tickets was so great that the publicized location of the dinner had to be changed to accommodate all of those who wished to attend and were on a waiting list after the original capacity of 50 registrants was exceeded.

Dr. Robert A. Baker was the recipient of the prestigious Cecil Award. Student awards, funded by Resources Conservation, Inc., Procter & Gamble and UCLA were presented as follows for the papers prepared especially for the student awards competition and not published elsewhere:

First Place: Jeffrey Kittrell, University of Massachusetts, a certificate and $250.00.

Second Place: Jay Turner, UCLA, a certificate.

Third Place: Jerry Maney, University of Kentucky, a certificate.

All awardees had expenses paid, including travel and hotel, by the above-mentioned sponsors.

Request for Award Nominees

The Palladium Medal Award is sponsored jointly by the Audubon Society and the American Association of Engineering Societies. The purpose of this award is to honor engineering achievement in environmental conservation. Bryce I. MacDonald, of the AAES Awards Committee and a former Chairman of the AIChE Environmental Division and Director of AIChE, has requested nominations of well-qualified candidates from the Environmental Division for this award, which has been presented in previous years to outstanding civil engineers and no chemical engineers to date. Nominations will come from the Executive Committee of the Environmental Division.

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Season's Greetings.
From one heart to another.

During this joyous season, your American Heart Association wishes you the happiest and healthiest of holiday greetings.

With our whole heart we're leading the fight against our nation's Number One Killer — heart disease and stroke.

We're leading the fight with research, professional and public education, and community service programs. And we're winning.

But more needs to be done.

You can help by making this holiday season "A Time To Remember." Send a friend or loved one a special occasion card from the American Heart Association, listed in your telephone directory.

American Heart Association

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ENVIRONMENTAL PROGRESS