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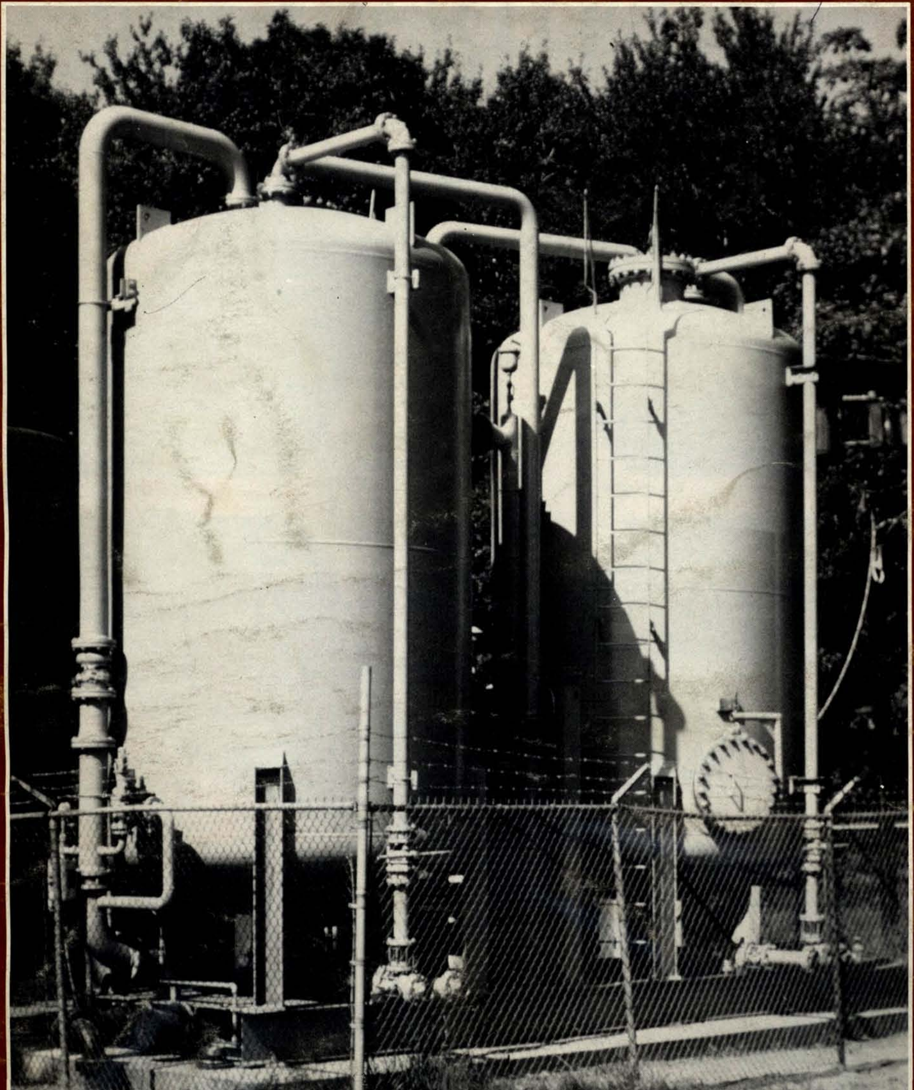
ENVIRONMENTAL PROGRESS



Carbon adsorption system for water treatment (see article on page 257).
Photo courtesy of Calgon Carbon Corporation, Pittsburgh, Pennsylvania.

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ENVIRONMENTAL PROGRESS

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

Publisher
Diane Foster

Editor
Gary F. Bennett
(419) 537-2520
Managing Editor
Maura Mullen
(212) 705-7327
Book Review Editor
Robert W. Peters
Software Review Editor
Ashok Kumar
Pollution Prevention/Waste
Minimization Section
R. Lee Byers
Editorial Assistant
Karen M. Simpson
Production Assistant
Maryanne S. Spencer

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Environmental Science and Technology to Meet The Challenges Of The 21st Century

John H. Skinner

Addressing the environmental problems of the 21st century will require an expanded scientific research program that focuses on the reduction of risks associated with pollution. Pollution prevention must be our highest priority. The research efforts of the Environmental Protection Agency (EPA) have been instrumental in addressing the environmental problems of the 20th century and will play a major role in our ability to address and effectively manage future problems.

In the past two decades, the pollution control efforts of EPA have been successful in improving the air quality in many cities, protecting thousands of miles of rivers and streams, and restoring and protecting thousands of acres of lakes. In addition, significant progress has been made in improving the management of hazardous wastes, toxic chemicals, and pesticides. EPA's past approaches have primarily focused on reducing environmental discharges or cleaning up contamination by employing engineering controls such as wastewater treatment plants, scrubbers for stacks, and treatment facilities for chemical waste.

Although these "end-of-pipe" strategies and remedial technologies have been somewhat successful in controlling pollution or cleaning it up once it is generated, further gains through technological treatment and control will be much more costly and difficult to achieve. Furthermore, as the nation approaches the 21st century, we face another level of environmental threats far more complex and widespread than can be addressed by "end-of-pipe" controls. We are facing a number of environmental problems — like municipal and hazardous waste disposal, ocean pollution, acid rain, global warming, stratospheric ozone depletion, and radon infiltration — that are not attributable to discrete sources of pollution and are not totally amenable to end-of-pipe solutions. Many cities do not meet federal air quality standards for ozone. Others are not in compliance with requirements for treatment of municipal sewage. Our oceans, estuaries, near-coastal waters and wetlands are victims of intensive coastal and upstream development and runoff from farms and cities. Urban areas face a mounting crisis over municipal garbage disposal.

Many of these environmental problems cannot be alleviated simply by more stringent regulatory standards and technological controls. Clearly, solutions of the past are not likely to be as effective as they have been. Addressing these future problems will require a major shift in our overall approach to environmental protection. Furthermore, our strategy for developing the knowledge needed to create and implement environmental protection programs. EPA must be enhanced. We cannot develop solutions without understanding what is happening to our environment and why. Research is the primary tool for enhancing our knowledge base and increasing our capability to respond to future environmental problems.

To meet the challenges of the next century, EPA must reshape its strategy for addressing environmental problems and refocusing its research program to ensure that we will have the fundamental scientific information needed to formulate solutions to these problems. EPA must be more than a regulatory and enforcement agency. It must also be a scientific research agency with responsibility for conducting a respected research program that supports the nation's ability to understand and respond to future environmental problems. EPA must also play a significant role in ensuring that environmental research results are transferred effectively to those who must implement environmental protection programs.

With this in mind the Office of Research and Development has proposed a new "core" research program designed to generate knowledge essential to all areas of environmental decision-making. The core research program will not only strengthen and expand existing efforts, but will initiate research in areas that are critical to addressing future environmental problems. The core research program consists of four components: (1) ecological risk assessment, (2) health risk assessment, (3) risk reduction, and (4) exploratory research. The two risk assessment components are designed to help EPA evaluate the risks that environmental contamination poses to our ecosystems and our health. This knowledge will guide the Agency in designing strategies to anticipate and reduce these risks using the technologies and methodologies generated by the risk reduction research. The fourth component is intended to ensure the continued strength of this nation's academic environmental research efforts.

The core research program redirects EPA's efforts toward preventing pollution. The program supports a risk reduction research hierarchy to help in setting research priorities and in achieving the agency's overall goal of protecting health and the environment. The first priority of the hierarchy is to reduce risk by reducing the generation of the quantities of waste, residues, and contaminants that are produced. The second priority focuses on reducing risks through or reduction of recycling or reuse. The third priority is to provide effective technologies to destroy, treat, or detoxify wastes or pollutants that are generated. Finally, the fourth priority is to minimize exposure to the residual wastes and contaminants that have not been destroyed or detoxified.

This core research program can provide the knowledge and understanding that we will need to wisely manage our environment in the coming decades.' It can provide decision-makers with the tools and information needed to make the difficult choices that we will face in the years ahead. Unless we redirect our research strategy to address preventing future problems, we will continue to implement short-term solutions that are ultimately more expensive and less effective than possible. EPA's core research program is an important step in arming the nation for the challenges that lie ahead.

John H. Skinner, PhD., is currently Acting Deputy Assistant Administrator for Research and Development at the U.S. Environmental Protection Agency. This editorial represents his personal views.

Canadian Official Calls for U.S. Action on Acid Rain And Details Efforts His Country is Making

Alex Manson, director of the Long Range Transport of Air Pollutants section of the Canadian government's environmental agency, recently called for bilateral action with the United States on acid rain. Speaking at the AIChE Summer National Meeting in Philadelphia last August, he detailed programs his government has instituted which are already improving conditions in Canada and in the Northeastern U.S.

But, Canadian action by itself can't solve the problem, Manson said, because "Mother Nature has quite literally put Eastern Canada's acid rain sensitive areas at the end of a huge exhaust pipe." "About 50 percent of the acid rain falling in Eastern Canada is directly manufactured in the United States and exported to Canada," Manson said. He added: "This is one area where Canada can do without 'free trade.' The 'balance of payments' is not favorable."

Manson pointed out areas that receive acid rain, in addition to damage to their lakes and forests, tend to have increased respiratory mortality and lung dysfunction. He also said that "damage caused by acid rain in Eastern Canada totals about $800 million per year." The natural resources at risk from acid rain account for eight percent of Canada's gross national product, he explained.

While the U.S. Congress is debating what action to take on acid rain and clean air, "Canada is well on the way to delivering its part of the bargain," Manson stated. "We have already reduced the amount of acid rain pollution we export (to the U.S.) by one-third," he said.

Since instituting an acid rain control program in 1985, Manson reported that 90 percent of the reductions needed to bring emissions to a level Canadian scientists consider acceptable have been approved and are in the process of being implemented. He predicted that Canada will achieve 100 percent of the emission reductions by 1994 at a cost of approximately $15 per person, per year.

Rather than legislating technology, Manson said the Canadian program lets the private sector and public utilities choose the most cost-effective means available to achieve emission targets. He believes this approach could be applicable to the U.S. even though our acid rain problems are different. For example, most Canadian emissions come from smelters, while most U.S. emissions come from power plants.

In conclusion, Manson said environmental concerns should be at the core of decisions made by governments, industries and individuals. "Just as we need to mange our monetary deficits, we need to manage our environmental deficits," he said.

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On-Site Hazardous Waste Treatment Technology Comes to Small and Medium Industrial Firms

Recent advances in recycling technology have brought a convenient, money saving on-site system for solvent waste reduction at the source, to small and medium-size businesses.

As new legislation requiring industrial firms to reduce their toxic wastes by 50% comes on line, this breakthrough has been achieved in the nick of time for many firms struggling to comply.

For as little as $2500, any firm generating only one drum or more per month of hazardous waste material can acquire the technological capability of a "stand-alone" portable system that will reduce its waste materials by 90%, exceeding imminent legislative requirements by a wide margin.

In addition to legal compliance, this new system allows the firm to have much greater control over the waste disposal aspect of its business, save on expensive hazardous waste removal and storage, minimize their liability in transport and disposal, and to recover their initial investment in the equipment in a matter of months rather than the traditional "pay back" period of several years.

Each year, as industrial waste minimization and source reduction has become a larger and larger social and political issue, industrial and environmental resources have been focused on offering a solution to both the large industrial concerns and to innumerable small and medium sized generators. However, until now, only the largest companies have been able to recycle their own solvent wastes, at the source, while smaller firms have relied on hazardous waste haulers to simply take the material away.

This new technology, marketed nationally by Solvent-Kleene, Inc. of Peabody, Massachusetts is available either for delivery or free demonstration and waste solvent testing upon request.

The system, according to Tom Kutai, President of Solvent-Kleene, Inc., "offers the easiest answer imaginable to a very pesky and disturbing problem. Our system allows companies an upfront savings on solvent purchases of at least 50%, and plus, our customers have the opportunity to clean their solvents and other chemicals more frequently, enhancing the production qualities at virtually no cost on an ongoing basis."

For complete information and detailed capability specifications contact Solvent-Kleene, Inc., Telephone (508) 531-2279, FAX (508) 532-9304.

Workshop on Estimation and Control of Volatile Organic Chemical Emissions

Sponsors: Maryland AIChE/Baltimore/Washington, D.C. Air and Waste Management Association

Workshop Dates: February 14, and 15, 1990

Place: The Sheraton Hotel, Inner Harbor
Baltimore, MD

Summary: This workshop addresses the technical issues involved with estimating and controlling volatile organic chemicals (VOC) emissions from stationary sources. State-of-the-art technologies and new methods of estimating air emissions from different sources (such as paint spray booths, coating processes, automobile refinishers, wastewater treatment facilities, chemical plants and landfills) are discussed.

The targeted audience for attending this workshop are industry environmental personnel, regulatory environmental program planners and technical personnel, and air pollution and waste management consulting personnel.

Contact: Bonnie J. Watts, Chairman (301) 631-3629

Book Reviews

Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants: Advances in Chemistry Series 219, I.H. Suffet and Patrick MacCarthy, editors. Published by American Chemical Society, Washington, D.C., 1989, 864 pages, U.S. List Price: $109.95

Clean water supplies are essential for many chemical and industrial process applications. When the available water is polluted, either by natural toxic elements or by human activity, treatment processes are required to produce the required quality of the needed water. The presence of humic substances in a water supply complicates the treatment processes involved, due to their interactions with other species in the environment, such as influencing the transport of heavy metals and the REDOX state of the metals. Humic substances also interact with nonionic compounds, immobilizing such compounds in sedimentary organic matter. This textbook provides a comprehensive discussion on the effect of humic substances in relationship to the area of water purification. The book is based largely upon a symposium entitled "The Influences of Aquatic Humic Substances on the Fate and Treatment of Pollutants," which was held at the 193rd National Meeting of the American Chemical Society, through the Division of Environmental Chemistry, in Denver, CO, on April 5-10, 1987.

The textbook, containing 45 chapters, is divided into eight major sections. The sections covered include: characterization, environmental impacts, interactions in natural waters with organic contaminants, interactions in natural waters with inorganic contaminants, influences of coagulation processes on water treatment, sorption onto activated carbon (influences on water treatment), influences on ozonation and chlorination processes on water treatment, and influences of ion exchange and membrane processes on water treatment. The vast backgrounds of the various authors of the respective chapters contribute and compliment the interdisciplinary nature of the subject material. A major emphasis of the textbook concerns humic substances and their reactions in natural waters and sediments and their influences on water treatment processes. Specific treatment processes, such as oxidation, enzymatic detoxification, photochemical oxidations, coagulation, ion exchange, and membrane processes are described, both from laboratory and pilot plant studies. The references are current through the time of publication (1987). The book presents an adequate blend of theoretical knowledge, experimental data, and practical applications.

This textbook should be a valuable asset for professionals involved in the areas of water-treatment specialists, environmental engineers, university environmental programs, and all industries concerned about the quality of their water supply.

Robert W. Peters, Ph.D., P.E.
Energy Systems Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Flocculation, Sedimentation & Consolidation, by Brij M. Moudgil and P. Somasundaran, Published by American Institute of Chemical Engineers (AIChE), New York, NY, 1986, 633 pages, U.S. List Price: $70

Flocculation, coagulation, sedimentation, and consolidation phenomena are extremely important for the fields of chemical, mineral, environmental, and coastal engineering. They are likewise important for applications such as wastewater treatment, coal liquefaction, tar sand processing, and electrophoresis. This textbook presents state-of-the-art reviews and recent advances in the areas of flocculation, settling, and consolidation of fine suspensions in aqueous and nonaqueous media. The book is based upon research papers which were presented at the Engineering Foundation Conference, held at Sea Island, Georgia, on January 27-February 1, 1985. All the papers included in this volume were accepted for inclusion, based upon a formal peer review process.

The book, containing 42 chapters, is divided into five major sections. The sections include plenary lectures, flocculation, sedimentation, consolidation, and research needs. The individual chapters are written by leading authorities in the field. The book describes such areas as the flocculating action of polymeric flocculants, aggregate breakage, floc characteristics, charge stabilization, equipment design, sedimentation theory, thickening and dewatering, and effects of chemical additives. Results are presented from many research studies, as well as from pilot plant and field studies. The references are relevant and current (through the time of the publication).

This book represents a welcome addition to the field of flocculation and coalescence phenomena. The book serves as a useful reference for those professionals involved in water and wastewater treatment, environmental engineers, coastal engineers, and those people concerned with the quality of their water supplies.

Robert W. Peters, Ph.D., P.E.
Energy Systems Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Red Book on Transportation of Hazardous Materials, 2nd Edition by Lawrence W. Bierlein, Van Nostrand Reinhold Company, New York, NY, 1988, 1203 pages, U.S. List Price: $104.95

Due to new developments and regulations governing the transportation of hazardous materials, the U.S. Department of Transportation (DOT) has revised many of the regulations. This second edition of the *Red Book on Transportation of Hazardous Materials* represents an update of the material contained in the first edition, published in 1976. These books are intended to serve as guides for the transportation of hazardous materials, including hazardous substances and hazardous wastes designated by EPA.

Federal safety regulation are written with the legal enforcement of the regulations in mind, rather than with the user or subject in mind. This book is not intended as a substitute for the regulations, but rather is used in conjunction with the regulations; frequent reference back and forth between the Red Book and the applicable EPA and DOT regulations is intended. The book contains 32 chapters and 4 appendices. Topics covered include hazardous materials transportation regulations; DOT-regulated hazardous materials; determination of proper DOT shipping name; hazardous materials packaging, marking, and labeling; shipping requirements; placarding of vehicles and containers; shipping requirements; inspection and enforcement; liability associated with shipment and transport, and various regulations associated with hazardous materials transportation. The book has as its goal to simplify the process of compliance with the regulations.

The book provides important information for those companies and personnel responsible for the shipment and transport of hazardous materials.

Robert W. Peters, Ph.D., P.E.
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

HWI: A Software For Hazardous Waste Incinerator Calculations

Ashok Kumar
Department of Civil Engineering, The University of Toledo, Toledo, Ohio 43606
and
H. S. Huang
Argonne National Laboratory, Argonne, IL 60439

The problem of hazardous waste disposal is a national problem. Extensive research is in progress to find safe methods of their disposal. One of the areas being investigated is incineration of hazardous waste. To assist in the preliminary design and analysis of incinerators, Professors Theodore and Reynolds from Chemical Engineering Department, Manhattan College, Riverdale, NY 10471, have developed a software HWI under the sponsorship of the United States Environmental Protection Agency (EPA).

The software package comes with two manuals [*1*, *2*]. Both the manuals are well written and are very helpful in understanding the theory behind the calculations and in running the program. The user guide is divided into five chapters. Chapter One gives an overview of the software and computer requirements. Installation of the program is discussed in Chapter Two. The instructions are easy to understand. The tutorial program HWI is explained in Chapter Three. The use HWI computer program is outlined in Chapter Four. Information on error and warning messages in HWI are also documented in this chapter. The last chapter provides directions on how to run the program in the "expert" mode.

A review of the basic principles involved in hazardous waste calculations is given in the reference manual. The reference manual is divided into five sections:

1. Introduction,
2. Calculation Concepts,
3. Program Details,
4. Chlorobenzene/Sulfur Mixture Example, and
5. Chlorobenzene/DDT/Water Mixture Example.

In order to test the program, two copies of the program were obtained; one from the U.S. EPA/Air Pollution Training Institute and the other from the authors. The program was tried after installation on a hard disk as well as using a floppy disk. It is straight forward to use, thanks to the clearly-written instructions. Two exercises are included in the tutorial program, which take you through all the steps in the program once and let

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Note from Editor: Please submit your software for possible inclusion in this section to Dr. A. Kumar.

you try a different problem afterward. Before the beginning of each step, however, a brief instruction is given. You are allowed to input the values of the process variables for the incinerator. And you can retreat and alter them if you wish.

To run the program, you will have to provide information about the composition and quantity of the waste feed, the amount of excess air or the final temperature desired, and other engineering requirements such as the volumetric heat release rate, heat losses through the furnace walls and the internal geometrics of the kiln. The composition of the waste can be entered either from an ultimate analysis or by the individual chemicals. And the net heating value of the waste feed can be either entered or calculated with the Dulong's formula.

The HWI program output includes the final flue gas composition, the mass and volumetric flow rates, flue gas temperature or the amount of excess air required, preliminary dimensions for the incineration chamber, and calculated gas residence time inside the chamber. During the calculations, the program assumes the final combustion products are CO_2 and H_2O, but also includes equilibria constants for the HCl-Cl_2 and SO_2-SO_3 systems so that these components can be reasonably calculated. The program, however, does not include calculations of the CO-CO_2 system.

Overall, we would rate the HWI program excellent. One inconvenience which was encountered is in obtaining the output in the form of a hard copy. The HWI output currently is only reported to the screen, and you have to resort to one of the utility programs to capture the output to a file.

Literature Cited

1. Theodore, L. and J. Reynolds, Reference Manual for Use with the HWI Software Package, Manhattan College, Riverdale, NY, 1989.
2. Reynolds, J. and L. Theodore, User's Guide for the HWI Software Package, Manhattan College, Riverdale, NY, 1989.

Introduction to Feature Column on Pollution Prevention/Waste Minimization

Pollution prevention and waste minimization are receiving considerable attention from all segments of our society—legislative bodies, regulatory agencies, the scientific and engineering communities, academia, industry, environmental groups and the public at large. The American Institute of Chemical Engineers is making a major effort to advance the concept of pollution prevention. The Institute will host in Washington, DC, Dec. 4-5, 1989 a conference on "Pollution Prevention: A Chemical Engineering Challenge." A study is underway to determine the feasibility of establishing an AIChE Center for Waste Reduction Technologies which would include joint venture research with a consortium of university research facilities.

Hazardous waste elimination was the featured subject in the June 1989 *Chemical Engineering Progress. Environmental Progress* has had several issues devoted to waste minimization and is pleased to initiate with this issue a feature column devoted to pollution prevention/waste minimization. The following is the first in a series of waste minimization case histories which will appear in the column.

R. Lee Byers
Environmental Progress
Editorial Advisory Board
and editor of
Pollution Prevention/Waste Minimization section.

Waste Minimization In A World Class Ethylene Plant

William B. Beck and R. B. McCampbell
E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

One of the hoped for benefits of reducing waste is that it will save money as well as satisfy environmental needs. But often, such benefits are non-existent, or aren't apparent, at the time a project is undertaken. This was the situation that arose in the ethylene plant at DuPont's Sabine River Works.

This single line plant, built in the 1960s, today produces a billion pounds of ethylene a year. As it grew in capacity over the years, the waste increased, especially the waste water from the quench system. Throughout this period waste water management was changed to accommodate the increases. The quench water was passed through a quench settler to remove small amounts of tars and emulsified solids. The partially clarified water leaving the settler was sent to an API separator in which the oil was separated from the water; and the "clean" water was sent on to the plant's bioponds for further treatment. Eventually, the oil removal system became overtaxed to the point where emulsions were being entrained in the effluent water. The emulsions had to be removed in a pretreatment basin to avoid operating problems in the bioponds. This basin became the focus of the waste reduction because of the frequent cleanings it required.

Various "cures," costing $500,000 to $1,000,000, were considered and tested, but none were acceptable: some were too costly; others were technically deficient. None would really do the job until a plant-team came up with a novel dissolved-gas-flotation (DGF) system.

In the DGF system, neutralized, chemically-treated wastewater from the quench settler is mixed with high-pressure, nitrogen-saturated, recycle water as it enters a flotation cell. Nitrogen bubbles carry oil and solid floc to the surface where it overflows into a centrifuge feed tank. The centrifuge separates the oil as an aromatic distillate. Water is recycled for further treatment and solids are collected in a dumpster for periodic disposal. Organic vapors stripped by the nitrogen in the DGF unit, are flared in the plant's existing flare system. Clean water exits the system for further treatment in the plant's bioponds.

When a project was undertaken to install the DGF system, there was no economic incentive. The recovered oils could be recycled, but had little value; and it was questionable whether the solids would be clean enough to be landfilled without greatly increased expense. However, without the DGF system the ethylene plant would continue to generate 10 million pounds per year of waste oil. The decision was made to proceed on the basis of reducing the amount of waste generated despite the lack of economic incentive; it seemed the "right thing" to do from an environmental and long-term liability perspective.

Coincident with the installation of the DGF equipment, changes were made in the operation of the ethylene plant which seemingly would have no effect on the waste characteristics. These changes, however, drastically altered the nature of the organics in the quench discharge from the ethylene plant. Fortunately, the DGF system works so well even on these organics which were not anticipated when the DGF unit was designed that it recovers essentially all of the oils in a form that enables them to be sold as aromatic distillate. Additionally, it cleans up the residual solids to the extent that they can be landfilled without difficulty. These altered organics, had it not been for the DGF unit, would have had to be incinerated at the cost of $2 million per year.

Thanks to the determination of a dedicated plant team and a management willing to invest in doing the "right thing," despite the lack of adequate financial return, the generation of 10 million pounds per year of waste oil was eliminated. A little luck, in the form of unexpected process modifications changing the nature of the waste such that it could be sold rather than incinerated, resulted in a $2 million per year savings. This waste elimination project proved to be an economic as well as an environmental success.

Washington Environmental Newsletter

CFC Phase-Out: A Pollution Prevention Activity

The imminent phase-out of ozone depleting chemicals such as CFC's and methyl chloroform may be one of the nation's most outstanding pollution prevention initiatives. As you know, virtually all U.S. production of the solvent CFC-113 (and possibly methyl Chloroform) is expected to cease in order to prevent further deterioration of the stratospheric ozone layer.

There has been some concern that this phase-out could result in industrial use of other highly toxic chlorinated solvents, but EPA, in a Federal Register notice warns users of CFC-113 that the Agency "does not want producers and users to replace them with solvents which also are ozone depleters or probable human carcinogens such as methylene chloride, perchloroethylene and trichloroethylene." (543 Fed. Reg. 15229). Now experts for industry and the government, working under the auspices of the United Nations Environment Programme (UNEP) have concluded that *safe* alternatives will be available for virtually *all* current users of these solvents.

Past experience in regulating CFC usage illustrates why it is necessary to treat the forthcoming phase-out as a prevention initiative. In 1978 Congress prohibited the use of CFC's as an aerosol propellant, but the legislation did not regulate the use of alternate propellants and much of the aerosol industry substituted hydrocarbons such as pentane, propane and butane, which are now considered to be contributors to the formation of ozone smog and the greenhouse effect. The failure to foresee the consequences of the 1978 regulation led to increased health risks, environmental damage and a strain on local governments as well as on the aerosol industry. The industry may now be forced to undertake a second, unanticipated, production change in 10 years. Treating the phase-out of ozone depleters as a priority pollution prevention effort will help insure that the phase-out reduces overall risks to human health and the environment, and avoids shifting risks among environmental media and human populations. It will also allow chemical users forced by the phase-out to change production processes, to find safe alternatives for the long term.

It is encouraging that large industrial users of CFC-113 and methyl chloroform are reporting excellent results with economical alternatives that sharply reduce (and in some cases eliminate) the use of heavily regulated chemicals. UNEP reports that more than 75% of current CFC-113 use could be replaced with "no clean" production technologies, aqueous cleaning, and terpene solutions. These alternatives are more cost effective than switching to chlorinated solvents and installing appropriate control systems.

Some examples:

AT&T has announced that it will replace practically all of its CFC-113 cleaning processes with closed-loop terpene systems by the mid 1990's.

General Dynamics reports great success in meeting zero discharge goals thru the use of closed-loop, aqueous cleaning systems for virtually all metal cleaning involved in aircraft production.

Northern Telecom has determined that up to 85% of its products can be manufactured using low solids fluxes that do not require cleaning, with the balance of its products made using new technologies such as inner gas soldering.

In effect, many users of ozone depleting chemicals are correctly concluding that reduced chemical use, not emissions control, is the future of industrial manufacturing.

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

Liquid Redox Sulfur Recovery Options, Costs, and Environmental Considerations

Dennis A. Dalrymple and Timothy W. Trofe
Radian Corporation, Austin, TX

and

James M. Evans
Gas Research Institute, Chicago, IL

Liquid redox chemistry has been employed for sulfur removal and recovery applications since the 1950's. The first process was the Stretford process, which was used commercially in the United Kingdom in the 1960's as a replacement for the iron sponge process in the treatment of sour town gas. The Stretford process has been joined in the United States' marketplace by several other liquid redox processes including the Unisulf, Sulfolin, LO-CAT, SulFerox, and Hiperion processes. This paper describes the chemistry and engineering options available with each process, as well as the environmental and cost considerations associated with these processes.

INTRODUCTION

Liquid redox sulfur recovery processes absorb H_2S from gas streams and produce solid sulfur for sale or disposal. These processes involve the overall reaction of H_2S with oxygen to form elemental sulfur and water. They can be used in a wide variety of sulfur treatment applications in the natural gas and other energy industries including: desulfurization of natural gas by direct treatment; off-gas from acid gas removal processes; Claus plant tail gas; coal derived (substitute) natural gas; enhanced oil recovery vent gas; and geothermal vent gas. Other non-energy applications range from treatment of distillery off-gases to vent gas streams in municipal wastewater treatment plants. For many applications liquid redox processes offer:

- Excellent sulfur removal, often reducing H_2S levels to 10 ppm or less;
- One-step conversion of H_2S gas to elemental sulfur;
- Ambient temperature and pressure operation;
- Ability to handle fluctuating inlet gas flow rates and H_2S concentrations;
- The capability of treating both low- and high-H_2S gas streams; and
- Regenerating catalysts.

For the last several years, the Gas Research Institute (GRI) and Radian, in cooperation with other organizations, have been conducting research into liquid redox sulfur recovery technology. To date, this research has focused primarily on the original technology—the Stretford process [*1*]. This paper provides information on Stretford and other major liquid redox sulfur recovery processes currently marketed domestically. It is based primarily on information provided by the process designers at a liquid redox conference sponsored by GRI in October 1987 and on information provided by the process designers in response to a questionnaire distributed to the designers in May 1988 [2].

The content of the questionnaire and the responses are described; an overview of the processes is explained; and the plant size, capital cost, chemical cost, and utility cost estimates provided by the designers are discussed. By-product sulfur salt formation and waste disposal considerations are discussed. A brief summary of research and information needs is also included.

It should be noted that this paper is based primarily on estimates supplied by the process designers, and represents a wide range of total experience and of experience with specific applications. Therefore, while this information provides many useful insights it should not be used to draw absolute conclusions. Instead, the intent is to provide potential process users with a basis for asking the right questions in areas that are unclear and to help guide research into areas that are unknown.

TABLE 1. SUMMARY OF CONDITIONS FOR THE FOUR COMPARATIVE CASES.

	Application			
	Natural Gas Direct Treatment	Geothermal Vent Gas	Claus Tailgas (COS Hydrolysis Reactor Effluent Cooler Outlet)	Rectisol Off-Gas in Coal Gasification Plant
Untreated Gas Characteristics				
Flowrate, kSCMD[a] (dry)	570	57	71	5700
Temperature, °C	27	49	60	38
Pressure, kPa (psig)	1240 (180)	ATM	34 (5)	34 (5)
H_2S, mole %	0.3	5.0	1.0	1.0
COS, ppmv	—[b]	—	20	—
CH_3SH, ppmv	—	—	—	100
CH_3CH_2SH, ppmv	—	—	—	50
CO_2, mole %	2.0	50.0	6.0	95.0
CH_4, mole %	97.7	5.0	—	3.0
N_2, mole %	—	40.0	93.0	1.0
Total, mole % (dry)	100.0	100.0	100.0	100.0
H_2O, mole %	—	12	9	—
Treatment Requirement	H_2S removal to 4 ppm	H_2S removal to 20 ppm	H_2S removal to 10 ppm	95% removal of H_2S
Sulfur in Feedgas, Metric Ton/D	2.3	3.9	9.7	78.1

[a] kSCMD = Thousands of standard cubic meters per day.

[b] = Not available.

INFORMATION REQUESTS TO THE DESIGNERS

While general chemistry and process description information for the major liquid redox processes marketed in the United States has been available publicly from the designers, information concerning capital and operating costs has either been lacking or not in a form that could be readily compared. In May 1988, several designers were asked to supply various pieces of information for application of their processes to the four treatment cases given in Table 1. The following information was requested:

- Capital investment required (installed cost including indirects, engineering, and contingencies);
- Plant size parameters (circulation rate and total solution inventory);
- Chemicals, catalysts, and additives requirements;
- Utility consumptions (electricity, steam, and cooling water); and
- By-product sulfur salts formation information.

They were also asked to identify any particular advantages or disadvantages associated with each application. Responses were received for all processes, and the cooperation of the companies is appreciated. These responses have been reviewed and tabulated. Comparative summary information was prepared and is shown in Tables 2 and 3.

PROCESSES OVERVIEW

Figure 1 is a process diagram for a generic liquid redox sulfur recovery process. In the absorption section, hydrogen sulfide is removed from the gas by contact with an alkaline scrubbing solution. The rich liquor flows to the reaction section where enough residence time is provided for completion of the sulfur forming reactions. The resultant elemental sulfur is then separated from the solution and the solution is regenerated by contact with air. In most systems, sulfur separation and solution regeneration

TABLE 2. PLANT SIZE AND CAPITAL COST ESTIMATES FOR FOUR COMPARATIVE CASES.

	Natural Gas Direct Treatment	Geothermal Vent Gas	Claus Tailgas (COS Hydrolysis Reactor Effluent Cooler Outlet)	Rectisol Off-Gas in Coal Gasification Plant
Solution Inventory, kL				
Vanadium-based processes[a]	235–255	370–424	800–970	6,300–8,000
Iron/quinone-based processes[b]	15–100	24–154	75–380	680-2,840
Circulation Rate, kL/hr				
Vanadium-based processes	165–285	270–340	680–825	5,500–6,500
Hiperion/SulFerox	52–136	70–160	450–760	4,000–5,600
LO-CAT	477	750	1,860	15,000
Residence Time, Minutes				
Vanadium-based processes	50–90	60–90	50–90	60–90
Iron/quinone-based processes	10–20	10–20	5–15	5–15
Installed Capital Cost $ Million				
Vanadium-based processes	3–5	3.5–5.1	6–9	20–36
Iron/quinone-based processes	0.8–1.2	0.8–1.9	1.2–3.7	9–10
Capital Recovery Charge, $/Day				
Vanadium-based processes	920–1,650	1,150–1,680	2,100–3,000	6,500–12,000
Iron/quinone-based processes	260–390	260–630	400–1,200	2,800–3,200

[a] Vanadium-based processes are Stretford, Unisulf, and Sulfolin.

[b] Iron/quinone-based processes are Hiperion, LO-CAT, and SulFerox.

TABLE 3. ESTIMATED CHEMICALS, UTILITY, AND CAPITAL RECOVERY COSTS IN $/METRIC TON OF SULFUR.

	Natural Gas Direct Treatment	Geothermal Vent Gas	Claus Tailgas (COS Hydrolysis Reactor Effluent Cooler Outlet)	Rectisol Off-Gas in Coal Gasification Plant
Chemicals Cost				
Vanadium-based processes[a]	5–40	5–25	5–30	5–30
Iron/quinone-based processes[b]	50–170	50–180	40–180	50–120
Utilities Cost				
Vanadium-based processes	110–160	50–150	40–125	50–150
Iron/quinone-based processes	40–80	15–50	11–50	14–50
Capital Recovery				
Vanadium-based processes	400–700	300–430	220–300	80–150
Iron/quinone-based processes	110–170	70-160	40–125	35–40
Total Cost				
Vanadium-based processes				
Stretford	515	351	264	233
Unisulf	716	615	448	306
Sulfolin	838	NR[c]	NR[c]	144
Iron/quinone-based processes				
Hiperion	202	137	92	101
LO-CAT	364	320	287	196
SulFerox	371	343	305	204

[a] Vanadium-based processes are Stretford, Unisulf, and Sulfolin.
[b] Iron/quinone-based processes are Hiperion, LO-CAT, and SulFerox.
[c] Not recommended for this application.

occur in the same aerated vessel. Typically, rising air bubbles perform the dual functions of oxygen mass transfer and sulfur flotation. Alternately, the sulfur can be separated by sinking if a surfactant is added to the solution.

In the process of oxidizing the H_2S from a valence of -2 to zero (elemental sulfur), the circulating solution is reduced. Depending on the process, either vanadium (V) is converted to vanadium (IV), Fe(III) becomes Fe(II), or an organic quinone goes from its oxidized to its reduced state. Again, depending on the process, other constituents in the solution may be needed to chelate the metal ions, modify reaction pathways, aid sulfur flotation or sinking, control biological activity, or aid H_2S/CO_2 selectivity. All processes require addition of caustic/bicarbonate to control the pH and alkalinity of the scrubbing solution.

There are six major liquid redox sulfur recovery processes competing in the United States market today: Stretford, Unisulf, Sulfolin, Hiperion, LO-CAT, and SulFerox. The following provides a brief overview of each.

Stretford

The Stretford process was the first liquid redox process, and it has been on the market since 1959. The original patents have expired and many companies can supply Stretford. Information was supplied by the team of British Gas plc and Peabody-Holmes, Ltd. Stretford uses vanadium as the primary catalyst for the sulfur reactions and anthraquinone disulfonic acid (ADA) to catalyze oxygen transfer in the regeneration of the reduced vanadium. Stretford has the vast majority of the experience with liquid redox processing both with respect to variety of applications and amount of operating time. There are over 120 Stretford plants in operation worldwide in western countries. A recent visit to the People's Republic of China by GRI and Radian indicates that there are at least 100, and maybe as many as several hundred Stretford units in that country treating a wide variety of H_2S-containing gas streams [3].

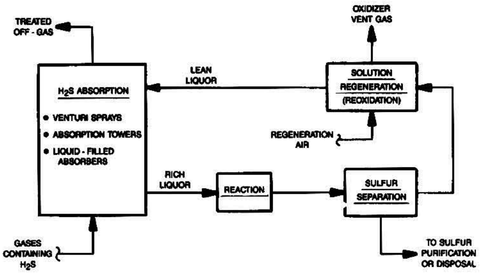

Figure 1. Liquid redox sulfur recovery process diagram.

Unisulf

The Unisulf process, marketed by Unocal, was commercialized in December of 1985. It is based on vanadium, but also contains thiocyanate, carboxylic acid (usually citrate), and an aromatic sulfonate complexing agent. Unocal states that the chemistry has been modified to virtually eliminate by-product salt formation and has supplied data from commercial plants to support this claim. Unisulf plants have no integral sulfur melter, which eliminates that high-temperature operation as a source of by-product salt formation. There are currently at least three commercial Unisulf plants in operation [*4*, *5*, *6*].

Sulfolin

The Sulfolin process, marketed by Linde AG, is similar to Unisulf in that it is a modification of the basic vanadium chemistry of Stretford. It was developed as a joint venture between SASOL South Africa and Linde AG, and is currently in use to treat Rectisol off-gas in the SASOL and Great Plains coal gasification plants. The SASOL Sulfolin plant came onstream in June 1985. In addition to vanadium, the solution contains organic nitrogen compounds. Low by-product salt make rates are claimed. Linde has supplied limited data in this area [*7*, *8*, *9*].

Hiperion

The Hiperion process, marketed by Ultrasystems, was developed as an improvement of the Takahax process that is widely used in Japan. In the Hiperion process, chelated iron is combined with naphthaquinone. The designer states that this results in greatly reduced residence times and thus smaller equipment sizes. Unique features of the process are removal of sulfur by a plate and frame filter and gas/liquid contactors featuring beds of "windy balls" that have been designed to be resistant to plugging. Hiperion's operating experience is limited to a one-year pilot unit test of anaerobic digester off-gas and a commercial plant that has been treating an H_2S-rich nitrogen stream in a refinery since 1986 [*10, 11*].

LO-CAT

LO-CAT is a chelated iron liquid redox process that was commercialized by ARI in the late 1970s and has achieved considerable market success over the last four to five years, especially in the smaller unit sizes. Around 40 LO-CAT plants are now in operation, in design, or under construction. LO-CAT solution compositions are maintained by regular additions of iron, two proprietary chelates, a biocide, and a surfactant to ensure that the sulfur will sink to the bottom of the oxidizer where it is extruded as a slurry. This sulfur removal method eliminates the need for a separate pump tank for the lean liquor. LO-CAT plants typically have iron concentrations of 500 ppm to 1500 ppm, as determined by cost trade-offs involving pumping costs and chemical costs. Applications where gas streams contain relatively high H_2S concentrations, such as regenerator acid gases from amine treatment, can use ARI's autocirculation unit. A single liquid-filled vessel replaces the absorber, reaction tank, and oxidizer. Solution circulation is achieved by utilizing fluid density differences resulting from different L/G ratios within the vessel [*12, 13, 14*].

SulFerox

A recent entry into the chelated iron arena is the SulFerox process, which was introduced in 1987 and is jointly licensed by Shell Oil and Dow Chemical. SulFerox solution contains 2–4 weight percent iron, which results in a very high H_2S removal capacity for a given volume of solution. As a result, system sizes and circulation rates are relatively low. Maintaining the iron ligand in solution was one of the primary challenges facing the designers. The resultant process utilizes proprietary chemical additives plus operating condition optimization to reduce ligand degradation. A cocurrent contactor was developed for the H_2S absorption section to take advantage of the high solution absorption capacity and to adjust for the low circulation rates. Nonfouling characteristics are claimed. Sulfur may be recovered as a cake or melted and purified, depending on the plant size and economics. To date, the only commercial experience is a plant built in 1987 that treats sour gas associated with heavy oil production [*15, 16, 17*].

RESULTS

The following summarizes the information provided by the designers in response to the May 1988 questionnaire.

Plant Size and Capital Cost Estimates

Table 2 gives ranges of the estimates supplied by the process designers for solution inventories, circulation rates, and installed capital costs for the four comparative cases. System residence times were calculated from the inventory and circulation rate values. Linde did not supply solution inventory and circulation rate estimates for Sulfolin, but these would be expected to be similar to the Stretford and Unisulf values.

The vanadium-based systems (Stretford, Unisulf, and Sulfolin) appear to require greater solution inventories (i.e., require larger equipment) and more capital investment than their iron- and quinone-based counterparts. LO-CAT is in the middle of the two groups of processes (vanadium-based and iron/quinone-based) with respect to size and has the highest circulation rate of all of the processes. The wide variations shown in Table 2 are due in part to differences in solution kinetics and in part to different process design approaches.

Chemicals, Capital, and Utility Cost Estimates

Table 3 shows a summary of the information supplied by the designers expressed in dollars per metric ton of sulfur in the feedgas. Common cost bases and pricing were used to convert the detailed information supplied by the designers into the summary information shown in Table 3.

The estimated chemicals costs for the iron systems are significantly higher than for the vanadium-based systems. One explanation may be the need for chelants, which tend to degrade, to keep the iron in solution. Another factor may be different approaches regarding blowdown and discharge of effluent wastes. The vanadium-based processes are now designed for very low discharges of vanadium, and consequently other catalysts and chemicals, due to environmental concerns and restrictions associated with vanadium. This is achieved through modifying the chemistry to minimize by-product salt formation thus minimizing the need for blowdown (as in Unisulf and Sulfolin) or by treating the effluent to recover and recycle the catalysts and chemicals (as in Stretford).

The utility cost estimates shown in Table 3 consist primarily of the cost of electricity to power the air blowers and the solution circulation pumps. These costs reflect the system volume and solution circulation rate estimates given in Table 2. Steam to melt the sulfur cake can amount to 25% of the utility cost for systems that produce molten sulfur.

The total costs shown at the bottom of Table 3 reflect the majority of the costs associated with these systems. Other costs would include operating and maintenance labor, maintenance materials, and waste disposal costs. The costs shown at the bottom of Table 3 reflect both the range of system designs and chemistries and a wide range of applications. As noted in the introduction, these values should not be regarded as absolute due to the site-specific nature of the designs for each of the processes.

By-Product Salt Formation and Waste Disposal Considerations

Some of the absorbed H_2S is converted to by-product sulfur salts (thiosulfate and sulfate) rather than the desired end product of elemental sulfur. These salts build up in solution and have been associated with process and chemistry problems when high levels are reached. The traditional approach has been to discard the entire inventory when excessive levels are reached, and/or to purge salts with the sulfur cake (if sulfur cake rather than elemental sulfur is being produced) or via a separate liquid blowdown stream. Discharge of solution, especially solution containing significant vanadium levels, has become environmentally unacceptable in some areas (e.g., California). Some plants are now sending their solution to off-site disposal firms and incurring substantial disposal costs ($130–$260 per kiloliter). As a consequence, the vanadium-based processes are now concentrating on modifying the reaction pathways to minimize sulfur salts formation or incorporating solution treatment/recovery in the design of new plants.

Several processes have been developed to treat blowdown from the vanadium-based processes. The British Gas Desalting Process, offered now as an integral part of Stretford plants designed by British Gas, recovers the vanadium and ADA in the form of a concentrated solution. Sodium thiosulfate is oxidized to produce Glauber's salt (Na_2SO_4 10 H_2O), a salable by-product. When combined with the desalting process, the Stretford is a zero-discharge process [3]. Dow has also developed a chemical recovery process that recovers 80–85% of the vanadium and 95% of the ADA, creating an inorganic purge stream of smaller volume and without the vanadium content of normal Stretford blowdown [3].

In addition, DuPont Company (through Envirodyne Corporation) is beginning to process Stretford liquid wastes at its PACT (Powdered Activated Carbon Treatment) wastewater treatment plant in Deepwater, New Jersey. This plant is capable of treating wastewaters containing both organics and heavy metals. Cri-Met is processing Stretford liquid wastes at a metals recovery plant in Plaquemine, Louisiana.

The iron-based processes seem to offer advantages in the area of liquid waste disposal since they do not contain vanadium, the constituent in these processes that has received the most attention to date. However, there is not enough information or experience accumulated to determine what the real situation is, or will be. While the faster chemistry of the iron-based processes would favor lower salt make rates, they do produce thiosulfate and sulfate salts, which would build up in their solutions.

A wide range of estimates concerning by-product salt make rates and recommended maximum salts levels was supplied by the designers:

	Percent Sulfur to S_2O_3	Percent Sulfur to SO_4	Recommended Maximum Salts Level, wt%
Stretford	1.38	0.62	21
Unisulf	None	None	—
Sulfolin	None	0.4	15
Hiperion	No Response	No Response	No Response
LO-CAT	2.0	<0.1 to <0.2, depending on the case	30
SulFerox	<0.1	<0.1	Not Applicable

These estimates, on the whole, provide an interesting view of the designers' perspectives, but probably do not represent accurate process-to-process comparisons. Obtaining reliable salts make rates on commercial units requires performing tests that yield accurate material balances on the sulfur species, which is quite difficult.

RESEARCH NEEDS

This summary of comparative information on a wide range of liquid redox sulfur recovery technologies and applications plus information from other investigations suggests several areas where additional information and/or research is needed including:

- Additional information regarding the application of liquid redox processes to a wide range of gas treatments, in particular information on sulfur fixation rates and high-CO_2/coal-derived gas treatment;
- Sulfur formation chemistry studies and investigations into sulfur properties;
- By-product salts formation and control studies;
- Investigations into blowdown treatment/disposal options:
- Comparative corrosion studies;
- Environmental, health, and safety considerations;
- Analysis of site-specific problems experienced by individual plants; and
- Increased communication and technology transfer to aid the user in making more knowledgable choices.

LIQUID REDOX SULFUR RECOVERY CONFERENCES

To support the open exchange of information and operating experience, GRI has sponsored three international conferences on liquid redox sulfur recovery technology, held in May 1986, October 1987, and May 1989 in Austin, Texas. These conferences are attended by process operators, researchers, governmental/regulatory representatives, process designers, chemical vendors, and equipment suppliers. Plant operators describe their experiences; researchers report on recent studies and testing; process designers give updates and describe process improvements; and new developments with respect to catalysts and equipment are discussed. Additional conferences are being considered.

CONCLUSIONS

For approximately 25 years, the market for liquid redox sulfur recovery technology was dominated by the Stretford process, a vanadium-based process. In the last five years, the market place has diversified to include several other vanadium- and iron/quinone-based processes and new applications have been developed. In addition, management of liquid and solid discharge streams has received increased emphasis.

The long-term environmental requirements associated with the discharges from these plants are not yet known. The environmental data is incomplete due to limited application experience, especially with respect to the newer processes, and because the environmental requirements are still evolving. Several options exist for the recovery or treatment of liquid wastes from these processes.

Each liquid redox sulfur recovery application has presented unique challenges and requirements. Problems have been encountered and adjustments have been made. The vanadium-based processes and options currently offered are substantially different from those offered in the past. The LO-CAT iron-based process has accumulated significant commercial experience over the last 4–5 years and has now been joined by other iron-based processes. These iron-based processes appear to have higher chemicals costs, but may offer equipment size, capital cost, and utility cost advantages. They have not, however, been evaluated commercially for the wide range of potential applications. Time and additional information gathering and research will be needed to see how these iron-based processes fit into the overall liquid redox sulfur recovery technology area.

Because of their flexibility and advantages in many diverse applications, liquid redox processes are being used in a growing number of desulfurization applications. This trend is expected to continue as new sulfur treatment needs are identified and as sulfur prices continue to rise in response to forecast shortages in the world supply.

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Utilization of Adipic Acid Byproducts for Energy Recovery and Enhancement of Flue Gas Desulfurization

C. T. Chi and J. H. Lester, Jr.
Monsanto Chemical Co., P.O. Box 12380, Pensacola, FL 32575

Beneficial utilization of two waste streams from adipic acid manufacture is described. The first stream, containing adipic, glutaric, and succinic acids, a mixture referred to as AGS, was found to be very effective in improving the efficiency of limestone scrubbers for removing SO_2 from coal-fired power plant flue gases. A small portion of the AGS stream is also used to convert a contaminated distillation residue from cyclohexanol manufacture into a clean boiler fuel. The residue is an oily waste which contains inorganics and a hard-to-separate aqueous phase. The inorganics and aqueous phase are removed by liquid-liquid extraction in a centrifugal contactor.

INTRODUCTION

At the Monsanto Pensacola site there is constant effort to reduce the waste from manufacturing processes. The following approach is taken:

1. Characterization of wastes at their sources.
2. Within process recycle and reuse.
3. External utilization.

This paper is a case study of combined internal and external utilization of two major waste streams. The first was a waste liquor from crystallization of adipic acid. The second was a refinement residue from cyclohexanol refining and recovery.

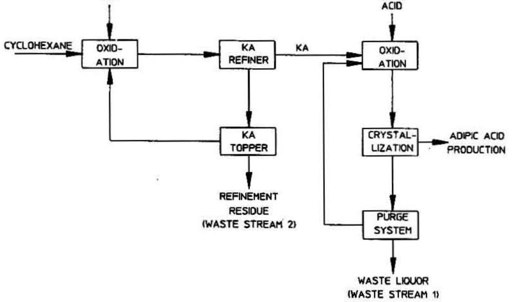

Figure 1. Sources of byproduct waste streams.

The sources of these two byproduct purge streams are illustrated in Figure 1. The waste liquor contains a total of about 25% dibasic acids, including adipic acid, succinic acid, and glutaric acid; the rest is comprised of water and minor impurities. The refinement residue contains primarily organic esters and various amounts of a second aqueous phase. Sodium and boron are also present in the second stream.

OVERALL SCHEMES

The overall scheme for the integrated approach is shown in Figure 2. Most of the waste liquor is directed to an evaporator for concentrating to over 50% organic solid for sales to coal-fired utilities for enhancement of flue gas

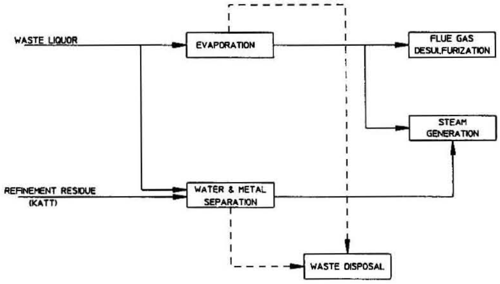

Figure 2. Overall scheme for byproduct utilization and waste disposal.

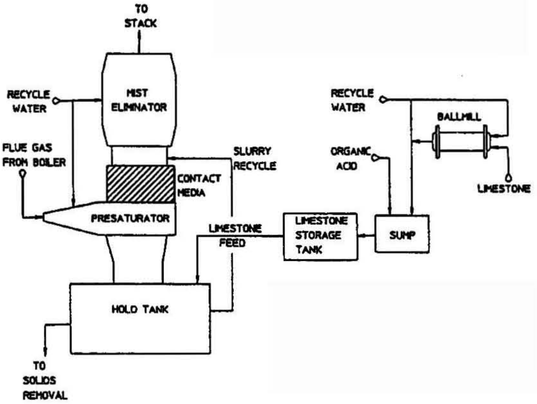

Figure 3. Flow diagram for a typical limestone scrubber, adapted from Hargrove et al. [4].

desulfurization. The product is sold as "AGS Mixture." A portion of the unconcentrated waste liquor is used to wash the refinement residue, which is subsequently burned in the plant boilers for energy recovery. The unused and unsold portion of AGS is also burned in the plant boilers for energy recovery. Other markets for AGS and sales of certain forms of the refinement residue are being actively pursued.

The above byproduct utilization scheme for these two streams achieves about 30% volume reduction and greater than 90% total carbon reduction. The scheme has converted a pollution control problem into a profitable operation. The three major segments, AGS for flue gas desulfurization, washing of the refinement residue, and energy recovery from excess waste liquor and the refinement residue, are discussed in the following sections.

AGS FOR FLUE GAS DESULFURIZATION

Background

A typical modern coal-fired power plant may emit as much as 2,000,000 ft^3/min (944 m^3/s) waste gas containing 2,000 ppm of SO_2. This sulfur dioxide must frequently be removed from the flue gas, usually with a scrubber, to meet governmental regulations. Sulfur dioxide emissions are associated with the acid rain problem. The majority of flue gas desulfurization (FGD) systems in operation or under planning are calcium-based lime or limestone processes because of system simplicity and economics [*1*]. A typical limestone FGD system is shown in Figure 3. Although this FGD technology has been under development for over 18 years, many of the existing limestone systems have problems in meeting design levels of reagent utilization and SO_2 removal [2].

Most problems with SO_2 removal and limestone utilization are symptoms of poor mass transfer. One explanation [3] is that limestone scrubber performance is limited by two pH extremes: 1. low pH near the gas-liquid interface, which decreases the SO_2 solubility and absorption rate; and 2. high pH near the liquid-solid interface, which lowers the limestone solubility and dissolution rate. These two extremes can be moderated by using a soluble buffer additive.

It has been known since 1977 [5] that certain organic additives are useful as buffers and are effective in enhancing mass transfer. Adipic acid and isophthalic acid were identified as "fully effective." Since then the EPA has sponsored pilot, prototype, and full-scale demonstration testing of adipic acid to quantify its effectiveness, loss, and other aspects as an additive. Adipic acid was selected because of its solubility in water, low volatility, chemical stability, non-toxicity, high availability, and low cost [*6*]. Demonstrated benefits of adipic acid enhancement include [7]: increased SO_2 removal; decreased limestone consumption; decreased waste sludge volume; reduced operating cost; and, expanded FGD system flexibility.

During the EPA's test program for adipic acid, the concept of using byproduct AGS (also called DBA, dibasic acids) as a lower cost alternative was introduced by Monsanto [8]. A separate program by the EPA was conducted to evaluate byproducts as alternatives to pure adipic acid.

Lab and Pilot Test Results

Following laboratory characterization, pilot plant (0.1 MW) tests were conducted by the EPA for byproduct organic acid from four sources, including two from adipic acid manufacture [7]. Figure 4, taken from the same reference, shows that both DBA's enhanced SO_2 removal significantly. With an addition of 50 meq/liter (about 3300 ppm) of DBA, the SO_2 removal efficiency was increased

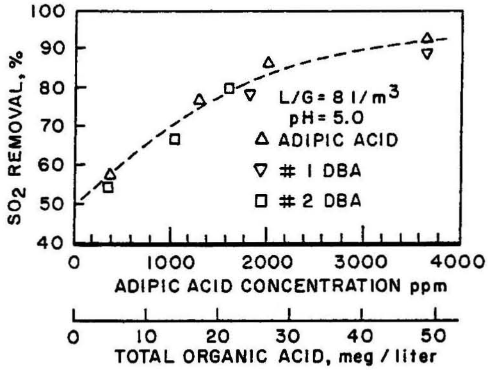

Figure 4. Effect of organic acid on SO_2 removal at IERL RTP pilot plant, Chang and Dempsey [7].

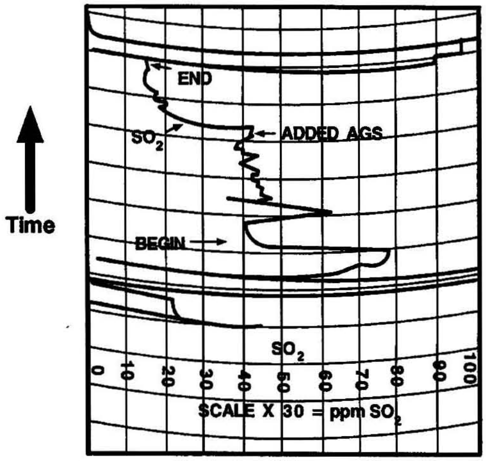

Figure 5. Reproduction of strip chart response to AGS addition at Monsanto bench scale SO_2 removal unit.

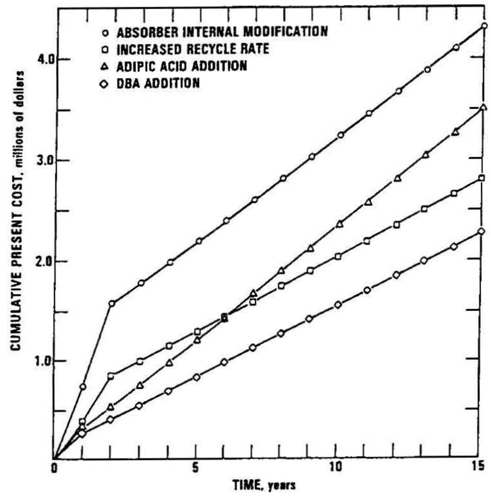

Figure 6. Cumulative present cost of options for improving Springfield City utilities' SWPP scrubber. Chang and Mobley [9].

from 50% to 90%. Figure 4 also shows that both DBA's can improve SO_2 removal as effectively as adipic acid.

A laboratory test on the effect of AGS addition was also conducted at Monsanto. The bench-scale apparatus had a 1 ft³/min (1.7 m³/hr) capacity, utilizing synthetic flue gas. A strip chart from one of the runs is shown in Figure 5. During this run, SO_2 removal efficiency increased from 59% to 85% in 10 minutes. The ultimate AGS concentration in the scrubbing liquor was 2200 ppm.

Commercial Application

The first commercial-scale test using byproduct DBA was conducted in Springfield City Utility's Southwest Power Plant (SWPP) utilizing AGS from Monsanto. This power plant has a 194 MW coal-fired unit designed to burn 3.5–4% sulfur coal. Prior to this test the plant's FGD system was unable to bring the SO_2 emission into compliance. Test results showed that addition of 530 ppm of AGS mixture increased removal efficiency from 58% to 85%, thus meeting the regulatory requirements [9]. An economic analysis was made to compare the cost of using DBA additive to other alternatives. As shown in Figure 6, the use of DBA was a clear winner [9]. It was decided to install permanent facility for operating with DBA additives. Thus, SWPP became the first commercial-scale facility to utilize DBA in FGD system application for enhanced SO_2 removal.

Two years after the first commercial application of DBA technology, SWPP reported not only meeting SO_2 emission limitations, but also having 98% FGD reliability as compared to 45% reliability prior to the change [*10*]. Today more than 11 power plants are either using or considering the use of DBA additives for improved FGD performance [*11*]. The sale of AGS for FGD had expanded into a multimillion-pound-per-year business and is growing. This kind of byproduct utilization solves two environmental problems at once.

KATT DECONTAMINATION FOR BOILER FUEL

Background

In a typical process for air oxidation of cyclohexane to produce cyclohexanone and cyclohexanol (KA), a refining step is usually included. In our process, the high boiling residue from the refining process is called KA Topper Tails, or KATT. KATT has a very high organic content, variable water content, and high metals concentration. In addition to dissolved water in the oil phase, there is a separate aqueous phase amounting to as much as 50% of the total weight. The relative density differential between the two phases would reverse with a change in temperature, making consistent phase separation difficult. Even if the phase separation were possible as a pretreatment for burning of the oil phase at the plant boilers, the high metal content (sodium and boron) would create boiler corrosion and tube fouling problems. As part of the waste reduction/recovery effort, a development program was undertaken to find ways to overcome these difficulties so that the heating value in this residue could be recovered and the waste disposal burden reduced.

Lab Screening and Column Test

A laboratory screening test was conducted to select the combination of factors for achieving desired responses. The manipulated factors and the responses are listed in Table 1. This lab screening identified that waste liquor was the best choice for consistent phase separation, good metal removal, and minimum loss of organics to the extractant. Qualitative temperature effects were understood and the minimum extractant/KATT ratio was determined.

Following lab screening, a batch simulation of two-stage continuous countercurrent extraction with simultaneous phase separation was conducted for planning a column test. The simulation run was made at 60°C and an extractant/residue ratio of 1:1. Results showed satisfactory metal removal. A column test using a 1-inch York-Schibel column was then conducted to optimize the process.

Full-Scale Operation

Data from the column test were used to scale up for a full-scale installation to separate water and metal from KATT. A patent application was filed and the patent was subsequently granted [*12*]. A centrifugal extractor was used to shorten the contact time and thereby reduce any chemical reactions between the two feed streams.

The washed KATT became a clean fuel for firing with primary fuel in one of the plant boilers for efficient recovery of the heating value. At the power house end, special stainless steel burner guns and tips were used because of the corrosive nature of the byproduct waste. This process of byproduct utilization has been in operation for four years.

EXCESS AGS INCINERATION

The excess waste liquor after sales for flue gas desulfurization and use in KATT washing is incinerated in the plant boiler for fuel value recovery. Prior to incineration,

TABLE 1. FACTORS EVALUATED IN LAB SCREENING STUDY FOR KATT.

Manipulated Factors	Responses
Method of creating density differential.	Density difference between two phases.
Extractant.	Time for complete separation.
Temperature.	Loss of organics.
Extractant/KATT ratio.	Metal removal.
	Undesirable chemical reaction.

most of the water content in the waste liquor is removed by evaporation. Low pressure waste steam is used for this water removal step. The same boiler is used for concentrated AGS and washed KATT. Because of the relatively low heating value from the highly oxygenated organic acids, primary fuel is always fired simultaneously to ensure flame stability.

As more and more process wastes are burned in the conventional industrial boilers, operator education becomes important because of the increased handling of chemicals that have different characteristics from the conventional fuels. Another point is that upper management's commitment in using boilers for byproduct waste disposal (and energy recovery) is very important. Their influence can facilitate acceptance of "chemical operations" by the utilities people.

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Decommissioning Old Plants (or, You Don't Close a Plant by Shutting it Down)

Dennis L. Caputo and Robert M. Zoch, Jr.
ENSR Consulting and Engineering, 3000 Richmond Ave., Houston, TX 77098

Evolving environmental regulations mean that closure of a plant entails more than simply shutting it down. Development and execution of a closure plan that will minimize cost, execution risks, and future liabilities must be approached as a major project for the owner company. This paper discusses the evolving impact of RCRA and CERCLA upon requirements for a plant, and describes a procedure for developing and implementing a closure plan.

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) regulates the generation, treatment, storage, and disposal of wastes, as well as the disposition of numerous "hazardous constituents" typical of many plant products and wastes. All plants generate wastes, and many have disposed of these materials on-site at some time during their life. The shutdown of your plant can trigger several facility closure requirements under RCRA and other environmental regulations that place serious financial and legal burdens upon the owner/operator of the plant.

In determining which of your facilities may be subject to closure under these RCRA requirements, several categories of plant units must be addressed. Those potentially subject to regulation are listed below.

- *Waste Management Facilities*—Hazardous waste treatment, storage and disposal units identified under various RCRA filings are subject to closure requirements. These can include storage and treatment facilities, as well as lagoons, waste piles, landfarms, landfills, and incinerators utilized for on-site hazardous waste management.
- *Process, Storage, and Transportation Equipment*—Hazardous waste generated in product or raw material storage and transportation equipment, or in process unit, are not subject to regulation until these wastes are removed from the equipment. However, 90 days after the plant ceases operation, residual waste materials still contained within the equipment could become subject to regulation.
- *Wastewater Treatment Facilities*—Most wastewater treatment systems are exempted from RCRA permitting requirements so long as they are regulated under the Federal Clean Water Act. Upon closure of the plant, and when your wastewater discharge permit is canceled, the liquid and solid residues of hazardous constituents resulting from "de minimus" losses during plant operations can place your treatment facilities under RCRA regulation.
- *Spills*—Releases of liquid products from leaking tanks (both below and above ground), pipelines, and process equipment frequently result in a "hydrocarbon pool" immediately beneath many older plants. Release of hazardous constituents (i.e., benzene, toluene, xylene, etc.) from this pool into groundwater or surface water can trigger regulatory action under several programs.

Two final issues are currently regulated under the Toxic Substance Control Act (TSCA).

- *PCBs*—The use of polychlorinated biphenyls in electrical and heat transfer equipment has been regulated for some time. However, electrical transformers and capacitors containing PCBs that are currently active, or in storage, also must be properly managed as part of closure.
- *Asbestos*—The use of asbestos for insulation of process equipment and piping was common until its potential health effects were discovered. The location of asbestos materials must be determined prior to any equipment dismantling so that worker protection and waste disposal plans can be developed.

It is the clear intent of Congress to further expand the regulatory impact of RCRA, which will further increase the burdens of plant closures. It is probable that regulations will be adopted to implement at least two additional closure requirements:

- *Groundwater Remediation*—The EPA groundwater protection strategy, which will be implemented over the next several years, will include provisions for remediating releases to groundwater, whether from hazardous or non-hazardous waste sources. This strategy could ultimately have an additional impact upon any subsurface oil pool in that it may require enhanced recovery to eliminate all water soluble species from the zone.
- *Clean-up Prior to Sale*—The state of New Jersey has already adopted an "Environmental Clean-Up Responsibility Act (ECRA)." This Act requires filing of a site remedial action plan as a precondition of closure, sale, or transfer of any industrial facility. It is probable that a form of federal regulation similar to ECRA will ultimately apply, even though it is already a prudent business transaction strategy.

These numerous regulatory requirements have a major impact upon most closures and even partial closures. They must be considered as part of a shutdown strategy. An outline of the factors to consider in developing a strategy is presented in the following sections.

ESTABLISH YOUR ALTERNATIVES (WHAT CAN BE DONE?)

Sufficient data must first be developed to determine feasible alternatives for closure of facilities. The types of data needed, and the sources from which they are frequently attainable, are described within this section.

Determine Operational History of the Facility

Many plants date back considerably, and they may have utilized several different process technologies during their operating life. The identification of specific raw materials and processes used over the years, and the products produced, is important in determining the types of waste materials that may have been generated. The use of by-products, and the procedures for on-site waste management, should be documented to the extent possible from plant records, aerial photography, and interviews with past or present employees. Any on-site disposal activities should be located and characterized relative to the types of waste and material handling procedures employed.

All findings under RCRA, both with the EPA and the State, as well as any filings under the requirements of the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA), should be reviewed for consistency with data developed from other plant records. Closure plans for active waste management facilities may require updating in preparation for implementation of closure. Older disposal facilities will require an assessment of the effectiveness of closure under current regulatory requirements. All process equipment, storage tanks, and transportation equipment from which hazardous waste residues may be generated should be identified well in advance of closure.

Determine the Regulatory History of the Facility

Data available from company files and public record files at the various agencies should be compiled into a regulatory history of the facility. Permit applications, issued permits, compliance actions, and inspection reports provide useful information to track the waste management history at the plant. These records include those maintained by federal, state, and local environmental regulatory programs that deal with air and water regulations as well as with solid waste. Pertinent data regarding on-site waste management should be summarized to reflect regulatory actions taken, with special attention to any permits or other authorizations regarding waste disposal facility operation or closure.

Characterize/Classify Wastes

Available analytical data should be utilized to properly characterize all waste material managed at the facility. For those materials managed on-site their probable classification under the hazardous waste guidelines should be established. Biodegradability or chemical degradation impacts should also be considered in estimating existing waste characteristics.

Classify On-Site Waste Management Facilities

From the above activities, you should identify each of your facilities which has been utilized to manage waste, or which will become a hazardous storage facility after closure.

Determine Geohydrologic Setting

One of the most critical issues in evaluating the status of your facility is the potential for waste constituent migration. Waste movement is typically based upon subsurface migration through porous media. Migration may be lateral to nearby surface water bodies, or vertical into usable groundwater. The soil stratigraphy (layering of sands, silts, and other strata) beneath the plant must be well understood in order to evaluate paths and the probable rates of migration. Permeable strata and confining zones must be characterized both in thickness and area for this purpose. The incidence and extent of groundwater should then be determined, along with local recharge and discharge locations and the identification of the "uppermost aquifer."

During the geohydrologic evaluation, the presence of any hydrocarbon pool beneath the plant must be determined. The approximate location and thickness of this zone should be evaluated and characterized.

Assess Possibilities for Future Use of the Site

The projected use of a site bears heavily upon closure requirements. Transfer of the property for some uses requires more complete clean-up than for other projected uses. Alternative uses of the site could range from industrial, agricultural, to residential. The cost of rendering the site suitable for an intended use must be balanced against the value to be obtained. Your analysis must be conducted on a site specific basis, including an evaluation of the extent of site contamination, adjacent land use, zoning, etc.

Assess Regulatory Policies and Attitudes

In today's regulatory environment, the continually evolving state of hazardous waste regulations produces a "moving target" with respect to policy interpretation. It is critical that both federal and regional agency attitudes be well understood with respect to the interpretation of relevant regulations. This is a subjective activity, and thus experience with the regulatory agencies is necessary in making a determination as to which alternatives for facility closure will be acceptable.

Determine Management Policies/Preferences

Corporate policies and attitudes regarding waste management vary significantly from company to company. This variation is not surprising in view of the rapidly and continually evolving requirements and the uncertainty that results. In view of the range of possibilities for closure, individual corporate preferences should be determined as "weighting factors" to be applied to various options.

Consider Alternative Closure Concepts

For each facility containing wastes or residuals, the closure alternatives can be reduced to these general alternatives:

- *In-Place Closure*—Some of your waste management units will allow in-place closure (i.e. lagoons, landfills, and landfarms), based upon various technical demonstrations. For these units, the requirements for controlling waste constituent migration and providing for post-closure care must be considered.
- *On-Site Consolidation*—Where regulations or existing conditions will not allow in-place closure, the consolidation of wastes to a regulated on-site disposal facility may be appropriate.
- *On-Site Treatment*—Some wastes may be treated on-site; for example, biological treatment of liquid hydrocarbon spills or oxidation of sulfide wastes.
- *Removal*—Site decontamination, and off-site disposal to a commercial waste management facility, is the fourth general alternative for consideration. Vari-

ous disposal or treatment technologies may be available to you under this category.

EVALUATE YOUR ALTERNATIVES (WHAT SHOULD BE DONE?)

Depending upon the results of the various inquiries conducted under the guidelines of the previous section, each identified alternative can be weighted for each facility that requires closure. The primary issues to be evaluated in developing strategies are described in this section.

Technical Feasibility

The technical feasibility of an option should be based upon the application of proven technology and the evaluation of the consequences generated by the option chosen. The application of innovative technologies should be weighed against available performance data for conventional techniques in order to determine their suitability.

Regulatory Complexity

Several overlapping regulations (RCRA, TSCA, State and Local) that may apply to implementation of each closure alternative must be considered in order to minimize regulatory complexity. The most direct regulatory framework for closure would be the alternative that minimizes the number of agency approvals to be negotiated, and does not require development of new policy or regulatory waivers. Any complicating agency requirements under a specific closure plan alternative will make that alternative less attractive.

Availability of Facilities

The capacity of any on-site waste management facilities and commercial disposal sites convenient to your plant should be assessed relative to the amount of waste material that must be managed during closure. Any major requirements for capacity increase, new construction, or special handling facilities would reduce the attractiveness or acceptability of those alternatives.

Completion Time

Available options should be evaluated by including reasonable construction related delays due to weather and equipment down-time. Any lead-time for permits or other authorizations, for equipment delivery, for site preparation, and so forth, should also be evaluated in considering the available alternatives. The intervening period between shutdown of operations and availability of the site for new use or sale is an important consideration in reviewing these impacts.

Expenditures/Results

An objective of your facility closure is that it be cost effective. The cost of an alternative must be compared to the reduction in potential risk of environmental degradation to establish a cost/benefit relationship. Ultimate use of the site weighs heavily in conducting this evaluation, since most on-site waste disposal alternatives detract significantly from future use options for the site.

Risk Assessment

The assessment of future risks related to your facility closure continue to be a subjective determination because of the evolving nature of the regulations and regulatory attitudes regarding waste management. The cost/benefit analysis previously discussed must be weighed against the risk of future regulatory action relative to the option(s) chosen. Closure options that continue to threaten usable groundwater resources should be closely scrutinized in terms of potential risk.

Public Acceptability

Public opinion based upon local perceptions of risk must be evaluated in choosing a waste management alternative. Since your plant closure will be public knowledge, and since hazardous waste facility closure is subject to some form of public notification, the possibility of community response must be considered. Possibilities for mitigating adverse public reaction by education and/or other programs should be assessed in evaluating the various alternatives.

Evaluation of closure alternatives under the above considerations obviously requires input from several sources of interest. The primary influences must be evaluated from:

Technical Experts
Regulatory Agencies
Legal Advisors
Accountants/Appraisers
Public Relations Specialists
Corporate Management

The collective input from these sources, appropriately weighted and applied to the various alternatives available, should result in a specific closure strategy for *each* of the facilities requiring attention.

DEVELOP YOUR STRATEGY (WHAT WILL BE DONE?)

After considering all the available alternatives, and the influences that direct the most feasible choice, a detailed plan must be developed. As this plan is developed, identify any major regulatory or public opposition. This will enable you to identify potential backup strategies should significant barriers be encountered. The elements of developing each formal closure strategy are summarized within this section.

Refine Site Condition Evaluations

Once a closure option is selected, additional site data may be required to support the technical or regulatory requirements of that strategy. A targeted program should be implemented to develop additional data necessary to satisfy requirements of the strategy.

Develop Engineering Plans

Preliminary engineering plans and specifications must be developed, to the extent that sufficient detail is established for budget considerations and for negotiating agency approval. At this point, conceptual engineering for closure and post-closure care, along with supporting graphics, should be developed.

Prepare Operating Procedures

Procedures to sequentially manage the implementation of the closure plan must be specified, along with safety plans and various contingency plans. To establish the credibility of the plan chosen, proposals must also be developed to document the effectiveness of the selected closure strategy (i.e., decontamination objectives, certification testing, etc.)

Sell the Plan

Approval of waste management facility closure plans is based upon several levels of review. Review and approval functions are typically conducted by

- *Company Officials*—In view of the economic and liability issues associated with waste management, internal reviews are usually conducted by company management with the support of technical, legal, and accounting staff. Before any plan is submitted for negotiation of outside approval, it must be acceptable to your company.
- *Regulatory Agencies*—All regulatory agencies identified as having jurisdiction over closure approval must be provided copies of the formal closure plan and then the required approvals must be negotiated. During these review activities, company approved backup strategies may be necessary in order to respond to agency concerns.
- *Public*—Depending upon the sensitivity of a particular closure strategy, it may be important to conduct a community relations program. This is most effectively developed through media advisors and meetings with selected public representatives. Should a public hearing be held, it may also be advisable to retain the services of a public relations firm to assist in community liaison.

IMPLEMENT YOUR PLAN (DO IT)

After all of the required approvals have been negotiated, implementation of the plan can proceed. The major elements of closure plan implementation follow.

Complete the Regulatory Package

Approval of a closure plan by the regulatory agencies frequently requires additional permits or authorizations for various components regulated under other programs. The concepts for these authorizations should have been approved during the regulatory review process, but formal permitting (if necessary) is a subsequent task. Any such permits should be obtained as soon as possible after approval of your closure plan.

Assemble a Detailed Engineering Package

A full construction package must be engineered in order to obtain contractor bids for plan implementation. This includes a complete set of construction drawings and specifications (with contractor bide documents) to solicit and evaluate competitive bids. Any additional site data (e.g., geotechnical data or topographical information) should be obtained during the development of this package.

Develop an Implementation Plan

A refined cost estimate and project schedule should be developed for final management approval prior to initiation of field activities. This schedule should optimize upon available resources to meet or beat the schedule approved by the agencies.

Identify and Qualify Contractors and Suppliers

Review and selection of competent mechanical contractors and equipment suppliers is critical to the successful completion of the closure activity. This review will ultimately result in contracts for equipment and construction of the closure plan, possibly including dismantling of production equipment. This element of the project is as significant as the original construction of your plant, since it will have an impact upon the value and/or liability associated with the closed facility. Contractors must be selected based upon their familiarity with the closure plan selected or, in the alternative, rigid supervision of field activities must be budgets into the program.

Provide On-Site Construction Supervision

Regardless of the experience of a construction or equipment contractor, it is prudent that company representatives monitor and supervise field activities. Auditing of construction and related progress payments under the construction contract will be required, together with field and laboratory testing to document compliance with the approved closure plan.

Prepare Closure Certification

Upon completion of all field activities, a verification report will be necessary, along with the certification by an independent registered professional engineer and the facility owner, that closure has been completed in accordance with the approved plan.

Manage Future Liability

Two aspects of facility closure may require post-closure monitoring, depending upon the closure option chosen:

- *Post-Closure Plan Implementation*—For on-site closure of regulated hazardous waste facilities, a 30-year post-closure care program may be mandated. Inspection of facilities and the procurement, interpretation, and submittal of post-closure monitoring data could be your continuing responsibility.
- *Monitor Site Integrity*—To minimize residual risks associated with any on-site closure, access control, erosion, and other long-term effects upon the closed facilities should be monitored. Any maintenance necessary to maintain the effectiveness of waste constituent containment will minimize your future liability.

SUMMARY

In considering shutdown and closure of a plant, it is imperative to plan not only the business impacts, but also the regulatory liabilities that will confront the owner company. The evaluation of closure alternatives based upon technical judgments, regulatory policies, public perceptions, and corporate objectives is a critical and complex decision that should be evaluated in advance of a shutdown. Expending a high level of effort early in the planning stages can significantly reduce the liabilities, risks, and costs of converting plant assets to alternative use or sale.

Soil Gas Survey Techniques for the Investigation of Underground Storage Tanks

Michael H. Schlender and Jerry Rowe
Golder Associates Inc., 4104 148th Ave., NE, Redmond, WA 98052

The sampling and analysis of near surface soil gas has shown great promise for the investigations of underground storage tanks. Trace to elevated concentrations of volatile organic components in soil gas samples have been used to identify source areas near buried tanks and map the migration of releases in groundwater and in the vadose zone. Soil gas surveys are also an effective tool to position soil borings, excavations, and monitoring wells, while support equipment (drilling rigs, backhoe, etc.) is still on site. Two examples are presented where soil gas surveys were used to direct the investigation of underground storage tanks.

INTRODUCTION

The Hazardous and Solid Waste Amendments of 1984 included provisions to deal with the mounting problem of leaking underground storage tanks. Recent estimates from government and industry indicate perhaps as many as 100,000 of the 1.5 to 3.5 million existing underground storage tanks are leaking [1]. The economic and environmental consequences of leaking underground tank storage systems can be quite significant, especially if the problem is overlooked or goes undetected for long periods of time. When considering, for example, the vast number of automotive service stations utilizing underground storage of petroleum fuels, it soon becomes clear that leaking underground storage tanks pose a very real environmental threat to soil, ground, and surface waters. Furthermore, hydrocarbon fuels can migrate through soils and invade below ground structures, possibly accumulating to toxic or explosive concentrations.

Various methodologies can be used to determine if underground tanks are leaking. Some of these methods have been incorporated into underground storage tank legislation as new requirements for existing and future tank installations. New regulations specify incorporating or retrofitting tanks to include product recovery, corrosion protection, and/or leak detection systems for tanks that will remain buried. However, in spite of these safeguards, experience has shown that losses to the environment still occur. Furthermore, when product or waste releases occur, determining the nature and extent of contamination can be costly, time consuming, and even disruptive if the project site is an active business. A soil gas survey is a good means of collecting preliminary information regarding subsurface contamination and has a successful track record evaluating underground storage tanks. Soil gas surveys are rapid, cost effective, and provide very little operational interference.

This paper describes two examples where field soil gas survey techniques have been used in a phased approach to determine subsurface contamination resulting from leaking underground storage tanks. The soil gas surveys are used to complement traditional sampling approaches and to enhance the effectiveness of the field work. Supplemental information from direct soil or water sampling is presented with each case study.

The first case study involves the delineation of subsurface contamination resulting from a leaking gasoline and diesel underground storage system (tanks and distribution lines). This study combines on-site gas chromatography for hydrocarbon analysis with unsaturated zone carbon dioxide analysis to account for hydrocarbon degradation due to subsurface oxidation. The second example shows the value of soil gas surveys in a phased subsurface investigation for petroleum hydrocarbons. The results of a soil gas survey are compared with soil sampling data collected from the same project site.

LEAKING GASOLINE AND DIESEL STORAGE SYSTEM

Background

The study involved an automotive service station and subsurface petroleum contamination resulting from a leaking underground storage tank system. The station was relatively new and the underground storage tanks, which had been installed within the last three years, included a leak detection system. Prior to the soil gas survey, several ground water monitoring wells had been installed at the project site. Three wells were located down gradient of the tank field and two wells were located within the surrounding tank backfill. The wells within the tank field and the well immediately down gradient contained free-floating petroleum product on the surface of the water table. The wells furthest downgradient showed no detectable concentrations of hydrocarbons.

Michael H. Schlender is presently at U.S. Environmental Protection Agency, 1200 6th Avenue, Seattle, WA. Jerry Rowe is currently at Golder Assoc., Inc., 200 Union Blvd., Lakewood, CO 80228.

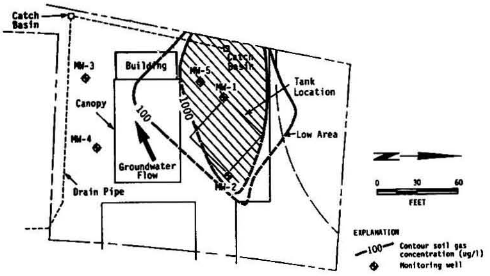


Figure 1. C_4-C_9 hydrocarbons in soil gas (2.0-3.0).

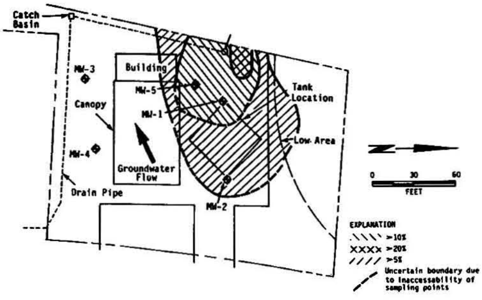


Figure 2. Carbon dioxide concentrations in soil gas (2.0-3.0).

The objective of the survey was to delineate vertical and lateral contamination near the tank storage area and to direct the placement of any additional ground water monitoring wells. An inspection of the monitoring well drilling logs indicated the subsurface geology was composed of interbedded clays and sandy-silty clays to a depth of approximately 7 meters. Ground water was encountered at depths from 3.2 to 3.3 meters, apparently moving in a southwesterly gradient. From the geologic and hydrologic information it was decided the survey would include depth profiling (sampling soil gas at successive depths) to determine the optimum sampling point. Furthermore, with ground water elevation data it was possible to keep a relatively consistent sampling distance above the water table.

Sampling Procedure

Soil gas samples were collected by driving 2.2 cm stainless steel probes to the desired depth using a rotary impact hammer. Depth profiling indicated the optimum sampling depth at approximately one meter (1.8–2.0 meters Below Land Surface (BLS)) above the water table. To estimate vadose zone petroleum sources, sampling was also performed at 1.7–1.8 meters (one meter BLS) above the water table. Static soil gas grab samples were collected using a high volume electric vacuum pump. The flow of the pump was reduced using a fine metering valve, monitored by a in-line rotameter. A consistent purge volume of 1 liter was removed during each sample collection. If a vacuum persisted after purging, an in-line vacuum gauge was monitored to establish when the probe pressure reached atmospheric and when the probe could be sampled. Probe pressure usually stabilized after a few minutes, at which time a sample for analysis could be collected in a gas-tight syringe and transferred to the field laboratory.

Instrumentation

Soil gas samples were analyzed by gas chromatography with photoionization detection (11.7 eV), using a HNU Model 321 field gas chromatograph (GC). Soil gas samples were separated with a GP 5% SP–1200/5.0% Bentone, 2 meter by 0.3 cm packed stainless steel column (Supelco, Bellefonte, PA) operated isothermally at 90°C. Data collection was accomplished with a Nelson Analytical Data (NAI, Cupertino, CA) system. The field GC laboratory and support equipment was set up in a rented van parked at the project site. The GC and data system received AC power during the two days on site.

In addition to the hydrocarbon analysis, qualitative carbon dioxide analysis was also determined at the deepest sampling points. The method of sampling and analysis used was similar to that described by Kerfoot, et al., and involved using a manual air-sampling pump and carbon dioxide detector tubes [2].

Discussion

The results of the soil gas survey are presented in Figures 1 and 2. Figure 1 illustrates the concentrations of C4-C9 hydrocarbons found at the deepest sampling point. Sampling at shallow depth produced only a few locations that showed measurable concentrations of hydrocarbons. Noticeable in almost all sample gas chromatograms was the reduced concentration of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes), with the presence of high concentrations of C4-C9 hydrocarbons. This absence of simple aromatic hydrocarbons correlated well with elevated concentrations of subsurface carbon dioxide. It is suggested from Figure 1 that the hydrocarbon plume originating from the tank field is diverting to the west-northwest, and away from the apparent down gradient ground water flow direction. In general, the hydrocarbons appeared to be moving into a low area near a storm sewer catch-basin located northwest of MW-5. This behavior is not surprising since the area surrounding the catch-basin was backfilled prior to station construction and would exhibit higher permeability relative to soils native to the site. Hydrocarbons may also be moving into this area as a free phase, since petroleum was noted to several centimeters in depth in MW-5.

The carbon dioxide data collected during the survey proved very useful toward the interpretation of C4-C9 hydrocarbon data. Site specific background concentrations were less than 1% carbon dioxide. As can be seen in Figure 2, the carbon dioxide contours generally followed those of the C4-C9 hydrocarbons, with an area just north of MW-5 showing significant concentrations of carbon dioxide exceeding 20%. Areas down gradient of MW-5 produced concentrations of approximately 5%. Carbon dioxide concentrations remained elevated in samples collected closer to the surface, although there was a decrease observed at some locations.

It was clear from the carbon dioxide data, the aliphatic hydrocarbon data, and the lack of aromatics in the soil gas that significant oxidation of the petroleum fuels was occurring. It has been reported that hydrocarbons composing gasoline are susceptible to biological and chemical oxidation and degrade at different rates, resulting in common oxidation end products such as n-butane, iso-octane, and carbon dioxide. Furthermore, aromatic hydrocarbons such as benzene tend to degrade rapidly to carbon dioxide, in comparison to aliphatic hydrocarbons [3].

If petroleum products were being diverted toward the catch-basin we might expect the highest hydrocarbon concentrations in this specific area. However, a slight decrease was actually observed in a northerly direction at the sampling points moved north along the western site boundary. This anomaly may be explained to some degree by the vicinity of the catch basin. This is understood to be a former discharge point or cross connection for seepage disposal and would be expected to contribute to increased biological activity, and higher degradation rates in the area.

The soil gas survey was used to direct the subsequent phase of groundwater monitoring well placement. The soil gas survey revealed that additional wells would be necessary to the north-northwest of the tank locations to verify localized groundwater flow patterns as influenced by backfilled soils, and to verify the extent of migration of petroleum hydrocarbons.

SUBSURFACE HYDROCARBON CONTAMINATION

Background

The second study involved another automotive service station. The station had been vacant for several months prior to the survey and the property was intended for resale. Several underground fuel and waste oil storage tanks remained buried at the site at locations shown in Figure 3. There was no record or available evidence of tank leakage and the tanks included a cathodic corrosion protection devise. Furthermore, no preliminary soil or water sampling had been performed at the site and at the time of the survey the tanks contained only residual amounts of petroleum. The objective of the field soil gas survey was to provide a preliminary screening of subsurface hydrocarbon contamination resulting from petroleum storage at the site.

The hydrogeological setting of the project site was determined from available records, which indicated the property was located over unconsolidated Quaternary glaciofluvial deposits comprising a regional unconfined aquifer. Ground water was predicted at a depth of 50 meters, moving northwest across the site.

Procedures

To design a comprehensive evaluation of the site, nearly 30 sampling locations were selected on a 10 by 10 meter grid, encompassing the tank field and most of the property. Sampling and analytical procedures used were similar to those discussed in the first case study. The sampling depth was determined from preliminary sampling and selected at 1.3 meters below ground surface. Electrical power for sampling and analytical equipment was supplied from two portable power generators.

Discussion

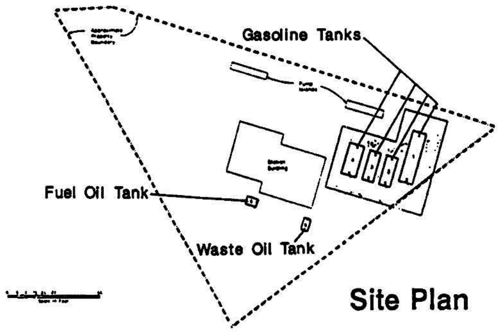
The results of the survey are presented in Figures 4–6 as individual concentration isopleths of C4-C9 hydrocarbons, benzene, and toluene. The survey results will be reviewed separately for clarity.

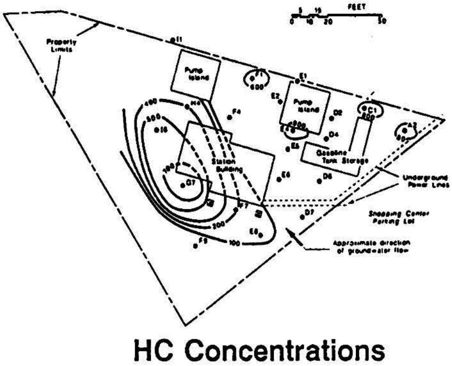
Figure 4 shows the C4-C9 hydrocarbon survey results. Overall, the hydrocarbon concentrations were low and did not indicate a potential for significant product losses to the soil. However, a pattern of hydrocarbons near the waste oil and fuel oil tanks (tanks 5 and 6, respectively) emerged from the survey results, apparently moving with ground water flow to the northwest. Because of the thickness of the vadose, the soil gas survey could not conclusively determine the vertical extent of contamination or if the petroleum residues had reached ground water.

As with the first area, the tank field showed only low concentrations of hydrocarbons in the soil gas. The concentrations found did not indicate the presence of significant product losses. The survey did find small confined discontinuous areas of elevated hydrocarbon concentration near the end of Tank 1 (see Figure 4), between the pump islands, and at the northwest corner of the tank field. In general, the benzene isopleths shown in Figure 5 followed the patterns established in Figure 4, however, a low concentration benzene plume was evident near the north end of the tank field.

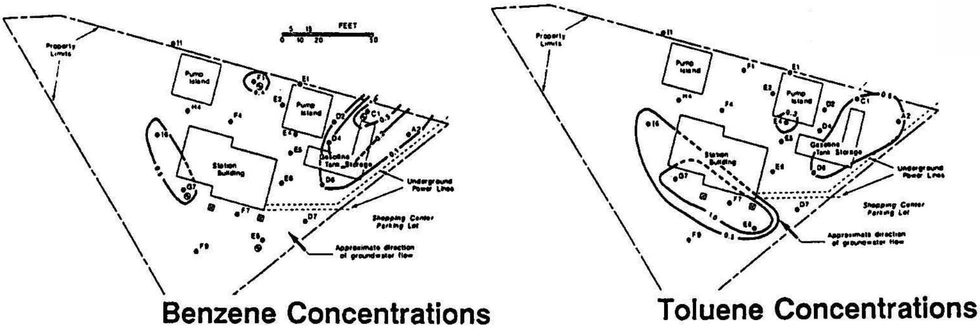
Toluene data, shown in Figure 6, resulted in concentration contours similar to those of benzene. In addition, the toluene isopleth shows slightly more spreading and higher concentrations overall in the tank area. Data for ethyl benzene and xylene isomers were also produced, but the results were often non-detectable. As a result, these compounds did not add significantly to the overall survey. In general, the soil gas survey indicated the tanks and distribution lines were contributing to only minor subsurface contamination.

There were primarily two areas of concern. One area was directly behind the station building, near the waste and fuel oil tanks, with a second area identified near the north end of gasoline Tank 1 (see Figure 3). At both locations it was uncertain as to the maximum depth of contamination. Therefore, soil sampling was scheduled for





Figures 3 and 4. Individual hydrocarbon concentration isopleths (all concentrations in μg/L soil gas).



Benzene Concentrations

Toluene Concentrations

Figures 5 and 6, Individual hydrocarbon concentration isopleths (all concentration in μg/L soil gas).

the next phase of the investigation to determine the vertical extent of hydrocarbon contamination at each area identified.

The soil sampling program was conducted when the storage tanks were excavated from the site. Observations and laboratory analytical results confirmed that the releases to the surrounding soils were confined to the vadose and minor in nature. For example, the plume originating near the rear of the station resulted from contaminated soils near the ground surface, produced from chronic tank overfill of the waste oil and fuel oil tanks. The contaminated soils were concentrated around the tank fill tubes and extended only a few feet in all directions. Soil samples were also collected from below each tank at a depth of 4–4.5 meters. The results were negative for petroleum residues. Furthermore, both tanks appeared in good condition, with no evidence of failure. It should also be noted that at the time of tank excavation the residue in the waste oil tank contained solvents in addition to waste oil. With the high permeability of the surrounding soils, and the distance between tank sources, what resembled a ground water contaminant plume from the soil gas survey, was most likely localized spreading from near surface hydrocarbon contamination.

Excavation of the gasoline tank field (Tanks 1-4, Figure 3) and associated distribution lines also showed several small shallow sources of hydrocarbons within the upper 2 meters of soil. These sources of the hydrocarbons were found near soil gas probe locations, which detected hydrocarbons. The sources were discontinuous with small pockets of contaminated soil, originating from loose pump or distribution line fittings, and from soils contaminated by tank overfilling. The tanks showed very little evidence of corrosion and appeared to be in good condition (estimated 20 years of burial). One exception however, was Tank 1, which showed a small seam failure at the bottom of the north end of the tank. This is the same area identified from the soil gas survey as exhibiting relatively higher soil gas hydrocarbon concentrations. A portable organic analyzer used to monitor soils during the excavation showed elevated concentrations of hydrocarbons in soils beneath the north end of Tank 1. At this location, soils were excavated to a depth of 5–6 meters, where a soil sample was collected. This sample showed nearly 2000 mg/Kg of petroleum hydrocarbon (USEPA Method 418.1) and low mg/Kg concentrations of xylenes. Benzene, toluene, and ethyl benzene were not detected in the sample. A shallow soil boring was drilled through the soil contamination and encountered clean soils at a depth of 13 meters. A ground water monitoring well was subsequently installed near this location. Soil sampling just above the ground water surface confirmed the negative results of the shallow soil boring. Ground water analysis results by method for 18.1 were slightly above detection.

This case study points out the benefits of confirmatory sampling methods phased with a soil gas survey. Many times, because of limited information regarding a project site, or inclusive survey findings, it is necessary to directly sample soil or water to confirm or further define preliminary soil gas information. In this case, the direct sampling defined the vertical component of hydrocarbon contamination whereas the soil gas survey defined the lateral extent in the vadose. In addition, because soil gas sampling and analysis can be completed rapidly, a survey can be used to accurately direct other methods of sampling.

SUMMARY

Although many applications are appropriate for remotely detecting contamination through soil gas monitoring, compound or site specific factors can significantly alter the outcome of a survey. The implications of these factors have recently been discussed in detail [*4*]. These factors include soil heterogeneity, porosity, moisture, and adsorptivity as well as the physical characteristics of the volatile organic compounds (VOCs) of interest. In addition, the degradation of VOCs, through chemical or biological oxidation, can produce compounds unlike those being monitored or may be converted to compounds which may not be appropriate for soil gas detection or analysis. Therefore, it is extremely important to select VOCs to monitor that are amenable to soil gas analysis and consider any site specific factors may influence their detection. Finally, because soil gas sampling and analysis only indirectly determines subsurface contamination it is often necessary to incorporate a survey into a phased investigative approach where the results of the survey can be confirmed and used to contribute to the overall effectiveness of a traditional soil or water sampling program.

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Oil Recovery and Waste Reduction by Microwave Radiation

C. S. Fang, Peter M. C. Lai, Bruce K. L. Chang
Department of Chemical Engineering, University of Southwestern Louisiana, Lafayette, LA 70504

and

W. J. Klaila
Electromagnetic Energy Corporation, Middleboro, MA

Oil-in-water and oil-water-solid emulsions, by-products of various industrial operations, often are environmental concerns. Laboratory and field tests have shown that these emulsions can be demulsified and separated into their individual layers by microwave radiation. The data also show that microwave separation is faster than gravity separation and can be faster than conventional heating at many conditions. After separation of emulsion into water, slop and oil layers, water can be discharged and oil is collected for recycle. The volume of slop is much smaller than the original volume of emulsion, therefore, the oily waste to be disposed is greatly reduced.

The zeta potential of oily droplets in water was measured and found that it is reduced by microwave radiation. This indicates that microwave provides heating and reduction of zeta potential in demulsification.

INTRODUCTION

In the petroleum refinery, natural gas processing, gas transmission, and oil and gas production industries oil-water emulsion is generated, which includes bottom sediment and water (BS&W) in crude oil transport facilities, oily slop discharged from flotation units, waste oil from gas compression stations, and emulsion left in pits and dump sites. Some of these emulsions are very old and "tight." They must be separated either for recycle of oil, or for the purpose of disposal required by the recent environmental regulations.

Two conventional methods of demulsification are: chemical addition and heating. Various chemical demulsifiers are available to break oil-water emulsion, such as alum and polyamines [*1*]. Demulsification by heat is usually carried out by gas- or oil-fired heaters [2].

An attractive alternative method of demulsification has been successfully tested in field operation and laboratory tests. This new technology is microwave demulsification of oil in water emulsion [*6*]. Patents were awarded to Klaila [3] and Nicholas [*4*] for their developments in this technology. The microwave demulsification can be used for oil recovery and waste reduction.

MICROWAVE RADIATION

Microwave frequencies allocated by the Federal Communication Commission for industrial and medical applications are shown in Table 1. These frequencies are referred to as ISM (industrial, scientific, and medical) frequencies. Two frequencies, 915 and 2450 MHz, are popular in industrial heating.

TABLE 1. ISM FREQUENCIES [5].

13.56 ± 6.68 kHz
27.12 ± 160.00 kHz
40.68 ± 20.00 kHz
915 ± 25 MHz
2450 ± 50 MHz
5800 ± 75 MHz
24225 ± 125 MHz

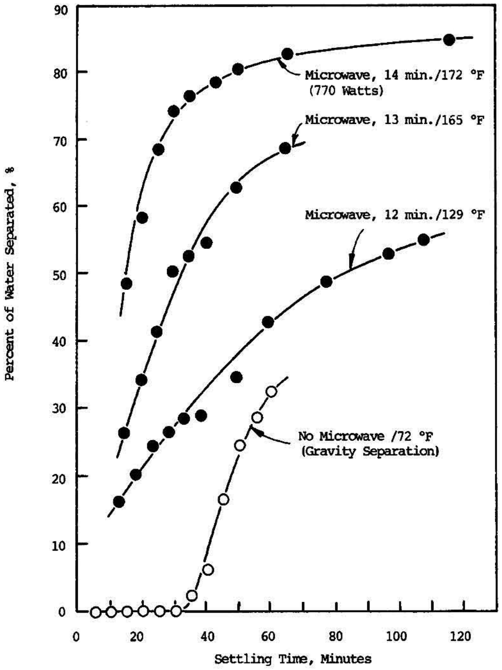

Figure 1. Separation of 20% water crude oil dispersed mixture. Reproduced from *Chem. Eng. Comm.* 73, pp. 227-239 (1988).

When an oil-water emulsion is heated, with microwave radiation, two phenomena take place simultaneously. The first phenomenon is reduction of viscosity. According to the force balance and Stoke's law, if water is the continuous phase, the rising velocity of oil droplets through water is given by:

$$v_{\text{oil}} = \frac{(\rho_w - \rho_{\text{oil}})g\, D^2}{18\mu_w} \qquad (1)$$

where D is the diameter of the droplets.

The viscosity of water, μ_w, is very sensitive to temperature. As temperature increases, viscosity decreases much faster than the density difference, $(\rho_w - \rho_{\text{oil}})$, does. Therefore, the heating, either by microwave or conventional heat, increases the velocity, v_{oil}, and consequently makes the separation of emulsion faster.

The second phenomenon is coagulation. The higher temperature and lower viscosity make the coagulation process easier. The results are larger particle diameters, D, and faster separation. Furthermore, microwave radiation is known to cause polar molecules to rotate rapidly. A number of experimental data presented previously [6], and in this work, indicate that the microwave-induced molecular rotation may neutralize zeta potential of colloidal droplets and help the coalescence of droplets.

Water-Crude Oil Dispersion

Water in water-crude oil dispersion can be separated from oil by microwave radiation [6]. As shown in Figure 1, the separation is much faster with microwave heating than the room temperature separation. A laboratory test showed that practically no separation was observed at the end of 30 minutes with no heating, while 12, 13, and 14 minute microwave radiation produced 28%, 48%, and 74% separation, respectively.

The dehydrated crude oil can be recovered for the refining process. In the case of 14 minute microwave radiation, the water content in crude oil can be reduced to 2–3%, which is near pipeline quality.

Oil Recovery from Oily Sludge

In laboratory tests, 100 grams of diatomaceous earth, 433 grams of vegetable oil, and 471.5 ml of distilled water were mixed using a hand blender with 2 minutes of agitation at its maximum speed. This sludge sample was divided into three parts: one for conventional-heating tests, one for microwave-heating tests, and one for gravity sedimentation tests at room temperature.

The above sample was further divided into 150 ml test samples and poured into 250 ml graduated beakers. Some of the test samples were heated with microwave radiation in a domestic microwave oven, and others were heated with a hot plate (conventional heating). After heating, the beakers were set on the bench for the water to settle. During the time of settling, volumes of oil separated from the sludge were read from the scale on the beaker.

Then, the percent of oil recovery was calculated from the following equation

$$\%\text{Oil Recovery} = \frac{\text{Vol. of Oil Separated}}{\text{Initial Vol. of Oil}} \times 100\% \qquad (2)$$

Figure 2 shows various percents of oil recovery by microwave heating and conventional heating. The microwave heating appears to heat the sample faster. Furthermore, at the same temperature, it provides the better end recovery than the conventional heating does. The recovery without any heating is poor. No separation was observed in the first 60 minutes.

Power Requirement

Power requirement and energy efficiency were studied. The electrical power inputs at various settings were measured with a voltmeter and ammeter. The initial and final temperatures of the test samples were measured for calculations of energy they received from microwave radiation. For 150 ml of test samples, 796 watts of electrical energy were supplied, and on the average, 20.4% of that energy was received by the samples.

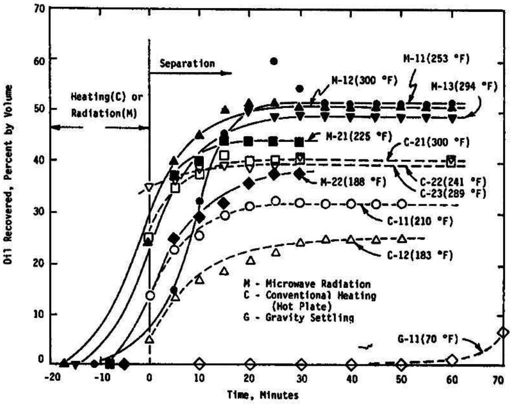

Figure 2. Separation of diatomaceous earth—vegetable oil emulsion.

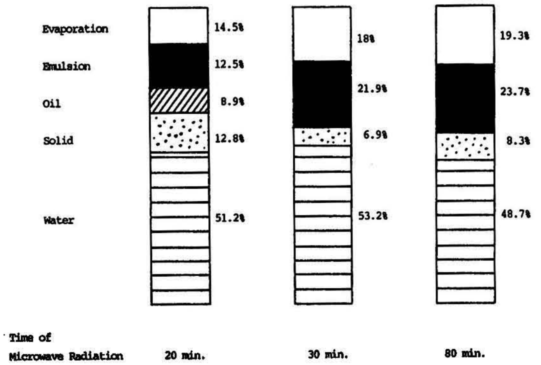

Figure 3. Separation of sludge by microwave radiation.

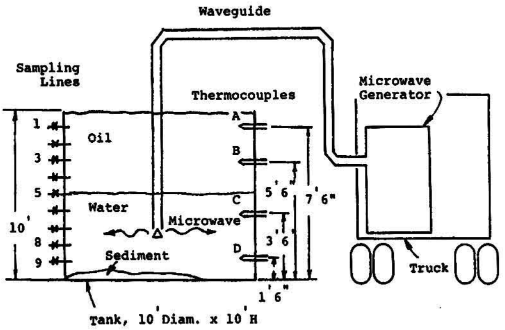

Figure 4. Apparatus used in field test. Reproduced from *Chem. Eng. Comm.*, 73, pp. 227-239 (1988).

Separation of Dump-Site Sludge

Thick, viscous, brown oil-water emulsion from a dumpsite of a compressor station was used in laboratory microwave experiments [6], similar to the bench tests described above. Its composition was 21.1% oil, 76.6% water, and 2.3% solid by weight. In each experiment, 300 grams of this emulsion in a beaker were placed in a domestic microwave oven for 20, 30, and 80 minutes of microwave radiation. Microwave energy inputs for these three samples were 58.3, 69.6, and 117.1 watt-hours, respectively. After microwave radiation, samples were placed on a bench for gravity separation. After a few minutes, three layers began to appear in the beakers.

The emulsion with 20 minutes microwave radiation produced four layers: water, oil, suspended solid, and slop layers. Material balances are shown in Figure 3. When the samples were heated longer, 30 and 80 minutes, three layers were observed: water, suspended solid and slop layers. No oil layer was found. In the three tests, emulsion was reduced to 12.5%, 21.9%, and 23.7% of its original amount. The excessive microwave radiation appeared to cause turbulence, resulting in poor demulsification.

FIELD TESTS

A commercial-scale microwave generator and wave guide were built and installed on a truck, which can be moved to reach a remote area for field tests. The maximum power output of the microwave generator is 50 KW and its frequency is 915 MHz.

One of the field tests were carried out in March 1984 in Coffeyville, Kansas [6] for 110 to 120 bbls of slop oil in a large tank, which was 10 ft in diameter and 10 ft high. Nine sampling lines, four thermocouples, and a microwave applicator were installed to the tank, as shown in Figure 4. There was one foot distance between two adjacent sampling lines. The slop oil was an emulsion of 50% oil, 22.5% bottom sediment, and 27.5% water.

Microwave radiation was applied to the tank on an on-and-off basis for 96 minutes in the morning to test the equipment. In the afternoon, microwave radiation was applied continuously at 20 KW from 1:30 p.m. to 9:55 p.m. The total energy applied was 228 KWH. The temperature readings of thermocouples A, B, and C rose steadily during the time of microwave radiation, from the room temperature to 80°F in C and around 100°F in A and B. After ten hours of microwave radiation, no water was found in samples drawn from sampling lines No. 2 through 6.

A similar field test was conducted in Louisiana. After draining off free water, there were 188 bbls of crude-oil/water emulsion left in a 210 bbl stock tank (10 ft diameter and 15 ft height). The emulsion was so thick that its pour point was 133°F. A 10-inch diameter circular microwave waveguide and a special applicator were inserted to the center of the tank. The applicator, which distributed microwave energy in all directions, was 3 feet above the bottom of the tank.

Microwave energy was applied to the oil-water emulsion, beginning at a power level of 16 KW at 915 MHz frequency. Gradually, the power level was increased to 25

TABLE 2. EFFECT OF MICROWAVE IN ZETA POTENTIAL OF OIL DROPLETS IN OIL-WATER EMULSION

Voltage Applied = 12.0 Volts (E = 1.569 volts/cm)

Voltage Applied = 20.0 Volts (E = 2.61 volts/cm)

Temp °F	Microwave Radiation	No. of Data Points	Average Electrophoretic Mobility, mm · cm/v · s	Zeta Potential, mv	Zeta Potential Reduction, %
116.8	Without	15	4.70×10^{-3}	43.3	
	With	15	4.23×10^{-3}	39.0	9.93
103.8	Without	15	5.79×10^{-3}	58.5	
	With	15	5.50×10^{-3}	55.6	4.96
96.0	Without	15	4.09×10^{-3}	44.6	
	With	15	3.73×10^{-3}	40.7	8.74
116.8	Without	15	5.99×10^{-3}	55.2	
	With	15	4.90×10^{-3}	45.1	18.3
103.8	Without	15	5.53×10^{-3}	55.9	
	With	15	4.53×10^{-3}	45.8	18.1
96.0	Without	15	3.48×10^{-3}	38.0	
	With	15	3.18×10^{-3}	34.7	8.68

KW. To avoid turbulence caused by microwave radiation, the power level was increased gradually. In 18.2 hours, the total energy applied was 417.5 KW-hr. At the end of 18.2 hours, the oil-water emulsion was separated to 146 bbls of dehydrated oil and 42 bbls of clear water. The clear water was drained from the tank.

Zeta Potential

A particle micro-electrophoresis apparatus, Model MK II, made by Rank Brothers (Cambridge, England) was used to measure electrophoresis velocities of crude oil droplets in oil-water emulsion. Measurements were made for the emulsion received microwave radiation, and for the emulsion heated with hot water. From measured electrophoresis velocities, electrophoretic mobilities and zeta potentials were calculated [7]. The results are summarized in Table 2.

Although the data are not consistent with the temperature, the effect of microwave radiation is obvious. The reduction of zeta poential can be considered as the result of microwave-induced molecular rotation neutralizing zeta potential of emulsified oil droplets.

CONCLUSIONS

Laboratory and field tests have shown that microwave radiation can be an effective tool to break oily emulsions for oil recovery and waste reduction. This new separation technology does not require chemical addition. Microwave radiation appears to provide faster separation than the conventional heating does. This may be an indication that the microwave-induced molecular rotation neutralizes the zeta potential of emulsified oil droplets. If this is the case, microwave radiation provides two contributions: reduction of viscosity and neutralization of zeta potential for coagulation. These two contributions are made separately by heating and chemicals in conventional demulsification.

ACKNOWLEDGMENTS

This paper is based on the results of an ongoing research project supported by the National Science Foundation. The support of NSF is greatly appreciated.

NOTATIONS

D = diameter of droplets
g = gravity acceleration
v_{oil} = rising velocity of oil droplets
μ_w = viscosity of water
ρ_{oil} = density of oil
ρ_w = density of water

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Evaluation of Membrane Processes for the Reduction of Trace Organic Contaminants

Sol Lyandres
TENERA, L.P., 1995 University Ave., Berkeley, CA 94704

John Meardon
Lawrence Livermore National Laboratory, MS L-499/PO Box 5508, Livermore, CA 94550

and

John Rees
TENERA, L.P., 1995 University Ave., Berkeley, CA 94704

Reverse osmosis (RO) was experimentally tested on liquid condensates produced from a pilot evaporative crystallizer. The condensates contained residual light organic compounds. The original sources of the condensate feeds were two solar evaporation ponds that received treated liquid effluents from a hazardous waste treatment and disposal facility. The objective of the tests was to reduce total organics concentrations (TOC) to levels acceptable for discharge into the local POTW or surface waters.

INTRODUCTION

The liquid feeds used in this study were complex chemically and have similarities with a wide variety of commercial waste streams. It is well known that reverse osmosis can be used to remove selected soluble compounds from liquid effluent. Reverse osmosis was, therefore, selected as one option among others for experimental removal of residual organics from the evaporative crystallizer condensate. The primary treatment of the feedstock by evaporation resulted in a condensate with few dissolved and suspended solids and no oil or grease. Pretreatment for reverse osmosis was therefore not required.

The economics of reverse osmosis for treatment of certain waste types, such as low concentrations of organics, is attractive. For average-sized full-scale reverse osmosis units of about 20–26 m^3 (75,000–100,000 gallons) per day, operational treatment costs will be about one cent per gallon. Installed 1988 equipment capital costs can be estimated by multiplying the gallons per day processed by the RO unit by \$2.50 (±15%).

A primary objective of this study was to investigate the effectiveness and feasibility of using reverse osmosis for the efficient separation of organic compounds present in the condensate. Additional objectives were to determine design criteria and operational parameters for a full-scale unit based on the experimental results of the pilot unit tests.

LITERATURE REVIEW

The first practical application of reverse osmosis membrane technology was performed in the early 1960's with the desalinization of sea water. Reid, *et. al.* [*1*] demonstrated that cellulose acetate membranes are capable of rejecting salts present in sea water, resulting in a greatly reduced concentration of salts in the permeate. Ionic rejection of organic species, which are small enough to pass through membrane pores, has further increased the efficiency of RO as a separation technique.

By 1983, commercial membranes had been developed for separation of organics, including carboxylic acids, phenols, and carbohydrates, etc. [*2, 3*]. It was demonstrated that the effectiveness of separation depended on a variety of factors, the principal one being the molecular size (molecular weight) of rejected compounds. The molecular weight cut-off point for membranes developed up to this time (given a 90% rejection) was about 100–110.

Improvements in materials since 1983 have led to membranes with enhanced ionic rejection properties. Acceptable rejection of organic species with molecular weights of about 50 can now be achieved successfully [*4, 5*].

The cost effectiveness of RO membrane performance can be improved by decreasing operational pressure. Recent developments in membrane technology have resulted in the use of low (above 1.0×10^6 N/m^2, or 150 psi) and ultra low (below 1.0×10^6 N/m^2 or 150 psi) operational pressures coupled with unique organic rejection characteristics [*6, 7*].

It has been shown repeatedly that the pH of the feed has a significant effect on membrane permeability. It has been demonstrated, for example, that 66% of acetic acid in an acetic acid waste was rejected at a pH of 2.7, whereas 99% was rejected at a pH of 11.1 [*8*].

Long-term use of full-scale RO units render the RO membranes susceptible to scale build-up and bacterial fouling. Membrane fouling due to scale accretion and biological activity can be prevented with low concentrations of chlorine [*9, 10*] as well as mineral acids and proprietary chemicals [*11*].

MATERIALS AND METHODS

Reverse Osmosis Feed

Two feeds were used during RO testing. The feeds originated from two solar evaporation ponds that received treated liquids from a hazardous waste treatment facility. These ponds were designated Ponds A and B. Condensates derived from these ponds were found to have TOC concentrations of 1500 mg/l and 500 mg/l, respectively. Pond A liquids were relatively "old" in the sense that they had been in the pond for some time and some biological degradation of organics had occurred. Pond B liquids were "new", and had been pumped into the pond relatively recently. Little biological degradation had probably taken place.

The feeds used for RO testing originated from pond water subsequently treated in an evaporative crystallizer, and then sent to the RO unit as evaporative condensate. The two RO feeds were designated A and B, named for the ponds from which they originated.

Samples of liquids from both ponds were sent to an evaporative crystallizer for initial bench-scale treatment. Extensive chemical analyses of the crystallizer feeds and condensates revealed complex organic mixtures. Due to interference during analysis, many of the compounds present were difficult to identify. Analyses of condensates from bench-scale tests indicated that the most common compounds were carboxylic acids and amines. Since the condensate was produced at about 110°C, most organics in the RO feed would be at the light end of the spectrum, with boiling points at 110°C or below. The pH of the condensate ranged from 6.4 to 6.8, depending on the batch. Feed pH was pond independent.

Chemical Analyses During Testing

Extensive chemical analyses for individual compounds during testing were difficult to perform due to the complex chemistry and analytical interference in the feed, condensate, the permeate. Analyses for TOC were performed as appropriate on the feed, concentrate, and permeate during testing. Standard methods for TOC analyses were applied. A Beckman TOC 540B analyzer was used for measurement of TOC concentrations. Accuracy of measurements was ± 10%. As a result of the evaporation of the original feed, inorganics were present only in trace amounts (80–350 mg/l), depending on the batch.

Definitions

In a generalized reverse osmosis scenario, feed enters the RO unit and exits as two flows—concentrate and permeate. Recovery is expressed as the percentage of feed which passes through the membrane and is recovered as permeate. Recovery can be calculated as follows:

$$\text{Recovery} = Q_p/Q_f \times 100\% \qquad (1)$$

where

Q_p = permeate flow rate

Q_f = feed flow rate

RO membrane rejection is measured by the extent of solute separation, given as:

$$\text{Rejection} = (1 - C_p/C_f) \times 100\% \qquad (2)$$

where

C_p = solute concentration in permeate

C_f = solute concentration in feed

Reverse Osmosis Membranes

Two brands of membranes were tested. Membrane selection was based on a review of available vendor information and the results of chemical analyses of condensates derived from bench-scale testing. The membranes

TABLE 1. FILMTEC AND TORAY MEMBRANES: MAJOR OPERATIONAL PARAMETERS.

Manufacturer:	FILMTEC	TORAY
Model:	SW30-HR2540	PEC-1000 SP110
Membrane Type:	Thin Film Composite Spiral Wound	Thin Film Composite Spiral Wound
Filtration Area:	2.32 m^2 (25 ft^2)	6.97 m^2 (75 ft^2)
Target Capacity:	1.14 m^3/d (300 gpd) (12 g/ft^2/d)	2.73 m^3/d (720 gpd) (9.5 g/ft^2/d)
Single Element Recovery:	10%	10%
Feed Flow:	13.25×10^{-5} m^3/sec (2.1 gpm)	31.55×10^{-5} m^3/sec (5.0 gpm)
Permeate Flow:	1.32×10^{-5} m^3/sec (0.21 gpm)	3.5×10^{-5} m^3/sec (0.5 gpm)
Concentrate Flow:	12×10^{-15} m^3/sec (1.89 gpm)	28.4×10^{-5} m^3/sec (4.5 gpm)

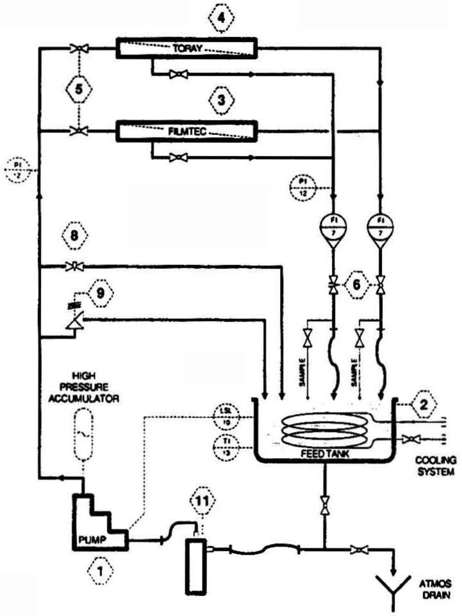

Figure 1. Reverse osmosis test stand.

selected had demonstrated in laboratory studies a high rate of rejection of carboxylic acids and amines. These two membranes types were Filmtec SW30 and Toray PEC1000. Both brands consisted of cartridges containing spirally wound membranes and were similar in performance characteristics. Filmtec is of American manufacture, while Toray is Japanese. The Filmtec cartridge membrane was a cartridge 12.7 mm (2 1/2") in diameter by 1.02 mm (40") in length, with 2.32 m^2 (25 ft^2) of filtration area. The Toray cartridge membrane was 101.6 mm (4") in diameter by 1.02 m (40") in length, with a working area of 6.97 m^2 (75 ft^2). The Toray membrane has some operational disadvantages as compared with Filmtec, such as the necessity for the addition of sodium bisulfite to the feed at concentrations of about 300 mg/l. Sodium bisulfite acts as an oxygen scavenger and protects the membrane material.

The principal operational parameters of each membrane type are presented in Table 1.

Test Unit Description

The reverse osmosis test unit is depicted in Figure 1. The entire RO system was skid mounted and employed a 3.16×10^{-4} m^3/sec (5 gpm) positive displacement pump (1) capable of maintaining a liquid system pressure of up to 7×10^6 (1000 psig). The 0.06 m^3 (16-gallon) feed tank (2) was equipped with cold-water cooling coils to remove heat generated during pumping. Membrane high pressure chambers held the Filmtec (3) and Toray (4) cartridges. Two block valves (5) isolated each RO membrane during testing.

Both concentrate and permeate lines were equipped with throttle valves (6) to regulate flow rate. Flow meters (7) were also installed in these lines. Excess feed was discharged back into the feed tank via a throttle valve (8). The test unit was operated such that the permeate and concentrate flow could be recirculated back into the feed reservoir.

The system was equipped with safety back-up mechanisms, including a high pressure relief valve (9) on the feed pressure line, a low liquid level cutout switch on the feed tank (10), and an in-line filter (11) on the pump suction line. These devices were installed for protection of the membrane pressure vessels and the feed pump. The system was also equipped with control units, including two pressure (12) and one temperature (13) gauges. Pressures gauges monitored on feed and concentrate lines, and temperature was measured in the feed tank.

Tests, Test Categories, and Results

A total of 14 individual tests were run with the RO system. These tests were grouped into five test categories based on tests goals. Test variables examined were feed source, membrane type, and operational parameters including feed pH, % recovery, and feed concentration. In all except the last category permeate recovery over a single pass through the membrane element was maintained at a level of 10%.

Table 2 presents the five test categories and the major operational parameters and conditions varied in each individual test. Experimental test results are presented in graphic form and discussed as appropriate to each test category.

Test category I: This category tested feed pH versus efficiency of organic rejection by the two RO membrane makes. Condensates from both ponds A and B liquids were tested. Three tests were run in this category. Mem-

TABLE 2. SUMMARY OF TESTS AND TEST CATEGORIES.

Test Category	Test Numbers	Condensate (Feed)	Membrane Brand	Feed pH	Pressure N/m^2 × 10^6 (psig) Feed	Concentrate	Recovery (%) Single Pass	Per Test
I	1	A	Filmtec	2-11	2.76 (400)	2.21 (320)	10	
	2	A	Toray	2-12	4.27 (620)	3.72 (540)	10	
	3	B	Toray	2-11	4.34 (630)	3.79 (550)	10	
II	4	B	Toray	6.4	4.38 (635)	3.83 (555)	10	50
	5	A	Filtec	6.8	2.83 (410)	2.27 (330)	10	55
III	6	A	Toray	6.8	4.34 (630)	3.79 (550)	10	90
	7	A	Toray	6.7	4.27 (620)	3.72 (540)	10	90
	8	A	Toray	6.7	4.21 (610)	3.65 (530)	10	90
	9	A	Toray	6.8	4.21 (610)	3.65 (530)	10	90
	10	B	Toray	6.4	4.34 (630)	3.79 (550)	10	90
	11	B	Toray	6.6	4.27 (620)	3.79 (550)	10	90
IV	12	B	Filmtec	6.5	2.90 (420)	2.34 (340)	10	95
	13	B	Toray	6.5	4.21 (610)	3.65 (530)	10	95
V	14	A	Toray	6.8	2.62–6.83 (380–990)	2.07–6.27 (300–910)	4–14	

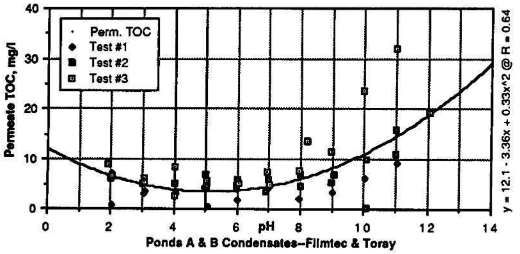

Figure 2. Test summary results: feed pH versus permeate quality (test nos. 1, 2, & 3).

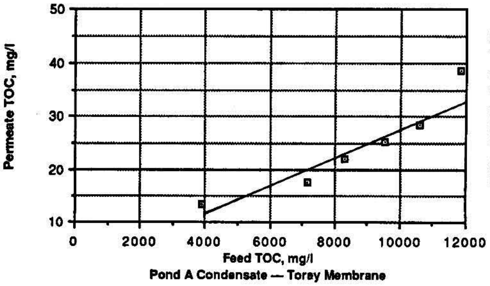

Figure 3. Test summary: permeate quality versus TOC concentration (test nos. 6-9).

brane rejection efficiency was measured by monitoring the TOC concentration of the permeate for different pH values of the initial RO feed. For each test, the pH was adjusted by increments of one from pH 2 to 12. Feed pH was adjusted via the addition of solutions of sulfuric acid or sodium hydroxide. At the beginning of each test, permeate and concentrate were returned to the feed tank, and the RO system was then operated until a steady state condition was reached. Samples of feed, permeate, and concentrate were then taken for analysis. Test results presented in Figure 2 give combined results for all tests.

The concentration of TOC in the permeate was below 10 mg/l for both membranes within a pH range of 2–8. In all runs, TOC removal was in excess of 98%. The Filmtec membrane was found to be slightly more efficient in removal of organics (TOC concentrations were slightly lower) than with the Toray under the same experimental conditions (compare test results 1 and 2).

Organics from pond B were found to have a slightly higher % rejection than those from pond A using a Toray membrane (compare test results 2 and 3). This result is thought due to the difference in the kinds organics species contained in the two ponds.

The summarized test data supports a second degree polynomial fit, which indicates a minimum of permeate TOC within a pH range of 3-8. This polynomial is well described by the equation:

$$y = 12.1 - 3.36 + 0.33x^2 \qquad (3)$$

$$@\, R = 0.64$$

Since the feed has a complex chemistry, the maximum pH rejection range is relatively wide. This pH range can be considered optimal for % TOC rejection for both membrane brands and both feed types.

The other practical conclusion resulting from these tests is that the condensate received from the evaporative crystallizer ranged from 6.4–6.8, which lies within the range for optimum TOC rejection. Based on this information, the original condensate feed could be used directly, without any pH adjustment.

Test Category II: This category included two tests. Rejection efficiency for both membrane brands was evaluated with respect to concentration of organics in feed. Both pond condensates were tested.

By returning the permeate and concentrate to the feed tank, each test was run until a steady state was attained. Samples for analysis were taken for feed, concentrate, and permeate. Three liters of permeate were then removed and replaced with 3 liters of original feed. A steady state operation was again attained, and the sampling and volume withdrawal/addition steps repeated. The result was a doubling of the feed TOC concentration.

Overall evaluation of both tests showed that Toray organics rejection averaged from 95% to 97% for the condensate of pond B with permeate TOC concentrations being about 20 ppm. Filmtec rejection was found to be slightly higher (99%) for condensate of Pond A, and permeate TOC concentrations here were below 10 ppm. There were no significant corresponding increases in permeat TOC concentrations as the concentration of both feed types were increased.

Test Category III: Because the tests of category II showed no detectible trend in the change of TOC concentration of permeate as TOC feed concentration was doubled, it was decided to increase feed TOC concentration. Six tests were run in this category to further explore the relationship between the TOC concentration of permeate and feed.

To attain high feed TOC concentrations, the test system was operated in a semi-continuous mode. During the test procedure the permeate was discharged from the system, while the concentration was returned back into the feed tank. The amount of permeate removed was replaced in the RO system with an equivalent inflow of condensate feed. Higher feed concentrations were attained by this means. Both pond condensates were tested. During testing samples of permeate, feed, and concentrate were taken for analysis. Samples of concentrate were large enough (500 mls) such that TOC concentrations in the concentrate flow were unintentionally lowered.

The Toray membrane was used in four of the tests to treat Pond A condensate. Summary results of these tests are presented in Figure 3. Overall membrane rejection was in excess of 99%. During the run, feed TOC concentrations ranged from 1500 to 12,000 mg/l, while corresponding TOC permeate concentrations ranged from 10 to 40 mg/l. Test results can be described by the straight line equation:

$$y = 1.22 + 0.0026x \qquad (4)$$

$$@\, R = 0.96$$

In the final two tests, the Toray membrane was used in conjunction with Pond B condensate. Feed concentration was increased from 500 to 4500 mg/l during the course of the tests. Summary experimental data for these two tests is presented in Figure 4. TOC rejection was in excess of 99%. Permeate concentration was seen to increase from 10 to 25 mg/l during the duration of the two tests. The test data can be described by the straight line equation

$$y = 5.9 + 0.005x \qquad (5)$$

$$@\, R = 0.98$$

It can be seen from comparing Figures 3 and 4 that permeate quality of feed A is less dependent on feed TOC concentration than permeate quality of feed B.

Test Category IV: Two tests were run in this category. The tests run were similar to those in test category III except for frequency of sampling and overall final percent recovery. In this test category, recoveries of 95% were ob-

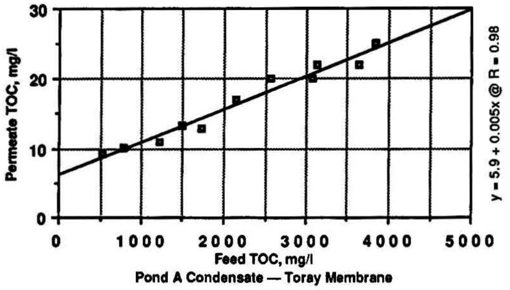

Figure 4. Test summary: permeate quality versus feed TOC concentration (test nos. 10 & 11).

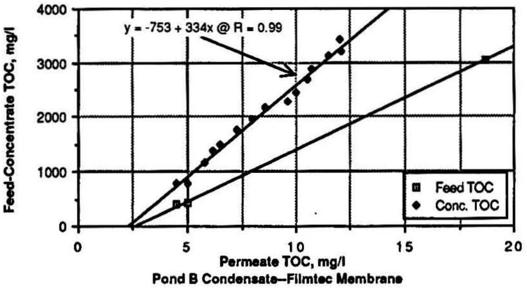

Figure 5. TOC feed-concentrate versus permeate quality (test no. 12).

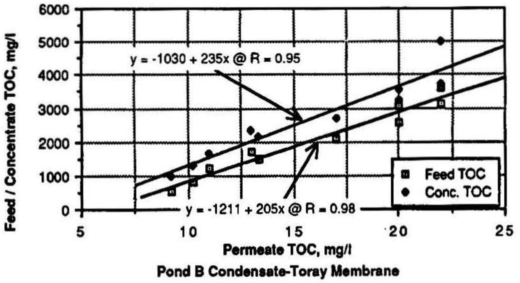

Figure 6. TOC feed-concentrate versus permeate quality (test no. 13).

tained by further working down the residual volume of feed in the feed tank. One test each was run on the Filmtec and Toray membranes. Condensate from Pond B was used as feed for both tests. The final test ratios of feed, permeate, and concentrate for the Filmtec and Toray membranes were 100:95:5 and 150:142.5:7.5 gallons (0.378:0.36:0.018 and 0.57:0.54:0.03 m^3), respectively.

Test results are presented in Figures 5 and 6. As evidenced by the data, TOC rejection of in excess 99% was found in both tests. The Filmtec membrane appears to give a slightly better percent rejection than the Toray. This observation is based on lower TOC concentration in the permeate from the Filmtec membrane (<10 mg/l) versus 10–20 mg/l for the Toray membrane at the same TOC feed concentrations. The TOC of the permeate is seen to be directly proportional to TOC concentrations of feed and concentrate. This dependency is demonstrated at TOC feed concentrations from 1,000–4,000 ppm. These relationships are given as a straight lines, and are described by appropriate equations (see Figures 5 and 6). The Filmtec membrane also requires lower feed operating pressure (up to 1.38×10^6 N/m^2 or 200 psi less) to achieve the same recovery as does the Toray membrane.

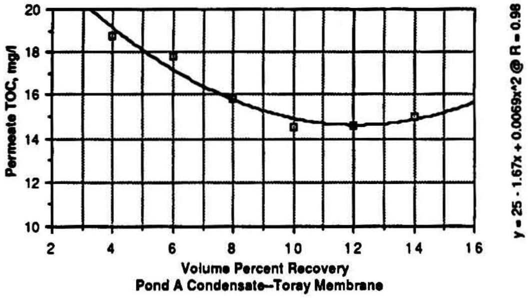

Figure 7. Recovery versus test operational parameters (test no. 14).

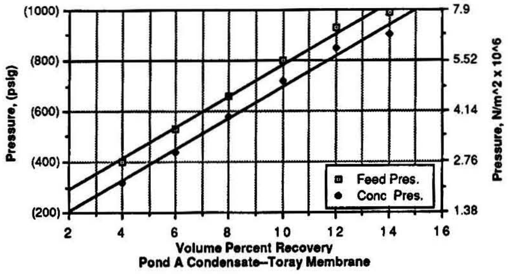

Figure 8. Recovery versus feed & concentrate pressure (test no. 14).

Test Category V: There was one test in this category. This test measured recovery versus operational parameters, such as feed and concentrate pressures and TOC in the permeate. The Toray membrane and Pond A condensate was used. Percent recovery was raised incrementally by two percentage points from 4% to 14% at each feed pass. The feed pressure was adjusted to attain each percentage recovery. Fourteen percent was the highest percent recovery for a single pass because the feed pressure was to be raised to a limit of 7×10^6 N/m^3 (1000 psig), the upper maximum membrane limit. After a steady state had been reached, pressure and temperature were recorded and samples taken for TOC analysis.

Experimental data are presented in Figure 7. Little effect was noted in TOC permeate concentration with increasing rate of recovery. At lower recovery rates, permeate TOC concentration was slightly higher as compared with higher recovery rates. This effect is thought due to membrane boundary layer solute build-up during the duration of the test. The data supports a second degree polynomial as given by:

$$y = 25 - 1.67x + 0.0069x^2 \tag{6}$$

$$R = 0.98$$

Recovery versus feed and concentrate pressures is shown in Figure 8. As expected, a rise in pressure followed a straight-line dependency with increasing recovery rates.

SUMMARY AND CONCLUSIONS

Results of the reverse osmosis pilot test program demonstrate that RO is a viable secondary treatment process for the removal of soluble organic compounds from liquid waste streams. Effluents with residual soluble organics are common in treated and untreated industrial waste streams.

Both RO membrane brands were used to successfully treat the two pond condensate feeds. The condensate feeds differed in types and concentrations of organic compounds. The Filmtec membrane exhibited a slightly higher rejection of organics than the Toray membrane. Both membranes exhibited 98 plus percent rejection of organics over a wide range of tested feed concentrations, a phenomenon known as constant rejection. Permeate qualities were consistently less than 50 mg/l of TOC with typical ranges from 10–30 mg/l. In all tests, the Toray membrane required higher operational feed pressures than Filmtec, up to 0.69–1.38 N/m^3 (100-200 psig). The Filmtec membrane does not require an oxygen scavenger to protect the membranes as does the Toray, and is lower in cost to purchase.

Rejection properties of both membrane brands tested were not effected to a great degree by changes in pH. Minor changes in permeate quality were noted over the wide pH range tested (2–12), and a pH of from 5–8 was found to be optimal for membrane rejection. Since the pH of the original feedstocks was between 6.4–6.8, no pH adjustment was required during testing.

Continuous testing of the RO unit for more than 30 days did not reveal any biological fouling or scale build-up problems on any of the membranes or within the system.

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Effluent Treatment for Alcohol Distillery: Thermal Pretreatment with Energy Recovery

S. S. Lele, P. J. Rajadhyaksha, and J. B. Joshi
Department of Chemical Technology, University of Bombay, Matunga,
Bombay, 400 019, India

Stillage from cane molasses based alcohol distillery was thermally treated at 160 to 250°C at high pressure and in the absence of air. A solid charred residue was precipitated that was easily separated by gravity filtration from a liquid suitable for anaerobic digestion or wet oxidation. The charred residue was comparable with typical lignite coal in terms of carbon content and calorific value. Effects of temperature and pH on COD reduction, biodegradability, and filterability were studied.

INTRODUCTION

Production of ethyl alcohol in distilleries based on cane sugar molasses is a very large industry in tropical areas such as Asia and South America. The world's total production of alcohol from cane molasses is more than 13 Mm^3/yr. The molasses is diluted and fermented with yeast and the resultant liquid, containing 6–8% alcohol by volume, is distilled to recover alcohol. The dealcoholized aqueous stream coming out of distillation unit is a dark brown, highly organic effluent known as stillage or vinase, and is about 12 to 15 times by volume of the product alcohol. The stillage is one of the most complex, troublesome, and strongest organic industrial effluents. It has a COD value of 100 kg/m^3 and BOD of 50 kg/m^3. It has been estimated that the BOD load of the stillage discharged by a typical distillery with a capacity of 30 m^3/d alcohol, is equivalent to the BOD load of sewage stream of a city having a population of 500,000. Thus, the alcohol distillery industry has posed a serious pollution problem and extensive research and development work is being carried out all over the world.

Due to the high concentration of organic load (COD) in the distillery stillage, it is a potential source of renewable energy. A countrywide cane-based alcohol production, along with energy equivalents is given in Table 1 [*1*].

Since most of the advanced countries produce 90% of the world's beet sugar and only 10% of world's cane sugar [2], most of the research has been concentrated on the treatment of stillage based on beet molasses. However, cane molasses-based stillage is twice in BOD and COD concentrations and hence, is a more difficult waste for treatment in comparison with the beet-based stillage. Further, sulphur dioxide is used for bleaching in the cane sugar process, which results in a large concentration of sulphate ions in the stillage, making the stream more difficult to treat biologically. Therefore, dilution before the treatment has been recommended [3]. It was thought desirable to undertake the treatment of stillage from sugar cane molasses with a novel approach for energy recovery.

The proposed method results in some dilution without adding any external water. Another attractive feature of the proposed method is that there is a drastic reduction in

TABLE 1. POSSIBLE ENERGY RECOVERY FROM THE CANE STILLAGE—COUNTRYWIDE STATISTICS

Country	Cane sugar production MT/yr	Cane based alcohol Mm^3/yr	Coal equivalent of stillage Mt/yr
C. America	27.0	3.7	5.4
N. America	3.0	0.4	0.6
S. America	22.0	3.0	4.4
Asia (excluding India)	24.0	3.3	4.8
Europe	1.2	0.2	0.2
India	8.0	1.1	1.6
Oceania	10.0	1.4	2.0
Total	95.2	13.1	19.0

(Alcohol capacity was estimated from cane sugar production. Specific energy of coal: 16.8×10^6 J/kg)

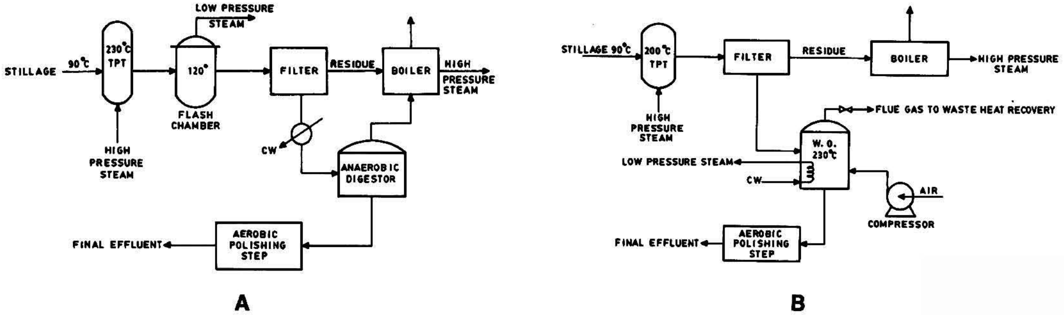

Figure 1. Modified flow-sheet: anaerobic digestion. 1B. Modified flow sheet: wet oxidation.

TABLE 2. ENERGY RECOVERY OF VARIOUS PROCESSES

Basis: Distillery capacity 30 m^3/d alcohol
Recoverable energy: 30 T/d (coal equivalent)

Process	Form of energy	Coal equivalent, T/d Stepwise	Coal equivalent, T/d Total
1. Anaerobic digestion	Biogas	13.0	13.0
2. Incineration	Excess steam	24.0	24.0
3. Wet oxidation	Excess steam	24.0	24.0
4. Modified anaerobic digestion	1. Charred residue	15.0	22.0
	2. Biogas	7.0	
5. Modified wet oxidation	1. Charred residue	15.0	27.0
	2. Excess steam	12.0	

the COD value from initial 100 kg/m^3 to 50 kg/m^3 in less than two hours. If this process can be implemented on plant scale, it will help in controlling the distillery environmental pollution and foul odor of the fermenting stillage for kilometers around. Also, contamination of surface and ground water by seepage of stillage can be prevented.

At present, stillage treatments are proposed by three different routes: concentration followed by incineration; anaerobic digestion with biogas recovery followed by a aerobic polishing step [*4*, *5*, *6*]; and direct wet oxidation of stillage by air at high temperature with generation of steam followed by aerobic polishing step [*7*, *8*].

The incineration process involves the use of a boiler of highly specialized design. This is to take care of the scaling problem during the combustion of concentrated organic wastes containing substantial amounts of inorganics like potash. The anaerobic process demands relatively high residence time, which results into enormous sized digesters. The wet oxidation process employs high-pressure, high-temperature air oxidation. This process needs autoclaves and large compressors and the capital investment is large. Further, the anaerobic as well as wet oxidation processes do not give the necessary effluent quality, and a secondary aerobic treatment is required. Thus, all these processes are highly capital-intensive. The incineration process involves an investment of the order of 400% of the distillery cost, whereas the other two processes along with the secondary treatment require an investment of 200% to 300% of the distillery cost. The unfavorable economics makes it very difficult to implement these treatment processes on the plant scale.

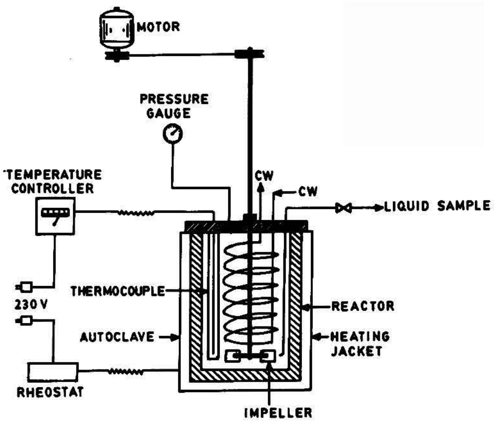

Figure 2. Experimental set-up.

Since the anaerobic digestion and the wet oxidation are relatively less expensive, these alternatives are more attractive. This paper discusses our efforts to modify these two processes, to make them more economic and by applying the following strategies: increase the net energy recovery by some modifications in the process, and reduce the capital investment. In order to achieve these objectives, the stillage was thermally pretreated to form a more suitable feed stock for the anaerobic digestion or wet oxidation. The thermal pretreatment was carried out in the absence of air at temperatures ranging from 160°C to 250°C. A charred residue was obtained, which could be easily separated by filtration. The stillage, having a COD value of 100 kg/m^3, was converted to a filtrate having COD value of 50 kg/m^3 in less than two hours.

The modified flowsheets of anaerobic digestion and wet oxidation processes incorporating the thermal pretreatment are shown in Figures 1A and 1B. The pretreated material may form a more suitable feed for anaerobic digestion and the digester volume may be much smaller. Lower COD of the filtrate will need correspondingly lower digester volume. Similarly, in the case of wet oxidation, since a large fraction of the COD is removed during the pretreatment, the compressed air requirement will decrease substantially and hence, the compressor cost will be much less. In order to compare the energy recovery, the different forms of energy recovered during the various treatment processes were expressed as its coal equivalent (specific energy: 16.8 × 10^6 J/kg). The estimated figures for a distillery having 30 m^3/d alcohol capacity are given in Table 2.

EXPERIMENTAL

Equipment

A schematic diagram of the experimental set-up is shown in Figure 2. The thermal pretreatment of the stillage was carried out in a 0.1 m inner diameter, 0.001 m^3

TABLE 3. TYPICAL COMPOSITION OF THE STILLAGE

Color	—	Dark brown
Odor	—	Molasses
pH	—	4.5
Total solids	—	11%
Chlorides	—	6.4 kg/m^3
Sulphates	—	4.7 kg/m^3
Potash	—	10.0 kg/m^3
COD	—	108.0 kg/m^3
BOD	—	50.0 kg/m^3

capacity, titanium autoclave. It was equipped with an electrical heating jacket, a thermocouple and temperature indicator controller, liquid side sampling port, pressure gauge, safety valve, and a cooling coil. It was also provided with a 0.055 m diameter, six-bladed pitched turbine impeller that was belt driven by an electric motor via a pulley system.

Materials

Cane molasses-based alcohol stillage was obtained from M/s Polychem Ltd., Neera, Maharashtra, India. The typical composition of the stillage used in this work is given in Table 3. Analytical grade reagents and distilled water were used during the analysis of all the samples.

Procedure

The autoclave was charged with 0.8 kg of stillage. The charge was preheated to the desired temperature with constant stirring at 6.33 rev/s. The time when the desired temperature was reached, was considered as zero time and the liquid samples were withdrawn at definite time intervals, up to 4 hours. The preheat period was 0.75 hours for attaining a temperature of 160°C and was 1.5 hours for 250°C. At the end of each run, the charge was cooled to room temperature in about 0.5 hours, by passing cold water through the cooling coils. The resultant slurry was gravity filtered using ordinary filter paper (no. 8032, grade-A, 80 gsm supplied by M/s August Ristelhueber, W. Germany) with the help of 0.15 m diameter ceramic buchner funnel. The rate of filtration was noted. The residue was washed with water, to remove filtrate if any, and dried at 80°C before analysis.

Parameters Varied

The pretreatment experiments were carried out under isothermal conditions at 160, 175, 200, 230, and 250°C. Each experiment was repeated two to six times to confirm the reproducibility of the results. The pressure of each experiment was the self pressure due to the temperature and hence, was different at different temperatures. Table 4 gives the experimental pressures. Vapor pressures of pure water are also given for comparison [9].

TABLE 4. EXPERIMENTAL PRESSURES

Temperature °C	Experimental pressure MPa	Vapor pressure of water MPa	Difference MPa
160	2.02	0.62	1.40
175	2.86	0.89	1.97
200	3.55	1.56	1.99
230	5.61	3.23	2.38
250	7.69	3.97	3.72

In the second set of experiments, the pH of the stillage was adjusted before the run. Different values of pH, ranging from 1.0 to 12.0, were employed and the desired pH was obtained by the addition of sulfuric acid or sodium hydroxide. The effect of pH was investigated at a temperature of 230°C. Each experiment was repeated two to three times.

Parameters Analyzed

Initial stillage was analyzed for BOD and COD. A sample of the stillage was evaporated at 50°C, to complete dryness and was then analyzed quantitatively for its elemental contents, namely C, H, N, S, chlorides. The ash content and specific energy values were also determined.

Stillage after thermal pretreatment was analyzed. The dry residue was analyzed for its chemical elements (quantitatively), specific energy, and ash. The filtrate was analyzed for BCD and COD. Liquid samples withdrawn during the run were also filtered and then analyzed for BOD and COD. In some experiments, a sample of the filtrate was evaporated to complete dryness and then analyzed in order to confirm the overall solid balance, component balance and the energy balance.

Analytical Methods

BOD of the sample was determined by incubating the seed sample for 5 days at 20°C. The COD was determined by dichromate method [*10*]. In the case of BOD analysis, the dilution water was seeded using the supernatent after primary settler of a municipal sewage treatment plant. Elemental analysis for C, H, N, S, etc. was conducted using standard methods [*11*]. The ash content was found by di-

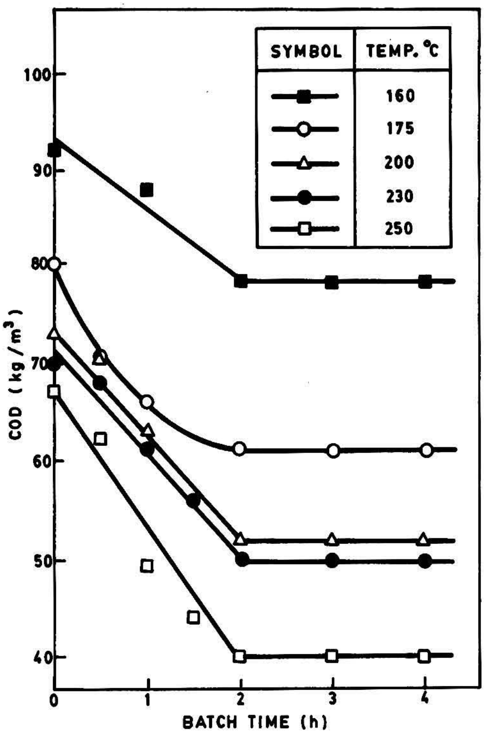

Figure 3. Isothermal plot of COD vs. batch time.

Table 5. Zero Order Rate Constants

Temperature °C	Rate constant $kg/m^3 \cdot h$
160	6.67
175	8.34
200	10.40
230	10.86
250	14.40

rect combustion using a burner or a muffle furnace. However, any correction for the decomposition of inorganic salts was not applied, due to lack of adequate information about the composition and nature of the inorganic salts. Specific energy of the residue was determined by preparing a suitable pellet and combusting it in standard adiabatic Bomb calorimeter [*12*]. Correction for sulphur and nitrogen content was applied to get the net specific energy of each sample.

RESULTS

Effect of Temperature

The experiments were conducted at different temperatures ranging from 160 to 250°C. Figure 3 shows the isothermal plots of COD of the filtrate as a function of batch time. As mentioned earlier, as the experimental temperature was varied, the pressure also changed correspondingly. Hence the results obtained were due to the combined effect of pressure and temperature. However, no experiments were performed to separate these effects.

It can be seen from Figure 3 that the final COD at 160°C was 78.5 kg/m^3 and that at 250°C was 40 kg/m^3. At all the temperatures, the COD attained a constant value after 2h. It can be also seen from Figure 3 that the COD reduction was linear from 0 to 2 h. implying that the process was zero order with respect to COD of the reactants. The zero-order rate constants obtained by least square fit are reported in Table 5.

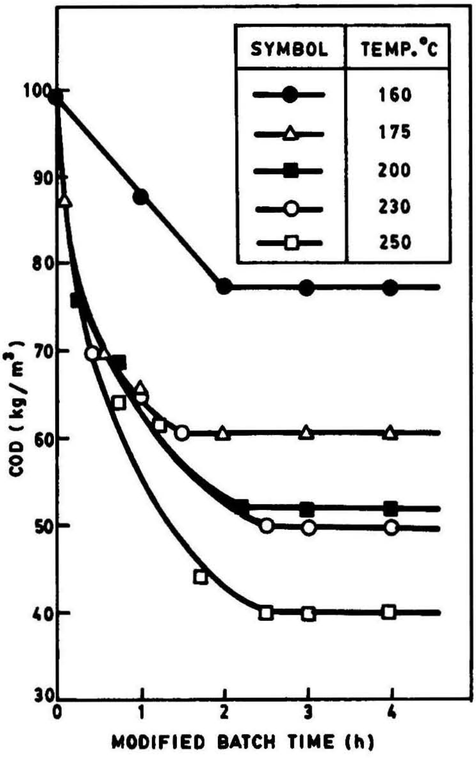

Figure 4. COD vs. modified batch time.

Since the preheat period at each temperature was different, the zero hour COD value changed for each temperature. For higher temperatures the preheating periods were larger and hence, substantial COD reduction took place during preheating. For better understanding of the process, the isothermal batch times were modified. As mentioned earlier, the lowest preheat period was 0.75 h corresponding to 160°C. This time was considered as zero for modified batch time calculations at all the temperatures. Thus, for 250°C, since the preheat period was 1.5 h, its previously described zero hour batch time was considered to be 0.75 h on the modified batch time scale. All other batch times were modified in similar fashion and the COD values as a function of the modified batch time were replotted in Figure 4.

The convertible COD at any temperature was calculated from the difference in COD values of the stillage and the final steady state COD of the filtrate and was expressed as the percentage of the initial COD. The convertible COD was found to be minimum at 160°C (27.8%) and was maximum at 250°C (63.0%).

The color of the final filtrate was dark brown at 160°C and was lighter at higher temperatures. At 250°C, the filtrate was orange-yellow colored.

The BOD values of the filtrate were found to be in the range of 30 to 40 kg/m^3, which shows that the BOD reduction was 20 to 40%. At all the temperatures, the percentage reduction in BCD was less by 10 to 20% than that in COD. This implies that the pretreated filtrate should have better biodegradability (lower ratio of COD:BOD) than the initial stillage. However, further biological treatment experimentation is required to study this aspect.

Filterability

Gravity filtration can be considered as constant pressure filtration (neglecting the change in the hydrostatic head), the force balance can be written to evaluate the rate of filtration [*13*]. The differential equation is as follows:

$$\frac{\Delta t}{\Delta V} = \frac{C \alpha \mu}{\Delta P A^2} V + \frac{\mu R_m}{\Delta P A}$$

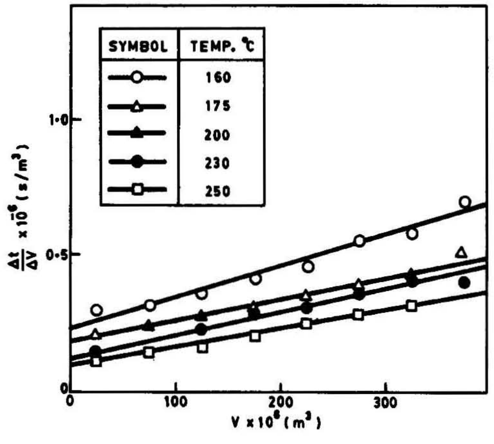

Figure 5. Effect of temperature on filterability.

TABLE 6. FILTERABILITY OF SLURRY: DIFFERENT TEMPERATURE EXPERIMENTS

Pretreatment temperature °C	Cake resistance, $\alpha \times 10^{-10}$ m/kg	Medium resistance $R_m \times 10^{-8}$ m^{-1}
160	9.36	10.15
175	6.24	7.95
200	6.24	7.95
230	6.71	5.30
250	5.46	4.40

where Δt = time interval of filtration, s
ΔV = volume of filtrate collected during Δt, m^3
V = cumulative average volume of filtrate collected up to that time intervals, m^3
ΔP = the pressure drop across the filter, Pa
μ = viscosity of the filtrate, Pa · s
C = concentration of slurry, kg/m^3
A = filtration area, m^2
R_m = resistance of filter medium, m^{-1}
α = average cake resistance, m/kg

A plot of $\Delta t/\Delta V$ versus V is a straight line. Values of α and R_m can be calculated from the slope and intercept respectively. Figure 5 shows the above plot for filtrate obtained during the pretreatment experiments conducted at various temperatures. All the filtrations were carried out at room temperature. Values of α and R_m were calculated from the graphs and are reported in Table 6. It can be seen from Table 6 that the values of cake resistance and medium resistance were highest for 160°C filtrate and were lowest for 250°C filtrate which implies that the filterability of the slurry increased with an increase in the pretreatment temperature.

At all the temperatures employed in this work, a solid charred residue was obtained after the thermal treatment. Compositions and properties of these residues are given in Table 7. For comparison, the percent of convertible COD as well as energy-recovery percentage (based on the total energy of the initial stillage) by way of residue, is also reported. It can be seen from Table 7 that the convertible COD percentages and energy recovery percentages are comparable for all the temperatures, except at 250°C. This implies that the COD reduction was due to the physical separation of solids. High values of COD conversion at 250°C may be due to the further decrease of COD by way of oxidation of COD by dissolved or chemical oxygen. This aspect was not investigated further.

TABLE 7. ANALYSIS OF RESIDUE pH—4.5

Temperature, °C	160	175	200	230	250
Wt. of residue, $\times 10^3$, kg	14	18	24	24	23
% Carbon	50.0	50.5	53.0	54.0	55.0
% Hydrogen	←		5.0 to 6.0		→
% Nitrogen	←		1.5 to 3.5		→
% Sulphur	←		2.5 to 4.0		→
% Ash	20.0	20.0	18.5	18.5	16.5
Color	←		black		→
Nature	Free flowing powder, bulk density <1009 kg/m³, True density 1220 kg/m³				
Approx. drying period, h	6.0	5.5	5.0	4.0	3.0
Specific enegy, $\times 10^{-6}$, J/kg	20.16	20.16	22.26	22.68	23.10
% Convertible COD	27.8	35.2	51.9	53.7	63.0
% Energy recovery	26.1	34.5	48.5	49.5	49.5

(Basis: 0.8 kg of stillage)

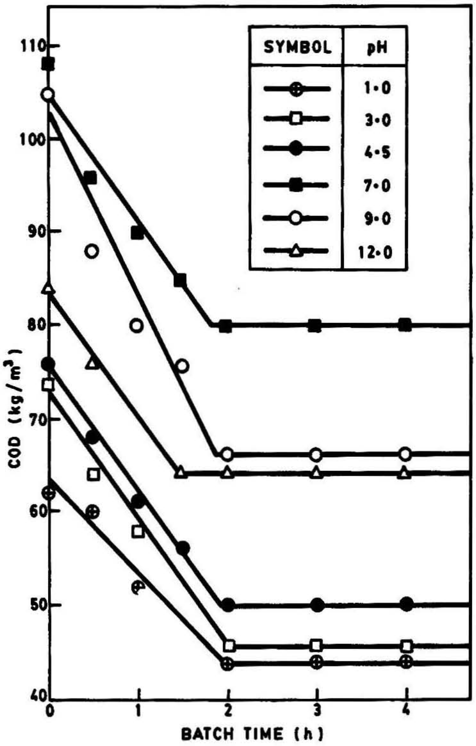

Figure 6. Effect of pH on COD of filtrate at 230°C.

Effect of pH

The pretreatment experiments were conducted at 230°C and at pH values of 1.0, 3.0, 4.5, 7.0, 9.0, and 12.0. The plot of COD of the filtrate as a function of the batch time is shown in Figure 6. The final filtrate COD was the highest for 7.0 pH (COD = 80 kg/m³) and was lowest for pH = 1.0 (COD = 44 kg/-m³). The plots had a similar nature, as in the case of temperature as the parameter. At each pH, the COD value decreased linearly with time up to two hours and was then constant.

The modified batch time was calculated and the COD versus the modified batch time was plotted in Figure 7. It can be seen from the plot that at 7 and 9 pH, the reduction in COD during the preheating was insignificant, unlike other pH experiments.

The percentage of convertible COD was calculated, as in the previous case. It was minimum at pH = 7.0 (26%) and was maximum at pH = 1.0 (59%). Similar effect of pH were reported by Joshi, *et al.* [*14*] for oxydesulfurization of coal.

The color of the final filtrate was darker as the pH was increased and was lighter as the pH was decreased. At pH = 1.0, filtrate was light orange colored.

The BOD of the final filtrate was in the range of 30 to 40 kg/m³. Under alkaline pH conditions, the percentage conversion of CODS and BOD was comparable. In the case of acidified stillage, the percentage conversion of COD was more than that in BOD, indicating that the filtrate was better suited for biological degradation than the original stillage. However, more experimentation is required for further investigation.

$\Delta t/\Delta V$ versus V for various pH experiments. Figure 8 shows the plot of and Table 8 gives the α and R_m values. It

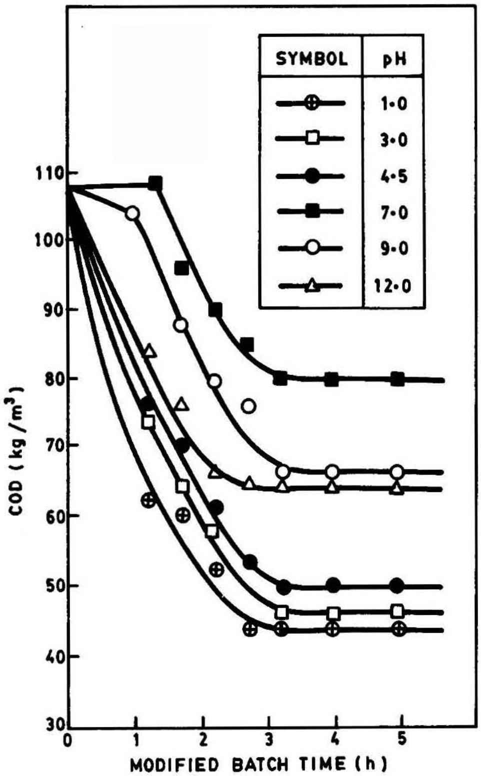

Figure 7. COD vs. modified batch time (different pH experiments).

is evident from these values that the filterability of the slurry was marginally improved under acidic conditions and it decreased significantly under alkaline conditions. For the experiment at pH = 12.0, the filterability was extremely poor.

The composition and properties of residue along with convertible COD percentages and energy recovery percentages is given in Table 9. The convertible COD and energy recovered percentages matched very well.

Overall Material Balance

To verify the overall as well as the component material balance, samples of initial stillage and final filtrate were dried and analyzed. The composition of the stillage, filtrate, and charred residue obtained in a typical experiment (230°C, 4.5 pH) are given in Table 10. The overall as well as component material balance (Total solids, C, H, Ash) was excellent. However, N and S balance was not very good. It was observed that at the end of the pretreatment, on cooling to room temperature, the system pressure was well above atmospheric pressure indicating formation of noncondensibles. The non-condensible gases had pungent and obnoxious smell and there is a possibility that N-S rich gaseous compounds might have been formed. These gases were not analyzed since the amount was small and the carbon balance was satisfactory without taking into account these gases. However, if similar process is to be implemented on larger scale, it may be necessary to install a suitable gas-scrubber to avoid air pollution.

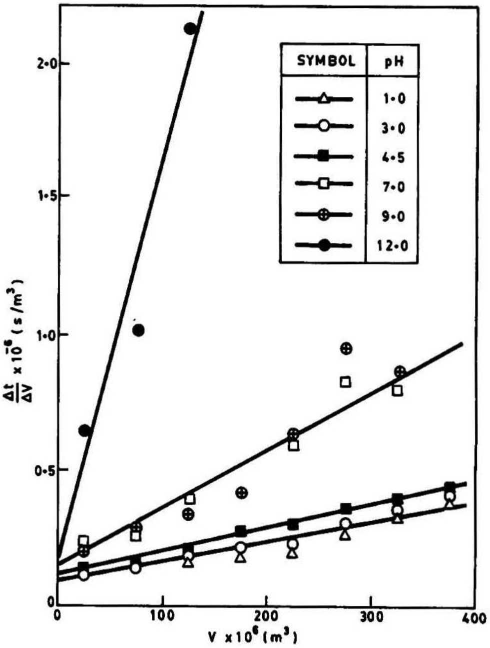

Figure 8. Effect of pH on filterability.

TABLE 8. FILTERABILITY OF SLURRY: DIFFERENT PH EXPERIMENTS—TEMPERATURE-230°C

Pretreatment pH	Cake resistance $\alpha \times 10^{-10}$ m/kg	Medium resistance $R_m \times 10^{-8}$ m^{-1}
1.0	5.83	4.4
3.0	5.83	4.4
4.5	6.69	5.3
7.0	16.89	6.7
9.0	16.89	6.7
12.0	115.26	7.6

TABLE 9. ANALYSIS OF RESIDUE—TEMPERATURE-230°C

pH	1.0	3.0	4.5	7.0	9.0	12.0
Wt. of residue, $\times 10^3$, kg	24	24	24	16	20	25
% Carbon	60.7	57.5	54.0	47.0	50.0	45.8
% Hydrogen	←		5.0 to 6.0			→
% Nitrogen	←		1.5 to 4.0			→
% Sulphur	←		2.5 to 4.0			→
% Ash	9.6	11.0	18.5	23.5	18.0	20.0
Color	←	black	→	←	brown	→
Nature	Fine free flowing porous powder			Fine sticky powder		1-2 mm grannules
Approx. drying period, h.	3.0	3.5	4.0	6.0	8.0	16.0
Specific energy, $\times 10^{-6}$ J/kg	23.94	22.68	22.68	21.84	21.42	17.64
% Convertible COD	59.3	51.9	53.7	25.9	38.9	40.7
% Energy recovery	52.5	49.5	49.5	31.7	36.0	37.0

(Basis: 0.8 kg of stillage)

	Total solids %	Dry basis composition, %						
		C	H	N	S	Ash	O*	Total
Stillage	11.0	32.0	6.2	2.3	4.3	33.8	21.4	100.0
Filtrate	8.0	21.4	6.4	0.1	1.8	40.2	26.1	100.0
Charred residue	100.0	54.0	5.6	3.5	4.0	18.5	14.4	100.0

* '0' was calculated from remaining components

MATERIAL BALANCE
Basis: 0.8 kg (Typical batch size)

	Total solids × 10^3 kg	Calculated amount, × 10^3 kg					Atomic ratio C:H
		C	H	N	S	Ash	
Stillage	82.4	26.4	5.1	1.9	3.5	27.8	1:2.3
Filtrate	60.0	12.8	3.8	0.1	1.1	24.1	1:3.6
Charred residue	24.0	13.0	1.3	0.8	1.0	4.4	1:1.2

DISCUSSION

Cane molasses distillery stillage contains all the dissolved impurities present in the cane juice, nutrients added during molasses fermentation, byproducts of fermentation and decomposed products. The suspended impurities like dust, cellulosic fibres, etc. are usually removed before the evaporation of the juice. However, water soluble hemicellulose, proteins, gums, organic non-sugars and minerals present in the cane juice are present in the stillage in the original or converted forms. Typical cane molasses contains 20% water, 62% sugars, 10% non-sugars (N-compounds, free and bound acids, gums etc.) and 8% inorganic compounds like potash [*15*]. About 95% of the sugar present in the molasses is fermented during the alcohol production and the remaining sugar may appear as caramel in the stillage which is obtained after separating alcohol by distillation. A small amount of glycerol and succinic acid formed as byproducts of yeast fermentation also comes along with the stillage. Further, traces of higher alcohols, furfural, etc. may also be present.

Thermal treatment of biomass has been extensively studied. These processes include the use of acids, alkali, steam, etc., to improve the biodegradability [*16, 17*]. It has been reported that the thermal pretreatment at 150–200°C for 1 hour results in improved dewaterability, odor control, etc., due to the breakdown of the gel structure and decrease in the bound water [*18*]. It has also been reported that the toxic compounds like furan may be formed [*19*]. Many processes involve alkali treatment at 120°C and 0.2 MPa pressure. Pyrolysis of biomass is a nonselective degradation carried out at 400°C or higher temperatures forming char, oils, and gases [*20*]. Hydrothermal treatment at 180–200°C is a selective degradation where hemicellulose and lignin degrade and cellulose remains unreacted. The products reported are xylose and furfurals [*21*]. This process is catalyzed by acids.

In the present work, stillage was treated under alkaline conditions with the idea of possible use of cheaper material of construction of the reactor. However, it was observed that the acidic conditions gave better results than the alkaline conditions, which is in contrast to the observations reported for cellulosic waste. The stillage differs from any other biomass since there is no cellulose or lignin present in the stillage. It is likely that the reactions involved in hydrothermal degradation of biomass may be similar to those involved in the present work. However, more basic research is necessary to propose possible mechanisms.

In the case of formation of crude oil from the biomass, an intermediate stage of formation of kerogene is recognized. Due to high temperature and high pressure, the underground bioorganic materials decompose to give two categories of compounds, namely a carbon deficient and a carbon rich compound. The ultimate products can be methane and graphite respectively (22, 23). For comparison, the atomic ratio of C:H of the stillage, filtrate and charred residue were evaluated and are given in Table 10. It can be seen that the initial stillage was converted into a carbon-rich charred residue and a carbon deficient filtrate. The C:H ratio also indicates that the initial stillage having highly substituted —CH_2— chain was converted into filtrate consisting of simpler and smaller molecules with CH_3-group. The decreased level of substitution of carbon atom in the filtrate is expected to result into a simpler and more biodegradable waste. The overall results obtained were in agreement with this observation.

CONCLUSIONS

Thermal pretreatment of stillage at 200°C for two hours results in 50% reduction in COD. The reduction in COD is primarily due to physical separation of residue. Energy equivalent corresponding to COD reduction is obtained in the form of charred residue which can be used as fuel.

Resultant lower COD stillage eliminates the need for its dilution before anaerobic digestion. However, more experimentation is necessary to study the suitability of pretreated stillage as a feed stock for secondary treatments.

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Myers Dump Case History: Innovative Utilization of Air Stripper-Activated Carbon Technologies

Jeffrey S. Binkley and Sally Matz
Roy F. Weston, Inc., Spill Prevention and Emergency Response Division,
Chicago, Illinois

Kenneth L. Myers
Conestoga-Rovers and Associates Limited, Chicago, Illinois

Kenneth Theisen
U.S. Environmental Protection Agency, Emergency and Remedial Response Division,
Chicago, Illinois

The treatment of residential well water contaminated with volatile organic compounds (VOCs) has typically included the use of granulated activated carbon (GAC) filters. The significant carbon replacement costs associated with filtration has prompted research into more cost effective alternatives. Another alternative for treatment of ground water contaminated with VOCs is air stripping. This process does not require extensive maintenance costs but it generally cannot achieve the required removal levels for small scale applications. The combination of these two technologies can result in achieving optimum removal levels while reducing carbon replacement costs. The case history described in this paper outlines the removal effectiveness monitoring program of a remediation technology utilizing air strippers in conjunction with GAC filters. Specific topics discussed in this paper include: site background, health effects, system design and installation, removal effectiveness monitoring, quality assurance program, and effectiveness and efficiency of the technology.

INTRODUCTION

The Myers Dump site covers 20,235 m^2 of rural St. Joseph County, Osceola, Indiana. The site topography is generally flat and surrounding land use is primarily agricultural. The soil is a typical glacial deposit, consisting of various interbedded sands and gravels associated with the valley-train deposits along the St. Joseph River outwash aquifer. The water table is shallow, approaching 3 m of the surface.

Past activities at the site involved uncontrolled dumping of drums containing waste solvents into unlined pits and subsequent recycling of the drums. Both the Indiana Department of Environmental Management (IDEM) and the local health department efforts to promulgate a responsible party cleanup of the site were unsuccessful. The death of the site owner in 1983 terminated the disposal operation. As a result of conditions at the abandoned site and the threats posed to human health and environment as outlined in Section 300.65 of the National Contingency Plan, the U.S. Environmental Protection Agency (U.S. EPA) conducted a removal action at the site in February 1985. The action involved the removal and disposal of the drummed solvent waste and contaminated soils from the site. Well water samples collected both on-site and in adjacent wells indicated traces of VOCs, including trichloroethylene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA). The concentrations were below the U.S. EPA "Suggested No Adverse Response Level" (SNARL), now referred to as a Removal Action Level (RAL). The ground water contamination was, therefore, not addressed during the removal.

In November 1986, the IDEM sampled 11 residential wells adjacent to the former dump site and identified two wells that contained concentrations of TCE up to 1.97×10^{-2} mol/m^3, exceeding the U.S. EPA RAL of 9×10^{-4} mol/m^3. The U.S. EPA Emergency Response Section was notified of the results in February 1987, and was requested to participate in a joint sampling program to delineate the plume, and; provide an alternative drinking water supply for affected residents.

The U.S. EPA confirmed the IDEM results by resampling five wells, with the highest concentration of a single VOC being 2.43^{-2} mol/m^3 of TCE. The U.S. EPA immediately supplied the affected residences with bottled drinking water. Between March 17, 1987 and April 1, 1987, 13 U.S. EPA and 15 IDEM residential well samples were collected. The U.S. EPA sampling effort began at the former dump site and radiated outward in the direction of the ground water flow. All samples collected by the U.S. EPA were analyzed for full scan [Hazardous Substance List (HSL)] VOCs and a limited number were analyzed for full scan HSL semi-volatile organics. Results of the sampling delineated a plume of contamination approximately 45 m wide and 804 m long. Within this area, three residential wells contained levels of TCE between 3×10^{-4} mol/m^3 and 3.57×10^{-2} mol/m^3. The nearest contaminated well, approximately 402 m south of the site contained TCE at a concentration of 2.43×10^{-2} mol/m^3. The well on the leading edge of the plume, approximately 804 m south of the site, contained 3.57×10^{-2} mol/m^3 TCE. The contamination ended abruptly at the leading edge of the plume with no indication of a gradational change in contaminant concentration. The affected wells were located directly south of each other in the direction of ground water flow.

Although well depth, construction, and pumping rates did not appear to influence the plume configuration, an adjacent roadbed and or utility line (possibly sand or gravel packed) provided a plausible explanation for the narrow width of the plume. It was also possible that a subsurface geological structure (e.g., clay lenses) restricted the plume's lateral extent.

The available alternative water supplies, including connection to a municipal water supply or installation of deeper wells, did not appear to be efficient for a project of this scale. Therefore, the U.S. EPA opted for utilization of GAC filtration as a remedy. The GAC treatment of residential well water contaminated with VOCs is a proven technology. However, the significant carbon replacement costs associated with filtration has prompted research into more efficient alternatives. Another alternative for treatment of ground water contaminated with VOCs is air stripping. The combination of these two technologies can result in achieving high removal levels while reducing carbon replacement costs. U.S. EPA Region III, which had successfully installed and monitored air stripper GAC filter systems at similarly affected sites, provided U.S. EPA Region V with data that indicated the air strippers had achieved approximately 85% removal of VOCs. Based on this data U.S. EPA Region V decided to install and conduct a removal effectiveness study.

HEALTH EFFECTS

Sampling initiated by the U.S. EPA in February 1987, identified two residential wells contaminated with TCE, 1,1,1,-TCA, trans-1,2-dichloroethene, and 1,1-dichloroethane. TCE was identified as the predominant contaminant of concern.

Approximately 91,000,000 kg of TCE are used annually in the United States, of which 80% is used as a solvent for the degreasing of metal parts. It has been estimated, based on nationwide sampling, that TCE is present in between 9% and 34% of all water supplies in the U.S. [1].

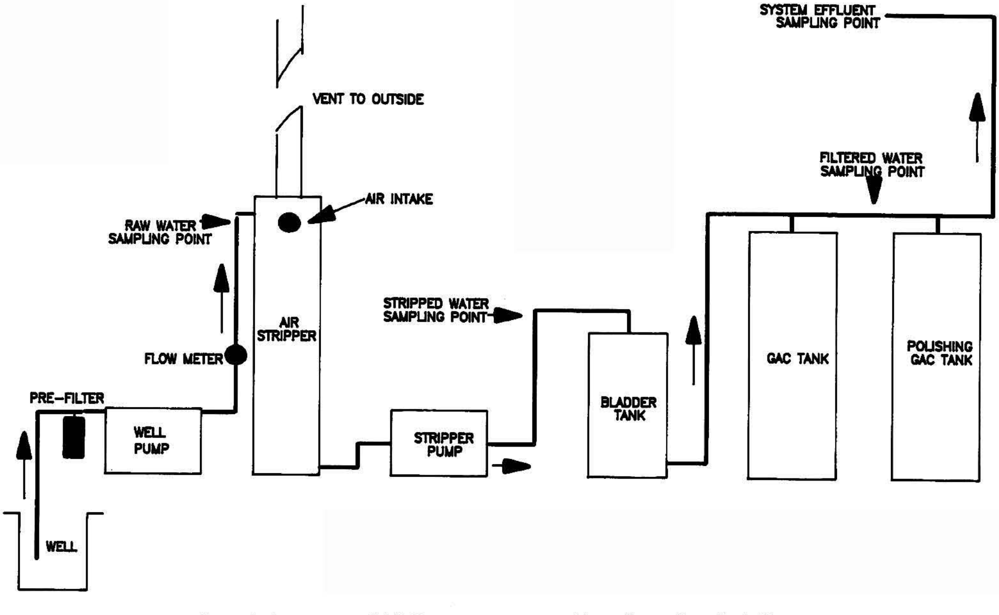

Figure 1. Air stripper—GAC filter treatment system Myers Dump, Osceola, Indiana.

TCE volatizes rapidly from water, although the exact rates are dependent upon temperature, water movement, water depth, air movement, and other factors. Estimated typical volatization half lives from various waters are as follows: rivers 1–12 days; ponds 11 days; and, lakes 4–12 days [2]. TCE is relatively mobile in soil and leaches readily into ground water [3, 4]. TCE persists, slowly biodegrading in ground water until it finds a path of release into the atmosphere. Once exposed to the atmosphere, TCE reacts with sunlight and produces phosgene, dichloroacetyl chloride, and formyl chloride [5].

A significant data base exists documenting health effects on animals and employees in the work place who inhale TCE vapors. The National Institute of Occupational Safety and Health has estimated that 3.5 million workers in the U.S. are exposed to TCE on a full or part-time basis. These studies indicate that TCE affects the central nervous system when inhaled in high concentrations, causing dizziness, headache, slowed reaction times, and facial numbness.

Based on this data the U.S. EPA's Office of Drinking Water has recently established a set of criteria to assess the risk at a particular site by using a particular chemical's: volatility, carcinogen group, maximum contaminant level, 10-day health advisory, the drinking water equivalent level, the 10^{-4} cancer risk level, and finally, its RAL. For TCE, those criteria are as follows: it is volatile, it is considered to be a probable human carcinogen; the maximum contaminant level is 3.8×10^{-5} mol/m^3; there is no 10-day health advisory currently established; its 10^{-4} cancer risk is 21×10^{-4} mol/m^3, and the RAL has been established at 9×10^{-4} mol/m^3. The acute effects of TCE ingestion and inhalation are well documented, particularly in studies with animals under laboratory-controlled conditions. However, the long-term human health effects are not as well documented [1].

Of primary concern in ground water contamination sites is the long-term exposure. Because minor amounts of TCE in well water cannot be detected by human senses, it could be ingested indefinitely. Although the risk of developing cancer from ingesting minor amounts of TCE over one's lifetime is relatively small, the U.S. EPA has expressed its concern by treating this problem with extreme caution.

SYSTEM DESIGN AND INSTALLATION

The design of the residential system implemented is a combination of two proven treatment methods: aeration, and adsorption (Figure 1).

The aeration portion of the treatment system is an air stripping column, or packed column, constructed of fiberglass reinforced plastic. The tower is 1.78 m high and has a 1.52 m total packing height. The raw water is pumped to the top of the tower and distributed over the entire surface area of the packing material where it cascades down by gravity. The packing material ensures that the water is formed into tiny droplets to maximize the surface area for air transfer. A countercurrent air flow is induced through the tower, volatilizing the VOCs from the water. The VOCs undergo mass transfer according to Henry's Law, which states that the amount of gas dissolved in a given amount of liquid is directly proportional to the partial pressure of the gas above the solution at a constant temperature and pressure. The Henry's Law constants for TCE and 1,1,1-TCA are 0.393 and 0.166 respectively, indicating that TCE is more readily removed by air stripping than 1,1,1-TCA. Design parameters for the packed column include type of compound, concentration, loading rate, air to water ratio, packing height, and packing material.

The adsorption portion of the system consists of two GAC filters, each containing 45 kg of GAC. Adsorption is the transfer of a dissolved contaminant to the surface of an adsorbent. Carbon is widely used as an adsorbent due to its extensive surface area, and affinity for organic constituents. GAC filtration is one of the most frequently applied technologies for treating waste streams contaminated with organics that have high molecular weights, low polarities and low solubilities. Typical carbon usage rates range between .45 kg and 3.18 kg of carbon per 3,785 L of water treated [6]. In this application, given the high levels of TCE, the carbon usage rate was calculated to be approximately 3.54 kg of carbon per 3,785 L of water.

By combining the two technologies, a high removal level is achieved while reducing costs associated with carbon replacement had GAC been used solely.

The following are required prior to installation:

- Availability of a separate 20 amp 110 volt electrical source.
- Availability of approximately .37 m^2 of floor space with a vertical clearance of 1.83 m.
- Access to an exterior wall for exhaust ventilation.
- A drain or sump pump.

It is recommended that the unit be located in proximity to either the well pump or the pressure tank to reduce the amount of plumbing required. If excessive sediment or iron is identified in the water supply, pre-filtration is recommended to prevent fouling of the packing material in the air stripper and or bacterial growth on the carbon bed.

Upon system demand, the existing well pump delivers water to the top of the air stripper and distributes it over the packing media. Simultaneously, the blower is initiated. The stripped organic constituents are exhausted to the exterior of the home. A secondary pump is activated by a float switch removing the water collected at the bottom of the stripper and delivering it to a bladder tank.

Water is allowed to collect in the bottom of the stripper to prevent untreated water distribution to the remainder of the treatment system. Prior to distribution to the house, the water passes through the GAC filtration units providing a final polishing of the air stripper treated water, achieving a total system removal level of 99.9999%.

EFFECTIVENESS MONITORING AND QUALITY ASSURANCE PROGRAM

The effectiveness monitoring program involved collecting water samples from four locations at each residence: raw water, stripped, filtered, and system effluent. Each system was sampled five times over a 90 day period. In addition, samples were collected from each system and analyzed for bacterial growth. Bacterial growth was not detected in either system during the monitoring program.

Because the data generated from this monitoring program was to be used to determine the removal effectiveness of the system, it was imperative that the data be valid and reliable. A strict quality assurance/quality control (QA/QC) program was implemented to ensure the validity and reliability of the data.

All samples were collected, stored, and shipped in accordance with U.S. EPA approved methodology. All samples were analyzed using U.S. EPA approved methodology through the U.S. EPA Contract Laboratory Program (CLP). In addition to the QA/QC maintained by the CLP laboratories, additional field QA/QC samples, including blanks and duplicates, were collected and analyzed.

EFFECTIVENESS OF THE TECHNOLOGY

Table 1 presents the analytical results and air stripper removal levels recorded during the monitoring program. During all sampling periods, 99.9999% removal was

Table 1. Effectiveness Monitoring Program—Myers Dump Site. (All concentrations in mol/m^3)

	Residence A				Percent removal	
Sample	1,1,1-TCA		TCE		1,1,1-TCA	TCE
date	Raw	Stripped	Raw	Stripped	(%)	(%)
10/01/87	96	30	4200	350	69	92
10/19/87	85	9.3	4300	360	89	92
10/29/87	74	9.1	3700	270	88	93
11/12/87	97	11	4300	430	89	90
12/09/87	92	11	3600	350	88	90
	Residence B				Percent removal	
Sample	1,1,1-TCA		TCE		1,1,1-TCA	TCE
date	Raw	Stripped	Raw	Stripped	(%)	(%)
10/01/87	110	17	3100	1300	85	59
10/19/87	100	21	7600	1400	79	82
10/29/87	110	14	6700	1200	88	83
11/12/87	130	20	7800	1400	85	82
12/09/87	130	18	7700	1400	86	82

achieved after the combination air stripper and GAC filter treatment. For ease of discussion, the following paragraphs will refer to average concentrations and average removal levels.

Raw water concentrations at residence A were 8×10^{-4} mol/m^3 of 1,1,1-TCA and 5×10^{-2} mol/m^3 of TCE. Stripped water concentrations were 1×10^{-4} mol/m^3 of 1,1,1-TCA and 1×10^{-2} mol/m^3 of TCE. Removal levels for the air stripper were 85% and 78% for 1,1,1-TCA and TCE, respectively.

Raw water concentrations at residence B were 6×10^{-4} mol/m^3 of 1,1,1-TCA and 3.05×10^{-2} mol/m^3 of TCE. Stripped water concentrations were 1×10^{-4} mol/m^3 of 1,1,1-TCA and 2.67×10^{-3} mol/m^3 of TCE. Removal levels for the air stripper were 85% and 91% for 1,1,1-TCA and TCE, respectively.

Air stripper removal effectiveness exceeded 85% at both residences for 1,1,1-TCA. TCE removal at residence A (78%) was significantly less than at residence B (91%). This variance is suspected to be a function of initial TCE concentrations (5×10^{-2} mol/m^3-residence A versus 3.05×10^{-2} mol/m^3-residence B). It is expected that removal efficiencies will be less at contaminant levels exceeding approximately 7.6×10^{-3} mol/m^3. It has been suggested by the air stripper manufacturer that at levels exceeding 7.6×10^{-3} mol/m^3, the air within the stripper becomes saturated with VOCs limiting the transfer of VOCs from the water to the air. Larger stripper blowers are available that increase removal effectiveness at contaminant concentrations greater than 7.6×10^{-3} mol/m^3 with the same packing tower design.

To exhibit the effectiveness of the air stripper in prolonging the life of the GAC filters the carbon usage rates for both alternatives were calculated: GAC filtration and air stripping with GAC filtration. As previously mentioned, it is estimated that 3.54 kg of carbon would be required to treat 3,785 L of water, assuming an absorptive capacity of 5.32×10^{-2} mol/m^3 TCE/g of carbon (7) and a maximum raw water concentration of 5×10^{-2} mol/m^3 TCE. This estimate is based only on TCE concentration because of the higher degree of TCE contamination relative to 1,1,1-TCA and the higher calculated carbon usage rate. Assuming an 85% air stripper removal level, the stripped water would only require .54 kg of carbon per 3,785 L of water extending the effective life of the carbon by a factor of 6.5.

To summarize, the option of GAC filtration alone would be able to treat a total of 97,047 L per carbon change and would require changing the carbon 2.8 times per year. The alternative of air stripping prior to GAC filtration would be able to treat a total of 630,846 L per carbon change, requiring changing the carbon once every 2.3 years.

CONCLUSION

As documented in this paper, the air stripper and GAC filter combination is an effective technology for treatment of VOC contaminated residential wells. The major factor in assessing the efficiency of air stripper utilization is the startup cost versus the extended effective life of the carbon. The air stripper GAC system used at the Myers Dump site can be installed for approximately $4,000. A GAC filtration system alone would cost $2,200. Replacement of the GAC in the carbon tanks costs approximately $450 per replacement period. Hookup to a municipal water supply, if water mains were present adjacent to the residence, could be completed for approximately $2,000 per residence. Other major factors affecting the efficiency of air stripper GAC filter treatment are VOC contaminant levels, the scope of the remedial action, and the availability of other remedies.

Air stripper use is most appropriate in instances where severe VOC contamination ($>7.6 \times 10^{-3}$ mol/m^3) would otherwise require short-term monitoring and frequent carbon replacement. A second factor is the scope of the remedial action: Is it an interim or final action? If the action is considered to be an interim emergency action (i.e., less than 180 days until an extent-of-contamination study is completed), air stripper use would not be efficient because of the limited number of GAC filter replacements necessary. Thirdly, the availability of alternative remedies affects the appropriateness of air stripper use. This factor is directly associated with the scope of the remedial action. If the scope of the action requires a long-term solution than an alternative such as hookup to a municipal water supply, if available is more efficient.

The air stripper GAC filtration combination was the most effective and efficient technology for utilization at the Myers dump site because of the elevated VOC levels and the lack of a nearby municipal water supply.

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Use of Carbon Adsorption Processes in Groundwater Treatment

Mark H. Stenzel and William J. Merz
Calgon Carbon Corporation, P.O. Box 717, Pittsburgh, PA 15230

One of the leading treatment technologies for reduction of organic contaminants in groundwater has become the adsorption process utilizing granular activated carbon (GAC). This paper presents a methodology for selecting the proper adsorption system design. The use of the isotherm test for evaluation of carbon adsorption is discussed, with new data on adsorption of VOCs presented. The use of the dynamic column study for system design and its relationship to the isotherm test is reviewed using actual case studies. Design and economics for full-scale GAC systems are discussed. The use of adsorption to remove organic contaminants from vapor sources resulting from groundwater treatment is also reviewed.

INTRODUCTION

The chemical process industry (CPI) may need to pump and treat groundwater for two different reasons: either to treat groundwater so it can be used as a resource, or to treat groundwater as part of a remedial activity. The treatment of groundwater so it can be used is becoming more common, as the CPI often faces the same problems as many municipal drinking water utilities in that even deep and heretofore clean aquifers have become contaminated with trace amounts of organic compounds. Removal of these compounds is often necessary before this water can be used. In the removal and treatment of groundwater as part of a remedial activity, the situation may reflect similarities to wastewater treatment, in that a CPI site cannot allow waste chemicals to migrate off-site, as would occur if contaminated groundwaters were allowed to flow untreated beyond the site boundaries.

In both categories, the organic contaminants of concern are, for the most part, chlorinated aliphatic and aromatic solvents, commonly referred to as Volatile Organic Contaminants (VOCs). These VOCs have become of primary concern as they have little affinity for soil, and thus rapidly pass through the soil and enter the aquifer. Once in the aquifer, the VOCs can migrate quickly in the groundwater and since they are often resistant to natural degradation, they can persist for long periods of time [*1*].

Adsorption with granular activated carbon (GAC) is a treatment technology that is now widely accepted for removal of these VOCs from groundwater. The acceptance of GAC adsorption is, in part, based on its long history of effectively removing organic contaminants from water and wastewater. The CPI has used the adsorption process to purify water and a wide variety of products, and has used it as a physical treatment process in wastewater treatment.

In evaluating the use of GAC for the treatment of groundwaters, either for use or as part of a remedial activity, the investigator needs to properly define the problem and determine the applicability of alternative treatment technologies, including GAC. If GAC is to be evaluated, methods are available to accurately predict the capital and operating cost of applying adsorption treatment. These costs can then be compared to other applicable technologies, so that the most cost-effective solution can be selected.

TREATING GROUNDWATER FOR USE

In treating groundwater for use, the CPI is faced with many of the same problems as the drinking water industry, where small amounts of VOCs have been detected in potable water aquifers. The EPA, under the 1986 Amendments to the Safe Drinking Water Act (SDWA), is to generate Maximum Contaminant Levels (MCLs) for 83 specific contaminants by 1989. Many of these specific contaminants are VOCs. Limits have already been issued for eight such compounds, Table 1 shows four of these. These compounds are specifically regulated for drinking water. Many of the listed VOCs, which are now being detected in nearly 20% of potable groundwater supplies [2], may be detrimental to processes and products produced by the CPI.

TABLE 1. MAXIMUM CONTAMINANT LEVELS FOR FOUR CONTAMINANTS

Compound	MCL (mg/l)
Trichloroethylene	0.005
Carbon Tetrachloride	0.005
1,2 Dichloroethane	0.005
Benzene	0.005

The success of GAC in removing these types of organic contaminants has resulted in the SDWA Amendments stating that other treatment techniques must be at least as effective as GAC in order to be considered as a "Best Available Technology" [3]. Thus, GAC has been established as the benchmark technology, and its use should be considered in any evaluation of technologies for treatment of groundwater.

Evaluation Techniques—Adsorption Isotherms

A basic evaluation technique for activated carbon is the liquid-phase adsorption isotherm. The adsorption isotherm is a batch test designed to determine the equilibrium relationship between the organic compound(s) in the water, measured as concentration, and the organic compound(s) adsorbed on the activated carbon, expressed as weight of contaminant per unit weight of activated carbon (carbon capacity).

Isotherms have long been used as a preliminary evaluation tool for the use of GAC in wastewater treatment. When considering the adsorption of very low levels of VOCs, however, test conditions need to be carefully controlled to prevent the volatilization of the solvents while equilibrium is being obtained. Over the past four years, Calgon Carbon Corporation has generated a family of single component VOC isotherms for use by the water treatment industry. Isotherm conditions were carefully selected so that reliable data points were obtained to better fix the isotherm plot. These conditions included the use of samples with no head space, long contact periods (20 hours) to assure equilibrium, relatively large quantities of powdered GAC to minimize weighing errors, and the use of relatively large concentrations of VOCs to minimize analytical errors [4], [5].

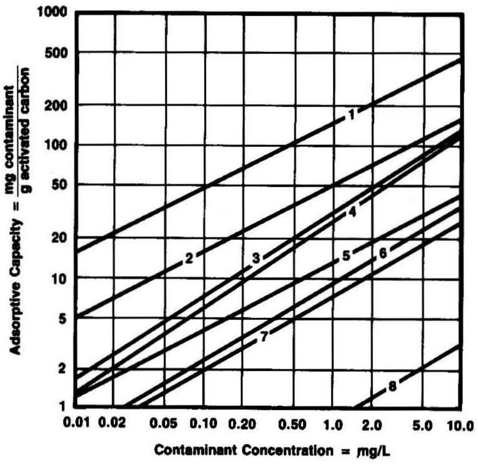
Figure 1 shows the results of single component isotherms for selected chlorinated aliphatic solvents. Figure 2 shows results of single component isotherms for some aromatic solvents. It is important to note that the testing protocol must be consistent when comparing the relative adsorbability of one compound to another, or when considering the effect of concentration changes.

Isotherms are useful in identifying whether activated carbon will be an effective treatment. In fact, when considering GAC treatment, isotherms such as these can be a valuable screening tool. Isotherms will also be useful in determining the effect of decreasing contaminant concentration, especially when used in conjunction with dynamic testing or actual operating results.

Prediction of Design and Usage Rates

The normal sequence of evaluation would be to follow the batch isotherm test with a dynamic column study to fix system size (contact time) and actual carbon usage rates so that a complete economic analysis can be done. If the contamination problem is simple, however, the isotherm test can be utilized to predict these parameters.

Often water drawn from deep aquifers is contaminated with only one or two organic compounds that require removal, and little background contamination from other organic material is present. In this situation, the investigator can have some confidence in determining the system design, using historical column test data to corroborate the estimates.



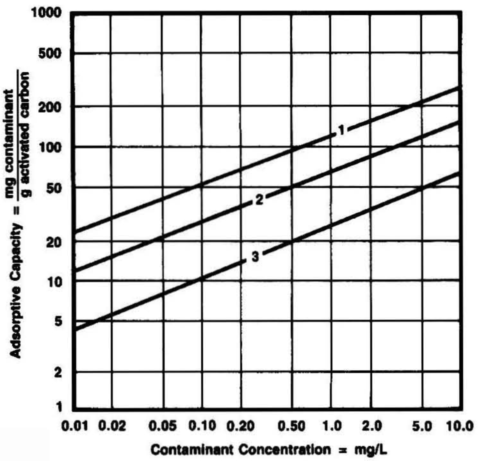
ISOTHERM CONDITIONS:

Sample Volume = 137 ml
Temperature = Ambient
Agitation Time = 20 hours
Carbon = Filtrasorb 300

ISOTHERM IDENTIFICATION

1. **Tetrachloroethylene**
2. **Trichloroethylene**
3. **Carbon Tetrachloride**
4. **1,1,1-Trichloroethane**
5. **1,1-Dichloroethylene**
6. **Chloroform**
7. **1,2-Dichloroethane**
8. **Methylene Chloride**

Figure 1. Single contaminant adsorption isotherms for chlorinated aliphatic solvents.



ISOTHERM CONDITIONS:

Sample Volume = 137 ml
Temperature = Ambient
Agitation Time = 20 hours
Carbon = Filtrasorb 300

ISOTHERM IDENTIFICATION:

1. **m-Xylene**
2. **Toluene**
3. **Benzene**

Figure 2. Single contaminant adsorption isotherms for aromatic solvents.

TABLE 2. ACCELERATED COLUMN TEST STUDIES LOW LEVEL/SINGLE CONTAMINANT CASES

Site:	Municipal groundwater	Synthetic groundwater	Synthetic groundwater	Municipal groundwater
Contaminant	Trichloroethylene	Trichloroethylene	Trichloroethane	Chloroform
Concentration, ppb	30	202	205	126
Effluent objective, ppb	1	1	1	1
Contact time, minutes	10	8.5	8.5	12
GAC usage rate, pounds/1000 gals.	0.07	0.12	0.36	0.9
Realized capacity mg/gm	3.6	14.1	4.8	1.2
Isotherm (equilibrium) capacity, mg/gm	8.0	27.0	8.8	2.6
Percent of equilibrium capacity realized	45%	52%	54.5%	46%

8.33 lb./1000 gallons = kg/m^3.

Calgon Carbon Corporation has conducted many column studies on contaminated potable groundwaters using a rapid small-scale column test [6]. These tests, using a single short column, small size granules, and mathematical modeling, have proven to be effective in predicting dynamic performance that has been shown to be similar to scaled-column studies [7] and actual system operation. The advantage of the rapid test is that the results can be obtained in a much shorter time frame, requiring less sample and less cost for analysis and manpower.

These "Accelerated Column Tests" (ACTs) have been used to model the system performance by evaluating contact times and determining carbon usage rates. Table 2 shows the results of ACTs run on actual and synthetic groundwater samples [5]. The actual groundwaters tested had low background organic contamination (<0.5 ppm TOC). These tests show that operating systems with short contact times can obtain 45–55% of the theoretical, or equilibrium, capacity of GAC at the time of "breakthrough," which is when the VOC first appears in the effluent. These tests also indicate that these contaminants adsorb in a relatively short adsorption zone, which means that little available adsorptive capacity will remain upon breakthrough.

Based upon the historical ACT data, a preliminary system design for removal of one or two VOCs from a "clean" groundwater would include a single-stable adsorber with 12–15 minutes contact time, calculated on an empty-bed basis. A single stage adsorption system will minimize equipment costs, and based on a low GAC usage, will optimize overall treatment costs. The operating GAC usage rate can be estimated at 45–55% of the capacity shown by the isotherm.

A column test such as the ACT would be recommended if there were more contaminants present or if there was a substantial amount of background organic matter. In some areas of the country, even clean groundwaters may contain up to 8–12 mg/l of background organic matter; reported as TOC, which may adversely affect adsorption of the specific contaminants of interest. An ACT is also recommended if a more accurate prediction of carbon usage, using the actual water to be treated, is deemed necessary.

Adsorption System Design and Economics

The downflow, fixed-bed adsorber is the simplest and most widely utilized design for groundwater treatment applications. The water enters the top of the adsorber, is equally distributed across the GAC by the packed, flooded-bed design, and is collected by slotted screen collectors across the bed cross-section at the bottom of the vessel. The fixed-bed design can be either of the gravity or pressure type. The pressure type is normally recommended as it will occupy less space because it uses higher surface loading rates (up to 10 gpm/ft^2, 0.0068 m/s), and generally, repumping of the treated water will not be required. A fixed-bed pressure adsorber is usually an ASME coded carbon steel pressure vessel with a corrosion resistant lining. A single-stage adsorber is often provided with in-bed sampling ports, if the breakthrough of contaminants needs to be anticipated.

Typically, 10 ft. (3.048 m) diameter adsorption vessels containing 20,000 lbs. (9080 kg) of GAC are used for groundwater treatment service. This size adsorber and GAC quantity has become an accepted standard size, as the spent GAC from a single unit can be transported from the site in a single trailer. The GAC quantity limitation is due to transportation considerations, as the entire quantity of GAC, retained pore water, and adsorbate will weigh approximately 40,000 lbs (18,160 kg). Each of these adsorbers can treat up to 350 gpm (0.022 m^3/s) at a contact time of 15 minutes, and an overall system pressure drop in the range of 15 psig (0.1 Mpa).

The following example shows how the preliminary economics can be obtained for a groundwater treatment scenario. The assumptions for the groundwater source are:

Flow:	300 gpm (0.019 m^3/s)
Contaminant:	Trichloroethylene
Concentration:	180 μg/l (ppb)
Desired Effluent Conc:	<5 μg/l (ppb)
Background Organic Content:	Negligible (<0.5 ppm)

Based upon the evaluation procedure and information provided, the following preliminary process design can be made:

Adsorbers:	One 10 ft. (3.048 m) dia. adsorber
GAC:	20,000 lbs. (9,080 kg)
Contact Time:	17 minutes (empty bed basis)
Equilibrium Capacity:	25 mg TCE/gm GAC (Figure 1)
% Equil. Capacity Expected to be Realized	50% at breakthrough
Estimated GAC Capacity:	12.5 mg TCE/gm GAC
Estimated GAC Usage:	0.12 lb. GAC/1,000 gal. (0.0145 kg/m^3)
Estimated Annual GAC Usage:	20,000 lbs. (9,080 kg)

A single adsorber, complete with process, utility, and

TABLE 3. ADSORPTION SYSTEM ANNUAL COSTS LOW LEVEL/SINGLE CONTAMINANT

Amortization of capital (8.75% interest/20 years)	\$13,400
Maintenance (5% of installed capital)	6,250
Energy costs (3.5 BHP for additional 15 psig; 8¢/KWH)	2,400
GAC usage[1] (20,000 lb. Calgon F-300; \$0.90/lb.)	18,000
GAC freight (one bulk delivery)	2,750
Total annual cost	\$42,800
Unit cost	\$0.27/1000 gal.

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[1] Assumes supplier of GAC can remove spent carbon and arrange for disposition or reactivation in an environmentally safe manner.

carbon transfer piping, and provided with 20,000 lbs (9080 kg) of GAC can be installed on an existing foundation for approximately \$85,000. A foundation, well pump upgrade (if necessary), tie-ins to the existing system, and project management might result in a total capital expenditure of approximately \$125,000 for a complete 300 gpm (0.019 m^3/s) system.

The annualized operating cost is shown in Table 3, which results in a complete treatment cost of approximately 27 cents for each 1,000 gallons treated. This amount assumes that the supplier of the fresh GAC will be capable of removing and safely handling the spent GAC, or possibly reactivating it for reuse. This cost is in general agreement with EPA estimates of 34 cents per 1,000 gallons (3.78 m^3), based upon systems below 1 MGD (3785 m^3/day) providing 99% removal of TCE at a 500 ppb or less initial concentration [8]. Also, in a survey of similar applications with low contaminant levels and single-stage adsorption, Calgon Carbon estimated treatment costs in the range of 22 to 55 cents per 1,000 gallons (3.78 m^3) [9].

TREATING GROUNDWATER FOR REMEDIATION

In dealing with remediation activities, the most important factor is that the groundwater is withdrawn at a rate at least sufficient to prevent the migration of the contamination, or preferably, to capture the contamination and eventually remove the contaminants from the site. After establishing the water pumping rate, there are numerous methods of treatment available, depending on site-specific situations. Of primary concern is the degree of treatment required. A checklist for degree of treatment would vary, depending on whether the water will ultimately be sent to a wastewater treatment facility, either in an existing plant or off-site POTW, whether it will be discharged under existing permits, or whether it will be recharged into the aquifer. If discharged to an existing treatment facility, for example, it is likely that point source treatment will be needed to reduce volatile and biologically resistant or toxic contaminants.

Once the flow, contaminants, and degree of treatment are fully defined, an evaluation of potential treatment processes can be made. For the type of organic compounds prevalent in contaminated groundwaters, especially chlorinated aliphatic and aromatic solvents, adsorption with GAC has proved to be a highly effective treatment.

The groundwaters withdrawn in remediation projects often contain a complex mix of contaminants. If drawn from a shallow aquifer, the groundwater may also contain other organic compounds, such as natural occurring humic substances. The type of other organic compounds present may influence carbon usage, even though their removal is probably not required. Poorly adsorbed compounds, for instance, will have little effect on usage rates, whereas more strongly adsorbed compounds will competitively adsorb with the contaminants of concern and adversely affect usage rates. For such cases, the isotherm evaluation can only be used as a preliminary screening tool. Published single-component isotherms can establish whether the compounds of interest are amenable to adsorption, and which compounds will likely control the cost-effectiveness of carbon treatment. Isotherms conducted on the specific groundwaters, and perhaps evaluated on a TOC (Total Organic Carbon) basis will show the presence of background organic compounds and will indicate what portion of these can be deemed non-adsorbable. If carbon treatment is viable, however, one needs to use more advanced evaluation to completely fix the performance and economic parameters.

Evaluation Techniques—Column Studies

If a review of the isotherm data establishes that GAC is a viable treatment technique, a scaled-column study can be conducted to observe the breakthrough characteristics. Based on proper selection of contact times, a carbon usage rate can be established for economic analysis. The isotherm review will also establish the least adsorbable contaminant of interest, so that a column study can be monitored for breakthrough of only that contaminant to simplify the analysis and reduce analytical costs. Although the scaled-column test is the best technique to define GAC system parameters, there can still be physical problems with the handling of water containing volatile contaminants, and the time and expense involved with such a study can be significant.

The rapid, small-scale column test, such as the ACT, is often a good means of obtaining dynamic data within a short period of time. Knowledge of the flow rate and influent characteristics is usually sufficient to select a contact time. This information, coupled with the understanding of what will be an economical adsorption system size for the actual site, would help select the contact time ultimately modeled. With the use of an actual field sample, the ACT will take into account actual operating situations; including the mass transfer zones as determined by the kinetics of adsorption and competitive effects of multiple components. The ACT will provide information on usage rates at breakthrough and saturation for the contaminants under consideration, which will be useful in determining system configuration and the degree of treatment for the economic analysis.

Table 4 shows the results of a variety of ACT studies conducted by Calgon Carbon on actual groundwater samples. These samples show a cross section of examples that might be expected in remedial activities, such as cleaning groundwaters from spills, leaking underground tanks or pipelines, leachates from dump sites, or from normal industrial activity. Before running these studies, it was determined that adsorption was an applicable treatment, but that more information was needed to confirm the system design and carbon usage rates.

Cases 1 and 2 show situations that are relatively simple and exhibit low GAC usage rates; indicating that a single-stage adsorption system would still be the optimum system. Case 1 also indicates that, due to the relatively higher concentration of trichloroethylene, a higher driving force toward equilibrium results in 60% of the equilibrium capacity of the isotherm being realized.

Case 3 covers a situation in which a poorly adsorbed contaminant is present in the mixture. Combined with

TABLE 4. ACCELERATED COLUMN TEST STUDIES GROUNDWATER FROM REMEDIATION SITES (ACTUAL SITE SAMPLES)

	Simulated conditions		Adsorbates		At breakthrough		At saturation	
Case	Loading gpm/sf	Contact time min.	Contaminant (order of breakthrough)	Concentration mg/l	GAC load mg/gm	lbs/1000 gallons	Effluent conc. mg/l	lbs/1000 gallons
1	3.8	18	Trichloroethylene	3.3	61	0.45	0.001	—
2	2.0	35	Benzene	0.024	0.5	0.4	0.002	—
			Toluene	0.116	2.4	0.4	0.002	—
			Xylene	0.630	13	0.4	0.001	—
3	3.5	20	Methylene chloride	0.007	0.014	5.8	0.001	5.2
			Chloroform	0.268	3.8	0.8	0.004	0.7
			Cis-1,2-Dichloroethylene	0.118	2.6	0.5	0.001	0.46
			Carbon tetrachloride	39.8	—	—	—	—
4	3.8	20	1,2-Dichloroethane	0.095	0.13	5.9	0.003	4.0
			Chloroform	0.223	0.37	5	0.010	4.0
			Carbon tetrachloride	3.08	6.4	4	0.010	—
5	1.3	100	Benzene	0.034	3.1	3.0	0.003	2.0
			Toluene	4.6	79.0	3.0	0.125	2.1
			Xylene	4.1	—	—	—	—
6	1.3	44	TOC	150	—	—	55	—
			Benzene	10.2	7.7	11	0.002	—
			Toluene	8.2	9.7	7	0.002	—
7	2.6	22	TOC	15	—	—	15	—
			Phenol	44	147	2.5	0.04	1.1
			Benzene	0.44	4.6	0.8	0.33	0.74

1470 gpm/sf = m/s

other VOCs, the presence of methylene chloride results in a relatively high carbon usage rate, if the methylene chloride is to be removed to non-detectable levels. The designer has several options available in designing an adsorption system for this situation. One option is to add a second stage to the process to allow the first stage to reach saturation, thereby reducing the carbon usage rate by approximately 10%. A second option, depending upon the disposition of the water and the applicable treatment limits, is to allow the methylene chloride to break through the carbon system and remain in the effluent or allow downstream mixing to reduce the concentration. Third, the use of a combination of technologies can be considered for a case like this. Finally, the designer may expect the concentration of the methylene chloride to diminish over time and disregard its effect on the usage rate. For the last two cases, the economic analysis would be based on removal of the remaining VOCs, which, in this example, would be determined by chloroform removal.

Cases 4 and 5 both exhibit the benefit in adding a second stage to an adsorption system, especially when working with a mixture of contaminants in the mg/l range. In these cases, a 30–32% decrease in carbon usage rate was realized by allowing the carbon to obtain full utilization for the contaminant. In Case 5, involving aromatic solvents, although benzene is more poorly adsorbed than toluene, both contaminants breakthrough and reach saturation at about the same time due to the much greater concentration of the toluene.

In some situations, one contaminant may be present to a much greater extent than the other compounds in a mixture. In certain examples, such as Cases 3 and 4, these contaminants will adsorb preferentially and other contaminants will breakthrough first. In other examples, such as Case 5, the predominant contaminant may breakthrough first. The designer may have to monitor for both the predominant contaminant and the less adsorbable contaminants in order to determine the carbon usage rate.

Cases 6 and 7 illustrate the effect of the presence of other organic compounds that need not be controlled by the treatment process. As discussed earlier, the adsorbability of these organic compounds may influence the adsorption of the contaminants of interest. The ACT test should determine the overall effect of such compounds on the usage rate for removal of specific contaminants under consideration. In Case 6, the presence of 150 mg/l TOC increases the carbon use rate for benzene and toluene above that which might have been expected after observing Case 5. In Case 7, a non-volatile contaminant, phenol, is adsorbed to a greater degree than benzene, but it will breakthrough first, due to its higher concentration and solubility. Due to the adsorption of phenol, the capacity of GAC for benzene is adversely affected. For this case, addition of the second stage will improve usage rates for the phenol and benzene.

These column studies illustrate some of the design decisions that need to be made when conducting an analysis of GAC treatment. Consideration of a second stage may improve carbon usage and optimize the treatment cost. Knowledge of effluent requirements will determine the proper control point for the adsorption process, and an understanding of impacts of change in influent levels may influence the selection of the treatment process.

Adsorption System Design and Economics

As a remedial treatment would likely encounter a mix of contaminants or contaminant concentration in the mg/l range, a staged adsorption system design would generally be recommended to minimize carbon usage and optimize treatment costs. Multiple pressure vessel systems, normally two units, will achieve the staged process design. The second unit will continue to adsorb contaminants, while the first stage is allowed to become more or less fully saturated for the contaminants. When the first stage is refilled with fresh GAC, it is then returned to service as the second stage unit. To allow for return of the spent GAC in the same trailer that delivered the fresh GAC, a transfer tank is often used to temporarily hold the spent GAC while the fresh GAC is unloaded into the adsorber. The GAC usage rate will normally determine whether the inclusion of a transfer tank is economically attractive.

Activated carbon treatment of groundwaters with contaminants in the mg/l range will likely result in higher

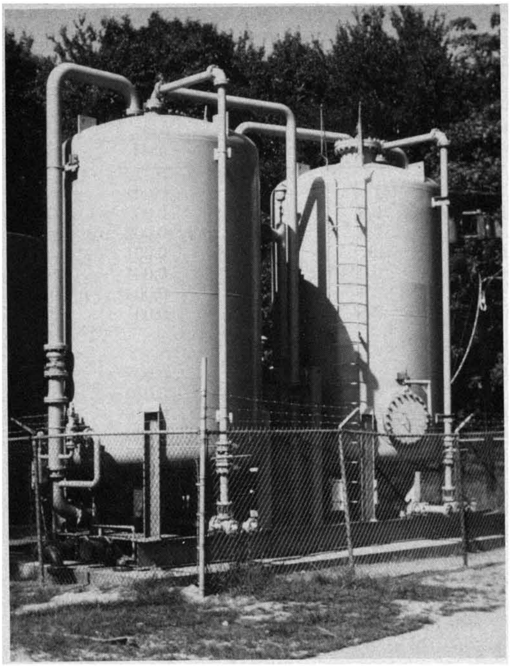

Figure 3. Two-stage adsorption system. This photo illustrates an installed two-stage adsorption system. Each adsorber is a 10 ft. (3.048 m)] diameter vessel containing 20,000 lbs. (9080 kg) of granular activated carbon. The system is skid mounted for ease of installation and pipe support. This site treats 350 gpm (0.022 m^3/s) for groundwater treatment.

carbon usage rates and greater contaminant concentrations on the spent carbon. The advantage of carbon adsorption is that these contaminants have been concentrated and can be retained in the carbon granule for transport. If the spent carbon is sent to a thermal reactivation process, the contaminants will be thermally destroyed in the process and the carbon can be reused.

Each individual adsorber in the staged system would be similar to the single-stage adsorber described previously, with a piping network utilized to effect the staging procedure. Figure 3 shows a typical two-stage adsorption system using two 10 ft. (3.048 m) diameter adsorbers, each of which contains 20,000 lbs (9080 kg) of granular activated carbon.

The following example illustrates an economic analysis, using Case 5 as a basis. Assuming that benzene, toluene, and xylene are to be reduced to non-detectable levels, a two-stage system is selected to assure both the achievement of this effluent level and to minimize GAC usage. The following process design was selected:

Flow:	200 gpm (0.0126 m^3/s) (24 hrs./day, 345 days/yr.)
System:	two-stage plus transfer tank
Quantity GAC:	20,000 lbs. (9,080 kg) per stage
Contact Time:	26 minutes/stage
GAC Usage:	2 lbs./1,000 gallons treated (0.24 kg/m^3)

TABLE 5. ADSORPTION SYSTEM ANNUAL COSTS REMEDIAL SITE—CASE 5

Amortization of capital (8.75% interest/20 years)	$ 37,600
Maintenance (5% of installed capital)	17,500
Energy costs (3.5 BHP for additional 15 psig; 8¢/KWH)	2,400
GAC usage[1] (20,000 lb. Calgon F-300; @$0.80/lb.)	160,000
GAC freight (10 bulk trailer deliveries)	27,500
Total annual cost	$245,000
Unit cost	$2.47/1000 gal.

[1] Assumes supplier of GAC can remove spent carbon and arrange for disposition or reactivation in an environmentally safe manner.

It is assumed for this example that the carbon usage rate from the column study is obtainable at shorter contact times. The capital cost for the two-stage system, with transfer tank, is predicted to be $350,000, utilizing the same assumptions as for the single-stage system.

The breakdown of the annualized operating cost is shown in Table 5 which results in a treatment cost of approximately $2.47 per 1,000 gallons (3.785 m^3) treated. The largest portion of this operating cost is due to the ongoing cost of GAC. Any reduction in influent concentration will be directly reflected in savings in carbon cost. In the survey cited earlier [9], Calgon Carbon estimated costs in the range of 48 cents to $2.52 per 1,000 gallons (3.785 m^3) treated for similar situations, using two-stage adsorption systems and recycling the activated carbon via thermal reactivation. The choice on how to handle the spent carbon is an important decision in any application of carbon adsorption, but particularly so in remedial treatment, where carbon usage is higher.

Reactivation offers a number of advantages over disposal, including lower cost in most cases, plus the assurance that reactivation, if properly done, will destroy the adsorbed contaminants in the process and remove them from the environment. While reactivation can theoretically be performed on-site, most of these types of projects will have too low a carbon usage to justify on-site reactivation, and reactivation will be performed off-site by a company offering reactivation services. Spent carbons from remediation projects, in particular, will often be considered a hazardous waste under the RCRA regulations. If the spent carbon is manifested as a hazardous waste, it is important that the company accepting the spent carbon have all requisite RCRA and other permits, and that the facility affords protection against occurrence of environmental incidents. It is also in the generators interest that the provider of reactivation services have the necessary insurance coverages and resources to properly indemnify the generator of the spent carbon against a potential liability for improper carbon handling.

Pretreatment for Carbon Adsorption Systems

At times, groundwaters from remedial activities may be complex in nature and multiple treatment steps may be required, of which carbon adsorption may be an integral part to remove specific organic contaminants to non-detectable levels. If the pre-treatment system to the GAC adsorption system includes precipitation of settling steps for metals or suspended solids removal, it is recommended that filtration be included in the design. While granular carbon itself is an excellent filtration medium, it may develop high-pressure drop faster than a unit process designed for more in-depth filtration. Also, pressure filters often utilize smaller diameter units operating at higher surface loading rates and, thus, required less backwash water. If a carbon unit is operating alone as a treatment step, however, it is recommended to include a backwash or backflush capability so that the unit can be kept in operation for the full life of the GAC.

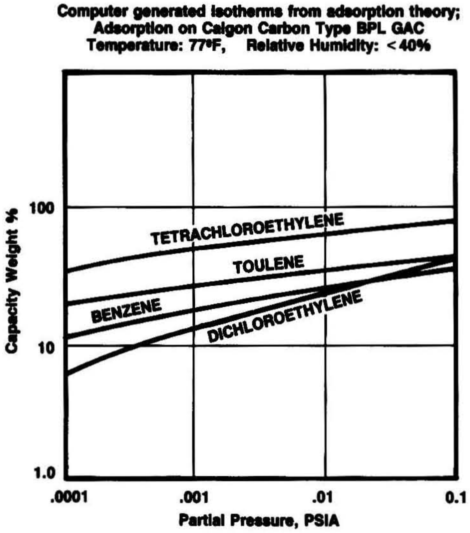

Figure 4. Vapor phase isotherms.

Another step that may precede adsorption is air stripping for removal of the most volatile contaminants. In many cases, the air stripping process can remove the bulk of the VOCs ahead of the adsorption unit, greatly reducing the carbon usage rate needed to remove the overall VOCs to non-detectable levels. This approach could, for example, be considered for the methylene chloride case (Case 3) previously discussed. If an air stripper system is considered, all of the operating expenses for an air stripper need to be taken into account. These expenses include downtime for cleaning and disposal of cleaning chemicals used for controlling scaling and fouling, and repumping the effluent. Possible influent variation, change in contaminant mix, effect of non-volatile contaminants, and potential requirements for off-gas treatment may result in the air stripper not reaching treatment objectives, and added expense for design changes or additional treatment.

For relatively clean groundwaters, it may be more economical to remove the VOCs by air stripping and use adsorption with GAC to remove them from the air stream, as vapor phase GAC has more capacity for organic contaminants adsorbed from air than liquid phase GAC has for the same contaminants in water.

ADSORPTION OF CONTAMINANTS FROM AIR SOURCES

Two aeration techniques that are finding acceptance in removing VOCs at remedial sites are air stripping for removing VOCs from groundwater, and *in-situ* soil air stripping that removes VOCs from the unsaturated zone above the water table. In both cases, VOCs are transferred to a vapor stream that may require treatment to remove the contaminants before they are released to the environment. Carbon adsorption is widely used in this application, as it has for many years been a well-established technology for removing organic compounds from vapor sources, such as solvent recovery operations in industry and odor control in wastewater treatment.

Evaluation Techniques—Adsorption Isotherms

As with the liquid phase evaluation, the vapor-phase adsorption isotherm is the basic evaluation technique for removal of organic contaminants from air. The compilation of single component isotherms in Figure 4 show the greater capacity for the contaminants in the vapor phase. This phenomena is partly explained by the structure of the vapor phase carbons compared to the liquid phase carbons, and partly due to the behavior of the solvents in their vapor state. In general, preliminary vapor phase carbon usage can be predicted by adding the carbon usage generated by each individual contaminant, as competitive adsorption effects are less of a concern in the vapor phase than in the liquid phase. The isotherm prediction assumes relatively low moisture in the vapor, as high moisture (greater than 50% RH) can cause the GAC pores to fill with water and adversely affect the predicted vapor phase capacity.

Design of Vapor Phase Adsorption Systems

The choice of vapor-phase adsorption systems is usually between one of two basic processes: regenerable and non-regenerable adsorption systems. The choice between the two systems is based on economics, with particular consideration given to the expected life of the remedial project. In *in-situ* soil-stripping processes, for example, the initial organic loading may be high, but then it often falls off rapidly in an asymptotic manner [*10*], so that the design of choice is nearly always a non-regenerable type when the project life is taken into consideration. For air stripper systems, however, a regenerable system may be more economical than one in which the carbon is replaced and disposed of on a frequent basis.

In a non-regenerable system, the contaminated air is passed through the adsorption system and discharged. If the contaminated air is from an air stripper, the air may be heated by approximately 25–30°F (14–17°C) to reduce the humidity to less than 50%, thus providing for greater adsorptive capacity by minimizing the tendency for water vapor to condense and fill the pores of the GAC. The capital cost for a non-regenerable systems is generally low, as adsorbers and duct are often constructed of FRP. The size of the vessel is determined by two factors. The vessel diameter is determined by the air flow rate, often in the range of 40–80 fpm (0.2–0.4 m/s) face velocity and the bed depth of GAC, normally 3 to 5 ft. (0.9–1.5 m) depth, depending upon the frequency of exchange required.

Vapor-phase adsorption occurs in a very short depth of the bed, so relatively short bed depths can be employed, as compared to the deeper bed depths normally used in liquid phase systems.

The equipment cost of a vapor phase adsorption system is approximately equal to the equipment cost of the air stripping equipment it is associated with. The cost of carbon on a per pound basis may be two to three times that of liquid phase GAC, as the price for vapor phase carbon is higher, and spent carbon handling costs may be higher due to the higher contaminant loadings obtained in the vapor phase.

In a regenerable vapor-phase adsorption system, the GAC can be regenerated in place. The regeneration of GAC in vapor-phase service requires less severe conditions than that required for regeneration of liquid phase carbons since there is a low level of mositure in the carbon particle. Also, the adsorbed organic compounds are volatile to begin with and are more easily desorbed from the carbon surface. Liquid-phase systems also will tend to adsorb many non-volatile compounds and other organic compounds that are not easily desorbed. The use of regenerable systems becomes economical when the carbon exhaustion rate is high, and the amount invested in regenerable systems is offset by the savings in the cost of purchasing replacement GAC.

The steam regenerable system, as is often used in solvent recovery operations, is the most common type of regenerable system. In this process, contaminated air is passed through one of two carbon adsorbers and then discharged. While one adsorber is on line, the second is regenerated by heating the GAC to about 220°F (105°C) with steam. The steam carrying the desorbed organic contaminants is then cooled in a condenser, and the condensate is collected for disposal.

The capacity of GAC for the contaminants in a steam regenerable system is often less than for fresh GAC. This working capacity of the GAC is determined by the type of contaminants being desorbed and the degree of removal required. In many cases, this working capacity may be less than 20% of the capacity of fresh GAC due to retention of adsorbed contaminants in the small carbon pores.

There are newer processes available that can be used when a more complete regeneration is desirable. A more complete removal of adsorbed contaminants can be effected using a hot inert gas, nominally at 350°F (175°C), for in-place regeneration. This hot gas regeneration recovers a greater portion of the working capacity than is obtained with steam regeneration. The organic contaminants desorbed and carried with the hot gas can be removed by cooling or can be oxidized by sending the gas directly to a thermal oxidizer. This type of regenerable system may be especially viable if disposal of condensate from a steam regenerable system becomes a major factor, or if the goal is to obtain complete destruction of contaminants at the site [*11*].

CONCLUSION

The need to remove organic contaminants from groundwater, either to insure safety of the groundwater resource or to remediate an underground wastewater problem, has become a widespread concern of the CPI. Adsorption with granular activated carbon is a widely accepted technology for removal of these contaminants, and normally should be an integral part of an investigation of treatment alternatives.

Both a historical data base for screening the applicability of GAC and evaluative techniques to determine the economics of treatment exist to establish the cost effectiveness of adsorption. The procedure presented here will hopefully be helpful as a point of reference to evaluate other treatment technologies and as a planning technique for the employment of activated carbon adsorption.

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Bench-Scale Testing of High-Temperature Desulfurization Sorbents

S. K. Gangwal, S. M. Harkins, M. C. Woods
Research Triangle Institute, Research Triangle Park, NC 27709

S. C. Jain and S. J. Bossart
Morgantown Energy Technology Center, Department of Energy,
Morgantown, WV 26505

Extrudates of regenerable mixed-metal oxide sorbents including zinc ferrite, copper-modified zinc ferrite, and zinc titanate were prepared and tested for their potential to remove hydrogen sulfide (H_2S) from coal gasifier gas in a high-temperature high-pressure (HTHP) fixed-bed reactor. Reductions in H_2S concentration from >10,000 parts per million by volume (ppmv) to <1 to 50 ppmv were achieved depending on sorbent, reactor temperature, and steam concentration. Zinc ferrite showed no apparent loss in capacity over 15 sulfidation-regeneration cycles, but underwent significant strength reduction at 5% steam due to soot formation. Zinc titanate exhibited excellent strength and capacity retention at 5% steam and temperatures up to 735°C.

INTRODUCTION

Integrated gasification combined cycle (IGCC) and gasifier/molten carbonate fuel cell (MCFC) are two of the most promising advanced systems for producing electric power from coal [*1*]. These systems offer the advantages of producing electric power at lower cost-of-electricity and lower pollutant emissions than conventional pulverized coal power plants. A critical component in both IGCC (Figure 1a) and gasifier/MCFC (Figure 1b) systems is hot gas cleanup at conditions that nearly match the temperature and pressure of the gasifier and power generator. This eliminates requirements for expensive heat recovery equipment and efficiency losses associated with fuel gas scrubbing. Particulate and sulfur control are of primary concern during hot gas cleanup.

Sulfur control is important for protection of turbine components, molten carbonate fuel cell components, and compliance with environmental regulations. Sulfur removal to meet Federal New Source Performance Standards (NSPS) will be required for IGCC systems. Removal to significantly lower levels than NSPS could be beneficial for gas turbine applications because alkali and sulfur may interact to cause corrosion and/or deposition on turbine blades. The MCFC system has much more stringent sulfur tolerances than those for the IGCC system due to the sensitivity of the fuel cell. Sulfur removal to less than 1 ppmv may be required to ensure fuel cell operability.

High-temperature desulfurization research over the past several years in the U.S. has concentrated on regenerable, mixed-metal oxide sorbents that can reduce the sulfur in coal gasifier gas to less than 10 ppmv and can be regenerated with air for multicycle operation. Zinc ferrite (an iron and zinc compound with a spinel-type crystal structure) is currently the leading sorbent candidate for application to power systems [*2*]. Zinc ferrite research was pioneered by Morgantown Energy Technology Center (METC), and sufficient progress has been made that zinc ferrite is now being evaluated using coal gasifier gas at the KRW pilot-scale gasifier in Madison, Pennsylvania [*3–5*].

The sulfur dioxide produced during regeneration of the zinc ferrite can be treated with one of several processes available for sulfur dioxide control. The objective is to re-

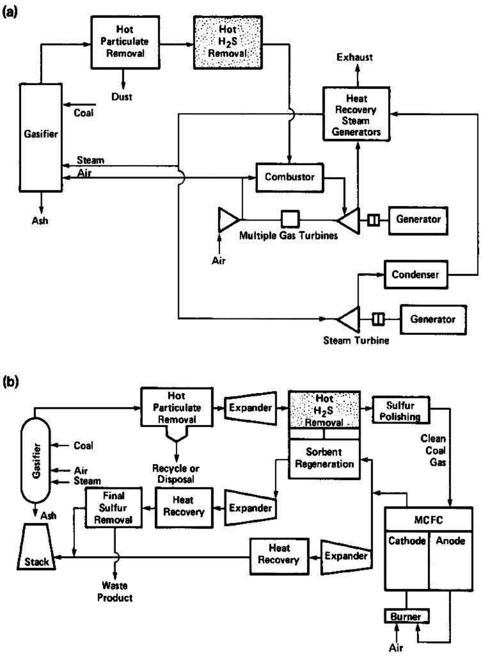

Figure 1. (a) Simplified IGCC system, (b) Gasifier/MCFC system.

cover the sulfur in an environmentally acceptable, resalable, or readily disposable form. Process options include conversion to elemental sulfur suitable for sale, production of sulfuric acid, conversion to a disposable sodium or calcium sulfate, or recycle of the sulfur dioxide-containing stream to the coal gasifier for reaction with the dolomite or limestone that may be incorporated as an in-bed desulfurization sorbent.

There are several potential improvements possible over existing zinc ferrite technology. These include extension of the operating temperature above 650°C, removal of coal-derived gas sulfur to less than 1 ppmv, simplified handling of regeneration off-gases, increased sorbent sulfur capacity, increased sorbent durability, and capability to control other coal-derived contaminants (ammonia, chloride, etc). Under METC sponsorship, Research Triangle Institute (RTI) is testing several high-temperature desulfurization sorbents [6]. This paper discusses the test conditions and results for zinc ferrite, copper modified zinc ferrite, and zinc titanate sorbents and the significance of these results for application to IGCC and gasifier/MCFC systems.

TABLE 1. SORBENT DETAILS AND THEORETICAL SULFUR CAPACITY

Sorbent	Chemical Formulae (UCI number)	Short form	Percent bentonite binder	Theoretical sulfur capacity (g S/100 g fresh sorbent)
Zinc Ferrite	$ZnO \cdot Fe_2O_3$ (T-2465)	ZF	3.1	38.7
Copper-modified Zinc Ferrite	$0.14\ CuO \cdot 0.86\ ZnO \cdot Fe_2O_3$ (L-2952)	(ZC)F	2.0	38.2
Zinc Titanate	$0.8\ ZnO \cdot TiO_2$ (L-3014)	(0.8Z)T	2.0	17.3
	$ZnO \cdot TiO_2$ (L-3139)	ZT	3.0	19.8
	$1.5\ ZnO \cdot TiO_2$ (L-3140 and L-3196)	(1.5Z)T	3.0	23.8
	$2.0\ ZnO \cdot TiO_2$ (L-3025)	(2Z)T	3.0	26.1

The copper-containing zinc ferrite formulation is essentially a modification of the zinc ferrite sorbent in which a small amount of the zinc oxide is replaced with copper oxide. Addition of copper oxide to zinc ferrite has been shown to reduce sulfur levels to less than 1 ppmv. This sorbent may be directly usable for MCFC applications without the need for a polishing sulfur sorbent. The zinc titanate formulations have the potential to extend the operating temperature range of zinc-based sorbents above 677°C. Addition of titanium to zinc-based sorbents is believed to stabilize the zinc in the crystal structure and minimize vaporization of zinc [7]. Zinc vaporization after reduction of zinc oxide to zinc metal can become a problem for zinc ferrite at temperatures exceeding 677°C.

SORBENT PREPARATION AND SCREENING

The sorbents were prepared as 3/16-inch (4.8 mm) extrudates approximately 1/2-inch (12.7 mm) long by United Catalysts, Inc. (UCI) Louisville, Kentucky, by high-temperature calcination of the oxide mixtures. Prior to preparing large batches for bench-scale testing, several small batches of each formulation were prepared with varying amounts of binder and screened using a thermogravimetric reactor (TGR). Additional details of the preparation and screening procedure are available [6]. Table 1 gives short-form designations for the purposes of this paper of the sorbents tested along with inorganic binder content and maximum theoretical sulfur capacity if all the reactive oxides were converted to stable sulfides ($ZnO \rightarrow ZnS$; $Fe_2O_3 \rightarrow FeS$; $CuO \rightarrow Cu_2S$). Sulfur capacity is defined as grams of sulfur per 100 grams of fresh sorbent.

Structural properties and X-ray diffraction (XRD) phases were measured for all sorbents. The radial crush strength (measured by ASTM D-4179) of the extrudates ranged from 3 to 4 lb/mm (14 to 19 N/mm). BET surface areas and pore volumes (cumulative at 408 MPa mercury intrusion pressure) were approximately 3 to 4 m^2/g and 0.25 to 0.4 cm^3/g, respectively. The median pore diameters (diameter at 50% intrusion) ranged from 0.25 to 0.6 μm, and porosities ranged from 58 to 66%. For the ZF and (ZC)F sorbents, $ZnFe_2O_4$ (franklinite) was the only XRD phase identified. The copper present in the (ZC)F sorbent was less than 5%, which was below the XRD detection limit. Its presence in the right amount was confirmed by atomic absorption spectrophotometry. The copper is believed to form copper ferrite ($CuFe_2O_4$), which is highly efficient for H_2S removal. For the zinc titanate sorbents, the desired $Zn_2Ti_3O_8$ and Zn_2TiO_4 phases were identified. As the zinc to titanium ratio increased from 0.8 to 2, the weight ratio of Zn_2TiO_4 to $Zn_2Ti_3O_8$ in the sorbent increased from approximately 0.18 to >9.

TEST EQUIPMENT AND PROCEDURE

The sorbents were tested in a HTHP fixed-bed bench-scale reactor (BSR), and the rate of sulfidation was measured in a HTHP TGR; details of the BSR are available [6]. Briefly, it consisted of a 7.75 cm diameter, 38 cm long Alon-processed (high-temperature aluminum vapor treatment) reactor with a rating of 843°C at 2.0 MPa. A battery of mass flow controllers, water pumps, and preheaters

Table 2. Bench-Scale Test Conditions

	Sulfidation Gas Composition (Volume %)	Regeneration Gas Composition (Volume %)
Pressure: 1–2 MPa	H_2: 10–14	O_2: 1.7–7.8
Temperature: 538–760°C	CO: 13–22	H_2O: 63–92
Sorbent Volume: 1.75 L	CO_2: 4.5–11	N_2: Balance
Linear Velocity: 2–7 cm/s	CH_4 0–0.6	
Space Velocity: 1000-	H_2O: 5–22	
(at 0°C, 0.1 MPa) 3000 h^{-1}	H_2S: 0.05–1.5	
	N_2: Balance	

were used to provide simulated KRW coal gasifier gas and regeneration gas. Sulfidation and regeneration were conducted in opposite direction, and inlet and outlet gases (after condensing the steam) were analyzed using a gas chromatograph system. Along with the major gas species, H_2S, COS, and SO_2 were also measured. Separate lines were used for sulfidation and regeneration to prevent contamination of the cleaned outlet gas from sulfidation. The range of test conditions used is shown in Table 2. Unless otherwise stated, the bench-scale tests were carried out at 1.5 MPa and 1,000 to 2,000 h^{-1} space velocity with 20% steam and $H_2S > 10{,}000$ ppmv in the inlet fuel gas.

A typical BSR run consisted of an initial 30-minute reduction with clean coal gas (sulfidation gas with H_2S replaced by N_2) followed by sulfidation to breakthrough. Breakthrough was indicated by a rapid increase of H_2S in the outlet gas exiting the reactor. Sulfidation was terminated when the outlet H_2S became 10 to 20 times higher than the prebreakthrough level. For the purpose of this paper, bed sulfur loadings are reported at the point when the H_2S concentration reached 100 ppmv in the cleaned outlet gas. The average loadings reported should only be used for comparative purposes between the sorbents because they apply uniquely to a reactor with the same height to diameter ratio as the RTI BSR. Following sulfidation, regeneration was carried out in an opposite direction starting with a high steam/air ratio and slowly decreasing it while maintaining the maximum temperature at approximately 760°C. The small amount of residual sulfate formed during regeneration was decomposed by reductive regeneration or by heating the entire bed to about 750°C. Successive sulfidation-regeneration cycles were then carried out in a similar fashion. Following the run, structural, mechanical, and chemical properties of the sorbents were measured from various levels in the fixed bed.

Details of the HTHP TGR are available elsewhere [8]. Single pellet kinetics were measured as a function of pressure by recording weight changes of a pellet suspended by a platinum wire from the TGR balance assembly. The gas atmosphere and conditions around the pellet were similar to those for the BSR shown in Table 2. The weight-temperature-time data were recorded using an automated data acquisition system and normalized on a weight fraction basis.

RESULTS AND DISCUSSION

Bench-scale tests were initially carried out with the (0.8 Z)T, (ZC)F, and ZF sorbents. The effect of temperature on the H_2S removal efficiency of the (0.8Z)T sorbent is shown in Figure 2. The effluent H_2S concentration was higher than that corresponding to the equilibrium of the $ZnO + H_2S \rightleftarrows ZnS + H_2O$ reaction. This indicated that the equilibrium was dictated by a zinc titanate phase rather than ZnO. However, since ZnS was the only sulfided phase identified, the overall reaction was deduced to be direct conversion of zinc titanate to ZnS. The (0.8Z)T sorbent was found to possess excellent durability at temperatures up to 735°C. Over 5 cycles, the average bed sulfur loading was about 7 g/100 g sorbent. The zinc loss from the bed was measured to be less than 1% per 1,000 hours of operation, and the sorbent showed essentially no decline in crush strength. These results, coupled to a prebreak through level of 40 ppmv sulfur, demonstrate the desirability of this sorbent for IGCC applications at temperatures up to 735°C.

The (ZC)F sorbent was found to be capable of reducing the H_2S concentration to less than 1 ppmv at temperatures up to 600°C, with 20% steam in the feed fuel gas. At 677°C, however, the H_2S concentration quickly rose to 20 ppmv before breakthrough. This indicated that the desirable copper ferrite phase is not stable at 677°C in reducing gas and the equilibrium is governed by ZnO formed from reduction of zinc ferrite to ZnO and Fe_3O_4. Significant precautions were required in running the (ZC)F sorbent to prevent falsification of outlet H_2S concentration by contamination. Although (ZC)F may be applied for MCFC without a polishing bed, it may be prudent to use a polishing bed to prevent fuel cell damage due to contamination. The sulfur content of the bottom section (bottom fifth of bed) and the average capacity of the (ZC)F sorbent at breakthrough are shown in Figure 3. In this figure, the weight % sulfur of the sulfided sorbent in the bottom section and the average capacity defined as grams of sulfur per 100 grams of fresh sorbent are plotted as a function of temperature. The results indicate that the capacity goes through a maximum at about 600°C. The crush strength of the (ZC)F declined about 20% over 4 cycles at 600°C and about 30% over 2 cycles at 677°C.

A comparison of regenerability of the (0.8Z)T and the (ZC)F sorbents is shown in Figure 4 in which the bed sulfur content is plotted against bed position following regeneration. The maximum temperatures achieved dur-

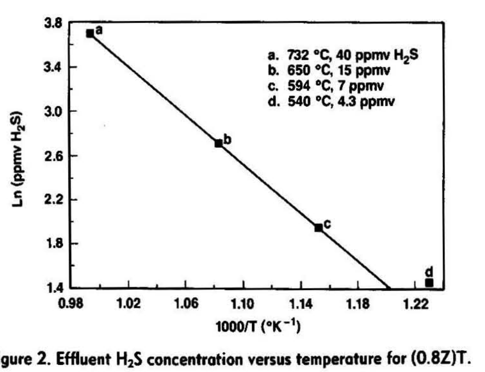

Figure 2. Effluent H_2S concentration versus temperature for (0.8Z)T.

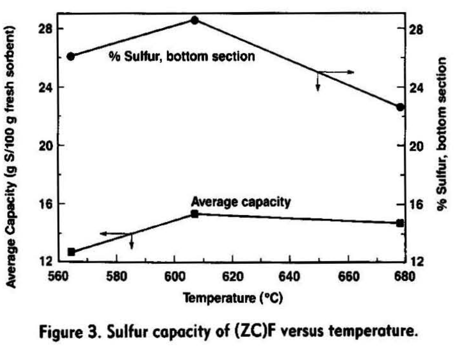

Figure 3. Sulfur capacity of (ZC)F versus temperature.

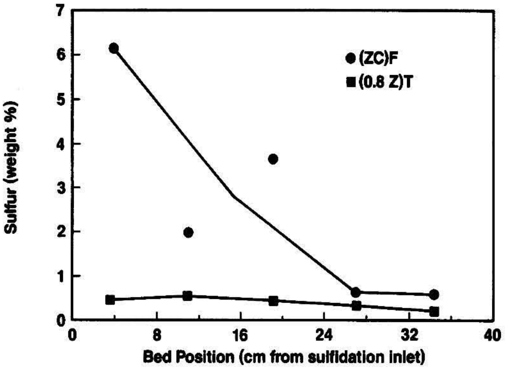

Figure 4. Bed sulfur distribution after regeneration of (ZC)F and (0.8Z)T.

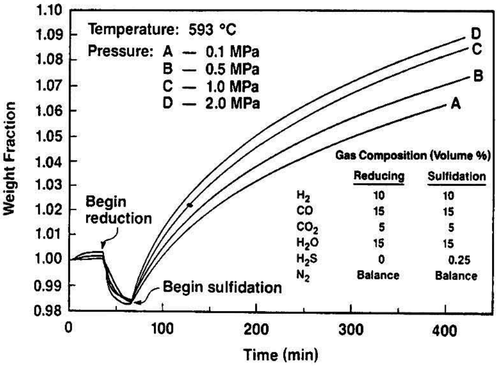

Figure 6. Effect of pressure on ZF reduction followed by sulfidation.

ing regeneration were 732°C and 785°C, respectively, for (0.8Z)T and (ZC)F sorbents. The results in Figure 4 are obtained from sulfur analysis of the bed prior to reductive regeneration or additional heating, and indicate the level of sulfate formation after the initial exothermic oxidative regeneration wave has traveled through the bed. Clearly, the (0.8Z)T sorbent possesses significantly superior regenerability than the (ZC)F sorbent.

As a leading candidate for IGCC, the ZF sorbent has been extensively tested at the KRW pilot plant and METC [*4*, *5*]. Special tests were conducted for further evaluation at RTI. A baseline test was first conducted at 600°C with 13,400 ppmv H_2S in the inlet fuel gas. The prebreakthrough H_2S level was 3 ppmv, and an average loading of 11.8 g/100 g sorbent was achieved. A test was then conducted at 600°C with only 500 ppmv sulfur in the inlet gas. The purpose of this test was to evaluate the ZF sorbent in the polishing mode of operation (KRW gasifier operated with limestone or dolomite injection for bulk sulfur removal within the gasifier). The prebreakthrough H_2S level was similar to the previous test, but a 25% higher loading was achieved. The bed sulfur distribution was found to be significantly more flat for the later test versus the earlier test, presumably due to a shorter reaction zone even though global sulfidation rates were much higher for the earlier test.

The ZF sorbent was also tested in the presence of KRW gasifier elutriated char fines. A 15 cycle test was conducted at 600°C with 15% steam in which the sorbent was mixed with 5 weight % fines prior to each sulfidation. The average sulfur loading did not decline with cycles, but was about 40% lower than the baseline capacity of 11.8 g/100 g sorbent. A small amount of carbon formation occurred, and the crush strength declined after each cycle. After 15 cycles the crush strength declined by 70%, the mercury pore volume increased from 0.25 to 0.34 cm^3/g, and the median pore diameter increased from 0.25 to 0.6 μm. Another test was conducted at 600°C with 5% steam. Over 5 cycles of this test, the average loading and prebreakthrough H_2S were consistently 15 g sulfur per 100 g sorbent and <1 ppmv, respectively. However, copious quantities of soot were formed during each sulfidation via disproportionation of CO to CO_2 and C. The sorbent was found to be severely decrepitated after the test, presumably due to reduction of the sorbent to metallic iron by the carbon. This seems to rule out the applicability of ZF to IGCC at 5% steam.

The high durability and excellent regenerability of the (0.8Z)T sorbent suggested its application at the severe low steam condition. However, in order to improve capacity, higher zinc to titanium ratio sorbents were needed. To compromise between temperature stability and capacity, four zinc titanate formulations, namely (0.8Z)T, ZT, (1.5Z)T, and (2Z)T, were tested using a TGR. Nonisothermal tests in reducing environment involving step temperature changes were conducted, as shown in Figure 5. Here the weight fraction normalized to 1.0 as initial weight is plotted against time. The results suggested that (1.5Z)T provided the best combination of

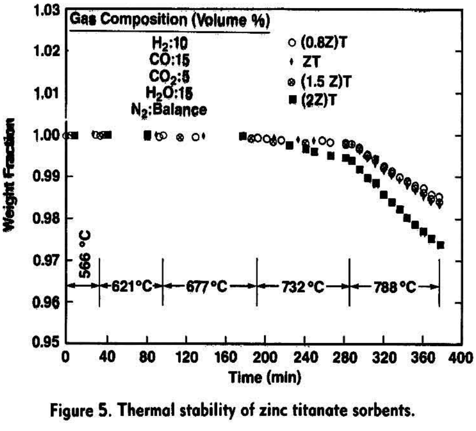

Figure 5. Thermal stability of zinc titanate sorbents.

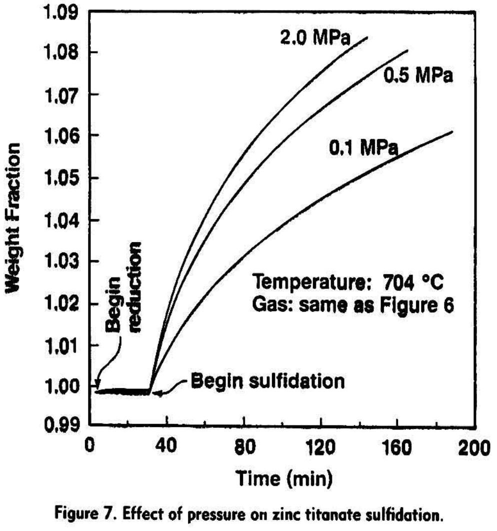

Figure 7. Effect of pressure on zinc titanate sulfidation.

capacity and temperature stability. The theoretical capacity of this sorbent, 23.8 g sulfur per 100 g sorbent, was only 10% less than that of (2Z)T (Table 1), while the thermal stability was measurably greater (Figure 5). On this basis (1.5Z)T was chosen for further TGR and BSR testing.

As an interesting sidelight, the effect of pressure on the sulfidation kinetics of the sorbents was measured using a HTHP TGR. These measurements are very important for scale-up of the BSR data. Typical results of ZF and (1.5Z)T sorbents are shown in Figures 6 and 7. These tests were conducted beginning with a 30-minute reduction at temperature in clean reducing gas followed by sulfidation. The ZF sorbent, as expected, reduces significantly more than (1.5Z)T, and the reduction rate is somewhat higher at higher pressure. The sulfidation rate increases between 0.1 to about 1 MPa, but remains essentially unaffected with further increase in pressure. The increase in sulfidation rate with pressure reflects the net increase in rate due to increased H_2S partial pressure and reduced effective diffusivity. If the sulfidation reaction is first order and molecular diffusion is controlling, the net increase in sulfidation rate should be nil. This is because rate of molecular diffusion is inversely proportional to pressure and H_2S partial pressure is directly proportional to pressure. The pressure effect would thus cancel itself out. On the other hand, if Knudsen diffusion is controlling, then the net increase in sulfidation rate should be directly proportional to H_2S partial pressure because rate of Knudsen diffusion is unaffected by pressure. The pellets under consideration thus reflected a diffusion regime that was somewhere between molecular diffusion and Knudsen diffusion.

The (1.5Z)T sorbent was tested at 600°C, with 5% steam in a 5 cycle test to ascertain if it could overcome the limitations of zinc ferrite. Unlike the ZF sorbent, essentially no carbon formation occurred, and the sorbent retained its crush strength even though the median pore diameter increased from 0.58 μm to 0.83 μm. The average capacity was consistently about 11.5 g/100 g sorbent, which is considerably higher than the capacity of the (0.8Z)T sorbent. Recent tests have shown that (1.5Z)T sorbent could also be successfully operated at 735°C, which is about 85°C higher than the highest operating temperature of zinc ferrite.

CONCLUSION

The most important conclusions based on the results reported are:

- Zinc-containing mixed-metal oxides are highly efficient high-temperature desulfurization sorbents for IGCC and MCFC applications.
- ZF possesses the highest capacity of the sorbents tested and retains its capacity over numerous cycles but suffers from decrepitation in the soot forming region, presumably catalyzed by iron oxide.
- Zinc titanate sorbents can be effectively used at 85°C higher operating temperature than the maximum operating temperature of ZF and do not decrepitate or catalyze soot formation at steam levels as low as 5% during sulfidation in a KRW-type gas.
- Addition of a small amount of copper oxide to zinc ferrite increases its H_2S removal efficiency to the point that it can reduce the H_2S level to <1 ppmv at 600°C with 20% steam in the fuel gas.
- Increase in pressure from 0.1 MPa up to 1 MPa increases the sulfidation rate of the sorbents. The rate remains essentially unchanged with further pressure increase.
- Higher average loadings prior to breakthrough can be achieved in a fixed-bed due to a significantly shorter reaction zone with 500 ppmv versus >10,000 ppmv sulfur inlet concentration, even though sulfidation rates are higher with higher concentration.

ACKNOWLEDGMENTS

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Reduction of Volatile Organic Compounds in Aqueous Solutions Through Air Stripping and Gas-Phase Carbon Adsorption

C. S. Fang and Sok-Leng Khor
Department of Chemical Engineering, University of Southwestern Louisiana,
Lafayette, LA 70504

Aqueous solution of volatile organic compounds (VOC's) is a waste stream of many chemical process industries. Conventionally, it is treated with a costly liquid-phase activated carbon adsorption process. An alternative process is studied, which is the combination of air stripping and gas-phase activated carbon adsorption. The removal of VOC's from waste-water can be as high as 99.8%, using a packed column for air stripping at room temperature. These VOC's include vinyl chloride, carbon tetrachloride, trichlorethylene, 1,1-dichloroethane, toluene, chloroform, 1,1,1-trichloroethane, benzene and xylene. These VOC's are separated from air and recovered through a carbon adsorption-regeneration cycle. The cost of VOC removal and recovery is in the range from \$0.457 to \$0.899 per 1000 liters.

INTRODUCTION

Dilute aqueous solution of volatile organic compounds (VOC's) is a waste stream of many chemical process industries, and often is a serious environmental concern. Conventionally, it is treated with a liquid-phase activated carbon adsorption process. The process is reportedly effective in removing VOC's from water [*1*], but its cost is high. The combination of air stripping and gas-phase activated carbon is an alternative process, and it appears to be efficient and cost-effective. Before any pilot-plant test, a preliminary design study was conducted to examine the technology and its cost. The results of the study are presented here.

VOLATILE ORGANIC COMPOUNDS

An organic compound, which has relative volatility of one or greater at room temperature, relative to water, is considered to be a volatile organic compound (VOC).

A survey of hazardous wastes generated in Louisiana in 1983 was conducted in 1985 by Jacobus [2]. It identified eleven VOC's which represented 79.5% of the identified organic wastes. They are listed in Table 1. Also shown in the table are five VOC's reported by other sources to be present in waste streams of many chemical process industries. Fourteen of these sixteen VOC's listed in the table are EPA priority pollutants.

HENRY'S LAW CONSTANT

Henry's law describes the distribution of a component in the gas and liquid phases at equilibrium condition. Henry's law, in commonly used units, is:

$$p_i = H_c \left(\frac{c_i}{M_i}\right) \quad (1)$$

where

p_i = partial pressure of component i in gas phases, atm
H_c = Henry's law constant, atm · m^3/g-mole
c_i = concentration of component i in liquid phase, mg/l
M_i = molecular weight of component i, g/g-mole

TABLE 1. VOLATILE ORGANIC COMPOUNDS

Volatile Organic Compounds	Tons/Year Reported in La. [2]	Relative Volatility 25°C
VOC's identified in La.:		
Vinyl chloride*	15,513	125.0
1,2-Dichloroethane*	13,356	3.353
Carbon tetrachloride*	2,396	4.843
Trichloroethylene*	1,775	3.150
1,1-Dichloroethane*	823	9.650
Toluene*	67	1.207
Methyl ethyl ketone*	61	3.825
Chloroform*	5.5	8.257
Acetone	3.8	9.751
Acrolein*	3.0	11.51
1,1,1-Trichloroethane*	2.5	5.653
	34,006 (total organic wastes identified: 42,774)	
Others:		
Benzene*		4.037
Methyl chloride*		179.3
Dichloromethane*		18.15
Acrylonitrile*		4.487
Cyclohexane		4.139

*EPA priority pollutants.

It also can be written in other terms. For example, if mole fraction is used,

$$y_i = m\, x_i \qquad (2)$$

where

y_i = mole fraction of the component i in gas-phase
x_i = mole fraction of the component in liquid-phase
m = Henry's law constant, dimensionless

Henry's law constant is a good indication whether a VOC can be removed from an aqueous solution by air stripping. Henry's law constants of eighteen VOC's are shown in Table 2. These values were reported by Thibodeaux [*3*], Dilling [*4*], and Mackay [*5*].

Henry's law constant for methyl ethyl ketone was reported to be 2.97×10^{-5} m^3 atm/g-mole, which appears to be too low. When this value is used in design calculations, the results are less than reliable.

PROCESS DESCRIPTION

Figure 1 shows the process flow diagram of the process to be studied. The process includes two parts: (1) air stripping operation, and (2) gas-phase activated carbon adsorption, including spent carbon regeneration. Equipment used in the air stripping operation includes a feed pump, air stripping column, blower and air filter.

The VOC laden air from the air stripping column is fed to one of two carbon adsorption columns to separate VOC's from air. Air after adsorption is vented to the atmosphere, while the VOC's are captured and collected in the adsorption column. When the concentration of VOC's in air reaches the break-through point, the feed is switched to the other column which has regenerated carbon. Spent carbon is regenerated either by hot air, electrical-resistance heater, or microwave radiation.

TABLE 2. HENRY'S LAW CONSTANT, 25°C

VOC's	Henry's Law Constant: Hc, m^3-atm/g-mole	Henry's Law Constant: m	Henry's Law Constant: H$_p$, atm
Vinyl Chloride	0.199	4,680	3,175
1,2-Dichloroethane	0.00123	68.3	12.4
Carbon Tetrachloride	0.0286	944.8	185
Trichloroethylene	0.0117	649.5	88.8
1,1-Dichloroethane	0.00577	320.3	58.1
Toluene	0.00688	370.8	72.3
Methyl ethyl ketone	(2.97×10^{-5})	(1.64)	(0.409)
Chloroform	0.00385	213.7	32.2
Acetone	1.16×10^{-4}	6.4	2.0
Acrolein	6.24×10^{-5}	1.1	3.5
1,1,1-Trichloroethane	0.030	991.1	224
1,1,2-Trichloroethane	9.11×10^{-4}	50.6	6.8
Benzene	0.00549	304.7	70.1
Acrylonitrile	3.19×10^{-4}	17.7	6.0
o-Xylene	0.00527	292.5	49.5
m-Xylene	0.00580	322	54.5
p-Xylene	0.00664	368.6	62.4

From Thibodeaux [3], Dilling [4], and Mackay [5].

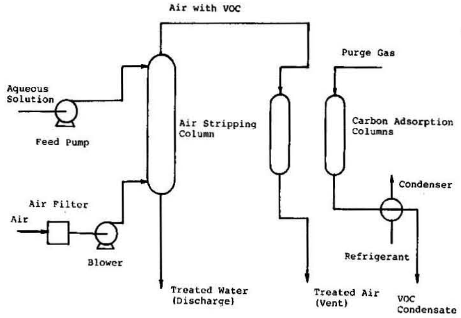


Figure 1. Process flow diagram.

AIR STRIPPING

Air stripping of an aqueous solution is a well established process. Recently, it has been used to remove various VOC's from the drinking water supply in a number of communities [6, 7, 8]. Basically, it is an operation providing inter-phase mass transfer of VOC from water to air. It can be accomplished with a tank and spargers, tray column, or packed column. In this work, both types of columns were studied; however, only the results of packed columns are reported here. The diagram given by Kavanaugh and Trussell [9] shows a comparison of tray and packed columns in the stripping operation. When Henry's law constants given in Table 2 are applied to this diagram, it is found that the diagram recommends a packed column for air stripping of most VOC's.

In air stripping of VOC's from drinking water supplies, the contaminated air is vented to the atmosphere. The more air is used in stripping, the VOC concentration in the effluent air of the stripping column is lower, which makes the operation look better. However, the VOC concentration in the effluent air from the stripping column in industrial wastewater treatment is too high to be discharged directly to the atmosphere. Dilution is not considered as a solution in industrial operations.

In this study, the contaminated air will be treated. Therefore, the less air is used in stripping, the cost of treatment of contaminated air will be less. The minimum gas-to-liquid ratio is equal to the reciprocal of Henry's law constant in [10]:

$$\left(\frac{G}{L}\right)_{min} = \frac{1}{m} \tag{3}$$

The actual value of gas-to-liquid ratio is found to be 1.5 to 6 times the minimum; that is: $(G/L)_{act} = n\,(G/L)_{min} = n/m$, where $n = 1.5$ to 6. The values of gas-to-liquid ratio of various VOC's are shown in Table 3. In air stripping of trichloroethylene and perchloroethylene for the drinking water supply of the city of San Bernardino, CA, the gas-to-liquid ratio is more than three magnitudes of order greater than the minimum [7].

Also shown in Table 3 is liquid loading, which is the flow rate of liquid fed to the air stripping column divided by the cross-sectional area of the column. It varies from 288 liters/min/m^2 [7.1 gpm/ft^2) for vinyl chloride to 6710 liter/min/m^2 (165 gpm/ft^2) for methyl ethyl ketone. The high liquid loadings for several VOC's are due to their low Henry's law constant.

The height of the packed bed is determined as follows [11]:

$$Z = N_{toL} \cdot H_{toL} \tag{4}$$

where

Z = height of packed bed
N_{toL} = number of overall transfer units (NTU), based on liquid phase
H_{toL} = height of overall transfer units (HTU), based on liquid phase

The values of NTU and HTU can be calculated from the following equation [11, 12]:

$$N_{toL} = \frac{\ln\left[\dfrac{x_{in} - (y_{in}/m)}{x_{out} - (y_{in}/m)}\left(1 - \dfrac{1}{S}\right) + \dfrac{1}{S}\right]}{1 - \dfrac{1}{S}} \tag{5}$$

$$S = \frac{mG}{L} \tag{6}$$

$$H_{toL} = H_L + \frac{L}{mG} H_G \tag{7}$$

$$H_L = 0.305\,\phi_h\,(S_c)_L^{0.5}\,K_3\left(\frac{Z}{3.05}\right)^{0.15} \tag{8}$$

TABLE 3. GAS-LIQUID RATIO AND LOADING OF STRIPPING COLUMN

VOC's	Gas-Liq. Ratio SCM/liter	Liq. Loading liter/min/m^2	Pressure Drop ($-\Delta$P) cm H_2O
Vinyl Chloride	1.64×10^{-3}	288.48	0.00279
1,2-Dichloroethane	0.0749	3,058.8	334.82
Carbon Tetrachloride	5.39×10^{-3}	724.47	28.85
Trichloroethylene	7.85×10^{-3}	488.95	0.267
1,1-Dichloroethane	0.0159	985.24	5.08
Toluene	0.0138	860.15	2.90
Methyl ethyl ketone	1.167	6,712.1	50.44
Chloroform	0.0239	1,395.6	33.76
Acetone	0.298	5,461.6	337.46
Acrolein	0.554	6,263.1	191.85
1,1,1-Trichloroethane	5.16×10^{-3}	686.98	0.239
1,1,2-Trichloroethane	0.101	3,587.7	304.8
Benzene	0.0168	1,030.5	6.60
Acrylonitrile	0.144	4,230.7	459.5
o-Xylene	0.0175	1,068.8	8.99
m-Xylene	0.0159	980.35	5.74
p-Xylene	0.0138	865.04	3.18

To convert SCM/liter to SCF/gal, multiply by 133.6809.
To convert liter/min/m^2 to gpm/ft^2, multiply by 0.024542.
To convert cm H_2O to in. H_2O, multiply by 0.3937.

TABLE 4. AIR STRIPPING COLUMN

Wastewater Flow Rate = 1000 gpm, VOC Reduction: 500 to 1 mg/l, Operating Temp. = 25°C

VOC's	HTU H_{toL} m	NTU N_{toL}	Stripping Column Height m	Stripping Column Diameter m	Installed Column Cost $
Vinyl Chloride	2.96	7.24	21.40	4.09	383,900
1,2-Dichloroethane	1.96	7.90	15.45	1.26	131,400
Carbon Tetrachloride	2.56	7.90	20.21	2.58	261,800
Trichloroethylene	3.36	7.90	26.61	3.14	384,100
1,1-Dichloroethane	2.12	7.90	16.75	2.21	192.000
Toluene	2.43	7.90	19.25	2.37	226,800
Methyl ethyl ketone	0.192	15.36	22.21	0.85	18,600
Chloroform	2.05	7.90	16.21	1.86	146,600
Acetone	1.29	15.36	19.75	0.94	94,900
Acrolein	0.576	15.36	8.85	0.87	42,800
1,1,1-Trichloroethane	2.68	7.90	21.20	2.65	277,800
1,1,2-Trichloroethane	2.01	7.90	15.90	1.16	110,000
Benzene	2.15	7.90	17.00	2.16	191,600
Acrylonitrile	1.92	11.05	21.20	1.07	117,500
o-Xylene	2.43	7.90	19.25	2.12	206,500
m-Xylene	2.49	7.90	19.71	2.22	221,800
p-Xylene	2.59	7.90	20.50	2.36	238,200

Cost is for 1988 second quarter.
To convert m to ft, multiply by 3.28084.

$$H_G = 0.011\,\psi_h\,(S_c)_G^{0.5} \left(\frac{D}{0.305}\right)^{1.11} \left(\frac{Z}{3.05}\right)^{0.33} \left(\frac{1}{L^*_w f_1 f_2 f_3}\right)^{0.5} \qquad (9)$$

L^*_w = liquid loading based on mass flow rate, Kg/m^{2}S

$f_1 = (\mu_L/\mu_w)^{0.16}$

$f_2 = (\rho_w/\rho_L)^{0.125}$

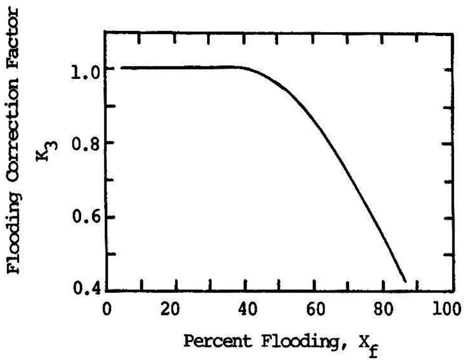
$f_3 = (\sigma_w/\sigma_L)^{0.8}$

Values of ϕ_h, ψ_h, and K_3 were given by Sinnott graphically [12]. They are converted to mathematical equations, so that they can be used in computer programs in this work. These mathematical equations will be presented later.

The diameter of the packed column is given by half of the cross-sectional area of the column at its flooding condition. The flooding condition is given by Peter and Timmerhaus [13] graphically. Again, the graph is converted to a mathematical equation for computer calculations.

Using these equations, the diameter and height of the air stripping column for various VOC's were calculated and are listed in Table 4.

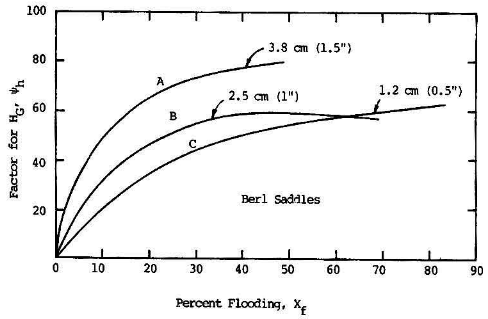
Pressure drop across the column was also calculated. It is small, less than 4.6 m of water (15 psi). A low pressure blower is sufficient to deliver the needed air in the column.



$$K_3 = a_o + a_1X_f + a_2X_f^2 + a_3X_f^3$$

a_o = 0.9989497
a_1 = -1.183564×10^{-3}
a_2 = 1.158558×10^{-4}
a_3 = -2.201115×10^{-6}

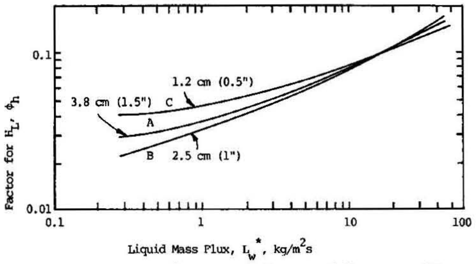
Figure 2. Flooding correction factor. (Curves are from Sinnott [12])



$$\psi_h = a_o + a_1X_f + a_2X_f^2 + a_3X_f^3 + a_4X_f^4 + a_5X_f^5$$

Constant	A	B	C
a_o	-8.403782×10^{-4}	8.752775×10^{-2}	-7.187484×10^{-2}
a_1	8.399757	4.454884	2.376368
a_2	-0.503881	-0.1624366	-3.575288×10^{-2}
a_3	1.793233×10^{-2}	3.583935×10^{-3}	1.680162×10^{-4}
a_4	-3.267907×10^{-4}	-4.234701×10^{-5}	1.249887×10^{-6}
a_5	2.305972×10^{-6}	1.950813×10^{-7}	-1.098742×10^{-8}

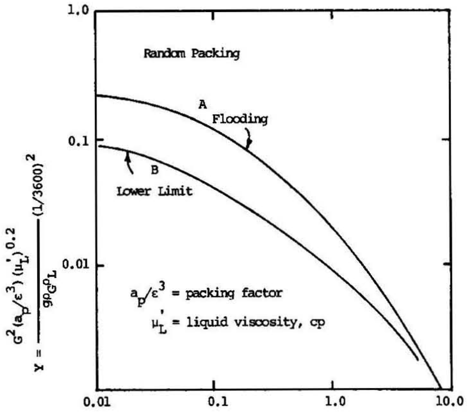
Figure 3. Factor for gas-phase HTU for Berl Saddles. (Curves are from Sinnott [12])



$$\phi_h = a_o + a_1 \ln(L_w^*) + a_2 \ln(L_w^*)^2 + a_3 \ln(L_w^*)^3 + a_4 \ln(L_w^*)^4 + a_5 \ln(L_w^*)^5 + a_6 \ln(L_w^*)^6$$

Constant	Curves A	Curves B	Curves C
a_o	3.690576×10^{-2}	3.180721×10^{-2}	4.671861×10^{-2}
a_1	1.015961×10^{-2}	9.436756×10^{-3}	7.357928×10^{-3}
a_2	1.592769×10^{-3}	7.922632×10^{-3}	2.918530×10^{-3}
a_3	-6.770780×10^{-4}	-1.946765×10^{-3}	-2.956231×10^{-4}
a_4	8.035873×10^{-4}	-2.391198×10^{-3}	-5.409217×10^{-4}
a_5	-8.266778×10^{-6}	1.770595×10^{-3}	4.292132×10^{-4}
a_6	-2.390407×10^{-5}	-2.712052×10^{-4}	-5.651553×10^{-5}

Figure 4. Factor for liquid-phase HTU for Berl Saddles. (Curves are from Sinnott [12])



$$X = \frac{L}{G}\sqrt{\frac{\rho_L}{\rho_G}}$$

$$Y = a_o + a_1X + a_2X^2 + a_3X^3$$

Constant	Curves A	Curves B
a_o	-3.92645	-4.726535
a_1	-1.092782	-0.8291371
a_2	-0.1407067	-0.06767819
a_3	-4.210557×10^{-3}	4.891963×10^{-3}

Figure 5. Correlation for estimating flooding rate in packed columns. (Curves are from Peter and Timmerhaas [13])

CORRELATIONS

Graphical correlations used in the packed-column design are converted to mathematical equations, using the least square fit, so that they can be used in the computer program in this work.

The flooding correction factor, K_3, used in Equation (8) is converted to the following polynomial:

$$K_3 = a_0 + a_1x_f + a_2x_f^2 + a_3x_f^3 \tag{13}$$

where x_f is percent flooding [12]. The values of a_0, a_1, a_2 and a_3 are shown in Figure 2.

The curves representing the factor for gas-phase HTU, H_G, for Berl saddles are converted to:

$$\psi_h = a_0 + a_1x_f + a_2x_f^2 + a_3x_f^3 + a_4x_f^4 + a_5x_f^5 \tag{14}$$

The values of coefficients, a_0, a_1, a_2, a_3, a_4 and a_5 are shown in Figure 3.

Similarly, the curves representing the factor for liquid-phase HTU, H_L, for Berl saddles are converted to, as shown in Figure 4:

$$\phi_h = a_0 + a_1 \ln L^*_w + a_2 (\ln L^*_w)^2 + a_3 (\ln L^*_w)^3 + a_4 (\ln L^*_w)^4 + a_5 (\ln L^*_w)^5 + a_6 (\ln L^*_w)^6 \tag{15}$$

Graphical correlation of flooding rates in packed columns [13] is converted to:

$$Y = a_0 + a_1X + a_2X^2 + a_3X^3 \tag{16}$$

where Y, X, a_0, a_1, a_2 and a_3 are given in Figure 5.

TABLE 5. SUPPORT FACILITY FOR AIR STRIPPING

Wastewater Flow Rate = 1000 gpm, VOC Reduction: 500 to 1 mg/l, Operating Temp. = 25°C

	Feed Pump		Blower		Air Filter	
VOC's	KW[(a)]	Installed Cost $	KW[(a)]	Installed Cost $	Flow SCMM	Installed Cost $
Vinyl Chloride	37.84	10,980	5.58	26.970	6.20	6,950
1,2-Dichloroethane	16.94	6,550	153.02	195,400	283.48	40,050
Carbon Tetrachloride	29.30	8,900	18,43	37,340	20.49	8,400
Trichloroethylene	28.93	8,800	26.81	43,700	29.80	9,320
1,1-Dichloroethane	18.34	7,000	54.37	62,900	60.43	12,730
Toluene	21.03	7,140	46.96	58,000	51.94	11,780
Chloroform	17.76	6,970	81.48	71,730	90.57	16,360
1,1,1-Trichloroethane	30.38	9,030	17.57	36,700	19.53	8,250
1,1,2-Trichloroethane	17.43	1,970	344.35	156,000	382.74	49,400
Benzene	18.61	7,000	57,14	64,670	63.51	13,100
Acrylonitrile	23.13	7,630	491.69	237,600	546.52	59,000
o-Xylene	21.03	7,140	59.52	66,200	66.16	13,400
m-Xylene	21.51	7,410	54.09	62,700	60.12	12,700
p-Xylene	22.37	7,500	47.24	58,200	52.51	11,800

[(a)] Actual kilowatt, assuming 60% efficiency.
Costs are for 1988 second quarter.
To convert KW to Hp, multiply by 1.341.
To convert SCMM to SCFM, multiply by 0.028317.

TABLE 6. COST OF AIR STRIPPING (1988, Second Quarter)

Wastewater Flow Rate = 1000 gpm, VOC Reduction: 500 to 1 mg/l, Operating Temp. = 25°C

VOC's	Total Equipment Cost[(a)], $	Utility Cost $/year	Labor Cost $/year	Total Stripping Cost $/year	Total Stripping Cost $/1000 liters
Vinyl Chloride	428,800	9,800	57,500	153,100	0.141
1,2-Dichloroethane	373,400	38,300	57,500	170,500	0.156
Carbon Tetrachloride	316,400	10,800	57,500	131,600	0.121
Trichloroethylene	445,900	12,600	57,500	159,300	0.146
1,1-Dichloroethane	274,600	12,270	57,500	124,700	0.114
Toluene	303,700	10,600	57,500	128,800	0.118
Chloroform	214,700	18,400	57,500	118,800	0.109
1,1,1-Trichloroethane	331,800	10,820	57,500	134,700	0.124
1,1,2-Trichloroethane	322,400	81,620	57,500	203,600	0.187
Benzene	276,400	17,100	57,500	129,900	0.119
Acrylonitrile	421,700	116,100	57,500	257,900	0.237
o-Xylene	293,200	18,200	57,500	134,300	0.123
m-Xylene	304,300	17,000	57,500	135,400	0.124
p-Xylene	315,700	15,700	57,500	136,300	0.125

[(a)] Including column, pump, blower, and filter; service time: 5 years.
To convert liter to gal. multiply by 0.26417.

COST OF AIR STRIPPING

Using the equations and computation procedures described above, equipment sizing and cost estimates were performed for an air stripping facility of 1000 gpm wastewater capacity and 99.8% VOC removal, from 500 mg/l to 1 mg/l. The operating temperature is 25°C (77°F), and pressure is 1 atm.

The sizes and costs of stripping columns for various chlorinated hydrocarbons, toluene and benzene are shown in Table 4. Cost data given by Guthrie [*14*] and Peters-Timmerhaus [*13*] are used. The costs are for the second quarter of 1988. The column costs include the costs of a shell, support and packing material. Table 5 shows the sizes and costs of the supporting facilities which include a feed pump, blower and air filter.

Table 6 shows the required capital investment, or the total installed equipment cost, for the air stripping of various VOC's. It includes the costs of air stripping, pumping and air supply. The utility cost is calculated, based on 10¢/KW-hr. The labor cost is based on two semi-skilled operators at $25,000 per year, plus 15% fringe benefits (total $28,750 per year). It is assumed that the facility is operated 16 hours per day, 300 days per year, and the service time of the facility is 5 years. It varies from $118,800 to $257,900 per year, or from $0.109 to $0.237 per 1000 liters ($0.39 to $0.90 per 1000 gallons) of VOC aqueous solution.

TABLE 7. SIZES OF ADSORPTION COLUMNS

Operation Time = 8 hrs; Superficial Velocity = 0.55 ft/sec.

VOC's	VOC Concentration (ppm by vol.) Influent	VOC Concentration (ppm by vol.) Effluent	Carbon Bed Diameter, D m	Carbon Bed Length, H m
Vinyl Chloride	98,434		0.93	13.96
Carbon Tetrachloride	13,257		1.62	5.43
Trichloroethylene	10,697		1.95	3.81
1,1-Dichloroethane	7,030		2.78	1.95
Toluene	8,726		2.58	2.22
Chloroform	3,901		3.39	1.37
1,1,1-Trichloroethane	15,992		1.58	5.60
Benzene	8,461		2.85	1.83
o-Xylene	5,991		2.90	1.81
m-Xylene	6,590		2.77	1.97
p-Xylene	7,537		2.59	2.23

To convert m to ft, multiply by 3.28084.

TABLE 8. FREUNDLICH-EQUATION CONSTANTS

	$k \frac{\text{g organic}}{(\text{g carbon})\,(\text{mm Hg})^n}$	n	Temp., °C
Carbon tetrachloride [*16*]	0.2928	0.20999	37.8
	0.1114	0.36462	100
Benzene [*19*]	0.2367	0.1780	33.3
n-Hexane	0.134*	0.08032*	25.0

* Estimated from ethane, propane and butane.

TABLE 9. COST OF VOC ADSORPTION

VOC's	Vessel Type[(a)]	Capital Investment 2 columns, $	 Carbon[(b)], $	 Total, $	Cost of Adsorption[(c)] $/1000 liters
Vinyl Chloride	V	111,000	21,000	132,000	0.0242
Carbon Tetrachloride	V	61,000	24,800	85,800	0.0157
Trichloroethylene	V	80,400	25,200	105,600	0.0194
1,1-Dichloroethane	H	40,800	26,000	66,800	0.0123
Toluene	H	39,600	25,600	65,200	0.0120
Chloroform	H	58,000	27,200	85,200	0.0156
1,1,1-Trichloroethane	V	97,000	24,400	121,400	0.0223
Benzene	H	39,600	25,600	65,200	0.120
o-Xylene	H	39,600	26,400	66,000	0.0121
m-Xylene	H	40,800	26,200	67,000	0.0123
p-Xylene	H	39,600	25,800	65,400	0.0120

[(a)] V: Vertical Vessel; H: Horizontal Vessel.
[(b)] Cost of Carbon: $1.00/lbm.
[(c)] 16 hr/day; 300 days/yr. Vessel service time: 5 years. Cost of make-up carbon excluded.
To convert liter to gal, multiply by 0.26417.

CARBON ADSORPTION

Gas-phase activated carbon adsorption has been used for two or three decades in the solvent recovery and odor control, removing alcohols, benzene, paraffins, trichloroethylene, chloroform and carbon tetrachloride from air streams (*15, 16, 17*). A recent field study by Nelson, et al., reported a high removal of VOC's from air using gas-phase carbon adsorption [*18*].

Air carrying VOC's stripped from aqueous solution is fed to an activated carbon adsorption column. The concentration of VOC in air varies from 3,901 ppm to 98,434 ppm by volume, as shown in Table 7. The concentration of VOC's in effluent air after adsorption is determined by the adsorption equilibrium. It is approximately 3 ppm for carbon tetrachloride, according to Parmele [*16*].

The adsorption equilibrium data of benzene and carbon tetrachloride were reported by Coolidge [*19*] and Parmele [*16*], respectively. These data were used to size the adsorption column.

The Freundlich isotherm equation is used to express the adsorption equilibrium. The equation is:

$$X = k\,p^n \qquad (17)$$

where

X = weight ratio, grams of VOC adsorbed per gram of activated carbon
p = partial pressure of VOC in gas-phase, mm Hg
k,n = Freundlich-equation constants

The values of k and n for carbon tetrachloride, benzene and n-hexane are shown in Table 8. The values of k and n of n-hexane are estimated from k's and n's of ethane, propane and butane.

Adsorption equilibrium data of other VOC's are not available. Therefore, k and n of n-hexane are used, as an approximation, in sizing adsorption columns for these VOC's. There are two reasons to use n-hexane; they are: the normal boiling point of n-hexane is comparable to that of many VOC's and the values of k and n of n-hexane give a conservative design.

Based on the concept of fixed-bed mass-transfer zone and Freundlich isotherm equation, the depth of the required carbon bed is obtained as follows:

$$L = \frac{M_0\,\dot{V}_{CA}\,y_{VOC}^{\,1-n}\,\theta_B 10^6}{A\,\rho_b\,k\,(P_{total})^n} \qquad (18)$$

where

L = depth of carbon adsorption bed, m
M_0 = molecular weight of VOC, g/g-mole
V_{CA} = flow rate of contaminated air, g-mole of air/min
y_{VOC} = mole fraction of VOC in the feed
θ_B = time to reach breakthrough, min
A = cross-sectional area of adsorption column, m^2
ρ_b = bulk density of carbon bed, g/cm^3
P_{total} = total pressure in adsorption column, mm Hg

The cross-sectional area and diameter of adsorption column are determined by fixing superficial velocity of air to be 0.17 m/s (0.55 ft/sec), which is about the midpoint of most industrial practices, 0.10-0.30 m/s (0.33-1.0 ft/sec). Table 7 shows the sizes of adsorption columns for various VOC's calculated from this superficial velocity and Equation (18).

COST OF ADSORPTION

Table 9 shows the capital investment and operating cost required for removing VOC's from air by carbon adsorption. The capital investment is for two adsorption columns, including initial charge of activated granular carbon. It varies from $65,200 to $132,000. The cost of activated carbon is $1.00 per pound. Based on the same basis, which is 5 year equipment service, 16 hours per day and 300 days per year, the costs of carbon adsorption of various VOC's are calculated. Depending upon the VOC involved, the cost varies from 1.2¢ to 2.4¢ per 1000 liters (4.6¢ to 9.2¢/1000 gal) of aqueous solution. This cost does not include the costs of spent carbon regeneration and make-up carbon.

TABLE 10. COST OF SPENT CARBON REGENERATION

VOC	Cost of Regeneration $/year	 $/1000 liter	Cost of Make-up Carbon $/day	 $/1000 liter	Total $/1000 liter
Carbon tetrachloride	174,500	0.160	582	0.160	0.320
Benzene	316,400	0.291	1,055	0.291	0.582
Others	400,600	0.367	1,335	0.367	0.734

REGENERATION

Regeneration of spent carbon is a supporting operation, which can be accomplished as a part of the process, or by an off-site commercial operator through a contract.

Spent carbon can be regenerated by hot air [*20*] or electrical-resistance heater [*21*]. Microwave regeneration is also a possibility [22]. However, the conventional steam regeneration is not considered, since it produces contaminated water.

Marquess and Nell, Inc. (New York) reported that their electrical-resistance heater can regenerate spent carbon at 13¢/Kg (6¢/lb) with only 4% carbon loss. Without committing to any specific regeneration method, the cost of regeneration and carbon loss are assumed to be, respectively, 22¢/kg (10¢/lb) and 10%. Based on these assumptions, the cost of regeneration operation is calculated and shown in Table 10. For carbon tetrachloride, benzene and other VOC's, it is, respectively, $0.320, $0.582, and $0.734 per 1000 liter ($1.21, $2.20, and $2.78/1000 gal) of wastewater.

MICROWAVE REGENERATION

The concept of using microwave radiation to regenerate granular spent carbon was first suggested by Schulin [23] in 1971. It was followed by more than a half dozen of patent awards in Japan, the United Kingdom, and the United States. However, there is no commercial application reported, and the literature in the public domain on this subject is scarce.

Two microwave frequencies, 915 and 2450 MHz, are popular in industrial heating and domestic cooking. When microwave radiation is applied to polar molecules, which includes all VOC's, molecules are heated by the induced molecular rotations, and separated from the carbon.

In laboratory tests [22], samples of 100 grams granular carbon loaded with acetone were placed in a domestic (Kenmore) microwave oven, and received microwave radiation for 48 minutes. The weight loss was monitored during the radiation. The weight loss represented the removal of acetone from spent carbon. The results are shown in Figure 6. All three tests showed the desorption of acetone, as shown by the three curves in the figure. The same microwave regeneration experiment was repeated for n-hexane. The results are also shown in Figure 6. The rate of desorption for n-hexane is slower than that of acetone. The dielectric constants of n-hexane and acetone are, respectively, 1.89 and 20.7 at the room temperature [*24*]. Therefore, the slower desorption rate of n-hexane is expected.

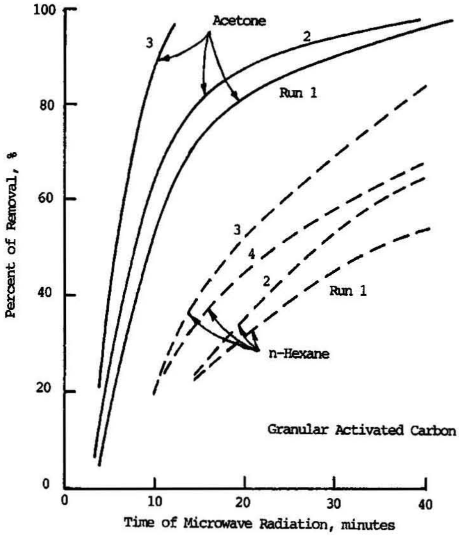


Figure 6. Microwave desorption.

The experiments show that microwave radiation can remove VOC's from spent carbon with very little purge gas, if any. This is the advantage of microwave regeneration over other types of carbon regeneration. The energy consumption of microwave regeneration is 7.3 KW-hr per Kg (11,230 Btu/lb) of acetone.

CONCLUSIONS

Neither air stripping nor gas-phase carbon adsorption of volatile organic compounds is new, but their combination shows a potential to remove VOC's from aqueous solutions economically, particularly from dilute solutions. Water involved in activated carbon is much less in gas-phase adsorption than that in liquid-phase adsorption. It makes regeneration of spent carbon easier and the recovery of VOC's from aqueous solutions possible.

The case of 3,785 liters/min. (1000 gpm) of aqueous solution containing 500 mg/l of VOC was studied. The 99.8% of VOC can be removed at costs ranging from $0.457 to $0.899 per 1000 liters of solution, depending on the VOC involved, as shown in Table 11. The cost can be reduced, if the credit for the reuse of treated water is considered. The recovered VOC's are in high concentrations, which can be recycled. The required capital investment is low, in the range of $580,000 to $840,000.

TABLE 11. TOTAL COST OF VOC STRIPPING AND RECOVERY

	Cost of Operation, $/1000 liters			
VOC	Air Stripping	Adsorption	Regeneration and Make-up Carbon	Total
Vinyl Chloride	0.141	0.0242	(0.734)	0.899
Carbon tetrachloride	0.121	0.0157	0.320	0.457
Trichloroethylene	0.146	0.0194	(0.734)	0.899
1,1-Dichloroethane	0.114	0.0123	(0.734)	0.860
Toluene	0.118	0.0120	(0.734)	0.864
Chloroform	0.109	0.0156	(0.734)	0.859
1,1,1-Trichloroethane	0.124	0.0223	(0.734)	0.880
Benzene	0.119	0.0120	0.582	0.713
o-Xylene	0.123	0.0121	(0.734)	0.869
m-Xylene	0.124	0.0123	(0.734)	0.870
p-Xylene	0.125	0.0120	(0.734)	0.871

Air stripping can be accomplished with much less air-to-liquid ratio than that in the air stripping of drinking water supplies. This means that equipment size and the cost for the treatment of contaminated air can be significantly reduced.

The cost of regeneration is the major cost of the process. Microwave regeneration has a potential to make the recovery of VOC's from spent carbon easier and less expensive.

ACKNOWLEGMENT

This work was supported by a grant from the Department of Environmental Quality, the State of Louisiana. The support is greatly appreciated.

NOTATION

A = cross-sectional area of adsorption column, m^2 or ft^2
c_i = concentration of component i in liquid phase, mg/l
D = column diameter, m or ft
D_L = diffusion coefficient of liquid, m^2/s or ft^2/s
D_v = diffusion coefficient of vapor, m^2/s or ft^2/s
f_1 = liquid viscosity correction factor
f_2 = liquid density correction factor
f_3 = liquid surface tension correction factor
G = gas flow rate, kg/hr-m^2 or lbm/hr-ft^2
H_G = height of a gas-phase transfer unit, m or ft
H_L = height of a liquid-phase transfer unit, m or ft
H_{toL} = height of an overall liquid-phase transfer unit, m or ft
k = Freundlich equation constant
K_3 = percentage flooding correction factor
L = liquid flow rate, kg/hr-m^2 or lbm/hr-ft^2
L = depth of carbon adsorption bed, m or ft
L^*_w = liquid mass flow rate per unit column cross-sectional area, kg/m^2s
m = Henry's Law constant, dimensionless
M_v = molecular weight of VOC, g/g-mole or lbm/lb-mole
n = Freundlich equation constant
N_{toL} = number of overall liquid-phase transfer units
p = partial pressure of VOC in gas-phase, mm Hg
p_i = partial pressure of component i in gas-phase, atm
P_{total} = total pressure in adsorption column, mm Hg
S = stripping factor
$(Sc)_L$ = liquid Schmidt number = $(\mu_L/\rho_L D_L)$
$(Sc)_v$ = vapor Schmidt number = $(\mu_v/\rho_v D_v)$
$\dot{V}_{CA}$ = flow rate of contaminated air, lb-mole of air/min
X = weight ratio, grams of VOC adsorbed per gram of activated carbon
X_{in} = mole fraction of solute in liquid-phase at entering condition, dimensionless
X_{out} = mole fraction of solute in liquid-phase at leaving condition, dimensionless
Y_{in} = mole fraction of solute in gas-phase at entering condition, dimensionless
Y_{out} = mole fraction of solute in gas-phase at leaving condition, dimensionless
y_{VOC} = mole fraction of VOC in the feed to the carbon adsorption bed
Z = height of stripping column, m or ft

Greek Letters

ψ_h = factor for H_G for Berl Saddles
ϕ_h = factor for H_L for Berl Saddles
μ_L = viscosity of liquid, kg/m-s or lbm/ft-sec
μ_w = viscosity of water, kg/m-s or lbm/ft-sec
ρ_b = bulk density of carbon bed, kg/m^3
ρ_w = density of water, kg/m^3
σ_L = surface tension of liquid, dyn/cm
σ_w = surface tension of water, dyn/cm
θ_B = time to reach breakthrough, min

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Electrophysical Sorption of Two Carbon Halogenated Solvents onto Soil

J. E. Mokrauer and D. S. Kosson
Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08855

Sorption of halogenated two carbon organic contaminants onto a sandy loam has been found to be controlled by the electrostatic attraction between a slightly negatively (δ^-) charged clay particle and a positively (δ^+) charged carbon atom within the solvent molecule. Adsorption isotherms for tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, and 1,2-bromochloroethane by a sandy loam indicate that the extent of sorption appears to have a direct functional relationship to the molecular charge distribution within the solvent molecule, and to the atomic radii of the molecular substituents of the contaminant. This theory of adsorption is defined as Electrophysical Sorption (EPS) because it reflects the combination of electrostatic and physical contributions to sorption.

INTRODUCTION

Groundwater contamination from inappropriate disposal of hazardous and toxic chemicals poses a major environmental problem to the United States. Testing performed on public water supplies as a consequence of New Jersey Assembly Bill A-280 has shown chlorinated aliphatic hydrocarbons to be present as contaminants in many New Jersey potable water resources. To fully understand contaminant attenuation in groundwater systems, all related processes (i.e., sorption, reaction, and dispersion) must be considered. Sorption most commonly involves the uptake of solutes (contaminants) by solid substrates (soil) [*1*]. The intent of this paper is to develop a mechanistic framework for the interpretation of contaminant partitioning in groundwater/soil systems.

As contaminated groundwater flows continuously through soil, some contaminants sorb to the surface of soil constituents, attenuating contaminant levels in the water. Furthermore, at equilibrium, for most priority pollutants, the soil concentration is at least that of the aqueous phase. In turn, this yields an apparent concentration at the soil water interface that is greater than or equal to the aqueous phase concentration [*1*]. Current theory describes adsorption of contaminants in an aqueous soil system as partitioning between an organic soil phase and an aqueous phase. In fact, it treats the partitioning of contaminants between soil phases and water in a manner similar to that of an organic solvent extraction [*2, 3, 4*]. However, recent studies on halogenated single carbon adsorption onto soil have produced results inconsistent with the prevailing theory. Isotherms for chloroform ($k = 0.4753$), bromodichloromethane ($k = 0.3218$), and methylene chloride ($k = 0.2168$) onto the sandy loam indicate that the extent of sorption appears to have a direct functional relationship to the molecular charge distribution within the solvent molecule and to the atomic radii of the molecular substituents of the contaminant [*5*]. Contrary to the prevailing theory of passive partioning, these results support a mechanistic theory of adsorption where a slightly positive (8) carbon atom forms an electrostatic bond with the clay particle.

The study described was carried out to expand a new model for the mechanism of adsorption. The model is based on the physical and electronic differences among adsorbing molecules. Chemical differences were ignored because no reaction occurs during the limited time period of simple adsorption.

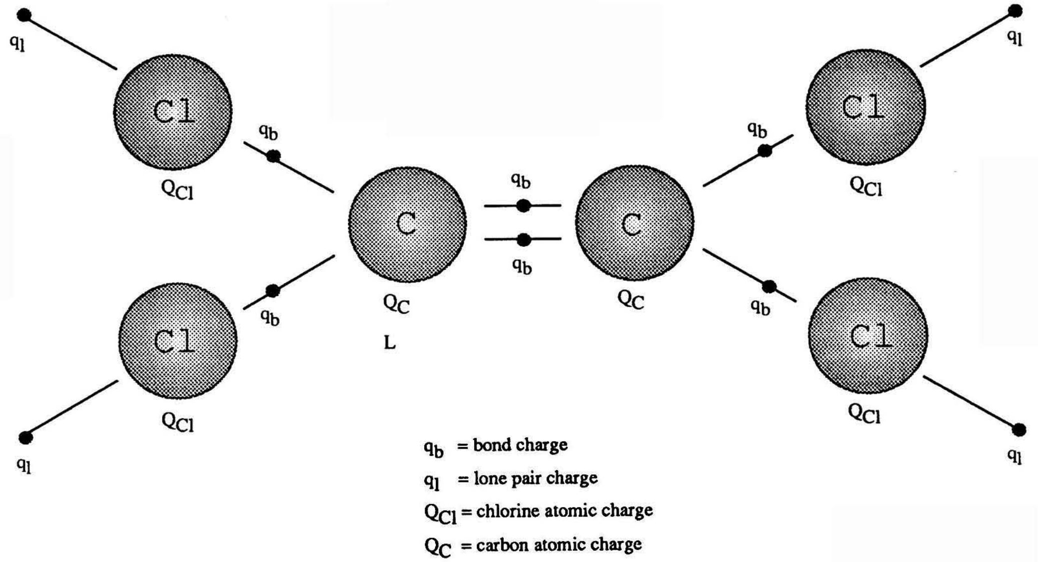

Figure 1. New point charge model.

EPS THEORY AND QUANTIFICATION

The clay mineral constituents of soil were chosen as the basis of the sorption theory because of high surface area and sorptive capacity [6]. Soils chosen for experimental verification were selected based on relatively low soil organic matter content. In addition, recent experimentation has shown aqueous adsorption of fluoridone (herbicide) to be related not only to organic matter, but also to clay content [7]. A plausible explanation for this is that, an electrostatic attraction exists between slightly negatively (δ^-) charged silicate clay molecules and slightly positively (δ^+) charged carbon atoms. The slightly negative charge on the clay surface is a result of unsaturated valence states surrounding the exterior of the molecule, and exposed oxygen and hydroxyl groups that behave as negatively charged active sites [6]. The slightly positive charge on contaminant carbon atoms results from highly electronegative substituents, e.g., chlorine atoms, attached to the carbon atom. In general, the greater the electronegativity and frequency of substitution of such substituents, the higher the local positive charge (δ^+) on the carbon atom. When the two oppositely charged particles are present in the same system, an electrostatic attraction between a δ^+ carbon atom and a δ^- clay particle acts to bind the contaminant to the surface of soil particles. Analogous theories have been used to explain cation adsorption to clays [8]. Consequently, according to the EPS theory, the greater the δ^+ charge on the carbon the greater the tendency to sorb. However, when the carbon atom is saturated with highly electron withdrawing groups other effects should be seen. The electronegative substituents surrounding the carbon atom create an electron cloud resulting in a negative shielding effect that leads to anion repulsion rather than the expected attraction.

TABLE 1. PARTITIONING COEFFICIENT VERSUS CHARGE ON CARBON

Compound	Partitioning Coefficient [10] (approximate)	Charge on Carbon (Rank by Inspection)
1,2-Dichloroethane	.25	4
1,1,2,2-Tetrachloroethane	.68	3
1,1,1-Trichloroethane	1.78	2
Tetrachloroethene	2.63	1

Electronegativity Values [11]: Carbon = 2.5, Chlorine = 3.0, Hydrogen = 2.1

Charge Quantification

To quantify the δ^+ charge on the carbon atom(s) of the molecules studied, the "New Point Charge Model" was used [9]. In this model atoms, bonds, and lone pairs are all compressed to point charges according to their electron density, as illustrated in Figure 1. The calculations of the point charges on the molecules are carried out with measurable dipole moments and core binding energies [9]. Unfortunately, these charges on the atom do not correspond to traditional atomic charges. To calculate the charge (Q_a), q_l, and the atom's share of q_b (bond charge) must be added to the atom point charge. The atom's share of the bond charge is inversely porportional to the ratio of the covalent atomic radii of the atoms [9]. Accurate values for q_b are not available. As outlined by Coppens and Hall [9], q_b can be assumed to be zero, although lesser accuracy is the result.

Sorption data obtained by other investigators is summarized in Table 1 [10]. In the two carbon molecules, the carbon with the higher charge was assumed to be the interacting carbon. Table 1 ranks, in order of increasing Q_c, the predicted relative adsorptivity for each molecule. This table illustrates the qualitative relationship between adsorption and point charge on the carbon atom [10]. (Note: Double bonds act as electron withdrawing substituents.)

In addition to these electronic effects, the size of the carbon substituents should play a major role in the adsorption of certain organic contaminants. The larger the substituent, the smaller the area available for attachment to the soil and the greater the substituent hindrance. The ratio of the atomic covalent radii of the substituents has been used to quantify these physical effects on sorption.

Correlating both the electronic and physical factors to sorption yields the EPS equation:

$$K_a/K_b = (Q_{ac}/Q_{bc})/\prod_{i=1}^{n} (r_{ai}/r_{bi}) \qquad (1)$$

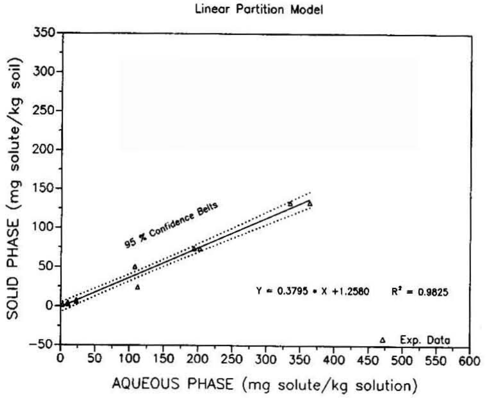

Figure 2. Adsorption of 1,2-dichloroethane.

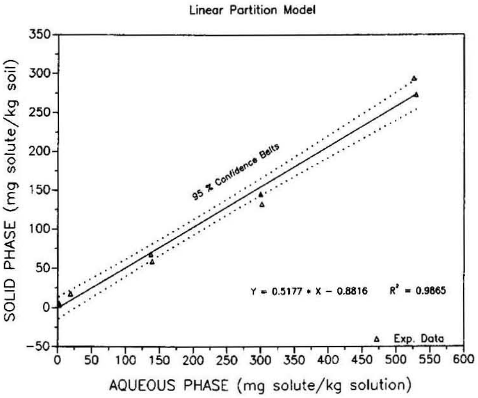

Figure 3. Adsorption of 1,1-dichloroethane.

where k_a represents the partitioning coefficient of contaminant a, Q_{ac} represents the charge on the carbon atom of contaminant a, n represents the number of substituents, π represents the product of the contaminants present, and r_{ai} represents the atomic covalent radii of substituent i on contaminant a.

Isotherm Model

To explore the EPS theory experimentally, the relative sorptive capacities of single carbon contaminants were determined. To correlate the results of sorption measurements, data for each solute was regressed to a form of the Freundlich model. The model is an empirical equation that takes the form:

$$q = k \cdot c^{1/n} \qquad (2)$$

where q is mg of solute per kg of soil, c is mg of solute per kg solution, k is the partitioning coefficient between water and soil, and n is the linearity constant. This model suggests that the energy of sorption decreases logarithmically as the fraction of surface covered increases [12]. A major problem with this model is that the slope of the isotherm should be finite at infinite dilution, but in reality is not unless n is equal to one [13].

The linear partition model is the Freundlich model with $n = 1$. It has the form:

$$q = k \cdot \mathrm{c} \qquad (3)$$

In the area of soil chemistry, this is the case for modeling adsorption onto soils and clays. As a result, all adsorptions studied were fit to this model.

EXPERIMENTAL AND ANALYTICAL METHODS

The following experimental procedures were used to quantify sorptive interactions of solute species (tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, and 1,2-bromochloroethane) with a sandy loam soil. This soil was assayed and found to have the following composition on a mass basis: 72% sand, 16% silt, 12% clay, and 1.8% organic matter. Initially, bottles were filled with sifted, air-dried soil and water and then sealed with teflon/silicone septa. Solute in methanol solution was injected, to attain concentrations of 2, 5, 10, 50, 100, and 200 ppm (within the solubility limit of all solutes used). Competition between methanol and the solute for sites on the clay particles has been found to be minimal at low methanol concentrations (0.1% in this case) [12]. Each concentration was run in duplicate, together with controls. Care was taken to minimize head space in all samples and controls to avoid vapor losses.

Samples were placed on an isothermal (25°C) shaker for at least 24 hours, at 250 rpm, to allow close approach to equilibrium. The equilibration time was calculated from a previous kinetic study [5]. Following equilibration and centrifuging, the aqueous phase was extracted with pentane and analyzed.

After shaking, soil samples were centrifuged at 3500 rpm for 4.0 hours to prepare them for extraction into pentane. Next, the aqueous phase was sampled and syringe filtered into an equal amount of chilled (4°C) pentane. Syringe filtration was utilized to minimize any losses through volatilization. This extraction step was the highest error-generating procedure in the experiment (9.4%), necessitating six extractions for each sample. An experiment, carried out using known amounts of halogenated hydrocarbons, pentane, and water to test this extraction procedure attained recovery in the pentane phase of greater than 97%.

Solute concentrations in pentane from the extraction step were determined using a Hewlett-Packard 5890A Gas Chromatograph (GC) equipped with an O.I. Model 4420 electrolytic conductivity detector (ELCD) and a 1% SP-1000 60/80 Carbopack stainless steel column. The GC utilized a 4-minute isothermal run at an oven temperature of 200°C, an injection temperature of 210°C and a detector temperature of 210°C. The detection limit for this method was less than or equal to 300 ppb for all halogenated hydrocarbons (utilizing a 1.0 μl injection).

To calculate aqueous phase concentrations, gas chromatograph output peak areas were compared to a standard curve. Standards for the development of standard curves were prepared in HPLC grade n-pentane on a volumetric basis. Data for the standard curves was linearly regressed and utilized to calculate sample solute concentrations. These concentrations were normalized for variance in water weight in each bottle. A total solute mass balance was utilized to calculate the concentration of sorbate on soil. The difference between the blank concentration and the aqueous phase concentration was the amount adsorbed. This concentration was renormalized for variance of soil weight in each bottle. Reduction of solute in the soil sample via degradative mechanisms was ignored due to the short period of this experimentation.

RESULTS OF TWO CARBON SPECIES ADSORPTIONS

Data for the sorption onto a sandy loam of 1,1-dichloroethane and 1,2-dichloroethane was regressed to the lin-

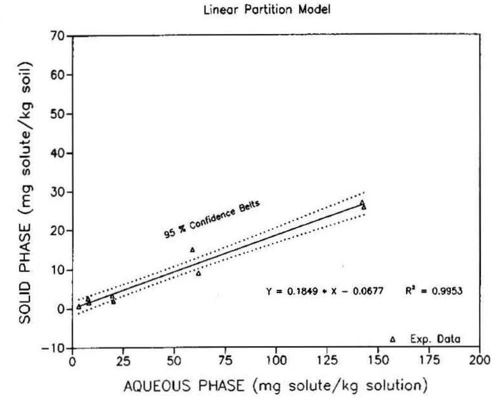

Figure 4. Adsorption of 1-bromo-2 chloroethane.

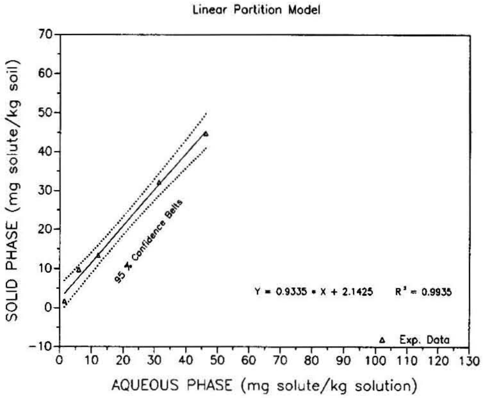

Figure 5. Adsorption of trichloroethylene.

ear partition model and confirmed that the data was linear over a broad range of aqueous concentrations. The dotted lines on the graphs indicate 95% confidence belts for the data. The isotherms have partitioning coefficients of 0.38 for 1,2-dichloroethane and 0.52 for 1,1-dichloroethane, as shown in Figures 2 and 3. The increased loading of 1,1-dichloroethane was attributed to the increased intensity of charge on one of the carbon atoms. With the major portion of the charge on one atom rather than spread out over two atoms, the electrostatic driving force for sorption was stronger.

Although not prevalent in most contaminated groundwater systems, bromochloroethane was investigated to further support the EPS theory. The similarity in structure to 1,2-dichloroethane and the presence of the bromine substituent should allow an extremely useful comparison between the sorptive data for bromochloroethane and 1,2-dichloroethane. Data for the adsorption of 1,2-bromochloroethane onto a sandy loam was regressed on the linear partition model and found to be linear over a broad range of aqueous concentrations. The linear isotherm has a partition coefficient of 0.1849, as shown in Figure 4.

Data for the sorption of trichloroethylene (TCE) and tetrachloroethylene (PCE) onto a sandy loam was regressed on the linear partition model and found to be linear over a broad range of aqueous concentrations. The linear isotherms have partition coefficients of 0.94 for TCE and 2.25 for PCE, shown in Figures 5 and 6. PCE's higher sorptive capacity was attributed to the additional chlorine present and thus the increased intensity of charge on the carbon atoms. In general, higher sorption was expected in these molecules for two reasons: the molecules have highly electron withdrawing double bonds, and the substituent hindrance is negligible due to the planar configuration of the molecules.

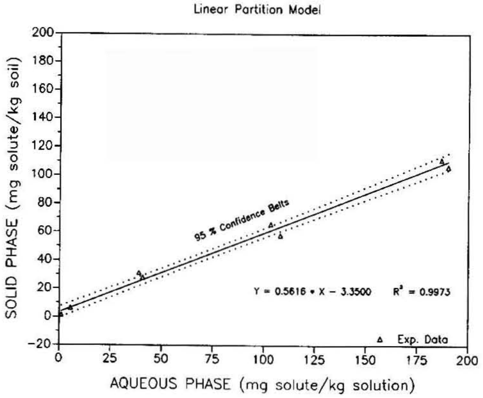

Figure 7. Adsorption of trichloroethane.

Data for the adsorption of 1,1,1-trichloroethane and 1,1,2-trichloroethane onto a sandy loam was regressed to the linear partition model and found to be linear over a

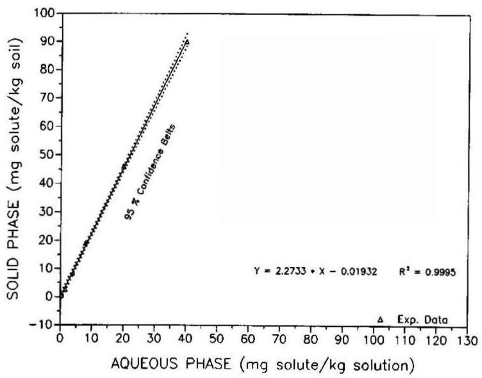

Figure 6. Adsorption of tetrachloroethylene.

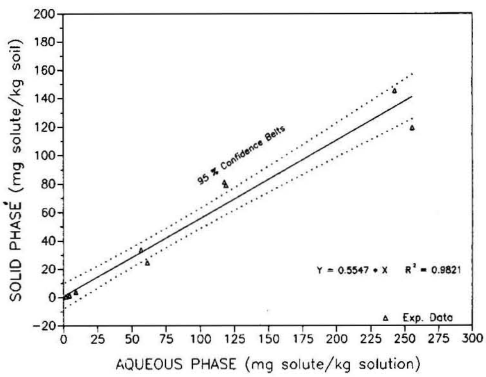

Figure 8. Adsorption of 1,1,1-trichloroethane.

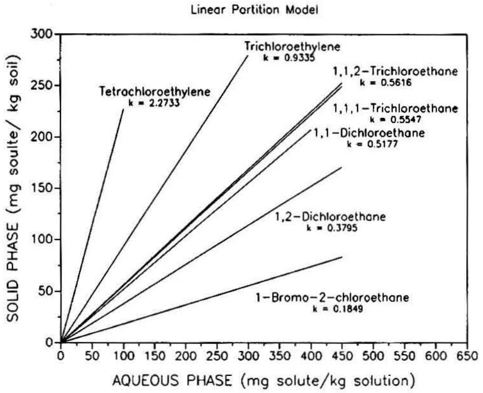

Figure 9. Adsorption of double carbon species.

large range of aqueous concentrations. The linear isotherms have partition coefficients of 0.5616 for 1,1,2-trichloroethane and 0.5547 for 1,1,1-trichloroethane, shown in Figures 7 and 8. The increased loading of both these compounds over both 1,1-dichloroethane and 1,2-dichloroethane was attributed to the additional chlorine present and thus the increased intensity of charge on the first carbon atom. However, comparison of sorption data for 1,1,1-trichloroethane and 1,1,2-trichloroethane was inconclusive.

Sorption data for all compounds is presented in Figure 9. Although specific charge data is not available for the two carbon molecules, the trend predicted by this molecule is illustrated.

CONCLUSION

Electrostatic attraction between δ^- charged clay particles and δ^+ charged carbon atoms is hypothesized to be the driving force for sorption of halogenated organic contaminants onto a sandy loam. In addition, the extent of sorption was found to be directly proportional to the molecular charge distribution on the contaminant and inversely proportional to the atomic radii of large substituents on the carbon atom.

ACKNOWLEDGMENT

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This is just one of the goals of our Global ReLeaf campaign. Can it be done? Certainly. But not without *your* support. For more information on how you can help, write Global ReLeaf, American Forestry Association, P.O. Box 2000, Dept. GR1, Washington, DC 20013.

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