ENVIRONMENTAL PROGRESS

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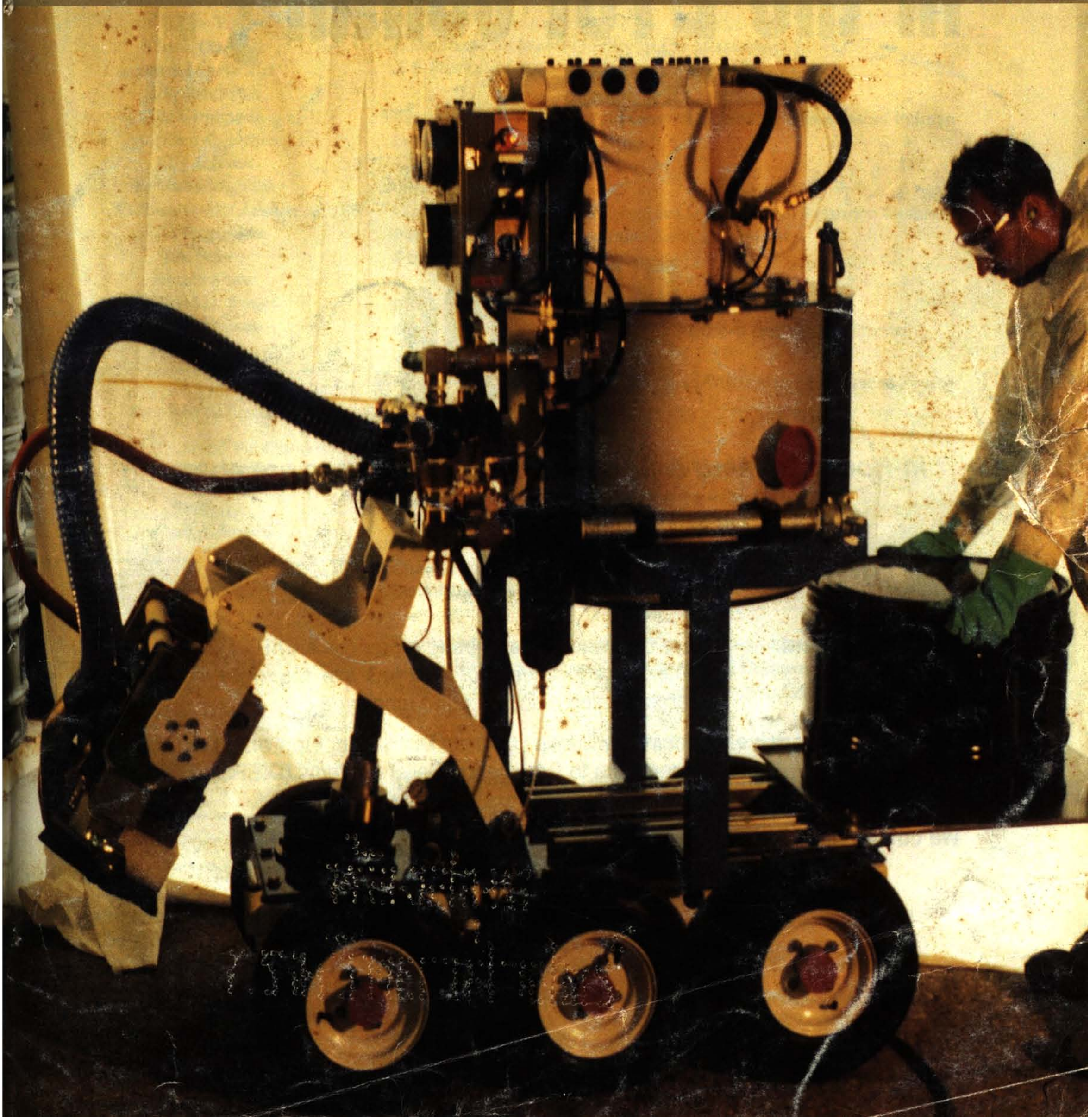

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Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multifaceted aspects of the pollution problem. It will provide thorough coverage of abatement, control, and containment of effluents and emissions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

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(419) 530-8103

Managing Editor **Maura N. Mullen**
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Manager, Technical Publications
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Cover: Pentek Moose Remote scabbler (see story on page F7) is equiped with pneumatic drum seal and a sliding drawer for a dustless drum changeout. Photo courtesy of Pentek Inc., Coraopolis, PA.

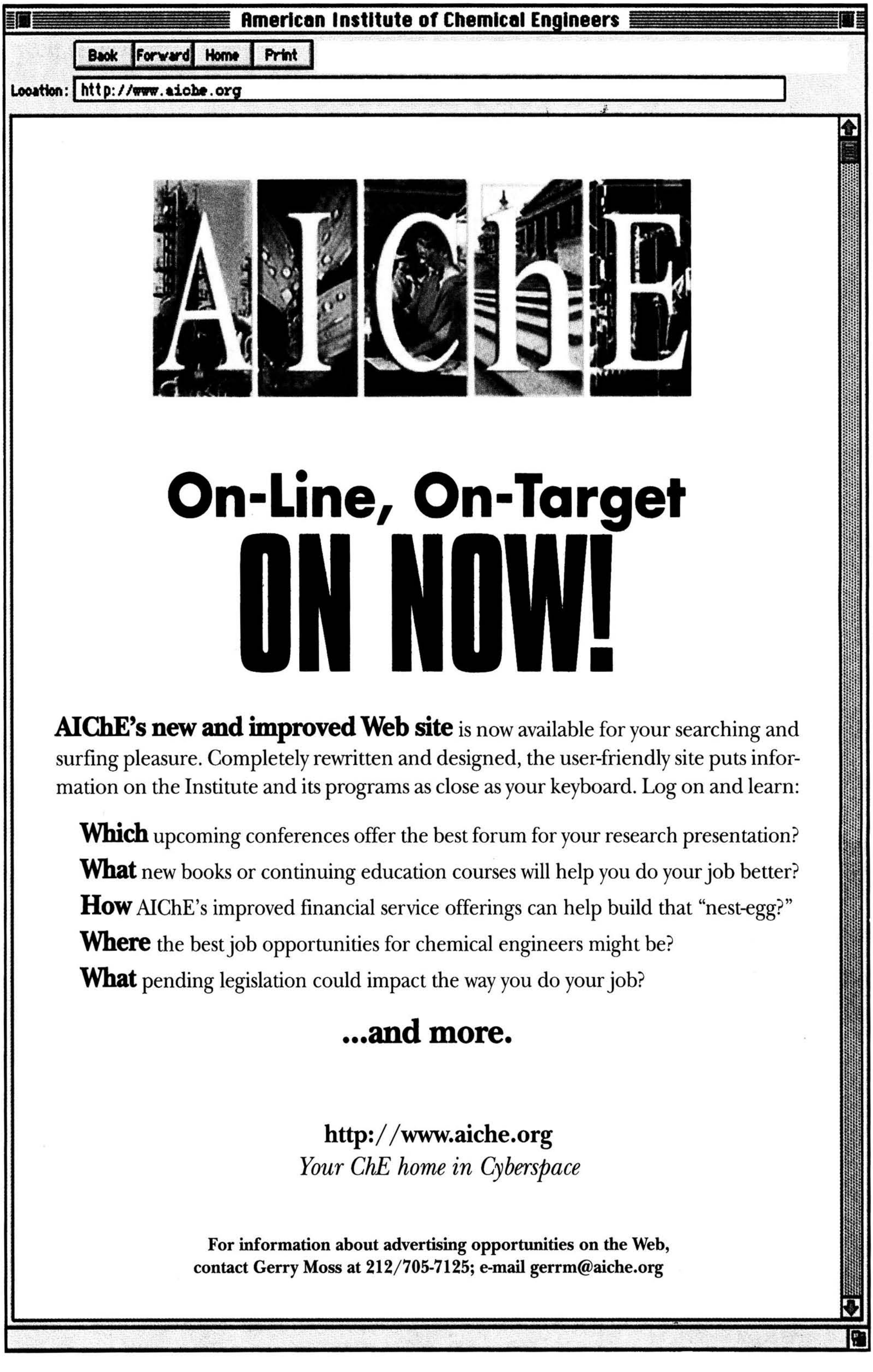
ENVIRONMENTAL PROGRESS

DEPARTMENTS

WATER

AIR

REMEDIATION



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Tapping Global Creativity to Drive Sustainable Development

Earl R. Beaver, Ph.D
Monsanto Company, St. Louis, Missouri

Still operating under conditions of relatively cheap energy, water and waste disposal, many modern corporations are beginning to understand the impact of their actions on the Earth as we are collectively perched on the verge of an ecological crisis. The traditional approach aimed at simply reducing the negative impacts of business operations cannot adequately address the approaching environmental discontinuities in the long run. This whole approach must change. Reinventing business approaches means searching out and embracing innovative business strategies unthought of just a decade ago.

Difficult problems demand innovative solutions. There is clearly a wealth of global creativity in science, technology and engineering that is yet to be tapped in the cause of accelerated environmental improvement. What is needed is the means to capture and apply this creative fountainhead to specific environmental problems that have vexed scientists and engineers for decades. The Monsanto $1 Million Challenge offers one model for tapping technological creativity.

Faced with a number of process dilemmas, Monsanto Company sought the help of the world's most gifted scientists. Through two $1 Million Challenges, Monsanto took a new step in addressing some long-standing environmental dilemmas. The $1 Million Challenges offered a major grant to the worldwide scientific community to develop cost-effective, commercially practicable technologies to separate and recover reusable chemicals from certain high volume wastewater streams.

Monsanto announced challenges in 1994 and 1995 to address separate wastewater treatment issues. The company was not facing any regulatory pressure; however, its environmental vision directs employees to "work toward the goal of zero environmental effect." It also says that we will "search worldwide for technology to reduce and eliminate waste from our operations."

Monsanto expected the $1 Million Challenge could make good on that commitment by getting the creative juices of researchers worldwide flowing to inject some fresh ideas into these nagging problems.

The first $1 Million Challenge, announced in August 1994, called for a technology to separate and recover ammonia from waste streams containing organic materials. Any breakthrough in this area is important because these mixtures contain very large volumes of potentially useful materials. Because the streams contain organics, salts and water, they are very difficult to treat.

A very real benefit would be recovery of useful materials rather than disposing of them. Such material recovery is key to realizing cyclical production processes that are more sustainable than traditional linear processes.

Likewise, the second challenge, issued in April 1996, called for a technology that would recover phosphorous acids, valuable chemical intermediates and a clean sodium chloride stream from another large volume waste water stream.

The challenges promised a win-win result - lowering treatment costs while also decreasing potential environmental effects of production processes. Additionally, because this was the first company-sponsored program of its kind and magnitude in the pollution-control arena, it has set a global precedent. This program suggests to the business world a productive mechanism for tapping public and private research.

The strong response to each of the challenges from scientists and engineers around the world and the quality of their proposals indicate that this sort of approach might be useful for accelerating the development of new technologies for other difficult pollution-control situations.

Response to both challenges was truly global, with more than 200 proposals submitted for the challenges. Monsanto received proposals from more than 20 countries ranging from Australia to Zimbabwe and from every continent except Antarctica.

Both challenges, judged by separate, independent panels, were won by SRI International, a private research, technology development and consulting firm based in Menlo Park, Ca. By winning the challenge, SRI received research contracts and $500,000 per proposal to further develop and demonstrate the effectiveness of each technology in a laboratory setting. When it is clear the technologies can be successfully applied to Monsanto manufacturing operations, Monsanto will award SRI a second $500,000 for each proposal.

Neither technology has been applied to manufacturing processes to date. The technologies are still in development and patent protection is being sought. Prospects for eventual application of all or part of the systems looks promising.

In developing the challenge, Monsanto worked closely with the Center for Waste Reduction Technologies (CWRT), an affiliate of the American Institute of Chemical Engineers (AIChE). In addition to providing and coordinating the panels of independent judges, CWRT provides a mechanism to fund "runner-up" proposals, thereby producing additional winners from the challenge.

Clearly, the cause of worldwide environmental improvement is larger than can be accomplished by any one solution or any one company. It requires that businesses and individuals think about the world in new ways. To this point in history, the global economy has operated predominantly as though nature had no limits. As the natural world has begun to reach some of those limits, it has become clear that this system is unsustainable.

A more sustainable future is only possible if everyone is willing to reinvent the way that the world does business. Realizing a sustainable world will require people to begin to think in unprecedented ways, to embrace innovative ideas, and to actively seek out and nurture creative thought. Monsanto's $1 Million Challenge is but one example of this new attitude. Movement toward sustainable development requires that this sort of innovation become a governing principle of day-to-day operations, rather than only a periodic occurrence.

***Earl R. Beaver, Ph.D**, is Director, Waste Elimination for Monsanto Company, 800 N. Lindbergh, St. Louis MO 63167. Earl is responsible for the identification, evaluation, development and application of waste elimination technology across Monsanto.*

On "Use of Ambersorb Carbonaceous Adsorbent for Removal of BTEX Compounds From Oil-Field Produced Water" by D.L.Gallup, E.G. Isacoff and D.N. Smith [*Environmental Progress*, 15, pp.197-203 (1996)]

TO THE EDITOR:

In the above study the authors look at the capabilities of activated carbon, two organoclays and several anion exchange resins of the Ambersorb type to remove BTEX compounds from reduced water. The following observations regarding the organoclays are in order:

1. We do not advocate organoclays as the primary removal mechanism for BTEX removal, unless these compounds are partitioned into oil.

2. Many case histories have shown organoclays to be an excellent material to reduce oil from water (7 times more than activated carbon, 50% of their weight).

Nonetheless, several preconditions must be observed:

1. In a laboratory study the column should ideally be 3 ft. long and 3 in. wide.

2. The flow should not exceed 5 gal/min/ft 3. The retention time must be 7-10 minutes, not 2 minutes as the authors used in their study.

4. The oil must first be de-emulsified, organoclays will not remove dissolved oil, in most cases.

5. Most of the time the oil content of the water should be less than 60 ppm, unless flow is low.

Organoclays are used as polishers, not as primary removal mechanism for oil. Had the authors used a lab column of appropriate size, with adequate retention time, the result would have been different. The organoclay should have been used after breaking the emulsion with the Magnifloc 494C. The authors state that Ambersorb can tolerate 1-2ppm of oil. That is true from a theoretical point of view. On the practical side, 1-2ppm of oil, at a flow of 200 gal/min, 24 hrs/day, 7 days/week, generates 130 lb of oil per month. Such flow rates are not uncommon at oil drilling sites. 135lb of oil can coat a resin quickly. Given the expense of such resins ($4. 00 lb) it makes sense for the operator to prepolish the water with organoclay, since frequent changeouts result in higher costs.

George Alther
President
Biomin Inc.,
P.O. Box 20028
Ferndale, MI 48220

AUTHOR'S REPLY:

In response to Mr. Alther's discussion on correct procedures for using Biomin, Inc., organoclays in our paper, we respectfully remind him that his local sales representative in California provided us with procedural recommendations. The following are our comments:

1. We were aware that organoclays extend the lifetime of granular activated carbon (GAC) by removing oil upstream therefrom. Since Ambersorb adsorbents may be attractive alternatives to GAC, we attempted to use organoclays to protect the adsorbents from pulling. While we agree that organoclays are not primarily employed for removal of BTEX, it was necessary for us to determine the extent to which organoclays affect BTEX removal to monitor the effeciency of Ambersorb adsorbents. This needed to be confirmed since our cited reference [9] (published in *Environmental Progress* in 1991) indicated that benzene is efficiently removed from water using organoclays.

2. We agree that prior studies have demonstrated that organoclays remove oil from water under certain circumstances, and as cited in reference [9], they may remove BTEX compounds. However, in our investigations, following recommendations from the sales representative, we were unable to effect high oil removal efficiencies. The organoclays removed up to 50% of the more emulsified crude oil inlaboratory and bench-scale tests. This led us to believe the filter cartridge form of the organoclays, supplied by Biomin's sales representative, would protect Ambersorb adsorbent from fouling withoil in the field demonstration tests.

3. Mr. Alther outlines how organoclays are best employed for removing oil. Although some of this information was provided to us at the time of testing , we were also informed by his sales representative that good results could be obtained (a) in smaller columns, (b) at higher flow rates, (c) at lower EBCTs, and (d) with emulsified or non-emulsified oils. As may be appreciated by these in the oil production industry, we had no control over the influent concentration of oil, nor its form. During field testing, the oil concentration and degree of emulsification varied significantly. The nature of our testing requires oil and BTEX removal processes to be flexible, to be applicable over a wide range of conditions, and to handle high flow rates. Otherwise, the process is too slow or too capital intensive to be practical.

We thank Mr. Alther for his suggestions about breaking the emulsion, polishing with organoclayand then removing BTEX with Ambersorb adsorbents. Unfortunately, we were unable to perform such a test due to time and operational constraints.

Darrel L. Gallup, Ph.D
Consulting Chemist
Unocal Corporation
1300 North Dutton Avenue
Santa Rosa, CA 95403

PANEL REVISITS AMUNDSON REPORT

Leading chemical engineers from academia and industry convened last June at Northwestern University, to revisit the groundbreaking report spearheaded by Dr. Neal Amundson in 1978 entitled "Frontiers in Chemical Engineering: Research Needs and Opportunities." Dr. Julio M. Ottono, the symposium organizer said "the report had a tremendous influence on funding policy and the way chemical engineering departments went about hiring faculty." The symposium focused on the significance of the Amundson report today, and how it will affect issues facing chemical engineers in the future. The primary issues considered by the panel were chemical engineering education, and cooperative partnership between industry and academia.

According to Dr. William Schowalter, Dean of the College of Engineering at the University of Illinois at Urbana-Champaign "chemical engineering has probably remained the most homogenous in its educational scope...The relative 'clubbiness' of our field has come at a price...Our curricula are still focused primarily on the chemical process industry, even though our graduates are entering an increasingly broad spectrum of industries. The disconnect between the education we provide and the actual and potential customers we serve can have serious undesirable consequences for the future of our profession. What is needed, he added, "is a professoriate more aligned with the range of possibilities inherent in our subject. When this happens, our faculties will again define the applications and products of the future, rather than react to them."

Professor Morton Denn, of the Department of Chemical Engineering, University of California at Berkeley, is concerned about the "shrinking core" of chemical engineering. He noted that "new areas of application put pressure on the core curriculum at the graduate level, as students increasingly need to study topics in basic science which are not part of the traditional core." He said he is particularly concerned "by the poor preparation in mass transfer which seems to have become universal in American chemical engineering programs; mass transfer is increasingly taught as an ajunct to heat transfer in the undergraduate curriculum, and rarely taught at all in the graduate curriculum."

On the other hand, Dr. David Tirrell of the Department of Polymer Science and Engineering of the University of Massachusetts at Amherst, said " advances in chemistry, biology, materials science and computational technology have provided new insights into the behavior of molecular systems and powerful new tools for manipulation and control of chemical reactions, cellular processes and materials properties. He asks, "What does this mean for chemical engineering? At the very least," he added, "it means that chemical engineers must be willing to venture farther than ever before from the traditional center of their discipline in order to acquire sufficient knowledge of the systems to which their methods can be applied most productively."

Nonetheless, Matthew Tirrell, Head of the Department of Chemical Engineering and Materials Science of the University of Minnesota said "The opportunities for chemical engineers entering the materials processing area have never been better. This is particularly true in electronic materials processing and in the emerging field of soft materials engineering." He added, "To educate a generation of chemical engineers optimally prepared to advance modern materials processing, the intimate connection with real materials science, and scientists during the education of chemical engineers is indispensable."

The education of chemical engineers for the last half century "has been a cooperative partnership between academia and industry" according to Dr. James Wei, Dean of Engineering at Princeton University. "The universities concentrated on teaching the fundamentals of mathematics, physics and chemistry; on the core subjects of thermodynamics, kinetics and transport illustrated by practical applications; and on giving a liberal education suitable for future leaders of society....The leading industries teach the new graduates the particular technologies that they engage in, such as oil refining and polymer processing, and the professional practices of engineering." He feels, however, that "this compact on engineering education is in serious jeopardy, if not totally broken. The downsizing of corporate research and engineering staff often means that the senior engineers who are the keepers of the flame in corporate technology, and who can be mentors to new college graduates, are either downsized or kept too busy to educate the fledging new engineers....The companies are talking about hiring graduates who can 'hit the ground running.' This could mean that the education of future engineers will stop at the academic side, just like MD's who know about anatomy and biochemistry, but have not done internships with experienced brain surgeons." Dr. Wei added that "we are in need of a forum and serious discussion on this matter."

James A. Trainham , Director Dacron Technology at E.I. DuPont de Nemours Company went on to say "The chemical industry is facing a large number of major challenges. These are challenges we look to chemical engineers to help us solve.... After decades of explosive growth, during the last ten years, the chemical industry as a whole is fairly stagnant....Margins have eroded and profitability is at the mercy of the gross world product...The mid-century growth of the chemical industry was essentially driven by one major chemistry breakthrough - synthetic polymers - a truly new class of materials - and the developed technologies that created a multi-billion dollar global industry." He added, "Growth in the next century will be driven by biotechnology, electrochemistry, our ability to model and simulate nature's processes, and out ability to measure key process parameters and use those measurements to control our manufacturing processes."

"Today's researchers have more linkage to product, work in cross-functional teams, and are closely accountable to those who provide their funding," according to Dr. Kathleen C. Taylor of General Motors Research and Development Center. "Their tools are increasingly computer-oriented as they exploit computer simulation for the design of new products and processes." Her advice to the chemical engineering student of today is "develop intellectual skills for lifelong learning - your current skills will be outdated in two years."

IChemE PIONEERS ONLINE ENVIRONMENTAL CONFERENCE

An Environmental Conference, sponsored by the Institution of Chemical Engineers of Great Britain (IChemE), will be held over two weeks, from November 3 through November 16, 1997. Environment97 may be the first environmental conference to be held entirely over the internet according to the *SEJ Journal*.

More than 150 technical and general papers will be presented dealing with subjects from climate change and urban air quality to pollution prevention and the future of wind power. Each keynote paper will have a corresponding online discussion group. There will be audio interviews with 10 environmental experts on future developments in environmental protection.

All of the conference proceedings will be free and will be online at the Environment97 web site: http://www.environment97.org.

EPA PROPOSES TIGHTER BOILER EMISSIONS STANDARDS

Under the new source performance standards of the Clean Air Act, the Environmental Protection Agency (EPA) is required to set emissions standards for new facilities inc ertain industrial categories. Recently, the EPA proposed tighter emissions standards for nitrogen oxides from new electric utility boilers to industrial boilers. The proposal is expected to become a final rule by September 1998. Seventeen utility boilers and about 380 new industrial boilers are planned for construction over the next five years according to the Environmental News Service.

The EPA last revised the new source performance standard for NOx from utility boilers in 1986. The proposed limits would reduce the projected growth in NOx emissions by approximately 42 percent from current levels.

INTERNATIONAL ENVIRONMENTAL AUDITING GROUP ESTABLISHED

A new association has formed to represent companies engaged in environmental auditing. The International Environmental Auditing Association hopes to unite both camps of environmental auditors: those based on the ISO 14000 series of environmental management systems and ISO9000 quality management systems; as well as those "technical auditors" who are also involved with compliance, site assessment, waste and pollution prevention, plus due dilligence environmental audits. The group, which has members from the U.S. and Canada, Turkey, Argentina and the Pacific Basin, will be headquartered in Zurich, Switzerland.

EPA AND CMA TO CONDUCT JOINT COMPLIANCE SURVEY

The Environmental Protection Agency (EPA) and the Chemical Manufacturers Association (CMA) have joined in a project to determine why chemical companies fail to comply with environmental laws such as TSCA and RCRA. The CMA/EPA survey, to be mailed to approximately 40 companies in September, is expected to yield written comments that EPA will use to determine whether the times and costs estimated for filing mandatory reports plus gathering the associated information are reasonable.

For more information please contact Sandy Farmer at EPA (202)260-2740 or Christing Franz at CMA (703) 741-5176.

EPA CONTEMPLATES REVISIONS TO CLEAN AIR ACT REQUIREMENTS

The Environmental Protection Agency (EPA) is considering revising its Clean Air Act risk management plan requirements under section (112r). A ruling to ease the reporting burden for certain facilities, such as public warehouses, and batch processors, is being considered. The agency is contemplating permitting companies to make "predictive filings" for chemicals based on its history and information from its customers but no implementation date has been specified.

Currently, all covered facilities are required to submit a risk management plan to EPA by June 21, 1999 for all processes that use more than a threshold amount of regulated substance.

SCABBLING ROBOT ACHIEVES DUSTLESS DECONTAMINATION

Pentek'a MOOSE scabbling robot (shown on the cover of this isssue) was recently leased along with a trained operatior, to remediate radiologically contaminated concrete floors at a Columbus-based nuclear research laboratory where Department of Energy (DOE) work had been conducted. The floors - 14,600 square feet ($1300m^2$) in total - were in two former metallurgical process buildings.

Areas in a former machine shop were covered with an adhesive tar residue that increased the difficulty of the project. The owner's operations manager said they had tried several methods - solvents, scraping, vacuum blasting - to remove the residue and concluded that the MOOSE was the most effective system for cleaning a large area in a single pass.

A remote scabbler, the MOOSE, removed contaminated concrete to the required depth with pneumatically-driven tungsten carbide-tipped bits and deposited waste into an integral collection drum. The process completely contains airborne particulates within an evacuated shroud. Therefore regular activities were able to proceed normally in other areas of the building while the decontamination was taking place.

For more information, please contact Pentek Inc., 1026 Fourth Avenue, Coraopolis, PA 15108; telephone (412) 262-0726 • FAX (412) 262-0731; e-mail: pentekusa@aol.com.

EPA COMPLIES WITH WORLD TRADE ORGANIZATION RULING

The Environmental Protection Agency (EPA) recently changed its ruling on imported gasoline in compliance with a ruling by a WTO (World Trade Organization) panel won by Venezuela and Brasil according to an Environmental News Service report. The two oil-exporting countries had challenged the different treatment EPA gave domestically refined oil in contrast to imported refined oil.

In 1990, the EPA assigned each domestic refiner an "individual base line" based on the volume and quality produced by that refiner. The refiner is required to produce gasoline no dirtier than the base line. All imported gasoline was assigned an average base line, called the "statutory base line" thus placing the responsibility on the U.S. importers to assure that the gasoline they imported was not dirtier than the statutory base line.

A foreign refiner can petition the EPA to establish an individual base line for it under the new ruling. If the EPA approves, then the foreign refiner must supply the same kind of evidence, the same quality of modeling, and the same quality of test data as domestic refiners.

Under the ruling domestic refiners test the gasoline just once, at the refinery gate prior to shipment. Foreign refiners having individual base lines must test the gasoline at the point it is loaded on ship and again at the point where it is discharged in the United States to assure that cleaner fuel is not switched or mixed with dirtier fuel in transit.

DIPPR TO ISSUE ENVIRONMENTAL SOFTWARE

AIChE's Design Institute for Physical Property Data (DIPPR®) will shortly release a new software entitled *AIChE/DIPPR Project 911 Environmental, Safety and Health Software, Version 2.3.* The software consists of critical environmental, safety, and health data for 283 regulated chemicals - including these found on the 1990 Clean Air Act Ammendments, OSHA process Safety Management, and EPA Risk Management lists, along with a selection of chemicals of interest to individual project sponsors.

Chemicals can be searched by name. synonm, CAS number, or family group. Users can customize the units in which the data is displayed, and can select from three reporter formats or, for temperature-dependent properties, graphs of the property over the temperature range.

For more information please call AIChE at (212) 705-7332

AIChE OFFERS COURSE ON WASTEWATER TREATMENT

AIChE is offering a course on Advanced Wastewater Treatment to take place in Los Angeles on November 18, and 19, 1997 and New Orleans on March 8, and 9, 1998. The course is designed for plant managers, project engineers, environmental managers and consulting engineers. A basic knowledge of wastewater principles is required.

Attendees will learn how to implement innovative wastewater treatment schemes in order to meet water quality requirements imposed by Federal and State legislation; apply physical-chemical methods in conjunction with biological treatment; become familiar with various applicable technologies which may be integrated into or added onto in order to treat contaminants; and review key concepts including design criteria, waste minimization and product life cycle analysis.

The fee is $845 for AIChE members and $945 for non-members. Formore information,or to register, please contact the AIChE*xpress* Service Centerat 1-800-242-4363; fax: (212) 705-8400; e-mail: xpress@aiche.org.

November 16-21, 1997

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- Separation Science and Technologies—42 sessions

SPECIAL EVENTS INCLUDING:

- **Fifty-Ninth Institute Lecture** Wednesday, November 19 - 11:45 AM - 12:45 PM
  Dr. Rutherford "Gus" Aris, University of Minnesota, will speak on a topic familiar to all chemical engineers - fudge factors. The title of his address is "A Fine Flurry of Fudge Factors and other Felicities of the Chemical Engineering Craft."
- **Professional Progress Award Lecture** Tuesday, November 18 - 11:45 AM - 12:45 PM
  This year's award lecture will be presented by Robert A. Brown, Dean of the School of Chemical Engineering, MIT
- **Graduate School Fair, Career Skills Help Sessions,** November 15 - 17
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ENVIRONMENTAL MODELING: FATE AND TRANSPORT OF POLLUTANTS IN WATER, AIR, AND SOIL

Jerald L. Schnoor, John A. Wiley & Sons, Inc., New York, NY, (1996),682 Pages, [ISBN No.: 0-471-12436-2], U.S. List Price: $69.95

As is often the case, this book has positive and some negative features. The primary negative feature is the title as the book is primarily concerned with crucial water quality areas. For example, very little is said about soil until Chapter 8.7, commencing on page 443. Chapter 9, on Groundwater, devotes much space to soil and related geohydrology. Tables 9.1 and 9.2 are especially useful to the non-geologist. Air is not addressed until Chapters 10 and 11. The material in these chapters is worthwhile but does not include information on micrometeorological (atmospheric boundary layer) processes, convective atmospheric transport, and dispersion/diffusion of stack emissions. In short, the air section does not address issues important to those responsible for compliance with primary air pollutant emission standards and NESHAP requirements. The fact that the book deals primarily with "crucial water quality areas" is reason enough to have it available as an environmental library resource.

More important to communication with the potential audience, the book is not too tightly focused on Environmental Modeling. The impression created by the title is that the book is an expansion on the numerous simulations and mathematical models of physical hydrologic processes, complete with floppy discs, that have appeared in book form. It appeared to offer expansion of existing models with species transport and chemical and physical chemical reaction and retention processes. It does this in a minor way. The book is primarily a compilation of important scientific and engineering fundamentals, together with the basic differential equations that describe Fate and Transport. The book is far more important than the title suggests.

Editing is casual; this weakness is distracting to the reader. The substitution of "ground water" for "groundwater" occurred about five years ago. The use of the incorrect form in a chapter title and repeated use in the text imply a feeling of disinterest on the part of the Editor and the Publisher. On a similar note, the artwork is of uneven quality. This is especially obvious in the figures that face each other on pages 152 and 153. Figure 4.3 is well done and Figure 4.4 is poorly executed; note, however, both figures were derived from books produced by the publisher of the subject book. A few pages further, Figure 4.11 on page 172 presented material comparable to that described in these other texts and is not of comparable (or adequate) quality.

The lengthy initial commentary on the inappropriate title follows from a great concern that the merits of a fine text are not communicated effectively to potential user communities. Subject book has great value, especially to chemical engineers. Dr. Schnoor reiterates the fundamentals of chemistry, chemical thermodynamics, reaction and sorption kinetics, and transport phenomena. These subjects are the backbone of undergraduate chemical engineering education. The profession is well trained in these areas of science. However, the book goes much further; it builds a bridge between basic science and the use of knowledge in the solution of environmental problems. The reader is educated to the jargon and techniques for analyses of the fate of wastes and wastewaters discharged to aquatic media, i.e., the receiving of waters of traditional sanitary engineering.

There are two large and eager communities ready for the subject text: chemical engineers with an interest in environmental issues and/or responsibility for compliance with regulations for discharges to the environment, specifically NPDES permits, and environmental scientists with concerns for fundamental chemical and microbial sciences and engineering principles.

Numerous examples are clear and detailed; these are at the core of demonstrations of methods for applications of fundamentals to the solution of practical environmental problems. This might be referred to as Process Design on an Environmental or Global Scale. The Streeter-Phelps equation and applications to the determination of acceptable stream loads and stream recovery processes, lake and reservoir eutrophication and reaeration processes, and interactions between contaminants and soil and ground water or aquifer systems are discussed within the context of basic science, mass balances, and rate relationships. Systems of differential equations are invoked to illustrate the systems-approach to problem formulation and solution. Modeling is a means of illustrating and analyzing issues, and is not an end unto itself.

Many typical problems are open-ended, i.e., possible solutions may be relatively obvious but no simple, unique solution is available. The reader or user is invited to ponder the problem; alternative selections of assumptions and methodologies may lead to different outcomes. The practice assignments are an area that requires thought and innovation.

This book is a welcome addition to the environmental literature. It is an important new resource for the environmental engineer and the environmental engineering bookshelf.

Robert C. Ahlert, Ph.D., P.E.
Distinguished Professor Emeritus
Chemical & Biochemical Engineering
RAMS Environmental Consulting, Inc.
P.O. Box 1982
Ormond Beach, FL 32175

EPA ENVIRONMENTAL ASSESSMENT SOURCEBOOK

J.Russell Boulding, Ann Arbor Press, Inc., Chelsea, MI, (1996), 386 Pages [ISBN No.: 1-57504-009-3],U.S. List Price: $69.95

J. Russell Boulding selected an assortment of Environmental Research Briefs and Groundwater Issue Papers from the U.S. EPA National Research Laboratories and put them in a book called EPA Environmental Assessment Sourcebook. Part 1 addresses contaminant behavior, transport processes, and modeling. It includes chapters on contaminant sorption, behavior of metals in soils, nonaqueous phase liquids, facilitated transport, reductive dehalogenation of organic compounds, and fundamentals of groundwater modeling. Part 2 deals with site characterization and monitoring, including specific chapters on measuring water depth, conducting pump tests, soil and groundwater sampling, and the importance of colloidal materials in sampling. Boulding, who took the time to make minor editorial corrections, including updated references and adding current affiliations of the authors, defends his selections noting that "many papers have become classics" and others are identified as "ground-breaking chapters... [that] have stood the test of time." That description is overzealous because the oldest paper here was first published in 1989; most of the papers were only four or five years old when this collection was published. However, the field is relatively new and there are some papers here that could become classics. Until then, I agree with the suggestion in the editor's overview that this collection should be a useful reference dealing with the broad area of site investigations.

My criticisms of this volume are relatively minor. For example, the preface says there are 20 papers included, in his overview the editor states there are 22 chapters, I count 19 chapters (not including the editor's overview), and in the chapter on "Ground Water Sampling for Metals Analysis", the reader is referred to an nonexistent Chapter 23. In addition, a heavier hand by the editor would have made the reading smoother. A couple of irritating grammatical uses show up a little too often. Some of us — who are probably standing in the way of the natural evolution of language — still believe the verb "to impact" means "to strike together", not "to influence". Several of the authors also invoke a passive sentence structure where phrases such as "It is recommended that..." or "It has been suggested that..." leave the reader pondering who made the recommendations or suggestions and why.

My biggest complaint, which is intrinsic to a collection of works by different authors, stems from the uneven level of content that the reader encounters moving from chapter to chapter. In a chapter on "Facilitated Transport", Huling note that "...complexation varies with the nature of [the] metal ion...", which is true, but not particularly helpful. In their chapter on "Fundamentals of Ground-Water Modeling, Bear, Beljin, and Ross discuss the application of two dimensional models for describing regional flow. In one paragraph, they note that "The error introduced by this assumption is small in most cases of practical interest." Three short paragraphs down on the same page, they caution that "When considering contaminant transport in aquifers, the model user must be cautious in attempting to utilize a two-dimensional model, because in most cases the hydraulic approach is not justified." Rawe and Hartley have a short chapter entitled "Technology Preselection Data Requirements" that skips lightly over a series of definitions of terms that can be used to characterize soil and water contamination at a site. The authors note, for example, that "Dissolved metals may be found at non-toxic levels or levels exceeded drinking water standards.", and that "Even low-solubility organics may be present at low concentrations dissolved in water." In a chapter entitled "Behavior of Metals in Soils", McLean and Bledsoe state that "Immobilization of metals, by mechanisms of adsorption ...will prevent movement of metals to ground water." Because they use the standard definition of adsorption (accumulation of ions at an interface), adsorption will retard but not prevent movement. In the same paper, the authors state that "A measure of the redox potential ...indicates whether the metals are in an oxidized or reduced state." There is, however, little discussion of how difficult it can be to measure redox potentials in natural aquatic environments. But these are all minor issues, many of which stand out only because they are in contrast to their surroundings.

The Sourcebook is at its best in papers where authors provide a critical review of a specific topic that is focused and documented with useful references. For example, Brusseau's chapter on "Complex Mixtures and Groundwater Quality" includes a critical literature review and discussion of how contaminant behavior can be influenced by complex mixtures, what to be aware of, and suggestions for areas of research. Sims, Sulflita, and Russell authored a chapter on "Reductive Dehalogenation of Organic Contaminants in Soils and Ground Water"; it is also thorough, well-organized, and includes good references. Part 2 is full of practical information on sampling and sources of error, contaminant interaction with well casing materials, and potential problems associated with colloidal transport. Osborne's chapter on "Suggested Operating Procedures for Aquifer Pumping Tests", for example, is a how-to manual for conducting aquifer pump tests, complete with an example and a typical field data sheet. (I am curious, however, why this chapter includes a warning that although a portable PC is handy for graphical evaluation, it is not a substitute for a manual-plot of the data).

In summary, Boulding's EPA Environmental Assessment Sourcebook is a conveniently organized collection of recent papers from EPA National Laboratories, providing a useful reference for people working with site characterization and site assessment. The material covers a broad range, from contaminant transport to site characterization and the potential pitfalls of trying to obtain a representative description of subsurface environments. I recommend this book as a useful reference for anyone working in this area.

Paul R. Anderson, Ph.D
Associate Professor of
Environmental Engineering
Department of Chemical and
Environmental Engineering
Illinois Institute of Technology
10 West 33rd Street
Chicago, IL 60616

WASTE MINIMIZATION AS A STRATEGIC WEAPON

David F. Ciambrone, CRC Press, Inc., Boca Raton, FL, (1996), 262 Pages, [ISBN No.: 1-56670-135-X],U.S. List Price: $65.00

The book has as its goal to provide a company with the tools necessary to implement the environmental resources management (ERM) program at their facility. This book contains ten chapters and seven appendices. The book is divided into two sections. The first section on ERM contains eight chapters. The second section containing two chapters addresses environmental audit introduction.

Chapter 1 provides an introduction describing pollution prevention trends in industry and government agencies and a description of the ERM program. Chapter 2 describe the waste minimization concept, management involvement, waste minimization programs, training, implementation concepts for management, and total quality management and just-in-time manufacturing as they relate to ERM. Chapter 3 describes design for the environment, giving the rationale involved, design for assembly and environmental concepts, development of environmental indices for materials and processes, and life cycle analysis. The fourth chapter addresses the environmentally responsible factory process. This chapter describes various waste minimization programs, systems approaches (addressing site characteristics, chemical consumption determination, hazardous index development, prioritization, process evaluation, and recommendations/implementation). This chapter also describes the EPA approach in developing waste minimization programs, and describes steps for implementation.

Solid waste management is addressed in the fifth chapter, and includes a discussion on sampling plans and procedures and identifying markets for recyclables. Chapter 6 discusses total quality management and the environmental factory process, including the steps involved for getting started. Chapter 7 addresses synchronous manufacturing and the environmental factory process and includes a discussion for setting up such a program. The next chapter describes "the green company".

Section 2 on environmental audits begins with a chapter on the facility compliance audit. An excellent discussion is presented on the preaudit activities, including the audit team selection, audit notification, the audit plan, regulatory review and update, developing the preaudit questionnaire and the checklists, and preparing for an audit. This is followed by a discussion on on-site audit activities, addressing record and document review, conducting staff interviews, facility inspections, and the exit debriefing. Included among the post-audit activities is the development of the audit report. The last chapter addresses the environmental management system audit. Included in the chapter are government guidelines for the U.S. EPA, the Department of Justice, and the U.S. Sentencing Commission.

The seven appendices include the following topics: (1) Examples of lesson plans for total quality manufacturing/synchronous manufacturing, (2) Waste minimization worksheet examples, (3) Assessment overview, (4) California self-audit checklist, (5) Self-audit format example for the printing industry), (6) Effectiveness of inspection demonstration, and (7) Example of a chemical approval form.

In summary, the book achieves its goal of describing the steps and tools required to implement the ERM program at a facility. The book is a worthwhile addition to the reference library for environmental and regulatory personnel involved in pollution prevention activities.

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

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Introduction to WWW.ISO14001.COM

Rishi Kumar.
Ontario Hydro, Toronto, Ontario, Canada M8Z5S4
and
Ashok Kumar
Department of Civil Engineering, University of Toledo, Toledo, OH 43606

INTRODUCTION

For the past three years, the International Organization of Standardization (ISO) has been developing a series of voluntary environmental standards that are likely to have a significant impact upon companies around the world in the years to come [1,2,3].

ISO 14000 series is a set of international voluntary standards recognized by major trading nations and trade regulating organizations such as GATT and World Trade Organization. It is not a law in the sense that no one is required to register (hence it is voluntary). However, no one has to do business with you, buy your products and services, or let your products and services into the other country if they have declared ISO 14000 registration a requirement for doing business with them or in their country. It is expected that many foreign trading partners will require registration by import manufacturers. This is a recognized legal trade barrier under international treaty. It is likely that registration will influence the enforcement stance of environmental regulators, and will likely influence insurance rates and lender practices.

The ISO 14001 standard is designed to assist organizations in implementing and maintaining an environmental management system (EMS), verifying conformance with their environmental policies and objectives and demonstrating such conformance to other organizations via certification by a third party or via self-declaration. While ISO 14001 specifies the essential elements of environmental management systems, it does not set required levels of environmental performance. On the other hand, the ISO 14001 standard is sufficiently vague to enable the standard to accommodate most business enterprises. A purpose behind the standard is cleaner production throughout the world.

The purpose of this paper is to introduce available information on the Internet. Over 1000 sites were visited to prepare this review. The information is outlined in two separate sections. The first section includes the sites which may provide required information on ISO 14001 and how to get registered and the second section sites are related to training and books on ISO14000.

ISO 14001 SITES

This section provides an overview of 36 useful sites for your work. E-mail addresses are given, if available.

Web site: www.aetsittc.com/iso13.htm
E-mail: ehornback@aetsitte.com

The site provides an update on the status of the ISO 14000/EMS implementation. The latest round of international voting is complete for the ISO 14001 environmental management system and its guidance document (ISO 14004), and the vote almost unanimous. Along with the environmental auditing standards (ISO 14010-12), the EMS Specifications and Guidance documents have now entered the final voting stage and will probably be published as final standards by the end of 1997. The site also provides information on AETS courses related to environmental management system auditor training.

Web site:
www.quality.org/ISO14000/index.html

This site provides detailed information on specific elements of ISO 14000 (such as, general guidelines on principles, systems and supporting techniques, auditing, etc.) and is presented in a column format. Information on interpretation of the standard's intent by section and the insight on auditing of environmental management system are outlined on this page.

Web sites:
www.realtools.com/fast/env/main.html
www.realtools.com/env/main.html
www.us.tuv.com/services/iso14000.html

These sites provide an overview of ISO 14000 Environmental Management System and describe how ISO 14000 can be used as a tool to create a fully integrated environmental management system to preserve the environment in your local communities and around the world.

Web site: www.conformance.co.uk/env
Email:environment@conformance.co.uk

Conformance, based in UK, provides a range of environmental consulting work, particularly in environmental management system. This web site is your guide to provide you details on, how Conformance can assist you to obtain 14001 registration, what is ISO 14001, how does ISO 14001 work, what is in it for my business, and more.

Website:www.greenware.ca/software/emp.htm
E-mail: greeninfo@greenware.ca

The site provides information on environmental information system, consulting and education/training. Details on variety of ISO 14000 software worksheets, such as environmental aspects and impacts, identification of legal and other requirements, objectives and targets, training program (s), emergency response procedures, monitoring of performance, etc. can be viewed on this site.

Website: www.isocenter.com/

From this site you can browse through a selection of material on ISO 14000, including certification requirements, specific information on ISO standards and recommendations on how you can implement quality and environmental management systems. This web site is developed by SCS Engineers and ETI Corporation.

Web site: www.edutec.ch/eiso.htm

The site provides useful information on how a company can introduce a successful management of environmental issues, and what the "environmental management system ISO 14001" is all about. The site offers you global solutions (computer based) and it can assist you with part of a project, be it counseling, project-management, screen designing, layout, storyboarding, digitalization, programming, installation, or training.

Website: www.swh.co.uk
E-mail: car@swh.co.uk

The site provides information on environmental management and how small and medium-sized businesses can register for ISO 14001. The company has developed a package to cover the implementation of a combined environmental and quality management system. This is an "off the shelf" system which can be fine-tuned as required.

Web site:
www.gasweb.org/gasweb/iso14000/intro.htm

An EMS is a part of the organization's overall management structure, which addresses the immediate and long-term impact that its products, services and operations have on the environment. Like the popular ISO 9000 quality management standards, the ISO 14001 environmental management system standard outlines a generic management system approach to an organization's operations.

Web site: www.bailey.ca/systems/eims.htm

This page is full of very interesting information related to ISO 14001. Information on environmental information management systems (EIMS) and emergency response, and environmental solutions and services are outlined on this web site. In order to maximize customer benefit, integration of technologies (ISO 14001 environmental regulatory requirements), with advanced application and services, such as product quality, safety, and productivity can be viewed on this site.

Web site: www.trst.com/iso1.htm
E-mail: haklik@trst.com

The site provides details on the benefits of an Environmental Management System registration ISO 14000 and is organized into categories such as (a) increased profits, (b) regulatory compliance, (c) marketing, and (d) operations.

Web site: www.trst.com/iso2.htm
E-mail: haklik@trst.com

The keys to success with ISO 14000 and Environmental Management System are compiled on this page.

Web site: www.trst.com/iso3.htm
E-mail: haklik@trst.com

This web site shares the benefits of implementing ISO 14000. This page features cases, stories and examples describing actual benefits from ISO 14000, environmental programs, and environmental management systems.

Web site: www.csa.ca/9-t.htm

The page outlines the listing of ISO 14000 and other quality system documents/standards, price and how to obtain them. Information on certification, testing and QMI - management system registration training is also available on this site.

Web site:
www.thurbergroup.com/audit.htm

The site provides information on how 'Thurber Environmental Consultants Ltd.' can assist you in performing environmental auditing in compliance with ISO 14001 environmental management systems requirements. Variety of professional services provided by this company in environmental and geo-technical areas are listed on this web site.

Web site:
www.quality.co.uk/quality/ecoadvic.htm
E-mail: help@quality.co.uk

This page provides an introduction to Environmental Management Systems and provides details on how your company can benefit by obtaining a registration for ISO 14001. Information on European Eco-Management & Audit scheme (EMAS), environmental auditors, and sustainable development can be obtained from this site.

Web site:
www.lilly.com/environment/envmgt.htm

Information on environmental performance review, environmental quality system, ISO 14000 audit program & compliance, emergency response, waste minimization and recycling is provided on this web site. The information can assist you in 'how to conduct an internal evaluation of your operations in compliance with environmental regulations, permits, and your own company policies'.

Web site:
www.smartsolutions.com/ssisso.htm

This site provides a variety of information related to ISO 14001 Environmental Management System. A list of services available to companies interested in getting certification for ISO 14001 are outlined on the web site. Information on Environmental Management Standard (EMS) groups of documents is also included on this site.

Web site:
www.gza.net/iso14000/iso14000.htm

The page reviews the importance of ISO 14000 and emphasizes that the ISO 14000 provides elements of an effective environmental management system, while integrating other management functions, to assist organizations with achieving environmental and financial goals. ISO 14000 advisory and consulting services, environmental management system development and implementation offered by GZA, to help you to meet your environmental management needs, are also outlined on this site.

Web site: www.gr-tech.com/iso14000.htm

The page provides information on ISO 14000 series of standards in a way, which may enable an organization to formulate an environmental policy and objectives taking into account legislation requirements and information with significant environmental impact. The discussion that if a company establishes an environmental management system, will probably depend on its current and targeted markets and on the environmental requirements is explained on this web site.

Website: qualitymag.com/0197fl.html

The page describes how a company can integrate both environmental-management-system (ISO 14000) and quality-management-system (ISO 9000) criteria into one set of procedures.

Web site: www.stoller.com/iso.htm
E-mail: Jholst@stoller.com

This is one of the sites, which can get you all sorts of details on ISO 14000. Information such as: so what is ISO 14000 anyway, what is ISO 14000 and what can it do for you, get ready for ISO 14000, and ISO 14000 Standards overview and description, can help you to develop environmental management system for your company. Information on ISO 14000 and the next generation of environmental protection tools provided on this page can assist you to prepare for future. Series of papers related to ISO 14000 are also given on this site.

Web site:
www.web.apc.org/ecoeco/iso14000.htm

Information on ISO 14000 Environmental Management Series and the steps to implement ISO 14001 is explained on this web site. The page also outlines the other issues related to environmental management system and the implications for management.

Web site: www.eaest.com/iso.html
E-mail: info@eaest.com

The page outlines the services, which EA Engineering can provide you to obtain ISO 14001 registration. The company's unique experience gained on diverse environmental audits, compliance, and EMS projects is listed on this web site.

Web site:
www.ercweb.com/BCDEC95.HTM

Beyond Compliance, a quarterly newsletter published by Environmental Resource Center is provided on this site. The newsletter publishes information on issues of regulatory importance related to environment management systems, waste management, and other topics. Information on "getting started on the ISO 14001 certification process" is also provided on this site.

Web site:
www.scc.ca/iso14000/infobref.html

This site provides reasons why companies should look into registering for ISO 14001 Environmental Management System. Some of the reasons outlined on this page are reduction of liability/risk, improvements in the company's image in the area of environmental performance and compliance.

Web sites: www.systemcorp.com/c/ and
www.interlex.com/

These two sites provide information on ISO 14000, ISO 14001 software (project management, business process improvement, best practices and management solutions) and how to obtain them. ALG System Corporation's software is produced on CD-ROM. Software on other quality systems (e.g.: QS 9000) is available on Interlex Technologies site.

Web sites:
194.177.160.201/standards/iso/14001/q1.htm
194.177.160.201/standards/iso/14001/q2.htm
194.177.160.201/standards/iso/14001/q3.htm
194.177.160.201/standards/iso/14001/q4.htm
194.177.160.201/standards/iso/14001/summary.htm

These five sites will be of interest to those who are considering implementing ISO 14001 Environmental Management System at their companies. These sites discuss in great length the so-called "five public policy questions for proponents of the ISO 14000 series.

Web site:
home.sportsite.com/sgma/international/environment/

If you are looking for information or research on environmental issues and programs concerning the sporting goods industry, this site can provide you useful information.

SITES FOR TRAINING/BOOKS

The following 17 sites provide information pertaining to training and books.

Web site: www.pncl.co.uk/mmi/

Services include inspection, expediting, procurement (purchasing), technical personnel recruitment, training (Lead Assessor, Internal Auditor, and Environmental Auditor), and a unique distance learning/home study course.

Web site:
home.inforamp.net/~qmi/courses/ems_lead.htm

The two day workshop on "ISO 14001-Environmental Management System Essentials", will give you the methods for auditing against ISO 14001 standard, and with the pre-requisites, provide you with the required skills and knowledge required for certification as an Environmental Auditor.

Web sites:
csf.colorado.edu/lists/elan/jan97/0010.html-
www.gr-tech.com/14oc.htm
www.xlp.com/

ProSolve Consulting is offering an online seminar on ISO 14000.

G.R.Technologies offers ISO 14000 orientation seminar.

Excel Partnership home page outlines training and consulting services available for customers for ISO 9000, QS-9000 and ISO 14000 and other international standards.

Web sites:
www.webpress.net/ttr/s013iaac.htm
www.mgmt14k.com/training.htm
www.qualimetric.com/prod02.HTM
www.yankee.com/iso14001.htm

These sites provide information on an "approved advanced EMS Auditors course". The courses are based on the international standards on Environmental Systems auditing (ISO 14010/14011/14012) and Environmental Management Systems standards (ISO 14001).

Web sites:
www.omninet.co.jp/isoworld/english/ENVIRON.HTM
www.iso14001.com/train.htm
www.smartersolutions.com/ssiso.htm

ISO 14001 Training Course - Building an Environmental Management System gives you an understanding of how to develop and implement ISO 14001. Also, the sites encompass a variety of information relating to the environment.

Web site: www.trst.com/iso4.htm
E-mail: haklik@trst.com

There is a growing library of books on ISO 14000 and environmental management systems. This page lists presently available books with comments where possible.

Web sites: www.opampbooks.com/ENG-
www.env.com/gbl/sample/brief3.htm
www.ait.ac.th/AIT/som/as/ec/EC.html
www.iso14000.com/issues.html

These sites provide review/detail on ISO 14000 related books.

CONCLUSIONS

It is easy to get lost on the information superhighway. This paper presents 53 sites based on a review of over 1000 sites. It is hoped that the paper will save time and the registration/certification process for ISO 14001 will be a bit easier/simpler.

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Air Pollution Control Cost Indexes

Update #1

William M. Vatavuk, P.E.
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

The article "Escalating Air Pollution Control Equipment Costs" [*Environmental Progress*, **16**, pp.S15-S18 (Summer 1997)] introduced the quarterly Vatavuk Air Pollution Control Cost Indexes (VAPCCI) and described how they can be used to adjust air pollution control equipment prices from one date to another. This article also presented equipment size-specific VAPCCI's for nine types of control devices, from first quarter 1996 through fourth quarter 1996 (preliminary) and first quarter 1997 (preliminary). Average VAPCCI for the years 1994 and 1995 were also listed for these nine devices, plus two more: fabric filters and mechanical collectors.

This update (the first in a regular series) presents final VAPCCI data for fourth quarter 1996 (Table 1) and preliminary indexes for second quarter 1997 (Table 3). For convenience, preliminary first quarter 1997 VAPCCI (Table 2) are also included. (The table 2 VAPCCI originally appeared in the Summer 1997 article.) Finally, an "Indexes Summary" (Table 4) is included. This table lists the average VAPCCI for the nine control devices, fabric filters, and mechanical collectors. Future VAPCCI updates will appear in upcoming issues.

Table 1. Vatavuk Air Pollution Control Cost Indexes: Fourth Quarter 1996 (Final)

Control Device	Equipment Cost Index (First Quarter 1994 = 100.00)				
	Small	Medium	Large	Average[1]	Range/ Average x 100%[2]
Carbon adsorbers	103.06	103.72	103.61	103.46	19.1
Catalytic incinerators	106.21	106.07	105.76	106.01	7.5
Electrostatic precipitators	108.21	107.93	109.00	108.38	12.8
Flares	105.44	105.14	104.98	105.18	8.9
Gas absorbers	106.91	107.40	106.87	107.06	7.5
Refrigeration systems	104.68	104.74	105.01	104.81	6.9
Regenerative thermal oxidizers	106.33	106.81	106.75	106.63	7.2
Thermal incinerators	108.16	108.21	108.49	108.29	4.0
Wet scrubbers	107.61	108.19	108.18	107.99	7.3

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[1] Arithmetic averages of the three ECI values.

[2] Calculated as follows:
R/A = {(High Index-Low Index)/|Average index-100|} x 100%

Table 2. Vatavuk Air Pollution Control Cost Indexes: First Quarter 1997 (Preliminary)

Control Device	Equipment Cost Index (First Quarter 1994 = 100.00)				
	Small	Medium	Large	Average[1]	Range/ Average x 100%[2]
Carbon adsorbers	103.70	104.43	104.31	104.15	17.6
Catalytic incinerators	105.96	105.64	105.23	105.61	13.0
Electrostatic precipitators	108.64	108.38	109.40	108.81	11.6
Flares	105.77	105.44	105.28	105.49	8.9
Gas absorbers	108.53	109.14	108.32	108.66	9.5
Refrigeration systems	104.95	105.05	105.24	105.08	5.7
Regenerative thermal oxidizers	107.00	107.44	107.36	107.27	6.1
Thermal incinerators	108.92	108.97	109.28	109.06	4.0
Wet scrubbers	108.06	108.54	108.41	108.34	5.8

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[1] Arithmetic averages of the three ECI values.

[2] Calculated as follows:
R/A = {(High Index-Low Index)/|Average index-100|} x 100%

Table 3. Vatavuk Air Pollution Control Cost Indexes: Second Quarter 1997 (Preliminary)

Control Device	Equipment Cost Index (First Quarter 1994 = 100.00)				
	Small	Medium	Large	Average[1]	Range/ Average x 100%[2]
Carbon adsorbers	105.54	106.02	105.89	105.82	8.2
Catalytic incinerators	108.03	107.99	107.84	107.95	2.4
Electrostatic precipitators	108.26	106.91	107.27	107.48	18.0
Flares	107.31	106.99	106.84	107.05	6.7
Gas absorbers	107.45	107.83	107.50	107.59	5.0
Refrigeration systems	106.08	106.20	106.36	106.21	4.5
Regenerative thermal oxidizers	107.46	107.86	107.78	107.70	5.2
Thermal incinerators	109.31	109.37	109.58	109.42	2.9
Wet scrubbers	109.13	109.68	109.57	109.46	5.8

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[1] Arithmetic averages of the three ECI values.

[2] Calculated as follows:
R/A = {(High Index-Low Index)/|Average index-100|} x 100%

Table 4. Indexes Summary

Control Device	Vatavuk Air Pollution Control Cost Indexes (1st quarter 1994 = 100.0)[1]							
	1994-avg[2]	1995 - avg[2]	1st Q' 96	2nd Q'96	3rd Q' 96	4th Q' 96	1st Q' 97[3]	2nd Q' 97[3]
Carbon adsorbers	101.2	110.7	109.2	107.5	105.2	103.5	104.2	105.8
Catalytic incinerators	102.0	107.1	107.7	107.0	107.1	106.0	105.6	108.0
Electrostatic precipitators	102.8	108.2	107.0	107.6	108.9	108.4	108.8	107.5
Fabric filters[4]	100.5	102.7	104.0	104.2	104.8	104.9	105.3	105.4
Flares	100.5	107.5	104.5	104.9	105.1	105.2	105.5	107.1
Gas absorbers	100.8	105.6	108.6	108.2	107.1	107.1	108.7	107.6
Mechanical collectors	100.3	103.0	103.3	103.3	103.3	103.3	103.5	103.6
Refrigeration systems	100.5	103.0	104.2	104.2	104.4	104.8	105.1	106.2
Regenerative thermal oxidizers	101.4	104.4	105.8	106.0	106.7	106.6	107.3	107.7
Thermal incinerators	101.3	105.9	108.0	108.0	108.3	108.3	109.1	109.4
Wet scrubbers	101.3	112.5	111.7	110.1	109.3	108.0	108.3	109.5

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[1] Except for fabric filters and mechanical collectors, each value shown is the arithmetic average of the size-specific index, rounded to the nearest tenth.

[2] Arithmetic average of quarterly indexes for year indicated.

[3] All first quarter and second quarter 1997 index are preliminary.

[4] For fabric filters and mechanical collectors, each quarterly value shown is the average of the Producer Price Indexes (PPI's) for the three months in question, divided by the average of the PPI's for January, February, and March 1994 (i.e, first quarter 1994).

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AIChE PUBLICATIONS

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A Database on Water Quality of the Mississippi River

Janet E. Preslan, Boumediene Belkhouche, Christopher M. Swalm, Janet M. Hughes, Hsiao-Lin Chen, Melanie Henry, Daryl Lin, Reda M. Bakeer, A. J. Englande, Irina Demtchouk, Mary B. Anderson, James L. Regens, Jay C. Means, James E. Bollinger, Laura J. Steinberg, Ronaldo Luna, Raul Hernandez, William R. Hartley, and William J. George*

Tulane University, New Orleans, Louisiana, and Tulane University/Xavier University Center for Bioenvironmental Research

A water quality GIS/database has been developed for the Mississippi River within the state of Louisiana. Existing ambient water quality data (1.3 million records) and records of river stage and discharge for the river and its tributaries have been acquired from government agencies, industry, and research projects. Data were initially reviewed to validate information quality. They have been incorporated into an Oracle® database created to provide rapid data searches and retrieval of information through a menu-format user interface. Descriptive information about sample collection and analysis methods are included, as well as government advisory criteria which provide ecological and human health perspectives to assist in data interpretation. GIS software utilizes electronic base maps which have been developed in Arc/Info® and ArcView® data formats to generate geographic displays and graphical representations of the data. Examples of the capabilities of the system are included for data on mercury, phosphates, and nitrates. The temporal trends in the concentrations of representative water quality parameters are tabulated for a selected segment of the river.

INTRODUCTION

Tulane University and the Tulane University/Xavier University Center for Bioenvironmental Research are developing a database of existing water quality data in the lower Mississippi River. The main focus of the study is the 500 miles of River south of the Louisiana-Arkansas border, but the included data to date have been gathered from as far north as Memphis and as far south as the receiving waters of the Gulf of Mexico. The database is designed as a tool to characterize current and historic conditions in this portion of the River and to compare reported concentrations of analytes to existing ambient water quality criteria established by state and federal agencies. Capabilities have been developed to display geographic and temporal trends in water quality by using geographic information system (GIS) software. The data are useful in the assessment of historical and present day conditions in the River.

The work to date represents the collaboration of researchers and students from Tulane University Departments of Toxicology, Biostatistics and Epidemiology, Electrical Engineering and Computer Science, Environmental Health Sciences, Civil and Environmental Engineering, Chemistry, Anatomy, and the Spatial Analysis Laboratory, as well as investigators from Xavier University.

This paper describes the design and content of the database, presents examples of graphical formats which have been developed to depict conditions in the River, and presents a brief overview of trends observed for selected water quality parameters over the past 3 decades.

THE STUDY AREA

The Mississippi River is the largest river in North America and one of the 10 largest Rivers of the world. As the River enters northern Louisiana, it transports more water than in any other section along its length. The discharge rate averages 575,000 cubic feet of water per second and provides drainage for 41% of the land mass of the southern 48 United States. In Louisiana, the River is confined by levees, so that drainage from the boundary lands is limited. The two largest tributaries which impact on the study region are the Arkansas River, draining the state of Arkansas from the west, and Yazoo River, entering from the east at Vicksburg, Mississippi. Additional smaller tributaries join from the state of Mississippi.

WATER QUALITY ISSUES IN THE RIVER

The lower Mississippi River serves people in many ways, and activities on the River are closely linked to water quality issues.

New Orleans and Baton Rouge are important port cities. Freighters, tankers, and barges travel the River in large numbers. Cargo terminals, marine supply companies, and barge cleaning facilities support the shipping industry. Fuel and cargo spills on the River are potential sources of water quality contamination. The dredging necessary to maintain river depths suitable for navigation resuspends bottom sed-

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**Address correspondence to William J. George, Department of Pharmacology, Tulane University School of Medicine, 1430 Tulane Avenue, New Orleans, Louisiana 70112.*

This project was supported by funding provided by Freeport McMoRan, Inc., New Orleans, LA.

iments and facilitates the exchange of materials between sediment and water.

A number of communities, as well as a variety of industries, are located along the Mississippi River and constitute a large user base for River water.

The River receives municipal and industrial waste streams, and agricultural runoff, and this use of the River carries the greatest potential impact on water quality. The River carries effluents from the heavily industrialized Ohio River valley, the farmlands surrounding the Missouri River, and the cities and towns along the length of the Mississippi and its tributaries. Currently, 106 sanitary discharge permits and 212 industrial discharge permits are issued by Louisiana, and over 2500 discharge permits have been issued by the state of Mississippi.

Pathogenic organisms and anthropogenic substances which reach the River are potential health concerns for humans and aquatic organisms. Twenty communities in Louisiana, including New Orleans, depend upon the River as a source of drinking water. The commercial fishing and oyster industries are influenced by constituents in the River, as is wildlife in the wetlands receiving diverted Mississippi River water. Organisms may bioaccumulate and biomagnify certain compounds present at very low concentrations in the water column.

GOALS OF THE PROJECT

The project general goal is the development of an information resource which consolidates existing knowledge and facilitates the analysis and interpretation of data concerning the ambient water quality of the River. This work is the initial effort in a long-term project which is planned to expand both in size and scope and to extend many years into the future.

The specific tasks of the current work are to acquire existing water quality data, to validate the data to assure its quality, to develop a database structure capable of organizing the information into a logical and utilitarian structure, to incorporate into the system the existing Louisiana and federal water quality criteria, to develop mapping and graphics capabilities to visualize the information, and to provide access to these capabilities to interested users.

DATA MANAGEMENT PROTOCOL

One of the first tasks of the project was to design a data management protocol for use during data acquisition and preparation phases of the project. The protocol developed insures: (1) the accessibility of the data to project researchers, (2) the security of the data from outside interference, and (3) the integrity of the data during processing. A flow diagram of the protocol is presented in Figure 1.

The project has been developed on the Tulane University RS6000 mainframe computer, which is readily accessible to staff and students from both Tulane University and Xavier University campuses. Two directories service the Mississippi River Project. The "riverdata" directory is the storage location for data sets during acquisition and processing. The "river" directory contains the finished database.

System security is maintained by restricting access to these directories and by frequent system backup. Through the coordinates efforts of a Tulane Computing Services System (TCS) Administrator and the River Project Coordinator, access to the directories is limited to project investigators and students. TCS provides full system backup 6 days per week, and investigators provide tape and disk backup at their personal computers and home directories.

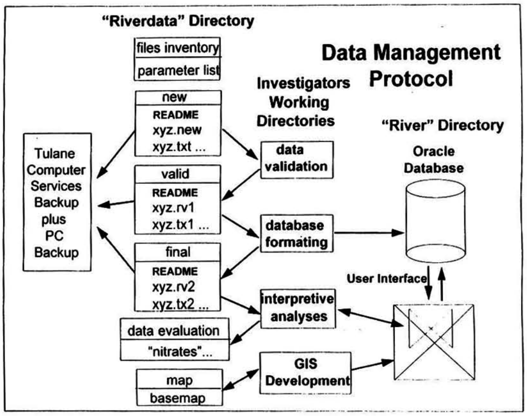


FIGURE 1 Two directories on the RS6000 mainframe computer are dedicated to the project. With "Riverdata," subdirectories permanently store each data file as originally acquired and as its successive revisions (.new, .rv1, . . .). Which are created as copies of the file undergo the preparatory validation and formatting steps. Modifications of the files are documented on the chain of custody (.txt). The finished Oracle database and user interface in "River" supply data for interpretive analyses and mapping via links to GIS software.

File tracking and a subdirectory organizational plan assist in maintaining data integrity during processing. An individual designated as the Gate Keeper, tracks the progress of file processing and ensures that changes to files are not made simultaneously by different investigators. The source and content of each file is documented when the file is acquired through using a chain of custody form, and as work on the file progresses, additional entries are made by the Gate Keeper to describe the nature of the changes made to the data and the names of the investigators who perform the work. The chain of custody is stored electronically as a text file named to correspond to the data file. A hard copy is retained by the Gate Keeper. Each data file has a unique name which includes a file name extension to identify the succession of revisions (rv1, rv2, etc.). Data files are not erased or overwritten. They are maintained in the directions in Read Only format, and ultimately all revisions are transferred for storage to permanent archives. For organizational purposes, the "riverdata" directory is divided into subdirectories each of which stores data at a particular stage of processing. There is a separate subdirectory for newly acquired files, validated files, and database formatted files, as well as summary data evaluations and mapping files.

DATA ACQUISITION

Several types of information have been acquired for the database including numerical data on ambient water quality, descriptive information about the data, and government reference criteria concerning water quality.

Numerical Data

At the present time, over 1.7 million data points have been acquired. Of these, 1.3 million records describe water quality of the River and its tributaries, almost 0.4 million records describe River stage and discharge, and a small number of records describe bottom sediments and fish tissues collected from the River.

Data were acquired from 35 different sources. The U.S. Environmental Protection Agency (USEPA) Water Quality Data Storage and Retrieval System, STORET [*1*], and the U. S. Geological Survey (USGS) National Water Data Storage and Retrieval System, WATSTORE [*2*], were consulted. Data were obtained directly from federal, state (Louisiana, Mississippi, Arkansas), and Louisiana parish sources, as well as various industries which monitor River water conditions. Data were retrieved from the published reports of the 1987 to 1992 USGS study of the River ([*3*–*7*], and others). In the database, the major organizations funding and/or overseeing the water quality investigations are designated as "Agencies," and a list of these is presented in Table 1. The individual investigations sponsored by the agencies, each with its own objectives and protocols, are designated as "Projects."

TABLE 1. Sources of Data

Federal Agencies
  U.S. Geological Survey Headquarters and Regional Offices
  Environmental Protection Agency Headquarters and Regional Offices
  Mississippi River Commission
  U.S. Army Corps of Engineers New Orleans District, Vicksburg District and Mississippi River Commission
  National Biological Service
  Department of Agriculture
Louisiana State Agencies
  Department of Environmental Quality
  Louisiana Geological Survey
  Department of Health and Hospitals
  Department of Natural Resources
  Louisiana State University
Agencies from Other States
  Arkansas Department of Pollution Control and Ecology
  Mississippi Department of Environmental Quality
  Mississippi Department of Natural Resources

Parish Water Works	Industry
Boothville	Domino Sugar
Dalcour	Dow Chemical
Donaldsonville	Exxon
Jefferson	Kaiser Aluminum
Lutcher	Monsanto
Orleans	Novartis
Point a la Hache	Shell Oil
St. Bernard	Vulcan Rubber
St. Charles	
St. James	
Westwego	

Generally data were acquired in electronic format. However, data available only as hard copy were manually tabulated, then independently reviewed twice to confirm the accuracy of the transcription.

Data concerning 403 compounds or water quality features are presently in the database. Data on the distribution of the compounds in different fractions of the water column (e.g., whole water, suspended material, water ultrafiltrate) and data generated using different analytical methodologies are uniquely identified. Thus a total of 759 parameter categories have been established. The parameters are grouped into classes as indicated in Table 2, and information can be queried from the database for an individual compound or by a parameter class. Conventional water quality parameters, such as temperature, pH, and conductivity, constitute a major portion of the data with records which date from 1960. Data available for inorganic constituents also cover 4 decades, whereas data for organic compounds are less abundant and sometimes extend only as far back as the late 1980's. For some compounds of current scientific and toxicologic interest, very few data are available. Examples of these include the latest generation of herbicides, alkyl phenols, and phthalates. The limited availability of such data are likely a result of slowly developing analytical capabilities for organic constituents existing at low concentrations.

Data originate from 643 different geographic locations along the River. These sampling stations are organized in the database according to their River mile designation, which is determined relative to a site called the Head of the Passes located at the downstream end of the main stem of the River. Sampling sites are distributed from River mile minus 25 in the Gulf of Mexico (downstream from the Head of Passes) to River mile 810 north of Memphis, Tennessee. Some sites have been repeatedly sampled over several decades, some other sites have been sampled on a short term basis for specific studies, and other sites have been sampled only a single time. In the database, each station identification number is uniquely associated with an agency.

To facilitate the summary of water quality information, the River was divided into 6 segment lengths, each with particular land use and population density characteristics. The distribution of the acquired data among the River segments is presented in Figure 2.

TABLE 2. Classes of Chemical Compounds in the Database

Inorganic Compounds and Basic Water Parameters
  Metals, rare earths, inorganics, nitrogenous and phosphorous compounds, oxygen parameters, and physical characteristics
Organic Compounds
  Volatile and semivolatile compounds, including halogenated compounds, polyaromatic and aliphatic hydrocarbons, polychlorinated biphenyls, and plasticizers (phthalates)
Pesticides
  Herbicides, chlorinated pesticides, organophosphorus pesticides, other pesticides
Radioactivity
Bacteria

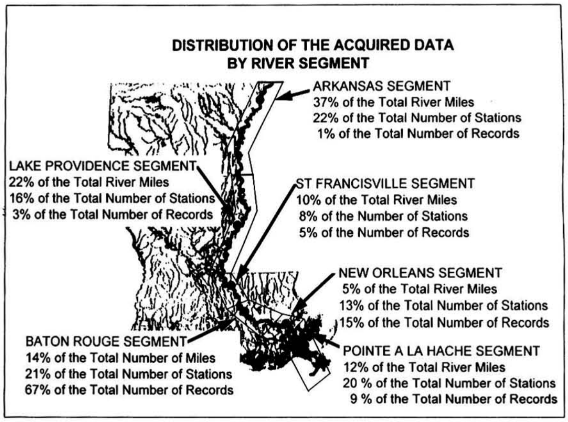


FIGURE 2 The designated River segments.

Segment Name	River Miles	Riverbank Land Use Characteristics
Arkansas	501 to 810	agricultural and municipal areas
Lake Providence	316 to 500	agricultural area
St. Francisville	231 to 315	small towns, some industry
Baton Rouge	111 to 230	large industry and municipality
New Orleans	71 to 110	large municipality and some industry
Pointe a la Hache	−25 to 70	wetlands

Descriptive Information

Metadata (data about data) are compiled as text, tables, and bibliographic references describing project objectives, quality control protocols, sampling site evaluations, collection procedures, and geographic reference points. Reported analytical detection (quantitation) limits, defined as the lowest concentration of a specific parameter which is accurately measured by an analytical method, were tabulated during the data validation process, as discussed later. While only limited metadata is available for historical projects, a more complete spectrum of information has been acquired for recent work, and the availability of this information to researchers is a unique feature of this database not presently available in the other existing water quality databases. The information is stored in the Projects section of the database.

The assessment of temporal trends for a parameter is an example of when information on data quality is helpful in interpreting numerical values. For some parameters, notably for heavy metals, data from the earliest sampling of the River reflect less sophisticated analytical technologies with high detection limits, and as test methods improve, detection limits become lower. Conversely, for some parameters and agencies, the reported detection limits have become elevated, occasionally by as much as ten-fold, as the understanding of detection limits issues has improved such as for Heptachlor, Aldrin and DDT. Therefore, numerical trends (in mean, for example) may be influenced by changing analytical methodology in addition to changing conditions in the River. Tabular summaries of detection limits provide, at a glance, perspective with regard to this type of question.

Look-up tables of descriptive information is useful in other ways too. A research study with documented analytical detection limits in the range of parts per trillion presents a different view of River water quality from either routine survey techniques in which detection limits are parts per billion or a source where detection limits have not been established. A sampling plan which integrates water from a cross-sectional area and depth profile of the River presents a more comprehensive picture of conditions than a surface grab sample. Differences or improvements in sampling protocols, such as the institution of the 1994 USGS methods for the collection of water samples for metal analysis [*12*], also can have an impact on the reported analytical values.

Reference Criteria

Federal and state freshwater advisory criteria are included in the database [*8–11*]. A criterion is the maximum concentration of a chemical to which aquatic organisms or humans can be safely exposed, as defined by the USEPA or the State of Louisiana Department of Environmental Quality (LDEQ). For carcinogenic compounds, it is the concentration level which poses a defined degree of added cancer risk. For metals, these criteria are applicable to the analyses of filtered water samples which depict the dissolved metal content of the water, for these are more representative of the concentrations of metal available for uptake into the biota. For certain metals, criteria are expressed as a function of water hardness which also influences the degree of metal uptake by organisms.

Two types of ambient water criteria are established to protect aquatic life. Chronic exposure criteria apply when exposure to a constituent is life-long or continues for several generations. Acute exposure criteria are established to protect aquatic organisms from short term, high dose exposure to a specific parameter, such as would occur during a chemical spill in the River. Such criteria are not designed to protect all life all of the time, but to protect "essential and significant life" as well as critical links in the food chain. Guidelines established by LDEQ are considered more conservative (permissible concentrations are lower) than those established by the USEPA for many compounds.

Several types of ambient water criteria are established to protect human health based on various water use designations for a specific water body. There are federal criteria for water bodies whose use is propagation of fish for ingestion alone or for the ingestion of both fish and water [*8*]. There are LDEQ guidelines established to protect a drinking water supply (water to be processed into finished drinking water), to protect individuals from exposure during primary and secondary contact recreation, and to protect the commercial oyster harvest. For some compounds, maximum contaminant levels (MCL's) for compounds in finished drinking water, as specified by the Safe Drinking Water Act, are the only established criteria. For a large number of constituents, now enforceable drinking water health advisories are provided under the Safe Drinking Water Act. These health advisories provide allowable levels of adults and children for short term exposure. For some parameters, no criteria have been established. Guidelines for general water parameters (chloride, dissolved oxygen, temperature, etc.) as well as those for potentially toxic constituents are included in the database.

Each criterion is established based on the current knowledge of the potential effects of parameter and water conditions on humans and aquatic organisms. As such, it is a good reference value for comparison to observed conditions in the River water.

DATA VALIDATION

All acquired data are reviewed prior to inclusion in the database. Data validation decisions are jointly made by a team of researchers with expertise in statistics, environmental engineering, analytical chemistry, and water quality. Exhaustive efforts by this team insure that the final database is of good quality.

The validation process includes removal of duplicate and unreasonable values (e.g. pH 71) and adherence to the convention of reporting negative results as "less than" [numerical value] the detection limit. The acquired data which already follow this convention is the source for established detection limits. However, in many cases zero values are reported, particularly in the older data sets. During validation, zeros are recoded to detection limits deemed appropriate for the agency and testing date, and notation of the recoding is stored with the data. Thus, for statistical evaluations, samples in which a compound is not detected can be treated uniformly and can be assigned values equal to one half the detection limit, the detection limit, or some other value. In this way, data can be viewed as either a more or a less conservative representation of conditions in the River, according to the needs of the researcher.

DATABASE DESIGN

Configuration of the Database

The configuration of the database system is presented in Figure 3. The basic system component is the Analysis Subsystem. It supports different water quality analysis procedures. The main part of the procedures is implemented as a set of nested and grouped queries. Query results from the environmental database are retrieved and transposed according to conditions specified by the analysis procedures and user. The analysis subsystem also provides inserting new data in the database and updating information.

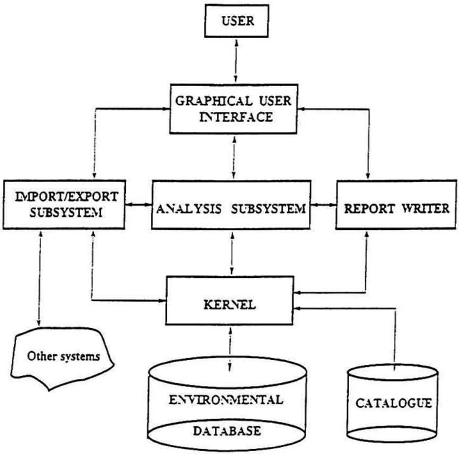


FIGURE 3 A diagram of the configuration of the elements of the water quality database.

The Graphical User Interface supports the interaction of users with analysis subsystem and other system components in a manner which is easy to learn and effective to use. It allows the users to directly manipulate windows, menus, controls and other graphic objects in specifying requests and responds interactively to the user's input actions.

The Report Writer is used to output the results of database querying and data analysis. The reports can be formatted by including headers and footers, forms, graphics, computing totals or data summaries, or performing computations on the data.

The Import/Export subsystem supports the interface with specialized software systems for data analysis such as the Geographical Information System used to create maps of river study areas, systems for sophisticated statistical and mathematical analysis and others. The Export module outputs stored data and results of retrievals into a format that can be processed by the specialized software. The Import module converts formats of data in an external file and inserts them into database files.

The Environmental Database consists of two types of files, data files and reference files. The data files contain information on: (1) the concentration of constituents in the water and references to the analytical methods used to generate the data, (2) physical characteristics of the river such as geographic data needed for mapping and hydrologic data on river stage and water discharge rate, (3) descriptive and geographic data about the sampling stations, and (4) descriptive information related to the environment of the river under study. Reference files contain: (1) sampling and analytical metadata for the various Projects, (2) descriptive information about the agencies collecting water quality data, (3) governmental advisory safety criteria, and (4) information on features along the riverbanks which serve as geographic reference points describing population distribution and land use.

The Catalogue stores database structural metadata such as environmental database definitions available for users as on-line system documentation. Metadata include descriptions of the database system schemas, users and their access rights, information on storage structures and access paths, database fields and record sizes, and usage statistics.

Structure of the Database

The ER schema modeling the system is displayed in Figure 4. Entities are shown in rectangular boxes. Each entity has attributes that are shown in ovals attached to their entities by straight lines. Composite attributes are linked to ad-

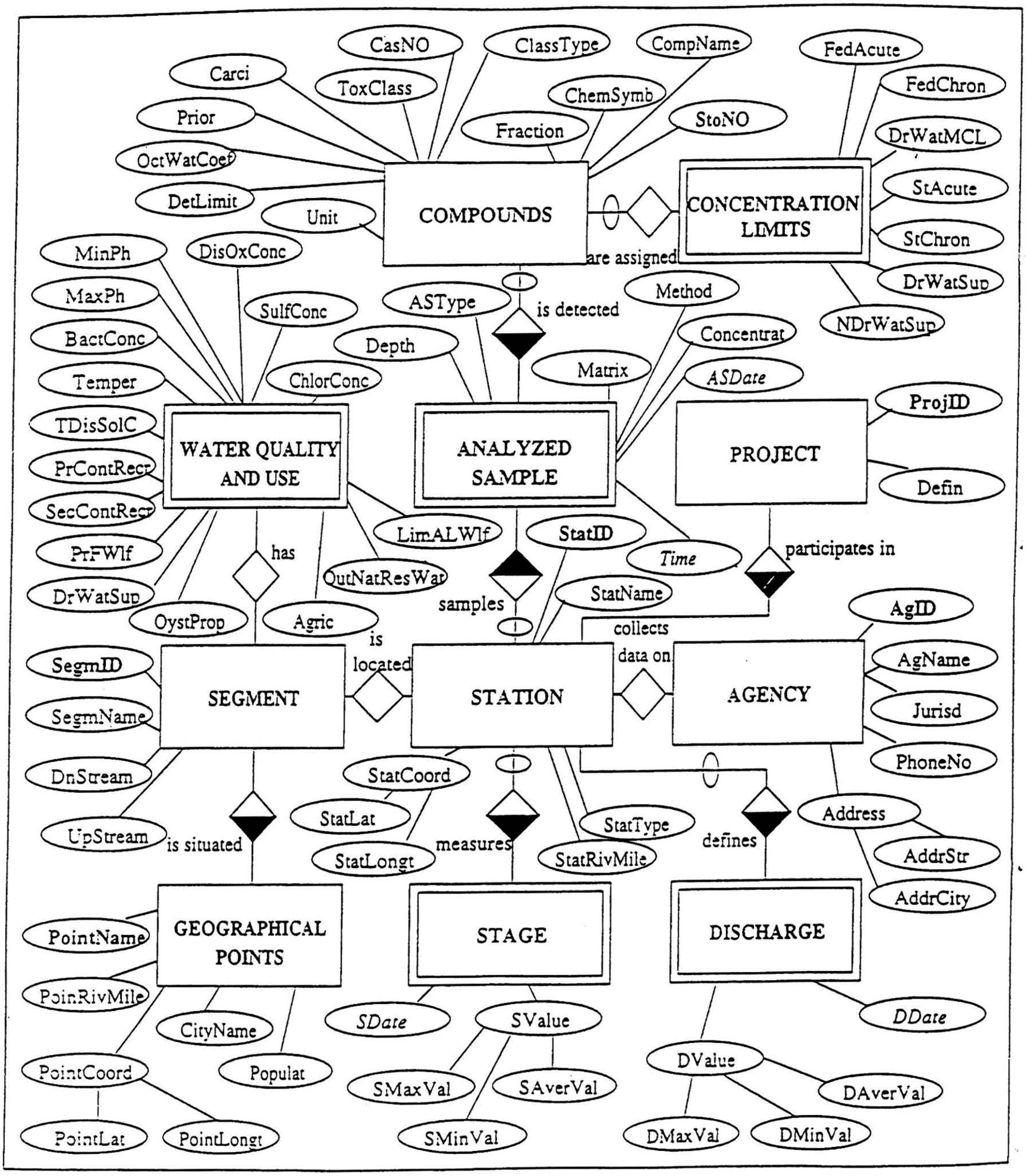


FIGURE 4 ER schema diagram for the water quality database. Rectangles are entities. Weak entities whose existence depends on the presence of some owner entity have a double border. Ovals are attributes. Key attributes are in bold type. For further description, see text.

ditional ovals representing the component attributes. For example, the entity STATION has the composite attribute Station Coordinates with the component attributes of Station Latitude and Station Longitude. Key attributes are in bold type.

Weak entities, whose existence depends on the presence of some owner entity, are depicted with a double-bordered rectangle. So STAGE depends on entity STATION. Two STAGE measurements may have the Sampling Dates, Maximum Value, Minimum Value, and Average Value and be distinctly identified only after determining the STATION to which each of stage data are related. ANALYZED SAMPLE has two owner entities: STATION and COMPOUND. Every ANALYZED SAMPLE entity occurrence may be uniquely identified after determining sampling STATION and detected COMPOUND.

Binary relationships are shown in diamond-shaped boxes attached to the participating entities with straight lines. The connectivity of each relationship is specified by shading the part of the relationship diamond on the side of the "many" associations. For example, the connectivity of COMPOUND and CONCENTRATION LIMITS in relationship to ARE ASSIGNED TO is one-to-one, whereas for STATION and ANALYZED SAMPLE, the connectivity is one-to-many. The participation of an entity in a relationship is defined as either total or partial. The partial participation is specified by a 0 on the line between an entity and a relationship. Hence, the participation of STATION in MEASURES is partial (not every station measures river stage), whereas the participation of STATION in COLLECTS DATA ON is total (every station is associated with an agency).

The version of the Database System on the RISC System supports a menu-based interface. The main system menu contains names of groups of analytical queries: queries about parameters, parameter concentration queries, queries about stations, queries about agencies, queries about segments, queries about time, and hydrographic queries. Future plans are to upgrade the user interface to a graphical user interface by employing PC software.

Issues Addressed in the Database Design

Issues of importance in the database design were expandability, longevity, and ease of maintenance.

The database was designed to be versatile and allow for future expansion of both the quantity and the variety of data. The design process began by surveying the wide variety of data pertinent to the study of any river system. Ambient water quality data were the initial focus of the project, but issues related to land use, point source discharges, hydrodynamics, epidemiology, geology, modeling, and satellite imagery were also considered. Interrelationships between different types of data were examined, and potential questions about the River were studied. Also evaluated was the impact of a dramatic increase in the size of the database, as would occur if the study area were extended upstream. Creating a format with adequate data storage capacity and efficient data search capabilities was a priority. It was also important that the system be easily updated. The database structure developed from this process was designed for utility extending many years into the future.

The Catalog information described earlier is another important resource that ensures an extended life for the database. It is a users' manual that supplies future investigators with the information necessary to use and to maintain the database, even if the system designers are no longer available.

GEOGRAPHIC INFORMATION SYSTEM PRESENTATIONS

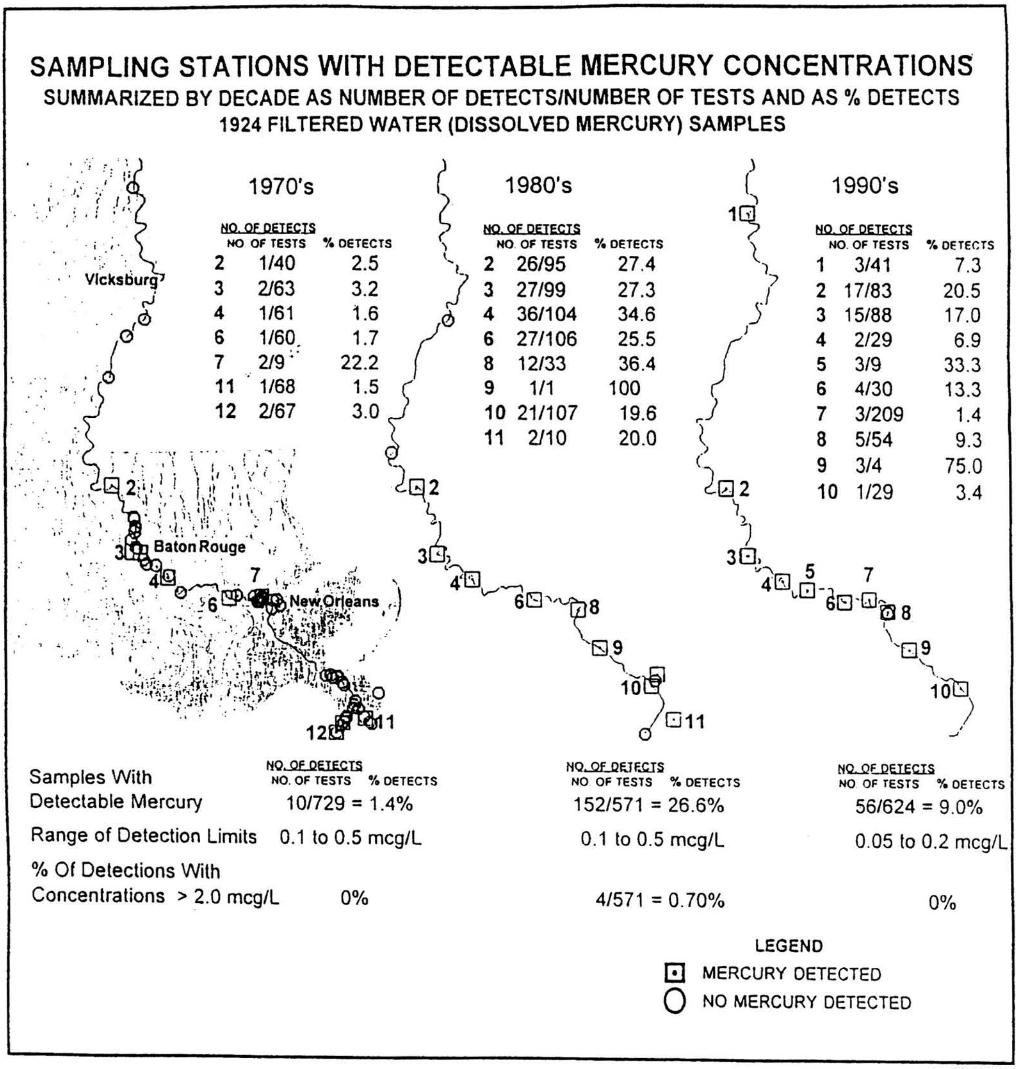
Electronic maps at the 1:2 000 000 and 1:250 000 scales were prepared using U. S. Geological Survey DLG (Digital Line Graph) data retrieved electronically and converted into Arc/Info® and ArcView® data formats. The Federal Geographic Data Committee Metadata Standards were used to track the development of the maps. Data sets include the state boundaries, transportation features, and hydrography of Louisiana, Mississippi, and a portion of Arkansas.

Three mapping strategies were developed. The 'snapshot' format is the simplest. It maps the values of a constituent at 10 mile intervals along the length of the River from data collected during a time span of just a few days; each mapped point presents the result from a single water sample. The snapshot identifies the localized geographic variability in the concentrations of a parameter at a given point in time. The 'sampling station' format summarizes test results by specific River Mile locations along the River using data which often have been collected over the span of many years. This format is useful for identifying sites with persistent high (or low) concentrations of a compound. The 'segment summary' format compiles test results by River segment, as defined earlier. It is useful for evaluating changes in the River as it travels through the state. The formats are easily adapted to meet the needs of specialized data sets, and can be used to present information on individual compounds or on whole classes of compounds.

MISSISSIPPI RIVER WATER QUALITY IN THE STATE OF LOUISIANA

GIS capabilities to visualize data are demonstrated in Figures 5 through 12. Two different data sets evaluating mercury levels in River water are presented (Figures 5–7). Mercury is a highly toxic metal which, when present under certain conditions in the water column and sediments in low concentrations, can readily accumulate in the tissues of aquatic organisms. Mercury is found naturally in soil and can enter the aquatic environment (via air deposition and drainage) as a result of the combustion of fossil fuels or from industrial wastes.

Existing data on phosphate-phosphorous in the River are viewed from three different perspectives (Figures 8–10). Phosphate is a constituent of fertilizers, detergents, and sewage which reach the River from agricultural, municipal, and industrial sources. Phosphorus is the limiting factor of primary productivity in fresh water systems. Figures 11–12 show data on nitrates from two perspectives. Nitrates originate from fertilizers and waste discharges. Finally, while an in depth evaluation of conditions in the River is not possible in this paper, data on a variety of water quality parameters in the Baton Rouge segment of the River are tabulated (Tables 3 and 4) to briefly characterize changes in River water quality which have occurred over the past three decades. Median values have been reported because they are most representative of conditions generally occurring in the River.



SAMPLING STATIONS WITH DETECTABLE MERCURY CONCENTRATIONS
SUMMARIZED BY DECADE AS NUMBER OF DETECTS/NUMBER OF TESTS AND AS % DETECTS
1924 FILTERED WATER (DISSOLVED MERCURY) SAMPLES

1970's

	NO. OF DETECTS NO OF TESTS	% DETECTS
2	1/40	2.5
3	2/63	3.2
4	1/61	1.6
6	1/60	1.7
7	2/9	22.2
11	1/68	1.5
12	2/67	3.0

1980's

	NO. OF DETECTS NO. OF TESTS	% DETECTS
2	26/95	27.4
3	27/99	27.3
4	36/104	34.6
6	27/106	25.5
8	12/33	36.4
9	1/1	100
10	21/107	19.6
11	2/10	20.0

1990's

	NO. OF DETECTS NO. OF TESTS	% DETECTS
1	3/41	7.3
2	17/83	20.5
3	15/88	17.0
4	2/29	6.9
5	3/9	33.3
6	4/30	13.3
7	3/209	1.4
8	5/54	9.3
9	3/4	75.0
10	1/29	3.4

	1970's	1980's	1990's
	NO. OF DETECTS NO. OF TESTS % DETECTS	NO. OF DETECTS NO OF TESTS % DETECTS	NO. OF DETECTS NO OF TESTS % DETECTS
Samples With Detectable Mercury	10/729 = 1.4%	152/571 = 26.6%	56/624 = 9.0%
Range of Detection Limits	0.1 to 0.5 mcg/L	0.1 to 0.5 mcg/L	0.05 to 0.2 mcg/L
% Of Detections With Concentrations > 2.0 mcg/L	0%	4/571 = 0.70%	0%

LEGEND
▣ MERCURY DETECTED
○ NO MERCURY DETECTED

FIGURE 5 The distribution of mercury in the River is described using both maps and statistics. For this data set, analytical detection limits ranged from 0.05 to 0.5 mcg Hg/L. Mercury is detected in a larger percentage of samples (26%) during the 1980's than during either the 1970's or 1990's. Only during the 1980's did mercury concentrations occasionally exceed the 2.0 mcg/L drinking water supply criterion (in 0.7% of the samples tested).

Mercury

Mercury is an example of a substance which is seldom detected in the Mississippi River. Figure 5 is a sampling station summary of dissolved mercury data from 1,924 water samples. The analytical detection limits for these data range from 0.1 to 0.5 mcg/L during the 1970's and 1980's, and decrease to 0.05 to 0.2 mcg/L during the 1990's. Testing at this sensitivity is sufficient to assess the distribution of mercury relative to the federal and state advisory criteria for aquatic organism acute exposure (2.4 mcg/L) and the Louisiana criterion for protection of the drinking water supply (2.0 mcg/L). The methods currently used for routine analyses of the River have detection limits which are not sensitive enough to evaluate water quality relative to federal and state criteria for aquatic organism exposure.

In the graphic presentation, if mercury was detected at a sampling location at any time during a decade, the site is marked with a square and the detection frequency is noted, expressed both as the ratio of the number of samples in which mercury was detected per total number of tested samples and as a percentage. Site identification numbers are consistent between the different decades. Stations where mercury was never detected are marked with a circle.

The map shows that there was a larger number of mercury sampling sites along the River in the 1970's than in other decades. In the 70's, mercury was detected at 12% of

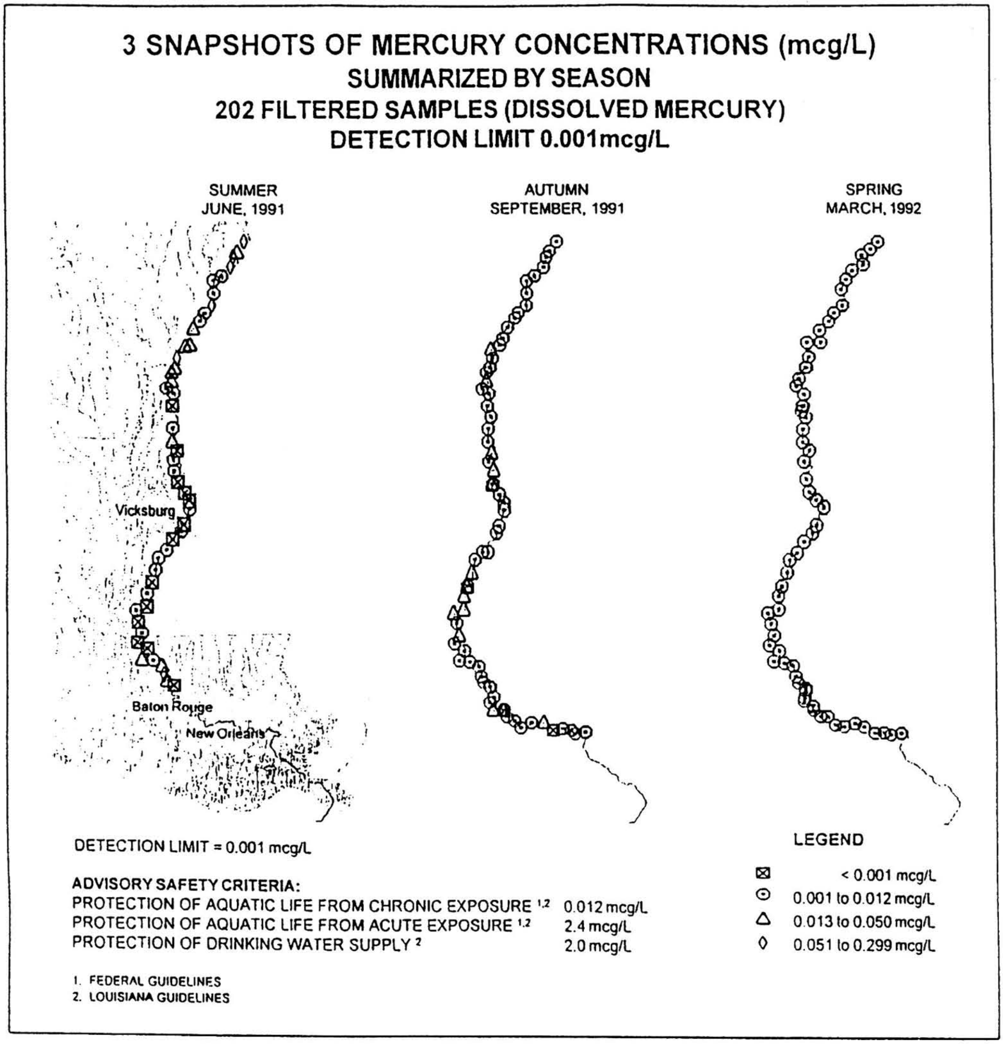


FIGURE 6 Snapshots of the distribution of mercury during 1991 and 1992, as determined by an analytical method with a detection limit of 0.001 mcg/L, show that mercury levels seldom exceed even the extremely low chronic exposure criterion of 0.012 mcg/L. Highest concentrations are detected during the summer sampling, and these were generally in the Arkansas River segment. Some samples with levels only slightly above the criterion concentration were also seen distributed at various sites along the length of the River during the Autumn sampling.

the locations (9 of 75). At the sampling sites where mercury was detected, it was present in only 1.5 to 3.2% of the samples, except for one station where the total number of samples tested was small (n = 9) and mercury was found in 22% of the samples. Overall during the decade, mercury was found in only 1.4% of the samples (10 of 729), and observed concentrations never exceeded the newly established 2.0 mcg/L drinking water supply criterion.

During the 1980's, when reported analytical detection limits were generally the same as those in the 1970's, mercury was detected in a 27% of samples (152 of 571), a substantial increase over the 1.4% in the 1970's. In the 1980's, 0.7% of all the samples have concentrations which exceeded the 2.0 mcg/L drinking water supply criterion. By the 1990's, however, the percentage of samples with detectable levels of mercury fell to one third of the 1980's level, even though testing methods were more sensitive, and never did the mercury level exceed 2.0 mcg/L criterion.

Figure 6 presents snapshots of the mercury data from 1991–1992 [*3*]. A more sensitive analytical procedure, with a detection limit of 0.001 mcg/L, produced data appropriate to evaluate the distribution of mercury relative to the low chronic mercury exposure advisory criterion of 0.012 mcg/L. The map shows that the majority of samples (84%) (171 of 203) had mercury concentrations below 0.012 mcg/L. The highest concentrations (up to 0.109 mcg/L) and the highest percent of samples with detectable levels

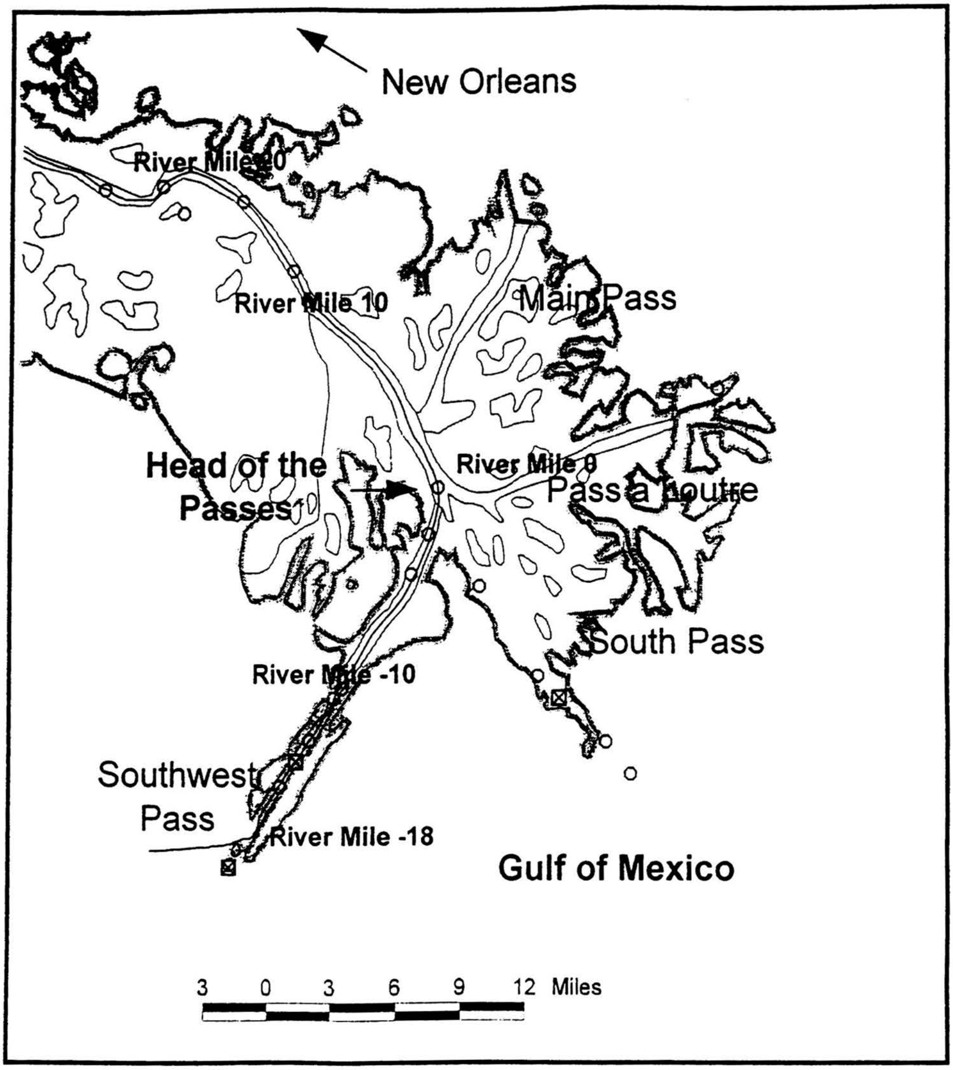


FIGURE 7 The GIS mapping software easily zooms in to permit inspection of map details. This enlargement of the bird-foot delta region from the 1970's data in Figure 9 shows mercury sampling station locations. The squares are sites where mercury was detected.

of mercury (34%) (17 of 50) occurred during the summer sampling which may be associated with decreased volume of water in the River during summer periods. Seventy-six percent (76%) of the sampling stations where mercury levels exceeded the chronic exposure criterion during summer are in the Arkansas segment. During autumn, the samples which exceed the chronic exposure criterion do so by only modest amounts (93% of the samples (14 of 15) with values above the criterion have concentrations of 0.018 mcg/L or less). Seventy-eight percent (78%) of the exceedences were located within Louisiana.

In summary, mercury was detected more frequently and at higher concentrations during the 1980's than during either the 1970's or the 1990's. Only during the 1980's did mercury concentrations occasionally exceed 2.0 mcg/L, the drinking water supply criterion. Recent tests, using more sensitive methods, show that at the majority of locations mercury levels are below the 12 parts per trillion aquatic organism chronic exposure advisory criterion. Based on ambient mercury water quality data, mercury contamination in the water column does not appear to be a problem in the River.

The electronic maps created by the GIS software easily zoom to close-up views. Figure 7 is an example, showing detail of the River distributaries near the Gulf of Mexico from 1970's mercury data presented in Figure 5.

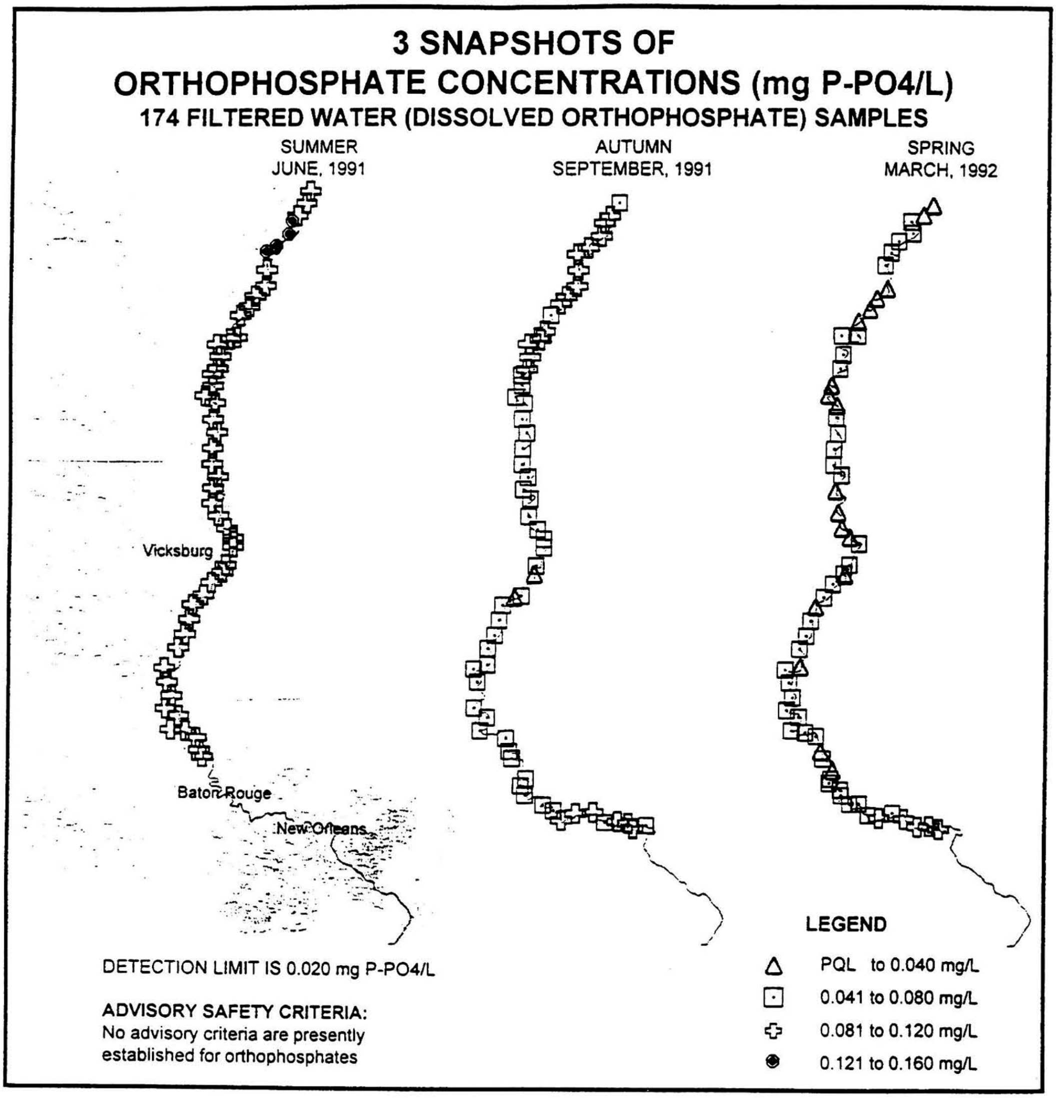
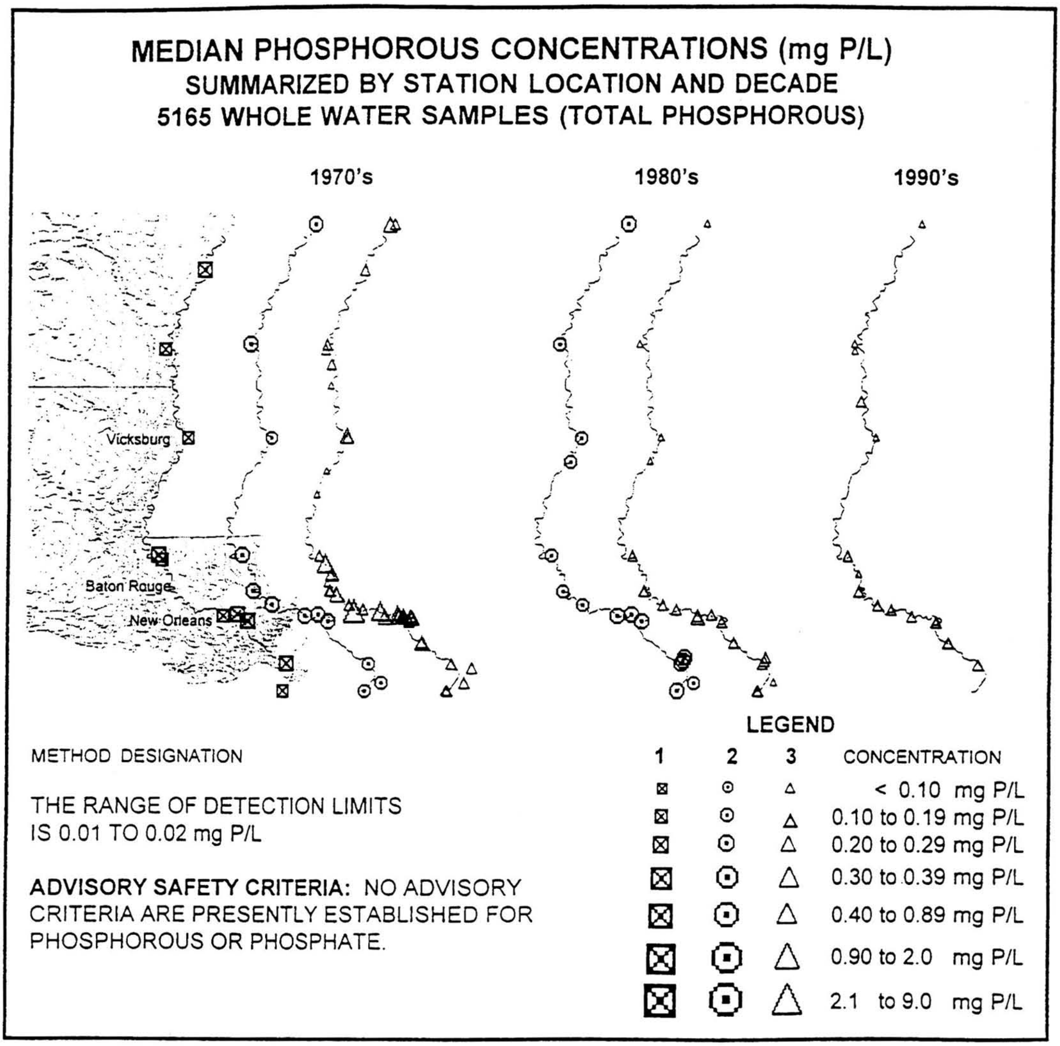


FIGURE 8 In a snapshot presentation, each symbol represents the analytical results from one water sample. In this data set, all samples for each season were collected during a 5-day period in 1991 or 1992. Phosphate-phosphorous levels are relatively low for all samples. The highest and most uniform values along the length of the River occur in the summer. Local variability in the phosphate levels is evident during the autumn and spring.

Phosphates

Figure 8 presents three snapshots of the dissolved phosphate-phosphorous concentrations during 5-day upstream cruises of the River conducted during three seasons in 1991 and 1992 [*3*]. The graphic conveys at a glance a seasonal pattern in the distribution of phosphorous, with highest levels in the summer (0.08 to 0.12 mg P/L).

In Figure 9, data on the distribution of phosphate-phosphorous in whole water samples is summarized by sampling station. For 5,165 samples, the median concentrations of data collected at each sampling station are mapped for three decades. Data from three slightly different methods are represented. During the 1970's, values at several sampling stations located in the Baton Rouge to New Orleans stretch of River exceed 0.5 mg P/L, and one site (a single sample) has a concentration of 8.7 mg P/L. Industrial and municipal waste streams are discharged into this section of the River. Localized high concentrations are particular noticeable in Method 3 data; however, based upon the variability and distribution of the data, sampling intensity rather than method bias appears to account for the differences. By the 1980's, phosphorous concentrations in this area of the River are considerably lower, and by the 1990's, median values from stations along the entire length of River are 0.2 mg P/L.

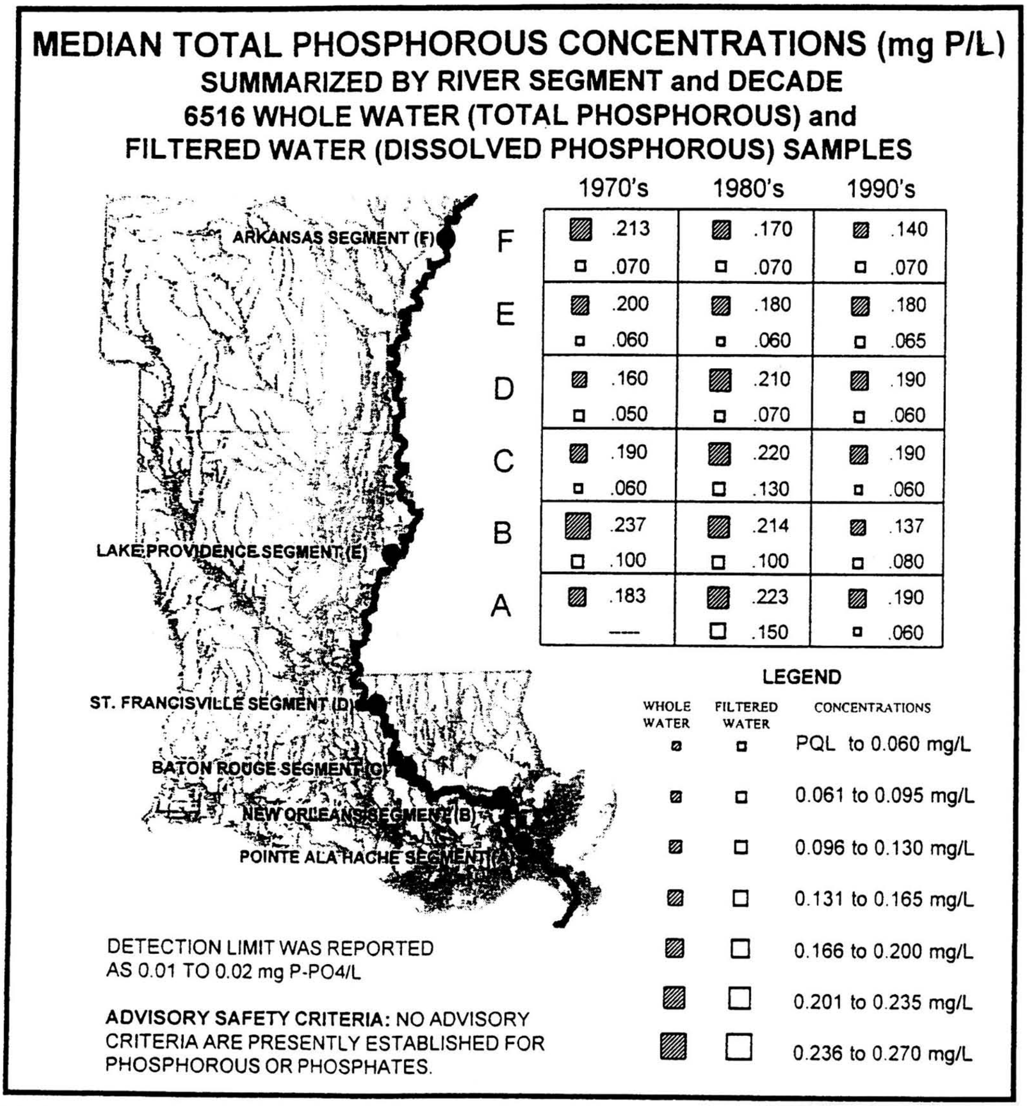

MEDIAN PHOSPHOROUS CONCENTRATIONS (mg P/L)
SUMMARIZED BY STATION LOCATION AND DECADE
5165 WHOLE WATER SAMPLES (TOTAL PHOSPHOROUS)

THE RANGE OF DETECTION LIMITS IS 0.01 TO 0.02 mg P/L

ADVISORY SAFETY CRITERIA: NO ADVISORY CRITERIA ARE PRESENTLY ESTABLISHED FOR PHOSPHOROUS OR PHOSPHATE.

FIGURE 9 In this Station Summary presentation, the results from 5,165 phosphate-phosphorous analyses are summarized as median concentration at each sampling location for each of the 3 decades. Data are presented for 3 different methods. Some stations between Baton Rouge and New Orleans show elevated phosphorous levels (Method 3) during the 1970's. By the 1990's, phosphorous values are substantially lower.

Figure 10 presents phosphate and nitrate data from whole water and filtered water samples within each River segment and for each decade. Median concentrations are represented graphically by square size, with whole water samples depicted as shaded squares and filtered water samples depicted as white squares. Concentration values are listed beside the squares. In the charts, columns track changes in the River as it travels to the Gulf, and rows track the changes in each segment from decade to decade. Results from 6,516 samples show that phosphates are largely associated with particulate matter suspended in the water, as median values for whole water samples are consistently higher than those for filtered water samples. Whole water samples from the New Orleans segment during the 1970's have the highest reported concentration, and the median value for filtered water samples is also highest for the decade in that segment. During the 1980's, phosphorous levels generally increase as the River passes through the state, with median levels in whole water samples increasing 31% and those in filtered water samples more than doubling between the Arkansas (F) and Point a la Hache (A) segments. Conditions are markedly improved by the 1990's, when phosphorous concentrations are more uniform along the length of the River and median values are generally lower than in the 1980's. The decline in phosphorous levels between the 1970's and the 1990's is steady and dramatic for both the Arkansas River segment (a 34% decline) and the New Orleans segment (a 42% decline).



MEDIAN TOTAL PHOSPHOROUS CONCENTRATIONS (mg P/L)
SUMMARIZED BY RIVER SEGMENT and DECADE
6516 WHOLE WATER (TOTAL PHOSPHOROUS) and
FILTERED WATER (DISSOLVED PHOSPHOROUS) SAMPLES

	1970's	1980's	1990's
F	▨ .213 □ .070	▨ .170 □ .070	▨ .140 □ .070
E	▨ .200 □ .060	▨ .180 □ .060	▨ .180 □ .065
D	▨ .160 □ .050	▨ .210 □ .070	▨ .190 □ .060
C	▨ .190 □ .060	▨ .220 □ .130	▨ .190 □ .060
B	▨ .237 □ .100	▨ .214 □ .100	▨ .137 □ .080
A	▨ .183 ---	▨ .223 □ .150	▨ .190 □ .060

LEGEND

WHOLE WATER	FILTERED WATER	CONCENTRATIONS
▨	□	PQL to 0.060 mg/L
▨	□	0.061 to 0.095 mg/L
▨	□	0.096 to 0.130 mg/L
▨	□	0.131 to 0.165 mg/L
▨	□	0.166 to 0.200 mg/L
▨	□	0.201 to 0.235 mg/L
▨	□	0.236 to 0.270 mg/L

DETECTION LIMIT WAS REPORTED
AS 0.01 TO 0.02 mg P-PO4/L

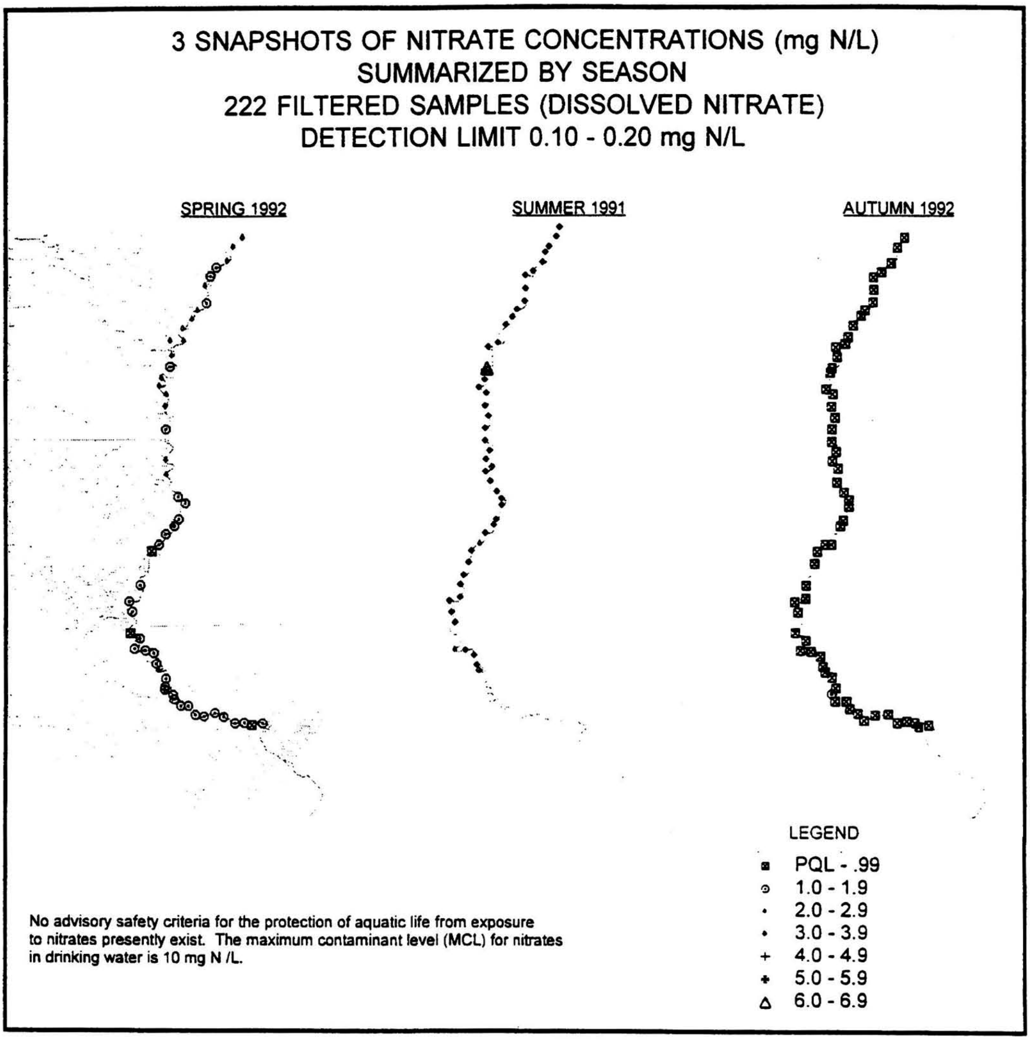
ADVISORY SAFETY CRITERIA: NO ADVISORY CRITERIA ARE PRESENTLY ESTABLISHED FOR PHOSPHOROUS OR PHOSPHATES.

FIGURE 10 In this segment Summary presentation, phosphorous data for all sampling stations within each River segment are compiled by decade. Square size graphically presents median concentration values. Whole water levels substantially exceed those from filtered water samples. During the 1980's, phosphorous levels increase as the River travels through the state. A dramatic decrease in phosphorous levels between the 1970's and the 1990's is evident for the Arkansas and New Orleans segments.

These presentations clearly depict salient features which characterize phosphates in the River. Phosphates are detected in most water samples, but concentrations in unfiltered water are currently near the median value for rivers across the United States (0.17 mg P/L) [*13*]. Higher levels of phosphate apparently reach the River at upstream locations during the summer growing season. Anthropogenic phosphate originating from multiple sources during the 1970's and 1980's has been substantially reduced resulting in decreased phosphate concentrations in the River in recent years. In the decade of the 1990's, there have been no detectable significant differences in phosphate levels entering and exiting in the state.

Nitrates

Data on nitrate concentrations in the River are presented in snapshot, and segment summary formats in Figures 11–12. The seasonal variability in nitrates is apparent in Figure 11, with lowest levels for dissolved nitrates in the autumn (< 0.99 mg N/L), higher levels in the spring (1–3 mg N/L), and highest levels in the summer (generally 2–4



No advisory safety criteria for the protection of aquatic life from exposure to nitrates presently exist. The maximum contaminant level (MCL) for nitrates in drinking water is 10 mg N /L.

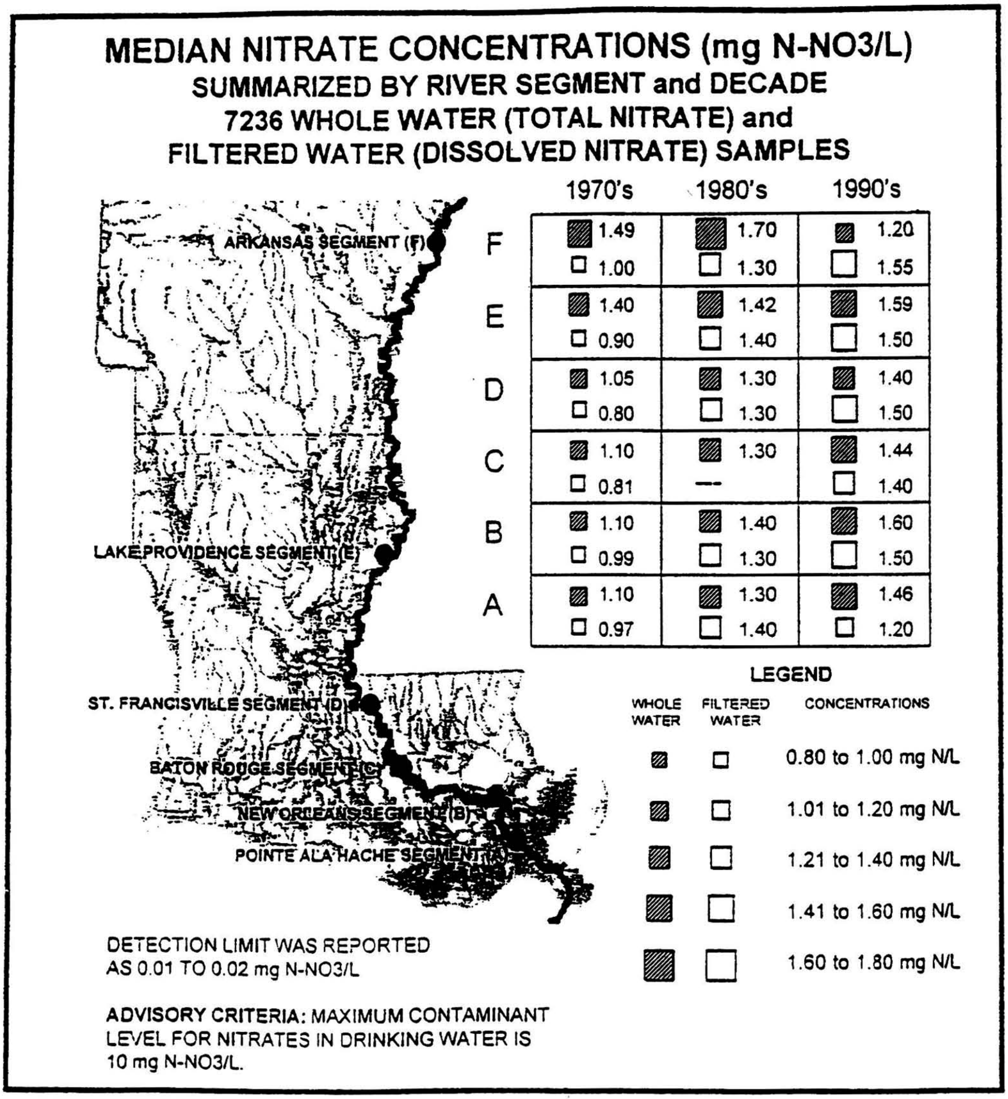
FIGURE 11 Snapshots of nitrate concentrations at 3 seasons show highest levels during summer, intermediate levels during the spring, and lowest levels in autumn.

mg N/L). This pattern corresponds to the pattern of application of nitrate fertilizers to agricultural fields in the Northern Mississippi River Basin. For each season, levels along the length of the River are quite uniform, with the exception of a localized site in the Arkansas segment in the summer time data.

Figure 12 shows temporal and geographic trends for nitrates in 7,236 whole water and filtered water samples. Median values for whole water samples are close to those for filtered water samples, indicating that nitrates are not associated with particulate matter as are phosphates. A small but steady increase in nitrate concentrations is apparent from the 1970's to the 1990's. Data for whole water samples in segment F and filtered water samples in segment A, which appear to be exceptions to these trends, have a disproportionately large number of samples collected during the lower nitrate autumn and winter months. Median values are therefore lower than would be expected if all seasons of the year were evenly represented. Present median values are 1.2–1.6 mg N/L which is above the 0.71 mg N/L median value for rivers across the United States. However, there is no significant difference between nitrate concentrations in water entering and exiting Louisiana. In addition, all nitrate levels are well below the drinking water MCL of 10 mg $N\text{-}NO_3/_L$.

Temporal Trends in Selected Water Quality Parameters

Tables 3, 4 and 5 focus on data from the Baton Rouge segment of the River. For selected water quality parameters the median values, and in some cases the percentages of samples in which the compound was detected, are sum-



	1970's	1980's	1990's
F	▨ 1.49	▨ 1.70	▨ 1.20
	☐ 1.00	☐ 1.30	☐ 1.55
E	▨ 1.40	▨ 1.42	▨ 1.59
	☐ 0.90	☐ 1.40	☐ 1.50
D	▨ 1.05	▨ 1.30	▨ 1.40
	☐ 0.80	☐ 1.30	☐ 1.50
C	▨ 1.10	▨ 1.30	▨ 1.44
	☐ 0.81	---	☐ 1.40
B	▨ 1.10	▨ 1.40	▨ 1.60
	☐ 0.99	☐ 1.30	☐ 1.50
A	▨ 1.10	▨ 1.30	▨ 1.46
	☐ 0.97	☐ 1.40	☐ 1.20

FIGURE 12 This Segment Summary presentation of nitrate concentrations show that whole water and filtered water levels are similar; nitrates are not associated with particulate material. Generally, values increase from the 1970's to the 1990's, but values for water entering and exiting the state do not differ significantly.

marized by decade. The "n" is the number of samples evaluated; almost 240,000 analyses are represented in the two tables. The arrows indicate whether the concentration of the chemical on water quality has become greater (↑), lesser (↓), or whether concentrations are unchanged (→) from decade to decade. The Baton Rouge segment was selected for this evaluation for three reasons: (1) a large quantity of data is available for this segment; (2) the segment is downstream from the junction with the River, the major source of agricultural runoff to the River within the bounds of the study; and (3) there is a concentration of various municipal and industrial outfall along the river in this region. Advisory criteria are listed in the right side of the table.

For inorganic compounds, as discussed earlier, nitrate concentrations steadily increased over the decades, and total phosphate-phosphorous in this segment were virtually unchanged. Nitrate and ammonia levels were quite low during all decades, with the 1990's median ammonia concentration at only one quarter of the level found during the 1970's. The lower ammonia levels probably reflect improvements in the treatment of sewage discharged into the River.

The concentrations of dissolved and total arsenic, cadmium, chromium, copper, lead and nickel in River water were consistently low throughout the three decades. Median values for cadmium and dissolved lead fell below the analytical detection limits. Chromium levels were elevated

TABLE 3. Summary of Data from Baton Rouge Segment of the River Nutrients, and Radioactivity

		Median Value by Decade (n = No. of Tests) Trends between Consecutive Decades Indicated by Arrows					Advisory Criteria Ambient Water Criteria			Finished Drinking Water MCL
Parameter	Units	1970s	*	1980's	*	1990's	Chronic Exposure	Acute Exposure	Drinking Water Supply	
				Nutrients						
Nitrate-N whole water samples	mg N/L	1.10 n = 577	↑	1.30 n = 1077	↑	1.44 n = 209				10.0 (F)
Nitrite-N whole water samples	mg N/L	0.01 n = 186	↑	0.02 n = 341	→	0.02 n = 107				1.0 (F)
Ammonia-N whole water samples	mg N/L	0.08 n = 50	↓	0.03 n = 134	↓	0.02 n = 823	(8)			
Phosphorous whole water samples	mg P/L	0.19 n = 361	→	0.22 n = 1156	→	0.19 n = 212				
				Radioactivity						
Gross Alpha Radiation whole water samples	pCi/L			12.5 n = 108	→	13.0 n = 88				15.0 (F)
Gross Beta Radiation whole water samples	pCi/L			19.0 n = 1108	↑	28.0 n = 88				50.0 (F)

in the 1980's, but levels measured during 1990's were low, particularly for dissolved chromium. Median copper levels were well below the freshwater criteria.

Measurements of radioactivity are made at sampling stations close to the nuclear power plants which withdraw water from the River and discharge effluent streams back to the River. Median levels were within the drinking water standards. Gross alpha radiation in the River near the power plant monitoring locations has remained essentially unchanged from the 1980's to the 1990's. Median gross beta radiation has increased 47% between the 1980's and 1990's. Both of these radiation parameters in raw river water are below treated drinking water MCLs.

With respect to organics, benzene and the chlorinated solvents have potential carcinogenic and toxic properties which make them of particular interest. The data for several of these compounds, presented in Table 4, originated from a variety of sources, including the Early Warning Organic Detection System (EWODS) network of industries and water works operating in connection with the LDEQ [*14*]. The sampling is frequent, at some sites hourly, as reflected in large number of samples included in the evaluation. The observed median concentrations of these organics such as benzene, carbon tetrachloride, chloroform and dichloromethane, when detected, have increased between the 1980's and 1990's although the values for most do not exceed drinking water supply criteria. The one exception found is chloroform whose median concentration is 32% higher than the drinking water supply criterion. The percentage of these samples in which the organic compounds were detected in recent years is, however, small (0.5 to 15%) and reflects periodic, short term presence of the compounds in the River. The percentage of detections also dramatically decreased between the 1980's and the 1990's. For the small number of instances when chemicals were detected in the water, however, median observed concentrations increased from the 1980's to the 1990's. Median levels were far below the ambient criteria for the protection of aquatic life (chronic and acute). They were also generally below the drinking water and drinking water supply criteria which are three orders of magnitude lower in concentration than the ambient criteria. Carbon tetrachloride was an exception. The median level of carbon tetrachloride, when detected in the River during the 1990's (0.290 mcg/L), exceeded the drinking water supply criterion of 0.22 mcg/L.

Atrazine, a pre-emergent herbicide extensively used on the corn crops grown along the full extent of the Mississippi River basin, was present at some level in more than 95% of River water samples tested for this compound. Median atrazine levels for acquired data from the three decades, 1.03, 0.79, and 0.49 mcg/L, are all well below the 3 mcg/L drinking water standard, the only established criterion [*15*].

Fecal coliform bacteria in the River originate from sources of untreated human and animal wastes. This parameter most consistently exceeds various advisory criteria for different water use designations. The strictest standards are established for primary contact recreation (a most probable number [MPN] of 200 bacteria per 100 ml of water), and for oyster propagation—applicable to the most downstream of the River twenty miles below the Head of the Passes (MPN of 43 bacteria per 100 ml of water). Secondary contact recreation and drinking water supply criteria have a much higher permissible level of 1000 bacteria/100 ml and 10,000 bacteria/100 ml, respectively. While the median fecal coliform concentration in River water increased 61% between the 1970's and 1980's, it decreased by 71% between the

TABLE 4. Summary of Data From Baton Rouge Segment of the River Organics and Bacteria

		% Detections and Median Values Summarized by Decade *Trends between Consecutive Decades					Advisory Criteria			
							Ambient Water Criteria			Finished Drinking Water MCL
Parameter Evaluated	Units	1970's	*	1980's	*	1990's	Chronic Exposure	Acute Exposure	Drinking Water Supply	
				Organic Compounds						
Benzene All tests	% Detection			1.6% n = 2075	↓	0.6% n = 51744				
Benzene Samples with detected levels	Median mcg/L			0.031		0.132	1125 (L)	2249 (L)	1.1 (L)	5.0 (F)
Carbon tetrachloride All tests	% Detections	0% n = 2	↑	4.6% n = 3402	↓	0.5% n = 38064				
Carbon tetrachloride Samples with detected levels	Median mcg/L			0.151	↑	0.290	1365 (L)	2730 (L)	0.22 (L)	5.0 (F)
Chloroform All tests	% Detections	80.0% n = 5	↓	15.0% n = 3403	↓	2.8% n = 38076				
Chloroform Samples with detected levels	Median mcg/L	2.0	↓	0.140	↑	0.250	1445 (L)	2890 (L)	5.3 (L)	
Dichloromethane All tests	% Detections	0% n = 1		3.4% n = 3403	↓	0.8% N = 38077				
Dichloromethane Samples with detected levels	Median mcg/L			0.230	↑	0.490	9650 (L)	19300 (L)	4.4 (L)	
Tetrachloroethane All tests	% Detections	50.0% n = 2	↓	6.6% n = 3403	↓	1.1% n = 38064				
Tetrachlorom=ethane Samples with detected levels	Median mcg/L	5.0	↓	0.230	→	0.256	645 (L)	1290 (L)	0.65 (L)	5.0 (F)
*Atrazine All samples	Median mcg/L	1.03 n = 101	↓	0.79 n = 104	↓	0.49 n = 260				3.0 (F)
				Bacteria						
Fecal coliforms	No./100 ml	490 n = 110		790 n = 601		230 n = 41	200/100 ml (L,5)	1000/100 ml (L,6)	10,000/100 ml (L)	

1980's and 1990's. Conditions have improved and now approach the primary contact recreation criterion.

We have briefly viewed an array of data on nutrients, metals, radioactivity, solvents, coliform bacteria and a heavily used herbicide in the River. While individual compound concentrations have occasionally exceeded applicable water quality criteria for short periods of time, the picture of overall water quality which emerges for the Mississippi River in Louisiana is a favorable one. Median concentrations of constituents generally fall well below applicable criteria established both for the protection of the ecological health of the River and for the protection of human health. Organic solvents and mercury are seldom present at a detectable level in the River, although frequency of testing is very high and the analytical detection limits are very low for these parameters. Fecal coliform bacteria levels do exceed the most stringent criteria, but levels in the 1990's are only 30% of what they were 1980's. Current nitrate levels exceed the 1980's levels. The concentrations of related nitrogenous nutrients, nitrites and ammonia, are negligible. Phosphate and atrazine levels, always low, have also shown significant decreases over the last three decades.

CONCLUSION

The Mississippi River water quality database/GIS described here is an important information resource concerning water quality of the Mississippi River in the state of Louisiana. It is a repository of 1.7 million data points compiled from authoritative sources, validated to an assured quality standard, and organized for ready accessibility and ease of handling. Water quality data and geographic infor-

TABLE 5. Summary of Data from Baton Rouge Segment of the River Metals

		Median Value by Decade (n = No. of Tests) Trends between Consecutive Decades Indicated by Arrows					Advisory Criteria Ambient Water Criteria			Finished Drinking Water MCL
Parameter	Units	1970's	*	1980's	*	1990's	Chronic Exposure	Acute Exposure	Drinking Water Supply	
Arsenic whole water samples	mcg/L	3.0 n = 224	→	3.0 n = 980	→	3.0 n = 146				
Arsenic filtered water samples	mcg/L	1.0 n = 451	↑	2.0 n = 457	↓	1.0 n = 147	190.0 (F,L)	360.0 (F,L)	50.0 (L)	
Cadmium whole water samples	mcg/L	U (2.0) n = 241	↑	0.5 n = 969	→	U (0.5) n = 146				
Cadmium filtered water samples	mcg/L	U (1.0) n = 457	↓	U (0.5) n = 459	→	U (0.5) n = 147	1.4 (L,2)	5.3 (F,2)	10.0 (L)	5.0 (F)
Chromium whole water samples	mcg/L	U (10.0) n = 258	→	10.0 n = 967	↓	6.0 n = 148				
Chromium filtered water samples	mcg/L	U (10) n = 29	↑	16.0 n = 124	↓	0.3 n = 54	11.0 (L,3)	16.0 (L,3)		
Copper whole water samples	mcg/L	16.0 n = 199	↓	10.0 n = 989	→	10.0 n = 146				
Copper filtered water samples	mcg/L	5.0 n = 168	↑	6.0 n = 462	↓	3.0 n = 147	14.8 (F,2)	22.7 (F,2)	1000 (L)	1300 (P)
Lead whole water samples	mcg/L	9.0 n = 233	↓	7.0 n = 968	→	7.0 n = 145				
Lead filtered water samples	mcg/L	U (2.0) n = 450	→	U (2.5) n = 310	↓	U (0.5) n = 147	4.4 (F,L,1)	114.0 (F,L,1)	50.0 (L)	5.0 (P)
Mercury whole water samples	mcg/L	U (0.25) n = 428	→	U (0.1) n = 785	→	U (0.05) n = 146				
Mercury filtered water samples	mcg/L	U (0.25) n = 206	→	U (0.05) n = 359	→	U (0.05) n = 141	0.012 (F,L)	2.4 (F,L)	2.0 (L)	2.0 (F)
Nickel whole water samples	mcg/L	10.0 n = 140	↓	8.0 n = 343	↓	6.0 n = 99				
Nickel filtered water samples	mcg/L	2.0 n = 160	→		→	2.0 n = 136	197 (F,L,2)	1771 (F,L,2)		

Legend for Tables 3, 4, and 5

F = A Federal Criterion, Environmental Protection Agency.
L = A Louisiana Criterion, Department of Environmental Quality Regulatory Code.
P = A proposed Criterion.
1 = Advisory criteria for ammonia is dependent on temperature and pH conditions.
2 = Criteria are dependent on water hardness. The values presented are the lowest concentrations applicable to the conditions generally found in the River.
3 = Criteria presented are for the more toxic hexavalent form of chromium.
4 = Criterion for primary contact recreation.
5 = Criterion for secondary contact recreation.
6 = Depends on pH and temperature [*16*].

mation are integrated in a variety of ways to create multidimensional displays of conditions in the River. Map presentations of data permit assessment of many aspects of conditions in the river, such as the spatial geographic or seasonal distribution patterns of a parameter, the temporal trends in a parameter over several decades, the comparison of results from various analytical methodologies, the partitioning of a parameter to various fractions of the water column, and the overview of the extent of testing conducted. The GIS/database capabilities are available through Tulane staff to individuals in the academic community, government, industry, and non-governmental organizations who need to study and understand past and present water quality conditions in the River. As the system expands in the future, direct access by outside users is planned through the Internet. The database is a tool to enhance the informed environmental management decision-making process maintaining high standards of water quality for the future protection of aquatic life and human health.

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Ultraviolet/Oxidation Treatment of Explosive Wastewaters Using a Commercial Process

Craig Hempfling

Indian Head Division, Naval Surface Warfare Center, 101 Strauss Avenue, Indian Head, MD 20640

The Indian Head Division, Naval Surface Warfare Center evaluated the performance of two pilot-scale ultraviolet/oxidation systems for treatment of nitroglycerin production wastewater, Solarchem Environmental Systems and Peroxidation Systems, Inc. A commercial-scale system was purchased from Solarchem and its performance compared to that of the pilot-scale system using standard reaction kinetics procedures. The first-order reaction rate expression for nitroglycerin decomposition was developed for the commercial-scale Solarchem system.

Studies were conducted using the commercial-scale UV/oxidation system to determine the treatment by-products from nitroglycerin decomposition. Nitroglycerin and partially nitrated derivatives of nitroglycerin, inorganic nitrates, nitrites, and ammonia, and total organic carbon analyses were conducted to determine the extent of nitroglycerin decomposition and probable by-products.

Studies were also conducted on nitroguanidine wastewater to determine the effectiveness of UV/oxidation wastewater treatment for the nitroguanidine production process.

BACKGROUND

In previous work ultraviolet/oxidation (UV/oxidation) treatment of nitrate ester contaminated wastewaters generated from the two nitration plants at Indian Head Division, Naval Surface Warfare Center (IHDNSWC) was studied (Hempfling [7]). It was determined that UV/oxidation treatment is most effective on wastewater generated by the transfer of emulsified liquid nitrate esters from one building to another and was effective on all nitrate esters studied: nitroglycerin (NG), propylene glycol dinitrate (PGDN), trimethylolethane trinitrate (TMETN), and triethylene glycol dinitrate (TEGDN). Wash waters used to neutralize residual nitrating acid and extract the resulting salts can be treated with UV/oxidation, but capital and operating costs are high due to high concentrations of carbonates, which scavenge hydroxyl radicals, and nitrates, which absorb ultraviolet light. Several systems were competitively evaluated, two under a pilot-study program, resulting in the purchase of a commercial-scale UV/oxidation system for treatment of NG wastewater at the IHDNSWC Biazzi Nitration Plant.

IHDNSWC is also a producer of high bulk density nitroguanidine (HBNQ), which is produced by dissolving low density nitroguanidine in a high temperature solution of methyl cellulose and water. The mixture is cooled under controlled conditions resulting in recrystallization of nitroguanidine (NQ) of the high density form. Wastewater produced from this process is saturated with NQ at nearly 3,000 ppm and is disposed of through a commercial vendor in 5,800-gallon truckload quantities at a cost of $442.72 per thousand gallons. The commercial-scale system was used to investigate the economic and technical feasibility of UV/oxidation treatment on NQ wastewater.

This report summarizes all efforts to date and includes:

- A competitive comparison of UV/oxidation systems available from two manufacturers, including system performance on NG wastewater
- A comparison of pilot-scale to commercial-scale performance on NG wastewater
- The reaction kinetics, by-products, and mechanism of NG decomposition via UV/oxidation treatment
- The reaction kinetics and inorganic by-products of NQ decomposition via UV/oxidation treatment
- UV/oxidation treatment costs of NG and NQ wastewaters compared to current or alternative treatment methods.

EXPERIMENTAL AND METHODS

Pilot-Scale Studies

The pilot-scale studies were conducted at the respective manufacturers' sites. The Solarchem pilot-scale study was conducted on an 18-kW (three 6-kW reactors) system treating 210-L batches. The Peroxidation Systems pilot-scale study was conducted on a 2-kW reactor, the cross section of which is identical to that of their commercial-scale systems. The batch volume for the Peroxidation Systems study was 8.3 L. Hydrogen peroxide was added in batch doses at the beginning of treatment in both studies.

Commercial-Scale Treatment Studies

The commercial-scale NG and NQ wastewater treatment studies were conducted on a 120-kW (four 30-kW reactors) Solarchem Rayox UV/oxidation system equipped with programmable logic control (PLC). Wastewater contained in a 1,000-gal batch tank was recirculated with a cantilever pump having no submerged bearings, through the UV system, then through an evaporative condenser cooling tower and back to the batch tank. The PLC automatically injects 50% hydrogen peroxide, as applicable, into the wastewater to the desired concentration, 1,000 ppm for NG and 3,000 ppm for NQ. The wastewater pH was allowed to decrease in both cases as treatment progressed.

After treatment of the NG wastewater the pH was adjusted with 50% sodium hydroxide to the permitted discharge range of 6.0 to 9.0, then discharged to the NPDES outfall. The NQ wastewater contained 106 ppm of ammonia (a decomposition by-product) after treatment, well in excess of the permitted discharge limit of 10 ppm. The NQ wastewater pH was increased and maintained between 10.0 and 12.5, converting ammonium ion (NH_4^+) to ammonia (NH_3), during which time compressed air was sparged through the wastewater to strip the ammonia from the water. When the ammonia concentration was less than 10.0, the wastewater was neutralized, then discharged to the NPDES outfall.

RESULTS AND DISCUSSION

Pilot-Scale Manufacturer Comparison

The competitive procurement process employed by IHDNSWC in the purchase of the commercial-scale system resulted in solicitations from four companies, two of which, Solarchem Environmental Systems and Peroxidation Systems, Inc. (PSI), were awarded contracts for treatability studies on NG wastewater based on the technical merit of their proposals. The results of the treatability studies were compared, then used as a basis of evaluation for award of the commercial-scale system (a contract option). The UV dose requirements for the two systems evaluated are shown in Figure 1 for UV/peroxide treatment.

PSI stopped the test before the NG concentration reached 1 ppm due to limitations in their pilot-testing apparatus. Although initial NG decomposition rates were similar, the Solarchem process increased in rate as concentration decreased, as evidenced by the increasingly steep slope as treatment progresses, while the PSI process was almost precisely linear.

The PSI process relies on hydroxyl radicals formed from UV exposure to hydrogen peroxide for attack of the organic material, but PSI states that energy from the UV light makes organic molecules more receptive to the hydroxyl radicals. The Solarchem process, however, demonstrated UV-only induced NG decomposition due to lamp output at short wavelengths in the region where absorbance by NG is high. The linear decomposition rate of the PSI process may more closely approximate exactly first-order since the decomposition is based primarily on chemical reaction. The data show that the Solarchem process may benefit from the added UV mechanism, especially at lower concentrations, while governed by hydroxyl radical based decomposition at higher NG concentrations. This would account for the similar initial decomposition rates of both processes and the eventual accelerated decomposition rate by the Solarchem process.

The pilot-scale Solarchem process effectively treated NG wastewater from over 1,100 ppm to less than 1 ppm with a UV dosage of 340 kWhr/1,000 gal. Extrapolation of the PSI curve shows that a UV dosage of approximately 530 kWhr/1,000 gal would be required to treat the same wastewater to a level of 1 ppm.

Pilot-scale to Commercial-scale Comparison

Previous efforts by IHDNSWC and Solarchem Environmental Systems during a pilot-scale, on-site treatability study resulted in decomposition curves for the nitrate esters NG, PGDN, TMETN, and TEGDN [7]. The pilot data were generated using an 18-kW system consisting of three 21-L, 6-kW reactors. The commercial-scale system later purchased by IHDNSWC and used to generate the data contained in this report is a 120-kW system (four 105-L, 30-kW reactors). The contract required the manufacturer to operate the commercial-scale system prior to government acceptance and that it perform to within 20% of the pilot-scale system. Data generated during the on-site pilot study and on the commercial-scale system after installation at IHDNSWC are shown in Figure 2.

As seen in Figure 2, the Solarchem commercial-scale system performed nearly identically in actual field operation to the pilot-scale system. Both reactions were first order, as expected, and the reaction rate constants agreed to within less than 1%. The process was successfully scaled up more than six times in lamp power output and five times in reactor volume. It is also worth noting that NG concentration during the pilot study was over 1,100 ppm while the concentration during actual production was less than 650 ppm.

NG Decomposition Reaction Kinetics

NG decomposition reaction order for the commercial-scale Solarchem Rayox UV system was determined by ana-

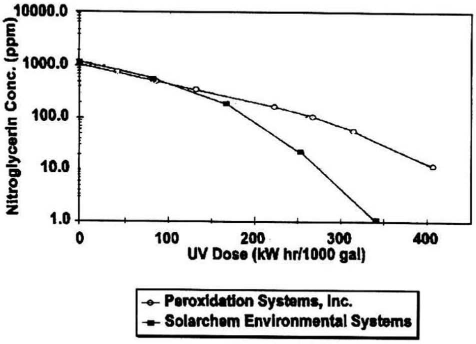


FIGURE 1 Manufacturer comparison of NG Wastewater Treatment

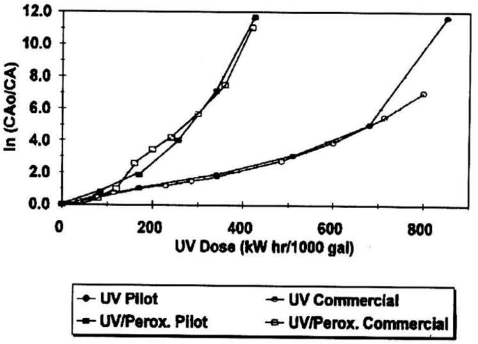


FIGURE 2 Pilot-Scale to Commercial-Scale Comparison of NG Wastewater Treatment

lyzing experimental concentration-time data as outlined by Fogler. Zero-order, half-order, first-order, and second-order batch correlations were plotted versus time, checking for linear or near-linear relationships:

Zero order:	$C_{NG} = C_{NGo} + kt$	Plot: C_{NG} vs. time
Half order:	$2(\sqrt{C}_{NGo} - \sqrt{C_{NG}}) = kt$	Plot: $\sqrt{C}_{NG}$ vs. time
First order:	$\ln(C_{NGo}/C_{NG}) = kt$	Plot: $\ln(C_{NGo}/C_{NG})$ vs. time,
Second order:	$1/C_{NG} - 1/C_{NGo} = kt$	Plot: $1/C_{NG}$ vs. time,

where:

C_{NG} = concentration of NG at time t,
C_{NGo} = initial concentration of NG,
k = reaction rate constant,
t = time.

The resulting graphs showed near-linear correlation for a first-order NG decomposition reaction for both UV-only and UV/peroxide treatments.

The procedure outlined above was developed from "pure" reaction kinetics methods, using time as the independent variable. However, by using time as the independent variable, a rate expression applying only to a specific experiment (a single volume of water treated by a given UV power source) can be derived. A more useful expression would incorporate these other variables into a more generic rate equation which could determine treatment time of any batch size using any number or power of similar UV lamps. Therefore, UV treatment is commonly expressed as a function of batch volume (V), power output (P), and, of course, time (t):

$$C_{NG} = f(V, P, t),$$

which can be arranged into a form of energy required per volume of wastewater (Pt/V), with the familiar units of kWhr/1,000 gal. To verify this relationship, the first-order relationship was replotted using Pt/V in place of t as the independent variable. An identical relationship was obtained in both cases and was corroborated on both pilot and commercial scale. Therefore, by expressing reaction rate in these terms, a generic rate relationship is obtained rather than a specific rate expression applying only to a single volume of wastewater and a single UV power output.

Next, the first-order data were fitted with an exact-linear correlation over the range of analytical detection. The slope of this line is the rate constant k. The first-order rate equations for UV and UV/peroxide treatment of NG wastewater by the Solarchem Rayox system are:

UV: $\ln(C_{NGo}/C_{NG}) = 0.00721\ Pt/V,$
UV/peroxide: $\ln(C_{NGo}/C_{NG}) = 0.0182\ Pt/V,$

with

P = UV power (kW),
t = time (hr),
V = batch volume (1,000 gal).

These are shown graphically in Figure 3.

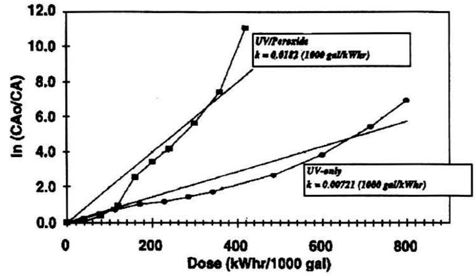


FIGURE 3 First-Order Reaction Kinetics of UV and UV/Peroxide Treatment of NG Wastewater

NG Decomposition Mechanism and By-Products

The intent of this study was to determine the extent of NG decomposition and probable by-products for both UV and UV/oxidation treatment using hydrogen peroxide. The analytical plan used is summarized below:

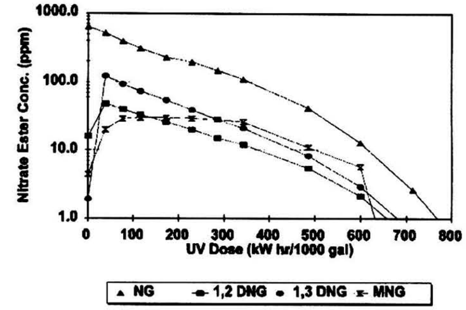
- Analytical standards for NG and its partially-nitrated derivatives, 1,2-dinitroglycerin (DNG), 1,3-DNG, and mononitroglycerin (MNG), were obtained and analyzed by HPLC as outlined previously.
- Inorganic compounds of nitrogen, nitrate, nitrite, and ammonia, were analyzed using ion chromatography.
- Total organic carbon was measured to determine the extent of carbon-carbon bond cleavage.

Figure 4 shows concentration curves for NG, 1,2-DNG, 1,3-DNG, and MNG for UV and UV/peroxide treatment. 1-MNG and 2-MNG were quantified under a single HPLC peak. In both cases, 1,3-DNG was preferentially formed under both UV and UV/peroxide treatments, even though 1,2-DNG was initially present in higher concentrations. This indicates that a primary initial step in the NG decomposition reaction is removal of the NO_2 group in the 2-position. MNG is rapidly formed indicating that NO_2 groups are removed rapidly and somewhat indiscriminately. The resulting decomposition curves for each of the NG derivatives follow generally first-order kinetics and all are effectively treated to less than 1 ppm. It is interesting to note that in both treatments, when the parent nitrate ester has been treated to less than 1 ppm, all partially-nitrated derivatives are less than 1 ppm as well, except possibly to a small extent in the case of MNG where the analytical detection appears to be slightly greater than 1 ppm, as evidenced by the sharp concentration decrease in the last sample.

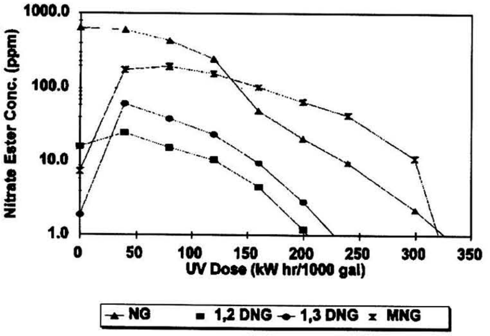
During both UV and UV/peroxide treatment, the wastewater pH decreased from neutral or slightly basic to approximately 2.4 after treatment. This is indicative of nitric acid formation by the following chemical reaction:

$$R - O - NO_2 + H_2O \rightarrow R - OH + HNO_3$$

Figure 5 shows total nitrate ester (including partially nitrated derivatives) concentration, inorganic nitrogen concentration (expressed as equivalent nitric acid), and pH. As nitrate esters are decomposed, NO_2 groups are evolved, forming nitrate ions (mostly in the form of nitric acid), resulting in the observed pH decrease.

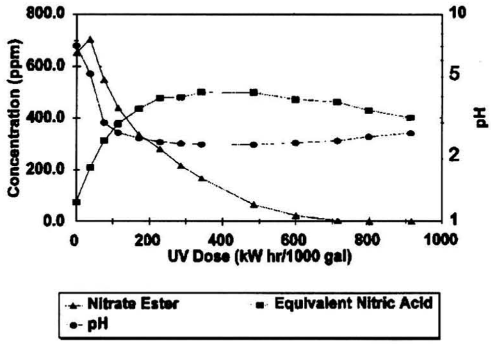


a. UV Treatment

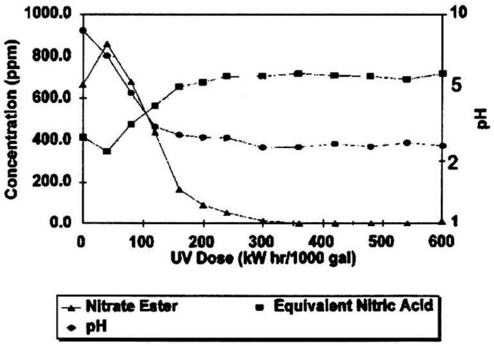


b. UV Peroxide Treatment

FIGURE 4 Nitrated By-Products of NG Wastewater



a. UV Treatment



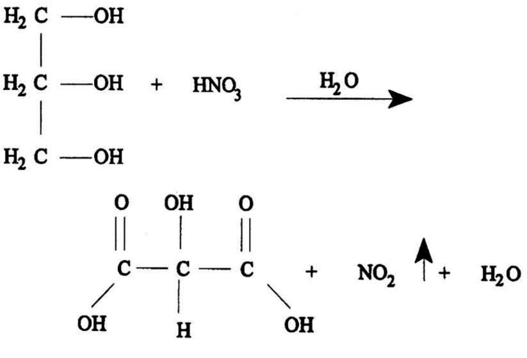
b. UV Peroxide Treatment

FIGURE 5 Nitric Acid from NG Decomposition

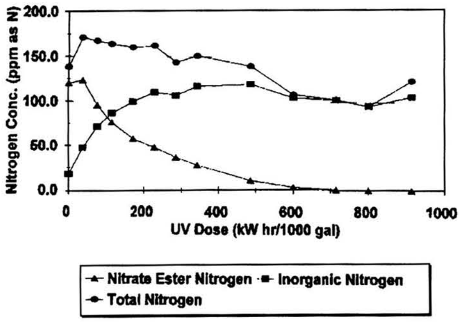
Figure 6 summarizes the treatment results in the form of a nitrogen mass balance. Nitrate ester nitrogen is the sum of the nitrogen present in the NG, DNG, and MNG. Inorganic nitrogen is the sum of nitrate, nitrite, and ammonia nitrogen.

To check the validity of the data, the nitrogen lost by nitrate esters should appear as inorganic nitrogen. The nitrogen balance between these two forms resulted in a 17.6% difference for UV treatment and a 9.5% difference for UV/peroxide treatment. In both cases, the inorganic nitrogen figure was lower, indicating that a form of nitrogen not detected by the analytical methods was formed. A gaseous form of nitrogen oxide NO_x could also explain this phenomenon since any gases would evolve from the wastewater during treatment.

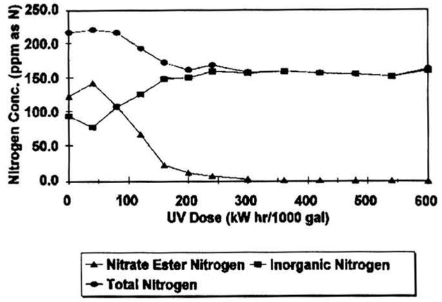
Total nitrogen is the sum of nitrate ester nitrogen and inorganic nitrogen and should remain constant as long as no gaseous nitrogen products are formed and all nitrogen is detected by the testing plan. However, in both cases, total nitrogen decreased. This could be indicative of a side reaction occurring which converts ionic nitrogen compounds into gaseous nitrogen compounds. This is further evidenced in the nitrate ion data, particularly for UV treatment, where nitrate ion concentration increased from an initial 55 ppm to a high of 493 ppm after 3 hours, then decreased to 395 ppm after 8 hours. Dilute nitric acid has been shown to oxidize alcohols with the evolution of nitrogen dioxide (NO_2) gas and water by the following reaction:



Next, samples were analyzed for total organic carbon (TOC) to determine the extent of carbon-carbon bond cleavage. Figure 7 shows the TOC data for both UV and UV/peroxide treatment. As might be expected, UV/peroxide treatment was more effective at TOC removal than UV treatment due to the added mechanism of hydroxyl radical attack. Both treatments, however, were effective at reducing organic carbon and show signs of substantial carbon-carbon bond cleavage. UV/peroxide treatment netted a 94% TOC reduction while UV treatment resulted in a 71% reduction. This is consistent with the above nitric acid oxidation of alcohols since the resulting carboxylic acid is convertible to carbon dioxide.



a. UV Dose (kW hr/1000 gal)



b. UV Dose (kW hr/1000 gal)

FIGURE 6 Nitrogen Balance of NG Wastewater

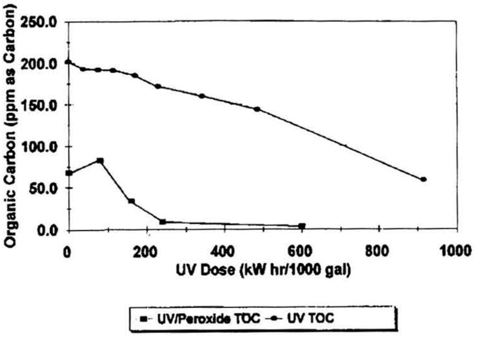


FIGURE 7 TOC Removal Testing of NG Wastewater

NQ Decomposition Reaction Kinetics

A similar decomposition kinetics procedure as used for NG was used to determine NQ reaction kinetics. It is interesting that, in this case, the reaction is zero order (linear when plotting concentration versus dose) rather than first order, as was found with all nitrate esters previously studied. The zero-order decomposition data were fitted with an exact-linear correlation to determine the rate constant *k*. The zero-order rate equation for UV/peroxide treatment of NQ wastewater by the Solarchem Rayox process is:

$$C_{NQ} = C_{NQo} - 1.402\ Pt/V,$$

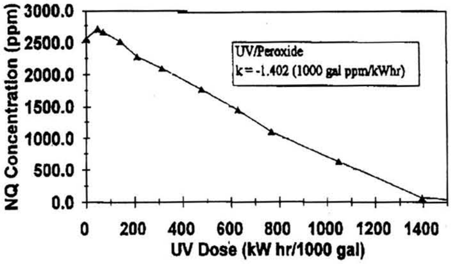


FIGURE 8 Zero-Order Reaction Kinetics of UV/Peroxide Treatment of NQ Wastewater

with

C_{NQ} = NQ concentration (ppm),
C_{NQo} = initial NQ concentration (ppm),

UV/peroxide
P = UV power (kW),
t = time (hr),
V = batch volume (1,000 gal).

This is shown graphically in Figure 8.

NQ Decomposition By-products

The intent of this study was to determine the inorganic by-products of NQ decomposition for UV/oxidation treatment with hydrogen peroxide. Treatment samples were analyzed for NQ, inorganic nitrate and nitrite ions, and ammonia. Figure 9 summarizes the treatment results except for ammonia, which remained relatively constant. Initial ammonia concentration was 76 ppm, reaching a final concentration of 105 ppm, while experiencing several slight increases and decreases during treatment time.

As in the case of NG the majority of NQ nitro groups form inorganic nitrates, with small amounts initially forming the toxic nitrite compounds which are subsequently oxidized to nitrate. Again the pH decreased due to nitric acid formation from an initial level of 8.36 to a final level of 1.80.

UV/Oxidation Treatment Costs

Prior to installation of the commercial-scale UV/oxidation system, NG wastewater was treated using activated carbon, purchased in loaded, plumbed 55-gallon canisters. NQ wastewater is currently disposed of through a com-

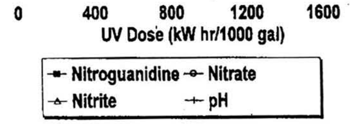


FIGURE 9 NQ Decomposition and By-Products

mercial vendor in tanker truck quantities. The costs of UV/oxidation treatment and the alternative treatment method are compared below.

Wastewater stream	Alternative treatment	Alternative treatment cost ($/1,000 gal)	UV/oxidation treatment cost ($/1,000 gal)
NG Transfer	Activated Carbon Adsorption	$246.48	$46.46
NQ Wastewater	Commercial Vendor IWTP	$442.72	$123.96

CONCLUSIONS

Manufacturer Performance Comparison

Pilot-scale systems manufactured by Solarchem Environmental Systems and Peroxidation Systems, Inc. were evaluated. The Solarchem process decomposed nitroglycerin in wastewater from over 1,100 ppm to less than 1 ppm with a UV dosage of 340 kWhr/1,000 gal. The Peroxidation Systems unit required 530 kWhr/1,000 gal to treat the same wastewater to a level of 1 ppm.

Commercial-Scale System Performance

The Solarchem commercial-scale system purchased by IHDNSWC performed nearly identically in actual field operation to the pilot-scale system. The NG decomposition reaction rate constants were calculated for both systems and agree to within less than 1%. The process was successfully scaled up more than six times in lamp power output and five times in reactor volume.

NG and NQ Decomposition Reaction Kinetics

NG and NQ decomposition reaction orders for the commercial-scale Solarchem Rayox UV system were determined by analyzing experimental concentration-time data. The NG reaction is approximately first order for both UV-only and UV/peroxide, while the NQ reaction is zero order. The following rate equations express contaminant concentration as a fraction of UV power, treatment time, and batch volume:

NG, UV treatment:

$$\ln(C_{NG_0}/C_{NG}) = 0.00721\ Pt/V,$$

NG, UV/peroxide treatment:

$$\ln(C_{NG_0}/C_{NG}) = 0.0182\ Pt/V,$$

NQ, UV/peroxide treatment: $C_{NQ} = C_{NQ_0} - 1.402\ Pt/V.$

NG Decomposition By-Products

In both UV and UV/peroxide treatment, 1,3-DNG was preferentially formed, even though 1,2-DNG was initially present in higher concentrations. The remaining NO_2 groups were removed as well, with MNG forming rapidly and subsequently diminishing as well. During both UV and UV/peroxide treatment, the wastewater pH decreased from neutral or slightly basic to 2.4 after treatment. Analysis showed formation of nitric acid and trace amounts of nitrite which were subsequently oxidized to nitrate ion. A nitrogen mass balance was used to check validity of the analytical results; the balance between inorganic nitrogen and nitrogen accounted for in the nitrate esters showed a 17.6% error for UV treatment and a 9.5% error for UV/peroxide treatment. It is proposed that a gaseous form of nitrogen is formed and subsequently evolved, which accounts for the difference. This is supported by an increase, then subsequent decrease, in nitrate ion concentration. Total organic carbon analyses showed that both UV and UV/peroxide treatments effectively reduce TOC, indicating some degree of carbon-carbon bond cleavage. UV/peroxide treatment was more effective at TOC removal than UV treatment due to the added mechanism of hydroxyl radical attack. UV/peroxide treatment netted a 94% TOC reduction while UV treatment resulted in a 71% reduction.

NQ Decomposition By-Products

As in the case of NG, nitro groups are stripped from the NQ molecules, forming mostly inorganic nitrates and causing the pH to decrease dramatically to levels less than 2.0. Initially formed nitrites are quickly oxidized to the nitrate form. Ammonia concentration remained relatively constant with both slight increases and decreases during treatment. All NQ from an initial level of over 2,700 ppm was successfully decomposed to less than 1 ppm with a UV dosage of 1,688 kWhr/1,000 gal.

Treatment Costs

In UV/oxidation treatment of both NG and NQ wastewaters a significant cost savings is realized over the current, or conventional treatment methods. In the case of NG, a cost savings of 81%, from $246.48 to $46.46 per thousand gallons, was realized through implementation of the UV/oxidation process. For NQ, a cost savings of 72%, from $442.72 to $123.96 per thousand gallons, could be realized.

The Solarchem system was installed in the treatment building for the NG wastewater and has been used to treat wastewater from NG production. The system was installed with the flexibility to perform treatability studies on other wastewaters and has been successfully used to treat NQ wastewater from 2,700 ppm to less than 1 ppm, suitable for discharge. IHDNSWC has plans to perform treatability studies on other wastewater sources to potentially expand the use of the system.

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Compliance Strategy for Cyanides in Petroleum Refinery Wastewater: Part 1—Source Characterization and Treatment

David Urban, Seth Frisbie, and Sarita Croce

ENSR, 35 Nagog Park, Acton, MA 01720

A small (< 8,000 m^3/day, < 50,000 bbl/day) petroleum refinery was having difficulty in complying with the 200 μg/L total cyanide limit in its NPDES permit. In addition, extensive cyanide corrosion was found during a turnaround of the fluid catalytic cracking unit (FCCU). Finally, the refinery was facing a NPDES permit renewal, in which the new total cyanide limit was expected to be 1.0 μg/L, the water quality standard for marine waters. The refinery, therefore, had both environmental and economic incentives for reducing cyanide in its FCCU process wastewater. The refinery undertook a multi-faceted approach to its cyanide problem, including consideration of source treatment, stripped sour water treatment, end-of-pipe treatment optimization, and discharge permit modification. This paper addresses the source characterization and treatment activities that were conducted as a part of the strategy.

Although the generation of cyanide in the FCC process is well documented, quantification of cyanides has historically been difficult due to analytical interferences from the high levels of sulfides in condensate streams from the unit. Measurements of cyanide by traditional analytical methods can be in error by orders of magnitude, and proper implementation of control technologies can be a guessing game. As a result, effective control techniques such as polysulfide injection are often avoided because of potential process upset.

Modified analytical techniques for cyanide (both free and total) and thiocyanate in refinery sour water and hydrocarbon liquids were developed. Water and hydrocarbon samples from the FCCU product distillation and gas compression systems were analyzed with these techniques, and a cyanide mass balance was developed. From the results, the following conclusions were drawn:

- *With certain process configurations, cyanides can spread far beyond the immediate condensate streams.*
- *The amount of cyanide generated in an FCCU may be higher than normally anticipated.*
- *Simple modifications to the existing system have the potential to substantially reduce cyanides, especially iron-complexed cyanides.*
- *Source treatment with polysulfide can be optimized with these improved analytical techniques.*
- *Polysulfide treatment at non-traditional, less risky locations may be adequate for meeting effluent discharge requirements.*
- *The degree of treatment required will also depend on final NPDES permit limitations. Negotiation of favorable limits can substantially reduce treatment needs.*

Follow-up studies to further optimize cyanide control are planned.

INTRODUCTION

A small petroleum refinery was out of compliance with its NPDES permit with respect to cyanide. With a total cyanide limit of 200 μg/L and typical discharge concentrations between 100 μg/L and 400 μg/L, the refinery needed to develop an effective compliance strategy. The refinery was also anticipating that the cyanide limits in its renewed NPDES permit would be lowered by two orders of magnitude to 1 μg/L, the marine water quality standard for cyanide. The primary source of cyanide was believed to be the fluid catalytic cracking unit (FCCU), operating at a throughput of approximately 1,600 m^3/day, or 10,000 barrels per day (bpd). With a typical wastewater flow rate of 1,300 m^3/day (350,000 gallons per day), the allowable cyanide discharge would be 1.3 grams (0.003 lb) per day. The strategy that was developed for cyanide compliance included two tracks: engineering controls and permit modification. This paper focuses on the engineering track, i.e., source control and/or treatment. Permitting activities are the subject of a separate paper.

ENGINEERING STRATEGY DEVELOPMENT

A feasibility study was conducted to identify engineering solution(s) that appear to be most appropriate for the facility to meet both current and future effluent cyanide limitations. Several candidate technologies were identified, including ion exchange, oxidation, and optimized biological treatment. Treatment locations included the FCCU sour water streams, sour water stripper bottoms, and refinery wastewater treatment system. Based on the technology evaluations, it was decided that a mass balance was needed to determine cyanide loadings from primary streams, the

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Seth Frisbie is now with The Johnson Co., Montpelier, VT and Sarita Croce is now with Hampshire Chemical, Nashua, NH.

extent of cyanide contamination, and the appropriate location(s) for treatment.

During a routine turnaround, the refinery determined that cyanide corrosion was a problem requiring attention. Because free cyanide is very reactive, it can accelerate corrosion in the refinery. Visible evidence of corrosion in the refinery includes: hydrogen blistering and/or cracking in the FCCU, corrosion in the amine regenerator, high amine make-up rates due to contamination by corrosion byproducts, foaming of amine system by corrosion byproducts, and hydrogen corrosion in the sour water stripper. Tell-tale blue staining (indicative of ferrocyanides) was noted at various locations in the facility. The FCC overhead system consequently became the focus of this study.

REFINERY INFORMATION

FCCU Configuration and Operation

The FCC produces higher quality naphthas from heavier feed stocks by catalytically cracking long-chain hydrocarbon molecules in a fluidized bed reactor. There are three main parts to the FCCU:

- Reactor;
- regenerator; and
- fractionator.

Reactor feed is pumped through a heater, mixed with the catalyst into a line called the riser that discharges at the bottom of a large reactor vessel similar in configuration to a water tank. By the time the feed reaches the reactor, the cracking process is well underway. The residence time in the reactor is only seconds. Because coke deposits on the catalyst reduce catalyst effectiveness, the catalyst is continuously sent to the regenerator, where coke is removed using heated air (600 deg C or 1100 deg F). The cracked product leaves the reactor vessel as a gas and is sent to a fractionating column dedicated to the catalytic cracker product. The product is typically separated into cracked gas (C_4 and lighter), cracked gasoline, cracked light gas oil, and cracked heavy gas oil.

Figure 1 is a simplified process flow diagram of the FCCU overhead system. The overhead gases from the FCCU fractionator, which are composed primarily of hydrocarbons and water vapor (from steam used in the reactor, regenerator, and fractionator), are cooled, and the condensate is collected in the FCCU Accumulator Drum. Condensed hydrocarbon is pumped to other vessels for further processing, and condensed water (sour water) containing hydrocyanic acid (HCN), hydrogen sulfide (H_2S), and ammonia (NH_3) is sent via a water boot to a holding tank (Degasser Drum), where other sour water streams are collected prior to being stripped in a Sour Water Stripper. The sour water feed enters the top of the stripper tower, and an ascending flow of stripping steam is introduced to remove hydrogen sulfide and ammonia.

The vapor phase (primarily hydrocarbon) from the FCCU Accumulator Drum is sent to a Compressor Suction Knock-Out Drum for removal of entrained or condensed liquid prior to the two-stage gas compressors. The two-phase liquid that accumulates in this Suction Knock-out Drum consists of hydrocarbon and water, and is periodically drained directly to the process sewer. The vapor phase from this drum is sent to a two-stage compressor system. In this system the vapor phase is cooled and partially condensed after each stage of compression. Wash water (fresh water) is injected after the first stage. Both vapor and liquid streams from the compressor system are sent to a Product Drum for further processing.

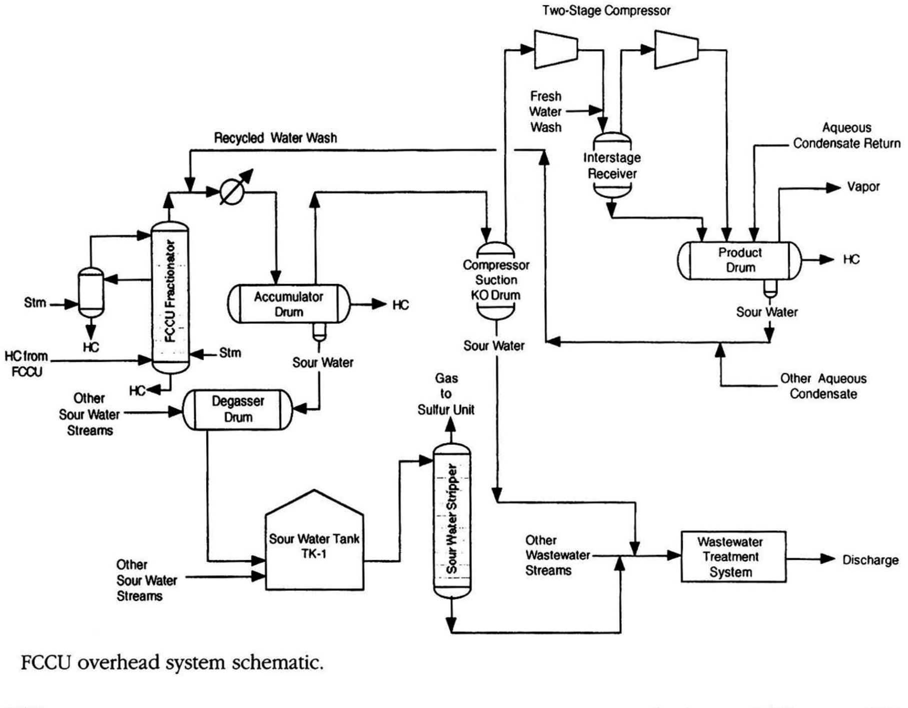

FIGURE 1 FCCU overhead system schematic.

Sour water from the Product Drum is recycled to the FCCU fractionator overhead condensers as wash water. Water flow from the Product Drum is controlled by a level control valve and is, therefore, variable. The liquid hydrocarbon as well as the hydrocarbon vapors from the Product Drum are further processed. Condensed waters from some of the downstream processes are returned to the Product Drum or injected into the recycle wash water system.

Wastewater Treatment System

The refinery wastewater treatment system consists of an API separator, Corrugated Plate Inteceptor (CPI), equalization, Induced Air Flotation Unit (IAF), two-stage activated sludge, polishing basin, and sand filtration. Typical flow rate through the system is 1,300 m^3/day (350,000 gallons per day).

MASS BALANCE

Objective

The objective of the mass balance was to determine the extent of cyanide contamination in the refinery. The information is to be used to develop an appropriate cyanide control strategy to help reduce corrosion and improve effluent quality at the refinery.

Procedures

The cyanide mass balance study involved sampling both water and hydrocarbon from 13 different locations in the facility. Water samples were analyzed for cyanides (both total and free*,**), thiocyanate, and iron. Also, pH and conductivity of the water samples were measured. Hydrocarbon samples were analyzed for total and free cyanides, as well as water content. Most of the analyses were done at an on site laboratory using the procedures described below. pH and conductivity measurements were taken with portable instruments. Because of the developmental nature of the cyanide analyses, selected split samples were analyzed by an off site laboratory for comparison purposes. Water content of hydrocarbons was determined by an off site laboratory using the Karl Fischer method.

All water samples were analyzed unfiltered. Filtered samples of the activated sludge system influent and clarifier effluent were also analyzed for free and total cyanides and thiocyanate.

During the course of the study, substantial negative interferences to the cyanide test were observed for the process wastewater samples. A procedure was developed to counteract the interferences and obtain results with reasonable level of confidence. A discussion of the analytical experiences and procedures is provided in the discussion of results.

Sample Locations, Procedures, and Analytical Schedule

Sampling locations for the mass balance study are indicated on Figure 2 and discussed below:

- FCCU Fractionator Overhead Accumulator Drum. This vessel receives the condensed hydrocarbon and water from the FCCU fractionator, along with recycled water from the product drum. The liquid hydrocarbon was sampled separately from the water.
- Compressor Suction Knock-Out Drum. This drum collects a small amount of hydrocarbon liquid and water that condenses or is entrained in the vapors from the accumulator drum. A two-phase sample was collected from this drum and separated into water and hydrocarbon phases prior to analysis.
- Interstage Receiver. This vessel receives the first-stage compressor discharge, which contains condensed hydrocarbons and water and uncondensed gases. As with the sample from the Suction KO Drum, a two-phase sample was collected from this vessel and separated into water and hydrocarbon phases prior to analysis.
- Product Drum. This drum receives the first stage compressor liquids and the second stage liquids and gases, which are separated and sent to downstream processes. This drum also receives aqueous condensates from those downstream processes. Separate liquid and hydrocarbon samples were collected and analyzed.
- Other process condensates. Other downstream aqueous condensates were sampled to determine the extent of cyanide contamination. These condensates are returned to the FCCU system or are discharged directly to the process sewer.
- Degasser Drum. Sour water from the Accumulator Drum and other sour water sources is collected in the Degasser Drum, where entrained oil can be separated. The water is sent to the Sour Water Tank prior to being treated in the Sour Water Stripper.
- Sour Water Stripper. Sour water from the Sour Water Tank is sent to the Sour Water Stripper to remove sulfides and ammonia. In the process some cyanide will be stripped. The overhead gases are sent to the sulfur recovery unit. Water samples were taken where the stripper discharges to the process sewer.
- Activated Sludge Influent. Water samples were taken at the effluent of the induced air flotation unit to represent the combined refinery wastewater prior to biological treatment.
- Clarifier Effluent. Water samples were taken at the effluent of the Clarifier to determine the effect of the activated sludge system on cyanide species.
- Sand Filter Influent. Water samples taken at the sand filter influent were intended to provide an indication of the impact of the polishing basin on the form and concentration of cyanide.

Additional notes on sample collection and analysis:

- In general, all samples were analyzed within 1 hour of collection.

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[*] *The analysis for weak acid dissociable (WAD) cyanide was considered to be the equivalent of free cyanide.*

[**] *Free cyanide is in a form that readily dissociates in weak acid, while total cyanide also includes stable metal-complexed forms of cyanide, such as iron cyanides, $Fe(CN)_6^{-2}$. The stable complexed cyanides cannot be measured directly, but are assumed to be the difference between total and free cyanide.*

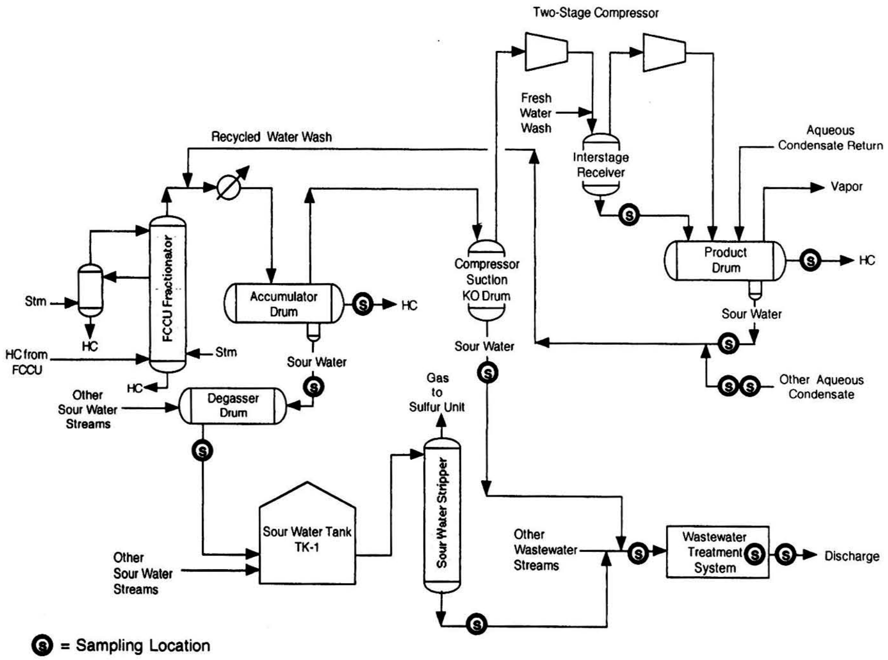

FIGURE 2 Cyanide study sampling locations.

- Cyanide was analyzed using modifications to the procedures in Standard Methods [2] for total and weak acid dissociable cyanides. Interferences with total cyanide analyses encountered during the study were attributed to sample matrix interference by organo-hydrogen sulfides. These compounds appear to distill over only during the highly acid distillation for total cyanide. The effect of this type of interference was eliminated by diluting the sample prior to distillation and/or diluting the distillate in the caustic trap.
- Several split samples were analyzed by an outside laboratory using Standard Methods for cyanide (Method 4500-CN$^-$) [2]. These results were intended to provide a comparison to the modified method developed for this study.
- Thiocyanate was determined with a modification to the procedures described in Standard Methods [2]. This modification is believed to eliminate the interferences in the matrix.
- The load of cyanide entering the main overhead accumulator is a combination of the cyanide generated during catalytic cracking, which exits the top of the fractionating column, and the cyanide recycled from downstream processes. The quantity of cyanide generated by the FCCU and exiting the fractionating column was not measured directly.
- Collection and analysis of vapor samples presented technical issues that were beyond the scope of this phase of the study. Therefore, vapor phase concentration of cyanide was not measured at any point in the system.

MASS BALANCE RESULTS

Overall Mass Balance Summary

The overall summary of analytical and mass balance results is presented in Table 1. Because of the limited number of samples and the dynamic nature of the FCCU, closure of the mass balance was not achieved, nor was it truly expected. Therefore, each key vessel and sampling point is discussed separately in order to more clearly present the sources, results, impacts, and uncertainties at each point.

Catalytic Cracker and Fractionating Column

Although no samples were taken from the FCCU or main fractionator, the evaluation of this portion of the process is important to understand potential cyanide loads and other pathways of cyanide distribution in the refinery.

In the FCCU process, steam is added to the unit charge, to the catalyst regeneration system, to the fractionating column, and side stripper on the fractionating column. The flow into the fractionating column consists primarily of the products from the catalytic cracker. The purpose of the catalytic cracking unit is to convert the heavy cuts of oil to gasoline. During this process, the nitrogen already in the crude reacts to form ammonia and hydrogen cyanide.

The fractionating column is designed to separate the lighter gases from the heavier products. Therefore, cyanide is expected to be in the vapor phase. The heavy fuel oil (bottoms of the fractionating column) is not expected to contain significant quantities of cyanide. The bottoms of the side stripper are expected to contain cyanides; these streams are further processed, and some of the cyanides are

TABLE 1. Cyanide Study Mass Balance Results

Sample Location	Accumulator Drum	Accumulator Drum	Compressor Suction KO Drum	Compressor Suction KO Drum	Interstage Receiver	Product Drum	Product Drum	Other Aqueous Condensate	Other Aqueous Condensate	Degasser Drum	Sour Water Stripper Bottoms	Activated Sludge Feed	Clarifier Effluent	Sand Filter Feed
Liquid Phase	Sour Water	HC	Sour Water	HC	Sour Water	Sour Water	HC	Sour Water	Sour Water	Sour Water	Waste Water	Waste Water	Waste Water	Waste Water
Concentrations, mg/L:														
Total cyanide	105	5	300	11	185	340	7	340	270	65	5.1	1	0.7	0.1
Free cyanide	95	3	195	11	125	330	8	140	200	54	1.7	0.25	0.15	0.09
Thiocyanate	375		475		1300	400		1200	410	120	35	4	< 0.1	< 0.1
(as CN)	169		214		585	180		540	185	54	16	2		
Mass Loading, kg/day														
Total cyanide	10.5	3.1	0.0016	0.0004	7.3	14.8	9.0	0.01	0.01	12.4	1.7	1.4	0.95	0.14
Free cyanide	9.5	1.8	0.0011	0.0004	5.0	14.4	10.2	0.01	0.01	10.3	0.6	0.3	0.20	0.12
Thiocyanate	37.3		0.0026		51.6	17.4		0.05	0.02	22.9	11.4	5.4		
(as CN)	16.8		0.0012		23.2	7.8		0.02	0.01	10.3	5.2	2.7		

returned to the sour water system. The fractionating column overhead gases, which are expected to contain elevated concentrations of hydrogen cyanide, are condensed, washed with recycled sour water from downstream processes, and collected in the overhead Accumulator Drum.

The quantity of hydrogen cyanide generated in the catalytic cracker was not measured. In a past study [*1*], a correlation was derived to estimate the cyanide produced as a function of the percent nitrogen in the crude. The crude typically used at this refinery, which has a nitrogen concentration of 0.22 percent, is below the range considered by Prather [*1*], and the correlation does not apply (a negative value results). It should be noted that the Prather study assumed that the vapors beyond the compressors (i.e., Product Drum vapors) do not contain cyanides, while results of this study indicate the potential for significant cyanide concentration in these vapors. Therefore, the Prather study probably underestimates cyanide generation rates, likely a result of analytical interferences.

Main Column Overhead Accumulator

The mass entering the accumulator drum is a combination of the fractionator overhead and the recycled wash water. The three streams exiting the accumulator include: sour water, which is pumped to the degasser; liquid hydrocarbon, which is further processed; and uncondensed vapors, which flow to the compressors. Of these three streams, sour water and liquid hydrocarbon samples were collected. The rate of cyanide entering the accumulator via the water wash was estimated to be 15 kg/day (33 lb/day) as total cyanide and 14.5 kg/day (32 lb/day) as free cyanide.

The Accumulator Drum sour water discharge contained 10.4 kg/day (23 lb/day) total and 9.5 kg/day (21 lb/day) free cyanide.

The Accumulator Drum hydrocarbon, which is further processed, contains approximately 3.2 kg/day (7 lb/day) total cyanide, and 1.8 kg/day (4 lb/day) free cyanide, based on cyanide-in-hydrocarbon analyses. It is important to note that the cyanide in this hydrocarbon stream is potentially distributed to other parts of the refinery, resulting in more difficulty in controlling cyanide impacts and discharges. If this stream has a high water content, then cyanides loads in the water can return to the water wash system via the Product Drum.

Although the cyanide concentration in the vapors was not measured, the minimum rate of cyanide mass flow in the vapors can be estimated based on known quantities. Assuming free cyanide and not complexed cyanide will be in the vapor phase, and that there is no accumulation of cyanide, the steady state mass balance is:

$$CN_{FCCU} + CN_{wash\ water} = CN_{sour\ water} + CN_{hydrocarbon} + CN_{Vapor}$$

Rearranging,

$$\begin{aligned} CN_{Vapor} &= CN_{FCCU} + CN_{wash\ water} - CN_{sour\ water} - CN_{Hydrocarbon} \\ &= CN_{FCCU} + 15\ \text{kg/day} - 10.4\ \text{kg/day} - 3.2\ \text{kg/day} \\ &= CN_{FCCU} + 1.4\ \text{kg/day} \end{aligned}$$

The minimum estimated rate of cyanide mass flow in the vapor phase exiting is 17.7 kg/day (39 lb/day), which represents the amount being recirculated in the wash water. The cyanide generation rate in the FCCU would be added to this amount to estimate the actual cyanide rate.

Because of the nature of thiocyanate, it will not be present in the vapor phase. Thiocyanate in the wash water was approximately 17.7 kg/day (39 lb/day) as SCN^-, or 7.7 kg/day (17 lb/day) as CN^-. Thiocyanate in the sour water to the degasser was approximately 37.2 kg/day (82 lb/day) as SCN^-, or 16.8 kg/day (37 lb/day) as CN^-. Because thiocyanate is not in the vapor phase, it can be assumed that it is not recirculated in the accumulator-compressor-wash-water system as free cyanide is. The resulting thiocyanate mass balance around the Accumulator Drum is a net increase of 19.5 kg/day (43 lb/day), or 13.6 kg/day (30 lb/day) as CN. This result is expected since the source of thiocyanate is the reaction of free cyanide with sulfur compounds that are present in high concentrations. It follows that the cyanide content of the thiocyanate discharged from the accumulator drum should be included in the estimate of cyanide generated by the FCCU. Therefore, the minimum cyanide generation rate in the FCCU becomes 1.4 + 19.5 = 21.3 kg/day (47 lb/day) cyanide.

Compressor Suction Knock-out Drum

The mass of cyanide exiting the Compressor Suction Knock-out Drum in the accumulated liquid is estimated to be 0.005 kg/day (0.01 lb/day) total and 0.001 kg/day (0.003 lb/day) as free cyanide. Although the amounts are low, a large fraction of the cyanide appears to be in the complexed form. This conclusion is supported by the relatively high concentration of iron (130 ppm) in the water, which also indicates that corrosion is occurring in this drum. The vapor phase, which flows to the two stage compressor system, is assumed to contain only free cyanide.

Thiocyanate cyanide was present in a concentration similar to free cyanide. It is assumed that thiocyanate is not in the vapor phase, so the presence of thiocyanate in the liquid is due to entrained liquid from the Accumulator Drum and/or reaction of cyanide and sulfur species in the liquid phase in the Knock Out Drum. The mass of thiocyanate discharged to the sewer from this source is negligible (0.005 kg/day or 0.01 lb/day).

Compressor Interstage Receiver Drum

The interstage receiver loads of free and total cyanide in the liquid were 9.1 and 6.3 kg/day (20 and 14 lb/day), respectively.

Thiocyanate was measured on only one sample of the Receiver Drum water. The concentration was 1300 mg/l, representing 57 kg/day (125 lb/day) as SCN^-, or 25 kg/day (56 lb/day) as CN^-. The concentration and mass appear to be high, indicating that the sample may not have been representative of normal operations. However, the presence of thiocyanate indicates that the conditions are conducive to promoting the reaction of cyanides with sulfur species.

Product Drum

The mass discharges of total and free cyanide from the Product Drum were 15 kg/day (33 lb/day) and 14.5 kg/day (32 lb/day) respectively in the water phase, and 9.1 kg/day (20 lb/day) and 10.4 kg/day (23 lb/day), respectively, in the hydrocarbon liquid phase. Based on Henry's Law and Raoult's Law, the cyanide that is in the vapor from this drum flowing to downstream processing was estimated to be 2.3 kg/day (5 lb/day). Much of this cyanide returns to the Product Drum via condensate returns from downstream processing.

The thiocyanate in the Product Drum sour water corresponds to a mass rate of about 17.7 kg/day (39 lb/day), or 7.7 kg/day (17 lb/day) as cyanide.

Downstream Hydrocarbon Units

There is the potential for trace levels of cyanides in both the liquid and vapor phases to become distributed throughout the refinery process units and products. Condensate streams downstream of the Product Drum had high concentrations of cyanides, but the liquid flow rates were very small. Although these loads were a small fraction of the overall loads, the results indicate that cyanides can be spread far beyond the immediate FCCU overhead system, and control to wastewater permit limitations could pose difficult challenges.

Degasser Drum

The cyanide load entering the degasser tank from the Accumulator Drum was calculated to be 10.4 kg/day (23 lb/day) total and 9.5 kg/day (21 lb/day) free cyanide. The loads from other sour water sources that enter this tank were not addressed in this study.

The degasser tank effluent cyanide mass loads were 12.2 kg/day (27 lb/day) total and 10.4 kg/day (23 lb/day) free cyanide, respectively. These results indicate that sour waters from the FCCU gas concentration unit are the main sources of cyanide, but that other sources may contribute to a small degree.

Thiocyanate mass load was 22.7 kg/day (50 lb/day) as SCN (10.4 kg/day or 23 lb/day as CN).

Sour Water Stripper

The effluent from the degasser tank, along with other sour water streams, is sent to a Sour Water Tank, which has a two day storage capacity. The Sour Water Stripper is fed directly from the Sour Water Tank. The overhead of the sour water stripper is sent to the sulfur plant and the bottoms of the sour water stripper is sent to the wastewater treatment plant. Average mass discharge of total cyanide in the stripper bottoms was 1.6 kg/day (3.6 lb/day), more than half of which is in complexed form. This result is significant because the discharge is sent to the wastewater treatment plant, and the complexed cyanides are difficult to treat. Thiocyanate and iron mass loadings were 11.3 kg/day (25 lb/day) and 1.8 kg/day (4 lb/day), respectively.

Wastewater Treatment Plant

The total and free cyanide concentrations in the *Biological Reactor Influent* averaged 1 mg/l and 0.2 mg/l, respectively. At an average wastewater flow rate of 1,300 m^3/day (350,000 gallons per day), the total and free cyanide mass rates were 1.3 and 0.3 kg/day (2.9 and 0.7 lb/day), respectively.

Thiocyanate concentration was approximately 4 mg/l in the reactor influent, corresponding to a mass loading of 5 kg/day (11 lb/day).

In order to indicate whether the cyanide was in a precipitated form, one influent sample was filtered and analyzed for cyanide. No difference was noted between filtered and unfiltered results, indicating that the cyanide was in a soluble form.

Total and free cyanide in the *Clarifier effluent* was 0.7 mg/l and 0.08 mg/l, respectively. These results indicate limited removal of cyanide across the reactor. Residual concentrations that remain are of potential concern.

Thiocyanate concentration was below detection (< 0.1 mg/l), indicating that it is degraded in the biological system.

Total and free cyanide measured in the *sand filter influent* was 0.1 and 0.09 mg/l, respectively, corresponding to a mass loading of approximately 0.14 kg/day (0.3 lb/day) cyanide.

Split Sample Results

Several samples were also analyzed by an off site laboratory to compare the modified method with the standard method for cyanide. The off site laboratory results indicated that the standard method for both total and weak acid dissociable cyanide can be low by more than two orders of magnitude, especially on process samples with high levels of sulfide. It was concluded that analytical methods were critical for obtaining a reasonable view of cyanide mass balances in the system, and that conventional analytical methods were inadequate for such mass balances.

MASS BALANCE DISCUSSION

The mass balance was intended to provide an indication of the loads of cyanide at various locations in the FCCU and the possible means of reducing cyanide loads to the wastewater treatment plant and, ultimately, in the discharge. In must be kept in mind that, in conducting the mass balances, closure was not achieved; this result was not unexpected, considering the variability in the processes and the sample holding times and analytical procedures that precluded the collection and analysis of simultaneous samples. Nevertheless, the study accomplished a major portion of the objectives, and, in the process, raised many more questions regarding appropriate strategies for cyanide control.

The key observations made from the mass balance results are the following:

- Modified analytical procedures are critical for understanding the true concentrations of cyanide in process sour waters.
- Much more cyanide appears to be generated in the refinery FCCU than correlations in the literature would predict. Based on the mass balance, the cyanide generation rate is about 17 kg per 1000 m^3 (6 lb per 1000 bbl) charged to the unit. This rate is much higher than would be expected based on the correlation developed by Prather. It can be concluded that either the Prather correlation underestimates cyanide generation rates (possibly because of analytical interferences) or the conditions in the FCCU at the refinery are conducive to higher cyanide generation rates than normal.
- Cyanide is recirculating in the FCCU main fractionator overhead system, thereby allowing additional reaction time for cyanide corrosion. The high concentration of cyanide in the main column overhead system is primarily the result of recycling cyanide from the Product Drum to the condensers as wash water, without adequately removing cyanide from the system in the Accumulator Drum sour water. Much of the cyanide in the water entrained in the Accumulator Drum hydrocarbon eventually reaches the Product Drum and is recycled. Because the Product Drum water is at higher pressure than the FCCU Fractionator overhead condensers, some of the free cyanide and other gases dissolved in the recycled water may be released from solution upon injection, thereby defeating the purpose of the water wash.
- The water wash is not effectively scrubbing cyanide out of the vapor phase hydrocarbon. Ideally a continuous water wash is effective at removing corrosive gases such as cyanide, since these gases are soluble in water. In this unit, the water wash rate at the overhead condensers is not constant, nor is it optimized based on the gas flow rate. The cyanide produced in the catalytic cracker is not scrubbed from the vapor phase consistently, and a significant amount of free cyanide remains in the vapor phase which flows to the Product Drum.

These results suggest that a clean water wash should be considered for the overhead condensers, and the rate and injection method should be optimized based on gas flow rates and process configuration. The sour water from the Product Drum and other downstream units should be sent directly to the Degasser Drum in order to remove cyanide from the system rather than recirculate the cyanide.

- In the current configuration, cyanide is present well beyond the Product Drum; the fraction of the total amount of cyanide that is spread to other parts of the refinery is unknown;
- Entrainment of water in hydrocarbon, as well as cyanide dissolved in hydrocarbon, can result in a relatively large load of cyanide being transported to downstream processing vessels;
- Significant cyanide removal occurs in the Sour Water Stripper;
- Although the thiocyanate concentrations and estimated loadings are considered to be somewhat qualitative, it appears that thiocyanate generation consumes a substantial portion of the cyanides from the FCCU. Based on the Accumulator Drum concentrations, more than half of the cyanide reacts to form SCN^-. Thiocyanate appears to be forming in each of the unit vessels. Because of the biodegradability of thiocyanate, this reaction helps to reduce effluent cyanide problems, and presumably reduces corrosion problems.
- Thiocyanate appears to be degrading completely in the wastewater treatment plant, which is consistent with available information. It follows that use of polysulfide (a common corrosion treatment strategy) to reduce free cyanide by forming thiocyanate is not expected to cause operational or effluent problems at the wastewater treatment plant; and
- Residual levels of both complexed and free cyanide remain in the wastewater treatment plant effluent.

RECOMMENDATIONS

This cyanide study has improved the understanding of cyanide sources, transport, and treatment at the refinery. However, the cyanide situation is complex, and additional steps are needed to adequately address corrosion and effluent quality. A phased approach to further efforts is recommended to achieve the project goals, as described below.

Phase 1: Reroute Product Drum Sour Water to Degasser

Initially, the sour waters from the Product Drum and other downstream condensates must be routed in the Degasser Drum to eliminate the recirculation and accumulation of cyanides in the system.

Concurrently, a clean water wash must be added to the overhead condensers.

The impact of these modifications can be far-reaching:

- The mass of cyanide in the Accumulator Drum sour water will decrease.
- Scrubbing of hydrogen sulfide and ammonia from the vapor phase will improve.
- The mass of cyanide entrained in the Accumulator Drum hydrocarbon will decrease, resulting in less cyanide being transported to downstream units.
- Cyanide concentration in the vapor streams downstream of the Accumulator Drum will decrease, re-

sulting in less cyanide being transported to downstream processes.
- Because the cyanide will be in the system for less time, the potential to form complexed cyanides will likely be reduced.

It is difficult to quantify the overall effect of these changes. Therefore, the modifications should be made and allowed to equilibrate prior to embarking on the next step in cyanide control. Ultimately, the time required to evaluate the effects can be quite long, considering that residual cyanides can be spread throughout the refinery, in products, tank water draws, as accumulated sludges in process equipment, and in the wastewater system.

Phase 2: Evaluation of Modifications

After the modifications have been made and the system reaches equilibrium, a new mass balance should be conducted to quantify the effectiveness of the changes and to further identify control strategies. At that point it may be clear whether potential cyanide corrosion concerns are still a factor, based on cyanide concentrations. It is likely that effluent concerns will remain, considering the anticipated low effluent discharge limits. The primary control strategy is expected to include polysulfide; the location for injection may be: 1) the water wash streams at either the overhead condensers or the interstage condensers; 2) the Accumulator Drum sour water boot; 3) the Product Drum sour water boot; and/or 4) the degasser tank. Selection of the appropriate location will depend on the degree of additional corrosion control required, the need to prevent formation of complexed cyanides as far upstream as possible for effluent considerations, and the need to reduce cyanide transport to downstream processes. For example, if water washing alone adequately scrubs cyanides into the sour water, and cyanides remain in the free form, then polysulfide injection into the water boot may be appropriate, and the issue of polysulfide injection into the hydrocarbon streams is avoided. However, if an unacceptable level of cyanide complexing occurs, then polysulfide injection at the water wash may be necessary.

Phase 3: Polysulfide Field Test Program

A polysulfide field test will then be conducted to evaluate the effectiveness of overall cyanide control and to develop design parameters. It is expected that a two-week field test will be adequate for this program.

Phase 4: System Installation

Upon completion of the test program, the polysulfide treatment system will be designed and installed, as appropriate.

NPDES PERMITTING AND OVERALL CYANIDE CONTROL STRATEGY

Although not a part of this paper, a separate concurrent activity was conducted to evaluate the anticipated permit limitation of 1 μg/L of cyanide in marine waters. The refinery in this study is pursuing a mixing zone which can result in much higher cyanide limitations, while still being protective of the environment. The ultimate cyanide control strategy will be a function of the impact of the permit negotiations, effectiveness of unit modifications and treatment technologies, and the need to further control process unit corrosion.

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Biological Treatment of Salty Wastewater

Gary Smythe

Syntex Agribusiness Inc., Kansas City, MO

Guy Matelli

Pace Consultants, 4828 Coop Central Drive, Houston, TX 77081

Mike Bradford and Carlos Rocha

Jacobs Engineering Group Inc., 4848 Loop Central Drive, Houston, TX 77081

Industrial wastewater containing high concentrations of salt can be treated in biological treatment systems. However, the high salt contents tend to add to the cost and sensitivity of the treatment system. Wastewater containing high concentrations of salt can be handled in the following types of treatment systems:

- *Conventional activated sludge systems can handle up to 5% salt.*
- *Anaerobic systems can handle up to 1.5% salt.*
- *Specialized systems, such as fluid bed/SBR/Zeno-Gem®, can handle up to 10% salt.*
- *Special bacteria can be used for treatment of wastewater containing up to 15% salt.*

This paper discusses three wastewater treatment projects that involved wastewater with high concentrations of salt, up to 10% salt. This paper also summarizes the information collected from literature searches conducted as part of the projects.

INTRODUCTION

High dissolved salt concentrations make the treatment of wastewater difficult for three reasons:

- Density differences becomes small, therefore, it is difficult to settle the bacteria and keep them in the treatment system.
- High salt concentrations can be toxic to bacteria which are not acclimated to the salt.
- Rapid increases/decreases in salt concentrations inhibit the growth and survival of bacteria due to extreme osmotic pressures to the organism's cell structure, which is some instances causes them to burst.

However, even in spite of these difficulties, wastewater containing high salt concentrations can still be treated using biological systems. The critical factor is to use a treatment system that keeps the bacteria in the system. An alternative to the use of special treatment equipment is a waste minimization program to remove the salt from the wastewater.

LITERATURE SEARCH

Prior to the start of the projects described in this paper, a literature search was conducted to determine treatment systems that had been successfully used in the past to treat wastewater with high salt contents. Significant information obtained during this literature search includes:

- Work conducted in Germany [*1*] demonstrated that nitrification does not occur at salt concentrations in excess of 1%. During the German tests, nitrification was documented at salt concentrations of 1%, but not at salt concentrations of 1.5% or 2%. This information was critical to one of the projects because it indicated that nitrifying bacteria could not be used to remove ammonia contained in the wastewater.
- Dow Chemical successfully operated an activated sludge system in their Sarnia, Ontario plant that treated wastewater containing 6% to 8% salt [*2*]. The system was seeded with municipal sludge, so acclimated bacteria were used. The system achieved an 80% TOC removal, but was sensitive to upsets and experienced high concentrations of suspended solids in the effluent. This project demonstrated that an activated sludge system can be successfully used to treat wastewater with significant salt concentrations, as long as suspended solids (TSS) can be tolerated in the effluent.
- Activated sludge pilot tests [*3*] were conducted to determine the feasibility of treating wastewater containing up to 12% salt. The tests demonstrated that an activated sludge system can at least partially treat salty wastewater; the unit was able to achieve a TOC removal of 28% to 43%. However, in addition to the low TOC removal, startup was difficult. It required 46 days to acclimate the bacteria, after which, tests determined that only two species of bacteria survived. The fact that only two species of bacteria survived further indicated the sensitivity of the system: large numbers of species are normally required to survive system upsets.

- Pilot sequencing batch reactors (SBRs) were successfully used to treat wastewater containing 15% salt [4]. This pilot treatment system had two special characteristics that allowed treatment of the salty wastewater:
    - A porous media was installed in the SBR. This media was used to diffuse oxygen into the bioreactor; it also provided a surface to which the bacteria could attach. Using this system, the bacteria were able to attach to a surface that kept them from floating out of the system, a surface that also provided them with good oxygen contact.
    - A special culture of bacteria was used which was cultured from the Great Salt Lake.

  During the startup of the pilot system, bacteria did not immediately attach to the porous system, in that bacteria were not observed on the surface for 11 days after startup. After acclimation, the system achieved a 90% removal of phenol.
- Bench scale SBR units were able to demonstrate at least partial TOC removal without support media for the bacteria, and without the use of "special" bacteria [5]. The bench scale tests achieved a 40% TOC removal treating wastewater containing 10% salt.

The above information demonstrates that special systems can be used to biologically treat wastewater containing up to 10% salt without specially acclimated bacteria and up to 15% salt using them.

SALT REMOVAL FOR A TREATMENT SYSTEM IN MEXICO

This project involved a pharmaceutical plant in Mexico. Located in an industrial complex, the plant is served by a regional, biological wastewater treatment system. The chemical reactions utilized in the plant resulted in the discharge of high concentrations of salt in the wastewater, violating the pretreatment standards of the regional treatment system. Either a new treatment system or removal of the salt from the wastewater was required to meet permit requirements.

A large percentage of the salt was known to originate during a specific step in the process. To confirm that this was the only source of the salt in the facility, however, a sampling program was initiated. The sampling program served two purposes:

- It confirmed that the pretreatment standards could be met if the discharge from the one reaction step could be removed from the wastewater.
- It provided information on wastewater flows and concentrations that could be used to design a treatment system for the plant wastewater.

Based on the results of the sampling program, two alternatives were considered:

- Alternative 1—design a wastewater treatment system that would allow direct discharge of the effluent, thus bypassing the regional treatment system.
- Alternative 2—installation of equipment to remove the salt from the wastewater at the source. This alternative included a number of sub-options such as evaporation and reverse osmosis.

Potential alternatives were sized and cost estimates prepared. The studies indicated that installation of a biological treatment system was technically feasible, but was not the most economical alternative. In this case, the economical approach was to collect the wastewater from the reaction step, before it mixed with the general plant effluent. An evaporator was installed to remove the salt for offsite disposal. The overhead from the evaporator, which contained the majority of the BOD in the plant effluent, was condensed and sent to the regional treatment system.

In this case, installation of a biological treatment system to handle the salty wastewater was feasible, but was not economical. The economical approach was removal of the salt before it mixed with the wastewater.

PHARMACEUTICAL PLANT WASTEWATER PRETREATMENT

This project involved a pharmaceutical plant located in Springfield, Missouri, and it encompassed characterizing the plant's waste streams, conducting a pilot test using the ZenoGem™ system, and developing various alternatives to reduce and/or treat the wastewater streams. Even though the existing treatment system utilized at the plant complied with the existing NPDES requirements, the impending promulgation of the proposed 1995 Pharmaceutical Effluent Guidelines (PEG) indicated that the plant would probably have to reduce its current discharge levels for specific organic compounds.

An analysis of the impending regulations showed that isopropanol (IPA) and methylene dichloride (MDC) required treatment to meet regulatory limitations. Based on wastewater characterization of in-plant waste streams, the combined stream's salt concentration averaged 7.4%. The major sources of salt (primarily inorganic species) were a process producing washwater with high organic and inorganic salt content, and cooling tower blowdown, which contributed up to 26% of the overall salt content of the combined wastewater stream.

The design basis adopted to evaluate different alternatives was derived from the waste characterization process, adjusted to reflect potential future production levels, and processes that may be installed at the plant. The design basis [6] was as follows:

• Average daily flow	390 m^3/day
• Maximum daily flow	780 m^3/day
• Maximum 14-day average	530 m^3/day
• Average COD	7,400 kg/day
• Maximum 14-day average COD	11,000 kg/day
• Average TDS	7.4%
• Maximum 14-day average TDS	9.8%

The alternatives analyzed included end-of-pipe treatment systems, with or without source reduction for IPA, MDC, and salts. Four alternatives were analyzed, each of which was capable of reducing the effluent concentration to required levels:

Option A: A central biological treatment system, with no source reduction.
Option B: A central biological treatment system, with source reductions in IPA and MDC and salts concentrations to within permit levels from *one* of the process' steps.

Option C: A central biological treatment system, with source reductions in IPA and MDC and salts concentrations to within permit levels from *two* of the process' steps.

Option D: This case is the same as Option C, except that a steam stripper would be used instead of a central biological treatment system.

For options A, B, and C, the biological treatment systems that were considered include the following:

ZenoGem^{TM} system,

a typical activated sludge system,

a typical anaerobic treatment system, and

sequential batch reactor (SBR).

An analysis of these alternatives indicated:

1. Options A and B were eliminated based on high investment and operational costs. Investment costs for Option A ranged between \$11.3 and \$21.8 million, whereas they ranged between \$8.7 and \$13.7 million for Option B. A reverse osmosis (RO) system was an integral part of these treatment trains in order to keep influent salt concentration below 5–7.5% in the bioreactors, depending on the biological process employed.
2. Option C, with a typical activated sludge system and source reduction, is the most attractive alternative for biological treatment. Its investment costs ranged from \$7.0 to \$8.5 million. Source reductions of organics (IPA and MDC) and dissolved solids accounted for the financial advantage of this option by eliminating the need for RO systems and by requiring smaller vessel sizes.
3. The investment costs for Option D is in the same range as for Option C, \$7.0 million. It is important to note, however, that the flexibility of a stream stripper, regarding flow rates and concentrations, is lower than that of a biological treatment system, plus operating costs for steam stripping are higher than for activated sludge.

Because of the uncertainty regarding the scope and timing of the proposed PEG guidelines, this project has been placed on hold.

CHEMICAL PLANT WASTEWATER CONTAINING 10% SALT PLUS TOXIC COMPONENTS

During 1995 and early 1996, a series of tests were run to determine if a biological treatment system could be used to treat the wastewater effluent from a hydrazine chemical plant containing 10% NaCl, 250 ppm organic Hydrazine as N_2H_4, 100 ppm of Ammonia, 100 ppm of Acetone and other toxic organic amines, Ketizones and Hydrozones. The average COD and BOD was 900 ppm and 120 ppm respectively. The average wastewater flowrate from this plant was 155 gpm.

Existing pretreatment of this waste stream prior to biological treatment involved chlorination with sodium hypochlorite addition which breaks the toxic hydrazine bond into organics that produce cyanides and chloroforms above acceptable biological treatment limits and make the wastewater expensive to treat.

A pilot plant study was conducted to take this hydrazine stream from a holding tank, neutralize it, and treat it biologically with a Fluidized Bed Bio Reactor. This treatment process (see Figures 1 and 2) is an attached growth type process utilizing carbon as the media for the microorganisms to adhere. Under normal conditions, the fluidized bed reactor would contain 25 times more microorganisms or mixed liquor volatile suspended solids (MLVSS) than a conventional activated sludge process. Therefore, the higher MLVSS makes the proposed process more viable in high salt environments.

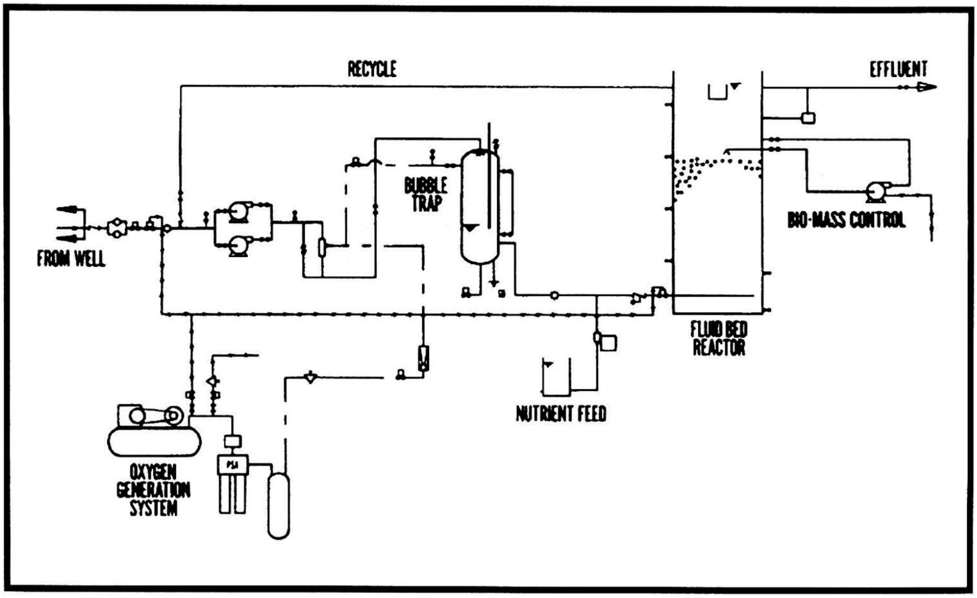
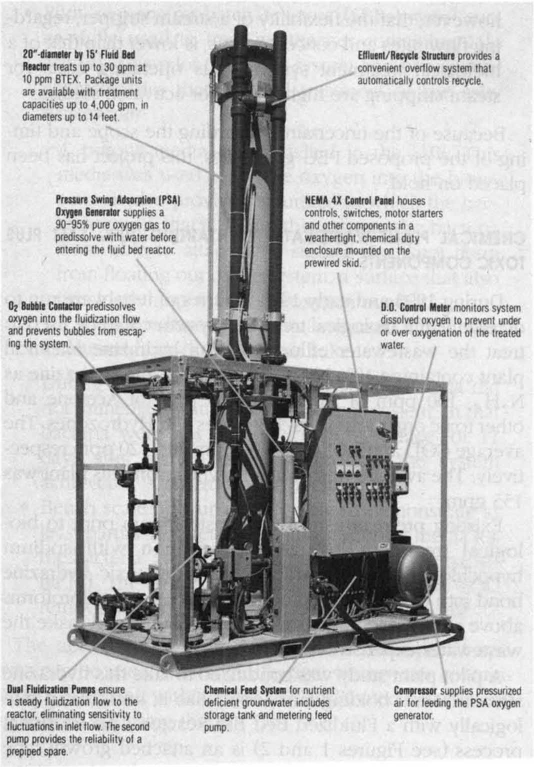


FIGURE 1 The fluid bed treatment process schematic. Reproduced by permission of Envirox Ltd. [7].



20"-diameter by 15' Fluid Bed Reactor treats up to 30 gpm at 10 ppm BTEX. Package units are available with treatment capacities up to 4,000 gpm, in diameters up to 14 feet.

Effluent/Recycle Structure provides a convenient overflow system that automatically controls recycle.

Pressure Swing Adsorption (PSA) Oxygen Generator supplies a 90–95% pure oxygen gas to predissolve with water before entering the fluid bed reactor.

NEMA 4X Control Panel houses controls, switches, motor starters and other components in a weathertight, chemical duty enclosure mounted on the prewired skid.

O_2 Bubble Contactor predissolves oxygen into the fluidization flow and prevents bubbles from escaping the system.

D.O. Control Meter monitors system dissolved oxygen to prevent under or over oxygenation of the treated water.

Dual Fluidization Pumps ensure a steady fluidization flow to the reactor, eliminating sensitivity to fluctuations in inlet flow. The second pump provides the reliability of a prepiped spare.

Chemical Feed System for nutrient deficient groundwater includes storage tank and metering feed pump.

Compressor supplies pressurized air for feeding the PSA oxygen generator.

FIGURE 2 Fluid bed pilot unit. Reproduced by permission of Envirox Ltd. [7].

The following tests were conducted prior to the pilot plant study:

- Laboratory treatability tests
- Bench scale anaerobic and aerobic treatability test
- Pilot test using a fluid bed biological treatment unit.

The following information was obtained from the tests:

- The laboratory tests confirmed that bacteria can live in the hydrazine wastewater, and can remove both hydrazine and TOC from the water.
- A review of the literature confirmed that biological treatment systems can be successfully used to treat wastewater containing 10% salt, as long as no other inhibitory compounds are present.
- The fluid bed pilot unit was able to achieve 80% and 50% removals of hydrazine and TOC, respectively, from the wastewater. However, the pilot unit was not able to develop a large population of acclimated bacteria (MLVSS) within the time frame of the tests, and could not sustain even moderate removal efficiencies.
- The difficulty in sustaining a bacteria population may have been caused by a combination of high salt and system upsets. The literature indicated that in 10% salt solutions, only a few species of bacteria survive, and that these few species are susceptible to upsets. This could explain why moderate removal efficiencies could be achieved for a short period of time, but could not be sustained. Even a minor upset or rapid change in salt concentration may have eliminated the few species of bacteria present.

CONCLUSIONS

While difficult, wastewater streams with high salt contents can be treated in biological treatment systems. Projects described in the literature:

1. Demonstrated that nitrifying bacteria will grow in salt contents up to 1%.
2. Demonstrated that activated sludge systems can be used in the 6% to 8% salt range, as long as a high TSS is allowed in the effluent. However, the biomass would be sensitive to upsets and may not be practical in many applications.

   A separate project demonstrated that only partial TOC removal is possible using an activated sludge unit to treat a wastewater containing 12% salt.
3. Sequencing batch reactors (SBRs) can be used with up to 15% salt if a media is installed in the SBR to allow a surface for the bacteria to grow without being washed out of the system. Partial TOC removal was experienced up to 10% salt with any media in the SBR.
4. For the above tests, bacteria acclimated from the Great Salt Lake was used in treatment systems containing up to 15% salt.

Pilot tests conducted as part of the projects described in this paper, demonstrated that:

1. An activated sludge system combined with an ultrafilter to remove the bacteria, in place of a clarifier, can handle at least 7.5% salt. The system was not tested with more than 7.5% salt. In theory this type of system could be expected to handle up to 10% salt, and possibly even up to 15% salt using specially acclimated bacteria.
2. It was not possible to get the bacteria to cling to the media in a fluid bed biological system, treating wastewater that contains 10% salt plus also containing a toxic compound. In theory, the fluid bed provides a surface the bacteria can cling to keep from floating out of the system, so a fluid bed system is a potential candidate for other salty wastewaters.

While the above information demonstrates that biological treatment is possible, none of the three projects described in this paper ended up installing biological treatment. Instead, two of the projects removed the salt at the source and the third project continued to use an existing physical treatment system. This occurred because the presence of the salt increased the cost of biological treatment and, thus, opened the door for other, more economically viable treatment options.

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Important Design Considerations in Wastewater Treatment Plants

Don Vacker

Bechtel Corporation, Houston, Texas 77056

Many wastewater treatment plants, over the years, have been designed and constructed with little thought being given to details that allow the whole to work as a system, and often provides little ease of operation and maintenance. Based on over 35 years experience in the field, the following are some observations of often overlooked details which a design engineer should consider. This will be categorized into the following: Front End Design, Treatability Studies, Primary Treatment, Biological Treatment, Secondary Clarification, VOC Control, Solids Dewatering and Disposal, Recycle/Reuse, and Spent Caustic Treatment.

FRONT END DESIGN

Very often not enough planning goes into establishing the appropriate design conditions. Establishing the "design basis" includes the following:

- Probability plots of historical flow and waste characteristics (BOD, COD, etc.); 50%, 90%, 99%, etc.
- Evaluation of company expansion plans or decommissioning.
- Source control and waste minimization efforts.
- Reductions via improved waste management practices, good housekeeping, improved monitoring, etc.
- Sewer segregation efforts: process from stormwater, stormwater from process.
- Sewer rehabilitation efforts, such as internal lining or replacement.
- Redundancy/risk: one 100% train; two 50% trains; etc.
- Equalization/spill tank requirements: on-line organic equalization; off-line spill containment; combination of both.
- Requirement for covering units: Benzene, etc.
- Effluent standards: Biomonitoring key issue today.
- Stormwater treatment: first flush, etc.

TREATABILITY STUDIES

In order to accurately size (without excessive conservatism) the biological treatment facilities, a bench scale treatability study should be performed utilizing at least three bioreactors. One should probably simulate the Zimpro PACT system especially given the emphasis on biomonitoring. These studies pay for themselves many times over in reduced biological system sizing, or conversely, in adequate sizing of the facilities or the correct carbon feed dose in the case of the PACT system. Enhanced biomonitoring can also result from adequate reductions in ammonia, i.e., the ability to maintain nitrifiers in the system. With totally enclosed biological systems, maintaining cool enough temperatures in the bioreactors is another challenge being faced, especially where nitrification is a factor. In some instances, direct heat exchange of the biological unit influent or of the aeration mixed liquor itself is practiced. Of course, if practical, location and cooling of few offending streams at-source is preferred.

PRIMARY TREATMENT

API Separators

There are numerous publications (including American Petroleum Institute) that discuss the proper sizing of API oil/water separators. Less discussed is the method of removal of the accumulated solids. These solids refuse to flow very well and require multiple hoppers with at least 45 degree side slope. Each hopper should be pumped individually, cycling between hoppers. The hoppers should have backflush water capability as well as water injection into the sides of the hoppers to stir the solids just prior to the pumping cycle. Refineries that have cokers and associated coke fines accumulating in the hoppers especially need this capability. This is also true of chemical plants that have a significant amount of silt and similar solids in their wastewater. Very often the water is pumped out of the bottom of the hopper through the fines, leaving the solids, and thus overloading the raking mechanism. Due to the very high maintenance requirement, internal screw conveyors are discouraged. The materials of choice of the sprocket, chain and raking mechanism is difficult at best in that neither the ferrous nor the composite materials seem to perform well. However, there are those operating facilities that attempt to operate without raking mechanisms, or abandoning them in place after some failure, find the solids accumulation problem has moved to another unit at much higher cost to remove. It is preferable to do routine preventive maintenance, as distasteful as that is in API separators, than to wait for failure. Perhaps the most important aspect of solids removal in these facilities is in the design phase: keeping suction line length at a minimum; eliminating any sharp bends; providing only long radius elbows;

and a positive displacement pump. A heavy duty double diaphragm type (typical of Dorr-Oliver and others) has proven successful, although not without their maintenance problems as well. Specification of the correct materials for the diaphragm is key as is routine maintenance and minimization of unnecessary pumping time. Additionally, one should consider a rotary drum oil skimmer on the discharge end of the separator, in addition to the slotted pipe skimmer.

Corrugated Plate Interceptors (CPI)

These oil/water separators are best suited for low solids applications. Even in low solids applications, one must be sure that the solids will not be so oil soaked that they simply stick to the plates, accumulate, and cause a catastrophic failure of the plates. Or, that the solids accumulation does not simply force the oil/water mixture through the plates so quickly (short circuit) that there is insufficient time for separation to occur. Only pilot testing can assess whether solids accumulation will be a problem in any given situation. Unfortunately, there are all too many cases where the installation of CPI's has been mandated and are currently inoperative. CPI's also have limited ability to capture and remove large spills of oil or other hydrocarbons compared to API separators. Space limitations may dictate their use. Also, with the advent of covered operating units, all too often observation hatches are not easily removable for the benefit of operations and maintenance personnel. Very often they are bolted in place. Observation ports/openings should all be equipped with sealed quick opening hatches. The material of the seal is very important as well. Solvents such as benzene, toluene, ethylbenzene and xylene tend to condense on the cooler cover inner surfaces and accumulate in high concentrations, much higher than in the wastewater, and can deteriorate the seal. All of the comments about solids removal in the above API separator section apply equally to CPI separators.

Dissolved Air Flotation (DAF)

Rectangular DAF's tend to have more maintenence problems, having chains, sprockets and more bearings to contend with. Insofar as possible, it would be preferable to have equipment with a minimum of moving parts, especially below the water surface. For most refinery applications, sizing is not difficult. Where high concentrations of emulsified oils/hydrocarbons, or solid particles, are encountered, pilot testing is recommended to establish the correct air/oil and air/solids ratios, recycles rates, overflow rates, etc. Dissolved air flotation has recently been successfully applied to high density and low density fluff and fines in a polyethylene plant.

Equalization/Spill Tank

The equalization/spill tank should be sized on the history of storm flow, and spills and dumps, having occurred at the facility. This can be obtained primarily from the probability plot of the flow and organic load or other parameter of concern, i.e. toxic materials. The size of the equalization/spill tank should be balanced against the cost of larger treatment facilities without the tank. When total treatment plant cost is plotted against increasing equalization tank size (with projected equalized organic load) vs. aeration tank/clarifier size, a minimum design point is determined. A fixed roof vs. a floating roof is often the next question. When required, floating roofs have been very successful. The key question past this point relates to the degree of mixing required. Generally, this translates in mixing terms to "mild blending" when full. As the level is lowered, any settled solids are slowly resuspended and carried forward, but equalized. Side entering mixers are very efficient. Today's designs minimize seal leakage and very effectively keep particles in suspension when properly positioned on the tank. The optimal arrangement generally means two mixers facing the same direction, placed several degrees apart horizontally and a few feet off the floor veritcally. Jet mixing has also found favor but may require more horsepower for the same water movement, and has more pumps and piping to contend with. In order for the tank to be utilized as a "spill" tank off-line, one needs some method to detect high organic load entering the treatment facility. This is most often done by an on-line TOC analyzer. The key to keeping this item up and running is proper design of the sample feed pump and, especially, a good filtration system. These analyzers can be maintenance intensive in that they have very small lines and chemical replacement to contend with, as well as repeated calibration. However, the benefits outweigh these disadvantages. There are quite a number of TOC analyzers on the market today.

BIOLOGICAL TREATMENT

Activated Sludge

Based on the treatability study, sizing of the aeration tanks is established. At least two should be installed for maintenance and redundancy. If not two 50% units, then two 75% units are installed, depending on the results of the probability plots and the degree of conservatism by the company. Generally speaking, course bubble diffusers are preferred over fine bubble in spite of the course bubble lower oxygen transfer efficiency. Most companies prefer not to contend with the added maintenance requirements of fine bubble diffusers. Oxygen transfer via jet mixers has an advantage of being able to curtail the supply of air from blowers when not needed without sacrificing minimum mixing requirements of the aeration tank. The disadvantage some companies feel is that there are more pumps to maintain. Alternatively, multistage blower capacity can be decreased to about 40% by closing the inlet valve somewhat or via throttling vanes. The deeper the aeration tank the better the oxygen transfer efficiency. That means multistage blowers are applicable to water depths of about 22 ft. (6.7 m) before they reach their shutoff point. High speed single stage blowers have applicability above this water level, however are considerably more expensive. Generally speaking then, taking into account the depth, size and cost of the aeration tanks together with the blowers, a maximum water depth of about 22 ft. (6.7 m) appears to be the most economical, incorporating amortized capital, operating, and maintenance costs. This is also on the basis of utilizing a jet aeration system. Of course, space considerations may dictate deeper tanks. Using deeper tanks, as with some commercial deep tank systems, there is the potential for sludge rising to the surface of the clarifier if there is inadequate degassing. With the introduction of air into the bottom of a 65 ft. (19.8 m) deep aeration tank, the pressure on the bubble of about 28 psig (194 kPa), and rise time, begins to simulate what happens in a DAF saturation tank —supersaturation. As the bubble rises to the surface, microscopic gas bubbles are released and tend to float the solids to the surface. Therefore, the need for incorporation of adequate degassing in the system.

PACT System

Where biomonitoring is of prime concern, this process very often can be used to improve the results via removal of toxic organic or refractory compounds. Bechtel specified the PACT system at two large refineries in California and Texas because of very stringent biomonitoring requirements. Also, a large DuPont plant and numerous other chemical plants utilize PACT as well. Where reuse of treated plant effluent is required and reverse osmosis (RO) is considered, PACT may very well be required to reduce the oil and grease and other materials to a level that is compatible with RO membranes.

SECONDARY CLARIFICATION

This is usually the last step in the treatment process and therefore much attention should be paid to all of its components. Starting with flow splitting and distribution into multiple clarifiers, this should not be taken lightly. For an example, one should not depend solely on assumed equal flow distribution based on equal sized piping. If possible, use a gravity flow splitter with weirs or other form of positive flow control. For enhanced settleability and proper flocculation, utilize a flocculating type influent well with a full circle flocculator designed with an appropriate velocity gradient (G) value. While an inboard mounted effluent trough has for many years provided enhanced effluent suspended solids quality, the Stamford baffle attached to the peripheral launder appears to show comparable effluent quality. The method of settled solids removal is very important as well. Based on the author's operating experience, the rake type sludge removal mechanism has outperformed the various hydraulic removal types. To improve performance even more, bottom slopes have been increased from the usual 1:12 to 1:8. Performance has been excellent. When sludge was settling average to poorly, both types of removal mechanisms performed comparably. When the sludge was settling and compacting especially well, the hydraulic types often plugged or removed sludge unevenly. This is common with polymer addition to secondary clarifiers. Those clarifiers with individual hydraulic pickup pipes performed poorly; plugged frequently.

VOC CONTROL

Regenerative thermal oxidizers (RTO) have been frequently installed for VOC control on streams having very low concentrations of VOC's, below the lower explosive limit (LEL). An example would be offgases from covered aeration tanks. Often, offgases from API separators and DAF's are added to this stream. Because safety must be first and foremost, a seal drum and on-line LEL and oxygen analyzers are minimum safety requirements. Other safety features must include: numerous thermocouples within the RTO and a method to introduce dilution air. The recuperative type of thermal oxidizer is said to require more maintenance.

SOLIDS DEWATERING AND DISPOSAL

Many years ago, vacuum filters were the standard for dewatering. Later, centrifuges came into vogue. Currently belt presses or recessed plate presses operate in a cost effective manner, depending on the level of dryness required for overall cost effective solids disposal. In addition, where required, rotary, screw, paddle and flash dryers are utilized to increase dryness to the 40% to 90% dry solids range. Gravity belt thickeners are proving cost effective over picket fence type gravity thickeners, achieving 4 to 6% dry solids on waste activated sludge. Very often waste activated sludge is very difficult to dewater in presses. An inexpensive filter aid the author has found which enhances dewaterability dramatically is the addition of about 5% (wt.) of bentonite clay, saving much more than the weight of clay in total tonnage to disposal. To reduce the total tonnage to disposal even further, aerobic or anaerobic digestion can reduce the original value by 25% or more. For those refineries having cokers and generating a low grade coke, disposal of oily solids and waste activated sludge to the cokers is often cost effective.

RECYCLE / REUSE

Ever more frqequently, Bechtel is being asked to provide facilities for wastewater effluent reuse and recycle. Although mechanical evaporators are available, reverse osmosis and related membrane systems are a cost effective method to accomplish reuse. Proper pretreatment is the key to long membrane life. These systems are being designed equally on highly saline oily groundwater being treated for reuse as boiler feedwater make-up and on treated wastewater for reuse in a refinery as boiler feedwater and cooling tower make-up.

SPENT CAUSTIC TREATMENT

Many refineries still continue to discharge spent caustic into the sewer system. For those where this would overwhelm the biological system, wet air oxidation and neutralization is often the solution. When discharging spent caustic directly to the sewer system one should take care not to do this immediately ahead of Archimedes type pumps, CPI separators or induced air flotation (IAF) units as the commingling of the calcium carbonate precipitate formed and the oil tenaciously adhere to the walls of the pumps, parallel plates or unit internals and result in overload and fouling conditions.

CONCLUSION

In summary, the companies and the design engineer must pay close attention to details to make the most cost effective use of any wastewater treatment system.

Modeling of Acetone Biofiltration Process

Shyh-Jye Hwang*, Hsiu-Mu Tang, and Wen-Chuan Wang

Department of Chemical Engineering, National Tsing Hua University, Hsin Chu, Taiwan, Republic of China

Biofiltration has been validated as a promising alternative to other conventional air pollution control technologies [1–3]. The objective of this research was to investigate the kinetic behavior of the biofiltration process for the removal of acetone, which was used as a model compound for highly water-soluble gas pollutants. Experiments were conducted in a laboratory-scale biofilter with a mixture of sieved compost and inert porous particles as the filter material. It was found that the elimination capacity of this biofilter could reach up to a high value of 80 g/(m^3 hr).

A mathematical model was developed by taking into account diffusion and biodegradation of acetone and diffusion of oxygen in the biofilm, mass transfer resistance in the gas film, and flow pattern of the bulk gas phase. The simulated results obtained from the proposed model indicated that mass transfer resistance in the gas phase was negligible for this biofiltration process. Analysis of the relative importance of individual rate steps indicated that the overall acetone removal process was primarily limited by the oxygen diffusion rate. Moreover, the gas phase acetone concentration profile along the biofilter and the elimination capacity predicted by the proposed model agreed well with the experimental results.

INTRODUCTION

The widespread use of acetone in many industrial processes, along with its high vapor pressure, releases tens of thousand tons of acetone per year to the environment. In light of increasingly stringent regulation of air emissions of volatile organic compounds (VOCs), an economical control technology should be developed. Biofiltration has been validated as a preferable alternative to conventional physical and chemical methods (e.g., incineration, scrubbing, and activated carbon adsorption) for the purification of large volumes of waste gases with low VOC concentrations [*1–3*]. Advantages of this process include low investment and operating costs, high removal efficiency for easily biodegradable compounds, and good operational stability. Furthermore, high destruction efficiency of pollutants in biofilters reduces secondary pollution to negligible levels [*3*].

Biofiltration is a process that utilizes microbial activity for the aerobic degradation of pollutants. A biofilter contains filter materials (mainly compost or peat) on which microorganisms are immobilized to form a biolayer. When waste gases pass through the reactor, target pollutants are absorbed into the biofilm and degraded aerobically to CO_2 and H_2O or incorporated into biomass.

Recent experimental investigations of the biofiltration process concerning the improvement of filter materials [*4–6*], operation and maintenance of biofilters [*7–10*], and reactor design [*11–12*] discuss the effects of design and operation parameters in detail. While these led to more extensive applications of the biofilter, proper design and improvement of the process depended upon quantitative understanding of the kinetic behavior in a biofilter. While much effort has been made toward model development for the biofilter [*13–17*], few investigations were conducted to established the quantitative criteria to determine the limiting step in the overall biofiltration process. Williamson and McCarty [*18*] have established criteria for determining relative importance of electron acceptor (oxygen) and electron donor (pollutant) in the mass transfer or biodegradation processes in the wastewater treatment systems. Shareefdeen *et al.* [*14*] derived criteria to determine the limiting step in the methanol biofiltration process. Based on a previous study [*18*], they suggested that the removal of methanol in a biofilter was primarily limited by oxygen diffusion rate and methanol degradation kinetics.

The objective of this research was to investigate the kinetic behavior of the acetone biofiltration process. Continuous experiments were conducted in a laboratory-scale porous clay/compost biofilter. A mathematical model was developed by taking into account the bulk gas flow, mass transfer in the gas film, and diffusion and biodegradation in the biofilm. Analysis of the effectiveness factor determined the relative importance of diffusion and biodegradation rate in the biofilm and indicated the limiting factor for the acetone biofiltration process under various operating conditions.

MATERIALS AND METHODS

The experimental apparatus used in this study is shown in Figure 1. The biofilter was divided into four 30 cm sections, each with an effective packing height of 25 cm. The filter material was a mixture of equal volume of compost (0.7–2.0 mm) and porous clay particles (4–5 mm). The total packing volume of the biofilter was about 5 L, and the bed porosity was 0.42. A mixed culture acclimated to acetone was used as the inoculum of the biofilter. $CaCO_3$ was used as a buffer salt to maintain the pH of the filter material at 7.0. Humidification of the inlet gas stream kept the water content of the filter material at about 50% (by weight). Artificial waste gas stream was made by injecting pure liq-

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* *To whom all correspondence should be addressed.*

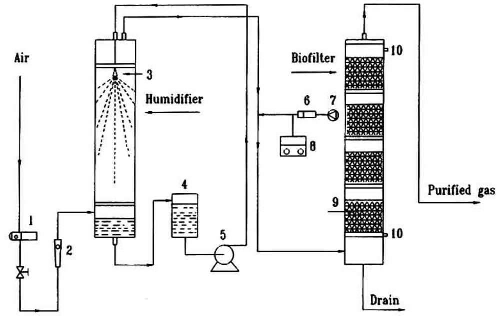

FIGURE 1 Schematic diagram of the biofilter system.
1. Air Filter
2. Rotameter
3. Nozzle
4. Water reservoir
5. Pump
6. Syringe
7. Syringe pump
8. Temperature controller
9. Filter material
10. Sampling ports

uid acetone into the effluent air stream from the humidifier by a syringe pump (Sage, Model 341B). Acetone concentration of the gas flowing into the biofilter was varied by adjusting the injection rate of the liquid and the flow rate of the air stream.

THEORY

A schematic representation of the biofilm model is provided in Figure 2. The overall kinetics in a biofilter is represented by the interactions among mass transfer in the gas phase, diffusion and microkinetics in the biofilm, and flow pattern of the bulk gas phase. Planar geometry is used since the biofilm thickness is substantially smaller than the particle size.

Material Balances

The material balance equations are established on the basis of the following assumptions:

(1) The diffusion of acetone and oxygen within the biofilm can be represented by effective diffusion coefficients, D_a and D_o (m^2/s).

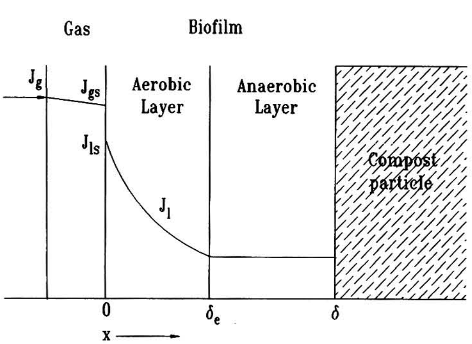

FIGURE 2 Schematic representation of the biofilm model. (J_g, J_l: concentrations of substrate J in the bulk gas phase and the biofilm; J_{ls}, J_{gs}: liquid phase and gas phase concentrations of substrate J at the gas-biofilm interface).

(2) At the gas phase-biofilm interface, acetone and oxygen concentrations in the gas phase are in equilibrium with those in the biofilm, respectively.

(3) The biofilm dry density is constant throughout the filter bed.

(4) The flow pattern of the bulk gas is plug flow.

(5) Microkinetics is characterized by a double-substrate limiting mechanism described by a Monod type equation. Thus the microbial specific growth rate, μ (l/hr), is given by:

$$\mu = \frac{\mu_m S_l}{K_a + S_l} \frac{O_l}{K_o + O_l} \tag{1}$$

where S_l and O_l are the acetone and oxygen concentrations (g/m^3) in the liquid phase, K_a and K_o are the half saturation constants (g/m^3) on acetone and oxygen, and μ_m is the maximum specific growth rate (l/hr).

The material balances of acetone and oxygen in the biofilm are:

$$D_a \frac{d^2 S_l}{dx^2} - \frac{X_v}{Y_{x/a}} \mu = 0 \tag{2}$$

$$D_o \frac{d^2 O_l}{dx^2} - \frac{X_v}{Y_{x/o}} \mu = 0 \tag{3}$$

where X_v is the biofilm dry density (kg/m^3), and $Y_{x/a}$ and $Y_{x/o}$ are the yield coefficients on acetone and oxygen, respectively.

The corresponding boundary conditions are:

$$x = 0, \quad D_a \left.\frac{dS_l}{dx}\right|_{x=0} = -k_{ga}(S_g - S_{gs}), \quad S_{gs} = m_a S_{ls} \tag{4}$$

$$D_o \left.\frac{dO_l}{dx}\right|_{x=0} = -k_{go}(O_g - O_{gs}), \quad O_{gs} = m_o O_{ls} \tag{5}$$

$$x = \delta_e, \quad \frac{dS_l}{dx} = \frac{dO_l}{dx} = 0 \tag{6}$$

where x is the position in the biofilm (μm), k_{ga} and k_{go} are the mass transfer coefficients of acetone and oxygen from the bulk gas phase to the gas-biofilm interface (m^2/s), S_{ls} and O_{ls} are the liquid phase concentrations of acetone and oxygen at the gas-biofilm interface (g/m^3), S_{gs} and O_{gs} are the respective gas phase concentrations of acetone and oxygen at the gas-biofilm interface (g/m^3), and δ_e is the effective biofilm thickness (μm).

The mass balances of acetone and oxygen in the bulk gas phase are:

$$u_g \frac{dS_g}{dz} + N_a A_s = 0 \tag{7}$$

$$u_g \frac{dO_g}{dz} + N_o A_s = 0 \tag{8}$$

where u_g is the gas superficial velocity (m/s), z is the axial position along the biofilter (m), A_s is the effective specific biofilm surface area (l/m), and N_a and N_o are the mass fluxes of acetone and oxygen into the gas-biofilm interface ($g/m^2 \cdot s$), respectively. Note that N_a and N_o are given by:

$$N_a = -D_a\left(\frac{dS_l}{dx}\right)\bigg|_{x=0} \tag{9}$$

$$N_o = -D_o\left(\frac{dO_l}{dx}\right)\bigg|_{x=0} \tag{10}$$

The corresponding boundary conditions are:

$$z=0, \quad S_g = S_{gi}, \quad O_g = O_{gi} \tag{11}$$

Solving equations (1)–(11) numerically yields the concentration profiles of acetone and oxygen along the biofilter and in the biofilm. The values of the parameters used in the model and the methods of their determinations are listed in Table 1.

Effectiveness Factor

The value of the effectiveness factor, η, indicates the relative importance of diffusion and reaction rates. The definition of η is [*24*]:

$$\eta = \frac{\text{actual consumption rate of substrate in the biofilm}}{\text{maximum consumption rate of substrate in the biofilm}} \tag{12}$$

Let

$$S_l^* = \frac{S_l}{K_s}, \quad O_l^* = \frac{O_l}{K_o}, \quad \theta = \frac{x}{\delta_e}$$

$$\phi = \left(\frac{\mu_m X_v \delta_e^2}{Y_{x/s} D_s K_s}\right)^{1/2}, \quad \lambda = \frac{D_s K_s Y_{x/s}}{D_o K_o Y_{x/o}}$$

The effectiveness factor is then given by:

$$\begin{aligned}\eta &= \frac{N_a}{(R_a)_{\max}} = \frac{1}{\phi^2}\left(\frac{\delta_e}{\delta}\right)\frac{1}{\left(\dfrac{S_{ls}^*}{1+S_{ls}^*}\right)\left(\dfrac{O_{ls}^*}{1+O_{ls}^*}\right)}\frac{dS_l^*}{d\theta}\bigg|_{\theta=0} \\ &= \frac{N_o}{(R_o)_{\max}} = \frac{1}{\phi^2\lambda}\left(\frac{\delta_e}{\delta}\right)\frac{1}{\left(\dfrac{S_{ls}^*}{1+S_{ls}^*}\right)\left(\dfrac{O_{ls}^*}{1+O_{ls}^*}\right)}\frac{dO_l^*}{d\theta}\bigg|_{\theta=0}\end{aligned} \tag{13}$$

where $(R_a)_{\max}$ and $(R_o)_{\max}$ are the maximum consumption rate of acetone and oxygen in the biofilm ($g/m^2 \cdot s$), respectively.

Criteria for Determination of the Limiting Step

Based on the criteria established by McCarty and Williamson [*18*], the criteria for determining the relative importance of oxygen and acetone in mass transfer or biodegradation process is derived and the limiting step in the acetone biofiltration process is determined

A. Kinetic limiting criterion

The following criterion is for oxygen kinetic limiting. If it is not satisfied, then acetone kinetic limiting occurs.

$$S_g < \frac{\dfrac{O_{gi}}{K_o m_o}\left(\dfrac{Y_{x/s} S_{gi}}{Y_{x/o} O_{gi}} - 1\right)}{\left(\dfrac{Y_{x/s}}{Y_{x/o} K_o m_o} - \dfrac{1}{K_a m_a}\right)} \tag{14}$$

TABLE 1. Values of the Parameters Used in the Model

Parameter	Value	Source	Unit
A_s	255.15	Adjustable parameter	(l/m)
D_a	$5.76*10^{-10}$	Fan et al. [*19*]	(m^2/s)
D_o	$1.22*10^{-9}$	Fan et al. [*19*]	(m^2/s)
k_{ga}	$2.71*10^{-2}$	Froment and Bischoff [*20*]	(m/s)
k_{go}	$5.46*10^{-2}$	Froment and Bischoff [*20*]	(m/s)
K_a	10.33	Batch culture experiment	(g/m^3)
K_o	0.5	Mid value of Minkevich and Utkina [*21*]	(g/m^3)
m_a	0.00028	Betterton [*22*]	(—)
m_o	34.4	Shareefdeen et al. [*14*]	(—)
O_{gi}	275	Ideal gas law	(g/m^3)
X_v	27.6	Mid value of Fujie et al. [*23*]	(kg/m^3)
$Y_{x/a}$	0.388	Batch culture experiment	(—)
$Y_{x/o}$	0.23	Mass balance	(—)
δ_e	20–100	Shareefdeen et al. [*14*]	(μm)
μ_m	0.0366	Batch culture experiment	(l/hr)

B. Diffusion limiting criterion

The following criterion is for oxygen diffusion limiting. If it is not satisfied, then acetone diffusion limiting occurs.

$$S_g > \frac{O_{gi}\left(1 - \dfrac{Y_{x/s} S_{gi}}{Y_{x/o} O_{gi}}\right)}{\left(\dfrac{D_a \nu_o M_o m_o}{D_o \nu_s M_s m_a} - \dfrac{Y_{x/s}}{Y_{x/o}}\right)} \tag{15}$$

where M_s and M_o are the molecular weights of acetone and oxygen, respectively, and ν_s and ν_o are the stoichiometric coefficients of acetone and oxygen, respectively in the following material balance equation for the biological reaction.

$$C_3H_6O + 3.04\,O_2 + 0.182\,NH_3 \rightarrow 0.91\,CH_{1.8}O_{0.5}N_{0.2} + 2.45\,H_2O + 2.09\,CO_2 \tag{16}$$

RESULTS AND DISCUSSION

Figure 3 shows the predicted acetone and oxygen concentration profiles and the experimental acetone concentration data along the biofilter at a constant gas superficial velocity of 0.01 (m/s) and inlet acetone concentration of 2.95 (g/m^3). As this figure shows, the simulated results with and without mass transfer resistance in the gas phase are very close. Thus, mass transfer resistance in the gas phase is negligible even for biofiltration of highly water-soluble compounds such as acetone. In addition, the acetone concentration profile along the biofilter is linear. Consequently, biodegradation within the biofilm follows zero order kinetics with respect to acetone under this operating condition. Note the satisfactory agreement between the experimental data and model predictions.

Figure 4 displays the effect of the acetone loading on the elimination capacity of the biofilter at a constant gas superficial velocity of 0.01 m/s. The maximum elimination capacity of the biofilter for acetone is approximately 80

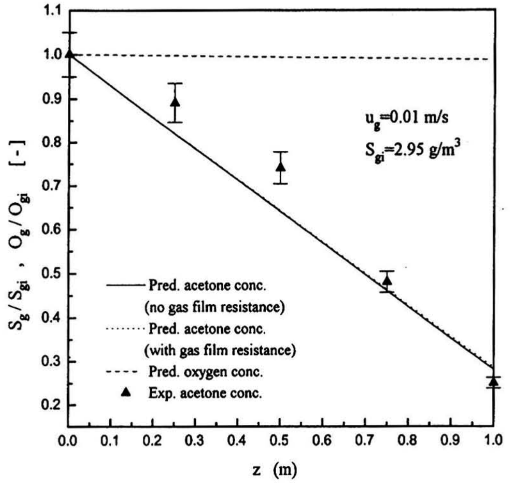

FIGURE 3 Gas phase concentration profiles of acetone and oxygen along the biofilter.

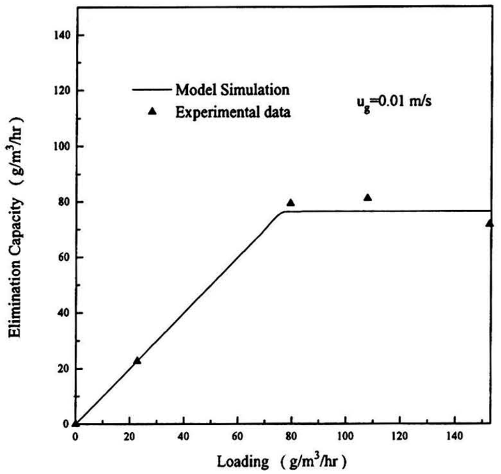

FIGURE 4 Effect of the acetone loading on the elimination capacity of the biofilter.

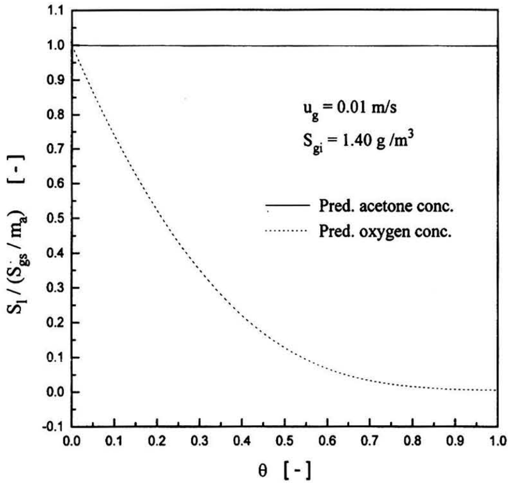

FIGURE 5 Concentration profiles of acetone and oxygen in the biofilm ($z = 0.5$ m).

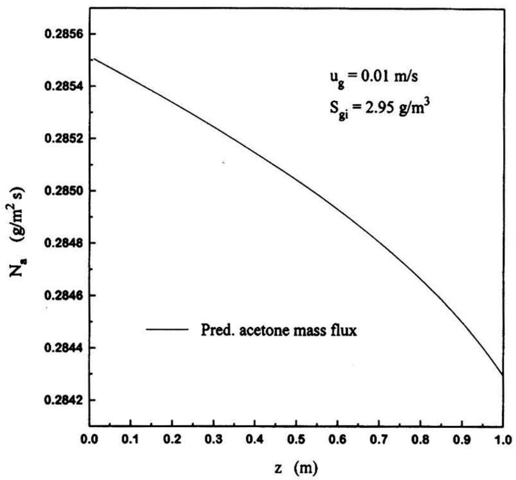

FIGURE 6 Acetone flux into the biofilm along the axial position of the biofilter.

g/(m^{3}hr). For a loading of acetone lower than 80 g/(m^{3}hr), the elimination capacity of the biofilter is equal to the acetone loading. However, when the acetone loading is higher than 80 g/(m^{3}hr) the system is overloaded and the removal efficiency decreases. This figure also indicates that the simulated results are in good agreement with the experimental data.

Figure 5 shows the dimensionless concentration profiles of acetone and oxygen in the biofilm located at 0.5 m from the bottom of the biofilter. The gas superficial velocity and inlet acetone concentration are controlled at 0.01 (m/s) and 2.95 (g/m^3), respectively. As a result, oxygen diffusion rate limits the acetone removal process because oxygen is depleted at some point in the biofilm, while a large amount of acetone is present throughout the biofilm.

Figure 6 illustrates the acetone flux into the biofilm along the axial position of the biofilter. The acetone flux, related to the slope of the concentration profile at the gas-biofilm interface, is higher near the inlet of the biofilter. As the waste gas flows upward through the biofilter, the radial acetone flux decreases gradually because the biodegradation rate in the biofilm decreases due to decreasing gas phase concentration along the biofilter. The effectiveness factor (η) for the biofiltration of acetone is between 0.27 to 0.35 under the operating conditions used in this study. Thus, the overall removal rate is limited by the diffusion rate of the substrate (acetone or oxygen) in the biofilm. Moreover, according to the derived diffusion limiting criterion (Eq. 15), the process is limited by oxygen diffusion for the operating conditions used in this study. Therefore, increasing the biodegradation rate of acetone by using specific organisms will have a minor effect on the overall acetone removal efficiency.

Figure 7 shows the effect of inlet acetone concentration

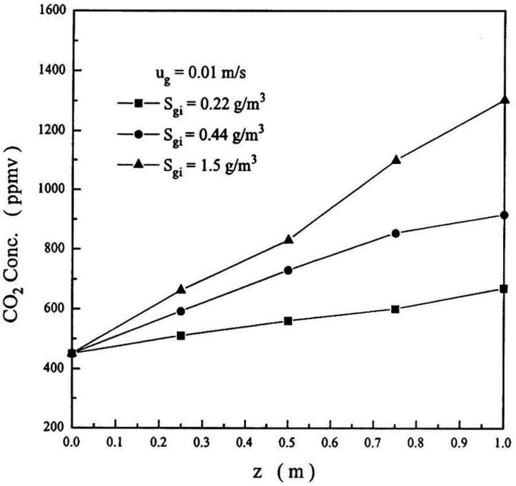

FIGURE 7 Effect of inlet acetone concentration on CO_2 concentration profile along the biofilter.

on the experimental CO_2 concentration profile along the biofilter. A background CO_2 level of 450 ppmv was measured in the inlet of the biofilter. In the biofiltration process, production of CO_2 results from biodegradation of the organic pollutants, mineralization of the organic matter in the filter material, and endogenous respiration of the biomass. As shown in this figure, increasing inlet acetone concentration results in a higher CO_2 production. The exit CO_2 concentrations for the inlet acetone concentrations of 0.22, 0.44, and 1.5 g/m^3 are 628, 905, and 1310 ppmv, respectively. This indicates that biodegradation of acetone actually occurs in the biofilter.

CONCLUSIONS

This study showed that a laboratory-scale biofilter with sieved compost and porous clay particles as the filter material was effective for the removal of acetone from the waste gas stream. The acetone elimination capacity of this biofilter could reach up to 80 g/(m^{3}hr). A biofilm model with mass transfer resistance in the gas film has been developed in this study. The accurate predictions of the gas phase acetone concentration profile along the biofilter and the elimination capacity of the biofilter by the proposed model were also demonstrated. Moreover, the simulated results indicated that mass transfer resistance in the gas phase was negligible for the acetone biofiltration process. Analysis of the effectiveness factor, along with the two criteria established for determining the relative importance of oxygen and acetone in mass transfer and biodegradation process, indicated that the removal of highly water soluble acetone was primarily limited by the oxygen diffusion rate. Results obtained in this study provide insight into the kinetic behavior of the biofiltration process and are useful guidance in biofilter design and operation.

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Chemical Evolution of Liquid Redox Processes

David DeBerry

Radian International LLC, P.O. Box 201088, Austin, TX 78720

A multitude of processes have been proposed for removal of hydrogen sulfide from gaseous streams. Removal of H_2S from sour natural gas streams is particularly difficult since low outlet concentrations must be reached before the gas is put into a pipeline. Liquid redox sulfur recovery (LRSR) processes use a solution containing an oxidizing agent that absorbs H_2S from the gas stream and oxidizes it to sulfur. The chemistry of these processes has undergone considerable evolution in the last 30 years.

A number of tradeoffs must be considered in designing LRSR processes. For example, the rate of reaction of the oxidized agent with H_2S often determines the scrubbing efficiency, but excessive rates of sulfur formation in the scrubber can lead to plugging. Systems based on vanadium and/or anthraquinone disulfonates (ADA) as the redox catalyst had several drawbacks, most of which can be traced to sluggish redox agent kinetics. Current LRSR processes use chelated iron as the catalyst for sulfur recovery. This gives faster scrubbing and reoxidation kinetics, but chemical degradation of the chelating agent can affect the economics of the process. Plugging of sorption vessels continues to be a problem in some applications. New nonaqueous solvent-based or biological processes may overcome these problems.

INTRODUCTION

Economical removal of hydrogen sulfide from gaseous streams is difficult, and many processes have been proposed and tested. Removal of H_2S from wellhead natural gas streams is particularly difficult since low concentrations (4 ppm) must be reached before the gas is put into a pipeline, and the locations are often remote. Liquid redox sulfur recovery (LRSR) processes use a near ambient (nominally 20–50°C) temperature solution to absorb hydrogen sulfide from the gas stream. This solution contains an oxidizing agent that converts the sulfide to elemental sulfur. The chemistry of these processes has undergone considerable evolution in the last 30 years. Since LRSR processes involve complex chemical processes, understanding their basic chemistry is key to ensuring reliable and economical operation. This paper discusses the issues which drive the chemical evolution of these processes and the changes that have resulted.

The overall reaction in LRSR processes is the same as for Claus process H_2S conversion [*1*, *2*, *3*].

$$H_2S(g) + \frac{1}{2}O_2(g) \rightarrow S(s) + H_2O(l) \qquad (1)$$

However, direct oxidation of H_2S by oxygen is slow and side reactions tend to form undesirable sulfur oxyanions as byproducts. Therefore, oxidation of H_2S in the LRSR absorber is carried out by an intermediate redox couple ("catalyst"), denoted Ox (for the oxidized form of the redox couple) in Reaction 2.

$$2\,Ox(l) + H_2S(g) \rightarrow S(s) + 2\,R^-(l) + 2\,H^+(l) \qquad (2)$$

The symbol R^- is used for the reduced form of the oxidizing agent, which is a one electron redox couple in this example. This reaction is most likely directly responsible for a large part of the removal of H_2S from the gas stream, although some removal can be attributed to neutralization of the acidic H_2S molecule by alkalinity in the scrubbing solution when the pH of the solution is greater than 7.

The reduced form of the redox couple produced in Reaction 2 is regenerated with air in the oxidizer, according to the overall Reaction 3.

$$4\,R^-(l) + O_2(g) + 4\,H^+(l) \rightarrow 4\,Ox(g) + 2\,H_2O(l) \qquad (3)$$

As shown, this reaction also consumes hydrogen ions, neutralizing the hydrogen ions generated in the sorption step (Reaction 2). The sulfur slurry is removed from the oxidizer and sent to a filtration unit for removal as a wet (approximately 50% solids) cake.

An excellent history of liquid redox processes has been given [*4*]. The present paper emphasizes the chemical issues in liquid redox sulfur chemistry and how they have evolved. This paper is organized by the following key topics:

- H_2S absorption efficiency;
- Redox "catalyst" regeneration;
- Byproduct formation rate;
- Chemical consumption;
- pH effects; and
- Sulfur formation.

These factors are interactive. For example, a strong oxidizing agent will readily absorb H_2S, but is difficult to regenerate with air. High rates of reaction of the oxidized catalyst with H_2S can provide good scrubbing, yet excessive rates of sulfur formation in the scrubber can lead to plugging. There are many other chemical tradeoffs in liquid redox sulfur recovery processes. Although commercial LRSR catalysts have high conversion efficiencies for each of these oxidation/reduction steps, even small chemical inefficiencies, degradation, or other chemical losses can affect process economics since the catalysts are recycled many times.

H_2S Absorption Efficiency

Redox driving forces are high, and LRSR processes have the potential for highly efficient H_2S removal. This implies that the concentration of H_2S in the treated gas can be reduced to low levels without the use of excessively large or high-energy absorbers. Much of this high efficiency is due to the electron transfer capabilities of the redox catalyst which reduces the liquid-phase concentration of H_2S to very low levels and thus practically eliminates "backpressure" effects [5]. For example, iron chelated by EDTA (ethylenediamine-N,N,N',N'-tetraacetic acid) has a standard redox potential (E^0) of about +0.1 V vs. SHE. This value is 0.34 volts positive of the E^0 for the redox couple $H_2S(g)$/sulfur (−0.24 V at pH 7.0). This provides enough driving force to reduce the H_2S equilibrium partial pressure to insignificant values (about 3×10^{-26} atm at equal concentrations of oxidized and reduced redox species and pH 7.0). The rate of reaction of the redox catalyst with H_2S is also important. For good scrubbing efficiency and small absorber size, this rate should be as high as possible. The more successful catalysts appear to rapidly form a complex with H_2S and then more slowly convert it to sulfur. The initial complex formation reduces the equilibrium backpressure of H_2S. The initial reaction rates of H_2S with several oxidizing agents are shown in Table 1. The values shown are second order rate constants derived primarily from the initial oxidation step or the rate of disappearance of sulfidic (sulfur in the −2 oxidation state) species. These rate constants range over six orders of magnitude, probably reflecting large differences in the chemical pathways of sulfide oxidation. The faster couples (such as Fe(III)EDTA) are used in commercial iron chelate LRSR processes. Oxidants which probably favor pathways involving radicals (such as O_2, H_2O_2, and MB^+) are the slowest reactants. This could be due to the high energy required to form HS • radicals. Catalysis of the oxygen reaction with cobalt phthalocyanine apparently provides an alternate reaction path and dramatically increases the rate of reaction. The Stretford process, an earlier LRSR process, used a mixture of vanadium and anthraquinone-2,7-disulfonate (ADA) salts as catalysts. The pathway for reaction of ADA with H_2S is not known. Since the reduction potential of ADA is fairly close to that of sulfide, the sluggish rate shown in the table may be due to the low available driving force. Vanadium(V) has an intermediate reaction rate, but is slow compared to the iron compounds. This is probably due to the difficulty in substituting a sulfide species for an oxygen species at the highly oxygenated vanadium metal center.

Also important is the capacity of the scrubbing liquid for H_2S as this can control the liquid circulation rate between the scrubber and oxidizer. A low liquid circulation rate is desirable, particularly for applications where the scrubber is operated at high pressure (such as a direct treat natural gas application). Use of a concentrated redox catalyst can increase the capacity of the sorbent for H_2S. However, high concentrations of catalyst could also lead to fast precipitation of sulfur in the scrubber and plugging. Control of sulfur formation is a key topic, as discussed later.

Redox Catalyst Regeneration

The reduced form of the redox catalyst must be converted back to the oxidized form in the regenerator, which is usually an air-sparged vessel. This vessel is usually large compared to the other vessels used in LRSR processes. In addition, the air compressors and energy needed to run the compressors can be significant. Thus, rapid regeneration reaction rates are needed for economical operation.

Generally speaking, the "stronger" (in the sense of higher oxidation potential) an oxidizing catalyst used for oxidation of H_2S, the slower and more difficult will be the regeneration step. This is because stronger oxidizing agents have more positive redox potentials. As the redox potentials get more positive, they approach the redox potential of oxygen, resulting in a decreased driving force for the reoxidation of the redox catalyst by O_2. A high driving force for air oxidation is needed to obtain acceptable regeneration rates since the reduction of oxygen requires multiple electron transfers and is thus an inherently slow process. Thus, redox catalysts with oxidation potentials just high enough to convert H_2S to sulfur are preferred. The catalyst redox potential should be high enough to give efficient H_2S

TABLE 1. Rates of Reaction of Some Oxidizing Agents with Hydrogen Sulfide

Oxidant	Second Order Rate Constant $k\ (M^{-1}sec^{-1})$	Notes and Source
O_2	1.5×10^{-3}	For $HS^- + O_2 \rightarrow HS + O_2^-$ according to Resch et al.; 20°C [16]
O_2 + CoPc	2.2×10^{1}	This is maximum k at pH 11.7; k = 1.9 at pH 8.3; 25°C, activation E unknown; Hoffmann [17]
H_2O_2	4.5×10^{-1}	From Resch et al., 20°C [16]
ADA	6.2×10^{-3}	From Thompson, adjusted to 20°C [18]
MB^+	1.0×10^{-1}	From Resch et al., 20°C [16]
MB	6.0×10^{1}	From Resch et al., 20°C [16]
V(V)	4.2×10^{-1}	Adjusted to 20°C; Radian
$FeOH^{2+}$	1.5×10^{3}	20°C, ferric ion at pH 2; from Asai et al. [19]
Fe(III)EDTA	6.2×10^{3}	Adjusted to 20°C, Radian
$Fe(CN)_6^{3-}$	1.0×10^{3}	Adjusted to 20°C; Radian based on disappearance of $Fe(CN)_6^{3-}$

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1. CoPc = cobalt(II), 4,4',4'',4'''-tetrasulfonatophthalocyanine, ADA = anthraquinone-2,7-disulfonate, MB^+ = methylene blue cation, MB = methylene blue radical.
2. All rate constants (except O_2/CoPc) were either measured at 20°C or adjusted to 20°C using known or estimated activation energy.

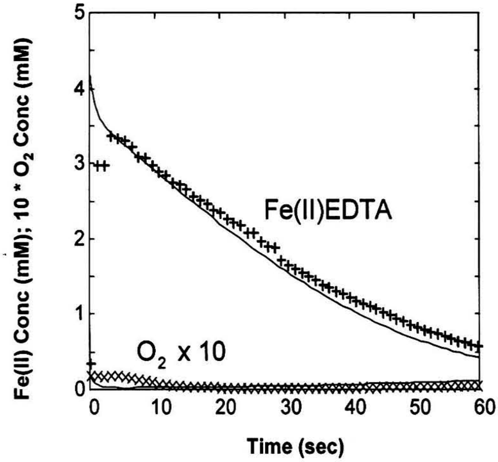


FIGURE 1 Air oxidation of Fe(II)EDTA at pH 7.33 and 25°C.

scrubbing (as discussed above) but low enough to allow efficient regeneration by air.

The oxidation rate of reduced iron chelates (used in current commercial processes) with oxygen is fast compared to the older vanadium-based (Stretford) processes. The chelate molecule plays a major role in the rate of regeneration of ferric iron [Fe(III)] from ferrous iron [Fe(II)] in the chelated iron LRSR processes. The air oxidation rate of uncomplexed ferrous iron (Fe^{2+}) is many orders of magnitude slower than that of Fe^{2+} chelated with ethylenediamine-N,N,N′,N′-tetraacetate (EDTA) or similar chelating agents. This is due in part to the large effect of the chelate on the reduction potential of chelated iron. Fe(III) chelated with EDTA is a much weaker oxidizing agent than simple aquated (complexed only by water molecules) Fe(III); the redox potential of FeEDTA is 0.6 V negative of uncomplexed $Fe^{2+/3+}$.

The redox potential does not tell the whole story. Specific kinetic effects must also be considered. The iron chelates rapidly form addition compounds with oxygen which then decompose to regenerate the oxidized form of the redox couple. These reactions are relatively fast and, in practice, the rates of regeneration are probably controlled to a significant extent by mass transfer of oxygen from the gas phase into the liquid. Figure 1 shows the rate of reaction of a low concentration of Fe(II)EDTA in an air-sparged vessel. The oxygen concentration falls to very low values during the run, and the Fe(II) is mostly converted to Fe(III) in about a minute.

Oxidation rates of several compounds by oxygen are compared to the rate of oxidation of Fe(II)EDTA in Table 2 where the second order rate constants are derived primarily from the overall or the slowest step.

The rate constants in this table range over six orders of magnitude. Note that both the uncatalyzed oxidation rate of H_2S by O_2 and the rate of reaction of O_2 with uncomplexed Fe(II) are very low. The rate of oxidation of tetravalent vanadium [V(IV)], used in the Stretford process, is much faster, but still significantly slower than the oxidation rates of the chelated iron compounds. The rates of oxidation of Fe(II)EDTA and Fe(II)HEDTA are high in part because of the favorable energetics of the process, but also because they can form oxygen-bridged intermediates (via the labile site described above) which lead to facile multi-electron transfers needed for efficient reduction of O_2. For comparison, the rate of direct oxidation of H_2S by oxygen is even more thermodynamically favored than that of Fe(II)EDTA, but is much slower because of the lack of suitable multielectron pathways. The rate of oxidation of Fe(II)DTPA is relatively slow since it is hindered by full occupation of labile sites on iron by the chelating agent.

The rate constant shown for the "biologically-enhanced" (in the presence of Thiobacillus ferrooxidans) oxidation of Fe^{2+} is based on the enhancement factor of 500,000 compared to Fe^{2+} alone [*6*]. The rate of biological reactions depends on many variables, so this comparison with the chemical systems must be made with caution. Although the oxidation potentials of the two cobalt compounds are in the general range of the iron chelates, they are somewhat higher (approximately 200 mV); and this, along with the lack of labile sites comparable to the iron chelates, may explain their relatively low reaction rates.

Overall control of regeneration rate by oxygen mass transfer can become important for the faster redox catalysts. However, it has been realized for some time that chemical reactions can have a significant (usually positive) effect on interfacial mass transfer. Chemical enhancement of the mass transfer of oxygen into chelated Fe(II) solutions was reported by Wubs and coworkers using an unsparged, stirred tank reactor [7]. Radian has investigated this phenomenon for air-sparged vessels (similar to com-

TABLE 2. Comparison of Rates of Oxidation of Species by Oxygen

Reactant	Second Order Rate Constant k ($M^{-1}sec^{-1}$)	Comments/Source
H_2S	1.5×10^{-3}	Resch, 1989 [*16*]
V(IV)	1.0	pH 8.8; Radian
Fe^{2+} (aq)	4.0×10^{-4}	Keenan as referenced in Lacey, 1970 [*6*]
Fe(II)EDTA	2.8×10^{2}	Radian
Fe(II)DTPA	1.4×10^{1}	Radian, based on data in Zang, 1990 [*20*]
Fe(II)HEDTA	6.0×10^{2}	Radian, based on data in Zang, 1990 [*20*]
CO(II)(o-phen)	8.0×10^{-2}	Chen, 1982 [*21*]
CO(II)(bpy)	2.9×10^{-2}	Chen, 1982 [*21*]
Fe^{2+} (biological)	2.0×10^{2}	Estimated from Lacey, 1970 [*6*]

mercial practice) using a new sophisticated model for chemical enhancement developed by Wilde and the kinetic model developed at Radian [8]. The main feature of this new model is the rigorous simulation of the effect of multiple chemical reactions on the gas-liquid mass transfer in the boundary layer. The enhancement factors calculated using a sparged tower model and iron EDTA catalyst were fairly small, on the order of 1.3 (the overall rate was enhanced about 30% by chemical reaction). An increase in key rate constants by a factor of 100 would be needed to produce an enhancement factor of approximately 3.

Byproduct Formation Rate

Oxidation of H_2S past the oxidation state of elemental sulfur results in the formation of soluble sulfur oxyanions which are difficult to purge from the LRSR process stream. If these salts reach high concentrations, they can cause scale formation and operating problems. The salts must be removed by "blowdown" or chemical treatment of the solution which results in loss of some of the catalyst and economic penalties. One of the main sources of this problem is the slow and/or incomplete oxidation of sulfide, which leads to elevated concentrations of polysulfides in solution. These polysulfides are readily converted to sulfur oxyanions when the solution contacts air in the regenerator.

The early anthraquinone sulfonate (ADA) and vanadium/ADA processes were characterized by relatively slow conversion of sulfide-to-sulfur at normal operating pHs. For this reason, an additional "reaction" vessel was usually inserted in the process between the H_2S absorber and the regenerator. This vessel allowed extra time for conversion of sulfide to sulfur before the liquid was contacted with air. Even so, it was difficult to obtain a low rate of sulfur oxyanion formation in the vanadium/ADA processes. Byproduct makes rates were typically 1–4% of the inlet H_2S. Chelated iron processes have much faster sulfide-to-sulfur conversion kinetics, and the concentration of polysulfide in these solutions is usually quite low. A comparison of polysulfide formation and reaction with vanadium and iron chelate redox catalysts is shown in Figure 2. The results are plotted as the total polysulfide sulfur (S0) normalized to the initial sulfide concentration. As can be seen, the formation of polysulfide is dominant in the vanadium case even though the concentration of V(V) (vanadate) is almost four times that of Fe(III)EDTA. As a consequence, the need for a separate reaction vessel was eliminated and byproduct make rates can be reduced to quite low values, ~ 0.1% of the inlet H_2S [9].

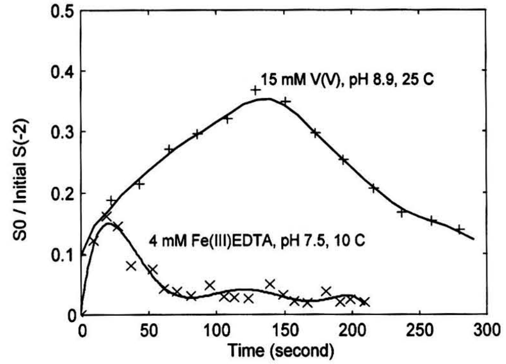


FIGURE 2 Comparison of formation and destruction of polysulfide in FeEDTA and vanadium solutions.

Paradoxically, one of the soluble sulfur oxyanion byproducts, thiosulfate, is a desirable constituent of current liquid redox processes since it is a very good inhibitor of chelate degradation, as described below. Thus the control and management of thiosulfate formation is a part of the operating protocol of such processes. The ARI LO-CAT II® (a registered trademark of Wheelabrator Clean Air Systems, Inc.) process uses a zoned oxidizer to provide better control of thiosulfate formation.

Consumption of Chemicals

There are several sources of chemical consumption in liquid redox processes. One of these, carry-out of chemical reagents with the sulfur product, is in large part a "physical" process, although some chemical binding to the surface of the sulfur may occur. This is also one of the main sources of surfactant losses for those processes which use surfactants for sulfur management. Another source of loss is blowdown of solution necessitated by byproduct formation (see above). This was mainly a problem with the ADA, vanadium/ADA, and arsenic-based LRSR processes which had relatively high byproduct formation rates. Various solution reclamation schemes have been developed for some of these processes. As noted above, byproduct formation is less of a problem with chelated iron systems.

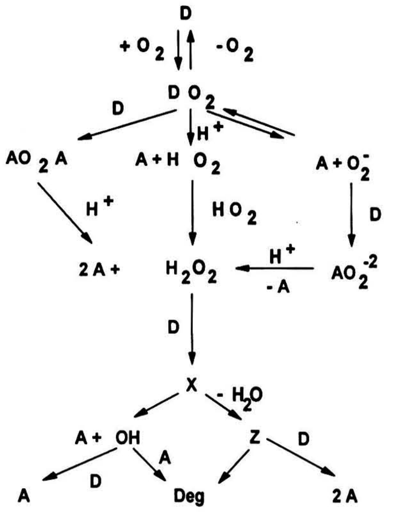
A major problem for iron chelate-based processes is chemical degradation of the chelating agent. The degradation is generally thought to be caused by hydroxyl radicals or other highly reactive intermediate generated in the air oxidation reactions. Formation of these reactive intermediates could be promoted by reaction of ferrous iron and hydrogen peroxide formed as a intermediate in oxygen reduction [*10*, *11*]. As discussed in a recent report, the picture is actually more complicated than this, and formation of tetravalent iron [Fe(IV)] intermediates may well be involved along with hydroxyl radial mechanisms [8]. The mechanisms of chelated iron regeneration and degradation are linked, as shown in Figure 3.

A number of compounds have been tested in an attempt to scavenge the hydroxyl radicals and thus protect the chelate. Most of these compounds are consumed more or less rapidly and thereby lead to a buildup of soluble salts in solution. This will eventually necessitate a blowdown or solution cleanup step similar to the sulfur oxyanion buildup. Thiosulfate has been proposed as an optimal degradation inhibitor [*12*]. Our results confirm the favorable effects of thiosulfate on chelate degradation [8]. In addition, the following reactions of thiosulfate with both hydroxyl radical and with iron(IV) were required to fit the degradation data with the kinetic model:

$$S_2O_3^{-2} + \cdot OH \rightarrow \cdot[S_2O_3OH]^{-2} \tag{4}$$

$$S_2O_3^{-2} + Fe(IV)EDTA \rightarrow \cdot[S_2O_3]^{-} + Fe(III)EDTA^{-} \tag{5}$$

A literature value ($7.80 \times 10^9\ M^{-1}s^{-1}$) was used for the reaction rate of hydroxyl radical with thiosulfate [*13*]. No lit-



A = chelated Fe(III) D = chelated Fe(II) Z = Fe(IV)

FIGURE 3 Fe(III) regeneration with degradation pathways.

erature rate constant was available for the reaction of thiosulfate with Fe(IV)EDTA, but a value of $3.0 \times 10^6\ M^{-1}s^{-1}$ provided a good fit to the data. Thiosulfate has the potential to undergo an interesting set of cyclic reactions which were also included in the model. These reactions could regenerate the original thiosulfate molecule, after it "neutralizes" a hydroxyl radical, through the reaction of ferrous EDTA with the thiosulfate radical anion:

$$\cdot[S_2O_3]^- + Fe(II)EDTA^{-2} \rightarrow Fe(III)EDTA^- + S_2O_3^{-2} \quad (6)$$

This pathway would allow thiosulfate to scavenge highly oxidized intermediate without undergoing a net consumption. Although this reaction has not been proposed before, it is reasonable to include it in the model since the thiosulfate radical anion is a good oxidizing agent ($E^0 = 1.35$ V) [*14*] and thus it should be able to react with Fe(II)EDTA at a high rate. This pathway should be investigated in more detail as it could provide a model for degradation inhibitors which are inherently regenerable, avoiding excessive sulfate or other soluble byproduct formation.

The BIO-SR process (NKK Corporation) is an iron-based system, but it does not use chelating agents and thus has no chelate degradation problems. To obtain sufficient iron solubility, the process is operated in the range of pH 1–2. Since the rate of Fe^{2+} oxidation is very low at this pH (see above), bacteria are added to catalyze the regeneration process. Little information has so far been revealed as to the issues involved in maintaining this bacterial colony and interfacing the regeneration process to the rest of the process.

pH Effects

Solution pH is often a key variable in LRSR processes. It can affect key chemical equilibria (such as H_2S/HS^-) as well as the rates of reactions. As noted above, a "compromise" operating pH was successfully in Stretford processes to simultaneously avoid sulfur plugging while giving acceptable sulfide-to-sulfur conversion rates and low byproduct make rates. The pH dependence of chemical processes is also complex in iron chelate systems. Figure 4 shows the pH dependence of initial Fe-S complex formation (assumed to be 1:1 in the figure) and also the pH dependence of sulfur formation for FeEDTA. Somewhat different results may be expected for other chelates.

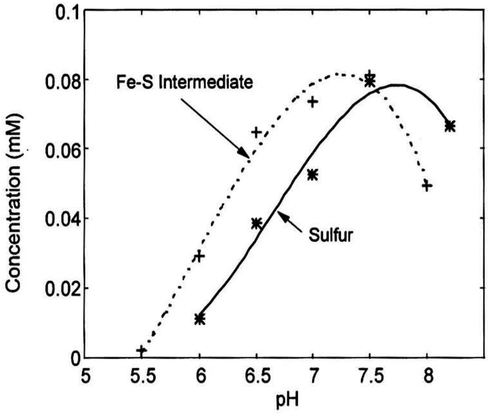


FIGURE 4 Effect of pH on rates of Fe-S intermediate and sulfur formation for Fe(III)EDTA.

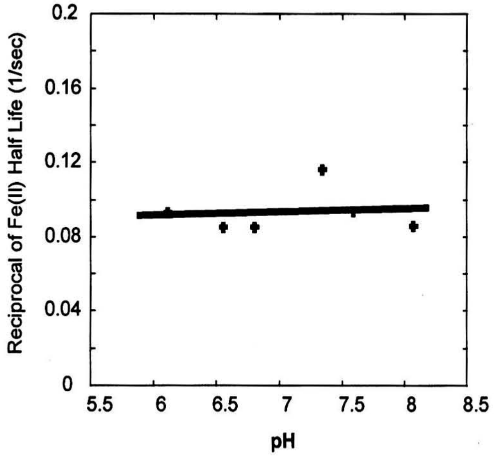


FIGURE 5 Effect of pH on rate of Fe(II)EDTA oxidation by O_2.

As can be seen in Figure 4, the rates of these reactions are slower in the acidic region and go through a maximum just above pH 7. The rate of the air regeneration reaction must also be considered. As shown in the Figure 5, however, this rate is relatively independent of pH, at least for FeEDTA.

Thus, if fast kinetics of H_2S reaction are desired, the iron chelate processes are probably best operated above pH 7, as also indicated by current practice.

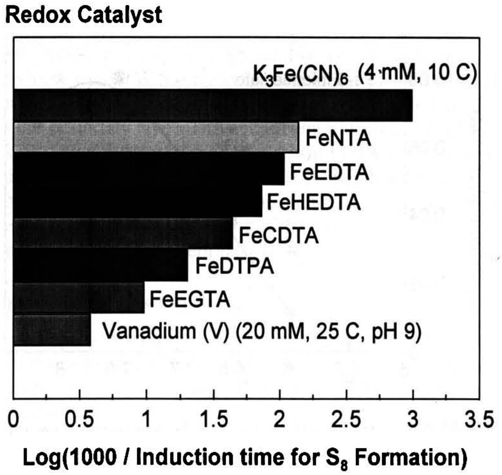


FIGURE 6 Comparison of sulfur formation rates using various oxidants.

Sulfur Formation

The formation of solid sulfur is a key step in LRSR processes. The efficient formation of a separable solid product is important to the economic, continuous operation of these processes. However, premature formation of sulfur in the H_2S scrubber can cause plugging of the scrubber internals (internals are necessary to get good gas/liquid mass transfer and high removal efficiency). Sulfur plugging problems with the Stretford process were usually handled by maintaining an elevated pH since the reaction of vanadium with H_2S becomes slower as the pH increases. The slower reaction at high pH, however, led to byproduct control problems as outlined above. The Stretford process was also not very tolerant of high CO_2 partial pressure as the locally low pH due to CO_2 absorption could cause sulfur plugging in the scrubber. Rates of sulfur formation using several redox catalysts are shown in Figure 6 [*8*].

As shown, current iron chelate-based processes have high reaction rates of H_2S with the redox agent and also high rates of sulfur formation. These processes commonly use additives and surfactants to modify the surface of the sulfur and give it better handling properties. However, such methods can be difficult to control and can cause foaming as well as produce an extra cost for the surfactant. Sulfur handling problems (primarily foaming and plugging in the high-pressure separator) could not be controlled by surfactant addition in a high-pressure, direct-treat natural gas pilot test of a chelated iron liquid redox process [*15*].

The basic problem appears to be that sulfur formed from aqueous systems has a small primary particle size and poor handling properties. This is because the solubility of sulfur in water is very low. The low solubility provides a high driving force for crystallization and this forces the rapid, uncontrollable nucleation of many small sulfur particles rather than the slow growth of large particles.

Since sulfur is much more soluble in most nonaqueous solvents than in water, elemental sulfur formed from nonaqueous solvents can have a much larger particle size, and thus better handling properties than sulfur formed from aqueous solutions. In addition, the higher solubility should make it easier to control the formation of sulfur from nonaqueous solutions than from aqueous solutions. However, nonaqueous solvents may also stabilize intermediate polysulfides and thus inhibit the formation of sulfur. On the regeneration side of the process, oxidation of redox couples in nonaqueous solvents with oxygen appears to be slow compared to the aqueous iron chelate systems, probably due to the importance of proton transfer steps which generally occur more readily in aqueous than in nonaqueous systems.

CONCLUSIONS

Liquid redox sulfur recovery processes offer inherently good H_2S removal and highly flexible operating properties at near-ambient temperatures. Economics are favorable in the capacity range of several tons of sulfur per day [*9*]. Process chemistry is complex and there are a number of possible tradeoffs for process optimization. Development of redox catalysts giving faster kinetics for conversion of H_2S to sulfur and faster regeneration of the catalyst with oxygen has solved several of the problems with earlier liquid redox processes. One unfortunate byproduct of this evolutionary step, catalyst degradation, is controlled in large part by inhibitors and management of solution chemistry. pH is a key variable in LRSR processes, and its effects are becoming better defined by research. Another byproduct of the faster kinetics associated with the new catalysts is difficulty in controlling the formation of solid sulfur. At least part of this problem may be inherent to aqueous-based processes due to the very low solubility of sulfur in water.

ACKNOWLEDGMENTS

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Countercurrent Absorption of CO_2 in a Real Flue Gas into Aqueous Alkanolamine Solutions in a Wetted Wall Column

Taiichiro Suda

General Office of Planstsiting and Environmental, The Kansai Electric Power Co., Inc., 3-22 Nakanoshima 3-chome, Kitaku,
Osaka 530-70 Japan

Masaki Iijima

Chemical Plant Engineering Center, Mitsubishi Heavy Industries, Ltd., 3-3-1, Minatomirai, Nishi-ku, Yokohama, 220-84 Japan

and

Hiroshi Tanaka, Shigeaki Mitsuoka and Toru Iwaki

Hiroshima Research & Development Center, Mitsubishi Heavy Industries, Ltd., 4-6-22, Kan-on-shin-machi, Nishi-ku,
Hiroshima 733 Japan

The countercurrent absorption of CO_2 from the flue gas into aqueous alkanolamines has been studied using wetted wall column equipment connected to the stack of a power plant. The absorption rates of CO_2 into aqueous alkanolamines were measured at 40°C, 10kPa partial pressure, and $2m^3/h$ of gas flow rate. From the rate of absorption and the absorption equilibrium results, the secondary amines have as large overall mass transfer coefficients as monoethanolamine. However, the coefficients of the hindered and tertiary amines are small even though the absorbed amounts of CO_2 at equilibrium are large. The CO_2 concentration profiles in a wetted wall column were estimated, and these results are due to the absorption process in connection with the degree of carbamate formation.

INTRODUCTION

Power plants are now considered to be one of the sources of large emissions of CO_2 into the atmosphere: the amounts of boiler flue gases are as large as 10^6 m^3 per hour. Therefore, it is important for the immediate counterplan of global warming to separate and remove CO_2 from the flue gas of combustion in the stack of a power plant. There are three ways to separate CO_2 from flue gas: membrane separation, physical adsorption and chemical absorption. The last method may be easily applied to the power plant compared to the other two methods. CO_2 removal advocates have been focusing in the development of utilization, underground storage, and ocean disposal of CO_2. At the present time, the CO_2 recovery process is limited to both general use for welding as an inert gas, food and beverage carbonation, and dry ice as a cooling agents, and partial use in the soda ash industry, urea production, and as enhanced oil recovery agents. In these processes, monoethanolamine has been used as one of the best solvents. Monoethanolamine, however, seems to be difficult to be used as a solvent for CO_2 removal at a power plant because this process causes the huge decrease in power plant efficiency due to its high energy consumption for regenerating the solvent [*1*].

Until now studies have been published on the recovery of CO_2 by alkanolamine [*1–6*], however, many important characteristics about the chemical absorption process when it is applied to a power plant remained uncertain. We have been developing the economical recovery of CO_2 from a power plant using a pilot test plant with the aid of new absorption packing since 1991 [*1*]. Moreover, a small-scale absorption unit comprised of a wetted wall column connected to the stack of a power plant (natural gas fuel) was constructed as the fundamental examinations about CO_2 absorption in the flue gas by various absorbents are essential for developing a CO_2 recovery plant.

In order to reduce the energy used to recover CO_2 at the plant, highly efficient absorbents are required which have a high absorption capacity, rapid absorption rate, and low heats of reaction at low CO_2 pressures besides a lower corrosiveness. Since considerable attention has been fo-

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Correspondence concerning this paper should be addressed to Taiichiro Suda.

cused on the process using the sterically-hindered amine, 2-amino-2-methyl-1-propanol, which Exxon developed [7, 7], the absorption characteristics on the above system have been examined in detail along with those of the tertiary amines [9, 10] from the point of view of their low interaction energies with CO_2. From a recent NMR spectroscopic study, secondary amines such as 2-(methylamino) ethanol have been found to have a moderate carbamate stability, resulting in increased absorbed amounts of CO_2 at low partial pressures [11].

In this study the countercurrent absorption kinetics of CO_2 in a real flue gas at an atmospheric pressure into several aqueous alkanolamine solutions using the wetted wall column were examined. The following amines were examined for comparison of their absorption characteristics by obtaining the total mass transfer coefficient and the liquid phase mass transfer coefficient: monoethanolamine (primary amine), 2-amino-2-methyl-1-propanol (hindered amine), diethanolamine(diol secondary amine), 2-(methylamino)ethanol, and 2-(ethylamino) ethanol (secondary amines), 2-(diethylamino)ethanol and 4-dimethylamino-1-butanol(tertiary amine), and 2-(2-amino ethylamino)ethanol(diamine). The absorption characteristics of these amines solvents were compared on the basis of the same aqueous concentration in wt% for industrial use and, for several of the amine solvents, the same in molar concentration for specific molecular properties. The CO_2 absorption equilibriums for each amine solution were also obtained. The liquid phase mass transfer coefficient of monoethanolamine obtained in this study is compared with that calculated from the reaction rate constant in the literature. Moreover, the CO_2 concentration profiles in the wetted wall column were estimated in order to provide information about the design of the absorption tower. These results were interpreted by referring to the carbamate formation stabilities.

EXPERIMENTAL

Apparatus and Procedures

Figure 1 shows a schematic diagram of the wetted wall column equipment which is connected to the power plant stack located at South Osaka Bay. This equipment has been used to obtain the kinetics of absorption as well as to control the concentrations of the absorbents and additives, flow rates and temperature of the flue gas, and absorbents in the CO_2 recovery plant. As shown in the figure, the reactor has a 15mm inner diameter and a 7.5m high wet wall absorption tower, with CO_2 in flue gas being contacted with a constant area of absorbents. The height of the column was changed to 3m in the case of absorption experiments done on a molar concentration basis. A fresh alkanolamine solution at a temperature of 40°C was fed at the top of the column. A part of the LNG-fired flue gas fed at the bottom of the wetted wall column came in contact with a countercurrent flow of liquid film falling down the column wall. The temperature of the alkanolamine solution was maintained at 40 ± 0.5°C by a water jacket outside the column. The CO_2 concentration in the flue gas at the bottom and top of the column was continuously monitored using an IR CO_2-analyzer (BIP-200, Best Instruments Co., Ltd.). After the CO_2 absorption became constant, the aqueous amine sample at the bottom of the column was analyzed as follows. The amount of CO_2 absorbed in the amine solution was determined by measuring the CO_2 gas evolved with an NDIR (TOC-5000), Shimadzu Co., Ltd.), at the injection point of the amine sample into the reaction tube packed with a phosphoric acid-mounted catalyst at 130°C. The concentration of the amine in the solution was obtained by the titration method using 0.1M HCl and methyl-red and bromocresol green as an indicator. The absorbed amount of CO_2 obtained from the differences in CO_2 concentration of the flue gas between the top and bottom positions of the column coincided well with that obtained from the liquid phase analysis. The specifications and the operating conditions for the CO_2 absorption test are summarized in Table 1.

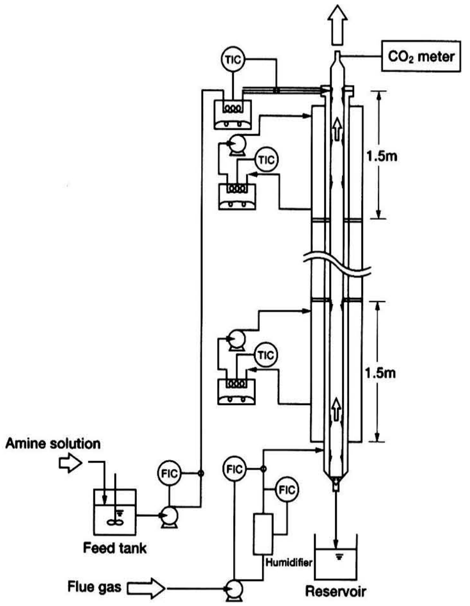

FIGURE 1 Schematic Diagram of a wetted wall column for countercurrent absorption.

TABLE 1. Specifications and Operating Conditions for CO_2 Absorption Tests

Wetted wall column	
ID	: 15 mm
Height	: 7.5 m and 3.0 m
L/G	: 2 d^3/m^3
Flue gas	
Flow rate	: 2.0 m^3/h
Composition	: 2 ~ 5% O_2, 85 ~ 89% N_2 9 ~ 10% CO_2
Pressure	: 1 atm
Amine solution	
Amine	: 8 kinds of alkanolamine
Concentration	: 30 wt% and 3 mol/l
Temperature	: 40 ± 0.5°C
Flow rate	: 4 dm^3/h

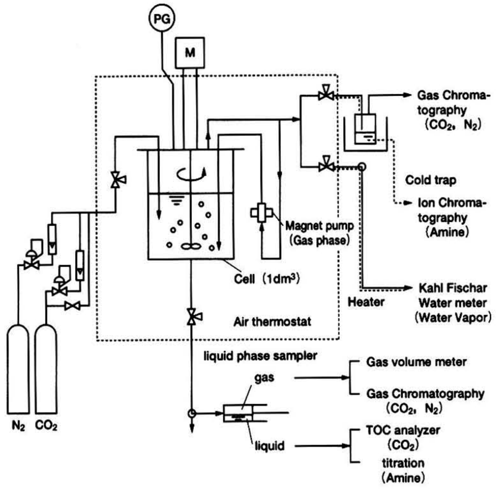

FIGURE 2 Schematic Diagram of a CO_2 absorption equilibrium apparatus and chemical composition analysis.

The gas liquid equilibrium apparatus is schematically shown in Figure 2. The equilibrium amount of CO_2 in the aqueous amine solution was measured in a 1 dm^3 stainless steel cell of at a total pressure of 1 atm. The temperature of the cell was kept at $40 \pm 0.1°C$. A 0.5 dm^3 of amine solution (30 wt% amine concentration) was poured into the cell, then the air remaining in the cell was purged using CO_2 gas before several compositions of CO_2/N_2 mixed gases used for equilibrium absorption test were introduced. The amine solution was continuously stirred and the gases were circulated through the liquid absorbent by means of a magnetic pump. The system was monitored for more than 6 h until both the pressure and the temperature became constant. The concentrations of CO_2, N_2, amine, and water vapor in a gas phase were measured by gas chromatography (GC-8A, Shimadzu Co., Ltd.). The concentration of CO_2 absorbed in the solution and total amine concentration were measured in the same manner as described for the absorption measurements with a wetted wall column.

Materials

The kinds and purity of the alkanolamine samples examined here are shown in Table 2. These amines were used without further purification. As for 2-(2-aminoethylamino)ethanol, the gas liquid equilibrium experiment was not done because of its corrosive property.

ANALYSIS

Evaluation of Mass Transfer Coefficient

The CO_2 absorption efficiency (η) was obtained according to the following equation,

$$\eta = \left(1 - \frac{y_{out}}{y_{in}} \cdot \frac{1 - y_{in}}{1 - y_{out}}\right) \times 100 \qquad (1)$$

TABLE 2. Alkanolamine Samples

	Alkanolamine	Purity (%)
A	monoethamolamine (primary amine)	99.8 [a)]
B	2-amino-2-methyl-1-propanol (hindered amine)	> 99[b)]
C	diethanolamine (diol secondary amine)	> 98[c)]
D	2-(methylamino)ethanol (secondary amine)	> 99[c)]
E	2-(ethylamino)ethanol (secondary amine)	> 99[c)]
F	2-(butylamino)ethanol (secondary amine)	> 99.9[d)]
G	2-(diethylamino)ethanol (tertiary amine)	> 99[c)]
H	4-dimethylamino-1-butanol (tertiary amine)	> 99[d)]
I	2-(2-aminoethylamino)ethanol (diamine)	> 99[c)]

[a)] Nihon Shokubai Co.
[b)] ANGUS Chem. Co.
[c)] Tokyo Kasei Kogyo Co.
[d)] Nihon Nyukazai Co.

where y_{in} and y_{out} are the molar fractions of CO_2 in the flue gas at the bottom and top of the absorption column, respectively. The absorption rate (r) of the CO_2 gas into the amine solution per unit absorber volume is expressed by

$$r = K_G a P_T (y - y^*) \qquad (2)$$

In this equation, K_G is the overall mass transfer coefficient for the CO_2 gas, a is the mass transfer area per unit volume of the absorber, P_T is the total pressure, y is the molar fraction of CO_2 gas in the flue gas, and y^* is the equilibrium molar fraction of CO_2 gas. The mass balance equation of CO_2 in both the liquid and gas phases is given by

$$L \cdot dx = rA\,dz \qquad (3)$$

where L is the flow rate of the alkanolamine solution, x is the molar fraction of CO_2 in the liquid phase, A is the cross sectional area of the absorber, and z is the absorber length. The overall mass transfer coefficient, K_G, is the sum of the gas phase mass transfer resistance and the liquid phase mass transfer resistance as follows,

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{\beta k_L} \qquad (4)$$

In this equation, k_G is the gas phase mass transfer coefficient, H is Henry's constant, β is the mass transfer enhancement factor, and k_L is the liquid phase physical mass transfer coefficient.

Chemical Reaction Equation

The reactions of CO_2 with primary and secondary amines in the liquid phase are:

zwitterion formation:

$$CO_2 + R_2NH \underset{k_2}{\overset{k_1}{\rightleftarrows}} R_2N^+HCOO^- \tag{5}$$

zwitterion deprotonation or carbamate formation:

$$R_2N^+HCOO^- + R_2NH \xrightarrow{k_3} R_2N^+H_2 + R_2NCOO^- \tag{6}$$

protonated amine formation:

$$R_2NH + H^+ \rightleftarrows R_2N^+H_2 \tag{7}$$

bicarbonate formation:

$$R_2NCOO^- + H_2O \rightleftarrows R_2NH + HCO_3^- \tag{8}$$

In the case of the tertiary amine, no carbamate forms because of the lack of a hydrogen atom bonded to a nitrogen atom on the amine molecule. The CO_2 hydration reaction proceeds by the catalytic action of the tertiary amine [*12*]:

$$R_3N + CO_2 + H_2O \xrightarrow{k_4} R_3NH^+ + HCO_3^- \tag{9}$$

This reaction is comprised of the following two simultaneous processes:

$$R_3N + H_2O \rightleftarrows R_3N^+H + OH^- \tag{10}$$

$$CO_2 + OH^- \xrightarrow{k_{OH}} HCO_3^- \tag{11}$$

Absorption Kinetics Equation

Assuming the concentration of an amine is constant in the rapid reaction region (Hatta number is greater than 5) [*13*], the absorption kinetics equations for primary, secondary and tertiary amines are expressed as follows:

primary and secondary amines [*14*]:

$$N_A = \beta k_L C_{Ai} = C_{Ai}\sqrt{\frac{C_B D_A}{\dfrac{1}{k_1} + \dfrac{k_2}{k_1 k_3 C_B}}} \tag{12}$$

tertiary amine [*15*]:

$$N_A = \beta k_L C_{Ai} = C_{Ai}\sqrt{(k_{OH} C_{OH} + k_4 C_B)\, D_A} \tag{13}$$

where the other reaction constants were eliminated because their reactions are negligibly small. The mass transfer rate of CO_2 gas per unit surface area, N_A, is proportional to both the CO_2 concentration at the gas-liquid interface in the liquid phase, C_{Ai}, and liquid phase mass transfer coefficient, βk_L, which is related to the CO_2 diffusibility in the liquid phase D_A. As seen from the above results, the liquid mass transfer coefficient, βk_L, is not dependent on the flow dynamics of the liquid but on the chemical reaction kinetics in the liquid phase regardless of the kind of amine species. The evaluation of the mass transfer coefficient, βk_L, can be first performed by obtaining K_G which is determined from y^* in the equilibrium absorption and equations (2) and (3), then by applying equation (4).

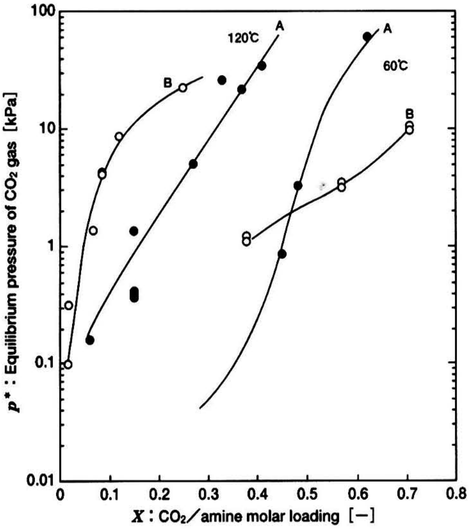

FIGURE 3 CO_2 absorption equilibrium curves for monoethanolamine and 2-amino-2-methyl-1-propanol solutions at 60 and 120°C: solid and open circles are obtained in the present experiments and solid lines from the literature [*7, 16*].

RESULTS AND DISCUSSION

Gas/Liquid Equilibrium

In Figure 3 are shown the results of the gas liquid equilibrium obtained with our equilibrium apparatus for the monoethanolamine and 2-amino-2-methyl-1-propanol samples at 60 and 120°C. These data are in good agreement with those reported in the literature [*7, 16*], indicating the reliability of our experimental methods. Figure 4 shows the relationship between the equilibrium pressure of CO_2 gas and the CO_2/amine molar loadings of the alkanolamines used in the experiment. The plots for the monoethanolamine and 2-amino-2-methyl-1-propanol samples in the figure are not the results of this study but those replotted by referring to the experimental data at 40°C available in the literature [*16–18*]. Using the method reported by Astarita et al. [*2*], the equilibrium curves were simulated and the resultant curves are indicated by the solid lines in Figure 4, where the curves of monoethanolamine and 2-amino-2-methyl-1-propanol are in the region below

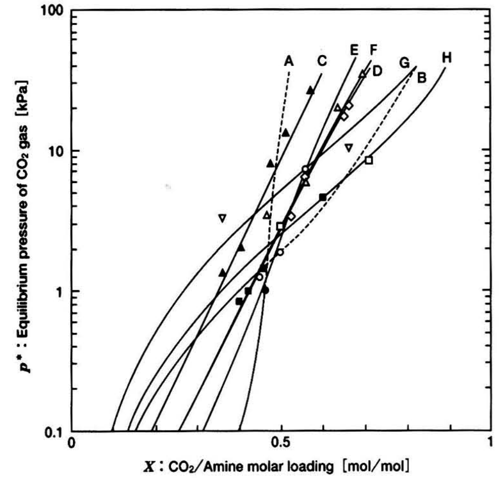

FIGURE 4 CO_2 absorption equilibrium curves for alkanolamine solutions at 40°C: open marks are present experimental data, solid marks obtained from the literature, solid lines simulated curves obtained according to eq. (14) ~ (17), and dotted lines, from the curves in the literature [*16–19*].

TABLE 3. The Calculated Values of C_1, C_2 and C_3

Amine sample	C_1 (kPa)	C_2 (kPam^3/kmol)	C_3 (kPam^3/kmol)
A	0.027	—	—
B	—	1.11*	—
C	—	2.53	4.75
D	—	1.03	2.62
E	—	0.369	7.75
F	—	1.01	4.34
G	—	4.05	—
H	—	1.98	—

*obtained by the equation (17) for tertiary amine.

the 0.5 CO_2 molar loading. These equilibrium relationships are expressed as follows:

for primary amine:

$$(X < 0.5) \quad p^* = C_1\left(\frac{X}{1-2X}\right)^2 \tag{14}$$

for secondary amines:

$$p^* = C_2 \frac{\left(1+\frac{1}{C_3C_B}-\sqrt{\left(1+\frac{1}{C_3C_B}\right)^2-4X(1-X)}\right)X}{\left(1-2X-\frac{1}{C_3C_B}+\sqrt{\left(1+\frac{1}{C_3C_B}\right)^2-4X(1-X)}\right)^2} \tag{15}$$

for hindered and tertiary amines:

$$p^* = C_2C_B\frac{X^2}{1-X} \tag{16}$$

where C_1 $(= H/K)$, C_2 $(= HK_P/K_{C1})$ and C_3 $(= K_C)$ are constant values as shown in Table 3, and C_B is the amine molar concentration, P^* is the CO_2 equilibrium pressure, and X is the CO_2/amine molar loading. In these equations, K is the carbamate formation equilibrium constant, K_P is the dissociation constant of the protonated amine, K_C is the carbamate stability constant, and K_{C1} the first dissociation constant of carbonic acid. As is shown in Figure 4, the absorption capacity at a low partial pressure of CO_2 of around 10kPa changes in the following order: tertiary amine > sterically hindered amine > secondary amine > primary amine, but, on the other hand, that at a much lower partial pressure of CO_2 of below 1kPa: primary amine > secondary amine > sterically hindered amine > tertiary amine. Since no carbamate forms in the dissolved states of CO_2 in both the tertiary amine and hindered amine, the CO_2 molar loading reaches 1.0 with an increase in the CO_2 partial pressure, while dissolved state of CO_2 in a primary amine bears a very stable carbamate, thus, bringing about half of the CO_2 molar loading below atmospheric CO_2 pressure. In the case of a secondary amine, the carbamate stability is moderate and bicarbonate forms even at low CO_2 pressures such as usual flue gas conditions; the molar loading is between those of the primary and tertiary amines. The carbamate formation of these secondary amines has already been quantitatively examined by NMR spectroscopy [*17*].

Absorption Ability in Wetted Wall Column

The absorption efficiencies of CO_2 in the amine solutions in the wetted wall column examined in this study are shown in Figure 5, where two kinds of amine concentrations, 30 wt% and 3M, are indicated for several amine samples. Under the condition of the same wt% concentration of amines, the secondary amine (D), primary amine (A), and diamine (I) have the high absorption efficiency above 90% while tertiary amines (G, H) have an extremely low absorption efficiency value below 20%, though other secondary amines (E, F) show about 70%.

On the contrary, under the same molar concentration with 3m high absorption column height, the secondary amine (E) has the highest absorption efficiency though the primary amine (A) also has a high absorption efficiency. The results of the total mass transfer coefficient, K_G, for amine solutions are also shown in Figures 5(c) and (d). The K_G value of the diamine (I) is postulated by neglecting the equilibrium pressure of CO_2 in equation (2). The gas absorption efficiency of CO_2 in each amine solution is significantly dependent on the total mass transfer coefficient as shown by the results in Figure 5.

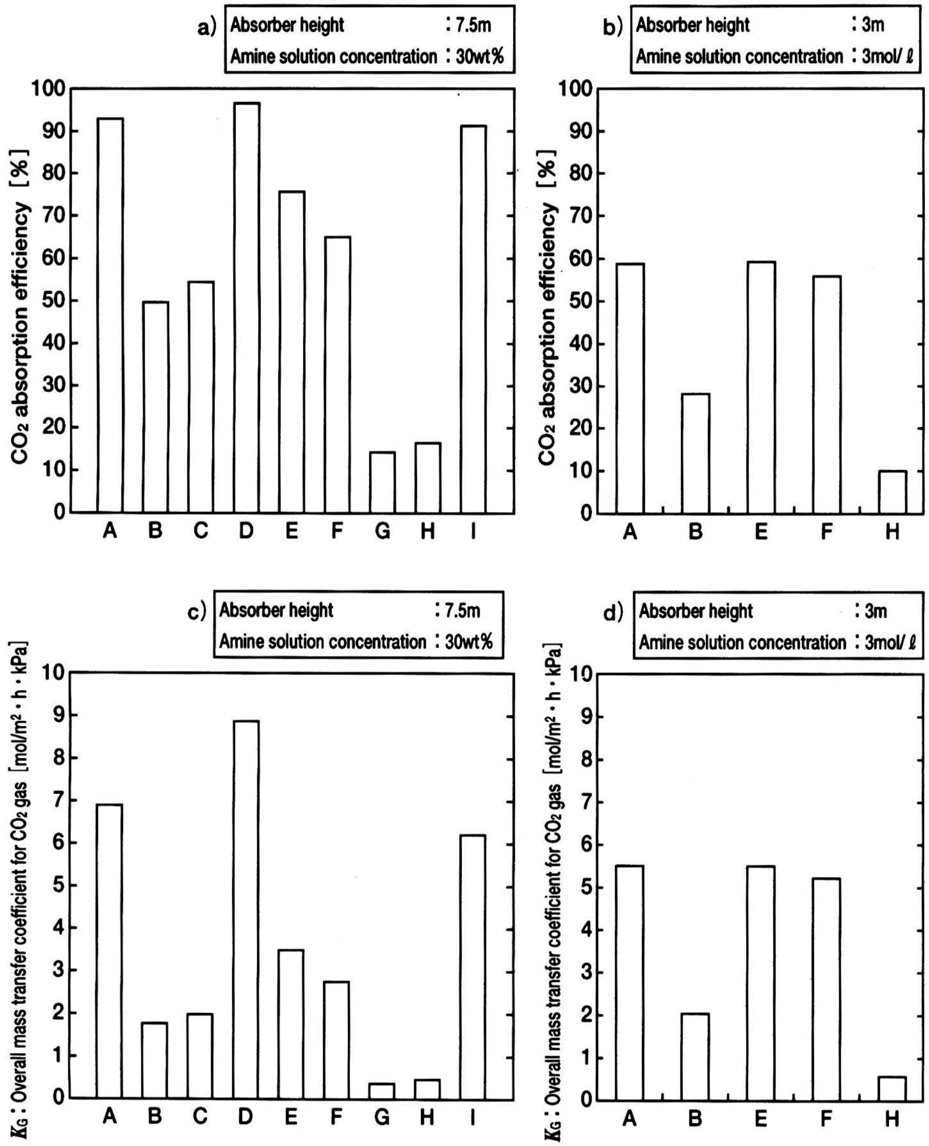

FIGURE 5 CO_2 adsorption efficiency and overall mass transfer coefficient for aqueous alkanolamine samples.

The liquid phase mass transfer coefficient, βk_L, of CO_2 in the monoethanolamine solution obtained in this wetted wall column test is compared with that obtained from the reaction rate constant given in the literature [*20*], the results being shown in Figure 6. The absorption ability at the wetted wall column is confirmed to be characterized by βk_L, which is independent of the flow dynamics of the liquid and dependent on the kinetics in the liquid phase because of the rapid chemical reaction region in this system. The representative values of βk_L (m/h) in the studied CO_2-amine system were found to be 43.7(A), 8.5(B), 19.0(E), 12.9(F), and 2.2(H) for the 30wt% amine solutions and 35.8(A), 10.9(B), 39.3 (E), 37.0(F), and 2.8(H) for the 3 mol/l amine solutions. These βk_L values are also directly related to the total mass transfer coefficient, K_G, because the gas phase mass transfer resistance, $1/k_G$, is very small as seen in eq. (4).

Both the liquid and gas phase CO_2 concentration profiles at each position in a wetted wall column for the 3M amine samples are shown in Figures 7(a) and (b), respectively. These curves are obtained by the successive calculation of the absorption rate at an interval of 0.03 m from the bottom position to the top one according to equations (1) ~ (3) using the experimentally obtained CO_2 concentrations at the top and bottom positions as the boundary conditions. The CO_2 absorption kinetics behavior of the sec-

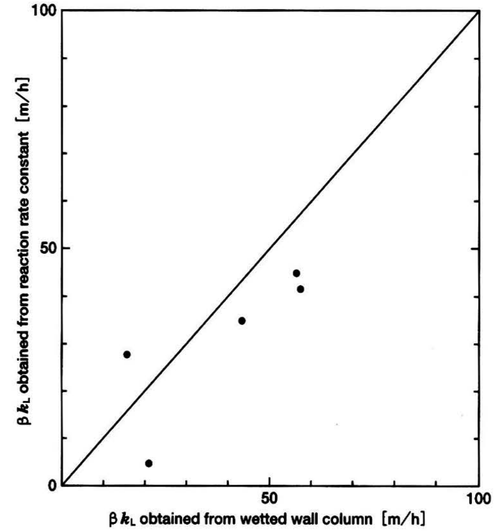

FIGURE 6 Comparison of βk_L obtained from a wetted wall column in the present study and that from the reaction rate constant for monoethanolamine-CO_2 system [*20*].

ondary amine, as shown in Figure 7, is not distinct from that of monoethanolamine, though the latter is superior to the former in total mass transfer coefficient on the basis of wt%. The concentration of CO_2 absorbed in each amine flowing solution in the column is almost dependent on the total mass coefficient, K_G, of each amine solution, while the mass transfer rate is proportional to both K_G and the concentration of CO_2 in the gas phase because the equilibrium CO_2 concentration in the absorption column is small ($y^* \rightarrow 0$ in equation (2)). A slightly lower mass transfer rate of the secondary amine, F, compared to that of primary amine, A, is responsible for the high equilibrium CO_2 pressures in the bottom part of the absorption column. Though the equilibrium absorption capacity of secondary amine at CO_2 pressures in the flue gas lies between the primary and tertiary amines, the absorption rate is comparable to the primary amine. Both the sterically hindered amine and tertiary amine have a low CO_2 absorption rate and βk_L values and may be considered to be unsuitable as CO_2 removal solvents. The secondary amine may be of great advantage for regeneration energy since it can immediately interact with CO_2 producing bicarbonate through the breakdown of carbamate at CO_2 pressures in the flue gas [*11*]. In addition, the tertiary amine and hindered amine, when other amines such as the secondary amines, which have high reaction rate are admitted as reaction promoters, possess the possibility as solvents at a power plant because of their low heat of absorption and high absorption capacity at CO_2 pressures in the flue gas.

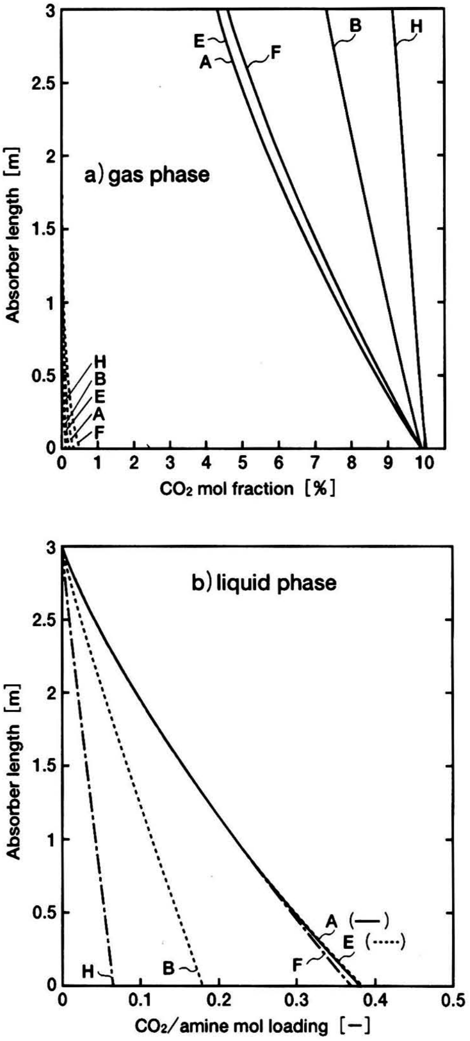

FIGURE 7 CO_2 concentration profiles simulated for gas (a) and liquid (b) phases at a wetted wall column: dotted lines in the figure (a) are equilibrium CO_2 mole fraction.

CONCLUSIONS

It was found in this study that the absorption behavior of CO_2 in a real flue gas into an aqueous amine solution is fully explained by referring to the total mass transfer coefficient and that the liquid film mass transfer coefficient is directly correlated with the chemical reaction rate in the liquid phase. The secondary amines have a CO_2 absorption rate high enough to be compatible with monoethanolamine and also have a high absorption capacity under real flue gas conditions, implying that these amines are applicable as solvents at a power plant, though tertiary and hindered amines possess the same possibility with the addition of the above amines.

ACKNOWLEDGMENT

The authors would like to express their grateful acknowledgment to Dr. Masakatsu Nomura of Osaka University for valuable discussion and suggestion.

NOTATION

a = mass transfer area per unit volume of absorber [1/m]
A = cross sectional area of absorber [m^2]
C_{Ai} = CO_2 concentration at gas-liquid interface in liquid phase [$kmol/m^3$]
C_B = amine concentration in bulk liquid [$kmol/m^3$]
C_{OH} = OH^- concentration in liquid phase [$kmol/m^3$]
D_A = CO_2 diffusivity in liquid phase [m^2/h]
H_A = Henry's constant of CO_2 gas [$m^3 \cdot atm/kmol$]
k_G = gas phase mass transfer coefficient [$kmol/m^2 \cdot h \cdot atm$]
k_L = liquid phase mass transfer coefficient [m/h]
k_1 = reaction rate constant defined in Eq. (5) [$m^3/kmol \cdot h$]
k_2 = reaction rate constant defined in Eq. (5) [1/h]
k_3 = reaction rate constant defined in Eq. (6) [$m^3/kmol \cdot h$]
k_4 = reaction rate constant defined in Eq. (9) [$m^3/kmol \cdot h$]
k_{OH} = reaction rate constant defined in Eq. (11) [$m^3/kmol \cdot h$]
K = carbamate formation equilibrium constant [$kmol/m^3 \cdot atm$]
K_C = carbamate stability constant [$m^3/kmol$]
K_{C1} = first dissociation constant of carbonic acid [$kmol/m^3$]
K_G = overall mass transfer coefficient of CO_2 gas [$kmol/m^2 \cdot h \cdot atm$]
K_P = dissociation constant of protonated amine [$kmol/m^3$]
L = amine solution flow rate [m^3/h]
N_A = mass transfer rate of CO_2 gas per unit surface area [$kmol/m^2 \cdot h$]
P_T = total pressure [kPa]
p = partial pressure of CO_2 gas [kPa]
p^* = equilibrium partial pressure of CO_2 gas [kPa]
r = mass transfer rate of CO_2 gas per unit absorber volume [$kmol/m^3 \cdot h$]
x = mol fraction of CO_2 in liquid phase [-]
X = CO_2/amine molar loading [-]
y = mol fraction of CO_2 gas [-]
y^* = equilibrium mol fraction of CO_2 gas [-]
z = absorber length [m]
β = mass transfer enhancement factor [-]

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Heavy Metal Soil Remediation: The Effects of Attrition Scrubbing on a Wet Gravity Concentration Process

Michael A. Marino

Metcalf & Eddy, P.O. Box 78301, Atlanta, GA 30357

R. Mark Brica

USAE Waterways Experiment Station, 3909 Halls Ferry Road, Vicksburg, MS 39180

and

C. Nelson Neale

Rice University, P.O. Box 1892, Houston, TX 77251

The US military has historically conducted activities which have either directly or indirectly contributed to environmental contamination. Metal contaminated soil at military sites has resulted from operations such as weapons production, small arms training activities, metal cleaning, and metal plating activities.

Soil washing is an effective approach to the treatment of contaminated soils employing both physical and chemical separation techniques. Physical separation methods encompass many different unit operations including screening, grinding, flotation, hydroclassification, attrition scrubbing and gravity concentration such as tabling and spiraling. The primary focus of this paper will be to address the effects of attrition scrubbing (an abrasive soil particle to soil particle interaction in a high solids environment), on a gravity concentration process.

Soil from an Army small arms training range with lead contamination in the bulk soil at approximately 40,000 mg/kg, was evaluated using a WEMCO® Laboratory Attrition Scrubber in conjunction with a Wilfley® Laboratory Wet Shaking Table. Results indicate attrition scrubbing enhanced the physical separation process on the wet shaker table by liberating the Pb contamination from the bulk soil, which resulted in a large volume of clean soil while simultaneously producing a small volume of Pb concentrated soil. Laboratory tests indicate over 96% of the contamination could be concentrated on 20% of the original soil mass.

INTRODUCTION

Background

It is estimated that thousands of sites in the United States have been polluted with organic and inorganic contaminants resulting from various activities including electroplating, metal working, ammunitions manufacturing, battery recycling, chemical processing, and solvent manufacturing. Many of these sites are current or formerly used federal facilities. The hazardous substances contained in the soil and water at many of these installations require remediation to avoid further environmental contamination.

Among the major contaminants of concern at many federal facilities are heavy metals. Heavy metal contaminants can be found at military operations including firing ranges, ammunition manufacturing facilities, metal plating facilities, and in open burn pits. Heavy metals currently constitute five of the six most cited hazardous materials at US army sites [*1*], and the three most prevalent metals at these sites are lead (Pb), cadmium (Cd), and chromium (Cr). All of these metals are potentially toxic to human health and many cause a variety of ailments including brain and neurological damage, liver and kidney damage, and cancer. Contaminant pathways include ingestion, absorption through the skin, and dust or vapor inhalation [*2, 3*].

Soil Washing Technology

To remediate these contaminated sites, a limited number of remediation technologies have been developed for treating and or disposing of soils contaminated with heavy metals. Soil washing is one such emerging technology currently being demonstrated for the removal of heavy metals from contaminated soils. Soil washing is a water based process for mechanically and chemically scrubbing soils *ex-situ* to remove organic and/or heavy metal contaminants from soil. While soil washing is a commonly used term, soil washing actually involves physical separation and chemical extraction techniques. Physical separation techniques, such as particle size and particle density separations, may reduce the volume of contaminated soil. Chemical treatment, which utilizes acids and chelating agents to dissolve or suspend the contaminants in solution, are generally used on the more recalcitrant soils, or soil fractions that could not be remediated with physical separation techniques. While many processes can be included in a study of physical separation and chemical extraction, this paper focuses on two physical separation processes to liberate heavy metals from contaminated soils.

General Description of Physical Separation Processes

Physical separation processes utilized in soil washing generally use mechanical energy and gravity concentration to separate particles of different densities and sizes from bulk soil material. The distribution of heavy metals throughout a soil matrix depends on the speciation of the particular metal. When the contaminant is in its elemental form, it may exist in any fraction of the soil as particulate matter. When the contaminant is in the form of a compound, it predominantly associates with the smaller, higher surface area particles, largely composed of hydrous manganese and iron oxides, organics, and clay minerals [1]. Since the contamination can be associated with a distinct fraction of the soil, the process of physically separating soil may effectively reduce the volume of soil requiring further treatment. Also, if the metals exist in elemental form as metallic particles, physical separation processes can be used to remove the metals for recycling.

The general physical separation remediation approach uses gravity concentration processes *ex-situ* which exploit differences in soil particle size and density to achieve a separation. A schematic of a typical physical separation circuit is illustrated in Figure 1.

In this process a prescreened excavated heavy metal contaminated soil is continually conveyed to a wet attrition scrubber. The scrubber breaks up agglomerated particles and potentially liberates contaminants from soil particles. The scrubbed soil is then sent to a trommel screen for sizing. The top product (material coming out of, or retained on the top of the unit operation) from the trommel is clean oversize material, and the bottoms product (material coming out the bottom of the unit operation) is sent to a jig. The jig pulsates and separates by employing buoyancy principals. The bottoms product from the jig is generally large metallic particles that can be recycled, such as lead bullet fragments. The lighter top product from the jig is sent to a hydrocyclone to again separate the soil by particle size. Typically, the fine fraction that contains the highly contaminated silts and clays is removed as the top product, dewatered, and sent for further treatment. The bottoms product from the hydrocyclone, largely sand, is fed to a spiral concentrator to separate the particles by density. The spiral is a helical screw which imparts centrifugal energy to a soil slurry as the slurry flows by gravity down the length of the spiral. The dense soil fraction is simply separated from the light fraction due to density variations. The contaminated dense fraction is dewatered and sent for further treatment.

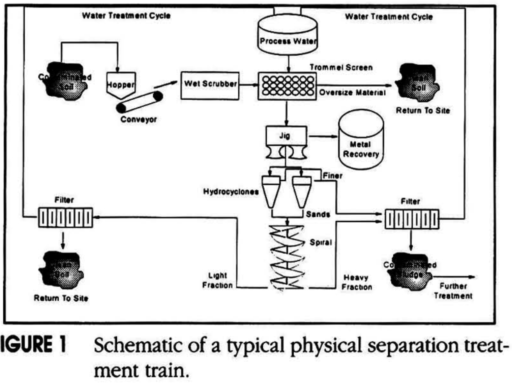

FIGURE 1 Schematic of a typical physical separation treatment train.

The lighter, typically clean fraction is dewatered and may be returned to the site as backfill. Process water used in the system can be treated to remove any accumulated metals, and then recycled back into the system. The ultimate goal of physical separation processes is to produce various soil product streams including a pure metallic stream, a small volume of concentrated contaminated soil, and a large volume of clean soil. Physical separation can be used as a total treatment technology or as volume reduction measure which involves additional treatment operations.

As discussed earlier, this paper focuses on physical separation techniques. The two unit operations evaluated in this study were a wet shaker table and an attrition scrubber. Details of each are discussed as follows.

Attrition Scrubbing

Attrition scrubbing employs a high energy mixer to impart a mechanical scrubbing action on a slurried soil. This mixing results in vigorous particle to particle scrubbing in a high solids environment. The two major effects of this particle scrubbing include scouring, and dispersion and disintegration. Scouring removes coatings or films from individual soil grains and produces clean soil surfaces. Dispersion and disintegration form a "slime" (ultra fine particles), or a dispersed slurry resulting from the break-up of agglomerated particles.

Attrition scrubbing can be utilized in a soil washing process after the large, oversize material has been removed by a grizzly and/or trommel. Attriting a heavy metal contaminated soil can either concentrate the contaminants into a particular soil fraction, or separate the soil particle from the metal surface, and increase the effectiveness of a particle density separation.

Wet Shaker Table

The wet shaker table is a rectangular or rhomboid shaped surface with raised strips of rigid material placed longitudinal along the surface to form "riffles." It is operated essentially in a horizontal plane. A schematic of the table surface is illustrated in Figure 2. A drive mechanism imparts an oscillating motion to the deck along its long axis as water flows perpendicular across the table. The separation produced on a wet shaker table is the result of several mineral processing principles simultaneously acting on the table feed. These principles include; flowing-film concentration, hindered settling, consolidation trickling, and asymmetrical acceleration [4].

Operationally, a solid slurry is fed to the upper edge of the sloping table. As the slurry moves across the table, its travel is slowed by the "longitudinal riffles" which allows the formation of pools behind the riffles. The oscillating action of the table causes size classification and specific gravity stratification. This result produces particles having simi-

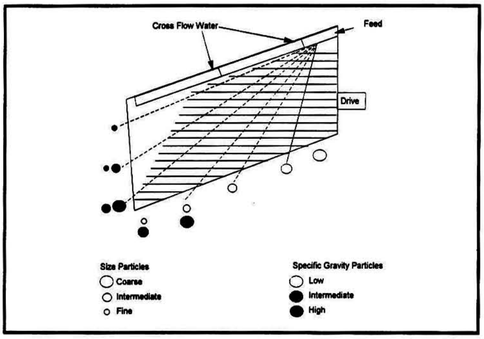

FIGURE 2 Map view schematic of size classification and density stratification for wet shaker table deck (adapted from Weiss, 1985).

lar specific gravities to arrange themselves vertically according to size as shown in Figure 2. The continuous addition of slurry and the action of the flow of cross water enables shearing of the top layers of the stratified particles. The table is designed so that the depth of the riffles decreases toward the left or discharge end of the table which allows the lighter coarser particles to pass over the riffles toward the downslope side of the table while the increasingly finer, denser particles move longitudinal along the table. The drive mechanism is designed to impart a faster return stroke than forward stroke which forces the particles to move toward the discharge end of the table. In summary, the heavy particles will discharge at the left side of the table, while the lighter particles will discharge toward the bottom of the table [5].

The effectiveness and speed of the separation is dependent on the operational factors of the shaker table and the properties of the soil. Such factors include: size and shape of the particles, difference in the particles specific gravity, the particle size range of the feed, the cross water and feed flow rates, and the mechanical settings of the shaker table which include the speed, stroke and slope of the table [4].

Objectives

This study examined the effectiveness of wet tabling in conjunction with attrition scrubbing on a Pb contaminated soil collected from an Army Small Arms Training Range (SATR). The objectives of this study were to 1) determine if a wet shaker table can successfully concentrate the heavy metal contaminant in smaller soil volumes, potentially rendering the bulk of the soil relatively free of contaminants, and 2) evaluate the effectiveness of attrition scrubbing as an aid to wet tabling to further concentrate the Pb contaminant into a smaller volume of soil.

The study was conducted in two parts: wet tabling without attrition scrubbing, and wet tabling with attrition scrubbing. Both the attrited and non-attrited samples were tabled using the same method, and both samples were subjected to the same physical and chemical analysis. These tests include table product distribution, particle density analysis (PDA), total metal analysis (TM), and contaminant mobility analysis, as discussed in the following sections.

MATERIALS AND METHODS

Soil Preparation

The bulk soil for this study was obtained directly from the impact berm of the SATR to insure that a highly contaminated sample would be collected. The bulk soil was initially thoroughly homogenized to ensure a uniform sample with respect to contamination concentration. The homogenization process was initiated by placing the bulk soil into shallow plastic containers (pools). The soil was mixed manually using a shovel and was allowed to air dry for approximately three days. During the air drying process, the soil was turned frequently and any large clumps of soil were broken up. Next the soil was passed through a mechanical sieve for separation of the large rocks and oversized lead particles from the bulk soil. A Sweco® 30 inch diameter mechanical sieve, model number XS30S6666 fitted with a $^1/_4$ inch aperture screen was used to make the separation. The $< ^1/_4$ inch soil fraction was utilized for experimentation throughout this study. After the soil was sieved, the $< ^1/_4$ inch material was passed through a Gilson® model SP-Z sample riffler to achieve a thoroughly homogenized soil. After these homogenization procedures were completed, the soil samples were then placed in 5 gallon containers and stored at 4°C to await further testing.

Attrition Scrubbing Experiment

The attrition scrubbing tests were performed using a WEMCO® Laboratory Attrition Scrubber fabricated with a high-torque variable speed drive motor and a stainless steel shaft. The variable speed drive was adjustable in the range of 650–1900 rpm and speeds were read directly from a tachometer. The attrition apparatus consisted of three, bladed impellers and a close fitting stainless steel tank with a lid. The impellers were fabricated into one piece with all the blades facing at opposing pitches and was attached to the end of the shaft (Figure 3). This type of configuration maximizes the particle to particle contact that produces the desired scrubbing action.

To optimize the effectiveness of the WEMCO® Laboratory Attrition Scrubber, a regulated volume of soil was added to the stainless steel tank. Approximately 1200 grams of moist $< ^1/_4$ inch soil was placed in tank. The appropriate amount of water was added to the soil to produce a 75% to 80% solid slurry. The speed was set to approximately 1100 rpm and the slurry was attrited for 15 minutes. After attrition, the slurry was removed from the tank and presized for use in the wet tabling experiment.

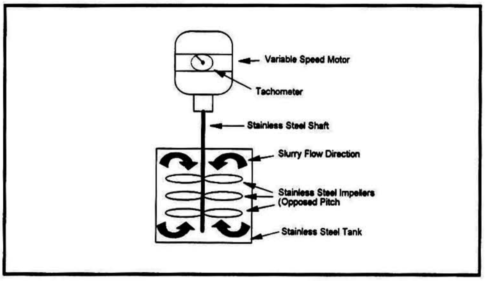

FIGURE 3 Schematic of a laboratory attrition scrubber.

Wet Shaker Table Experiment

The shaker table experiments conducted in this study utilized a Wilfley® Laboratory Concentrating Table with a model 13A Sand Deck. The differential shaking motion was provided by a gear connected to a pulley which was driven by an electric motor. The table deck, gear box, and the pulley-motor system were mounted in line. A trough with multiple sampling point was also attached to the table mount. The deck and sampling ports were made of polyester resin reinforced fiberglass material. A schematic of the experimental apparatus is presented in Figure 4.

Optimization of the operating parameters was essential to achieve the maximum performance of the Wilfley® Concentrating Table. Previous studies indicated that the feed soil particle size range should be between 2.00–0.063 mm. The presizing was accomplished by wet sieving to remove the > 2.0 and < 0.063 mm particles. It was determined through pretesting that approximately 2500 grams of dry presized feed was sufficient to conduct a tabling experiment. Attrited samples used in the wet tabling analysis were prepared as previously discussed. In contrast to the unattrited sample to be tabled, the attrition-tabling sample was first attrited, then presized as described previously.

The presized soil was slurried to form a 20% solids mixture and fed to the table. Table feed rate, cross water flow, table tilt, speed and stroke were adjusted to obtain proper separation based on visual inspection. A good separation was determined by observing distinct bands of material at the left end of the table deck. Once a good separation was achieved, and the adjustable parameters were fixed, the process was at "steady state" and ready for sampling. The "bands" of material flowing off the table were isolated by sample cutters and were discharged into 5 gallon containers as tabled samples. The presized feed was separated into 3 fractions: concentrates (cons), middlings (mids), and tailings (tails). These terms are commonly used in the mining industry and have been adopted for use in this study. The particles with the highest densities were typically associated with the cons fractions and were discharged at the left end of the table. The tails fraction usually contained the lightest density particles and was discharged at the bottom-right side of the table. The mids fraction contained the medium density particles and was discharged at bottom, left end of the table.

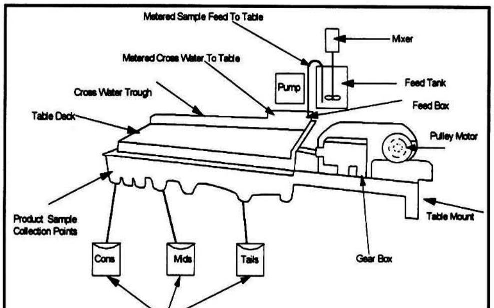

FIGURE 4 Schematic of a wet shaker table experimental apparatus.

Table Product Distribution Analysis

The dry mass of the tabling products (cons, mids, and tails) was needed to determine the distribution of the products as well as to provide a homogeneous sample for further analysis.

The dry mass was obtained for each fraction by dewatering the samples using a custom made air pressure filter. The pressure filter utilized Sharkskin® filter paper with an average pore size of 8–12 μm. The maximum pressure used to filter the samples was approximately 80 psi. The pressure filter produced a filter cake, which was further dewatered by drying the cakes in a VWR® model 1370G vented oven at 104°C for 24 hours. After the soil cakes were dry, they were weighed and stored in plastic sample bottles.

Particle Density Analysis

Particle density of soils refers to the density of solid particles collectively, or the ratio of total mass of the solid particles to their volume, excluding pore spaces between particles [6]. Published data indicates that on an average, soil has a particle density range of 2.45–2.80 g/cc [7]. A significant deviation from this range may give insights to the treatability potential of a contaminated soil using physical separation. Particle densities were determined for each fraction of soil including the presized bulk soil, using a Micrometrics AccuPyc® 1330 Pycnometer.

Total Metal Analysis

The total amount of metal contaminant was determined for all fractions obtained from the wet tabling analysis. Pb was the primary contaminant of concern for this study, although copper (Cu) and zinc (Zn) were also analyzed.

Three sub-samples from the bulk soil were used to determine bulk concentrations, while two sub-samples from the tabled soil samples were utilized for contaminant analysis. Using a Carpco® SS-16-3X, and SS-32-6X sample splitter, a representative 30 gram sample of each soil fraction was obtained. Each 30 gram sample was ground to approximately 75 μm in size using a mortar and pestle and stored in 20 ml glass vials. A small representative sample of the ground 75 μm material, was further prepared for TM analysis using microwave assisted acid digestion. A Floyd® Microwave Digester, model RMS-950 in conjunction with EPA method 3051 for solids, and EPA method 3015 [8] for aqueous samples was used to digest the samples. The determination of the total metal contaminant was accomplished using a Perkin Elmer® Model 5100 PC atomic adsorption spectrometer with direct aspiration and EPA methods 7420, 7210, and 7950 for Pb, Cu, and Zn, respectively [8].

Contaminant Mobility

The contaminant mobility testing was performed using the Toxicity Characteristic Leaching Procedure (TCLP) [9]. The test basically consists of mixing a sample in a 20:1 liquid-to-solid ratio, with a mild acidic or basic solution, depending on the pH of the sample, and tumbling the mixture for a given amount of time. The sample is then filtered to capture the leachate and analyzed for contaminant concentration.

Pb was the only metals analyzed in this study that EPA regulates according to the provisions under the Resource Conservation and Recovery Act (RCRA). The regulations state that the TCLP limit for Pb is 5 mg/l. Any solid that leaches more than the limit has failed the TCLP test, and the solid is deemed a hazardous waste. Such solid must be disposed of in a hazardous waste landfill, or treated to reduce the contaminants to acceptable levels [9]. TCLP tests were performed in duplicate on all samples generated in the study. The TCLP leachate produced was analyzed for Pb, Cu, Zn, using the same methods described above.

RESULTS AND DISCUSSION

Tabling Soil Mass Distribution and Total Metal Analysis Results

The effectiveness of the wet tabling experiment with and without attrition scrubbing was based on three factors including soil and Pb mass distributions, and leachability based on TCLP tests. These results are presented in Figures 5, 6, and 7, respectively.

Wet tabling of the Pb contaminated soil produced three fractions: cons, mids, and tails. Figure 5 provides the weight distribution of each of these fractions for both the attrited and non-attrited samples. The results indicate that the majority of the soil mass pre and post-attrition was separated into the mids fraction. The cons fraction contained the next largest amount of soil, while the tails received the least amount of soil. Inspection of Figure 5 reveals attrition scrubbing affected the separation in all three tabling products. For example, the cons experienced as 12.5% decrease in soil mass from 33.2% to 20.7%, the mids increase by 14.9%, and the tails decrease by 2.4%.

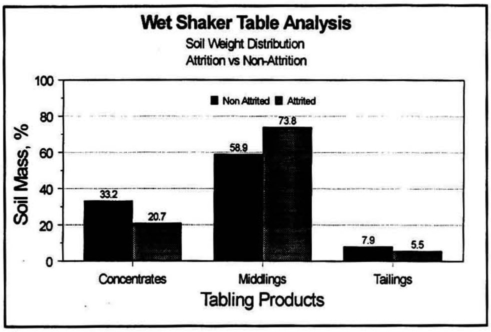

FIGURE 5 Table product distribution for the wet shaker table analysis.

The Pb mass results presented in Figure 6, indicate the vast majority of the Pb was concentrated on the cons fraction, while the mids and tails split the remaining Pb mass almost evenly. Although Figure 6 indicates attrition scrubbing only slightly affected the distribution of Pb mass between the tabling products, the Pb TM concentrations presented in Table 1 reveal more significant results. The concentrations given in Table 1 are averages of two or more samples. Copper and zinc results are presented as well. Table 1 indicates attrition scrubbing increased the Pb concentration in the cons and decreased the concentration in the mids and tails. Although the actual mass % of Pb was relatively unchanged pre and post attrition for all fractions, attrition scrubbing prior to tabling produced a smaller, more concentrated cons fraction, and a larger, less contaminated mids fraction.

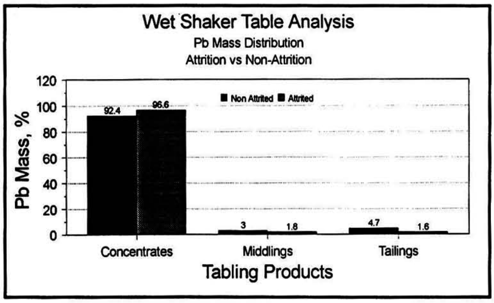

FIGURE 6 Pb mass distribution between the tabling products for the wet shaker table analysis.

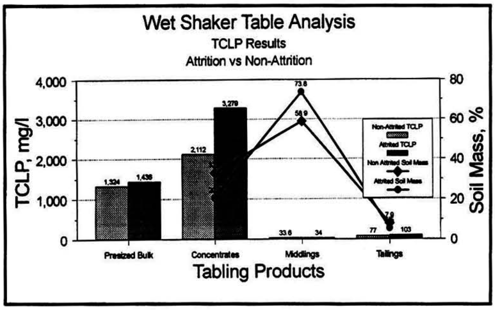

FIGURE 7 Pb TCLP results for the wet shaker table analysis.

TABLE 1. Total Metal Concentrations for Attrited and Non-Attrited Wet Tabling Analysis Samples

	Pb		Cu		Zn	
Tabling Component	Non-Attrited mg/kg	Attrited mg/kg	Non-Attrited mg/kg	Attrited mg/kg	Non-Attrited mg/kg	Attrited mg/kg
Presized bulk	41,623	52,517	904	4,068	206	449
Concentrates	81,906	202,333	4,233	28,939	456	2,814
Middlings	1,487	1,049	149	146	149	43
Tailings	17,373	12,476	1,841	1,259	315	172

TABLE 2. TCLP Concentrations for Attrited and Non-Attrited Wet Shaker Tabling Analysis Samples

	Pb		Cu		Zn	
Tabling Component	Non-Attrited mg/l	Attrited mg/l	Non-Attrited mg/l	Attrited mg/l	Non-Attrited mg/l	Attrited mg/l
Presized bulk	1324.0	1436.0	3.5	2.1	0.8	0.8
Concentrates	2112.0	3279.0	0.6	0	0.4	0.9
Middlings	33.6	34.0	1.2	2.5	0.5	0.6
Tailings	77.0	103.0	2.4	10.6	0.4	3.1

TCLP Analysis Results

Figure 7 presents the Pb TCLP results from the wet tabling experiment for both the attrited and non-attrited SATR soil. TCLP tests were also conducted on Cu and Zn and the results are presented in Table 2.

The data in Figure 7 reveals the Pb concentrations for all of the tabling components failed the TCLP limit of 5.0 mg/l. Although the middling fraction, pre and post attrition failed the TCLP, their concentrations of 33.6 mg/l and 34.0 mg/l respectively, are significantly lower than those in the cons and tails fractions. It is also observed in Figure 7 that attrition scrubbing increased the TCLP concentrations in the cons and tails and the mids remained unchanged. The latter proves to be the most significant result of Figure 7 since attrition scrubbing prior to tabling produced a larger mids fraction.

As stated previously, the bulk soil used in this study was collected to ensure a highly contaminated sample. In actual pilot testing, or full scale treatment, excavation and blending techniques of the feed soil would produce a less contaminated stock, and hence, probably passing TCLP concentrations for the mids fractions.

Particle Density Analysis Results

Particle density measurements were obtained for each of the tabling components for both the attrited and non-attrited soils as shown in Figure 8. Pb is considered to be the driving force influencing the density of the fractions for two reasons: 1) Elemental Pb has a specific gravity of 11.33, compared to Cu and Zn with 8.92 and 7.14 respectively [*10*]; 2) Pb was the predominant contaminant based on TM analysis shown in Table 1. In fact, the Pb TM concentrations in the cons fraction pre and post attrition, translate into 8.2% and 20.2% total Pb, respectively.

Figure 8 indicates the cons fraction had the highest densities with 2.9748 g/cc for the non-attrited sample, and 3.5784 g/cc for the attrited sample. The distinct increase in the particle density of the cons fraction post-attrition, is a result of the decrease in the cons soil mass after attrition (Figure 5), and the large increase in Pb TM concentration (Table 1) after attrition. Figure 8 also shows the middling fraction densities to be very close to that of the average density of mineral surface soil, which is 2.65 g/cc. The tailing fractions measured densities below the average at 2.4734 g/cc and 2.4379 g/cc for non-attrited and attrited samples, respectively.

Discussion of Results

Comparing Figures 5 and 6, reveals that the vast majority of the Pb contamination is concentrated on the cons fraction, which is a relatively small portion of the initial bulk soil mass. It is also observed that attriting the bulk soil prior to tabling produces a smaller, more concentrated fraction (cons), while simultaneously producing a larger, cleaner fraction (mids), which is the goal of this treatment.

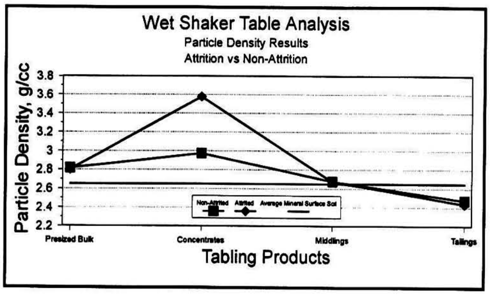

FIGURE 8 Particle density results for the wet shaker tabling analysis.

The results in Figures 5 and 6 indicate that attrition scrubbing enhances the separation achieved on a wet shaker table. These results suggest that attrition scrubbing liberates the Pb from the soil, producing a more discrete Pb constituent within the bulk soil, making the soil matrix more amenable to physical separation. By separating individual Pb particles from the soil particles with attrition, a sharper more distinct visual separation was achieved on the shaker table between the mids and the cons. This result helped produce the smaller more concentrated cons and larger, less contaminated mids illustrated in Figures 5 and 6. The TCLP data in Figure 7, and the particle density data in Figure 8 both support the attrition scrubbing concept described above, by showing large increases in concentration after attrition. Both of these results are due to the increase in the cons TM concentration, from 81,906 mg/kg to 202,333 mg/kg post attrition.

CONCLUSIONS

This study investigated the ability of the wet shaker table, with and without the aid of attrition scrubbing, to physically separate Pb contamination from a SATR soil. The following conclusions were drawn from this study:

a) The wet shaker table successfully concentrated the majority of the Pb contamination onto a small volume of the original presized bulk soil, in the 2.0–0.063 mm size range.

b) The wet shaker successfully produced a larger fraction of soil which was relatively free of Pb contamination.

c) Attrition scrubbing greatly enhanced the physical separation process on the wet shaker table by liberating the Pb contamination from the soil and producing a larger cleaner fraction while simultaneously producing a smaller, more Pb concentrated fraction.

d) Low TCLP concentrations on the large, slightly contaminated middling fractions indicate that this fraction is basically free of mobile Pb. In pilot of full scale soil washing conditions, it is highly probable that a density separation on this soil would produce a fraction that would pass TCLP for Pb.

e) Further studies are needed to support the trends observed in this study and provide data to develop pilot scale physical separation processes.

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A Simplified Approach for Preliminary Design and Process Performance Modeling of Soil Vapor Extraction Systems

Jeff Staudinger and Paul V. Roberts

Department of Civil Engineering, Stanford University, Stanford, CA 94305-4020

and

James D. Hartley

CH2M-Hill, Inc., 2485 Natomas Park Dr., Suite 600, Sacramento, CA 95833

While soil vapor extraction has been widely utilized as a remedial action technology over the past decade, design and associated process performance modeling of full-scale systems continues to be frequently based on the results of pilot-scale treatability tests. To aid engineers in conducting preliminary scoping studies without the benefit of such treatability data, a relatively simple approach, consisting of linked design and process performance elements, was developed and subsequently incorporated into a spreadsheet format for rapid project evaluation purposes. Under this approach, a preliminary design is specified via a set of baseline values which vary based on the predominant soil type encountered at a particular site. Process performance is then mathematically modeled by a semi-empirical relation accounting for non-equilibrium (mass transfer) effects via use of a lumped parameter, the venting efficiency factor (η). Values for η vary based on characterization of soil heterogeneity. The low values cited for η (on the order of 0.02–0.20) reflect the relative inefficiency of field venting operations (due to inherent mass transfer limitations) when compared to idealized conditions. Validation results, considering two case studies reported in the literature, indicate that the approach developed provides reasonably accurate predictions. Evaluation of a hypothetical case study reveals that the number of extraction vents required as well as the number of pore volumes of soil vapor that must be extracted for effective remediation can vary by an order of magnitude depending upon the particular soil matrix encountered.

INTRODUCTION

At many hazardous waste sites, as well as sites that have experienced gasoline or other hydrocarbon fuel spills, remediation of soils contaminated with volatile organic compounds (VOCs) is required. In such situations, soil vapor extraction (SVE) is the current technology of choice for VOC removal from permeable soils (i.e., most sands and some silts).

SVE is a relatively new remedial technology, with first reports regarding its implementation surfacing during the early 1980s. Over the years, SVE has been applied at thousands of sites across the nation, its use expanding due to its cost-effectiveness and ease of implementation, particularly for cases involving fuel spills from leaking underground storage tanks. In response, the United States Environmental Protection Agency (USEPA) issued a reference handbook specifically for SVE [*1*]. In addition, several SVE-focused vendors are active in the current marketplace.

Despite being "an every day part of our environmental strategy" [*2*], design of full-scale SVE systems continues to be based principally on the results of pilot-scale treatability tests. This empirical approach historically has been justified because of the varying subsurface conditions encountered and complexities of the dynamic SVE process [*3*]. The USEPA has acknowledged the necessity of pilot studies, having issued an interim guidance for conducting SVE treatability studies under the Superfund program (i.e., CERCLA) [*4*].

During project scoping activities, when such pilot study information is unavailable, it is desirable to have a quick means of generating a preliminary design and estimating system performance. In this paper, we detail a relatively simple approach which has been incorporated into a spreadsheet format for rapid project evaluation purposes. This approach also has been utilized in a prototype of a knowledge-based (i.e., expert) system developed to both select appropriate remedial technology and provide design and time/cost estimates for clean-up of "real-world" waste sites when limited information is available [*5*]. Known as "Haztimator," this expert system was developed in part as a potential next-generation system to replace the well-known Cost of Remedial Action (CORA) model initially developed in 1987 by CH2M-Hill Inc. for the USEPA [*6*].

KEY ENGINEERING PARAMETERS

The key engineering parameters for SVE and their associated significance are as follows:

Design:

- Extracted Air Flow Rate: Affects sizing of vacuum pump unit(s).
- Vent Design Radius (Effective Radius of Influence): Affects number of extraction vents required.

Process Performance:

- Mass Removal Versus Time Profile: Determines required system operation time (i.e., remediation time).

Determination of the two design-related engineering parameters noted requires characterization of the subsurface air flow regime; determination of the process performance-related engineering parameter cited requires coupling contaminant transport/removal with air flow regime characterization. A discussion of the simplified approach developed through this work is presented below within the context of the general approach typically employed. Process performance (i.e., contaminant transport/removal) is addressed first as it ultimately guided selection of the design method employed under this approach.

PROCESS PERFORMANCE

Based on mass balance considerations, the fundamental governing process performance equation for predicting contaminant removal during SVE operations is:

$$\frac{dm_{i,\text{tot}}}{dt} = -QC_{i,\text{vap}} \qquad (1)$$

where $m_{i,\text{tot}}$ = total mass of contaminant i present in the soil (g); t = time (day); Q = extracted air flow rate (m^3/day), and $C_{i,\text{vap}}$ = mass concentration of contaminant i in extracted air (g/m^3).

Equation (1) can be solved if the relationship between $m_{i,\text{tot}}$ and $C_{i,\text{vap}}$ is known.

Such a relationship can be established via use of an advection-only (A) or an advection-diffusion (A-D) differential equation. Under this approach, a numerical technique (e.g., a finite element or finite difference method) is typically required for solution of the governing A/A-D equation.

The A/A-D equation method is commonly taken; a review of literature-reported SVE models (Table 1) yielded twenty-two coupled air flow/contaminant transport and removal models [*7–28*], as well as six air flow-only models [*29–34*] based on this approach.

The major advantage of A/A-D equation modeling lies in the ability to utilize detailed, site-specific knowledge of the subsurface structure and spatial distribution of the contaminant(s) to make "accurate" (at least on a theoretical basis) predictions. However, the focus of this effort was to develop a method designed for use at the project scoping stage, when such detailed information is not available. Therefore, A/A-D equation modeling was eliminated from further consideration. Instead, a simpler, albeit less accurate, approach utilized by both Roy and Griffin [*23*] and Johnson et al. [*24*] was selected. These investigators simplified the problem by assuming that the contamination is uniformly distributed (i.e., completely mixed) throughout the soil *at all times.* $m_{i,\text{tot}}$ thus represents the total mass of contaminant i as calculated by multiplying the average soil concentration of contaminant i by the volume of contaminated soil. Although the uniform distribution assumption is clearly not valid in field situations, it was felt that use of an average contaminant concentration would still yield performance predictions reasonably accurate for project scoping activities.

The specific process performance model developed based on the uniform distribution assumption is presented below. An initial discussion examines the validity of the Local Equilibrium Assumption (LEA) in field situations; based on the subsequent finding that the LEA frequently is not a valid assumption, the mathematical model is modified to incorporate kinetic limitations, thus relaxing the LEA.

Validity of the Local Equilibrium Assumption

Early SVE modeling work considered the LEA to be valid (see Table 1). In addition, a laboratory soil column study using a clean, medium sand and three separate air flow rates gave results which closely matched those predicted using a LEA-based model [*27*]. However, non-equilibrium-type tailing effects have been observed in many other laboratory and field studies [*16, 21, 35–38*]. As a result, non-equilibrium models have appeared in the literature (see Table 1).

Significant overestimation of SVE system performance, most clearly manifested in the underestimation of the time required for remediation, can result when the LEA is inappropriately applied. Modeling efforts in one particular case resulted in the predicted cleanup time being five times greater using a non-equilibrium model when compared with a LEA model [*39*]. The USEPA has cautioned practitioners that when mass transfer limitations exist, actual cleanup times can be as much as two orders of magnitude greater than those predicted using the LEA [*4*].

Given this situation, it was considered mandatory that non-equilibrium effects be taken into account under this effort. The resultant model so developed is detailed below.

Non-Equilibrium Process Performance

Conceptual Framework

It is readily recognized that natural soil heterogeneity affects air flow patterns and thus, contaminant transport, during SVE operations. For modeling purposes, a simple framework capturing that fundamental concept divides the soil media into two distinct domains based on relative air permeability, as follows:

- Advective domain (coarser-grained materials possessing a relatively high air permeability) containing mobile gas and aggregates composed of immobile water and solid soil phases.
- Non-advective domain (finer-grained material possessing a relatively low air permeability) comprised of (relatively) immobile gas and aggregates composed of immobile water and solid soil phases.

Principle mass transfer rate limitations present are:

- Advective domain: Grain-scale (sorption-related) limitations resulting from either chemical non-equi-

TABLE 1. Summary of Literature-Reported Soil Vapor Extraction Models

Model	Lit. Ref. No.	Equilibrium?	No. of Dimensions	No. of Phases	No. of Contaminants	Initial Contaminant Distribution	Soil Conditions	Surface Boundary	Analytical Solution Method	Validation	Notes
Air Flow Coupled with Contaminant Removal											
Gomez-Lahoz et al. (1995)	7	NE	2-D	3	1	U	I, H	C	FD	None	
Rodriguez-Maroto et al. (1995)	8	NE	2-D	3	1	U	I, H	UC	FD	None	
Wilson et al. (1994)	9	NE	2-D	3*	1	U	I, H	UC	FD	None	
Rodriguez-Maroto et al. (1994)	10	NE	2-D	3*	1	U	I, H	UC	FD	None	1
Gomez-Lahoz et al. (1994)	11	NE	2-D	3*	1	U	I, H	UC	FD	None	2
Wilson et al. (1994)	12	NE	1-D	3*	1	U	H	UC	FD	None	
Gomez-Lahoz et al. (1994)	13	NE	1-D	3	Multi	U	H	UC	FD	None	3,4
Benson et al. (1993)	14	LEA	2-D	4	Multi	U	A, NH	C, UC	FD	NM, AM	5
Falta et al. (1993)	15	LEA	2-D	3	1	U	I, H	C	SA	NA	
Gierke et al. (1992)	16	NE	1-D	3	1	NU	H	UC	OC	LSC	
Kayano & Wilson (1992)	17	LEA	2-D	2	Multi	U	I, H	UC	FD	None	1
Lingineni & Dhir (1992)	18	NE	1-D	2	Multi	U	H	C	FD	LSC	6
Brusseau (1991)	19	NE	1-D	3	1	U	NH	UC	FD	LSC	
Gomez-Lahoz et al. (1991)	20	LEA	2-D	3	1	U	A, H	UC	FD	None	2, 3
Rathfelder et al. (1991)	21	LEA	2-D	4	Multi	U	I, H	UC	FD	LSC, AM	
		NE	2-D	4	Multi	U	I, H	UC	FD	None	
Rodriguez-Maroto & Wilson (1991)	22	NE	1-D	3	1	U	H	UC	FD	None	3
		NE	2-D	3	1	U	A, NH	C, UC	FD	None	3
Roy & Griffin (1991)	23	LEA	0-D	3	1	U	H	C	AN	NA	
Johnson et al. (1990)	24	LEA	0-D	4	Multi	U	I	C	FD	FS	
Stephanatos (1990)	25	LEA	2-D	4	1	U	I, H	C	FD	FS, NM, AM	
Wilson (1990)	26	NE	1-D	3	1	U	H	UC	FD	None	3, 7
		NE	2-D	3	1	U	A, NH	C, UC	FD	None	3, 7
Baehr et al. (1989)	27	LEA	1-D	4	Multi	U	H	C, UC	FD	LSC	
Wilson et al. (1988)	28	LEA	1-D	3	1	U	H	UC	FD	None	3
		LEA	2-D	3	1	U	I, H	UC	FD	FS	3
Air Flow Only											
Mohr & Merz (1995)	29	NA	2-D	NA	NA	NA	A, NH	C, UC	FD	FS	
Gamliel & Abdul (1993)	30	NA	2-D	NA	NA	NA	I, H	C, UC	FE	None	
Sepehr & Samani (1993)	31	NA	3-D	NA	NA	NA	A, NH	C, UC	FD	FS, AM	
Shan et al. (1992)	32	NA	2-D	NA	NA	NA	A, H	UC	AN	NA	
Baehr & Hult (1991)	33	NA	2-D	NA	NA	NA	A, H	C, UC	AN	NA	
Kuo et al. (1991)	34	NA	3-D	NA	NA	NA	I	C, UC	FD	FS	

No. of Dimensions: 0—D assumes uniform contaminant distribution (e.g., complete mixing) at all times.
No. of Phases: 2–Vapor and NAPL.
3–Vapor, dissolved, and adsorbed.
3*–Vapor, dissolved, and NAPL.
4–Vapor, dissolved, adsorbed, and NAPL.

NOTES: 1–Separate models for horizontal and vertical wells.
2–Applicable to horizontal wells.
3–Adsorption indirectly modeled via effective Henry's Law constant.
4–Accounts for biodegradation.
5–Accounts for soil water depletion with time.
6–Accounts for non-isothermal effects.
7–Applicable to fractured bedrock.

ABBREVIATIONS: General:
NA: Not Applicable
Equilibrium?:
LEA: Local Equilibrium Assumption
NE: Mass-transfer rate limitation
Initial Contaminant Distribution:
U: Uniform
NU: Non-uniform

Soil Conditions
I: Isotropic
A: Anisotropic
H: Homogeneous
NH: Non-homogeneous
Surface Boundary Conditions:
C: Confined
UC: Unconfined

Solution Type:
AN: Analytical
SA: Semi-Analytical
FD: Finite Difference
FE: Finite Element
OC: Orthogonal Collocation
Validation:
FS: Field Site
LSC: Lab Soil Column Study
NM: Numerical Model
AM: Analytical Model

librium (rate limited sorbate-sorbent interactions) or physical diffusion.

- Non-advective domain: Large-scale (transport-related) limitations arising from physical transport phenomena (i.e., slow diffusional release from the non-advective to the advective domain).

Overall, during soil venting, the advective domain undergoes active remediation, while the non-advective domain effectively acts as a contaminant source.

Of course, more detailed conceptual outlines have been developed to support advanced modeling efforts (see any of the studies listed in Table 1, for example). One such framework, generated based on the work of Brusseau [*19*] and supplemented by that of Gierke et al. [*16*], is given in Figure 1.

Quantitative Modeling

From the two-domain, multi-transport process conceptual framework given in Figure 1, theoretically-based, quantitative modeling of SVE system performance under real-world (e.g., non-equilibrium) conditions represents a daunting task, even for sites which are "well-char-

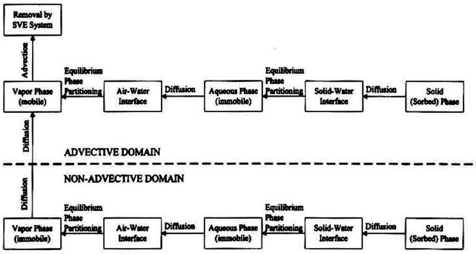

FIGURE 1 Example conceptual model of non-equilibrium contaminant transport during SVE operations (assumes no NAPL present).

acterized." Thus, for preliminary project scoping studies, a much simpler (but less accurate) approach must be adopted. This is achieved by characterizing non-equilibrium effects via a single lumped parameter (the "venting efficiency factor"), defined as follows:

$$\eta = \frac{C_{i,\mathrm{vap}}}{C_{i,\mathrm{vap}}^{\mathrm{eq}}} \tag{2}$$

where η = venting efficiency factor (dimensionless), $C_{i,\mathrm{vap}}$ = actual mass concentration of contaminant i in extracted air (g/m^3), and $C_{i,\mathrm{vap}}^{\mathrm{eq}}$ = predicted mass concentration of contaminant i (g/m^3) in the extracted air, calculated based on the LEA being a valid assumption. Values for η can range from (essentially) 0 to 1, with 0 indicating that overwhelming mass transfer limitations exist (i.e., worst case—no removal), while 1 reflects a lack of mass transfer limitations (i.e., best or ideal case), a situation where the LEA is valid.

$C_{i,\mathrm{vap}}^{\mathrm{eq}}$ is calculated as follows depending on whether an immiscible phase (i.e., Non-Aqueous Phase Liquid—NAPL) is present in the soil:

If NAPL is present:

$$C_{i,\mathrm{vap}}^{\mathrm{eq}} = \frac{x_i P_{i,\mathrm{sat}} MW_i}{RT} \tag{3}$$

If NAPL is absent:

$$C_{i,\mathrm{vap}}^{\mathrm{eq}} = \frac{k_{i,\mathrm{vap}}^{\mathrm{eq}}\ m_{i,\mathrm{tot}}}{\theta_a\ V_{\mathrm{tot}}} \tag{4}$$

where x_i = mole fraction of contaminant i in the NAPL (mole/mole); $P_{i,\mathrm{sat}}$ = saturated vapor pressure of contaminant i at temperature T (Pa); MW_i = molecular weight of contaminant i (g/mole); R = universal gas constant (8.315 N · m/mole · Kelvin); T = temperature (Kelvin); $k_{i,\mathrm{vap}}^{\mathrm{eq}}$ = vapor-phase equilibrium partition coefficient for contaminant i (g in vapor/total g present in soil); θ_a = volumetric air content of soil (m^3/m^3), and V_{tot} = total volume of contaminated soil (m^3).

Equation (3) is derived from the ideal gas law, and Equation (4) is based on multi-phase equilibrium considerations. For Equation (4), $k_{i,\mathrm{vap}}^{\mathrm{eq}}$ is calculated as follows:

$$k_{i,\mathrm{vap}}^{\mathrm{eq}} = \frac{H_i \theta_a}{H_i \theta_a + \theta_w + K_i \rho_{s,b}} \tag{5}$$

where H_i = Henry's Law constant (air-water partition coefficient) of contaminant i at temperature T ((mole i in air/m^3 air)/(mole i in water/m^3 water)); θ_w = volumetric water content of soil (m^3/m^3); K_i = soil-water partition coefficient of contaminant i (mole i in soil/kg soil)/(mole i in water/m^3 water)), and $\rho_{s,b}$ = bulk density of soil (kg/m^3). In this derivation, a linear adsorption isotherm was assumed.

Equation (5) was derived (as detailed in [6]) via substitution of appropriate equilibrium relationships into a simple mass balance expression followed by re-arrangement of terms. For a given contaminant/soil matrix, $k_{i,\mathrm{vap}}^{\mathrm{eq}}$ will be a constant value.

A direct analytical solution to Equation (1) (substituting in Equations (2) through (5) as appropriate) is obtained when the following assumptions are made:

- Single predominant contaminant (thus, x_i = constant = 1 in Equation (3)).
- Isothermal operating conditions.
- Constant soil water content.
- Biodegradation effects ignored.
- η values independent of contaminant concentration.

Under these assumptions, solution of Equation (1) yields:

If NAPL is present:

$$m_{i,\mathrm{tot},t} = m_{i,\mathrm{tot},t=0} - \left(\frac{\eta P_{i,\mathrm{sat}} Q MW_i}{RT}\right) t \tag{6}$$

If NAPL is absent:

$$m_{i,\mathrm{tot},t} = m_{i,\mathrm{tot},t=0} \exp\left[-\left(\frac{\eta k_{i,\mathrm{vap}}^{\mathrm{eq}} Q}{V_{\mathrm{tot}}}\right) t\right] \tag{7}$$

where $m_{i,\mathrm{tot},t}$ = total mass of contaminant i present in the soil at time t (g); $m_{i,\mathrm{tot},t=0}$ = total mass of contaminant i present in the soil at time = 0 (g), and t = remediation time (days).

Equations (6) and (7) can be easily converted to a mass concentration basis after dividing through by the total volume of contaminated soil, yielding:

If NAPL is present:

$$C_{i,\mathrm{tot},t} = C_{i,\mathrm{tot},t=0} - \left(\frac{\eta P_{i,\mathrm{sat}} Q MW_i}{RTV_{\mathrm{tot}}}\right) t \tag{8}$$

If NAPL is absent:

$$C_{i,\mathrm{tot},t} = C_{i,\mathrm{tot},t=0} \exp\left[-\left(\frac{\eta k_{i,\mathrm{vap}}^{\mathrm{eq}} Q}{V_{\mathrm{tot}}}\right) t\right] \tag{9}$$

where $C_{i,\mathrm{tot},t}$ = total mass concentration of contaminant i present in the soil at time t (g/m^3); $m_{i,\mathrm{tot},t=0}$ = total mass concentration of contaminant i present in the soil at time = 0 (g/m^3).

Each of the terms contained in parentheses in equations (6) and (7) represent constant values. Thus, in the case of NAPL being present, a plot of predicted contaminant mass removal versus time using Equation 6 would yield a straight line with a slope equal to ($-\eta$ $P_{i,\mathrm{sat}} Q MW_i/RT$). When NAPL is absent, a semi-log plot of predicted contaminant mass removal versus time using Equation 7 will yield a straight line with a slope equal to $(-\eta k^{\text{eq}}_{i,\text{vap}} Q/V_{\text{tot}})$. Similar plots can be generated using Equations (8) and (9).

The appropriateness of either Equation (6) or (7) (or equivalently, Equation (8) or (9)) depends on whether a NAPL is present in the soil at a given time during cleanup efforts. The following equation defines the minimum level at which a single contaminant i can exist as a NAPL in a given soil:

$$m_{i,\text{NAPL}} = \left[\left(\frac{P_{i,\text{sat}} \theta_a MW_i}{RT} \right) + (\theta_w C_{i,s.l.}) + (K_i \rho_{s,b} C_{i,s.l.}) \right] V_{\text{tot}} \tag{10}$$

where $m_{i,\text{NAPL}}$ = amount of contaminant i at incipient NAPL formation (g) and $C_{i,s.l.}$ = aqueous solubility limit of contaminant i at temperature T (g/m^3).

The terms in parentheses in Equation (10) represent the mass concentration of contaminant i present (in [g/m^3]) in the vapor, aqueous, and adsorbed phases, respectively, at the condition of incipient NAPL formation.

Equation (10) presumes that the contaminant is uniformly distributed at a scale relevant to the problem (i.e., the volume sampled in a core). However, if preferential pathways exist in the soil (as often occurs), NAPL may be present at levels less than that calculated by Equation (10). Because such preferential flow regimes are difficult to detect and characterize, Equation (10) is utilized as a rough approximation for project scoping purposes.

For a given scenario, Equation (10) is employed as follows. $m_{i,\text{NAPL}}$ is calculated and compared to the initial total mass of contaminant, $m_{i,\text{tot},t=0}$. This comparison dictates use of Equations (6) and/or (7) as follows:

1) If $m_{i,\text{tot},t=0} > m_{i,\text{NAPL}}$, then NAPL is presumed initially present and:

- For the period when $m_{i,\text{tot},t=0} > m_{i,\text{NAPL}}$:
  Equation (6) is used for time versus contaminant mass removal calculations.
- For the period when $m_{i,\text{tot},t=0} \leq m_{i,\text{NAPL}}$:
  Equation (7) is used for time versus contaminant mass removal calculations.

2) If $m_{i,\text{tot},t=0} \leq m_{i,\text{NAPL}}$, then NAPL is presumed absent and:

- Equation (7) is exclusively used for all time versus contaminant mass removal calculations.

A similar methodology can be employed to determine appropriate application of either Equation (8) or (9).

Often in field situations, the initial amount of contaminant present, $m_{i,\text{tot},t=0}$, is unknown. In such cases, process performance typically is monitored by plotting the profile of contaminant concentration measured in the extracted air over time. Appropriate vapor phase concentration modeling equations analogous to Equations (6) and (7) are as follows:

If NAPL is present:

$$C_{i,\text{vap},t} = \text{constant} = \frac{\eta P_{i,\text{sat}} MW_i}{RT} \tag{11}$$

If NAPL is absent:

$$C_{i,\text{vap},t} = C_{i,\text{vap},t=0} \exp\left[-\left(\frac{\eta k^{\text{eq}}_{i,\text{vap}} Q}{\theta_a V_{\text{tot}}} \right) t \right] \tag{12}$$

Equation 11 predicts that vapor phase contaminant concentrations will remain at a constant value if NAPL is present, while Equation (12) predicts an exponential decay when NAPL is absent. In the latter case, a semi-log plot of vapor phase concentration versus time using Equation (12) will yield a straight line with a constant slope equal to $(-\eta k^{\text{eq}}_{i,\text{vap}} Q/\theta_a V_{\text{tot}})$.

Field-observed results are often correlated by practitioners using the simple exponential decay function:

$$C_{\text{vap},t} = C_{\text{vap},t=0} \exp(mt) \tag{13}$$

where m = constant (day^{-1}), as determined from best-fit regression analysis of monitoring data. Thus, field results correlated using Equation (13) can be compared to model predictions given by Equation (12). As discussed later under model validation, two such case-study comparisons were performed as part of this effort.

Values for η

A detailed review [*40*] of non-equilibrium (i.e., diffusion and inter-phase mass transfer) theory identified three variables potentially affecting η:

- Subsurface conditions (both predominant soil type and amount of heterogeneity).
- Contaminant concentration.
- Specific contaminant present (contaminant properties).

For the case when NAPL is absent, further analysis indicates that the latter two variables likely have only secondary impact when compared with the first, subsurface conditions. When NAPL is present, analysis based on applying work investigating NAPL dynamics in the saturated zone [*41*] to the unsaturated zone, also found subsurface conditions to be the major variable expected to influence η. Thus, for both NAPL and no-NAPL cases, the process performance model developed assumes η to be principally dependent on the subsurface conditions (both predominant soil type and amount of heterogeneity present) encountered at a particular site.

At this point, typical preliminary design practices were considered in developing the framework for selecting specific numerical values for η. As noted above, the subsurface conditions variable consists of two components, predominant soil type and the degree of heterogeneity present. With respect to predominant soil type, values historically utilized in practice for key design parameters (i.e., design radius, airflow extracted per unit vent screen length and vacuum applied) are based on achieving cleanup in roughly the same time frame for different soil types. Thus, in practice, non-equilibrium effects due to differing predominant soil types are taken into account through differences in design values, eliminating the need to vary η based on the predominant soil type present. Therefore, in this effort, values for η were determined based solely on characterization of the heterogeneity of the subsurface environment.

TABLE 2. Process Performance Model η VALUES*

Characterization of Soil Homogeneity	Average	Range	
		Min.	Max.
Relatively Homogeneous	0.17	0.14	0.20
Heterogeneous	0.10	0.07	0.14
Highly Heterogeneous	0.04	0.02	0.07

*Not recommended for cases involving small initial contaminant level (≪ 100 mg/kg) combined with high removal required (≫ 90%)—see text for details.

Numerical values associated with η were then estimated based on reconciliation with observed field results. Using the process performance model developed, a series of hypothetical cases was evaluated utilizing a range of η values. The results were assessed for reasonableness based on general field experience. From this exercise, an "average" and anticipated range of values for η were selected, as summarized in Table 2.

Discussion of Modeling Assumptions

Isothermal Operating Conditions: The SVE process appears relatively unaffected by temperature changes, based on the observation that subsurface temperatures generally do not vary by more than 10°F (6°C) from summer to winter [*36*]. As the typical time-frame for SVE operation is on the order of 1 to 2 years, input of a representative average yearly surface temperature value should not significantly affect ultimate cleanup predictions.

Constant Soil Water Content: Dehydration potentially could occur in cases involving shallow contamination where no surface cap (e.g., asphalt pavement) is present—conditions where relatively dry air from the atmosphere may be drawn into the soil. In most areas, however, precipitation events likely would provide sufficient recharge of moisture into the soil. As with temperature, because the typical time-frame for SVE operation is on the order of 1 to 2 years, input of a representative average yearly soil water content value should not significantly affect ultimate cleanup predictions.

Biodegradation Effects Ignored: At fuel-spill sites, significant contaminant removal attributed to biodegradation (estimated at 15 to 25% of the total mass removal achieved) has been observed [*42–45*]. Indeed, soil bioventing has recently emerged as a new technology based on this biodegradation phenomenon, with encouraging field results (up to 85–90% reduction due to biodegradation) reported [*46–49*]. Following common design practice, however, the model developed ignores the positive effects of biodegradation as a form of design safety factor to offset the negative effects that mass transfer limitations impose on the removal process.

η Values Equivalent for Both NAPL-present and NAPL-absent Cases: It can be argued that the presence of NAPL will dictate lower values of η owing to the extremely non-uniform contaminant distribution associated with NAPL-contaminated soils. However, there is a lack of information concerning NAPL-contaminated soils that could guide selection of separate numerical values for cases involving NAPL. Thus, for this effort, it was assumed that the differences between the two cases were negligible; future research work can lead to refinement of this assumption.

η Values Independent of Contaminant Concentration: Under the two-domain conceptual framework previously presented in Figure 1, the application of constant, concentration-independent values for η implies that the fraction of relatively quickly- and slowly-released sorption sites present on soil solids remains constant throughout the cleanup process. Recent experimental work by Farrell and Reinhard [*50*] with laboratory columns (using three natural soils, four different silica gels, glass beads, and montmorillonite) has indicated, however, that the slowly desorbed contaminant fraction increases with decreasing initial contaminant concentration (although not in direct proportion), indicating preferential sorption to the slow sites. Such results imply that η is concentration-dependent, with values decreasing as the cleanup proceeds. Similarly, Wilson et al. [*12*] attributed field-observed tailing effects to a decrease in the effective diffusion rate constant with time.

Unfortunately, no method has been reported for predicting the apparent decrease in η values with time and/or initial contaminant concentration. Farrell and Reinhard [*50*] reported that measurable solid properties, such as internal porosity, natural organic matter, internal surface area, pore size, and particle size did not correlate with the slow desorbing fraction. The data provided by those researchers, however, can be used to roughly divide the two desorption regions noted (i.e., fast and slow) as follows:

- For relatively large initial concentrations (on the order of 100 to 10,000 mg/kg):
  90 to 95 + % of the initial mass was removed relatively quickly.
- For relatively small initial concentrations (on the order of 1 to 100 mg/kg):
  10 to 90% (generally from 70 to 90%) of the initial mass was removed relatively quickly.

Using this information, an initial guide for selecting an appropriate value for η based on the average and range given in Table 2 would be as follows:

- Large initial concentration (≫ 100 mg/kg) AND low removal required (≪ 90%):
  Use the upper end of the range.
- Small initial concentration (≪ 100 mg/kg) OR high removal required (≫ 90%):
  Use the lower end of the range.
- Small initial concentration (≪ 100 mg/kg) AND high removal required (≫ 90%):
  The appropriate value lies below the lower end of range. Caution is urged in such cases—detailed investigation (e.g., laboratory and/or field studies) of potential mass transfer limitation effects is warranted.
- All other cases: Use the average value.

SYSTEM DESIGN

For system design (i.e., airflow and design radius prediction), the general governing steady-state vapor flow equation is [*14*]:

$$\nabla\left(k_g \nabla P^2\right) dx\,dy\,dz = \left(\frac{2\mu\rho_g RT}{MW_g'}\right) Q \qquad (14)$$

TABLE 3. Design Parameter Baseline Values

Predominant Soil Type	Soil Permeability		Applied Vacuum ["Hg]	Pressure in Well [atm]	Initial*		Final*		Volumetric Water Content [—]	Volumetric Air Content [—]	Fraction Organic Content [—]	Soil Bulk Density [lb/ft^3]
	Intrinsic [darcies]	Air [ft/s]			Unit Airflow** [cfm/ft]	Design Radius [ft]	Unit Airflow** [cm/ft]	Design Radius [ft]				
Coarse Sands, Gravels	100	2×10^{-3}	3	0.9	16	50	20	50	0.09	0.31	0.01	105
Medium Sands	10	2×10^{-4}	6	0.8	8	28	8	30	0.12	0.28	0.01	107
Fine Sands, Silty Sands	1	2×10^{-5}	9	0.7	4	16	3	18	0.18	0.22	0.01	110
Clayey Sands, Silts	0.1	2×10^{-6}	15	0.5	2	9	1.5	13	0.25	0.15	0.01	115

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*See text for explanation of initial and final values for unit airflow and design radius.

**Unit airflow is total airflow divided by vent screen length.

1 darcy = 9.87×10^{-12} m^2; 1 ft/s = 0.305 m/s; 1 atm = 30"Hg = 101×10^3 Pa; 1 cfm/ft = 0.0929 (m^3/min)/m; 1 ft = 0.305 m; 1 lb/ft^3 = 16.0 kg/m^3

where k_g = vapor-phase relative permeability tensor (m^2); P = soil gas pressure (Pa); x, y, z = length dimensions (m); μ = soil gas viscosity (kg/m · sec); ρ_g = vapor density (kg/m^3); T = temperature (Kelvin); Q = extracted air flow rate (m^3/sec); MW_g' = molecular weight of the vapor (kg/mole).

Numerical solutions to this general equation are available (see Table 1). As with the process performance modeling situation, however, detailed, site-specific knowledge of the subsurface structure is required, information not available at the project scoping stage targeted for this application. Thus, a simplified alternative approach was adopted. Appropriate numerical values for basic design parameters were selected based on general field experience, as summarized in Table 3.

The required vacuum cited was derived using a baseline of 0.1 atmosphere (3 inches of mercury or 10 kPa) for coarse sand and gravel soils. For the remaining soil types, values were developed assuming a 0.1 atmosphere (10 kPa) increase in vacuum required per one order-of-magnitude (i.e., 10x) decrease in soil permeability. The volumetric air content values listed are based on an assumed total porosity of 0.4 for all soils minus the assumed water contents listed in Table 3. The soil bulk density was calculated assuming a solid density of 0.16 lb/ft^3 (2.6 kg/m^3).

For unit airflow (total airflow divided by the vent screen length) and design radius, two entries are listed in Table 3, "initial" and "final." Initial values were developed based on the following criteria as derived from an assessment of results from various field installations:

- Unit Airflow: 50% decrease in unit airflow per one order-of magnitude (10x) decrease in permeability.
- Design Radius: The log of the design radius varies in proportion to one-quarter the log of permeability.

The initial values thus calculated then were used in preliminary simulations (based on available case study data) with the developed process performance model. As was previously discussed, in practice, "optimal" system design generally seeks to achieve cleanup in roughly the same time frame for different soil types; thus, the predicted time to cleanup (using the process performance model) should correspondingly be approximately equal. Based on the preliminary simulations conducted, this objective was met after minor modification of the initial values for unit airflow and design radius, resulting in the value listed as "final" in Table 3.

Based on the information contained in Table 3, the number of pore volumes of extracted air that would be removed after one year of continuous operation range from approximately 4400 (for coarse sands and gravel) to 10,500 (for clayey sands and silts). This difference reflects the relative ease that contaminants can be removed from coarse, sandy materials (thus, requiring much less air be extracted to achieve a specified removal target) as compared to fine, clayey materials which tend to "hold" onto contaminants (resulting in greater volumes of air needing to be extracted to achieve equal removal in the same time frame).

It should be noted that the design radius values cited in Table 3 assume the absence of significant short-circuiting effects (i.e., surface leakage). Short-circuiting is not expected to be significant if the contamination is located at least 20 ft (6 m) below the ground surface (bgs) [*4*]. If the contamination is relatively shallow (i.e., < 20 ft bgs), however, potential short-circuiting must be addressed by either using engineering controls (e.g., applying a surface seal) to reduce/eliminate such effects or by appropriately reducing the design radius value used from those provided in Table 3.

VALIDATION

General Approach

Validation efforts focused on two of the three key system engineering parameters previously identified: extracted air flow rate and contaminant removal versus time profile (the latter parameter quantified by the venting efficiency factor). The general methodology employed involved taking a given system design (as outlined in separate case studies), using the approach developed to predict system performance, and comparing predictions to actual (i.e., field-observed) values.

Field data reported for the following two sites were used in the validation:

- Groveland Wells (Massachusetts) Superfund Site.
- An unnamed New Jersey industrial site.

The validation results for each of these two sites are presented below.

Groveland Wells Superfund Site

The results of a two-month (56-day) demonstration test at this site were reported as part of the USEPA's Superfund

TABLE 4. Validation Case Study Summary Table: Groveland Wells Superfund Site

	Shallow Extraction Vent				Deep Extraction Vent				
	#1	#2	#3	#4	#1	#2	#3	Units	Notes
Site Soil Conditions									
Soil Temperature	40	40	40	40	40	40	40	°F	
Bulk Soil Density	110	110	110	110	105	105	105	lb/ft^3	1
Volumetric Air Content	22	22	22	22	31	31	22	—	1
Volumetric Water Content	18	18	18	18	9	9	18	—	1
Fraction Organic Content	0.01	0.01	0.01	0.01	0.01	0.01	0.01	—	1
SVE Design/Operating Conditions									
Air Flow per Unit Screen Length									
Field Achieved	3.8	4.8	2.4	3.0	21.4	15.4	4.2	cfm/ft	
Model-Predicted	3	3	3	3	20	20	3	cfm/ft	1
Effective Design Radius	18	18	18	18	50	50	18	ft	1
SVE Peformance									
Actual Performance Curve									2
Initial Vapor TCE Conc. (C_0)	0.859	0.627	3.83	10.4	0.859	0.627	3.83	g/m^3	
Slope (m)	−0.051	−0.035	−0.031	−0.013	−0.036	−0.027	−0.025	day^{-1}	
Number of Data Points	64	34	34	34	64	34	34	—	
Regression Coefficient (r^2)	0.62	0.56	0.62	0.70	0.42	0.56	0.47	—	
Slope of LEA-Predicted Performance Curve (m')	−0.26	−0.33	−0.17	−0.21	−0.21	−0.15	−0.29	day^{-1}	3
Venting Efficiency Factor (η)	0.194	0.105	0.187	0.060	0.174	0.181	0.086	—	4

Deep Extraction Vent #4 not evaluated as it ceased operation after 3 weeks due to siltation problems.
1–Assumed baseline value from Table 3 as follows:
All Shallow Vents & Deep Vent #3: Fine sands, silty sands.
Deep Vents #1, 2: Coarse sands and gravels.
2–Calculated based on best-fit regression analysis of monitoring data using Equation (13).
3–Calculated using Equation (12) with $\eta = 1$.
4–Calculated as actual slope (m) divided by LEA-predicted slope (m').
40°F = 4.4°C; 1 lb/ft^3 = 16.0 kg/m^3; 1 cfm/ft = 0.0929 (m^3/min)/m; 1 ft = 0.305 m.

Innovative Technology Evaluation (SITE) program [*36, 51*]. The principal contaminant of concern was trichloroethylene (TCE); weighted average values at individual vent locations ranged from approximately 3 to 100 mg TCE/kg soil. The demonstration test system consisted of four nested extraction vents, three of which were characterized as barrier vents (designed to prevent further contaminant movement), while the fourth was designated as the main extraction vent. At each of the four locations, two nested vents were installed, a shallow vent and a deep vent. The shallow vents were screened in a medium-to-fine sand, while the deep vents were screened in a coarse sand. In between the two sandy layers was a clay layer, 3 to 7 ft (1 to 2 m) in depth, which provided an effective barrier to air flow between the two sandy layers.

A summary of site soil conditions, SVE design/operating conditions and system performance is given in Table 4. Field-achieved air flow rates (per unit screen length) were in reasonable agreement (within 25% on average) with the baseline values cited in Table 3 for six of the seven vents evaluated. For the seventh vent, similar agreement is seen if the soil is re-classified as a fine sand rather the coarse sand cited by the original investigators.

Turning next to the η values, field-achieved efficiencies were calculated using Equation (10), assuming baseline design values (i.e., Table 3 values) for most site soil conditions as well as for the effective design radius. The η values thus obtained ranged from 0.06 to 0.19, with the average being 0.14. These values are in agreement with those cited in Table 2 for heterogeneous soil (average of 0.10; range from 0.07 to 0.14) and relatively homogeneous soil (average of 0.17; range from 0.14 to 0.20).

New Jersey Industrial Site

The results of a year-long (227 non-consecutive operating days) pilot study at this site were reported by Clarke et al. [*52*]. The principal contaminant of concern was 1,1,1-trichloroethane (TCA); TCA levels averaged over 5-ft (1.5 m) depth intervals ranged from approximately 3 to 27 mg/kg. The pilot-scale unit consisted of a single extraction vent, completed in a sandy soil mixed with fill material.

A summary of site soil conditions, SVE design/operating conditions and system performance is given in Table 5. The field-achieved air flow rate (per unit screen length) of 17 ft^3/min/ft (1.6 m^3/min/m) was in good agreement (within 15%) of the baseline value cited in Table 3 for coarse sands and gravels.

Turning next to the η value, the field-achieved efficiency was calculated using Equation (10), assuming baseline design values (i.e., Table 3 values) for most site soil conditions as well as for the effective design radius. The η value thus obtained was 0.055. This value is in agreement with the value cited in Table 2 for a highly heterogeneous soil (average of 0.04; ranging from 0.02 to 0.07), but it is significantly less than that cited for a heterogeneous soil (average of 0.10; range from 0.07 to 0.14).

TABLE 5. Validation Case Study Summary Table: New Jersey Industrial Site

	Value	Units	Notes
Site Soil Conditions			
Soil Temperature	50	°F	
Bulk Soil Density	105	lb/ft^3	1
Volumetric Air Content	31	—	1
Volumetric Water Content	9	—	1
Fraction Organic Content	0.01	-	1
SVE Design/Operating Conditions			
Air Flow per Unit Screen Length			
Field-Achieved	17	cfm/ft	
Model-Predicted	20	cfm/ft	1
Effective Design Radius	50	ft	1
SVE Field Performance			
Actual Performance Curve			2
Initial Vapor TCA Conc. (C_0)	0.724	g/m^3	
Slope (m)	−0.0169	day^{-1}	
Number of Data Points	4	—	
Regression Coefficient (r^2)	0.96	—	
Slope of LEA-Predicted Performance Curve (m')	−0.31	day^{-1}	3
Venting Efficiency Factor (η)	0.055	—	4

1–Assumed baseline value from Table 3 for coarse sand and gravel.
2–Calculated based on best-fit regression analysis of monitoring data using Equation (13).
3–Calculated using Equation (12) with $\eta = 1$.
4–Calculated as actual slope (m) divided by LEA-predicted slope (m').
50°F = 10°C; 1 lb/ft^3 = 16.0 kg/m^3; 1 cfm/ft = 0.0929 (m^3/min)/m; 1 ft = 0.305 m.

A possible explanation for the relatively low η value is that the initial contamination level was relatively small ($\ll 100$ mg/kg), and a relatively high contaminant removal (approximately 98% reduction in contaminant concentration in extracted air) was achieved. As previously discussed, recent experimental work by Farrell and Reinhard [50] has suggested that the venting efficiency factor significantly decreases under such a combination of conditions. The values listed in Table 2 are appropriate for less extreme cases.

PREDICTIONS FOR A HYPOTHETICAL CASE

Table 6 summarizes predictions using the approach presented for a hypothetical 1/3-acre (14,500 ft^2 or 1350 m^2) site requiring 90% removal of TCE from a 5-ft (1.5 m) deep soil layer. Employing the baseline design values provided in Table 3, the total number of vents required ranges from 2 (for coarse sands and gravels) to 28 (for clayey sands and silts). Utilizing the average η values cited in Table 2, the estimated clean up time ranges from 40 (for coarse sands and gravels) to 175 (for clayey sands and silts) days. Note that under this approach, if NAPL is not present, the initial contaminant level does not affect calculated results.

SUMMARY

The simplified preliminary design and process performance modeling approach developed can be summarized as follows:

Preliminary Design (Estimation of Extracted Air Flow Rate and Vent Design Radius): Typically observed values, assigned based on predominant soil type ("clayey sands, silts," "fine sands, silty sands," "medium sands," or "coarse sands, gravel") are given in Table 3.

Process Performance Modeling (Estimation of Mass Removal Versus Time Profile): Equations (6) and (7) (or, alternatively, Equations (8) or (9)) define the profile for cases where NAPL is present and absent, respectively. Equation (10) is used to determine the presence/absence of NAPL at a particular site, and if initially present, at what point during the remediation will it disappear. Non-equilibrium effects are modeled via use of a single, lumped parameter η, the venting efficiency factor. Specific values for η were derived based on the relative homogeneity of the subsurface environment ("relatively homogeneous," "heterogeneous," or "highly heterogeneous").

TABLE 6. Model Predictions for 90% Removal of TCE from a Hypothetical Site

Predominant Soil Type	Total No. of Vents Required [—]	Total Air Flow Rate [ft^3/min]	Characterization of Soil Homogeneity					
			Relatively Homogeneous		Heterogeneous		Highly Heterogeneous	
			Time [days]	PV [—]	Time [days]	PV [—]	Time [days]	PV [—]
Coarse Sands, Gravels	2	200	40	500	70	850	175	2100
Medium Sands	5	200	40	600	70	1000	175	2500
Fine Sands, Silty Sands	14	200	40	800	70	1350	175	3400
Clayey Sands, Silts	28	200	40	1200	70	2000	175	5000

PV–Pore volumes.
Average η values cited in Table 2 utilized.
Baseline design values cited in Table 3 utilized.
Assumed Site Conditions:
- 1/3 acre (14,500 ft^2 or 1350 m^2).
- 5 ft (1.5 m) layer of contamination.
- No NAPL present.
- Subsurface temperature of 50°F (10°C).

1 cfm = 0.0283 m^3/min.

The assumtions incorporated in development of this simplified approach are as follows:

- Uniform contaminant distribution at all times (including when NAPL is present).
- Single predominant contaminant.
- Isothermal operating conditions.
- Constant soil water content.
- Biodegradation effects ignored.
- Linear adsorption isotherm.
- Values for η are independent of contaminant concentration.
- Values for η are equivalent for both NAPL and non-NAPL cases.
- Values for η are contaminant-independent.

This approach is not recommended for use in the following cases:

- Low level of contamination initially ($\ll 100$ mg/kg) combined with a high removal ($\gg 90\%$).
- Arid or semi-arid regions expected to have a low ($\leq 5\%$) natural soil moisture content.
- Shallow contamination (< 20 ft bgs) (< 6 m bgs) yielding significant short-circuiting effects (e.g., surface leakage).

In these cases, predicted cleanup times may be significantly less than the actual time required. For the first two cases, detailed investigation (e.g., laboratory and/or field studies) of potential mass transfer limitation effects is warranted, while the last case warrants consideration of appropriate engineering controls (i.e., installation of an impermeable cap).

CONCLUSIONS

As a result of this work effort, the following two significant insights were gained:

- The low values cited for the venting efficiency factor (on the order of 0.02–0.20) underscore the relative inefficiency of field venting operations (due to inherent mass transfer limitations) when compared to idealized conditions. Development of more sophisticated models (such as those cited in Table 1) therefore must account for non-equilibrium mass transfer effects to be of significant value to practicing engineers.
- The hypothetical case study evaluation indicated that the number of extraction vents required (as well as the number of pore volumes of soil vapor that must be extracted for effective remediation) can vary by an order or magnitude depending upon the particular soil matrix encountered at a given site.

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Remediation of Polychlorinated Biphenyl Contaminated Soils/Sediments by Supercritical Fluid Extraction

P. Chen, W. Zhou, and L. L. Tavlarides*

Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, NY 13244

Studies of polychlorinated biphenyl (PCB) desorption from soils have been conducted in a laboratory scale supercritical fluid extraction (SFE) unit to provide information for soil remediation. The results demonstrate the effectiveness of SFE as a promising technology for the clean up of PCB contaminated soils/sediments. After 30 minutes of extraction at 40°C and 100 atm, more than 86% of PCBs in real world Hudson River sediment and 92% in St. Lawrence River sediment were removed. The extraction of PCBs from spiked samples showed even higher efficiencies. Various effects such as temperature, pressure, cosolvent, sample water content, and soil/sediment type on PCB desorption have been investigated. The sample water content and the presence of cosolvent were shown to be the most important factors affecting desorption of PCBs. The results show that PCBs in real world samples are more tightly bound than in spiked samples. The desorption behavior of individual PCB congeners in various samples has been investigated. The results demonstrate no relative accumulation of the most environmentally threatening PCB congeners throughout the extraction process.

INTRODUCTION

It has been estimated that about 385 million pounds of polychlorinated biphenyls (PCBs) exist in landfills and other storage media, and another 24 million pounds exist in sediments, soils, vegetation, and animals [*1*]. The potential environmental threat of the large amount of PCBs has called for the development of effective PCB cleanup techniques. Although some PCB remediation technologies such as incineration and in-situ vitrification have been commercially available, many efforts are still being conducted in order to develop more economically and socially acceptable methods [*1*]. Among these efforts, the application of supercritical fluid extraction (SFE) to the removal of toxic organics from environmental samples is receiving much attention due to the unique properties of supercritical fluids (SCFs) such as low viscosity, high diffusivity, and easily tunable solvent power [*2*].

Using SFE in analytical chemistry to replace conventional liquid extraction has been widely reported [*3–15*]. Some researchers [*5, 13*] have obtained quantitative recovery of organics such as PCBs and polycyclic aromatic hydrocarbons (PAHs) from environmental samples. However, the results of analysis oriented research may not be able to be used directly for waste remediation, because, (a) in order to obtain quantitative recovery, impractical conditions such as high temperature and pressure [*6–14*], non-CO_2 SCFs [*5, 10, 14*], toxic cosolvents [*13, 14*], and additional chemicals [*12*] are employed in many of these studies, and (b) there may exist significant discrepancies between the results of analytical studies and those of remediation studies because of the difference in objectives and concentration levels of contaminants [*16*].

The broad applicability of SFE to remediate environmental pollutants has been demonstrated in several laboratories. Kothandaraman et al. [*17*] studied the adsorption and desorption properties of PAHs from soil in the medium of supercritical CO_2. Erkey et al. [*18*] investigated the extraction of naphthalene, phenanthrene, hexachlorobenzene, and pentachlorophenol from soil. Ghonasgi et al. [*19*] reported the success of removing benzene, phenol, *p*-chlorophenol, and *m*-cresol from aqueous streams by using SC-CO_2.

For the case of remediation of PCB contaminated soils by SFE, the pioneering studies were conducted by Brady et al. [*20*] and Dooley et al. [*21, 22*]. Both real world and laboratory spiked samples were used in these studies and no significant difference was found between those samples. Although effects of cosolvent, temperature, SCF flow rate, soil water content and organic matter have been investigated in those studies, the scatter in the results suggests a need of a firmer foundation for future design of SFE processes. Recently, similar studies were conducted by Liu et al. [*23*] and Markowz et al. [*24*] based only on spiked soils. Also, solubilities of PCB congeners in SC-CO_2 have been reported by Yu et al. [*25*] which augments the above data base.

This paper investigates the effects of various important factors such as temperature, pressure, cosolvent, soil water content and soil properties on the desorption of PCBs from soils/sediments. The difference between spiked and real world samples and the behavior of single PCB congeners during the extraction are also discussed. The objectives of this paper are to systematically address these issues and provide additional information to a data base for the eventual design of a process unit for soil remediation. The final objective of this study is to design and install a mobile

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* *To whom correspondence should be addressed.*

demonstration SFE unit for the remediation of PCB contaminated soils/sediments.

EXPERIMENTAL SECTION

Materials

Aroclor 1248, a commercial product of a mixture of fifty PCB congeners with certified purity of 99%, was purchased from AccuStandard, Inc. Liquid CO_2 with purity of 99.8% was obtained from Matheson, Inc. All other chemicals used as cosolvents and for analysis were obtained from Fisher Scientific, Inc.

Sample Preparation

Till, sand, clay, and St. Lawrence River sediments were obtained from sites in vicinity of the Superfund site near Massena, New York [*26*]. Two Hudson River sediments were obtained from SUNY GSPH, Albany [*27*]. The physical characteristics of these soils and sediments are listed in Tables 1 and 2. All the clean samples were ground and sieved through a No. 30 mesh screen prior to spiking. Soils were then spiked according to the following procedure. Air-dried soils (at ambient temperature) were totally submerged into a predetermined amount of Arolcol 1248/hexane solution, stirred with a spatula thoroughly, and put in a venting hood for more than 48 hours to evaporate the solvent. Initial PCB concentration of each batch of sample was analyzed via the procedure discussed below. Spiked samples were then stored in sealed containers for future extraction. When applicable, a desired amount of water was added to air-dried samples prior to the experiments except for the real world Hudson River sediment which was obtained as wet sample with 20–23 wt % water content. All sample water contents were calculated based on the weight difference between wet and air-dried samples.

TABLE 1. Soil Properties

	Composition[a] (%)			TOC[b]	Surface Area[c] (m^2/g)	
Soil	Sand	Silt	Clay	(%)	BET	Langmuir
Till	81.2	12.5	6.3	0.25	6.22	9.37
Clay	0	75	25	2.65	6.43	11.30
Sand	100[d]	0[d]	0[d]	—	—	

[a] Obtained by using pipette method.
[b] Obtained by using CARLO ERBA Elemental Analyzer E. A. 1108.
[c] Measured by N_2 at liquid N_2 temperature in volumetric apparatus.
[d] Estimated value.

Apparatus

Experiments were conducted in a laboratory scale unit which was designed and machined at Syracuse University. A fixed bed extractor (1.2 cm id by 5 cm length) with a capacity of about 6 grams of soil/sediment was maintained in an air bath box for isothermal operation (±0.5°C). The temperature was measured with a thermocouple placed at the entrance of the soil bed within the extractor. Liquid CO_2 was compressed (compressor Model 46-13421-2, Newport Scientific, Inc.) to the desired pressure and delivered continuously. The pressure was controlled by a back pressure regulator and monitored by a Heise digital pressure indicator (Model 901A, Dresser Industries). Cosolvent could be added to the CO_2 stream through a syringe pump (Model 100D, ISCO, Inc.) at an accurate flow rate. The SCF then flowed downwards through the extractor. Two micrometering valves (Model 30VRMM 4812, Autoclave Engineers) controlled the flow rate and decreased the pressure to atmospheric. A cold trap precipitated the PCBs and condensed the cosolvent. CO_2 volumetric flow was measured by a dry test meter (Model DTM-200A, American Meter Company). After depressurization of each experiment, the sample was removed and weighed for gravimetric analysis of water content (relative error ±10%) and the analysis of residual PCB concentration which combined with the initial PCB concentration gives extraction efficiency. For all experiments, CO_2 flow rate was controlled at 0.07 g/s. Further details are provided elsewhere [*28*].

The laboratory scale unit simulates industrial SFE systems and, as such, is equipped with various safety devices (rupture disks, emergency relief piping, etc.). As a result, the system possesses a relatively large dead volume which results in batch extraction periods during pressurization and depressurization. Care was taken to achieve a sharp start and shut-down to reduce this batch extraction during periods. A special valve arrangement permitted a pressurization within 0.5 minutes and a depressurization within 1.5 minutes. Batch extraction during these transient periods could be monitored through "zero time extraction" which was conducted by depressurizing the system immediately after the operating pressure had been achieved. The PCB concentration after "zero time extraction" was taken as $C_{t=0}$ which is smaller than the initial concentration (C_0).

Sample Analysis

The concentrations of PCBs in soils were analyzed via the following method provided by our co-workers at State

TABLE 2. Sources and Properties of Sediments

Sediment	Source	C_0 (ppm)	TOC (%)
Contaminated Hudson River sediment	SUNY, GSPH, Albany	71.2	6.79
Spiked Hudson River sediment	SUNY, GSPH, Albany	485	3.92
Contaminated St. L. River sediment	General Motors, SPDES 001, 25 yds offshore, 6/22/92	370	1.97
Spiked St. L. River sediment #1	Cove sediment, 0–10 inch below cove bottom, St. L. River, 6/24/92	500& 1893	2.41

TABLE 3. Precision Tests of the System

Conditions[a]				Experimental Number				
T (°C)	H_2O (wt %)	SCF[b]	Time (min.)	#1	#2	#3	#4	RSD (%)
				Residual Concentration (ppm)				
40	Air-dried	A	30	4.9	4.3	4.5	4.5	5.6
40	Air-dried	A	3.5	38.5	36.3	40.6	37.7	4.7
50	10	A	30	450	419	430	434	3.0
50	10	A	3.5	948	942	931	959	1.2
40	10	B	30	3.6	6.1	9.8	12.6	49.9
40	10	B	3.5	922	904	835	869	4.3

[a] P = 100 atm, spiked till, $C_0 = 1299$ ppm. [b] A—Pure CO_2; B—CO_2 + 5 mol % MeOH.

University of New York (SUNY) at Albany [29]. The PCBs in soils were dissolved into an acetone/hexane solution (1:1 by volume) using a sonicator (Model W-380, Ultrasonics, Inc.). The acetone was removed from the solution by addition of water. The hexane phase containing PCBs was then concentrated. Sulfur was removed from the concentrate with mercury, and impurities were removed through a florisil column (Magnesium silicate activated 60–100 mesh, Sigma Chemical Co.). The PCB concentration of the hexane solution was determined by a Hewlett-Packard 5890 series II gas chromatography (GC) equipped with a splitless injector, an electron capture detector (ECD), and an ultra performance capillary column (Ultra 2, Crosslinked 5% Ph Me Silicone, 25 m × 0.20 mm id, 0.33 μm film thickness, Hewlett-Packard, Inc.). GC was calibrated every 4 samples with a standard solution containing 88 PCB congeners. Precision of the analytical method was evaluated as relative standard deviation (RSD) of 2.9% based on 39 initial concentration analyses. Based on this analysis and the detail of analytical procedure of this study, PCB concentrations greater than 0.1–0.5 ppm fall within these RSD values for the soil samples and PCB patterns encountered.

The precision of the entire experimental process which includes both the SFE process and the analytical process was determined with a series of duplicate runs. The results are given in Table 3. The RSD values range from 1.2% to 5.6% for all the experiments except the long-time (30 min) extractions of wet samples with cosolvent for which the RSD is 49.9%. This high RSD value is possibly related to the observation that, during the extractions of wet soils, a condensed phase would drain below the bottom of the bed in variable amounts. The amount of dissolved PCBs in the condensed phase is unknown, and apparently, is sufficient to cause this large error. Generally, this problem occurs only for long-time extractions where the absolute values of residual concentration are low (viz., 3.6 ppm to 12.6 ppm). Hence, the total precision of the process is considered acceptable.

RESULTS AND DISCUSSION

Initial Concentration Effect

To investigate the effect of initial PCB concentration, till and St. Lawrence River sediment No. 1 were spiked at two different initial concentrations. For each set of samples the desorption conditions were the same. The results are given in Figure 1 which shows that, even though there exists more than three fold differences of initial concentrations, the desorption rates of PCBs are essentially identical for the same soil. These data demonstrate that the solubility of PCBs in the supercritical fluid is not a limiting factor for the extraction of PCBs under these experimental conditions. A similar conclusion was previously reported by Hawthorne et al. [9].

It is interesting to note that Figure 1 shows an initial (0 ~ 7.5 min) linear desorption period for all of the desorption curves. A linear desorption curve generally indicates a desorption process controlled by solubility limitation, partition equilibrium limitation, or both [30].

Accordingly, it would appear that the partition equilibrium of PCBs between soil matrices and SCF might be a controlling factor for the desorption processes. However, as discussed later, it is shown that the partition equilibrium cannot be achieved under the conditions studied here for dynamic extraction of PCBs from wet soils. Based on these results, it appears that the linear desorption period could

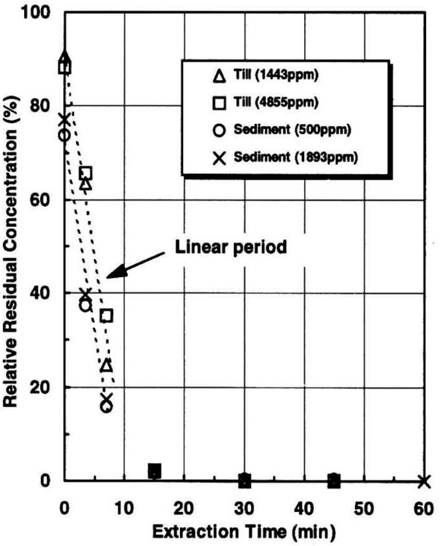

FIGURE 1 Initial Concentration Effect. SCF: CO_2 + 5 mol % methanol. Conditions: 40°C (sediment), 50°C (Till); 100 atm; 10 wt % H_2O

be caused by a constant overall mass transfer rate which is the result of the combined effects of a decreasing average PCB loading in soil (reduces the mass transfer rate) and a decreasing water content in the matrix (decreases the mass transfer resistance).

Water Content Effect

As naturally occurring soils/sediments contain a significant amount of water, it is important to study the effect of soil/sediment water content on PCB desorption. This effect was investigated by extracting both air-dried and wet (10–20 wt. % water) samples. Figures 2 and 3 give the results for spiked till and real world Hudson River sediment. It is found that the presence of water reduces PCB desorption rates dramatically for both real world and spiked samples. Similar results were presented by Brady et al. [*20*]. Cosolvent effects shown in these two figures will be discussed later.

It is interesting to note that, in contrast to the above results, some researchers [*15, 17, 23, 31*] have reported that the presence of water would enhance the desorption of solutes due to the abilities of water to compete with the adsorbed solutes for matrix active sites and to swell the soil matrices. The contradictory water effects shown here may be related to the difference in experimental methods. In this study, PCBs were extracted dynamically from wet soils. The pre-existing water films covering both inside and outside surfaces of soil particles may have exerted large mass transfer resistances on PCB molecules and prevented PCBs from reaching an equilibrium partition between the SCF and the soil matrices. In contrast, for the studies which show positive water content effects, one group of extractions [*17, 31*] were conducted dynamically from air-dried samples using wet SC-CO_2, where mass transfer resistances due to the presence of pre-existing water films on matrix surfaces are absent. The other group of extractions were conducted statically from wet samples [*15, 23*], where the equilibrium partition of solutes should be achieved. Therefore, these processes might be controlled mainly by thermodynamic limits instead of transport limitations. Based on the above analysis, it can be expected that, for static extraction of PCBs, the presence of water will increase the extraction efficiency. To support this contention, quasi-static experiments were conducted on a real world St. Lawrence River sediment ($C_0 = 96.8$ ppm) using another apparatus with small dead volume. The experiments include two cycles which involve a 15 min static contacting period followed by a dynamic sample step at the same temperature and pressure of the static period. CO_2 flow rate for the sampling step was controlled at ~ 100 ml/min (1 atm and room temperature) using a 25 μm silica restrictor. For each sampling step, a total of 30 ml of CO_2 was allowed to pass through a solvent trap for PCB collection. The extraction efficiencies for both dry and wet samples are given in Table 4 which shows that wet samples give better extraction efficiencies for static extractions. The above discussion raises the important issue as to the effects of water on the extraction efficiencies. Other studies, such as equilibrium distri-

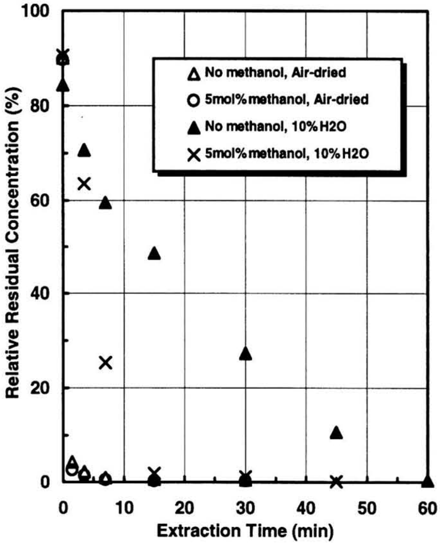

FIGURE 2 Cosolvent and Water Content Effects on SFE of Spiked Till ($C_0 = 1443$ ppm). Conditions: 50°C; 100 atm.

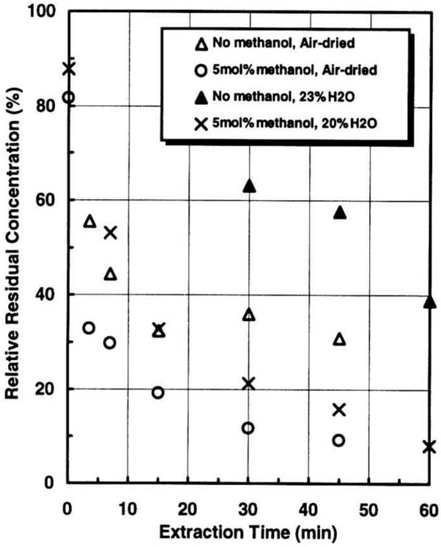

FIGURE 3 Cosolvent and Water Content Effects on SFE of Real World Hudson River Sediment ($C_0 = 71.2$ ppm). Conditions: 40°C; 100 atm.

TABLE 4. Results of Quasi-static Experiments[a]

	Extraction Efficiencies (%)				
Sediment[b]	1	2	3	4	Average
10% H_2O	14.7	12.6	12.7	14.0	13.5
Air dried	5.9	7.3	7.1	-	6.8

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[a]: Conditions: 50°C, 100 atm.

[b]: A real world St. Lawrence River sediment with a PCB initial concentration of 96.8 ppm.

bution experiments for wet and dry matrices, would be needed to further clarify these issues.

Temperature Effect

The temperature effects were investigated for both spiked till and real world sediment over the range of 40–50°C, which was chosen based on the consideration of practical applications. The results (not presented) show very little temperature effects over the temperature range studied.

It is reported that the increase of temperature may retard the desorption of PCBs because of the reduction of SCF density and the accompanying decrease in solubilities of PCBs in SCF [*22*], or, oppositely, facilitate the extraction of PCBs by yielding larger PCB vapor pressures [*8*] and/or decreasing mass transfer resistance [*23*]. The trivial temperature effect showed here may be a consequence of the narrow temperature range examined. According to the results reported by Langenfeld et al. [*8*], the temperature effects on SFE became important only when the temperature was increased from 50°C to 200°C.

Pressure Effect

The pressure effects on PCB extraction are given in Figure 4 which, in accordance with the results of other researchers [*9*, *32*], shows that high pressures facilitate PCB desorption especially for wet samples. The pressure effects on dry samples are not clearly demonstrated in Figure 4 because of the very quick desorption rate of spiked PCBs in dry samples and the very low PCB residue levels compared with the initial concentrations. It was also found that for extraction from wet samples the enhancement of PCB desorption rate was not proportional to pressure increment. As is evident in Figure 4, the greatest pressure effect on PCB desorption from wet samples occurred when pressure was raised from 90 atm to 178 atm. In contrast, further increase of pressure from 178 atm to 400 atm only provided marginal PCB desorption improvement. These results clearly demonstrate that as a means of improving extraction efficiencies, increasing pressure is effective only in a limited pressure range. Specifically, it seems that the employment of pressure higher than 170–200 atm is not necessary in the sense of enhancing PCB extraction efficiencies.

A possible reason for the significant pressure effect on PCB extraction from wet samples is that the soil water content was removed slowly when low pressure was employed. For example, the soil water content for the 90 atm, 178 atm, and 400 atm experiments were 8.1%, 6.1%, 6.4% at 15 minutes, 6.3%, 2.7%, 2.8% at 30 minutes, and 4.4%, 0%, 0% at 45 minutes, respectively.

Cosolvent Effects

The choice and application of cosolvents are proven to be very important for SFE. Preliminary experiments in our laboratories show that methanol and acetone are better than toluene as cosolvent for the extraction of PCBs from wet till. Further investigation of the effects of four cosolvents (methanol, *n*-propanol, *n*-butanol, and hexanes) on the extraction of PCBs from wet till (10 wt % water content) was conducted by adding the same amount (5 mol %) of each cosolvent to the SC-CO_2 fluid stream. The results presented in Figure 5 indicate that the ability of a cosolvent to improve the PCB desorption rate is strongly related to the miscibility of the cosolvent with water. As shown in Figure 5, hexanes, which are immiscible with water, do not enhance the extraction of PCBs. In contrast, the most significant PCB desorption rate enhancement is found when

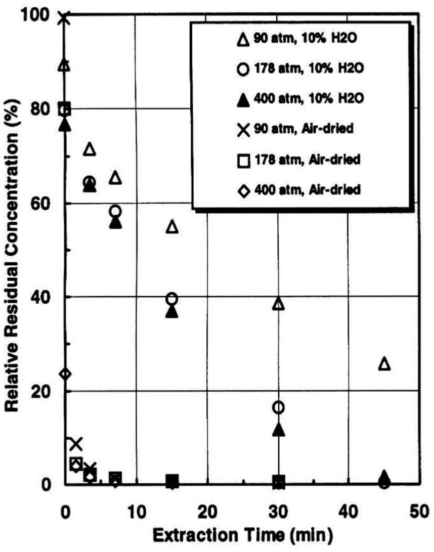

FIGURE 4 Pressure Effect on SFE of Spiked Till. SCF: CO_2. Conditions: 45°C; $C_0 = 1299$ ppm (90 and 400 atm), 1314 ppm (178 atm).

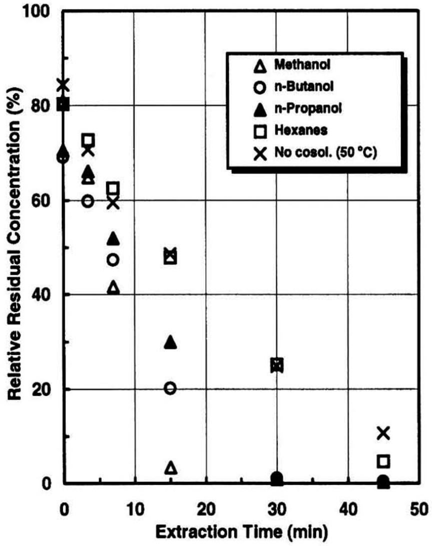

FIGURE 5 Cosolvent Type Effect on SFE of Spiked Till. SCF: CO_2 + 5 mol % cosolvent. Conditions: 40°C; 100 atm; 10 wt % H_2O; $C_0 = 1299$ ppm (n-butanol, n-propanol, and hexanes), 1443 ppm (methanol and no cosolvent).

methanol is used as cosolvent. The possible reason that cosolvent power is related to its miscibility with water is that when PCBs are extracted from wet samples, the cosolvent must have the ability to increase the removal of water from the samples. A cosolvent which is miscible with water may increase the solubility of water in SCFs and consequently enhance the removal of water from the samples [*33*]. The effects of *n*-propanol and *n*-butanol are intermediate to those of hexanes and methanol. *n*-Butanol shows slightly stronger PCB desorption rate enhancement than n-propanol even though it is less miscible with water. The cause of this inconsistency is unclear.

The effects of methanol as cosolvent were then studied in detail for both spiked and real world samples. The results are shown in Figures 2 and 3. It is found that the impact of methanol on wet samples is more significant than that on air-dried samples. Also, different effects of methanol are found between spiked samples and real world samples. For the spiked till, Figure 2, the main effect of methanol is the enhancement of the desorption rate. The methanol effect on the final residual PCB levels reached through SFE is negligible. In contrast, for the real world Hudson River sediment, the presence of methanol not only increases PCB desorption rate but also reduces the final PCB residual concentration significantly (Figure 3).

The effects of cosolvents on SFE have been investigated by many people [*5, 15, 21–23, 32, 34–35*]. Generally, cosolvents are thought to improve the extractabilities of the compounds studied by increasing the solubilities of these solutes in the supercritical fluids [*34*], competing with solutes for active sites on the matrices [*5*], and by swelling the soil matrices and increasing the accessibility of the solutes [*15*].

For extraction of air-dried samples, the enhancement of PCB extraction efficiencies caused by the addition of methanol may be mainly related to the interactions between methanol/PCB molecules/sediment matrices, instead of the increase in PCB solubilities in the SCF. As mentioned earlier, the extraction of PCBs is not limited by PCB solubilities in SCF. Also, according to the results of Chiou et al. [*36*], the dry soil sorption capacities of organic compounds could be dramatically reduced when a polar solvent is introduced. They contend that the major fraction of the capacity (adsorption on soil mineral matter) could be suppressed by the strong interaction of the polar solvent with the polar minerals. Therefore, methanol might have interacted with the polar segments of soil matrices and competed with PCB molecules for active sites during the processes. These possibilities suggest that the presence of methanol improves the desorption rates of weakly adsorbed PCBs and makes portions of strongly bound PCBs desorbable. The details of these interactions are unknown and further studies are needed. The significant reduction of the final PCB level in the real world sample also indicates that PCBs are more tightly bound in real world samples than in spiked samples.

As for the extraction from wet samples, it is shown in Figure 1 that the solubilities of PCBs are not a limiting factor. Also, it has been reported [*23, 33*] that the presence of methanol for the extraction of PCBs from wet samples does not increase solute solubilities because methanol in the SCF would dissolve in the sample water and lose its cosolvent power. Therefore, the improvement of PCB desorption rates from wet soils caused by the addition of methanol could not be the result of incrementally increasing PCB solubility. On the other hand, the strong interactions between polar methanol and sediment matrices/PCB molecules cannot be the major mechanism of the cosolvent effects, otherwise, the presence of sample water would have enhanced PCB extraction efficiencies because of the strong polarity of water.

To further analyze the function of methanol on the extraction of PCBs from wet samples, the trends of soil water/methanol content during the extraction are given in Table 5. It is shown that the soil water content decreased monotonically along with the increase of extraction time in the absence of methanol. In contrast, the soil water/methanol content increased (0–7 minutes) and then decreased (longer than 7 minutes). This phenomenon implies that part of the methanol in SCF condensed in the soil matrix during the extraction. Even though the exact water concentration in the soil is unknown, clearly the soil water was removed more quickly in the presence of methanol (see the long time data). Based on the above discussion, the possible reasons for the dramatic enhancement of PCB desorption rate from wet soils are (a) the presence methanol facilitates the removal of soil water which, as discussed earlier, would retard the PCB extraction; and (b) the formation of a condensed water/methanol phase increases the mass transfer rate of PCBs from the soil matrix to the SCF stream due to higher solubilities of PCBs in the water/methanol mixture than in pure water [*37*].

TABLE 5. Soil Water / Methanol Content During Extraction[a]

	Sample Water/Methanol[b] (wt %) at Different Extraction Time							
SCFs	Initial	0 min	3.5 min	7 min	15 min	30 min	45 min	60 min
CO_2[c]	10	9.6	9.1	8.4	7.0	4.3	1.6	—[e]
CO_2 + 5%MeOH[c]	10	9.7	11.0	14.3	12.5	2.2	0.9	—
CO_2[d]	20	—	—	—	—	16.2	13.0	9.2
CO_2 + 5%MeOH[d]	20	19.5	—	23.1	26.2	16.5	8.7	2.8

[a] Conditions are same as Figure 2 or 3.

[b] $$\text{Soil water/methanol} = \frac{\text{Weight after extraction} - \text{Air dried weight}}{\text{Weight after extraction}} \times 100\%$$

[c] Spiked till.

[d] Real world sediment.

[e] No experiments made at these conditions

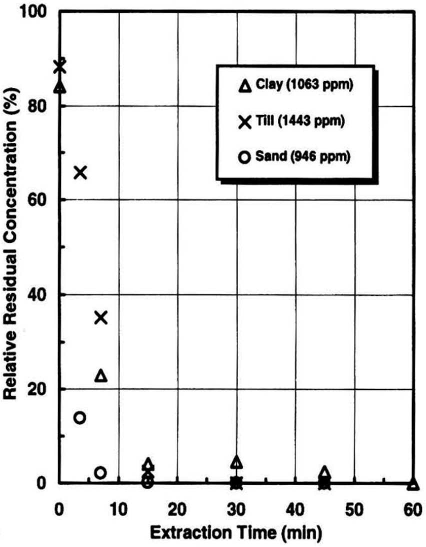

FIGURE 6 Soil Type Effects. SCF: CO_2 + 5 mol % methanol. Conditions: 50°C; 100 atm; 10 wt % H_2O.

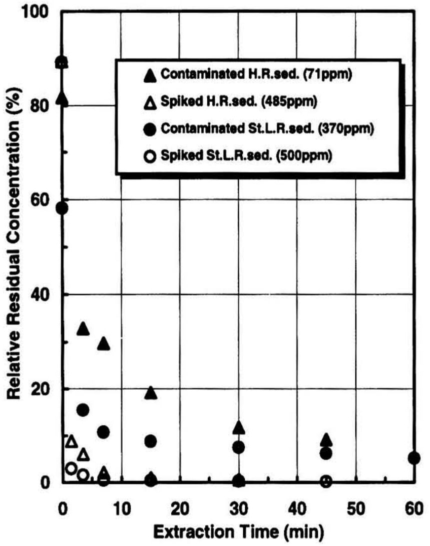

FIGURE 7 Effect of Contaminating Procedure. SCF: CO_2 + 5 mol % methanol. Conditions: 40°C; 100 atm; Air-dried.

Soil Property Effects

Matrix properties have been shown to influence solute extractabilities [*6*, *23*, *38*]. For example, differences in solute extraction efficiencies have been observed under similar SFE conditions for soils of different mineral compositions [*6*, *15*]. Also, the organic matter in soils is shown to affect the extraction rate and efficiency of solutes from matrices [*20*, *23*]. To investigate these effects, three types of soil (sand, till, and clay) were studied and results are given in Figure 6. High soil organic matter and clay content were found to retard the extraction of PCBs. As is evident in Figure 6, sand distinguishes itself from the other two samples by the fastest PCB removal due to the absence of clay and organic matter. The difference between clay and till is unclear in this figure, possibly because the strong effects of soil water on the mass transfer process mask the effects of the matrix properties. Experiments for air-dried samples (results are not presented) did show that the desorption rate of PCBs in clay is lower than that in till due to the higher clay and organic matter content.

In addition to soil/sediment composition, the processes by which the matrix is contaminated also affect the extraction of PCBs. Due to the difficulty of getting proper real world samples, spiked samples are broadly employed in many remediation oriented researches. However, at present little attention has been paid to the investigation of the difference between spiked and real world samples. Dooley et al. [*22*] claimed comparable extraction efficiencies from spiked and real world samples. In contrast, Burford et al. [*6*] reported that spike studies may overestimate the effectiveness of SFE.

Comparison between real world and spiked sediments from both the Hudson River and St. Lawrence River is given in Figure 7. It is found that, compared with the results for real world samples, spiked sediments show more rapid PCB desorption rates and lower final residual concentrations.

The observed difference could be caused by the property inconsistency between spiked and real world sediments and/or by the inability of the spiking process to represent the actual situation experienced by real world soils/sediments.

The most important property distinction among the four samples is the sediment organic matter which ranges from 1.97 to 6.79% (Table 2). As shown in Figure 7, this property variation between the samples cannot be the major cause of the observed desorption difference, otherwise the real world St. Lawrence River sediment should show the quickest PCB removal.

In contrast, since it is impossible for the spiking procedure to exactly simulate the conditions experienced by PCBs in river sediments, the spike study may not demonstrate the same results as those obtained from real world samples [*5*–*6*]. Based on these results, it is concluded that, to properly evaluate a SFE process, it is necessary to test the effectiveness of extracting pollutants from real world samples.

Distribution of PCB Congeners in Soils

It is reported that among the 209 possible PCB congeners, only a small number of them are both environmentally prevalent and demonstrably or potentially toxic [*39*]. In the work by McFarland and Clarke, 16 PCB congeners were listed as the most environmentally threatening congeners. Since the extraction efficiency of total PCBs has been a broadly employed criterion for the evaluation of the SFE of PCBs, there remains a concern over the potential relative accumulation of the most environmentally threatening PCB congeners during the SFE processes. Accordingly, the relative abundance ($C_{congener}/C_{total}$) of PCB congeners in the two real world sediments and spiked till has been investigated.

The behaviors of PCB congeners were different during the extraction process for the three samples. For the Hudson River sediment, as shown in Table 6, higher molecular

TABLE 6. PCB Congener Distribution in Real World Hudson River Sediment

Time (min) →		Initial	0	3.5	7.0	15.0	30.0	45.0
C_{total} (ppm) →		71.2	58.2	23.4	21.2	13.7	8.3	6.5
IUPAC No.	Congeners	$C_{congener}/C_{total}$ (%)						
1	2	4.27	4.76	5.94	6.65	7.79	9.53	9.89
3	4	—	—	—	—	2.98	3.29	3.93
4 + 10	22′ + 26	34.7	31.4	28.9	28.6	27.7	24.9	23.7
7 + 9	24 + 25	0.24	0.29	0.39	0.78	0.50	0.54	0.64
6	23′	1.15	1.40	1.91	2.41	2.39	2.77	3.11
5 + 8	23 + 24′	3.38	4.02	5.59	7.29	7.09	8.66	9.24
19	22′6	7.54	6.64	5.64	5.14	4.69	4.20	3.67
18	22′5	1.18	1.24	1.49	1.58	1.58	1.58	1.82
15 + 17	44′ + 22′4	2.77	3.07	3.60	3.87	3.90	4.12	4.44
24 + 27	236 + 23′6	5.66	5.41	5.16	4.74	4.25	3.79	3.51
16 + 32	22′3 + 24′6	3.21	3.23	3.20	3.25	2.97	2.75	2.83
26	23′5	1.98	2.18	2.55	2.48	2.33	2.35	2.39
25	23′4	0.27	0.32	0.43	0.43	0.43	0.46	0.47
31	24′5	4.94	6.04	7.48	7.81	7.48	8.09	8.80
33	2′34	3.19	3.09	2.82	2.72	2.52	2.53	2.40
22	234′	0.54	0.66	0.86	0.98	0.90	1.01	1.10
45	22′36	0.49	0.46	0.42	0.42	0.36	0.32	0.29
52	22′55′	5.36	5.11	5.08	4.43	4.12	3.93	3.79
49	22′45′	2.66	2.56	2.59	2.19	2.09	1.89	1.87
47 + 48	44′ + 22′45	2.30	2.17	2.08	1.76	1.56	1.37	1.36
44	22′35′	0.61	0.67	0.75	0.73	0.72	0.71	0.74
37 + 42 + 59	344′ + 22′34′ + 233′6	1.07	1.83	2.09	1.97	2.07	2.27	2.26
64	234′6	1.28	1.34	1.23	1.24	1.17	1.09	1.03
40	22′33′	0.28	0.25	0.22	0.21	0.21	0.20	0.21
74 + 94	244′5 + 22′356′	0.39	0.42	0.48	0.43	0.41	0.44	0.44
70	23′4′5	0.39	0.45	0.56	0.55	0.55	0.61	0.53
66	23′44′	2.11	2.10	1.99	1.76	1.67	1.70	1.46
56 + 60	233′4′ + 2344′	0.91	0.85	0.76	0.67	0.60	0.58	0.55
101*	22′455′	0.85	0.81	0.75	0.66	0.58	0.59	0.53
99*	22′44′5	—	0.28	0.28	0.24	0.18	0.20	0.15
97	22′3′45	0.13	0.14	0.12	0.11	0.10	0.10	—
	DDE	0.11	0.12	0.10	.089	.082	7.05	—
136	22′33′66′	0.13	0.12	—	—	—	—	—
77* + 110	33′44′ + 233′4′6	2.00	2.08	2.10	1.84	1.80	1.92	1.88
82 + 151	22′33′4 + 22′355′6	0.31	0.30	0.19	0.16	0.15	0.13	—
135	22′33′56′	0.11	0.11	.061	.060	5.06	—	—
149	22′34′5′6	0.38	0.36	0.25	0.20	0.20	0.16	0.16
118*	23′44′5	0.33	0.36	0.39	0.34	0.35	0.36	0.36
146	22′34′55′	0.12	0.12	.083	.064	.058	—	—
132 + 153*	22′33′46′ + 22′44′55′	0.50	0.51	0.30	0.23	.066	0.18	0.17
141 + 179	22′3455′ + 22′33′566′	0.10	.099	—	—	—	—	—
138*	22′344′5′	1.09	1.71	0.93	0.92	0.80	0.87	1.00
182 + 187	22′344′56′ + 22′34′55′6	0.15	0.14	.081	.059	.093	—	—
128* + 167	22′33′44′ + 23′44′55′	.065	.066	.054	—	.041	—	—
174	22′33′456′	.070	.072	—	—	.058	—	—
177	22′33′4′56	.065	.066	—	—	.035	—	—
180*	22′344′55′	0.13	0.13	.086	.064	.012	—	—
170* + 190	22′33′44′5 + 233′44′56	.077	.084	—	—	.052	—	—
201	22′33′455′6′	.068	.071	—	—	.051	—	—
194*	22′33′44′55′	.044	.048	—	—	.037	—	—
206	22′33′44′55′6	.026	.029	—	—	—	—	—

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*: Among the most environmentally threatening congeners as listed in reference 39.

—: Peaks were not detected.

Conditions: 40°C; 100 atm; Air-dried sediment; SCF: CO_2 + 5 mol % methanol.

weight congeners seemed more likely to be removed. Among the congeners (or congener mixtures) detected in the Hudson river sediment, both of the mono-CBs and 3 of the 4 di-CBs increased their relative concentrations with the increase of extraction time; only 5 of the 9 tri-CBs showed the same behavior; for all tetra- or higher chlorinated PCB congeners, the relative abundance either decreased or did not show much variation. Similar results have been reported by Hawthorne et al. [9]. However for St. Lawrence River sediment and the spiked till (results not presented), most of PCB congeners showed no significant relative concentration shift as extraction time increased.

As for the most environmentally threatening PCB congeners detectable in the above mentioned three samples, no relative accumulation was observed throughout the extractions. It is interesting to mention that the PCBs in the two sediments consisted of primarily mono-, di-, and tri-CBs (~75 wt % and ~78 wt % for Hudson River and St. Lawrence River sediments respectively), possibly caused by natural dechlorination.

CONCLUSIONS

The following conclusions can be drawn from this study over the range of parameters investigated. It is demonstrated that the desorption of PCBs from soil/sediments appears to be controlled by the PCB transfer rate from soil matrices to the SCF stream rather than the solubility limits. The most important factors affecting the extraction process are sample water content and the presence of cosolvent. The presence of 10–20 wt % water content in the soil matrix retards the initial PCB extraction rate sharply as compared to dry soil matrices. In contrast, the addition of methanol in SC-CO_2 enhances PCB desorption rates and reduces the ultimate PCB residual levels in sediments. Among all the cosolvents studied, the polar, water soluble solvent methanol is the most effective for the extraction of PCBs from soils/sediments.

The results also demonstrate that a significant difference exists in PCB desorption behaviors between spiked and real world samples. All spiked samples showed faster and more complete PCB removal than real world samples. For the two real world sediments, PCB concentrations can be reduced to 10–20 ppm after 30–45 minutes of extraction. This capability meets most US EPA requirements [40] for PCB decontamination. Finally, although preferential retention of lower chlorinated congeners was found in Hudson River sediment, no relative accumulation of the most environmentally threatening congeners was found for all the samples studied.

Based on the results of this study, the suggested ranges of extraction conditions are: pressure of 100–200 atm, temperature of 40–50°C, methanol as cosolvent at about 5 mol %. For the remediation of wet soils/sediments, a drying process prior to the extraction is recommended. The two important factors which are not covered in this paper are the flow rate effect and the adsorption/desorption characteristics of cosolvent on treated soils. Studies on these two factors will be conducted and the results will be presented later. The recommended remediation conditions will be tested for several types of real world soils in a bench scale SFE unit with a fixed bed extractor of 2 liter capacity. An economic analysis of the process and the design of a mobile demonstration unit will be presented after the bench scale experiments are concluded.

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