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OIL SHALE
RESEARCH AND COORDINATION
Progress Report 1980 - 1981
DOE Contract #EV-10298

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PROGRESS REPORT: 1980 - 1981
INTRODUCTION AND SUMMARY OF RESEARCH

Willard R. Chappell
Center for Environmental Sciences
University of Colorado, Denver

The purpose of this research program is two-fold: to conduct research on the environmental impacts of an oil shale industry and to develop strategies to mitigate these effects; and to perform field coordination of the Data Base Development and Risk Analyses portions of the DOE RD&D program. The environmental research program has focused primarily on a comprehensive study of the sources, release mechanisms, transport, fate, and effects of toxic trace substances principally the trace elements, in an oil shale industry. The study group is a multi-institutional, interdisciplinary team from the University of Colorado, Colorado State University, and the Colorado School of Mines, and the New Mexico Institute of Mining and Technology. The coordination task is performed through the DOE Oil Shale Task Force which involves membership from all of the national labs (LANL, LLNL, PNL, LBL) and universities (CU, CSU) which are major participants in the DOE oil shale program. Professor Willard R. Chappell, Director of The Center for Environmental Sciences, is the Chairman of the Task Force.

The program is conducted under the auspices of the Center for Environmental Sciences of the University of Colorado at Denver. The Principal Investigator is Dr. Willard R. Chappell. The senior investigators involved in the environmental research program are:

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The present report describes the progress of the fifth year of funding as of February 15, 1981.

The major objective of the program is to evaluate the environmental and health consequences of the release of toxic trace elements by shale and oil production and use. Clearly, it is impossible to study in detail all possible trace elements. At the beginning of the program we chose five priority elements on the basis of their occurrence in oil shale, the likelihood that they would be mobilized by the process involved, and the likelihood that if released they would cause deleterious effects; these elements were As, B, F, Mo, and Se. While all of these, except possibly As, are essential to plants and/or animals, they can all be toxic to plants and/or animals at sufficiently high levels. At the same time that we were conducting in-depth studies of these elements we were also evaluating the potential for problems to arise from other elements. Where ever the opportunity arose to obtain information about other elements for little or no additional cost, we took advantage of the opportunity. For example, before we obtained ERDA (later DOE) funding, we received a small grant from the Colorado Energy Research Institute. Dr. Ronald Klusman was able to interest the U.S. Geological Survey in cooperating with us to the extent of analyzing his early samples for a number of elements such as Zn and Li. In other cases, we have come to realize that other contaminants such as reduced sulfur species (see e.g., Dr. Runnells' report) play an important role and we shifted effort into these areas. Thus, the reader will often encounter a statement such as "this study has concentrated on Se, Mo, As, B, and F", and yet somewhere else will find data on Zn, Li, or some other element or organic compound.

From a trace element point of view (and others as well) the single most important characteristic of the oil shale process is the large amount of material that must be processed. To obtain a million barrels of oil per day, 480 million tons per year of shale must be processed. The total estimated amounts of the five "priority" elements contained in this amount of material are shown in Table 1 and are compared to the annual U.S. industrial consumption.

Thus, rather prodigious amounts of trace elements will be handled. The other important characteristic that a future oil shale industry will have is that most, if not all, of the processing will probably take place within the Piceance Creek Basin in Colorado, an area of perhaps 1,350 square miles. Thus, even if a very small percentage of the amounts shown in Table 1 are released, the impact could be very significant.

TABLE 1

Element	Contained in Shale	Industrial Consumption
As	20,000	22,000
Mo	10,000	100,000
F	1,000,000	600,000
Se	1,000	500
B	20,000	70,000

The progress is described in detail by the various investigators in the following sections of the report. Some of the particularly significant results obtained during the previous four years are:

- The baseline geochemical survey shows that stable trace elements maps can be constructed for numerous elements and that the trends observed are related to geologic and climatic factors.
- Shale retorted by above-ground processes tends to be very homogeneous (both in space and in time) in trace element content. This implies that the number of analytical determinations required of processed shales is not large.
- Leachate studies show that significant amounts of B, F, and Mo are released from retorted shales and while B and Mo are rapidly flushed out, F is not. On the other hand, As, Se, and most other trace elements are not present in significant quantities.
- Significant amounts of F and B are also found in leachates of raw shales.
- Very large concentrations of reduced sulfur species are found in leachates of processed shale. Upon oxidation a drastic lowering in pH is observed. Preliminary data indicates that this oxidation is catalyzed by bacteria.

- Very high levels of B and Mo are taken up in some plants growing on processed shale with and without soil cover. These amounts depend upon the process and various site specific characteristics. In general, the amounts taken up decrease with increasing soil cover. On the other hand, we have not observed significant uptake of As, Se, and F into plants.
- There is a tendency for some trace elements to associate with specific organic fractions, indicating that organic chelation or complexation may play an important role. In particular, most of the Cd, Se, and Cr in shale oil is associated with the organic fraction containing most of the nitrogen-containing compounds.
- Many of the so-called "standard" methods for analyzing trace elements in oil shale-related materials are inadequate. These inadequacies have been eliminated in many cases by modification of the "standard" method or by development of new methods. This is a highly significant result because the "standard" methods tend to be used in many environmental assessments.
- A new combination of methods was developed for separating the minerals in oil shale into different density fractions. Mineralogical and chemical analyses then give the distribution of trace elements as a function of density. The heavy metals (e.g., Ni, Cu, and Pb) were found in the heaviest fraction; F was found in the lightest fraction associated with the mineral Illite.
- Microbial investigations have tentatively identified the existence of thiobacilli in oil shale materials such as leachates. Laboratory investigations have shown that the potential exists for microbial thiosulfate oxidation and the concomittant side reactions of pH decline and possible pollutant solubilization.
- ✓ ● Other microbial research indicates that micribiological growth in spent shale, in the presence of added soil and nutrients, can lead to increases in arsenic present in solution after 5-6 weeks of incubation.
- A sampling of plants from the intensive study site in the Piceance Creek Basin showed that some plants grown on Paraho spent shale covered to a depth of 30.5 cm of soil contained levels of molybdenum that could be hazardous to grazing livestock. Some plants also contained levels of boron that might be harmful to the plants.
- Leaching experiments involving the application of retort water to spent shales indicated a potential for the solubilization of Se if retort waters are applied directly to spent shales.

Some of the significant results and accomplishments in the past year were:

- Published a DOE report (DOE/EV 10298-2) "Sampling Designs for Geochemical Baseline Studies in the Colorado Oil Shale Region: A Manual for Practical Application", authored by Dr. Ronald W. Klusman of the Colorado School of Mines.
- Dr. Klusman found that ridge top soils absorb significantly more Hg^0 and HgO than valley floor soils and that Hg^0 is absorbed to a greater degree than HgO . All soils studied showed a great affinity for Hg.
- During the past year Dr. Runnells and his students had the opportunity to study some freshly retorted TOSCO samples. Their leaching studies indicate some significant differences with the results obtained on TOSCO shale that had been weathered. The freshly retorted material shows much higher levels of F (5 - 10 times) than previous studies. At the same time they see higher levels of bicarbonate and lower levels of dissolved calcium than observed previously.
- The studies by Dr. Runnells involving passing leachate through native soils indicate significant levels of F, B, As, and Al. While subsequent amounts of F and B can be rinsed out by subsequent leaching with deionized water, the results indicate that the local soils may offer protection from As and Al contamination of water supplies. On the other hand, very little removal of Mo was observed.
- Dr. Lindsay's studies of B toxicity indicate that the B levels observed in plants on some revegetation studies may be causing chronic toxicity in certain plant species as revealed by decreased productivity in greenhouse experiments.
- Dr. Sievers' group found that arsenic can be effectively removed from process waters by passing it through retorted shale.
- The Brierleys' have determined that the potential does exist for microbial thiosulfate oxidation and the concomittant side reactions of pH decline and possible pollutant solubilization.
- Dr. Klein has found that under aerobic conditions it appears that bacteria can lead to the release of volatile forms of As from spent shale.

These and other results obtained in the past year are discussed in detail in the following sections of this report.

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PROGRESS REPORT -- June 1980 - May 1981

U.S. Department of Energy
THE OIL SHALE TASK FORCE

Project #EV - 10298

Willard R. Chappell
Kathy Petersen
Center for Environmental Sciences
University of Colorado at Denver

INTRODUCTION

The Oil Shale Task Force, formerly the DOE/EV Modified in Situ (MIS) Task Force, was formed in June 1978 to coordinate environmental research on oil shale.

Dr. Willard R. Chappell, as Chairman of the Task Force, provides planning, field coordination, and management assistance for DOE/ASEV sponsored oil shale research. The professional staff of the Task Force includes an Associate Chairman, Kathy Petersen; a Staff Scientist, Eleanor Werbe; and a University of Colorado chemistry faculty member, John Lanning. (Dr. Lanning was involved during the summer of 1980 for 20% time.) In addition, Dr. Chappell is coordinator for the Data Base Development Subactivity, with the Task Force serving as the coordinating tool for that subactivity. The Task Force is composed of individuals from major national laboratories, universities, and the State of Colorado. Table 1 lists all members, with new members indicated along with a notation on who they replaced, if applicable.

OBJECTIVES

Planning

Rio Blanco Oil Shale Co. (RBOSC)--

A research plan was developed and implemented for Rio Blanco Oil Shale Co's. Tract C-a. Retort O was ignited in October 1980 and several task force members were on site to collect data for the proposed studies in the areas of source characterization; health effects -- sampling, monitoring and characterization, and biological testing; air quality; water quality; land disturbance; and environmental control technology.¹ In addition, during the start-up of Retort O, RBOSC encountered difficulty with their instrumentation. Several members of the Task Force, particularly Mike Tompkins, monitored process gases for RBOSC, information that was vital to RBOSC's analysis of the burn. At the March 1981 Task Force meeting, the first progress report was drafted. The anticipated publication date is early fall 1981.

Geokinetics--

Two initial planning meetings were held with Task Force members, Geokinetics personnel, and other related DOE supported program personnel to discuss a

TABLE 1
The Oil Shale Task Force Members

Willard R. Chappell, Chairman University of Colorado at Denver Denver, Colorado	Chips Barry*** State of Colorado Department of Natural Resources Denver, Colorado
David Sheesley* Laramie Energy Technology Center Department of Energy Laramie, Wyoming	L.M. Holland Marvin Tillery George Voelz Paul Wagner Los Alamos Scientific Laboratory Los Alamos, New Mexico
Phyllis Fox Lawrence Berkeley Laboratory Berkeley, California	Richard Ragaini Hector Timourian Lawrence Livermore Laboratory Livermore, California
Jonathan Fruchter Ira Levy** Richard Pelroy Raymond Wildung Battelle-Pacific Northwest Laboratories Richland, Washington	Ed Redente† Colorado State University Fort Collins, Colorado
Robert Siek Council of Energy Resource Tribes Eaglewood, Colorado	Larry Gratt† IWG Corporation San Diego, California

DOE Project Managers

Ralph Franklin, Ecological Research
and R&D Coordinator

Joseph Blair, Human Health Assessments

Gerald Goldstein, Pollutant Character-
ization and Safety Research

Charles Grua, Environmental Control
Technology

David Smith, Health Effects Research
Office of Environment
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Arnold Harak
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U.S. Department of Energy
Washington, D.C.

Jack O'Brien
Denver Project Office
Lakewood, Colorado

Professional Staff

Kathy Petersen, Associate Chairman
John Lanning, Assistant Professor, Chemistry Dept.
Eleanor Werbe, Staff Scientist
University of Colorado
Denver, Colorado

* Replaced David Farrier, ** Replaced Daryl Hessel, *** Replaced Walt Hecox

† New members

coordinated research effort. A plan was developed and implemented on December 15, 1980.² This is a modest effort concentrating on how to avoid the release of fugitive emissions from the ground surface, characterization and quantification of constituents released during the retorting process, and bioassays and treatability studies of the wastewaters.

Occidental Retorts 7 & 8--

On June 10, Task Force members met with State of Colorado representatives and Carole Stover, Occidental Oil Shale, Inc. The purpose of the meeting was to assist the State in compiling a shorter list of monitoring parameters for Logan Wash.

Union Oil--

On December 10, Dr. Willard R. Chappell, Chairman of the Task Force, Kathy Petersen, Associate Chairman, Drs. Ralph Franklin and Art Hartstein of DOE met with officials of Union Oil in Grand Junction to discuss the feasibility of developing a research effort involving Task Force members and Union Oil. Other meetings are planned in the future (see Proposal).

Executive Committee--

Recently, an Executive Committee of the Task Force was formed to facilitate coordination among the diverse groups and activities thereby developing an effective mechanism for identifying, formulating and implementing programs. In addition, the Committee will coordinate activities with other contractors. Members of this committee represent each major contractor and research area associated with the environmental research programs (Table 2). The first meeting of the Executive Committee was February 11 in Gaithersburg, Maryland. Several major topics were addressed, and further plans for work with Rio Blanco, Geokinetics, and Occidental were designed.

Since the last reported Task Force meeting of February 1980, the Task Force has met four times to further develop research plans, strategize implementation of the plans, and report on the progress of on-going research:

- May 1980 in Laramie, Wyoming. The Task Force was briefed on the raw shale lysimeters at Tract C-a by Glen Miller, AOSO/USGS; the Tract C-a oil shale run at the LETC retort by Dave Sheesley, LETC; and the Sandia Lab instrumentation at Logan Wash by Al Stevens. The majority of the meeting was devoted to finalizing the research plans and sampling efforts for research on Tract C-a following comments by Rosielea Gash of RBOSC. The sample agreements between RBOSC and the individual researchers were also discussed.

- June 1980 in Gaithersburg, Maryland. Each Task Force member presented a status report on current and planned research. The peer review process was described by Ralph Franklin and there was some discussion on the management design of the Task Force. L.M. Holland, LASL, briefed the Task Force on a proposal to construct an experimental bench scale retort at LASL for occupational health investigations and other Task Force studies. In preparation for anticipated environmental research plans to be developed with Geokinetics and Equity, Gerry Roberts of Aerospace briefed the Task Force on their in situ oil shale processes and potential areas of research need/interest.

TABLE 2
Executive Committee
The Oil Shale Task Force

Marv Dickerson Lawrence Livermore Laboratories	Air
Phyllis Fox Lawrence Berkeley Laboratory	Water, Retort Abandonment
Larry Gratt IWG Corporation	Risk
Marty Holland Los Alamos Scientific Laboratory	Health
Edward Redente Colorado State University	Reclamation
Dave Sheesley Laramie Energy Technology Center	Control Technology
Ray Wildung Battelle-Pacific Northwest Labs	Solid Waste

• November 1980 in Denver, Colorado. Briefings were given by Larry Gratt on IWG, Inc. on the newly implemented Risk Analysis Program; Werner Frei, UCS, on remote sensing; Jon Fruchter, PNL, on the RBOSC sampling activities; and Marv Tillery, LASL, on Geokinetics plans. Chips Barry, Colorado Department of Natural Resources, addressed the Task Force on the State's primary concerns with oil shale development (socio-economic, air quality, and water quality impacts). The majority of the meeting involved developing proposal outlines for future research in the areas of ecological impact, health effects, retort abandonment, water treatment, solid waste management, and emission control.

• March 1981 in Seattle, Washington. Progress reports and updates were presented on the work with Geokinetics, Occidental's Retorts 7 and 8, the Risk Analysis program and recent Risk Analysis workshop, and the Executive Committee meeting. Most of the meeting was devoted to writing the first draft of the progress report for Task Force research on RBOSC's Retort 0.

Two public meetings were held in April 1980 to communicate the planning and research efforts of the Task Force and other DOE-sponsored oil shale environmental programs. The meetings were co-sponsored by Club 20, a western Colorado Association of Communities and Industries, and the League of Women Voters. The same meeting was conducted in Grand Junction and Denver in order to reach the widest audience. Poster sessions were set up illustrating various research efforts and a panel discussion was conducted addressing some of the most frequently asked questions about oil shale development (see Table 3). Dr. Martin Robbins, Director of the Colorado Energy Research Institute, was the keynote speaker in Denver. Although Ms. Nancy Dick, Lieutenant Governor of Colorado, was scheduled to give the keynote address in Grand Junction, airplane delays prevented her from doing so. Appendix A includes copies of the announcement flyers, agendas, list of participants and summary of the evaluation forms.

Overall, the meetings were well received by the attendees (187 in Grand Junction; 75 in Denver). Most expressed an interest in attending future meetings of this nature, although preferably using a workshop format.

A major symposium on "Oil Shale: the Environmental Challenges" was held in Vail, Colorado, August 10-14, 1980. The meeting was designed to convene the producers and users of information being generated from DOE sponsored research efforts on the environmental and socio-economic impacts related to oil shale development.

There were major review presentations in thirteen technical areas:

- The Scottish Shale Oil Industry
- Chemical Analysis for Inorganic Constituents of Oil Shale-Related Materials: An Overview
- Characterization of Oil Shale Retort Effluents
- Industrial Hygiene Concerns Associated with Oil Shale Development
- Studies of the Biology and Toxicology of Oil Shale Materials
- Ecological Effects of Oil Shale Development — Problems, Perspectives and Approaches
- Retort Abandonment: Issues and Priorities
- Retorted Oil Shales Characteristics and Reclamation
- Geochemistry/Hydrology of Solid Waste Disposal

TABLE 3

THE POSTER SESSIONS

GEOLOGICAL DEVELOPMENT OF OIL SHALE
U.S. Geological Survey

GEOCHEMICAL BASELINE STUDIES

Ronald Klusman
Colorado School of Mines
Golden, Colorado

WESTERN OIL SHALE FACILITIES

Carol Nieuwenhius *
University of Colorado
Denver, Colorado

OIL SHALE DEVELOPMENT TECHNOLOGIES

Laramie Energy Technology Center
Department of Energy
Laramie, Wyoming

CHARACTERIZATION

Jonathan Fruchter*
Battelle-Pacific Northwest Laboratories
Richland, Washington

ANALYTICAL METHODS FOR OIL SHALE SAMPLES

Robert Meglen
University of Colorado
Boulder, Colorado

INDUSTRIAL HYGIENE AND
OCCUPATIONAL MEDICINE

Marvin Tillery*
Los Alamos National Laboratory
Los Alamos, New Mexico

BIOLOGY AND TOXICOLOGY

L.M. Holland* and Julie Wilson
Los Alamos National Laboratory
Los Alamos, New Mexico

WILDLIFE

Tom Hakonson and Gary White
Los Alamos National Laboratory
Los Alamos, New Mexico

RECLAMATION

Walt Ruzzo and Wayne Cook
Colorado State University
Fort Collins, Colorado

THE PANELISTS

MODERATOR: WILLARD R. CHAPPELL
Chairman, The Oil Shale Task Force
Denver, Colorado

SUMNAR BARR—Air
Los Alamos National Laboratory
Los Alamos, New Mexico

ARTHUR HARTSTEIN—Technologies
Office of Fossil Energy
U.S. Department of Energy
Washington, D.C.

L.M. HOLLAND*—Health Effects
Los Alamos National Laboratory
Los Alamos, New Mexico

WILLIAM McDONALD—Water Quantity
Colorado Department of Natural Resources
Denver, Colorado

CAROL NIEUWENHIUS*—Water Quality
University of Colorado
Denver, Colorado

EDWARD REDENTE—Reclamation
Colorado State University
Fort Collins, Colorado

DAVID SHEESLEY*—Air
Laramie Energy Technology Center
Department of Energy
Laramie, Wyoming

ERIC STENEHJEM—Socioeconomic Impacts
Denver Research Institute
Denver, Colorado

RAYMOND WILDUNG*—Water Quality
Battelle-Pacific Northwest Laboratories
Richland, Washington

MEETING PLANNER AND MANAGER:

Kathy Petersen
The Oil Shale Task Force
University of Colorado at Denver
Denver, Colorado

* MEMBERS OF THE OIL SHALE TASK FORCE

- Water Management Strategies: Issues and Priorities
- Air Emission Control Strategy
- The Socio-Economic Research and Implementation Needs Related to Oil Shale
- Compliance Plans

Each presentation was followed by a panel discussion assessing future research requirements and addressing existing and anticipated problems associated with developing the oil shale industry. Panels were composed of representatives from federal, state, or local government; industry; academic, environmental groups; and private consulting firms. Table 4 lists all the speakers and panelists.

The keynote speaker at the Symposium was Mr. Fraser Cook, Perthshire, Scotland, who discussed the 100 year oil shale industry in that country. Mr. Cook had worked for several years in the industry. He was associated with F.I. Petroleum since 1939 and was manager of the Pumpherstons Oil Shale Works when the company ceased mining shale oil in 1962.

Of the 200 people who attended the Symposium, 20 oil companies were represented as were 36 consulting firms, 7 national labs, 7 universities, 8 federal agencies, 11 State of Colorado departments, and 3 environmental groups. In addition, individuals attended from Australia, Scotland, and Spain. Appendix 3 is a listing of all participants at the meeting and includes related materials.

The proceedings from the Symposium will be published by Colorado School of Mines as hard back publication. It will include all presentations which were initially distributed as draft preprints to all symposium participants plus an edited version of all panel discussions.

The symposium was well received by all participants, so much so that another symposium is being planned for August 1981. Appendix B also includes a summary of the evaluation forms distributed at the conference.

Other activities which have transpired related to planning efforts included:

- Water Treatment Meeting. On April 15, 1980 a meeting was held to coordinate the testing of wastewater treatment at Oxy's Logan Wash Retorts 7 and 8. The Chairman and several Task Force members attended the meeting where DOE, EPA, Oxy and their contractors agreed to interchange information on the development and testing of wastewater treatment.
- Leaching Meeting. In September 1980 the Chairman of the Task Force, in cooperation with the Task Force Staff Scientist, convened a meeting to gather perspective in the development of a coherent program for future leaching activities. A report is being written recommending additional studies closely tied to the LLNL simulated retorts (Appendix C for minutes).
- On October 7, 1980 DOE-funded researchers met with representatives from the Division of Mined Land Reclamation, State of Colorado to discuss permitting problems encountered by MLR and ways in which the Task Force might be of assistance (Appendix D for minutes).

TABLE 4

Chemical Analysis for Inorganic Constituents of Oil Shale-Related Materials:
An Overview

Robert Meglen
Center for Environmental Sciences
University of Colorado at Denver
Denver, Colorado

and

Characterization of Oil Shale Retort Effluents

Johathan Fruchter
Battelle-Pacific Northwest Laboratories
Richland, Washington

Panelists:

Bruce Clark
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Robert Heistand
Paraho Development Corp.
Rifle, Colorado

Haven Skogen
Occidental Oil Shale, Inc.
Grand Junction, Colorado

Harold Stuber
U.S. Geological Survey
Denver, Colorado

Facilitator:

Art Hartstein
Department of Energy

Industrial Hygiene Concerns Associated with Oil Shale Development

Harry Ettinger
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Panelists:

Stan Ferguson
Colorado State Department of Health
Denver, Colorado

Howard Runion
Gulf Science and Technology Co.
Pittsburgh, Pennsylvania

William Wagner
Rocky Mountain Center for Occupational and Environmental Health
University of Utah
Salt Lake City, Utah

Panelists (cont'd):

William Wallace
NIOSH
Morgantown, West Virginia

Facilitator:

Art Hartstein
Department of Energy

Studies of the Biology and Toxicology of Oil Shale Materials

L.M. Holland
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Panelists:

Elias Balbinder
American Medical Center
Denver, Colorado

Harold MacFarland
Gulf Sciences and Technology Co.
Pittsburgh, Pennsylvania

David Smith
Office of Environment
U.S. Department of Energy
Washington, D.C.

Ed Wrenn
University of Utah
Salt Lake City, Utah

Facilitator:

Willard R. Chappell
The Oil Shale Task Force

Ecological Effects of Oil Shale Development -- Problems, Perspectives and Approaches

Tom Hakonson and Gary White
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Panelists:

A. William Alldredge
Department of Wildlife
Colorado State University
Ft. Collins, Colorado

W. Jack Clark
Rio Blanco Oil Shale Co.
Rifle, Colorado

Don Dietz
U.S. Fish and Wildlife Service
U.S. Geological Survey/Area Oil Shale Office
Grand Junction, Colorado

Panelists (cont'd):

Al Whitaker
Colorado State Division of Wildlife
Denver, Colorado

Facilitator:

Ralph Franklin
Department of Energy

Retort Abandonment: Issues and Priorities

Phyllis Fox and Peter Persoff
Lawrence Berkeley Laboratory
Berkeley, California

and

Paul Wagner and Gene Peterson
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Panelists:

Kevin Markey
Friends of the Earth
Denver, Colorado

Glen Miller
U.S. Geological Survey/Area Oil Shale Office
Grand Junction, Colorado

Allan Sass
Occidental Research Corp.
Irvine, California

George Watson
Standard Oil Co. Research and Development
Naperville, Illinois

Facilitator:

Art Hartstein
Department of Energy

Retort Oil Shales Characteristics and Reclamation

E.F. Redente, W.J. Ruzzo, C. Wayne Cook, and W.A. Berg
Range Science Department
Colorado State University
Ft. Collins, Colorado

Panelists:

Paul Kilburn
International Environmental Consultants, Inc.
Denver, Colorado

Panelists (cont'd):

David Shelton
Mined Land Reclamation Division
Colorado State Department of Natural Resources
Denver, Colorado

Dick Ward
Botany Department
Colorado State University
Ft. Collins, Colorado

Facilitator:

Willard R. Chappell
The Oil Shale Task Force

Geochemistry/Hydrology of Solid Waste Disposal

Raymond Wildung and John Zachara
Battelle-Pacific Northwest Laboratories
Richland, Washington

Panelists:

Frank Haas
TOSCO
Golden, Colorado

Glen Miller
U.S. Geological Survey/Area Oil Shale Office
Grand Junction, Colorado

David Shelton
Mined Land Reclamation Division
Colorado State Department of Natural Resources
Denver, Colorado

O. James Taylor
U.S. Geological Survey
Denver, Colorado

E. Jenne
Battelle-Pacific Northwest Laboratories
Richland, Washington

Facilitator:

Art Hartstein
Department of Energy

Water Management Strategies: Issues and Priorities

Trudy Phillips
Laramie Energy Technology Center
Laramie, Wyoming

and

Phyllis Fox
Lawrence Berkeley Laboratory
Berkeley, California

Panelists:

Bob Shukle
Water Quality Control Division
Colorado State Department of Health
Denver, Colorado

Fred Lee
Environmental Engineering Department
Colorado State University
Ft. Collins, Colorado

Basil Mercer
Battelle-Pacific Northwest Laboratories
Richland, Washington

Gary Rawlings
Monsanto Research Corp.
Dayton, Ohio

Ernest Turner
Occidental Oil Shale, Inc.
Grand Junction, Colorado

Facilitator:

Ralph Franklin
Department of Energy

Air Emission Control Strategy

David Sheesley
Laramie Energy Technology Center
Laramie, Wyoming

and

E. Leonard
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Panelists:

Chuck Bray
Occidental Oil Shale Inc.
Grand Junction, Colorado

Gary McCutcheon
Air Pollution Control Division
Colorado State Department of Health
Denver, Colorado

Panelists (cont'd):

W. George N. Slinn
Battelle-Pacific Northwest Laboratories
Richland, Washington

Terry Thoem
U.S. Environmental Protection Agency, Region 8
Denver, Colorado

Facilitator:

Ralph Franklin
Department of Energy

The Socio-Economic Research and Implementation Needs Related to Oil Shale

Eric Stenehjem and Jack Gilmore
Denver Research Institute
Denver, Colorado

Panelists:

William E. Davis
Office of Technology Assessment
U.S. Congress
Washington, D.C.

Carol Edmonds
Colorado State House of Representatives
Grand Junction, Colorado

Barry Gale
Office of Resource Applications
U.S. Department of Energy
Washington, D.C.

Ira McKeever
Colowyo Coal Co.
Meeker, Colorado

Duane Rehborg
Rio Blanco County Development Department
Meeker, Colorado

Steve Schmitz
Colorado State Department of Local Affairs
Denver, Colorado

Facilitator:

Willard R. Chappell
The Oil Shale Task Force

Compliance Plans

Larry Harrington
Laramie Energy Technology Center
Laramie, Wyoming

Panelists:

Larry Kronenberger
Exxon Co., USA
Houston, Texas

Pete Rutledge
U.S. Geological Survey/Area Oil Shale Office
Grand Junction, Colorado

Terry Thoem
U.S. Environmental Protection Agency, Region 8
Denver, Colorado

Carole Stover
Occidental Oil Shale, Inc.
Grand Junction, Colorado

Kevin Markey
Friends of the Earth
Denver, Colorado

B. Curtis Smith
Bureau of Land Management
Meeker, Colorado

Facilitator:

Ralph Franklin
Department of Energy

- Air Quality Research Meetings. On October 6 members of the Task Force and other DOE-supported individuals met to delineate issues and specify the type of research that needs to be performed in the air quality area. A follow-up meeting occurred on October 7 with the Colorado State Department of Health to discuss the kinds of permitting issues encountered by that agency with oil shale development (Appendix E for minutes).

- November 5, 1980 Task Force researchers and others met with representatives of the Colorado Department of Health to consider what roles if any, the State can or should play in occupational and public health problems (Appendix F for minutes).

Information Dissemination—

Newsletters have continued to be published describing Task Force activities. A resource library on all phases of oil shale research has been assembled and catalogued. The Staff Scientist is currently reviewing the status of the library holdings and publications will be procured where deemed necessary to ensure the library is complete. This library will be continuously updated and serve as a central point of information

FIELD COORDINATION

The Task Force received one quarter of a core taken between Occidental's Retorts 7 and 8. This material is archived at LASL. Results from experiments performed on the permeability of the material have been completed by Dr. Paul Wagner, LASL and are reported in his progress report to DOE.

In addition, core material was acquired from Rio Blanco Oil Shale Co. and the results of planned experiments on this material will be discussed in the RBOSC progress report (to be published by the Task Force in early fall 1981).

Further field coordination efforts involve working with Occidental Oil Shale on identifying additional sampling ports in the engineering design of Retorts 7 and 8 for future sampling programs.

MANAGEMENT ASSISTANCE

The Chairman of the Task Force is a member of DOE's management team for DOE's environmental activity in oil shale research as coordinator of the data base development and risk analysis subactivity. In that capacity he is responsible for developing detailed plans for the technology base program in that area. During implementation he ensures the research is in place, proceeding on schedule, and that DOE's objectives are being accomplished. The Task Force interfaces closely with the Management Team and serves as the focal point for coordinating environmental activities. In concert with this management assistance, the Chairman has been involved in a variety of communication activities:

- The liaison group formed to facilitate information transference among various interest groups met in July 1980 with the Task Force Chairman,

Associate Chairman, and Staff Scientist. (See Table 5 for advisory group membership). The meeting concentrated on a group discussion of key environmental and health issues relating to oil shale development addressing the question of whether enough research is being performed and if not, what should be done. Also, W.R. Chappell briefed the group on the recent Task Force activities.

- On October 16, 1980, W.R. Chappell, Chairman of the Task Force, briefed the Advisory Group to the Assistant Secretary for Environment on the Task Force, its purpose and functions. On October 17 he traveled with the group to four oil shale facilities in western Colorado.

- Dr. Chappell briefed several members of Utah State Government on September 17 in Salt Lake City.

- Dr. Chappell briefed the DOE Fossil Energy Research Working Group on May 6 in Denver and July 11 in San Diego.

- The Chairman has presented several papers on the work of the Task Force.

CONTROL TECHNOLOGY

The Chairman and the Associate Chairman have been assisting David Sheesley, Laramie Energy Technology Center, in the control technology subactivity. An oil shale environmental control technology team is being organized, patterned after the Oil Shale Task Force, which will be responsible for assessing the research needs and coordinating subsequent programs.

TABLE 5
Advisory Group
The Oil Shale Task Force

Mr. Bob Arnott
Colorado Department of Health
Denver, Colorado

Mr. John Cavanaugh *
U.S. Department of Labor
Grand Junction, Colorado

Dr. R. Merrill Coomes
TOSCO Corporation
Los Angeles, California

Ms. Carol Edmonds
Colorado House of Representatives
Denver, Colorado

Dr. Bobby Gunther
U.S. Public Health Svc.
Denver, Colorado

Ms. Rosielea Gash
Rio Blanco Oil Shale Co.
Denver, Colorado

Mr. Glen Miller
U.S. Geological Survey
Grand Junction, Colorado

Mr. Rafael Moure
Oil, Chemical and Atomic Workers
International Union
Denver, Colorado

Dr. Daniel Luecke
Environmental Defense Fund
Denver, Colorado

Mr. Ed Piper
Energy Development Consultants, Inc.
Golden, Colorado

Dr. Martin Robbins
Colorado Energy Research Institute
Golden, Colorado

Dr. Allan Sass
Occidental Research Corporation
Irvine, California

Mr. Terry Thoem
Office of Energy - Region VIII
Denver, Colorado

Ms. Anne Vickery
Colorado Mountain Club
Boulder, Colorado

* Mr. Cavanaugh recently resigned from MSHA; a replacement will be named in the near future.

References

1. The Oil Shale Task Force, "Environmental and Health Research Plan for the Retort O at Tract C-a, Rio Blanco Oil Shale Company", Appendix C to "Proposed Environmental Research Program for Modified In-Situ Oil Shale Processes", The Oil Shale Task Force, University of Colorado, Denver, May 1980.
2. The Oil Shale Task Force, "Environmental and Health Research Plan for Geokinetics Inc. Oil Shale Facility", Appendix D to "Proposed Environmental Research Program for Modified In-Situ Oil Shale Processes", The Oil Shale Task Force, University of Colorado, Denver, December 1980.

APPENDIX A

OIL SHALE: WHAT'S IT ALL ABOUT?

Two public meetings sponsored by the U.S. Department of Energy, hosted by The Oil Shale Task Force, and co-sponsored by the League of Women Voters and Club 20.

OBJECTIVE

To increase public awareness of research activities related to oil shale development in the western United States, concentrating on the areas of water-related problems, types and amounts of pollutants, human health effects, reclamation, and socioeconomic impacts.

In order to maximize participation, two meetings have been scheduled—one in Grand Junction and one in Denver. The same agenda will be followed at each meeting.

TENTATIVE AGENDA

- Poster session: Displays illustrating work at various national laboratories and universities. There will be the opportunity to discuss this work with individual scientists.
- Convene Formal Session.
 - Key Note Address.
 - Panel discussion of the most frequently asked questions about oil shale.
 - Adjourn formal session.
- Poster session continues.

Note: A formal agenda noting speakers, panelists, poster session participants, and topics to be addressed during the panel discussion will be forwarded to all who have preregistered, and will be available at the meeting.

GRAND JUNCTION MEETING

DATE: Thursday, April 10

TIME: 1:00 pm-5:00 pm; formal session convenes at 1:45 pm

LOCATION: Two Rivers Plaza Convention Center
2nd and Main Street
Grand Junction, Colorado

Transportation: A bus will be available from Rifle to Grand Junction, returning to Rifle following the meeting. If you would like to reserve a place on the bus, please check the appropriate box on the preregistration form. Preregistration is required for those requesting transportation.

DENVER MEETING

DATE: Saturday, April 12

TIME: 12:30 pm-4:30 pm; formal session convenes at 1:15 pm

LOCATION: Student Center Auraria Campus
10th and Lawrence
Denver, Colorado

Please direct all inquiries regarding the meeting to:
Kathy Petersen
The Oil Shale Task Force
University of Colorado at Denver
1100-14th Street, Campus Box 136
Denver, Colorado 80202 303/629-3460

DETACH AND RETURN—PREREGISTRATION IS URGED!

_____ I will attend OIL SHALE: WHAT'S IT ALL ABOUT?

in

_____ Grand Junction _____ Denver

_____ Reserve a place for me on the bus from Rifle to Grand Junction and send me detailed information.

_____ I cannot attend but please send the written summary of the meetings.

NAME _____

ORGANIZATION _____

ADDRESS _____

CITY _____ STATE _____ ZIP _____

PHONE _____ office/home (circle)

OVERVIEW

A RESOURCE

LARAMIE ENERGY TECHNOLOGY CENTER

TECHNOLOGIES

MANAGEMENT

DISPLAY

Jon Fruchter's Display

LOS ALAMOS SCIENTIFIC LABORATORY

OIL SHALE INDUSTRIAL HYGIENE CONCERNS

Development of Oil Shale technology will involve determination of work practices and control requirements to provide a healthy working environment. The experience provided by existing mining and petrochemical industries provides a basis for identifying controls and work practices for initial Oil Shale development. Health evaluation, research and toxicology studies are paralleling process development to ensure that potential health concerns are resolved prior to full scale operations. The Oil Shale industries and several Departments of Energy laboratories are active in identification of unique problems, determination of control requirements and collection of potential exposure materials for toxicology studies. These studies are coordinated between industry experts, concerned with the health of their employees, and National Laboratories, to assure efficient control of potential problems.

These posters detail some activities which LBL is currently involved in. They are aimed at: (1) providing industrial hygiene information for each process, (2) evaluating the occupational health status of Oil Shale workers and (3) providing input data for toxicology studies.

A. MILING

- Dust Inhalation
- Exposure to Trace Metals
- Exposure to Gases
 - CO
 - Hydrocarbons
- Noise
- Releases from Milling operations
- Diesel Exhaust

Dust in Mine

B. MATERIAL TRANSFER MINE TO RETORT

- Dust Inhalation
- Exposure to Trace Metals
- Noise
- Respiratory Protection Requirements

Dust Generated by Truck Transporting Raw Shale

C. CRUSHING

- Dust Inhalation
- Exposure to Trace Metals
- Noise
- Exposure Arising from Maintenance
- Respiratory Protection Requirements
- Waste Handling

Fugitive Emissions from Crusher
(Respirators Used to Assure Adequate Worker Protection)

D. RETORTING

- Exposure to Trace Metals
- Exposure to Hydrocarbons and Organic Vapor/Solvent on Dust
- Maintenance
- Respiratory Protection Requirements
- Protective Clothing
- Exposure Resulting from Continuous Mining and Retorting
- Noise
- Waste Handling
- Heat
- Gases SO_2 , SO_3 , H_2S

Above Ground Retort

E. WASTE MANAGEMENT

- Dust Inhalation
- Exposure to Trace Metals
- Exposure to Gases
 - CO
 - Hydrocarbons
- Exposure to Hydrocarbons and Organic Vapor/Solvent on Dust
- Respiratory Protection Requirements

- Total Dust
- CO
- Respirable Dust
- Gases and Vapors

- Rinsing
- Animal Inhalation
- Skin Penetration

Some of the data obtained is shown below.

	Total Psychiatric Patients	CGI	H ₂ S	H ₂ N	CGI ₂	Scale ₂
1. Age (year)	Mean 50.0	78	70	8	100.0	100
2. Sex (male)	1	5	6.2	100	100	100
3. Treatment (months)	78	100	100	100	100	100
4. Duration (months)	100	100	100	100	100	100

Location	Total Load (kg m ²)	% Temperature Increase	Maximum Temperature (°C)
Shelf	1.0 31.9	65	2
Center	2.0 42.2	50	2-9
Box Storage	4.2 112.0	85	5
Refract	9.0 302.8	4-25 1-5	8 7
Refrigerated Shelving	5.2 84.0	10-37	5

Variable	76	80	87
Mean Age (Years)	38	37	40
Sex Problems (Left report)	1	4	0
N. S. C. 17 (Left report of masturbation)	0	0	0
Sex C. 17 (Left report)	0	0	2
Polymenorrhea Problems (Left report)	3	4	3
Chlamydia (Left report of Chlamydia 2 rep)	1	0	0

Table
Medical Examination Summary

Shale-Oil Environmental Hurdles Outlined

By ROBERT TWEEDELL

Denver Post Western Slope Bureau

GRAND JUNCTION — Environmental hurdles on the track leading to commercial production of shale oil in Colorado, Utah and Wyoming were set up for public view in Grand Junction last week.

During a meeting sponsored by the U.S. Department of Energy, with assistance from the Oil Shale Task Force, the League of Women Voters and Club 20, experts from the Energy Department and other organizations took turns outlining needs that have been established for a shale-oil research, development and demonstration program.

Among the needs are development and solid-waste disposal, water treatment and air quality-control systems, programs to alleviate impact on the environment and on the social and economic fabric of communities, guidelines for the health and safety of shale-oil industry workers and the public, methods to control or prevent land

subsidence, and a plan for abandoning underground retorts that have served their purpose.

Ralph Franklin, shale-oil research coordinator for the Energy Department, said at a news conference before the meeting Thursday that the timetable for getting over these hurdles is five to 10 years.

He added that he expects "some significant data" will be available by 1984-85, and that failure to reach any one research goal isn't likely to interfere with shale-oil development. He pointed out that small-scale commercial plants are in fact a necessary part of the Energy Department project.

BRIAN HARNEY, a technology expert in the Energy Department's Office of Fossil Energy, also said construction of commercial facilities should proceed in conjunction with the research program. He said the department expects the first such plants to be pilot-size, with a production capacity of 6,000 to 12,000 barrels of oil a day.

From that beginning, he said, the industry probably will proceed on an incremental basis toward the higher production levels that have been judged necessary for profitable operation.

Availability of water is a key factor in development of a full-scale shale-oil industry. David Walker of the Colorado

Department of Natural Resources reviewed the recent study done for the Water Resource Council and said that a number of questions still are unanswered, particularly with regard to the effects on agriculture, fishing and wildlife. He also stressed the need for storage and distribution facilities.

Glenwood Post 04/11/80

Questions remain over oil shale impacts

By Gary Schmitz
Post staff writer

GRAND JUNCTION — Although confirming that numerous questions remain over the effects of large scale oil shale development, scientists here Thursday for a U.S. Department of Energy (DOE) seminar expressed confidence that the first series of commercial scale oil shale plants will not cause serious harm to the environment.

Speaking at a program which detailed the DOE's ongoing work on the environmental, social and economic effects of massive oil shale development projected for Western Colorado, researchers suggested operation of the "first generation" of oil shale plants — which several corporations say could begin construction this year — may be necessary before the answers can be known.

The program, entitled "Oil Shale: What's It All About," was attended by about 100 people from a variety of backgrounds. A bus chartered by the Garfield-Eagle League of Women Voters brought 25 members of that group and other local residents to the seminar.

"There are a lot of public misconceptions about what we know and what we're doing in the oil shale field," said Ralph Franklin, who heads the DOE's environmental work on oil shale. Thursday's program was part of an ongoing effort to rectify that, he added.

"There appear to be no environmental problems of overwhelming consequence,

but there are questions that have yet to be answered," Franklin said.

"We should learn enough in the next five to ten years from the first set of plants to come up with the right technology to meet the long-range development of the resource," Franklin said.

And it can occur without serious environmental degradation in the interim, Franklin said, adding, "We have enough knowledge and safeguards to ensure that."

For example, almost no definitive studies have been done on what oil shale development will do to the relatively pristine air now enjoyed on the Western Slope.

According to David Sheesley of the DOE's energy technology center at Laramie, Wyo., the terrain of western Colorado complicates the potential for air pollution. Pockets of stagnating air, especially at high altitudes, could present significant pollution problems, Sheesley noted.

Researchers are currently developing a computer model of the atmospheric conditions above the region, he reported, to answer the unknowns surrounding dust from mining, gases and particles from the retorting and refining process — as well as the population growth the industry will bring.

Sheesley, however, pointed to the Clean Air Act, which places limits on the cumulative amount of pollutants which can be discharged into the air, as an

adequate safeguard.

Storage and revegetating vast areas of spent shale, material left after the oil is removed, also remains a major concern, researchers said.

While some companies contend they have successfully grown native plants on spent shale piles without problems, research by Colorado State University indicates serious gaps in reclamation knowledge.

"It's not as simple as some would have us believe," said Ed Redente of the CSU Range Science Department, which has conducted experiments at the federal oil shale facility at Anvil Points, near Rifle.

While noting some oil shale corporations dispute his findings, Redente said preliminary data suggests that some form of top soil will be needed to cover spent shale piles before vegetation can be successfully grown.

Toxic substances within the spent shale, which is planned to be dumped in the canyons surrounding local oil shale reserves, could be leached into underground water and become another pollution hazard. Redente said research in that area is also inconclusive.

The social and economic impacts that Western Colorado would face in an oil shale boom may be more serious than the environmental effects, several researchers affirmed.

Kevin Markey, director of the Colorado chapter of Friends of the Earth, told the Post his group supports the DOE's en-

vironmental research program, as well as its current effort toward public education.

Asked if he believed the current research effort was adequate in light of corporate reports that major construction will soon occur, Markey responded: "I don't know if it's adequate, it is still too early to tell. I will say the evidence so far isn't conclusive, and they don't pretend it is."

Friends of the Earth, a nationwide environmental organization, has consistently been involved in ecological issues surrounding oil shale development.

Markey, who organized a DOE-funded oil shale workshop in Denver late last year, said more public education is needed if Coloradans are to be aware of and respond to the problems that will come with oil shale development.

Paraho Development Corp. spokesman Harry Pforzheimer III agreed that further education is needed.

"It's hard to get the public motivated," Pforzheimer said. "So many people have heard so much for so many years, they think they know it all. But that's not accurate," said the representative of the Grand Junction-based company, which operates the Anvil Points facility in conjunction with DOE.

"Though some research is still needed, I have no doubt oil shale can be developed safely...and will be within this decade," Pforzheimer predicted.

78 attendees

Denver

23 pgs. returned

OIL SHALE: WHAT'S IT ALL ABOUT?

EVALUATION

We would appreciate your filling out this form before leaving today. Please give it to any of the registration personnel (orange ribboned name tags) or the meeting manager (red ribboned name tag). Thanks!

1. How did you learn about this meeting:

Mailer - 9 League WV - 2 FOE - 2 Friend - 1
Sierra CWB - 3 CES staff - 2 Village Spire - 2

Displays

2. Did you find the display(s) to be informative?

Not At All 0 Moderately 13 Very 9

3. Which display(s) did you find most useful:

Comments:) see attached

4. Which display(s) did you find least useful?

Comments:) see attached

Panel Discussion/Presentations

5. Was the panel discussion informative?

Not At All 0 Moderately 14 Very 9

6. Which presentation(s) was most informative?

Comments:) see attached

7. Which presentation(s) was least informative?

Comments:) see attached

8. Did you have the opportunity to talk with scientists/research people in your area of interest? yes 15 no all others

Were the discussions useful? yes 15 no

9. How much did you learn about oil shale and oil shale research at this meeting?

none 1 little 2 some new information 16 considerable 4

10. What concerns do you have regarding oil shale development?

SEE attached

What wasn't addressed at this meeting that you would like to hear about?

SEE attached

11. Would you attend other public meetings on this topic?

yes 22 no

Should such meetings be an annual event or held more frequently?

annual event 7 more frequently 16

Would you prefer the presentation format similar to today's meeting or a workshop format?

presentation 14 workshop 14

Would you like to see displays of a similar nature at any future meetings?

yes 20 no

12. How could this meeting have been improved?

SEE attached

13. Please circle the constituency you represent:

Local Government -1 State Government ☐ Federal Government -0

Industry -4 Public Interest/Service Organization -3

Citizen -3 Academic -1 Environmental Groups -6

Other: 5

Questions 3 & 4

<u>DISPLAYS:</u>	<u>A. Most Useful</u>	<u>B. Least Useful</u>
I. Reclamation (CSU)	3	0
A. o Slide Program useful (2)		
o Availability of publications		
Good general background		
II. Geological Development of Oil Shale (USGS)	0	2
III. Western Oil Shale Facilities (Nieuwenhuis)	2	0
A. o Excellent		
IV. Oil Shale Development Technologies (LETC)	6	0
A. o Good for basics - good for lay person (2)		
V. Characterization (Fruchter)	0	1
VI. Analytical Methods (Meglen)	1	0
VII. Occupational Medicine (Ettinger)	0	0
VIII. Biology & Toxicology (Holland)	2	0
IX. Wildlife (Hakenson)	3	0
A. o Informative		
o Clever idea and easy to understand		
X. Geochemical Baseline Studies (Klusman)	0	0

GENERAL COMMENTS ON DISPLAYS:

- o Some displays down at 3:15 pm
- o Handouts should have been available for each display
- o More technical displays somewhat interesting but didn't relate to impacts
- o Technology displays too confusing; chart would have been useful:

	Union	Colony	Tosco	etc.
types of retort	--	--	--	--
etc.	--	--	--	--

Questions 6 & 7

PRESENTATIONS:

	<u>A. Most Useful</u>	<u>B. Least Useful</u>
I. Harney (Technologies)	0	1
II. Holland (Health)	0	2
III. McDonald (Water Availability)	4	0
Air:	1	4
B. o Minimal information difficult to follow		
IV. Sheesley (Air)	0	1
V. Barr (Air)	0	0
VI. Nieuwenhuis (Water Quality)	1	0
VII. Wildung (Water Quality)	2	0
VIII. Redente (Reclamation)	5	0
A. o He needed more time		
IX. Stenejhem (Socio-Econ)	6	0
A. o Needed more time for discussion		
<u>All:</u>	6	0
<u>M. Robbins</u>	0	2
B. o Said four major environmental problems but neglected to mention them		
o Too general, not applicable		

GENERAL COMMENTS:

- o More detail needed
- o Copies of presentations would have been useful
- o Not enough time for panelists or questions
- o Too many subjects to handle in afternoon session
- o Too superficial given time constraints but otherwise o.k. (2)

What concerns do you have regarding oil shale development?

Question 10A

- o Social impacts (6)
- o Air quality (4)
- o Water Resources (3)
- o Total impacts (3)
- o Soil
- o Net energy (2)
- o Research after permits(?)
- o Resource value (?)
- o Premature development
- o Need newer technology
- o Management concerns
- o Commercial delays

What wasn't addressed at this meeting that you would like to hear about?

Question 10B

- o Socio-econ (2)
- o Conservation alternative cost analysis (2)
- o Industry money maker/answers to plans (2)
- o DOE relation to state government permits
- o Spent shale usage
- o Management and solutions
- o Processing
- o Wildlife
- o More detail in layman's terms
- o Is Kathy available

How could this meeting have been improved?

Question 12

- o Should have been more publicity, more public awareness, involvement/attendance (6)
- o Too general, too much in a short period (3)
- o Need to define goals (2)
- o Coffee and donuts (2)
- o Public getting pushed aside in interest of DOE monopoly
- o Considering time and complexity, pretty good
- o More government to industry interaction information necessary

How could this meeting have been improved? (cont'd)

- o More question & answer time
- o Answer the questions
- o More local input
- o Need industry rep to answer responsibility impacts
- o Deal with management & solutions
- o More time/start earlier
- o Excellent procedure
- o More detailed information on international and future approaches
- o Audience couldn't hear questions

187 Attendees

60 Q&A returned.

Grand Junction

OIL SHALE: WHAT'S IT ALL ABOUT?

EVALUATION

We would appreciate your filling out this form before leaving today. Please give it to any of the registration personnel (orange ribboned name tags) or the meeting manager (red ribboned name tag). Thanks!

1. How did you learn about this meeting:

Work - 7 Brochure - 18 Friend - 3 Energy Office - 2 Word-of-mouth - 1
League WV - 16 Newspaper - 12 Club 20-1 Fox News - 1
Displays

2. Did you find the display(s) to be informative?

Not At All 4 Moderately 36 Very 17

3. Which display(s) did you find most useful:

Comments:)

SEE attachment

4. Which display(s) did you find least useful?

Comments:)

SEE attachment

Panel Discussion/Presentations

5. Was the panel discussion informative?

Not At All 6 Moderately 38 Very 12

6. Which presentation(s) was most informative?

Comments:)

SEE attachment

7. Which presentation(s) was least informative?

Comments:)

SEE attachment

-continued-

8. Did you have the opportunity to talk with scientists/research people in your area of interest? yes 30 no not asked, obviously

Were the discussions useful? yes 23 no —

9. How much did you learn about oil shale and oil shale research at this meeting?

none 3 little 15 some new information 28 considerable 12

10. What concerns do you have regarding oil shale development?

see attachment

What wasn't addressed at this meeting that you would like to hear about?

see attachment

11. Would you attend other public meetings on this topic?

yes 49 no 5

Should such meetings be an annual event or held more frequently?

annual event 19 more frequently 31

Would you prefer the presentation format similar to today's meeting or a workshop format?

presentation 12 workshop 41

Would you like to see displays of a similar nature at any future meetings?

yes 44 no 9

12. How could this meeting have been improved?

see attachment

13. Please circle the constituency you represent:

Local Government -5 State Government -2 Federal Government -7
Industry -6 Public Interest/Service Organization -17
Citizen -14 Academic -2 Environmental Groups -4
Other: 3 (1 pers)

Citizen and Public Service Const. = 51%

DISPLAYS:

	<u>A. Most Useful</u>	<u>B. Least Useful</u>
I... Geological Development of Oil Shale (USGS)	4	2
A. o Most interesting, easiest to comprehend		
B. o Vague and general		
o I'm already familiar with USGS info		
II. Geochemical Baseline Studies (Klusman)		
III. Western Oil Shale Facilities (C. Nieuwenhuis)	11	1
A. o Carol provided a good commentary		
o Too much information but I'm slow (2)		
o Very informative and understandable (2)		
o Very thorough in explaining facts		
IV. Oil Shale Development (LETC)	9	4
B. o Elaborate display did not convey much new information		
o No personnel available to interact		
o Ill defined, could have been clarified to some extent by expansion of display (me - ???)		
V. Characterization (Fruchter)	1	2
A. o Relationship to end products clear		
B. o Not impressed (2)		
VI. Analytical Methods (Meglen)	1	4
B. o Too technical		
o Too technical, not related		
VII. Occupational Medicine (Ettinger)	1	
VIII. Biology and Toxicology (Holland)	3	5
A. o Very informative and understandable (2)		
B. o No specific compounds were identified		
o Too technical - not related		
IX. Wildlife (Hak nson)	11	3
A. o Showed an interesting research tool; provided interaction; learned something new (2)		
o Displays with direct implication to mitigative effects & results most informative		

A. Most UsefulB. Least Useful

IX. Wildlife (Hakenson) cont'd.

- A. o Very informative and understandable (2)
- o My specific area of interest (2)
- B. o Do not believe all information was presented - only that which would make a desired point (2)
- o Wildlife stressed too much - they will adjust to development if not harassed (2)

X. Reclamation (CSU)

8

1

- A. o Specific application to public concerns
- o Future impact of past activity
- o Very informative & understandable

DISPLAYS:

General Comments

- o Need more hand-out material
- o Good program
- o All good - want more
- o All subjects were pertinent. It takes alot of time to absorb the message of each so it was hard to get all around.
- o Far too technical to be understood by the layman
- o Some studies still too new to show results but were interesting and informative to know something being done in the area
- o The ones I had difficulty understanding because of technical information or complexity
- o Those too technical, but basically they were all good
- o All about equally interesting
- o All were very informative
- o More technical ones

PRESENTATIONS:

A. Most Informative B. Least Informative

I.	Harney (Technologies)	4	
	A.	o Good speaker, easy to follow	
		o Not enough emphasis on technologies; and current company involvements in doing development in saline zone	
		o Good review, easily understood, good graphics	
II.	Holland (Health Effects)	7	2
	B.	o Not enough detail, probably because studies are still underway	
III.	Walker (Water Availability)	5	2
	A.	o Effects on water supply and other uses are very important. He had too many facts and figures to absorb in one hearing. He should have used some slides giving figures and gone more slowly so we could take notes	
		o Need more time	
	B.	o Speaker stated that unallocated water is available - did not address the real constraints to developing this water - 1) environmental impacts, 2) endangered species, 3) salinity problems downstream	
		o Difficult to track	
IV.	Water Quality (Nieuwenhuis & Wildung)	4	4
	B.	o Wildung - mainly because speaker mumbled and very difficult to understand so presentation was lost	
		o Wildung - difficult to hear; boring	
		o Wildung - hard to understand speaker; was disappointed because I am concerned with impacts on surface water. Also need to identify definite impacts	
	General Comments: Too much emphasis on water; not any on multi-mineral development of oil shale and its associated benefits.		
V.	Air (Sheesley & Barr)	3	9
	B.	o particularly Sumner Barr	
		o both	
		o Sumner Barr; could not understand him - actually don't think he had too much to say of any substance	
		o Sumner Barr (2)	
		o Detrimental effects unknown? Yet to be learned?	
		o Boring; i.e., scientific community talking to each other (or itself)	

PRESENTATIONS: (cont'd)

A. Most Informative B. Least Informative

VII. Stenehjem (Socio-Econ) cont'd

- A. o Jane Quimby, Mayor, Grand Junction,
 wants to rap with Stenehjem re: this
 presentation
- o Particular area of interest to many people
- o One of the better presentations I have
 heard in a while. I've heard quite a
 few!
- o Well presented and site specific to this
 region's concerns
- o Well done and easily understood
- B. o Nothing new; over talked
- o Overbearing, lengthy, laden with mis-
 information

VIII. Franklin (Introduction)

2

- A. o Didn't know DOE was doing that much
 work

Question 10 (A)

Concerns Re: Oil Shale Development

Air Quality: (7)

Retention of Existing Wildlife: (4)

Orderly Development: (1)

Impact on Land Use: (1)

Socio-Econ: (21)

- o Econ: impact on economic sectors in the region, primarily agriculture and recreation
- o Lack of capital
- o How fast will area communities grow
- o Econ: will this industry be self-supporting or will it be subsidized through our taxes
- o Lack of private sector preparedness for any growth
- o Recreation
- o Econ: what portion will it cost me for DOE to help big oil
- o Econ: waste of tax dollars - subsidy of private industry
- o Mitigation of impacts
- o Influx of people (training of the people)
- o Economic; and growth and development

Reclamation: (7)

- o Retaining integrity of environment to the extent that natural processes have enough viability to restore themselves over time

Quality of Life: (3)

Too Much Planning; Not Enough Action: (4)

- o Why so slow coming
- o Oil shale being studied to death, need production demonstrations

Business Concerns Will Be Ignored by Government: (1)

Water Availability: (4)

- o If there were a water shortage in the future similar to a few years back and the oil shale industry was full scale who would get the water? Oil shale or agriculture? Will we sacrifice agriculture to produce oil?

Water Quality: (10)

- o And aquatic life
- o Ground water impacts

Production Cost Kept at a Minimum: (1)

Production of Oil From Shale Feasible: (1)

What Area Will be Like When Oil Shale Industries Exhaust the Available Resources: (2)

Addressing (mentioning) Specific Rather Than Contaminants in General: (1)

Massive Government Inducements to Produce Large Uncontrolled Industry Rather Than Selecting Promising Technologies and Proceeding to Pilot Commercial Demonstration of Economic and Environmental Feasibility: (1)

More Public Information Through Our News Media: (2)

Impact Mitigation Strategies: (1)

When Going to Happen: (3)

- o How much
- o How developed

Would Federal Dollars be Better Spent on Solar: (2)

- o Government waste of dollars on development

Research Goals: (1)

- o i.e., conclusions and data compilation deadlines

Approach to Development is Disorganized: (1)

Am Concerned that Widespread Lack of Public Knowledge Concerning What is Known About Environmental Effects of Synfuels Technology Will Stand in Way of Real Progress in Meeting Demand for Liquid Fuels: (1)

Question 10 (B)

What wasn't addressed at this meeting that you would like to hear about?

More interest in meeting public concerns toward the negative problems of oil shale: (1)

How R & D interfaces with policy. Policy issues: (1)

Cumulative costs: (2)

- o Who will bear? Where will benefits of development go
- o Cost/benefit

Odors associated with a large industry: (1)

Government subsidy of private industry: (3)

- o Would there be development if government left all to private industry

The years of research that has been carried out on the C-a and C-b tracts: (1)

Much more emphasis on Socio-Econ: (2)

- o What will DOE's role be in attempting to eliminate or mitigate these impacts

Progress industry is making: (2)

Tax money use: (1)

- o How much for research? How much does big oil turn back into the economy?

Total time span for full production: (1)

Cumulative effects of all development in the region: (1)

Mitigations on aquatic impacts: (1)

How long does it take DOE to write an EIS: (1)

That development will occur: (1)

Development of saline zone of basin: (1)

The amount of energy used to recover/refine the oil: (1)

Positive steps which have been made in area of environmental and socio-econ assessment, mitigation and monitoring: (1)

Potential problems, dangers, uncertainties: (3)

- o Impression given that environmental hazards are minimal and controllable, not my understanding from other workshops attended and from reading the entire text of DOE's 5 year plan
- o Sounds like all problems have been solved, hard to believe

Soil amendment - microbial effects: (1)

How development is to be coordinated with local government: (1)

Transportation: (2)

What is the big picture? Where are we?: (1)

Industry viewpoint: (5)

Comparison with other energy alternatives: (1)

More about exact extraction processes: (1)

o Is one better than another

DOE stand on future leasing in Piceance Basin: (1)

Question 12

How Could Meeting Be Improved?

Format: (25)

- o More small groups
- o Poor
- o Panel method awkward
- o Prefer workshop
- o Panel information but doesn't lend to good dialogue which is absolutely necessary
- o Most of seminar should have been question and answer
- o Reflected disjointed presentation
- o More direct contact with panel - workshop - or question and answer meeting
- o Fewer topics more intensely covered
- o Question and answer, focusing on fewer things with more opportunity to discuss them fully
- o Too long
- o Chance to ask questions
- o Too long to set without scheduled break
- o Too many speakers - talks too superficial
- o No chance for discussion and group interaction
- o Separate workshops in specific areas
- o Use public comments/questions for future orientation
- o Group question and answer
- o Use public forum format
- o 5-10 min/speaker; then question and answer
- o Shorter
- o Focus on one topic/meeting
- o Do two day workshop; have presentation on the displays
- o Organized to allow better absorption of information through more time or fewer speakers

Panelists: (14)

- o Talking at, not to the audience
- o Difficult to understand (diction) at times
- o Difficulty in hearing clearly (4)
- o Some poor speakers

Panelists: (cont'd)

- o Many too wordy and number oriented
- o Moderator should be able to communicate
- o Better speakers (2)
- o Presentations need to be zippy and a bit shorter
- o Most speakers need public address system instruction
- o Boring talks to lay person's level
- o Some slides too busy

Acoustics/Public Address System: (6)

- o Hand held mike might have helped

Room Too big: (1)

Timing: (5)

- o Start earlier
- o Could have started and finished earlier
- o Start earlier with break for lunch - too much of a marathon
- o Hold later so more public can attend

Spotlight On Speaker Podium: (1)

Better Public Notification: (1)

More Involvement of Industry: (3)

Get Down to Specifics - Interests and Conflicts: (2)

GENERAL COMMENTS:

- o Need to develop commercial plants post haste - too much planning, not enough implementation
- o Chariman needs to learn how to enunciate: mushy mouthed
- o #6 - All presentations too long, hence not enough time for question and answer and discussion
- o In all cases, question and answer should follow presentation
- o No presentation particularly informative - researchers tend to be very lackluster in public presentations, impression impartial ? of inordinate problems at every turn. The entire group session preoccupied with reinventing the wheel of environmental research
- o Could not hear clearly, panelists often mumbled and just rambled on and on. Only trying to influence or brain wash rather than present information - it is stupid to reseed sagebrush and other nonbeneficial and poisonous plants!
- o Too technical for lay people
- o Most presentations too technical; panelists didn't seem interested and were coming from a point of view that oil shale is good and not really addressing the problems associated with increased oil shale production.
- o Very one-sided (presentations) without "blind faith" to mitigation of the environmental problems. Why no questions from the floor?
- o Some of these folks need public speaking courses

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OIL SHALE: WHAT'S IT ALL ABOUT?

A PUBLIC MEETING SPONSORED BY THE U.S. DEPARTMENT OF ENERGY, HOSTED BY THE OIL SHALE TASK FORCE, AND CO-SPONSORED BY THE LEAGUE OF WOMEN VOTERS AND CLUB 20.

THURSDAY, APRIL 10, 1980

TWO RIVERS PLAZA CONVENTION CENTER
2ND AND MAIN STREET
GRAND JUNCTION, COLORADO

AGENDA

- 12:30 PM Registration
 Poster Sessions *Displays illustrating aspects of oil shale development and research activities at various national laboratories and universities.*
- 2:00 PM Formal Session Convenes
 Introductory Remarks: *Ralph Franklin
 Office of Environment
 U.S. Department of Energy
 Washington, D.C.*
- 2:15 PM Keynote Address: *Nancy Dick
 Lieutenant Governor
 State of Colorado*
- 2:30 PM Panel Discussion *Each panelist will address a question regarding oil shale development and briefly describe the activities in that area.*
- 5:00 PM Formal Session Adjourns
 Poster Sessions Continue
 No-Host Reception (in room across hall from main meeting room)
-
-

THE POSTER SESSIONS

GEOLOGICAL DEVELOPMENT OF OIL SHALE
U.S. Geological Survey

GEOCHEMICAL BASELINE STUDIES
Ronald Klusman
Colorado School of Mines
Golden, Colorado

WESTERN OIL SHALE FACILITIES
Carol Nieuwenhuis *
University of Colorado
Denver, Colorado

OIL SHALE DEVELOPMENT TECHNOLOGIES
Laramie Energy Technology Center
Department of Energy
Laramie, Wyoming

CHARACTERIZATION
Jonathan Fruchter*
Battelle-Pacific Northwest Laboratories
Richland, Washington

ANALYTICAL METHODS FOR OIL SHALE SAMPLES
Robert Meglen
University of Colorado
Boulder, Colorado

INDUSTRIAL HYGIENE AND
OCCUPATIONAL MEDICINE
Marvin Tillery*
Los Alamos National Laboratory
Los Alamos, New Mexico

BIOLOGY AND TOXICOLOGY
L.M. Holland* and Julie Wilson
Los Alamos National Laboratory
Los Alamos, New Mexico

WILDLIFE
Tom Hukunson and Gary White
Los Alamos National Laboratory
Los Alamos, New Mexico

RECLAMATION
Walt Ruzzo and Wayne Cook
Colorado State University
Fort Collins, Colorado

THE PANELISTS

MODERATOR: WILLARD R. CHAPPELL
Chairman, The Oil Shale Task Force
Denver, Colorado

SUMNAR BARR—Air
Los Alamos National Laboratory
Los Alamos, New Mexico

ARTHUR HARTSTEIN—Technologies
Office of Fossil Energy
U.S. Department of Energy
Washington, D.C.

L.M. HOLLAND*—Health Effects
Los Alamos National Laboratory
Los Alamos, New Mexico

WILLIAM McDONALD—Water Quantity
Colorado Department of Natural Resources
Denver, Colorado

CAROL NIEUWENHIUS*—Water Quality
University of Colorado
Denver, Colorado

EDWARD REDENTE—Reclamation
Colorado State University
Fort Collins, Colorado

DAVID SHEESLEY*—Air
Laramie Energy Technology Center
Department of Energy
Laramie, Wyoming

ERIC STENEHJEM—Socioeconomic Impacts
Denver Research Institute
Denver, Colorado

RAYMOND WILDUNG*—Water Quality
Battelle-Pacific Northwest Laboratories
Richland, Washington

MEETING PLANNER AND MANAGER:
Kathy Petersen
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Denver, Colorado

* MEMBERS OF THE OIL SHALE TASK FORCE

APPENDIX B

Appendix B

OIL SHALE
the environmental challenges

Vail, Colorado

August 11-14, 1980

program

general information
registration forms

To present and discuss research on the environmental and socio-economic impacts related to oil shale development. Major review presentations will focus on an evaluation of the present state of knowledge and include recommendations for mitigation strategies based on current information. Extensive discussion will be encouraged to assess future research requirements to address existing and anticipated problems associated with developing the oil shale industry.

*Sponsored by The Oil Shale Task Force
and the U.S. Department of Energy*

CENTER FOR ENVIRONMENTAL SCIENCES

The Oil Shale Task Force

OIL SHALE: THE ENVIRONMENTAL CHALLENGES

August 11-14, 1980

EVALUATION FORM

200 attendees
66 forms returned

We would appreciate your filling out this evaluation form. Please give to Kathy Petersen before you leave Vail.

1. How did you learn of this meeting?
 - 22 - Invitation from Task Force (written & oral)
 - 10 - Word of mouth
 - 5 - Invited speaker/panelist
 - 18 - Publications (Science-10/Energy Insider-2/ES&T-6)
 - 4 - Doe circular, 1 - FOE, 1 - University circular
2. Oil Shale Tour:

Did you find the tour to be interesting and useful?

Yes 23 No 2

In what way would you change the tour, if any?

- 5 - More comfortable transportation
 - 4 - Ride to site too long (more on site time)
 - 8 - Better guides, less PR People
 - 7 - One bus
 - 2 - Better drivers, 6 - Include: 1-USBM/1-Colony/2-Anvil/1-Paraho/1-TOSCO
3. Technical Sessions:

- A. Please rate both the presentation and the panel -- A rating of 1 indicates very informative; a rating of 5 indicates not at all informative.

Average of all talks = 2.4

Average of all panels = 2.2

Overall Rating		Very informative					Not at all informative	
		1	2	3	4	5		
2.4	Chemical Analysis for Inorganic Constituents of Oil Shale Related Materials: An Overview - Meglen	1	2	3	4	5		
2.4	Characterization of Oil Shale Retort Effluents - Fruchter	1	2	3	4	5		
1.8	Panel Discussion	1	2	3	4	5

Comments: (1) Brought out basic problems
 (1) Meglen - Informative
 (1) Fruchter - Too technical
 (5) Papers lacked direction, too vague, needed more detail

Overall Rating		Very informative			Not at all informative	
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2.3	Industrial Hygiene Concerns Associated with Oil Shale Development - Ettinger	1	2	3	4	5
-----	--	---	---	---	---	---

2.4	Panel Discussion	1	2	3	4	5
-----	------------------	---	---	---	---	---

Comments:
 (1) Couldn't read slides
 (1) Next year data application, guidelines, new proceedings
 (2) Good presentation & discussion but got trivial
 (1) Need clarification
 (1) Good pts brought out
 (1) To defensive
 (2) Selfish
 (1) Old stuff

2.2	Studies of the Biology and Toxicology of Oil Shale Materials - Holland	1	2	3	4	5
-----	--	---	---	---	---	---

2.2	Panel Discussion	1	2	3	4	5
-----	------------------	---	---	---	---	---

Comments:
 (3) Best presentation
 (2) Interesting/good
 (1) Add environmental toxicology
 (2) Too general/clarify
 (1) Panel too short
 (1) Couldn't read slides

3.2	Ecological Effects of Oil Shale Development--Problems, Perspectives, and Approaches - Hakonson	1	2	3	4	5
-----	--	---	---	---	---	---

2.5	Panel Discussion	1	2	3	4	5
-----	------------------	---	---	---	---	---

Comments:
 (6) Vauge/uninformative
 (1) Hakonson good/but lacked exp.
 (1) Dietz poor, but had good pts
 (2) Author poorly informed
 (1) Dominated by a few (tempest in a teapot)
 (1) Dominated by unknowledgable facilitator
 (1) Should have been lead-off
 (1) Good point to continue from next time
 (1) Exciting

(In general, most felt title/speaker/subject matter did not correlate)

Overall Rating		Very Informative					Not at all Informative	
		1	2	3	4	5		
1.8	Retort Abandonment: Issues and Priorities - Fox	1	2	3	4	5		
1.8	Panel Discussion	1	2	3	4	5		
	Comments:							
	(12) Well organized/good discussion							
	(3) Very relative area							
	(2) Hartstein rude to Fox							
	(2) Kevin Hogged time/Kevin - shut up							(In general, most very impressed with Phyllis)
	(1) Good slides							
	(2) Old stuff/limited							
	(1) Unrealistic							
	(1) Poor speaker							
2.1	Retorted Oil Shales Characteristics and Reclamation - Redente	1	2	3	4	5		
2.0	Panel Discussion	1	2	3	4	5		
	Comments:							
	(5) Excellent, well organized							
	(2) Stress uncertainties							
	(2) More Dave Shelton							
	(1) Old stuff							
	(1) Terrible speaker							
	(1) Conflict between industry & research obvious							
	(1) More specific							
2.1	Geochemistry/Hydrology of Solid Waste Disposal - Wildung	1	2	3	4	5		
2.1	Panel Discussion	1	2	3	4	5		
	Comments:							
	(4) Good, informative							
	(3) Good Panel							
	(2) Need more specific, realistic applications							
	(1) Industry/research discrepancies							
	(1) Shelton Good							
	(1) Panel better than speaker							
	(1) Panel too long							
	(1) Old stuff							
2.1	Water Management Strategies: Issues and Priorities - Fox	1	2	3	4	5		
2.1	Panel Discussion	1	2	3	4	5		

Comments:

- (5) Good speaker/presentation (1) Give Trudy more
- (3) More specific/too general (1) Title/subject misleading
- (3) Limited speaker/uninformed of total data
- (4) Facilitator dominated
- (1) Good video
- (1) Unequal representation
- (2) Panel better than speaker
- (1) "Naive"
- (1) Good panel
- (1) Should have been lead-off

Overall Rating		Very informative					Not at all informative				
		1	2	3	4	5	1	2	3	4	5
3.5	Air Emission Control Strategy - Sheesley	1	2	3	4	5					
2.7	Panel Discussion	1	2	3	4	5					
	Comments:										
	(6) Lacked research						(1) Sparked response				
	(4) Dominating facilitator						(1) Opinionated panel				
	(4) Very bad						(1) Very informative of problems of DOE research				
	(3) Too general										
	(2) Agree with Slinn										
	(1) Title/subject confusing										
	(1) Good comments										
	(1) Should have been lead-off(again)										
	(1) LETC slide snow										
2.2	The Socio-Economic Research and Implementation Needs Related to Oil Shale - Skenejhem & Gilmore	1	2	3	4	5					
2.0	Panel Discussion	1	2	3	4	5					
	Comments:										
	(6) Good/interesting/well org.						(1) "Edmonds-1/Schmitz-5"				
	(4) Good panel										
	(3) More time & attention										
	(2) Best paper										
	(1) More state										
	(1) Panel too long										
	(1) Good facilitator										
	(1) Too general										
	(1) Naive										
2.5	Compliance Plans - Harrington	1	2	3	4	5					
2.2	Panel Discussion	1	2	3	4	5					
	Comments:										
	(3) Good panel (Kevin)										
	(2) Too general										
	(2) Excellent										
	(1) Dominating facilitators										
	(1) Title/subject not correlated										
	(1) Poor										
	(1) State rep.										
	(1) More time										
	(1) Terrible (embarassment to LETC)										

- B. Would you have preferred a more usual symposium format -- more papers of shorter duration with a brief question and answer period following each paper?

Yes 7 No 59

Would you have preferred concurrent sessions with smaller groups?

Yes 14 No 48 Maybe 3

4. The Facility

- A. Were your lodging accommodations:

Excellent 35 Adequate 23 Poor 2 Good 2

- B. What was the quality of the food and service:

Excellent 50 Adequate 13 Poor Good 1

- C. How would you rate the meeting set-up (room set-ups, audio and visual, temperature control, access, spaciousness, etc.)

Excellent 13 Adequate 28 Poor 25

Comments:

Majority: room too long for audio & visuals
Complained about P.A. system
Instructions for microphone use needed prior to meetings
Elevate speakers and projection screen
Outside noise distracting
Room too warm

5. Social Gatherings

Did you find the social gatherings useful in promoting informal exchange of information?

Yes 64 No 1 Kind of 1

Please rate the number of social events:

Too many 5 Just Right 56 Maybe just right 2 More 1

Comments:

Most felt they gained as much from social functions as meetings. Gave them a chance to meet new people and people outside their immediate areas. Provided a stimulating interaction.

Some thought social functions to "cliquey":

(1-DOE clique) (1-General break-up of groups- restrictive to interaction)

6. General comments on the meeting including suggestions on how the meeting could have been improved:
- (14) Overall planning excellent
 - (9) Need more time for informal discussions
 - (2) Open up discussion groups more
 - (1) Technical information too intimidating (3) more technical (5) good balance
 - (6) Speaker time - more controlled
 - (3) Too much Art & Ralph & (2) facilitators too dominating
 - (2) Speakers too process oriented
 - (2) Smaller panels/fewer subjects
 - (1) More equal time to all factions/(1) More industry representation
 - (1) Too much quibbling
 - (3) Speakers reaction to papers & title to papers misleading
 - (2) Coffee in meeting room before meeting begins-longer breaks
 - (6) Would like more "free time to explore Vail ("end at four"/spread out another day/shorter meetings", etc.) (more time for informal interactions informal meetings...)
7. Please circle the constituency you represent:

Federal Government -9	University -14
State Government -2	National Lab -12
Local Government -0	Private Consulting Firm -13
Industry -9	Environmental Groups -3
Other <u>4</u>	

6. (cont'd)

- (2) Ski season/night sessions
- (1) Stay in Vail
- (1) No luncheon speakers
- (1) List panelists also
- (1) Name tags on folders
- (1) Good family provisions

A few were comments made about the "lengthy" check-out time (extend check-out time, more staff, etc.)

CENTER FOR ENVIRONMENTAL SCIENCES

The Oil Shale Task Force

List of Attendees

OIL SHALE: THE ENVIRONMENTAL CHALLENGES

August 11-14, 1980

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August 11-14, 1980

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APPENDIX C

CENTER FOR ENVIRONMENTAL SCIENCES

508

The Oil Shale Task Force

LEACHING MEETING
Berkeley, California
9/24/80

In Attendance:	Bill Chappell	Fred Ramirez
	Esmail Esmaili	Al Rothman
	Phyllis Fox	Clyde Sisemore
	Tom Garland	Paul Wagner
	Florence Harrison	Nonie Werbe
	Peter Persoff	Ray Wildung
	Gene Peterson	

This meeting was called to gather perspective on the development of a coherent program for future leaching activity. The first order of business called for a presentation by each researcher of his/her work carried out so far.

Activities and Purpose

J.P. Fox

Four past and present activities were described. These consist of:

1. The use of spent shales from the small (125 kg) Livermore retort to study the behavior of TDS and TOC as a function of certain parameters. The studies consisted of both batch and column work, and resulted in a Ph.D. Thesis for Amy and a manuscript in the July, 1980 issue of ES & T.
2. An experiment whose purpose was to develop a kinetic model of TOC and TDS. This was done by Hall and made use of the LETC 10 ton retort. Batch and column studies were used. A model has been constructed.
3. An effort which is designed to generate large volumes of leachate for benchscale treatability studies. The purpose here is to study the feasibility of intentional leaching as a control technology. Clearly this would require the ability to treat the leachates.
4. A study of arsenic speciation in leachates from the OXY 3 and LLNL spent shales.

R.E. Wildung

These studies have used a multidisciplinary approach (mineralogy, chemistry, microbiology, plant physiology, hydrology) focusing upon above-ground retorting. The objective of the program is to establish the important chemical/microbiological processes influencing the mobility and form of inorganic and organic residues in wastes disposed to the ground in order to (1) assess the availability of residuals to plants, (2) determine the hydrologic transport and impact of percolates on soil and water quality and corresponding biological effects, and (3) develop appropriate revegetative and remedial measures for use in solid waste management. Emphasis on development of experimental and field data necessary for predictive chemical and hydrologic models is focused on the Anvil Points site, but also includes investigations at Logan Wash and the Piceance Creek Basin. Recent studies have been initiated on above-ground retorting operations at Rio Blanco. They have been looking at surface and alluvial ground waters above and below retorted shale disposal sites and have completed an elemental and hydrological balance on retorted shale lysimeters. Lab studies have been used to answer questions raised by field studies. Briefly, the results are:

1. Leachate compositions are influenced by the volume of the leachate, but major effects are through highly complex mineral weathering sequences which have been identified for a number of elements. Microbial processes have been shown to play a role in the behavior of both carbon and nitrogen in retorted shale residuals.
2. Weathering reactions are largely independent of water movement. Initially, measurements indicated a high pH in the leachates (collected from the lysimeter). After a winter of weathering, the pH dropped significantly. The laboratory experiments have duplicated the field results, and showed that the pH reduction was due to the oxidation of reduced sulfur species through thiosulfate intermediate. This was verified in the field and shown to have secondary influence on a number of solubilization processes affecting the composition of the leachate over the long-term.
3. Inorganic ions, trace metals and organic species capable of distinguishing the effects of water solubilization of retort water, shale oil, and retorted shale on surface and groundwaters have been defined in the laboratory and verified in the field.

They are now emphasizing longer term weathering/microbial effects on the composition of the leachates using chemical modeling as a tool. They have found a significant weathering effect upon chemical composition of Paraho retorted shale leachates over a four-year period. Concentrations of carbonate, calcium, and magnesium are increasing relative to sodium and sulfate due to mineral weathering processes which are being defined. The goals of the new work at Rio Blanco are similar to those of the Paraho work.

D. Runnells

(Esmaili - Graduate Student Report)

This group focused mostly on surface-retorted shale and raw shale. The objective has been to determine the mobility of a selected group of trace elements (As, B, F, Mo, and Se) as a function of leaching volume, time, and weathering. These elements are chosen because they can be soluble under the pH conditions of the leachates and because they are potentially toxic to plants and/or animals.

The results show that F and B can be leached in significant quantities from raw shales. The retorting of oil shale by low to moderate temperature surface methods results in a significant increase in TDS compared to raw oil shale. Equilibration times are quite long - up to a year. In general, concentrations of As and Se are not significant. However, with repeated wetting and drying of the oil shale, the concentration of Se increases significantly while those of B, F, and As are reduced and TDS and Mo remain unchanged. Comparisons among Paraho, TOSCO II, and MIS retorted shales indicate the TDS, F, B, and Mo decrease with increased temperature. While the initial high concentrations of TDS, Mo, and B decrease substantially with the passage of one or two pore volumes, that of F remains high (15-20 mg/L) after several (30-50) pore volumes. Runnells' group showed that most of the F resides in the mineral illite, which is in the lightest fraction of the oil shale.

Computer modeling indicates that aqueous Mo is present chiefly as MoO_4^{--} , boron as $\text{B}(\text{OH})_3^0$ and F as free F^- . Powellite (CaMoO_4) may control the solubility of dissolved Mo and fluorite (CaF_2) probably controls dissolved F.

Reduced S species, principally thiosulfate ($\text{S}_2\text{O}_3^{--}$), were found in several samples of leachate from retorted oil shale. Thiosulfate is oxidized to elemental sulfur and sulfuric acid (possibly by means of bacterial action). It does not appear that this acid-producing reaction will have a significant impact in the carbonate-rich rocks and waters of the oil shale region.

The results of this work indicate that the potential for migration of leachate from surface disposal piles of oil shale depends, to a large extent, on the annual precipitation. Based on this work, the most suitable locations for surface disposal of spent shale in the Piceance Creek Basin are small gulches at low elevations, such as those at Tracts C-a and C-b. The greater amount of precipitation at higher elevations, such as the Colony disposal site, could alter water quality significantly.

Runnells' group has now finished collecting samples of soils and bedrock from several areas in the Basin. Leachates will be passed through these samples to determine the ability of soils to remove contaminants from leachates and thereby protect ground and surface waters. This work should provide additional data for the selection of disposal sites. The leachate will be generated in laboratory shaker experiments. The emphasis will be on TOSCO II shales.

W.F. Ramirez

This program has just started. It is designed to relate leaching behavior to transport mechanisms and pore size distribution of the spent shale. One of the sets of experiments will be to determine how much is flowing and how much is in dead space. Both internal and gross porosities will be studied.

Preliminary data on TOSCO spent shale pore size volume shows a uni-model peak.

P. Wagner

What are the chief contaminants (in particular, trace elements) in the leachate and what mitigation strategies are available? Their focus is on the relationships among the character of the raw shale, the retorting parameters, and the final leachate.

At this point, they feel they are getting an understanding of the mineralogy of the OXY spent shale. They see no major anomalies and have found some significant trends. Their results disagree with OXY's in that while there can be a decreased TDS, there is not necessarily a decrease in some important trace elements. Basically the suite of important trace elements is the same as in surface-retorted material. There seems to be an inverse relationship between some trace elements (As, B, V, F) and TDS or Ca. Whereas B, V, and Se have no secondary solubility controls, the concentration of a variety of elements, including F⁻ and Mo (as MoO₄²⁻) builds until the solubility products of a "secondary" mineral, not present in the original suite of minerals, is exceeded. At this point, the solubility of the secondary mineral controls the concentration of the trace element in the leachate, thereby clarifying the inverse relationship between Ca and F⁻ ion concentrations in the 3E leachates.

Discussion on Use of LLNL Retort

There was unanimous agreement that spent shales from the LLNL retorts will provide DOE with the single most important means of proceeding with the leaching program. Because of the instrumentation allowed by these retorts, we should be able to improve upon our understanding of the role of retorting parameters, such as maximum temperatures and heating rates. Also, there is less likelihood of the contamination that is encountered in the field, and the material is apt to be more uniform. One important consideration which has not received much attention is the effect of the rate of cooling of MIS spent shales. It may take very long periods of time for these materials to cool and this may have a significant impact on the mineralogy.

Whether the LLNL spent shales will serve all of the research needs of all those attending this meeting deserves more thought, however. Examination of the LLNL inventory of past experiments is recommended, as well as an inquiry into their plans for future retorts. Al Rothman's description of four retorts planned for next year spurred agreement on

two that would be of interest: the slow retorting rate experiment and, perhaps, the run with lean shales. Primarily, the LLNL retort could be used to complement field-generated materials with laboratory-generated materials. However, the LASL research effort on characterization and leaching behavior of spent shales might also be well served on the laboratory retort now being constructed by Marty Holland. In addition to simulated retorting, experiments could be aimed at inducing mineralogic transformations which are known to occur during processing. The information generated from these laboratory experiments could be compared with that from pilot scale experiments to provide for the development of a predictive capability for impact of leachates in abandoned retorts.

APPENDIX D.

CENTER FOR ENVIRONMENTAL SCIENCES

The Oil Shale Task Force

Minutes of the
MLR - DOE Researchers - DOH Meeting
October 7, 1980
Denver, Colorado

This meeting was called to allow for the free exchange of ideas between the Division of Mined Land Reclamation and DOE-funded researchers in areas that pertain to the permitting problems encountered by the MLR staff. Members of the Department of Health were invited because there is considerable overlap shared between the DOH and MLR.

MLR's two biggest concerns are that any mining process will require some surface retorting, and that each retorting operation has slightly different, if not unique, problems. They are currently engaged in the permitting process for the Colony project, which calls for possibly the first commercial production of shale oil at a level of 47,000 bbl/day.

Colony's proposed disposal of spent shale over approximately 900 acres of land constitutes one of the more immediate problems. The piles will have a maximum depth of 600-700'. The slope profile of 3:1 at its bottom and 4:1 at the top should be seen as a compromise between reducing the angle of the slope and disturbing less total area. Six to eight inches of topsoil was originally prescribed to overlie the spent shale, through which 40" of water will be passed annually - the depth of soil has been adjusted to between 18 and 24 inches. Native grass species will be seeded to initiate reclamation. Spent catalysts and other industrial wastes are planned for disposal within these piles. The spent shale has a range of electrical conductivity between 12 and 18, and thus is alkaline. It is also apt to have considerable accumulations of trace elements such as boron, which is readily taken up by some plants.

The experimental nature of the oil shale development makes the regulatory process a best-guess venture; the laws were not written to accommodate the tremendous size of this industry, when mature. MLR needs to address many specific problems, of which the following are representative:

- o MLR wants to determine where leached salts go, specifically whether they move upwards via the forces of evapotranspiration, or directly down into the soil.
- o Trace elements such as boron and molybdenum could be taken up by plants which are suitable forage for animals; thus, in reclamation research, it is uncertain whether grasses should be emphasized rather than shrubs, and whether species palatable to wildlife should be minimized.

- o Compaction of spent shale over rough terrain is difficult to achieve, especially TOSCO spent shale. Since Colony intends to dispose of spent shale over one or more stream channels, it is imperative to understand the long term hydro-geology of the spent shale piles. Is it a problem if water enter the piles, and if so, how can that be prevented?
- o Matters of subsidence may not fall within the jurisdiction of MLR, and thus may possibly not even be addressed.
- o The creation of new land forms is critical, in that their behavior over time is unknown. What will be the downstream and upstream effects of these geomorphological changes?
- o There is such a lack of information regarding long-term geochemical leaching, that permits should be issued as contingent upon the results of ongoing research.
- o Problems in revegetation are both short term and long term; how much cover is needed, and what kind should it be? Is a capillary break necessary? What about uptake of toxic materials?

In conclusion, MLR is expected to issue permits in areas in which their confidence levels aren't very high. They need ongoing monitoring to provide the answers to the above questions, and they need help in identifying the most critical items which warrant monitoring. MLR would like to avail themselves of the technical expertise amongst Task Force members so that they can plan for specific programming per facility.

Hartstein inquired whether MLR considered either open pit or underground mining as environmentally more sound. Shelton responded that open pit mining on a mid-size scale has distinct advantages:

- o subsidence problems are considerably less
- o spent shale may be disposed into the area from which its raw form was taken
- o allows rebuilding of stratigraphy
- o the end product is known, thus predictable
- o higher recovery of resource
- o less land disturbance per barrel of oil

Shelton emphasized that open pit on a large scale is prohibitive and counter-productive.

Richardson asked a number of questions pertaining to reclamation:

- o how deep should the overlying layer of topsoil be
- o how will salt-tolerant species fare when exposed to the shorter growing seasons of higher elevations

- o will evapotranspiration in plants cause salts to rise to the soil surface
- o how might threatened and endangered species be established elsewhere so that their propagation is ensured
- o how will raw shale fines be handled
- o where does water in a spent shale pile go - does it percolate to great depth or is it lost in runoff
- o can hazardous wastes be distributed throughout the spent shale pile

Cook emphasized that there is a void in data pertaining to spent shale as a suitable substitute for soil. What happens if the soil laid down over the spent shale erodes? How should the topsoil be stored? How long can it be stockpiled before it becomes "inert"?

Some time was spent discussing the merits of a capillary barrier. Runnells warned that the reactivity of spent shale may constitute more of a problem than uranium tailings does. Water must not be allowed to percolate through the soil and into the spent shale, and then to pass upwards, again; water should be kept out of the piles. Colony's disposal of spent shale over streambeds is the worst possible scenario. Spent shale piles should be covered to prevent water from infiltration. Raw shale also dissolves, so that lean stored shale should not be applied over soil as a protective cover.

Zachara proposed looking at some small spent shale piles that are already on the western slope; the USGS (AOSO) has a catalogue of their locations. The problem is that there is no original baseline information on them.

The meeting was concluded when Bill Chappell suggested that the Task Force review some of the work submitted to MLR to ensure its accuracy and applicability.

CENTER FOR ENVIRONMENTAL SCIENCES

The Oil Shale Task Force

MLR/DOE Meeting
Denver, Colorado
October 7, 1980

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MLR/DOE Meeting

Denver

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APPENDIX E

CENTER FOR ENVIRONMENTAL SCIENCES

The Oil Shale Task Force

Minutes of Air Quality Research Meeting
October 6, 1980
Denver, Colorado

This was a seed meeting to discuss the formation of an atmospheric research plan in oil shale development. Many feel that the DOE support in this area should be amplified and organized more coherently. We met to delineate the issues, and specify the kind of research that needs to be done.

Hartstein introduced the discussion by observing that the air program is probably the least sophisticated of the environmental research programs. With the formation of the Synthetic Fuels Board, the Office of Fossil Energy has recently shifted its emphasis from pilot plant development to environmental research. The \$3 million budget cut taken by Fossil Energy in 1981 will not compromise the environmental research, although additional funds for 1982 are not available yet. Art will be needing a formal paper proposing an air quality research program, in the event that the money does become available.

Ballantine opened the discussion further by reviewing the ASCOT (Atmospheric Studies in Complex Terrain) Program, which has focused on drainage winds in the Geysers area of California for the last 2 years. ASCOT can probably shift into oil shale with few modifications during FY 1981. This effort has been directed by Dickerson (LLL), with support from LLL, PNL, LASL, ORL, BNL, EML, SRNL, and ANL.

EPA Role in Air Quality Regulation

Chappell reviewed a recent briefing given by Terry Thoem to various state agencies. The PSD is granted when certain requirements for preventing significant degradation of ambient air are met. Whereas NAAQS pertains to protection of Public Health, the PSD is based upon standards for two regulated substances, which have been averaged over 24 hours. These are SO₂ and Particulate Matter, for which there are 3 classes:

			SO ₂	mg/m ³	PM
PSD	Class I	(pristine)	5		10
	Class II	(average)	91		37
	Class III	(heavy)	182		71
NAAQS			365		150

Most of the state of Colorado falls within Class II designation; there are 10 Class I areas, but no Class III areas. Federal Class I areas receive visibility protection, although state Class I areas do not.

There are two types of visibility problems. Plume Blight results when a single plume travels across the landscape; Regional Haze is more broadly dispersed. Standards for Plume Blight are being developed this fall, although Regional Haze standards will be developed at a later date.

Views are classified as one of 3 types: within the Class I area, from without-to-within the Class I area, and from within-to-without the Class I area. The Federal Land Manager makes the key recommendation as to whether a view is or is not impaired. For visibility to be impaired, the pollutant must be:

- 1) perceptible in terms of contrast, color, or extinction coefficient.
- 2) adverse in terms of frequency, duration, spatial extent, or time of year.
- 3) significant in terms of cost, energy, or degree of improvement.

The question of how much oil shale development can be tolerated has been skirted for lack of scientific evidence. In 1976, EPA used the Valley Model to calculate rough concentrations of SO₂ and TSP at a 200,000 bbl/day level of production:

	mg/m ³	
	SO ₂	TSP
Dinosaur National Monument	5	18
Colorado National Monument	<1	<3
White River National Forest	<2	~8
Ashley National Forest	~1	~5

Calculations for the Flattops Wilderness Area indicated the following breakdown among oil shale industrial concerns:

	bbl/day	mg/m ³	
		SO ₂	TSP
C-a	1000-2000	<.3	<.1
C-b	1000-2000	<.1	.5
Colony	50,000	1.1	1.4
Union	10,000		
	<hr/> 62,000	<hr/> 1.5	<hr/> 2.0

$$\frac{5}{1.5} \times 62,000 \text{ bbl/day} = 207,000 \text{ bbl/day}$$

= allowed before PSD limits
for SO₂ would be exceeded

Problems with extrapolating from these numbers include the fact that Colony emissions constitute most of the impact and are emitted closest to the Wilderness Area. Secondly, emissions from Utah would be dispersed more widely. Thirdly, these numbers are based on the worst possible case. Thus, the interpretation can be made that a level of 200,000 bbl/day could be allowed; it does not imply that the level could not be increased at some future date.

EPA used the Box Model (40 km) to calculate concentrations of SO₂ and TSP, assuming the following criteria are applied:

- o 400,000 bbl/day
- o Colony type of operation
- o no chemical transformation
- o no deposition
- o no dispersion beyond the box
- o homogeneous mixing

		mg/m ³	
mixing height	wind velocity	SO ₂	TSP
2500 m	6m/sec	.5	.4
1000 m	5m/sec	1.6	1.3
500 m	5m/sec	3.2	2.6
500 m	3m/sec	5.4	4.4
400 m	4m/sec	5.0	4.1

Mean conditions are:

AM mixing height	400m
PM mixing height	2500m
AM wind velocity	4m/sec
PM wind velocity	6m/sec

EPA Contracts

Systems Applications, Inc. agreed to identify what would be needed to develop a better model. Their calculations were extrapolated to a 24-hour period from data generated in one-hour increments, and were based upon a 600,000 bbl/day level of production by 1990, and a level of 900,000 bbl/day by 1995. They anticipated that the threshold of tolerance for the Piceance Basin could be elevated because there is little likelihood that interactions will occur between winds crossing the Basin at any one time, and also because pollutants which have been concentrated under inversion conditions will not be likely to reach the Flattops.

EPA has also enlisted the help of LASL and L³ who are making runs on regional models. PNL is under contract to EPA to develop an improved meso-scale Box model for the Piceance Basin.

Possible Breakdown of Issues

Sheesley referred to a series of meetings held early in 1980, during which 8 air issues were defined (health is distributed across them all):

- 1) Regulated pollutants
- 2) Unregulated pollutants
- 3) Visibility
- 4) Precipitation Quality
- 5) Regional Climatology
- 6) Meteorological Studies
- 7) Process Emissions
- 8) Model Development

Review of Research Programs

Natusch has been funded by Ballantine to collect gases and particulates emitted from stacks. His purpose is to determine how the organic species, once generated, are transformed. Using material from Laramie, he has made two runs and foresees one more; he hopes to get some material from Rio Blanco. So far, he has identified 60 species, but there are approximately 200 in all. His biggest problem is getting hands-on, i.e., representative, material. Because his information is probably inaccurate, he also can't focus on rates of transformation. These two problems might well be solved if Dave could gain access to the Livermore retort. His structure for further research employs good field science to answer these questions: a) what if anything, is coming out of the stacks, b) what direction is it headed, c) how is it transformed, and d) so what? What are the effects?

Drake has been working with fugitive emissions in oil shale, using dual tracer techniques to look at dry deposition. This August, he worked with LASL in the Yellow Creek watershed (Corral Gulch). He's had some EPA funding to characterize larger regions in the Piceance Basin in terms of winds, temperatures, and other standard air quality parameters. EPA will shift its emphasis from field work to model development from now on. He feels the biggest problem is the threat to Class II standards close in, rather than to Class I areas, 40 miles away, for the simple reason that some valleys won't clear up diurnally. We must know when flows couple and decouple; only field work will give us the right kind of data.

Slinn directed his remarks to the topic of modeling accuracy. The Gaussian model took 30 years to develop, is good up to 10 km, and on simple terrain. Likewise, the oil shale project requires an investment on the order of 100 million dollars and a time scale of 20-30 years. The first step must be a 20 best-man workshop, with participants having been informed as to what is wanted and how much money is available. The focus should be on whatever obstacles are holding up the industry: visibility, siting of plants, PSD, the lack of baseline data, and potential risk to health.

Streit objects strongly to the emphasis on modeling at the expense of chemistry; aerosols contribute significantly to the visibility problem. His proposal embraces the following points in the development of a new program:

- 1) a literature search which includes photochemical and atmospheric chemical research
- 2) baseline modeling to measure natural level of pollutants
- 3) retort monitoring, during which all emissions are broken down
- 4) laboratory photochemical simulation

Ondov remarked that air pollutants of interest are going to be on small particles, such that we cannot afford to ignore aerosol dynamics. He endorses seeking epidemiological data to demonstrate toxicological effects.

Fox cautioned that the orientation of a new program should be toward developing solutions to the problems that limit industry, as well as to the identification of those problems. We must be certain to include the Risk Analysis and Control Technology in our proposal.

All present agreed that the Flattops issue is separate from the drainage wind/valley issue because of scale; one huge mathematical model will not address both issues.

CENTER FOR ENVIRONMENTAL SCIENCES

The Oil Shale Task Force

DOE Air Quality Research Meeting
1020 9th St.
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October 6, 1980

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CENTER FOR ENVIRONMENTAL SCIENCES

The Oil Shale Task Force

Minutes

Department of Health - DOE Air Quality Researchers Meeting
October 7, 1980
Denver, Colorado

Members of a Department of Energy team of air quality researchers met with Colorado Department of Health members to learn about the kinds of permitting issues encountered by the Health Department in the development of oil shale. The Health Department is eager to participate fully in the permitting process, but does not yet have the kinds of information that will be necessary to solve some of their problems.

Among the areas of concern are acid rain, visibility, the SO₂ emission standard, secondary impacts of rapid growth, and inadequacies of modeling for complex terrain. From the state's perspective, however, no one issue is of greater importance than any other. Some of the issues the state's Air Quality Control Commission must address include 1) whether the technology exists to meet the emission standards, 2) what would be the cost of meeting them, and 3) whether there are exotic pollutants to be as or more concerned about than SO₂. It was reported that Occidental has applied to the AQCC for replacement of the 0.3 lb per barrel SO₂ standard with Best Available Control Technology (BACT) as of September 12 in Meeker, Colorado, and October 16 in Denver.

Ballantine of DOE summarized the activity conducted so far at the national labs. The first task of any air quality program is the characterization of emissions. Site-specific and regional studies, such as the SO₂ conversion to aerosol sulfate problem in oil shale development, and the nocturnal drainage winds research in the Geysers of California, follow sequentially. Areas of research that warrant further investigation include:

- o the mode of particulate formation in the atmosphere
- o the removal of pollutants from the atmosphere
- o possible interactions between pollutants and vegetation
- o transport and dispersion of pollutants in complex terrain
- o chemical transformation of pollutants

He emphasized that there is no documented evidence at this point of a link between SO₂ and public health; SO₂ is primarily a visibility problem. Air quality is one of four research areas that are now under study for definition of carrying capacity.

Hartstein of DOE explained that the Office of Environment (EV) is responsible for the development of a data base, whereas the Office of Fossil Energy (FE) is responsible for the development of control technology,

such as the application of the petroleum industry's Stretford process to the oil shale industry. He also referred to the EPA-DOE memo of understanding to develop a quality Pollution Control Guidance Document (PCGD). Arnott remarked that if PCGD's are implemented, there will be considerable state involvement.

Visibility regulations will be determined in November of this year. Of primary concern to the state is the validity of the EPA air models, which they are mandated to use. Governor Lamm's office is interested in assigning some mechanism other than first-come, first serve in use of the PSD increment.

Slinn (PNL) asked whether the state would possibly allow one plant to go on line by issuing a temporary permit; this would allow researchers to focus on the photochemistry aspect of the modeling problem at a commercial-sized facility. The request would have to go before the state AQCC. He also suggested that establishing a more accurate baseline than that which has already been contributed is necessary, as well as a broader look at mountain meteorology.

Dickerson (LLL) remarked that the physics of drainage winds at the Geysers is applicable to the oil shale region in principle, but numbers could not be transferred directly. Drake (PNL) and Slinn concurred that empirical studies were much better for the time being than any modeling work.

In response to the question of whether the Task Force should help with setting up program goals or merely review any work submitted for accuracy and applicability, the state indicated that it needs to know what to track and why to track it.

CENTER FOR ENVIRONMENTAL SCIENCES

The Oil Shale Task Force

Health Department/DOE
Air Quality Meeting
Dept. Health, Denver
October 7, 1980

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Air Quality Meeting

October 7, 1980

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APPENDIX F

Minutes of Meeting
Department of Health and Department of Energy Researchers
Health Effects
November 5, 1980

This meeting was one in a series called to explore the problems encountered by the State of Colorado in the development of the oil shale industry. While the other meetings have been designed to address issues related to air quality, water quality, and mined land reclamation, the purpose of this meeting was to consider what roles, if any, the State can play in occupational and public health problems. This is important because the State's regulatory authority with respect to health issues was eliminated when the Colorado legislature discontinued the Colorado Occupational Health and Safety Program. The Department of Health's main health arm is currently the Division of Epidemiology.

The Department of Energy-sponsored health research focuses on occupational and public health issues. It is designed to identify biological effects resulting from contact via inhalation, skin exposure, or ingestion of materials such as raw or spent shale dusts, process waters or gases, or residual by-products. David Smith presented a brief overview of this effort, explaining that data are obtained for the purpose of extrapolation to humans. Paul Cho then summarized the Risk Assessment Program, which is charged with providing a top quality analysis of health and environmental effects resulting from oil shale development. The first step towards accomplishing this goal is the development of a data base. This task has been undertaken by the Oil Shale Task Force, which is chaired by Bill Chappell. Larry Gratt of IWG Corporation, San Diego, will provide the analytical framework. The end product will be an annual Health and Environmental Effects Document (HEED).

It was suggested that, in the absence of a regulatory function, the State could become involved with the formation of a registry in an effort to track any long-term health effects on people working in the oil shale industry. One obstacle to this plan is the fact that no U.S. facility has been in operation for longer than two years. In addition, it is difficult to isolate the effects of exposure to oil shale as opposed to other resources in the area, e.g., coal or uranium.

It was suggested that another way the State could become involved is through researching the history of its interactions with other energy industries. Past performance could present other needs that have yet to be addressed in the developing oil shale industry.

Marty Holland reviewed the Los Alamos Scientific Lab (LASL) program in DOE-funded health research. As the leading national lab in this effort, LASL has focused primarily on occupational concerns, although these blend readily into the public sector. The LASL team is working with pilot projects in an effort to determine the probable hazards to individuals as a result of commercial levels of production. So far, they have worked with inhalation of raw and spent shale dusts, determined that hydrotreated shale oil is less carcinogenic than crude shale oil, and detected mutagenic activity in product oil and sludge oil.

Meeting Minutes
November 5, 1980.

The foreign literature suggests that the primary risk to humans is skin disease, either cancer or irritation. The Russians have accumulated considerable epidemiological data over 30 years of operation, but are apt to be guarded about releasing the information. The Scots, on the other hand, might be interested in participating in epidemiological studies; this would be valuable because of their 100 year long history in oil shale. In addition, it is interesting to note that there is no record of pulmonary disease among workers in Scotland. George Voelz (LASL) then recapped his recent visit to Scotland.

Relations among industry, state agencies, and the DOE seem to be improving, as illustrated by the recent development of an Oil Shale Task Force research plan for Geokinetics, a small concern located 70 miles south of Vernal, Utah. This program evolved because Geokinetics has been consistently producing oil at low levels for some time, but continues to experience problems that warrant some outside expertise. These problems revolve around fugitive emissions, waste water disposal, and regional hydrology. The team from Los Alamos is planning to launch a research effort, in conjunction with the University of Utah, to investigate the following areas of interest:

- 1) The toxicity of retort water and other waste materials upon organ systems in mice and rats.
- 2) Altered drug metabolism in workers as a result of exposure to gas and liquid waste products of the oil shale recovery process.
- 3) Definition and characterization of potential inhalation exposures associated with the oil shale recovery method by means of air sampling for dust, gases, fumes, and vapors.
- 4) Tests for short term mutagenicity and cytogenetic effects, oral toxicity, and acute/chronic skin applications with product oils or aqueous products.

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PROGRESS REPORT

1980 - 1981

MICROBIAL THIOSULFATE OXIDATION AND ITS EFFECT ON THE
QUALITY OF WATER IN OIL SHALE RETORTING

for the

U.S. Department of Energy

by

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January 26, 1981

INTRODUCTION

The most critical environmental problem associated with oil shale development in the western United States could be water quality. Water pollution from the industry can arise from underground and in-situ mining, process waters derived from retorting of shale condensate water, waste water from cooling tower and boiler blowdown, sour water from refining, and run-off water from processed shale (11). The quality of retort water, i.e. water co-produced with shale oil, and backflood water, i.e. water accumulating in retorted areas due to seepage of ground water, is low and will have to undergo extensive treatment before reuse or discharge is feasible. Retort waters may be generally characterized as having a high pH (8 - 9.5) and containing high concentrations of dissolved organic compounds (which are primarily polar) and inorganic constituents (e.g. HCO_3^- , CO_3^{2-} , F^- , Mg^{2+} , Na^+ , SO_4^{2-} , and NH_4^+). The principal sulfur species in retort waters is thiosulfate. Other species in decreasing amounts are sulfate, thiocyanate, tetrathionate, and sulfite. Sulfides are absent (4, 5).

There is evidence that microorganisms are present in the retort waters, and that these organisms could be responsible for alteration of the water (3, 6, 15). Among the organisms present in the waters, those that transform reduced sulfur compounds are of interest. Microbes capable of oxidation of thiosulfate with formation of sulfate, polythionates or sulfur have been discussed in several reviews (7, 8). These microbes include the chemolithotrophic bacteria of the genus Thiobacillus as well as some heterotrophic microbes of the genera Pseudomonas, Achromobacter, and Micrococcus (9, 13). These microbes could either be directly responsible, or initiate a succession which results in production of sulfuric acid (2). Characteristics of the thiobacilli species which oxidize thiosulfate are summarized in Table 1. The conditions existing in retort and backflood waters are suitable for the development of microbes capable of oxidizing thiosulfate and the intermediary tetrathionate. Available are sources of organic carbon for heterotrophic bacterial development, carbon dioxide for autotrophic activity, and a suitably alkaline pH (4). This creates a potential situation for acid production.

Research during the period 1 June 1979 - 31 May 1980 was aimed at determining the presence of thiosulfate-oxidizing microorganisms in a variety of retorted and raw oil shale samples, leached raw and retorted shales, leachates from these shales and soils from oil shale areas. The potential for development of thiosulfate-oxidizing microorganisms in these samples was also examined. In the present (1 June 1980 - 31 May 1981) studies raw and retorted oil shales are being leached in the presence of thiosulfate-oxidizing microbes. Changes in pH, Eh, and thiosulfate concentration are being monitored, and differences in these parameters between inoculated shales and sterile controls are being compared. The fate of selected trace elements is being examined. This report summarizes data collected from these studies and assesses the significance of these results.

Table 1. Characteristics of the species of
Thiobacillus which oxidize thiosulfate

<u>Species</u>	<u>pH range for growth</u>	<u>Products of thiosulfate oxidation</u>	<u>Metabolism</u>
<u>T. thioparus</u>	4.5 - 7.8	SO ₄ ⁼ , S, polythionates	autotrophic
<u>T. denitrificans</u>	6.0 - 8.0	polythionates	autotrophic
<u>T. neapolitanus</u>	3.0 - 8.0	SO ₄ ⁼ , S, polythionates	autotrophic
<u>T. thiooxidans</u>	1.0 - 3.5	SO ₄ ⁼	autotrophic
<u>T. ferrooxidans</u>	2.5 - 5.8	SO ₄ ⁼	autotrophic
<u>T. novellus</u>	5.0 - 9.2	SO ₄ ⁼	facultative autotrophic
<u>T. intermedius</u>	1.9 - 7.0	SO ₄ ⁼	mixotrophic
<u>T. perometabolis</u>	2.8 - 6.8	SO ₄ ⁼	obligate mixotrophic

EXPERIMENTAL PROCEDURE

ANALYSIS FOR PRESENCE OF THIOSULFATE-OXIDIZING BACTERIA

Thirty samples, including raw oil shale, retorted oil shale, column leached raw and retorted shales, leachates from laboratory columns, and soils from the Piceance Basin were provided by Mr. Kenneth Stollenwerk of the University of Colorado. See Table 2 for a description of the samples. This series of samples was used to determine the presence of chemolithotrophic thiosulfate-oxidizing bacteria.

One gram or one-milliliter of sample was placed in 100 ml of culture medium with incubation at ambient temperature (20 to 25°C). Initial enrichment media (1) for thiosulfate-oxidizing bacteria consisted of (g l^{-1}): Na_2HPO_4 , 1.2; KH_2PO_4 , 1.8; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1; $(\text{NH}_4)_2\text{SO}_4$, 0.1; CaCl_2 , 0.03; FeCl_3 , 0.02 g; MnSO_4 , 0.02; and $\text{Na}_2\text{S}_2\text{O}_3$, 10.0, for aerobic bacteria and the following were added for culture of anaerobic bacteria (g l^{-1}): NaHCO_3 , 0.5; and KNO_3 , 5.0g. Anaerobic conditions were maintained with a BBL Gas-Pak system. Media for enriched growth of selective species of Thiobacillus had the following components (g l^{-1}): for T. thioparus and T. neapolitanus (14), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$, 10.0; K_2HPO_4 , 2.0; KH_2PO_4 , 2.0; MgSO_4 , 0.8; NH_4SO_4 , 0.4; and 5.0 ml of trace metals solution; for T. intermedius (1), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 10.0; NH_4Cl , 1.0; MgSO_4 , 0.5; K_2HPO_4 , 0.6; KH_2PO_4 , 0.4; yeast extract, 1.0; and 2.0 ml of trace metals solution. The medium for T. denitrificans was a composite of four solutions (1): A, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 5.0g; NH_4Cl , 1.0g; KNO_3 , 2.0g; and 250 ml distilled water; B, KH_2PO_4 , 2.0g; and 250 ml distilled water; C, NaHCO_3 , 2.0g; and 250 ml distilled water; D, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.8g; 2.0 ml of trace metals solution, and 250 ml distilled water. The four solutions were combined aseptically following sterilization. Gas production by T. denitrificans was evaluated using a Durham tube inverted in the medium. The pH of all media was adjusted to 6.9 to 7.0.

Goodfellow's broth (in g l^{-1}): peptone, 5; yeast extract, 1.0; $\text{Fe}(\text{SO}_4)_3$, 0.01; $\text{Na}_2\text{S}_2\text{O}_3$, 2, at pH 7.2 was used for enrichment and culture of heterotrophic thiosulfate-oxidizing bacteria. Phenol red (15 ml l^{-1} of a 0.02% ethanol-water) was added as an indicator for acid production.

Microbial growth was monitored by microscopic observations of the culture media and acid production as indicated by change in the color of the indicator present in all the media.

Upon growth of an enrichment culture a 1.0 ml sample of the medium was transferred to the same medium for subculture. Subcultures were maintained by routine transfer for up to 10 transfers (6 months) before isolation of the aerobic thiosulfate-oxidizing bacteria was made on agar plates prepared with the various enrichment media. All isolates were evaluated by colony characteristics, cell morphology and Gram reaction.

Samples which did not yield thiosulfate-oxidizing bacteria were inoculated with cultures of T. denitrificans, (incubated anaerobically), T. neapolitanus and T. intermedius (incubated aerobically). The samples were inoculated in order to determine if some inherent quality prevented growth of particular

Table 2. Samples analyzed for presence
of thiosulfate-oxidizing microorganisms

<u>Sample Designation</u>	<u>Sample</u>	<u>Description</u>
1	Geokinetics:	Retorted oil shale
2	INOS-1:	Fresh oil shale, Rio Blanco tract c-a
3	SS-1:	TOSCO II, retorted oil shale
4	SS-3:	TOSCO, retorted oil shale
5	SS-3/49:	Column leached SS-3
6	POS-1:	Paraho plant oil shale
7	Lys. soil:	Anvil Points soil cover plot
8	Lys. soil:	Column leached lysimeter soil
9	Oxy cores; 3,4:	Retorted oil shale
10	Oxy cores; 14,15:	Retorted oil shale
11	RS5866-4:	SS-3 column leached shale
12	RS5867-4:	SS-3 column leached shale
13	RS5868-4:	SS-3 column leached shale
14	RS5869-4:	SS-3 column leached shale
15	PSS-1:	Paraho retorted shale
16	RS5887-4:	PSS-1 column leached shale
17	RS5884-4:	PSS-1 column leached shale
18	RS5889-4:	PSS-1 column leached shale
19	RS5890-4:	PSS-1 column leached shale
20	PSS-1/46:	Column leached PSS-1
21	RW5780:	Leachate from POS-1
22	RW5887:	Leachate from PSS-1
23	RW5888:	Leachate from PSS-1
24	RW5849:	Leachate from INOS-1
25	RW5850:	Leachate from INOS-1
26	RW5866:	Leachate from SS-3
27	RW5867:	Leachate from SS-3
28	CWG:	Soil, Cottonwood Gulch
29	RDGL:	Soil, lower Rinky Dink Gulch
30	APBZG:	Soil, Anvil Points-Balzac Gulch

thiosulfate-oxidizing microbes. After 40-days, the cultures were examined for presence of the microbes and acid production as indicated by color change in the added indicator, bromcresol purple.

Oil shale samples from which thiosulfate oxidizing bacteria were obtained were recultured in the autotrophic media with 1.0 ml of formalin added. These samples were incubated in excess of one month and observed visually for color change and microscopically for growth.

Thiosulfate-oxidation was followed by determination of the thiosulfate remaining in the cultures compared with uninoculated controls after incubation. An iodometric titration (10) was used for measuring thiosulfate concentrations. A modification (Personal Communication, Public Service Company of New Mexico San Juan Station) of the standard iodometric titration was used for thiosulfate measurement in Goodfellow's medium. This modification required addition of a formaldehyde solution to the sample.

LEACHING STUDIES

Two column studies have been initiated.

Experiment #1

An airlift percolator column (1 in. x 9 in.) was filled with 66.2 g of equal quantities of SS-1 and SS-2 TOSCO retorted shale (Table 1). Forty ml of sterile water were recycled at a rate of 1.1 ml hr^{-1} . After pH stabilization, 0.15 mg ml^{-1} thiosulfate were added. pH and thiosulfate were monitored at frequent intervals. Thiosulfate was assayed using a colorimetric technique (12).

Experiment #2

Five columns (1 in. x 9 in.) were each filled with a blend of 25 g of TOSCO II spent shale, sample SS-4 (E. Esmaili and D. Runnells, University of Colorado). The following solutions (45.5 ml per column) were added and recycled over the shale:

1. Distilled water
2. Distilled water + 50 ppm panacide (an antibacterial agent)
3. Distilled water + 1% thiosulfate
4. Distilled water + 1% thiosulfate + 50 ppm panacide
5. Distilled water + 1% thiosulfate

Column #5 was inoculated 64 days after start-up with all thiosulfate-oxidizing isolates obtained from samples described in Table 7. Eh, pH, and thiosulfate concentration (12) were periodically examined.

RESULTS

AUTOTROPHIC, THIOSULFATE-OXIDIZING BACTERIA IN OIL SHALE SAMPLES

Enrichment Cultures

Results of enrichment cultures of the 30 oil shale samples are summarized in Table 3. The initial enrichment cultures for the chemolithotrophic thiobacilli indicated that most samples do contain microorganisms capable of oxidation of thiosulfate (Table 3) as determined by decrease in levels of thiosulfate. Concurrent with thiosulfate-oxidation, in the aerobic cultures was a pH decrease. A slight pH decrease was observed in some anaerobic cultures. The lowest pH achieved was 4.3 with sample 24--a leachate from column leached Rio Blanco tract c-a oil shale. Since the pH did not decrease below 4.3 for any samples, it is a presumptive indication that only T. thioparus and/or T. denitrificans were found in aerobic cultures. Although T. denitrificans will grow anaerobically if nitrate is present, the oxidation of thiosulfate in aerobic conditions indicates T. denitrificans was present in some samples. However, a word of caution must be expressed. It is not certain if the source of microbes was indeed the samples. Aseptic procedures were not used in sample collection and handling. It is possible that the sample containers could be a source of the microorganisms, or they could have been introduced through handling of the samples. The absence of microbial thiosulfate oxidation for samples 10, 17, 28, 29 and 30 would indicate that the source is not the containers and handling procedures, or all samples should have yielded positive results. The areas with samples containing aerobic, thiosulfate-oxidizing microbes include: Paraho, plant shale (#6), column leached retorted shale (#15, 16, 18, 19, 20), and leachate (#21, 22, 23); Oxidental retorted shale (#9); Rio Blanco, tract c-a shale (#2), leachate (#2, 25); TOSCO, and TOSCO II, retorted shale (#3, 4, 5), column leached shale (#11, 12, 13, 14), leachate (#26, 27); and Anvil Points soil (#7, 8). This suggests wide distribution of the aerobic, thiosulfate-oxidizing thiobacilli. No cultures of soils from Cottonwood Gulch, Rinky Dink Gulch or Anvil Points - Balzac Gulch were positive. The anaerobic, thiosulfate-oxidizing microbes were not as widely distributed. Only samples of Rio Blanco oil shale (#2), Anvil Points soil (#8) and TOSCO column leached shale (#5, 11, 12, 13, 14) and leachate (#27) had presumed T. denitrificans activity. These results indicate that thiosulfate-containing waters exposed to aerobic conditions have potential for microbial thiosulfate oxidation and acid production.

Selective Cultures

Media which favor the growth of particular species of thiobacilli, but do not necessarily preclude the development of others, were inoculated with the original samples. This was done to obtain information regarding the types of thiobacilli which might be present in the samples. These cultures were incubated up to 6 months. When a culture demonstrated growth by change in color (pH decrease), decrease in thiosulfate concentration, and microscopic evidence of microbial growth, the culture was transferred to fresh medium. Table 4 shows those samples which yielded organisms. Most aerobic cultures

Table 3. Effect of enrichment cultures of samples on thiosulfate concentration and pH

Sample	Aerobic conditions ¹		Anaerobic conditions ²	
	pH	mMS ₂ O ₃ ⁼	pH	mMS ₂ O ₃ ⁼
uninoculated control	6.6	23.5	7.9	25.0
1	7.8	14.5	7.9	25.2
2	5.8	3.8	6.5	7.2
3	6.6	9.0	8.1	20.0
4	5.8	2.5	7.8	27.5
5	5.4	3.5	7.0	5.0
6	6.4	4.3	7.9	22.5
7	6.1	2.5	7.9	22.2
8	5.1	3.0	6.9	5.2
9	6.7	8.2	7.5	25.0
10	8.0	23.7	8.3	27.2
11	5.4	3.0	6.3	2.8
12	5.4	3.0	6.4	5.0
13	5.3	3.5	6.3	3.5
14	5.4	3.7	6.3	0.9
15	6.4	3.0	8.3	29.8
16	7.2	4.4	8.0	25.2
17	7.0	20.5	7.9	24.8
18	6.8	16.2	7.5	25.2
19	6.3	3.0	7.9	25.0
20	6.2	2.5	7.7	20.2
21	6.8	5.0	7.4	27.2
22	7.7	11.8	7.3	22.5
23	7.2	3.8	7.2	22.7
24	4.3	2.9	7.3	22.5
25	5.9	3.0	7.0	24.8
26	5.2	3.9	7.0	22.8
27	7.4	3.2	7.0	7.8
28	6.7	21.9	7.0	22.5
29	6.7	22.5	7.1	27.2
30	8.7	23.3	7.2	25.2

¹ incubated for 38 days

² incubated for 55 days

Table 4. Growth from oil shale samples of specific microbial types on selective media.

<u>Sample</u>	<u>Aerobic</u>		<u>Anaerobic</u>
	<u>T. intermedius</u>	<u>T. thioparus</u> <u>T. neopolitanus</u>	<u>T. denitrificans</u>
Uninoculated Control	-	-	-
1	+	+	-
2	+	+	+
3	+	+	-
4	+	+	+
5	+	+	+
6	+	+	+
7	+	+	+
8	+	+	+
9	+	-	-
10	-	-	-
11	+	+	+
12	+	+	+
13	+	+	+
14	+	+	+
15	+	+	-
16	-	-	-
17	-	-	-
18	-	-	-
19	-	-	-
20	-	-	±
21	+	+	-
22	+	-	+
23	-	+	-
24	+	+	+
25	+	+	+
26	+	-	-
27	+	+	+
28	-	-	+
29	+	-	±
30	+	+	+

± inconclusive results

indicated presence of the T. thioparus-/T. neapolitanus-type microbes. Some samples were positive for T. intermedius. The previous data regarding pH after growth (Table 3) had suggested that T. thioparus was a likely microorganism to be present. The anaerobic cultures indicated presence of T. denitrificans.

After incubation of the aerobic selective media for 54 days and the anaerobic selective medium for 68 days, those samples which did not exhibit growth were recultured in selective media and inoculated. Color changes (pH decrease) in aerobic media and gas production in anaerobic medium were noted. These results are summarized in Table 5. Several shale samples did prohibit the growth of some of the organisms. These included samples 19 (Paraho column leached retorted shale) and 29 (soil, lower Rinky Dink Gulch) for T. thioparus and T. neapolitanus; and samples 10 (Oxy retorted shale), 16 and 18 (Paraho, leached retorted shale), 21 (leachate from Paraho plant shale), and 22 (leachate from Paraho retorted shale) for T. intermedius. All samples inoculated with T. denitrificans demonstrated growth or inconclusive results.

Samples, which were positive on selective media after 54 days incubation aerobically and 68 days anerobically, were recultured in selective media, but formalin was added to inhibit microbial growth. This experiment was designed to show that acid production resulted from microbial activity rather than being chemically mediated. Table 6 illustrates these results. No acid or gas was produced in any samples.

After repeated transfers of up to 6 months of the oil shale cultures on selective media, transfers were made from aerobic cultures to solidified media to observe colonial characteristics of the microbes. Diverse colony types were obtained from each sample indicating a heterogenous microbial flora. Samples which yielded colonies are noted in Table 7. All colonies were pin-point, dry and yellow in appearance. Acid production in the media was observed. The organisms were all small, Gram- negative rods.

HETEROTROPHIC, THIOSULFATE-OXIDIZING BACTERIA IN OIL SHALE SAMPLES

Table 8 summarizes the oil shale samples which demonstrated thiosulfate oxidation in the heterotrophic Goodfellow's broth. Positive cultures were transferred in Goodfellow's broth for a period of 4 months. Cultures remaining positive were transferred to agar plates of Goodfellow's medium. Colony description, Gram reaction and cellular morphology of the isolates are summarized in Table 8. These is evidence that 5-7 isolates were obtained from the samples.

COLUMN LEACHING STUDIES

Experiment #1

Thiosulfate concentrations and pH values measured over a period of 179 days in the leachate of a column leaching study are shown in Table 9. pH

Table 5. Growth of specific thiosulfate-oxidizing bacteria inoculated into media containing selected shale samples.

<u>Sample</u>	<u>Aerobic Inoculum</u>		<u>Anaerobic Inoculum</u>
	<u>T. neopolitanus</u>	<u>T. intermedius</u>	<u>T. denitrificans</u>
1	+	+	+
3	NI	±	+
6	+	±	ND
7	+	+	ND
9	+	NI	+
10	+	-	+
15	+	+	±
16	+	-	±
17	+	+	±
18	+	-	+
19	-	+	±
20	+	+	+
21	+	-	+
22	+	-	ND
23	+	±	+
24	NI	+	ND
25	NI	NI	+
26	+	NI	+
27	+	NI	+
29	-	+	ND
30	NI	+	ND

+ growth

± inconclusive results

ND not determined

Table 6. Acid or gas production with formalin added to shale samples exhibiting the presence of thiosulfate-oxidizing autotrophic bacteria.

<u>Sample</u>	<u>Aerobic</u>		<u>Anaerobic</u>
	<u>T. intermedius</u>	<u>T. thioparus</u> <u>T. neopolitanus</u>	<u>T. denitrificans</u> ³
2	ND ¹	-	-
4	- ²	-	ND
5	ND	-	ND
7	ND	ND	-
8	-	-	-
11	-	ND	-
12	-	-	-
13	-	-	-
14	-	-	ND
24	ND	-	-
25	ND	-	ND
30	ND	-	ND
Uninoculated Control			

¹ ND - not determined

² - - no acid production

³ Examined for gas production

Table 7. Isolates of thiosulfate-oxidizing bacteria obtained after repeated transfer on selective media and culture on agar plates.

<u>Sample</u>	<u>T. intermedius</u>	<u>T. thioparus</u> <u>T. neapolitanus</u>
uninoculated control	-	-
2	-	+
4	-	-
5	-	+
6	-	-
7	-	-
8	+	+
11	-	-
12	-	-
13	+	+
14	+	+
24	-	-
25	-	-
26	-	-
27	-	-
29	-	-
30	-	+

Table 8. Oil Shale samples yielding heterotrophic, thiosulfate-oxidizing bacteria and characteristics of these isolates.

<u>Sample</u>	<u>Colony Characteristics</u>	<u>Gram Reaction</u>	<u>Cell Morphology</u>
2	C, R, RA, T, M, St	+	Cocci
6	C, I, RA, WH, M	-	Cocci
8	S, I, T, M	-	Cocci
22	I, W, TR, D	+	Cocci
	C, R, O, M	+	Cocci
24	C, R, RA, T, M, ST	+	Cocci
	C, R, RA, O, M	+	Cocci
25	C, R, T, M, S	+	Cocci
26	C, R, RA, T, M	+	Cocci
	C, R, RA, O, M	+	Cocci
27	C, R, RA, O, M	+	Cocci

Legend: C - Circular
R - Regular edges
I - Irregular edges
S - Spreading
RA - Raised
W - Wrinkled
O - Orange

T - Tan
WH - White
TR - Translucent
M - Moist
D - Dry
ST - Sticky

Table 9. pH values and thiosulfate concentrations of leachate from column experiment #1.

Day	$S_2O_3^{2-}$ Added (mg ml ⁻¹)	Measured $S_2O_3^{2-}$ (mg ml ⁻¹)	pH
0			7.2
7			7.1
13		0.005	
18		0.002	
27		0.002	6.8
32	0.15	0.002	7.1
33		ND ¹	
35		0.357	6.9
39	0.30	ND	6.4
41		0.69	6.8
43		0.63	
47			6.4
48		ND	
66			6.0
67		ND	
75			6.5
81	0.30	ND	6.6
84		0.38	6.7
88	0.30	ND	6.5
92		0.34	6.7
98	0.60	ND	6.7
102		0.79	6.3
104		0.74	6.3
116	1.20	ND	
124		3.00	6.3
133		0.28	
145	2.10	ND	
154		6.30	5.9
158		2.80	5.9
165		1.00	6.1
179		ND	6.3

¹ ND = Not detectable

Table 10. pH and Eh values and thiosulfate of leachate from 5 columns of experiment #2.

<u>Day</u>	<u>pH</u>					<u>Eh (mv)</u>					<u>S₂O₃²⁻ Concentration (mg ml⁻¹)</u>				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
34	8.5	8.0	8.9	8.4	8.4	+256	+258	+249	+250	+271	0.38	0.04	12.00	8.40	8.40
62	8.5	8.0	8.7	8.8	8.5	+419	+453	+435	+414	+399	0.19	0.05	1.2	4.2	6.3

values were observed to remain stable; thiosulfate concentrations decreased after each addition of the reduced sulfur compound.

Experiment #2

Data collected from the series of 5 columns in experiment #2 (Table 10) showed that the pH stabilized between pH 8-9. The Eh increased with time. Thiosulfate concentrations diminished in all columns except #2 containing distilled water and panacide. The thiosulfate in columns #1 and #2 represent that which was leached out of the retorted shale. Less thiosulfate leached out of the material containing panacide (column #2).

Experiment #2 has produced very preliminary data. It can be noted from the data (Table 10), however, that as in Experiment #1, thiosulfate is being oxidized in the columns, but the pH remains alkaline. The increase in oxidized species is evident from the increasing Eh values. Little more can be concluded from existing data.

SUMMARY

From studies on the development of heterotrophic and autotrophic, thiosulfate-oxidizing bacteria in enrichment and selective media from 30 diverse oil shale samples it is clearly evident that potential exists for microbial thiosulfate oxidation and the concomittant side reactions of pH decline and possible pollutant solubilization. Column leaching studies currently underway will identify quantitatively the extent of acid production in selected retorted and raw oil shales and concomittant trace element mobilization. pH decrease in oil shale samples and leachates is clearly dependent on the chemistry. Acid-consuming material may in fact be present in some samples in such concentrations as to neutralize the acid produced by biological oxidation of thiosulfate. In other samples biological acid production may reduce alkalinity and in effect aid in restoration of water quality.

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PROGRESS REPORT 1980-81

Nutrient Effects on Microbial Mobilization of Arsenic from Retorted Oil Shale

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INTRODUCTION

Microorganisms are known to carry out important functions in the global cycles for arsenic (2, 5, 7, 8, 12, 14, 15). This metal is a common constituent of soils, plant materials, and higher organisms (4), and has been used in a wide range of industrial and agricultural applications. Oil shale is of particular environmental interest due to the higher levels of arsenic found in this material, with values in the range of 60 ug/gm having been reported (9). During the retorting process, the major portion of the arsenic found in shales appears to remain in the residual solid material and only minor amounts will be released to the retort waters (9). Managing the disposal and reclamation of retorted shale is of particular concern because of the possible release of this metal to the environment.

A critical factor in microbial mobilization of arsenic will be the availability of organic matter to serve as a carbon and energy source for microbial growth. Studies which have been completed to date in the Piceance Basin (11), where surface soil at varying depths has been placed over retorted shale, suggest that with plant growth into the surface soil-shale interface, organic matter release can result in increased microbial activity. This can provide an energy source which would allow microbial modification and solubilization of a wide range of environmental metals to take place, including arsenic.

Another source of organic substrates which can influence possible mobilization and solubilization of arsenic in retorted oil shales involves water movement into retorts after in situ or modified in situ processing. Under these conditions, large volumes of water from surrounding aquifers and surface sources which contain dissolved organic carbon may mix with retorted shale.

In either of these situations, the possible presence of organic matter with sufficient available moisture may lead to increased microbial activity and changes in the form and/or mobility of arsenic. Possible effects of microorganisms on the solubilization, oxidation, reduction, or alkylation of arsenic have been documented (1, 3, 5, 8, 12, 13, 15). Of particular interest for the development of this research is the documentation of specific nutrient addition effects on the mobilization and volatilization of arsenic. Cheng and Focht (3) showed that microorganisms in water-logged soils produced gaseous arsenial products from arsenate, arsenite, and mono- and di-methyl arsenate. These were only detectable when urea and glucose were added to soil slurries. The present studies were carried out

to provide information on possible effects of microbial growth in the presence of added nutrients on arsenic mobilization from retorted shale-soil mixtures, and to provide information on the usefulness of a KI/I₂ trapping system for monitoring arsenic volatilization from retorted oil shale.

METHODS

RETORTED SHALE AND SOIL

Retorted oil shale and soil samples were derived from materials placed in storage during the construction of the oil shale successional plots at the intensive study area in the Piceance Basin, supervised by the Range Science Department at Colorado State University. The soil and retorted shale were sieved through a 32 mesh screen prior to use in these experiments.

GLASSWARE AND IMPLEMENT PREPARATION

All sieves, spatulas and glassware used in these experiments were soaked in 10% analytical grade nitric acid for at least 16 hours and rinsed in deionized water until a neutral pH of the rinse water was obtained.

MOBILIZATION EXPERIMENT DESIGN

Soil and shale samples were mixed in the following manner: 5.0 g shale, 5.0 g shale plus 5.0 g soil, 5.0 g shale plus 100 mg soil, or 5.0 g soil, with 110 ml of sterile basal salt medium containing minerals for a 130 ml volume. Stock solutions of 10% w/v glucose and 1% w/v NH₄NO₃ were prepared and filter sterilized through 0.45 μ m membrane filters. The stock solutions plus sterile deionized water were added to a total volume of 20 ml to yield the following final concentrations: 0.8% w/v glucose, 0.1% w/v NH₄NO₃, and 0.8% w/v glucose plus 0.1% w/v NH₄NO₃. Sterile controls with 0.8% w/v glucose plus 0.1% w/v NH₄NO₃ and deionized water were also prepared and treated in the same manner as test samples.

All flasks were weighed and shaken at 200 rpm on a New Brunswick Gyro-rotary shaker at 25 C. Prior to analysis, the flasks were weighed and any water lost as a result of evaporation was replaced by the addition of sterile deionized water.

MICROORGANISM ENUMERATION

Fungi were enumerated using rose bengal agar plates consisting of 10.0 g of glucose, 5.0 g peptone, 1.0 g KH₂PO₄, 0.5 g MgSO₄·7H₂O, 0.033 g of rose bengal, 20.0 g of agar, and 1000 ml of deionized water. This medium was sterilized, and after cooling to 45 C, 3 ml of a streptomycin solution was added to the medium using the procedures of Martin (6).

The bacteria were enumerated with sodium caseinate agar which consisted of 1.0 g sodium caseinate, 1.0 g glucose, 0.2 g MgSO₄, 0.2 g K₂HPO₄, 0.1 g FeSO₄, 15.0 g agar, and 1000 ml of deionized water (10). The samples were diluted using phosphate buffer dilution blanks and plates were inoculated with 0.1 ml inocula and spread using an alcohol-flamed curved glass

rod. Plates were incubated for one week at 25 C. The fungi were counted on rose bengal agar and the bacteria were counted on the sodium caseinate medium. At the time of sampling, the pH values were measured using a Fisher Accumet pH meter with buffer standards of pH 7.0 and 9.0.

METAL SAMPLES AND ANALYSIS

For the analysis of metals in the supernatant solutions, at three week intervals, 30 ml of each slurry was centrifuged for 30 minutes at 10,000 rpm at 12 C. Using acid-washed pipettes, 20 ml of the supernatants were removed and placed in 30 ml Sybron/Nalgene bottles with 0.1 ml of 3X distilled HNO_3 . The HNO_3 was held in FEP Nalgene bottles presoaked for three days in 6N reagent grade HNO_3 . The samples were analyzed for arsenic levels by Dr. R. R. Meglen of the Environmental Trace Substances Laboratory, University of Colorado.

VOLATILE ARSENICAL TRAPPING SYSTEM

The trapping system used in this experiment was a modified version of the system used by Woolson (16). A single apparatus consisted of a 500 ml Erlenmeyer Flask connected to two 150 mm x 25 mm test tubes in series. The connections were made with glass and polyethylene tubing. Premoistened air or U.S.P. grade nitrogen was passed over the soil or shale in the flask and then bubbled through trapping solutions contained in the test tubes. Neoprene stoppers were used throughout since rubber has been reported to adsorb volatile arsenicals (5). All glassware was soaked in 10% analytical grade nitric acid and rinsed in deionized water before use.

VOLATILE ARSENICAL EXPERIMENT PREPARATION

Low pH soil, retorted oil shale, and dimethylarsinic acid (DMA) were mixed in 500 ml flasks in the following manner: 100.0 g soil plus 2.94 mg DMA, 100.0 g shale plus 2.94 mg DMA, or 100.0 g shale without DMA. All flasks were amended with 6.0 g of soybean meal as a microbiological nutrient source and adjusted to approximately 0.3 bar water tension with 34.0 ml of deionized water. Duplicate flasks were prepared for each variable.

Volatile arsenicals were trapped in 20 ml of an 0.01 N KI solution contained in each of the test tubes. The trapping solutions were kept at equilibrium by the periodic addition of solid I_2 .

All flasks were weighed and incubated without shaking at 23 C in the light. One set of flasks was incubated anaerobically by continual flushing with U.S.P. grade nitrogen at a flow rate of approximately 35 ml per minute. A second set of flasks was incubated aerobically by continual flushing with air at an equivalent flow rate. Periodically, the flasks were weighed and any water lost as a result of evaporation was replaced with deionized water.

At three week intervals the trapping solutions were collected in 30 ml Sybron/Nalgene PP bottles and held at 12 C until arsenic analysis was completed by Dr. R. R. Meglen of the Environmental Trace Substances Laboratory, University of Colorado.

RESULTS

SUPERNATANT ARSENICAL EXPERIMENTS

Based on previous studies which suggested that nutrient additions and microbial growth could influence supernatant arsenic levels, additional experiments were completed in which specific carbon and/or nitrogen sources (glucose and ammonium ion) were added. These experiments were also carried out to determine if retorted shale is able to serve as a carbon or nitrogen source if other nutrients are not limiting microbial growth.

The responses of the bacteria and fungi to nutrient additions are shown in Figure 1. Retorted shale, to some extent, appears able to serve as a source of nitrogen, but this material apparently is an extremely poor source of carbon for the support of microbial growth. With added nitrogen in the form of NH_4NO_3 , essentially no increases in viable counts were observed in comparison with the controls. However, as noted in the previous report, this material appears to serve to some degree as a nitrogen source, as microbial increases did occur after glucose additions. With the addition of both glucose and NH_4NO_3 , bacterial populations increased to 10^8 - 10^9 /ml, indicating that nitrogen was limiting microbial growth with added 0.8% w/v glucose. Similar results were observed when 100 mg of soil was present with 5.0 g of retorted shale.

The microbial responses to similar amendments with a 5.0 g shale plus 5.0 g soil mixture are shown in Figure 2. Under these conditions, the soil served as a source of nitrogen to supplement the nitrogen deficiency in retorted shale created by the addition of 0.8% w/v glucose (Figure 2). Bacterial populations of the glucose-amended slurries increased to the level of the populations in the glucose plus NH_4NO_3 -amended slurries. The soil constituents may have helped to relieve the carbon deficiency in the retorted shale to some extent, although only a small increase in the viable population of the NH_4NO_3 -amended slurries occurred in comparison with the controls.

The pH values for the retorted shale slurries also changed in response to those amendments (Figure 3). In the control and nutrient-amended slurries, sharp increases to higher pH values occurred during the first three weeks of incubation. These slurries continued to show gradual increases in pH up to twelve weeks. The glucose plus NH_4NO_3 -amended slurries also had an overall trend of increasing pH, although the rate was variable in some cases. An interesting pH trend was noted with the NH_4NO_3 amendments. After an initial increase to 8.0, the pH steadily dropped to 6.7 at the end of twelve weeks. This change can best be explained by the growth of nitrifying bacteria, which oxidize ammonium ion to nitrate with the loss of protons, in a carbon-limited system. Similar pH trends were seen in slurries with 5.0 g shale plus 100 mg soil and 5.0 g shale plus 5.0 g soil, as noted in Figures 4 and 5. However, the decreases observed in pH values of nitrogen-amended shale slurries were not seen in the soil slurries. This is consistent with the hypothesis that the soil used can to some extent serve as a carbon source resulting in a decrease in the rate of nitrification.

Figure 1. The effects of glucose and/or ammonium ion additions on bacterial and fungal viable populations in a 5.0 g re-torted oil shale slurry.

Figure 2. The effects of glucose and/or ammonium ion additions on bacterial and fungal viable populations in a 5.0 g re-torted oil shale plus 5.0 g soil slurry.

Figure 3. The effects of added glucose and/or ammonium ion additions on pH in 5.0 g retorted oil shale slurries.

Figure 4. The effects of added glucose and/or ammonium ion additions on pH in 5.0 g retorted oil shale plus 100 mg soil slurries.

Figure 5. The effects of added glucose and/or ammonium ion additions on pH in 5.0 g retorted oil shale plus 5.0 g soil slurries.

The supernatant arsenic values for 5.0 g shale plus 100 mg soil slurries indicate that the highest arsenic levels, 0.47 ug/ml and 0.64 ug/ml were found in control and nitrogen-amended slurries, respectively (Figure 6). Interestingly, these conditions also resulted in the least amount of bacterial and fungal growth. Glucose and glucose plus NH_4NO_3 -amended slurries contained the largest viable populations, but the lowest supernatant arsenic levels with 0.44 ug/ml and 0.1 ug/ml being detected, respectively. Similar relationships were found with the 5.0 g shale and 5.0 g shale plus 5.0 g soil slurries (Figures 7 and 8). These trends indicate that arsenic may be immobilized by increases of bacterial and fungal biomass. This immobilization could occur by many different mechanisms, but is most likely caused by adsorption to biomass or biological transformation, which might result in a loss of arsenic by volatilization.

It was not possible to establish a relationship between pH shifts and supernatant arsenic levels. However, for shale and shale plus soil slurries, supernatant arsenic levels exceeding 0.45 ug/ml were found in slurries amended with NH_4NO_3 and having pH values of less than 8.1.

The Piceance Basin soil used in this experiment appears to be extremely low in arsenic. Less than 0.02 ug/ml of supernatant arsenic was found in soil slurries, suggesting that the surface soil is not a major contributor of this metal to the environment.

VOLATILE ARSENICAL EXPERIMENTS

The amounts of volatile arsenicals trapped over a three week time period are shown in figure 9. Volatile arsenic compounds were detected at levels of 7.2 ug/100 g soil and 7.0 ug/100 g shale after only one week of aerobic incubation with added DMA. No arsenic above detection limits was recovered from anaerobic systems or systems without added DMA at one week.

By three weeks of incubation, the aerobic soil system with added DMA had lost 81.0 ug As/100 g soil, while the corresponding system with shale lost nearly double that amount, possibly indicating that the high pH values associated with retorted shale may be more favorable to arsenic volatilization than lower pH values. The anaerobic shale system with added DMA lost 3.4 ug As/100 g shale, far less than found under aerobic conditions. This finding is consistent with that of Woolson (16) who found that volatilization occurred much more slowly with anaerobic conditions. Of special interest was the observation that by three weeks, the aerobic shale system without added DMA had lost by volatilization 2.8 ug As/100 g shale.

The primary trapping solutions were found to contain all of the volatilized arsenic, whereas the secondary trapping solutions contained less than detectable levels of arsenic. This seems to indicate that the trapping efficiency of this system is acceptable, although the exact efficiency has not yet been determined.

These results suggest that measurable amounts of arsenic can be mobilized, with a relatively greater amount released in supernatant rather than in volatile forms. There is some indication that microbial growth in the presence of more optimal growth substrates can also lead to arsenic immobilization and decreased levels of supernatant arsenic in these shale-soil mixtures.

Figure 6. The effects of added glucose and/or ammonium ion additions on supernatant arsenic levels in 5.0 g retorted oil shale plus 100 mg soil slurries. $\sigma = 0.020$ ug/ml.

Figure 7. The effects of added glucose and/or ammonium ion additions on supernatant arsenic levels in 5.0 g retorted shale slurries. $\sigma = 0.020$ ug/ml.

Figure 8. The effects of added glucose and/or ammonium ion additions on supernatant arsenic levels in 5.0 g retorted oil shale plus 5.0 g soil slurries $\sigma = 0.020$ $\mu\text{g/ml}$.

Figure 9. The amounts of volatilized arsenic recovered from aerobic retorted oil shale and soil systems.

DISCUSSION

Based on results obtained to date, it appears that with nutrient additions and subsequent microbial growth, changes in arsenic mobilization can occur involving both volatile and supernatant forms.

The following observations have been made concerning microbial arsenic mobilization processes:

- With carbon (glucose) additions to shales, some increases in microbial populations occurred, suggesting that retorted shale, to a limited extent, was able to serve as a nitrogen source for microbial growth.
- With nitrogen additions, no major increases in microbial populations occurred indicating that retorted shale is a particularly poor source of carbon for microbial growth.
- High supernatant arsenic levels appear to be related to low levels of bacterial and fungal biomass as seen in control and nitrogen-amended slurries.
- The trapping and analysis methods employed appear to be satisfactory for monitoring the release of volatile arsenicals from soil and retorted shale samples.
- Under aerobic and anaerobic conditions, microbial growth on retorted shale with added DMA and nutrients can lead to the release of arsenic forms at levels of 152.0 ug/100 g shale and 7.0 ug/100 g shale after three weeks, respectively.
- With aerobic conditions and nutrient amendments to retorted shale without added DMA, release of volatile arsenic forms at levels of 2.8 ug/100 g shale has been detected after three weeks. These results suggest that in the presence of organic substances, either as a result of plant growth or surface water penetration into abandoned retorts, arsenic volatilization may be able to take place.

The objective of the work which is planned in the next research period is to more fully define the effects of varied environmental conditions on these processes, to make it possible to more effectively mitigate and manage such possible arsenic releases to the environment.

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PROGRESS REPORT 1980-1981

Adsorption of Mercury by Soils from Oil Shale Development Areas in the Piceance Creek Basin of Western Colorado

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INTRODUCTION

BACKGROUND

The anticipation of an oil shale industry in Colorado, Utah, and Wyoming has generated considerable interest and concern for the potential environmental impact which may result from extraction of shale oil. As a result of this concern, baseline studies of various types are being carried out by several groups including the tract lessees and university groups. These baseline determinations must precede studies dealing with the changes in distribution of elements and compounds resulting from energy resource development.

Based on geologic and geochemical conditions of formation of the oil shale, some predictive capability as to which elements are likely to be of environmental concern can be made. Those elements which are toxic to plants and animals and mobile as anions under alkaline conditions are a potential hazard. The trace elements As, B, F, Mo, Se are of prime concern, although additional elements have been analyzed in many of the samples. Elements which are volatile under the reducing conditions of retorting are also a potential hazard, and include Hg and to a lesser extent Zn and Cd. Arsenic, Se and F which are mobile under alkaline conditions are also volatile under certain reducing conditions.

PREVIOUS ACCOMPLISHMENTS

Initial funding by the Colorado Energy Research Institute, ERDA, and cooperation with the U.S. Geological Survey, enabled studies by Ringrose and others (1), McNeal and others (2), Ringrose (3), Klusman and Ringrose (4), and Dean and others (5). These studies have provided considerable useful data on the occurrence of trace elements in soils and stream sediments in reconnaissance work over the entire Piceance Creek Basin. The regional studies have enabled the proper planning of studies funded by DOE which have focused on areas of prime potential for development. With this information, a sampling plan was developed for surficial materials on Tract C-a by Candito (6), Candito and Klusman (7), Tract C-b by Zuccaro (8), and the Anvil Points area by Rutherford (9). Segments of all of these studies are incorporated into a manual for sampling design in environmental studies for the oil shale region (10).

More recently, Tuttle (11) is nearing completion of a study under U.S. Geological Survey sponsorship to verify the sampling design methods used by

Ringrose and others (1) and to add more information. The Ringrose and others (1) study only considered total composition of soils. Tuttle (11), in a completely independent sampling, determined total soil composition for selected elements, available concentrations of the same elements, and concentrations in two common plant species.

PRESENT RESEARCH

Due to the reducing conditions and elevated temperatures experienced during the retorting of oil shale, the volatilization and dispersion of metallic Hg vapor is greatly facilitated. Previous work by Fox and others (12) have confirmed extensive loss of Hg vapor during experimental retorting. Mercury in the atmosphere and possible sorption of metallic Hg vapor by soils surrounding oil shale facilities is therefore of great concern in regard to the potential environmental impact it poses.

The areas of interest in this study are those in Western Colorado, within the Piceance Creek Basin, which are currently undergoing construction of retort facilities. Surface soil samples were collected from locations on oil shale Tracts C-a, C-b and near Anvil Points. (Figure 1).

Brown (13) is evaluating the trace element composition of stream sediments from the eastern Uinta Basin, Utah, which will provide data analogous to that developed by Ringrose (3) for the Piceance Basin.

OBJECTIVES

The objectives of the study are:

- 1) To investigate the extent of Hg adsorption and desorption by these soils, and to identify the parameters affecting Hg adsorption.
- 2) Determine whether cultivated soils in the Piceance Creek Basin have chemical characteristics different from those of the uncultivated soils at baseline composition.
- 3) Collect and analyze predevelopment baseline stream sediment samples from the eastern portion of the Uinta Basin in Utah. The Utah oil shale area is the prime area for horizontal in situ experimentation outlined in the Oil Shale RD & D Program as well as the location of several other sites likely to undergo development.

MATERIALS AND METHODS

MERCURY ADSORPTION

Six representative surface soils were collected from non-cultivated sites on Tracts C-a, C-b, and the vicinity of Anvil Points (Rutherford, unpublished work). The samples were collected from the top 5cm, air dried, and sieved to -80 mesh. The -80 mesh fraction is the fine fraction which normally will have

Figure 1. Location of Piceance Basin prototype oil shale development sites. Tract C-a, C-b and Anvil Points.

the highest adsorptive capacity. The Anvil Points soils were both collected from areas east of the experimental retorting facility and on Wasatch Formation parent material. At these three locations, a soil was collected from a ridge top with pinion-juniper cover and a soil from a sage-covered valley floor. The textural differences in the soils and dominant vegetation cover between ridges and valleys suggested chemical and physical characteristics may be different. Gross chemical differences were not found by Ringrose and others (1) but Barth (14) found substantial differences in soluble constituents, apparently caused by vegetation development.

A wide variety of determinations were made on the soils in order to characterize their physical and chemical properties. Determinations include; soil pH (1:2 soil:water), cation-exchange-capacity (1N NaOAc (15)) and organic carbon (Walkley-Black wet oxidation). Iron and manganese oxides were determined using a partial extraction (ammonium oxalate $(\text{NH}_4)_2 \text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, pH 3-4). Surface areas (B.E.T.- N_2) and clay mineralogy (x-ray diffraction, glycol-treated) were also determined. Soluble anions (distilled H_2O leach) and total elemental analysis of the soils was determined by inductively-coupled plasma spectrometry.

Mercury soil concentrations > 1 ppm were analyzed by flameless atomic adsorption spectrometry after digestion with 5:1 $\text{HNO}_3:\text{HClO}_4$ for 2 hrs at 75°C (Hatch and Ott (16)). Samples with Hg concentrations < 1 ppm were analyzed using the Jerome Model 301 Au film mercury detector. Samples for the background Hg concentration study were collected in a similar manner and analyzed using the Jerome Instrument.

Approximately 1 gram portions of air-dried soil were placed in 5 mm diameter glass vials. This resulted in a soil layer in the bottom of the vial approximately one centimeter deep. A total of 1080 samples were prepared, enough to allow triplicate analyses of ridge and valley soils from each of the study areas over 12 distinct periods of Hg vapor exposure. A total of 216 vials, 36 ridge and 36 valley samples from Tracts C-a, C-b and Anvil Points, respectively, were supported by a styrofoam holder and placed into a tupperware container. Five containers were employed, two containing elemental Hg^0 , two containing the red HgO , one each for lab and field exposure conditions. The field conditions are similar to those which might be found on the Roan Plateau in the Piceance Creek area. The fifth container was not exposed to mercury and served as a control series. The containers were then closed until samples were taken for analysis. The soils are exposed to ambient temperature and humidity and the Hg vapor pressure of either Hg^0 or HgO .

Those samples experiencing lab exposure were subjected to temperatures ranging from 20°C - 30°C . No attempt was made to regulate the meteorological variations (i.e. temperature, humidity, barometric pressure, etc.) experienced by the field-exposed samples. The field-exposed samples experienced the normal daily and seasonal variations in meteorological conditions. Temperature, relative humidity, and barometric pressure were continuously recorded.

Samples were taken at 2, 5, 8, 11, and 13 month intervals for analyses of Hg adsorption. In addition, at the end of eight months of adsorption, three sets of field-exposed Hg^0 , HgO samples, and control samples were removed from

Hg exposure and allowed to undergo desorption under ambient field conditions. These samples were then analyzed at 1, 3, and 6 month intervals of desorption for elemental Hg concentrations.

CULTIVATED AND UNCULTIVATED SOILS

Ninety additional samples of soils were collected from alluvial valley in the Piceance and Yellow Creek drainage at 15 locations (Figure 2). At each location three soils were collected from an actively cultivated or recently cultivated field and three uncultivated soils on the slope immediately adjacent to the cultivated fields. The samples will be analyzed for the selected trace elements; Hg, Mo, B, F. Since trace element impact may be concentrated in valley floors by non-uniform atmospheric dispersion, the composition of these cultivated soils will be compared with baseline soil composition.

STREAM SEDIMENTS

Approximately 220 composite stream sediment samples were collected from the eastern portion of the Uinta Basin in Utah (Figure 3). The area includes all of the Utah sites for oil shale development likely to occur in the near to mid-term. The area includes Prototype Lease Tracts U-a and U-b, TOSCO properties, Westco properties, Geokinetics property, and Federal In-Situ Sites Nos. 7, 8, 9. The streams sampled include all those labeled in Figure 3, except Green River. The area includes the outcrop of the Parachute Creek Member (which contains the oil shale) of the Green River Formation and the area where the Parachute Creek Member is in the relatively shallow subsurface and commercially recoverable.

Each of the 16 named streams and their major tributaries included in Figure 3 was divided into one km segments. For most streams, this results in 30-150 segments. Ten segments were selected at random for smaller streams and 20 for the larger streams. A composited sample was collected from each of the randomly selected segments. The composite consists of at least ten grabs from the stream channel spread over the entire one km segment. This sampling scheme allows characterizing each individual drainage and outlines regional trends, while reducing the smallest scale variance which is not of interest in a regional study. The sample design allows adequate characterization of sediments in an area of approximately 2000 mi² utilizing only 220 samples and provides a data base for sound planning of local studies.

The composite sample consists of material sieved to -4 mesh during collection. The -4 mesh is a size that can be sieved wet if necessary, eliminates large pebbles, and will allow future mineralogical studies if deemed necessary. A split is sieved to -80 mesh in the field for Hg analysis. This smaller split is stored in a sealed vial to prevent Hg loss. The finer grain size is necessary so that the sample can be analyzed without grinding, which can cause Hg loss from the sample.

The 220 samples have been analyzed for B, F, Mo, organic carbon, and pH. The analysis of 50 randomly selected samples for Mn, Fe, Mg, Al, Ca, Ti, V, Sr, As, Cr, Zn, Pb, Cd, Ni, Co, Cu, and Ba has been completed by the

Figure 2.
Location Map for
Background Hg soil
study.

Figure 3. Streams in the eastern Uinta Basin selected for sediment sampling.

Project Central Analytical Facility at the University of Colorado. Mercury is yet to be determined at CSM. It is expected that the analysis and interpretation will be complete by December, 1981.

RESULTS AND DISCUSSION

MERCURY ADSORPTION

The chemical composition and physical characteristics of the six soils are summarized in Tables 1, 2, and 3. In successive tables of experimental data, the samples are labeled as follows; CaV - Tract C-a valley floor soil, CaR - Tract C-a ridge top soil, CbV - Tract C-b valley floor soil, CbR - Tract C-b ridge top soil, ApV - Anvil Points valley floor soil, ApR - Anvil Points ridge top soil. This data will be used in the interpretation of the Hg adsorption characteristics of the soils. The relative order of mercury adsorption by the soils over a 13 month period was $ApR > CaR > CbR > ApV > CaV > CbV$. In all the areas which were studied, the ridge-top soils were found to contain higher concentrations of elemental Hg⁰ than did the corresponding valley floor soils. Due to the topographic similarity of these soils, it was decided to group all ridge-top and all valley-floor soils together. Figure 4 represents the general trend which was observed. Mean Hg concentrations due to Hg⁰ exposure for ridge and valley soils are presented in Table 4. The data of Tables 1,2,3 represent the mean of a triplicate exposure and analysis.

Both types of Hg exposure (Hg⁰ and HgO) reflect this same pattern, namely ridge > valley in adsorbed Hg. However, Hg concentration levels in soils exposed to elemental Hg⁰ were considerably higher than those exposed to HgO (Figures 5 and 6). It has been assumed that the species which is being sorbed is elemental Hg⁰ vapor in both cases. A possible explanation for the observed differences in Hg concentrations between the forms of Hg exposure comes from a thermodynamic consideration. There is a substantial greater vapor pressure from the Hg⁰ species than from the HgO. Koksay and others (17) have also shown that sorption of HgO by soils is very unlikely.

Data obtained on the physical and chemical properties of these soils do not reflect significant differences in parameters such as organic carbon, pH, surface area, clay content or cation exchange capacity, to lend support to these variables as having a major role in controlling the Hg adsorption. The most significant factor appears to be the amount of amorphous material present in these soils (Table 1).

The relative amount of amorphous material between ridge and valley soils suggests considerable leaching of the ridge soils. Barth (14) has reported that differences in local vegetation in these areas play a significant role in altering the physical and chemical properties of soils. Pinon pines (Pinus edulis), which are common to the ridges in the Piceance Creek Basin, have an extensive leaching ability.

Results of the partial extraction of these soils employing ammonium oxalate, reflect a good correlation between reducible Fe and Mn oxides (Table 1) with the observed behavior of Hg adsorption. The correlation of Mn concentration is especially strong, and due to its scavenging properties,

TABLE 1. Chemical and Physical properties of soils from selected Western Colorado oil shale development sites.

Soil	pH	Organic Carbon %	Mean Back-ground Hg ppb	Cation Exchange Capacity meq/100g.	Fe ppm	Mn ppm	Surface m ² /g	*Clay wt %	*Amorphous %
CaV	7.65	1.90	28.7	9.95	33.5	6.55	3.7	9.5	13
CaR	7.77	2.48	34.2	13.54	39.6	15.3	3.3	8.0	20
CbV	7.71	1.89	27.5	11.26	5.60	3.78	3.3	19.0	16
CbR	7.93	1.90	29.2	12.05	9.94	13.5	3.5	4.5	22
ApV	7.85	1.17	33.2	8.73	78.1	13.4	11.5	14.8	8
ApR	7.18	1.16	16.5	6.89	50.7	22.0	8.7	3.5	16

*Values are semi quantitative weight percent estimates

TABLE 2. Water Soluble Anions (µg/ml)

Soil	Cl ⁻	Br ⁻	F ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₂ ⁻	NO ₃ ⁻
CaV	0.6	<1	<.25	1	3	0.5	7.4
CaR	0.3	<1	<.25	<1	<1	<.5	4.0
CbV	0.8	<1	<.25	1	<1	<.5	15.8
CbR	0.6	<1	<.25	1	<1	<.5	4.0
ApV	0.7	<1	<.25	1	<1	<.5	4.8
ApR	0.8	<1	<.25	1	<1	<.5	3.2

TABLE 3 Total Elemental Analysis for selected Western Colorado Soils
(ppm).

<u>µg/g</u>	<u>CaV</u>	<u>CaR</u>	<u>CbV</u>	<u>CbR</u>	<u>ApV</u>	<u>ApR</u>
Al	51800	65800	75900	58700	56600	47700
Ba	700	670	850	760	540	530
Ca	76900	10300	30400	76900	41400	8200
Co	7	<5	4	7	9	25
Cr	21	7	31	12	13	14
Fe	20400	24700	37600	25900	24100	32800
Mg	11500	6800	12400	10900	11100	4900
Mn	470	480	600	990	430	370
Na	21300	22800	41800	20500	12200	14200
Ni	56	52	88	67	81	23
Pb	20	<10	69	12	50	<10
Si	268000	323000	308000	281000	398000	391000
Sr	430	162	275	402	205	160
Ti	2400	3200	3800	3000	3100	3900
V	66	80	99	76	111	98

TABLE 4 Logarithm of mean Hg concentration (ppb) in adsorption
experiment of Ridge and Valley Soils.

Type	Exposure	2 months	5 months	8 months	11 months	13 months
Hg ⁰ lab	Ridge	4.83	5.84	6.07	6.04	6.77
	Valley	4.34	5.45	5.75	5.86	6.34
Hg ⁰ field	Ridge	3.32	3.42	4.12	5.28	5.17
	Valley	2.54	3.07	3.38	3.33	3.47
HgO lab	Ridge	3.33	3.29	3.54	3.48	3.71
	Valley	2.73	2.94	2.98	2.99	3.19
Hg ⁰ field	Ridge	2.47	2.71	2.81	.325	3.82
	Valley	1.90	2.17	2.83	3.11	3.30

TABLE 5 Logarithm of mean Hg concentration (ppb) in desorption
experiment of Ridge and Valley Soils.

<u>Type Experience</u>		<u>No desorption</u>	<u>1 month</u>	<u>3 months</u>	<u>6 months</u>
Hg ^o	Ridge	4.12	3.71	3.12	2.65
	Valley	3.38	2.92	2.71	2.39
— HgO	Ridge	2.81	2.82	2.53	2.31
	Valley	2.83	2.79	2.57	2.25

Figure 4. Adsorption of Hg by soils exposed to Hg vapor under laboratory conditions.

Figure 5. Adsorption of Hg by soils exposed to Hg vapor from elemental Hg and HgO under field conditions.

Figure 6. Adsorption of Hg by ridge-top soils exposed to Hg vapor from elemental Hg and HgO under laboratory conditions.

Figure 7. Desorption of Hg by ridge-top soils previously exposed to vapor from elemental Hg or HgO under field conditions.

appears to be largely responsible for the Hg adsorption. Reducible Fe and Mn oxides may be a significant portion of the amorphous component of the soils.

Data from the desorption study are presented in Table 5. Soils exposed to elemental Hg^0 were found to initially lose Hg at a faster rate than those exposed to HgO . However, after six months of desorption, both appear to be converging to a similar rate of Hg loss (Figure 7). These results lend support to the singular adsorption process, that of elemental Hg^0 . The greater initial loss of Hg from soils exposed to elemental Hg^0 vapor is thought to be due to a concentration phenomenon. These data are also derived from a triplicate desorption and analysis.

CULTIVATED AND UNCULTIVATED SOILS

Background Hg concentration data obtained from cultivated and non-cultivated soils are summarized in Table 6. A t-test was employed on this data to observe any statistical difference in the mean background Hg concentrations. Results obtained did in fact show that cultivated areas did indeed have a higher Hg background. The most plausible explanation seems to be the larger accumulation of organic matter in the cultivated soils. The other trace element data for these soils have not been adequately evaluated at this time.

TABLE 6 Data summary of cultivated vs non-cultivated soils

<u>Soil Type</u>	<u>Mean Hg ppb</u>	<u>Std. Dev.</u>	<u>Calculated t value</u>	<u>Degree of Freedom</u>	<u>t value $\alpha = .01$</u>
Cultivated	42.59	23.01			
			2.90	43	2.42
Non-Cultivated	31.73	12.00			

SUMMARY AND CONCLUSIONS

The soils studied show a high affinity for elemental Hg^0 . Under both types of exposure, Hg^0 and HgO , ridge-top soils were found to adsorb higher amounts of Hg vapor than did the valley-floor soils. Results from the physical and chemical studies reveal higher amounts of amorphous material in ridge-top soils. A strong correlation between reducible manganese oxides and adsorbed Hg was found to exist. This suggests that Mn-oxide coatings may be the controlling factor in the observed behavior of Hg^0 adsorption.

Results from this study indicate that Piceance Creek Basin soils will serve as one possible mechanism in the removal of atmospheric Hg vapor present in the off-gas of retorting facilities. However, further work is needed in the investigation of the atmospheric dispersion of Hg before its full environmental impact can be ascertained.

Data presented here on the background Hg concentration differences between cultivated and non-cultivated soils shows that significant differences do

exist. These results will aid in future environmental monitoring on the impact of the oil shale industry in these areas.

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CONCENTRATION OF CHEMICAL ELEMENTS IN PLANTS GROWING ON RETORTED OIL SHALES

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INTRODUCTION

During the past year we completed a second season of analyses investigating plant uptake of many elements as affected by depth of soil covering retorted oil shale. Data from the 1979 sampling season demonstrated that the potentially toxic elements (selenium, arsenic, lead, cobalt, and chromium) were not accumulated by the plants to any significant extent. Plant concentrations of boron were approaching phytotoxic levels but showed no effect of soil cover. Uptake of the nutrient elements (phosphorus, potassium, calcium, magnesium, zinc, iron, manganese, and copper) also showed no effects of soil cover. Some of the nutrient elements' concentrations appears to be very low, but data are not available which document the nutrient status of native plant species. Elevated levels of molybdenum were observed in several of the plant species, and molybdenum concentrations decreased with increasing soil cover. The copper-to-molybdenum ratio of the plants (a critical parameter for molybdenosis in grazing ruminants) was low, but increased with increasing soil cover. We felt a second year of sampling was necessary to observe trends in uptake by these plants as their roots began penetrating the shale beneath the soil.

OBJECTIVES

The purpose of our sampling and analyzing native plants growing on retorted oil shale was to determine the effects of the presence of retorted shale on the uptake of environmentally significant elements. This includes elements which are phytotoxins as well as elements which are toxic to grazing wildlife. By examining the native species for two consecutive years, it will be possible to observe trends in uptake as a function of time. This data will then allow us to evaluate the environmental hazards and fertility status of plants growing on retorted oil shale.

MATERIALS AND METHODS

SAMPLING SITE

The site sampled in 1979 was sampled in 1980. The revegetation site of Cook et al. (1), as shown in Figure 1, was sampled for native species from the intermediate fertilizer mixture in Panels 2 through 6. The soil covers are one foot (30.5 cm), two feet (61 cm), and three feet (91.5 cm) of topsoil over retorted (Paraho) shale. There is also a panel with two feet (61 cm) of soil plus one foot (30.5 cm) of gravel over retorted shale. To fill the need for a "control" plot, one panel consists only of subsoil.

PLANT SAMPLING

On July 1, 1980, six native plant species were sampled from the three replicates within each panel. The species sampled are listed in Table 1. Plants were not available on Panel 1 due to poor growth. Plants were cut with grass clippers and pruning shears and stored in coolers with dry ice. After being taken to Colorado State University, the plants were washed using the following procedure: 1) soaked for 1 to 2 minutes in distilled water; 2) washed in phosphate-free soap solution; 3) rinsed in distilled water; 4) soaked for 30 seconds in dilute HCl; 5) rinsed twice in distilled-deionized water. The sampling in Piceance Basin was performed in a driving rainstorm, and the plant samples were somewhat muddy. As a result, the washing solutions needed to be changed after every 6 samples. This procedure removed all superficial "dirt", and not soil particles were observed in the final rinse.

The washed samples were dried in a forced-air oven at 70°C for 48 hours and ground in a stainless steel mill to pass a 20-mesh sieve.

Table 1. Common and scientific names of plants analyzed in this study.

Common Name	Scientific Name
Indian ricegrass	<i>Oryzopsis hymenoides</i>
Fourwing saltbush	<i>Atriplex canescens</i>
Western wheatgrass	<i>Agropyron smithii</i>
Sherman's big bluegrass	<i>Poa ampla</i>
Utah sweetvetch	<i>Hedysarum boreale utahensis</i>
Winterfat	<i>Ceratoides lanata</i>

Figure 1. Profile configuration for retorted shale successional study Paraho retorted shale.

PLANT ANALYSIS

Dried, ground plant material was digested for ICP-OES analysis using the following procedure: 2.0 g of plant material was placed in a 75 ml digestion tube. Ten milliliters of HNO_3 was added, and the plants were allowed to predigest overnight. Five milliliters of HNO_3 was then added to help break up the partially decomposed plant material. The tubes were placed in a block digester and the temperature kept at 90°C for one hour. The temperature was increased to 130°C and maintained for another three hours. By this time the volumes of the samples were about 50% of their original 15 ml. The tubes were removed from the block, cooled, diluted to 12.5 ml with concentrated HNO_3 , and diluted to a final volume of 50 ml with distilled water.

The above nitric acid digestion procedure was recommended by the CSU Soil Testing Laboratory. Although it is recognized that this is only a partial digestion, the temperature encountered in ICP-OES analysis should be great enough to destroy partially digested organics in the solution. To ensure that the digestion and analytical methods were yielding proper results, NBS standard plant materials were included. The elemental concentrations reported by the Soil Testing Laboratory agreed quite well with NBS values for all elements except for iron and aluminum. The values for these elements were 30-50% lower than the values reported by NBS. It has been postulated that some of the iron and aluminum is incorporated in the remaining silica fraction of the digest. This digestion procedure is, therefore, quite satisfactory for all elements except iron, aluminum, and possibly titanium. If these three elements are critical in a given plant analysis, the nitric acid digestion procedure is not recommended. To overcome this, the data reported within for aluminum, iron, and titanium come from nitric-perchloric-sulfuric digests analyzed by Bob Meglen. Meglen had much better agreement for these elements in NBS digests than did the CSU Soil Testing Laboratory.

As will be seen in the Results and Discussion section, the problems encountered in the analysis for iron, aluminum, and titanium were greatly overshadowed by this year's findings.

DATA ANALYSIS

The data for 1980 was statistically analyzed as a split-plot factorial design. The statistical program STAT 41V programmed into a CYBER computer assisted in the numerical analysis. For all elements, a significant soil treatment x plant species interaction was observed. Therefore, we were able to compare the three-replicate means within each panel for a given species. The means were broken into nonsignificant groups using Bayes-LSD (2). Copper-to-molybdenum ratios were computed and the mean ratios were compared.

The combined data for 1979 and 1980 were also statistically analyzed. Sampling year was analyzed as a separate treatment. Only the results for those elements which showed significant soil treatment x plant species x year interactions were discussed in this report. The three-replicate means were broken into nonsignificant groups using Bayes-LSD. Elements whose concentrations showed non-significant three-way interactions showed little variance in concentration from 1979 to 1980.

RESULTS AND DISCUSSION

Several elements discussed in 1979 were not analyzed in 1980. Cobalt, cadmium, lead, and fluorine were below detection limits in 1979 and were not being accumulated above 5 ppm in the plants. These elements were not pursued in 1980. Mercury, arsenic, and selenium were also not analyzed in 1980 because of the prohibitive expense required for the detection of these elements. The concentrations of mercury, arsenic, and selenium were within detection limits in 1979, as detected by vapor and hydride methods; however, all levels were well below concentrations which provide environmental hazards. The exclusion of these elements from this year's discussion should not suppress any pertinent data. It is recommended that mercury, arsenic, and selenium be monitored in the future at least on an intermittent basis.

MACROELEMENTS

In this section, calcium, magnesium, phosphorus, potassium, and sodium concentrations will be discussed. Figures 2 through 6 illustrate the plant concentrations of these elements as affected by soil depth for 1980. Although there are significant differences between species, there are no observable trends in relation to soil depth. These elements are important plant nutrients. By analyzing the native plant species for these elements we can estimate the fertility status of the plants and observe trends over the two years' samplings. The mean concentrations and ranges for calcium, magnesium, phosphorus, potassium, and sodium for 1980 are listed in Table 2. Typical concentrations for similar native species (as reported in the literature) are also in Table 2 for comparison. Allowing for environmental differences, the levels of uptake for 1980 are very similar to the literature values. Although little or no data have been published on the critical concentrations of these elements as related to plant fertility, the levels we have observed in the revegetation plants would be well within the "sufficient" range for similar cultivated plants (5). This is consistent with visual observations on the growing plants.

The statistical analysis of the combined data for 1979 and 1980 showed significant differences between years for phosphorus, potassium, and magnesium. A difference between years is considered significant

CALCIUM

Figure 2. Calcium concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 0.27%.

MAGNESIUM

Figure 3. Magnesium concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 0.22%.

PHOSPHOROUS

Figure 4. Phosphorus concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 0.062%.

POTASSIUM

Figure 5. Potassium concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 0.72%.

SODIUM

Figure 6. Sodium concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 0.029%.

Table 2. Means and ranges of concentrations of calcium, magnesium, phosphorus, potassium and sodium for various plant types. Numbers listed in the source column refer to the numbers given in the Literature Cited section.

Element	Plant Type	Mean	Range	Reference
		%	%	
Ca	grass	0.23	0.16 -0.35	3
		0.23	0.11 -0.40	this work
	forb	1.84	0.50 -5.33	3
		0.84	0.54 -1.28	this work
	shrub	1.24	0.54 -1.71	4
		0.66	0.46 -1.30	this work
Mg	grass	0.11	0.08 -0.17	3
		0.12	0.09 -0.16	this work
P	grass	0.08	0.04 -0.17	3
		0.13	0.08 -0.17	this work
	forb	0.20	0.12 -0.51	4
		0.11	0.07 -0.16	this work
	shrub	0.20	0.12 -0.29	4
		0.13	0.05 -0.24	this work
K	grass	1.20	0.72 -1.60	3
		1.21	0.78 -2.03	this work
	forb	3.92	1.28 -5.85	4
		1.20	0.70 -1.69	this work
	shrub	1.77	1.38 -2.64	4
		2.91	1.81 -3.97	this work
Na	grass	0.003	0.000-0.014	4
		0.008	0.003-0.046	this work
	forb	0.019	0.000-0.124	4
		0.058	0.005-0.020	this work
	shrub	0.008	0.000-0.028	4
		0.016	0.007-0.030	this work

when one obtains a significant F value at the 5% level for the year x panel x species interaction term in the analysis of variance table. Figures 7 through 9 show a definite decrease in some of the plant concentrations for magnesium, phosphorus, and potassium in going from 1979 to 1980. Fourwing saltbush, winterfat, and to some extent Utah sweetvetch show this decrease. The concentrations in the grasses remain essentially constant from one year to the next, which indicates that the decreases in concentrations seen in fourwing saltbush and winterfat cannot be explained by changes in soil-availability of these elements. More likely, we are observing a dilution effect within the plant as the shrubs and forbs continue to grow from one year to the next. Similar decreases in concentration were observed for calcium and sodium, but the decreases were smaller and not statistically significant.

MICROELEMENTS

In this section plant nutrient elements (zinc, iron, manganese, and copper) are discussed. Nonnutrients (aluminum and titanium) are included, but nutrients molybdenum and boron are discussed in the Toxic Elements section. The concentration data for zinc, iron, manganese, copper, and aluminum are plotted in Figures 10 and 14. As with the macroelements, no real trends are observed with soil cover. The concentration values are compared with values in the literature for similar species growing under similar circumstances (Table 3). The iron and copper values for the 1980 sampling agree very well with values in the literature. Manganese concentrations for our study are approximately twice those found in the literature, but still an order of magnitude below toxic levels (5). Our zinc values are much less than literature values and are approaching values of zinc deficiency for cultivated plants (5). However, there are no visual symptoms of zinc deficiency. Figures 15 and 16 illustrate the changes in manganese and iron concentrations between 1979 and 1980. The trend for manganese is similar to that for the macroelements-manganese concentrations decrease between 1979 and 1980 for winterfat and fourwing saltbush but remain constant for the other plants. Thus, even if manganese concentrations in winterfat and fourwing saltbush were near phytotoxic levels, the passage of time tends to lower these concentrations.

Figure 16 shows the radical changes in iron concentrations with time. Without exception, iron concentrations have increased between 1979 and 1980. There are two explanations for this observation. First, we may assume that iron, unlike the other nutrient elements, actually increased in concentration between years. Table 3 supports this idea by showing that other researchers have found similar concentrations of iron in native species. The second explanation is soil contamination. Most soils have a total iron content of approximately 3%. The presence of only 0.01 g of soil per gram of plant material will introduce 300 ppm Fe contamination. As we mentioned in the Methods section, we were forced to sample the plants under very muddy conditions. Although the samples were washed,

MAGNESIUM

Figure 7. Magnesium concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 0.183%. Unshaded bars are 1979 and shaded are 1980.

PHOSPHOROUS

Figure 8. Phosphorus concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 0.070%. Unshaded bars are 1979, shaded bars are 1980.

POTASSIUM

Figure 9. Potassium concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 0.494%. Ushaded bars are 1979, unshaded bars are 1980.

ZINC

Figure 10. Zinc concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 5.80 ppm.

IRON

Figure 11. Iron concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 173 ppm.

MANGANESE

Figure 12. Manganese concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 27.3 ppm.

COPPER

Figure 13. Copper concentrations in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 1.82 ppm.

ALUMINUM

Figure 14. Aluminum concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 171 ppm.

Table 3. Means and ranges of concentrations of zinc, iron, manganese, aluminum, and copper for various plant types. Numbers listed in the source column refer to the number given in the Literature Cited section.

Element	Plant Type	Mean	Range	Reference
		ppm	ppm	
Zn	grass	26	18 - 32	3
		15.8	8.5- 23.9	6
		8.5	5.9- 10.9	this work
	shrub	17	12 - 22	7
		25.1	12.0- 41.0	this work
Fe	grass	290	120 -740	3
		305	80 -802	6
		164	53 -930	this work
	shrub	200	100 -300	7
		75	47 -169	this work
Mn	grass	38	19 - 60	6
		39	23 -140	3
		70	21 -152	this work
	shrub	32	27 - 39	7
		85	43 -183	this work
Al	grass	1100	410 -3700	3
		163	35 -930	this work
	shrub	645	330 -960	7
		68	41 -147	this work
Cu	grass	3.9	0.8- 5.4	6
		3.2	1.6- 5.9	3
		3.4	1.0- 5.4	this work
	shrub	8.2	6.5- 10.0	7
		6.4	3.9- 10.2	this work
	legume	7.3	6.0- 9.0	8
		5.1	4.2- 6.4	this work

MANGANESE

Figure 15. Manganese concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 36.4 ppm. Unshaded bars are 1979, shaded bars are 1980.

IRON

Figure 16. Iron concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil, 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 121 ppm. Unshaded bars are 1979, shaded bars are 1980.

contamination on such a small scale remains possible. Careful scrutiny of the publications in Table 3 reveals that their plants were not washed at all.

If one compares aluminum and iron concentrations for 1980 (Figures 11 and 14), one sees that the concentrations are nearly identical. To pursue the possibility of contamination of the plant samples with soil, regressions were run to compare apparent plant concentrations of elements present in the soil in high concentrations - aluminum, iron, and titanium. The combination of high soil concentrations and normally low plant concentrations makes aluminum, titanium, and iron excellent indicators of contamination. Table 4 shows the results of the regression analysis. Note the high r^2 values (0.99). There is no prior evidence that plant uptake of aluminum, iron, and titanium are so closely linked, especially at such high concentrations. Lindsay (9) and Brady (10) reported that average ratios for Al:Fe:Ti in the soil are about 15:7:1. This is consistent with the slopes of the regression lines which have ratios of 11:8:1. We must assume that the increases in iron concentrations are due to soil contamination.

Although the above discussion has diverged somewhat from the theme of this report, we are trying to emphasize that soil contamination is easy to encounter, hard to avoid, but possible to detect by monitoring the proper plant constituents.

Table 4. Results of regression analyses for plant concentrations of iron, aluminum, and titanium.

Regression	Slope	Intercept	r^2
Al vs Fe	0.763	-8.87	0.99
Fe vs Ti	0.116	-2.40	0.99
Al vs. Ti	0.088	-3.59	0.99

POTENTIALLY TOXIC ELEMENTS

This section deals with elements which are potentially harmful either to plants or grazing wildlife. Boron, molybdenum, and the copper-to-molybdenum ratio are discussed. As mentioned at the beginning of the Results and Discussion, cobalt, cadmium, lead, selenium, arsenic, fluorine, and mercury will not be discussed this year.

Boron plays a dual role for plants. Boron is an essential element and needed in concentrations of 5 to 15 ppm to maintain proper plant growth (5). However, if plant concentrations become

too high, boron can be phytotoxic. The concentration needed varies from approximately fifty to several thousand parts per million depending on the plant. The work of Klusman (11) and Runnells et al. (12) has indicated that boron is a potential problem in the revegetation of retorted shale. Figure 17 represents the plant concentrations of boron in 1980 as a function of soil treatment. All plants were in the 10 to 60 ppm boron range which is similar to concentrations in plants in the surrounding regions (11). These concentrations are also similar to those found by other researchers (Table 5). Since the boron concentrations in our plants remained unchanged from 1979 to 1980, boron does not appear to be a problem in this study.

Plant concentrations for molybdenum in 1980 are given in Figure 18. This figure shows a significant decrease in molybdenum concentrations with soil depth for winterfat and Utah sweetvetch and similar, nonsignificant trends for the other four plant species. Molybdenum can become toxic to grazing animals if the plant concentration exceeds 5 ppm (13) or 2 ppm under the proper circumstances (14, 15). Figure 18 indicates that all plants growing on the one-foot soil cover have the potential of inducing molybdenosis and that this potential decreases with increasing soil depth. Only small differences in molybdenum concentrations were observed between 1979 and 1980.

Some researchers believe that it is not the concentration of molybdenum alone which induces molybdenosis, but the ratio of copper-to-molybdenum (8). Ratios of copper-to-molybdenum above 5:1 are considered safe, and ratios below 2:1 will likely cause molybdenosis symptoms to develop. With this in mind, Figure 19 was constructed. The dotted line represents the critical ratio of 2:1. At a soil depth of one foot, all plants show a copper-to-molybdenum ratio less than 2:1. Only in the grasses does increasing soil cover increase the ratio significantly above two. For Utah sweetvetch, increasing soil cover has no effect on the copper-to-molybdenum ratio.

Figure 20 shows the changes in the copper-to-molybdenum ratios from 1979 to 1980. The overall trend is the ratio decreasing, and in many cases this decrease is statistically significant. The passage of time is not improving the situation, but making it worse. In 1979, a three-foot soil cover was adequate to maintain a safe copper-to-molybdenum ratio for all plants except Utah sweetvetch. This was not true for any plants in 1980. This is a serious situation which deserves careful consideration and periodic monitoring in the future.

BORON

Figure 17. Boron concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 9.19 ppm.

Table 5. Means and ranges of concentrations of boron and molybdenum and the copper:molybdenum ratios for various plant types. Numbers listed in the source column refer to the number given in the Literature Cited section.

Element	Plant Type	Mean	Range	Reference
		ppm	ppm	
B	grass	17	11 -48	3
		12	6 -25	this work
	shrub	22	18 -24	7
		28	17 -46	this work
Mo	grass	0.43	0.39- 0.84	3
		1.46	0.1 - 4.5	this work
	shrub	0.60	0.45- 0.90	7
		4.20	1.20- 9.0	this work
	legume	7.0	3.0 -13.0	8
		15.0	3.0 -38.0	this work
Cu:Mo	legume	1.44	0.6 - 2.4	8
		0.65	0.1 - 1.6	this work

MOLYBDENUM

Figure 18. Molybdenum concentration in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 4.91 ppm.

COPPER TO MOLYBDENUM

Figure 19. Copper-to-molybdenum ratio in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 gravel; S is subsoil. Bayes LSD = 3.6.

COPPER TO MOLYBDENUM

Figure 20. Copper-to-molybdenum ratio in the plants as a function of treatment: 1 is 30.5 cm soil; 2 is 61 cm soil; 3 is 91.5 cm soil; 2G is 61 cm of soil plus 30.5 cm gravel; S is subsoil. Bayes LSD = 3.2. Unshaded bars are 1979, shaded bars are 1980.

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EFFECT OF BORON ON PLANTS GROWING IN RETORTED OIL SHALE

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BACKGROUND

Elevated levels of several trace elements have been found in both retorted oil shale and plants growing thereon. Boron (B) and molybdenum (Mo) are of particular concern in this respect. Available B levels appear to be high enough to pose problems in establishing plants on retorted shale sites, while excessive uptake of Mo by plants may reduce the quality of forage and impose hazards to grazing livestock (Kilkelly, 1979).

A greenhouse study was set up to investigate the uptake of B and subsequent yield of plants growing on direct retorted Paraho shale to which various levels of B were added. Another study was undertaken to examine the solubility and fate of added B to retorted oil shale.

PLANT RESPONSE TO BORON IN DIRECT RETORTED PARAHO SHALE

A greenhouse study was conducted to evaluate the effects of added B on plants growing in direct retorted Paraho shale. Dry matter yield and uptake of boron were examined as a function of calcium chloride soluble and ammonium acetate available B. In addition dry matter yield versus plant uptake of B was also examined.

MATERIALS AND METHODS

Unleached Paraho shale of less than $\frac{1}{4}$ " aggregate was placed in a large plastic container with drainage holes in the bottom. Water was leached through the shale until the electrical conductivity (EC) of the leachate fell below 2 mmhos/cm. The leached shale was dried, mixed, and divided into 1.5 kg portions. Appropriate quantities of a 25 ppm B stock solution of H_3BO_3 were added to the dry shale to provide 0, 25, 50, 100, 200, and 400 μg B/g shale. The treated shale was allowed to dry and was mixed in a V-blender to distribute the added B throughout the shale. The following native plant species were seeded in the treated shale: fourwing saltbush (*Atriplex canescens*), Indian ricegrass (*Oryzopsis hymenoides*), Utah sweetvetch (*Hedysarum boreale*), western wheatgrass (*Agropyron smithii*), and winterfat (*Ceratoides lanata*). All plants received periodic addition

of 55 ppm phosphorus (P) and 45 ppm nitrogen (N) as diammonium phosphate to supplement the low levels of these nutrients in the retorted shale. The plants were harvested approximately six months after planting and both dry matter yield and B contents were determined. The 0.01 M calcium chloride soluble and 1 N ammonium acetate available B were determined for all levels of added B in the retorted shale (Table 1). Boron was determined by the Azomethine-H method (Gupta and Stewart, 1975).

RESULTS

Both winterfat and Utah sweetvetch either failed to germinate or died shortly thereafter, leaving only the three species. No plants germinated in the shale receiving 400 $\mu\text{g B/g}$ and winterfat failed to grow in shale receiving greater than 100 $\mu\text{g B/g}$. The three surviving species exhibited visual symptoms of B and/or salt toxicity at all levels of B addition.

Distinguishing between salt and B damage is difficult and improvements in leaching of soluble salts from the shale will be necessary in future studies to more clearly distinguish between the two.

Table 2 shows that western wheatgrass accumulated an average of 58.3 to 887 $\mu\text{g B/g}$ when grown on shale containing 0 to 200 $\mu\text{g B/g}$. Similarly, fourwing saltbush accumulated an average of 80.5 to 580 $\mu\text{g B/g}$. Winterfat accumulated 47 to 450 $\mu\text{g B/g}$ when grown on shale containing 0 to 100 $\mu\text{g B/g}$. Plant uptake of B increased as calcium chloride soluble and ammonium acetate available B increased in the Paraho shale. Plotting plant uptake versus soluble and available B in shale revealed a high correlation between plant uptake of B and soluble and available B levels in the shale (Figures 1 through 6). Inspection of the graphs illustrating dry matter yield versus calcium chloride soluble and ammonium acetate available B reveals a depression in dry matter yield as soluble B increased (Figures 7 through 12). Fourwing saltbush may be exhibiting B tolerance at the lower levels of B in the retorted shale (Figures 7 and 10).

The relationship between dry matter yield and plant uptake of B was also plotted (Figures 13, 14, and 15). All plants showed an obvious reduction in yield with B additions to the shale over the non-B amended shale.

In addition to the immediate effects of excessive B uptake by plants, the elevated B uptake may be of long-term concern as plants accumulate and deposit B and other elements on the soil surface upon their death, thereby increasing the availability of potentially hazardous elements to newly germinated plants. The phenomena of salt cycling has been observed on some saltbush (*Atriplex*) species (Sharma and Tangway, 1973).

SOLUBILITY OF BORON IN RETORTED OIL SHALE

A study was conducted to determine whether soluble and available B levels in retorted shale will change with time. The capacity for spent shale to "fix" B was also examined. A lowering of soluble and available B over a period of time may indicate a potential decrease in plant-available B and a corresponding decrease in plant toxicity. However, the capacity for direct retorted Paraho shale to fix B in compounds of low solubility may have some significance as the shale weathers and again releases plant-available B.

MATERIALS AND METHODS

Paraho direct retorted shale was leached by the method discussed in Part I of this report. Appropriate amounts of a 25 ppm B as H_3BO_3 stock solution were added to the leached shale to provide 0, 25, 50, 100, 200, and 400 μg B/g shale. The treated shale was dried and then mixed in a V-blender to thoroughly distribute the B. The treated shale underwent a wetting and drying cycle for a period of 8 weeks. Both soluble and available B were determined at two-week sampling intervals at each level of added B. Boron was determined colorimetrically by the Azomethine-H method (Gupta and Stewart, 1975).

RESULTS

The amount of B recovered by calcium chloride and ammonium acetate extraction revealed a tremendous capacity for the retorted shale to "fix" B (Table 3). Average values for percent recovery of added B were 3.4% and 20.9% for calcium chloride and ammonium acetate soluble B, respectively. This indicates a capacity for the retorted shale to retain from approximately 79 to 97 percent of added B in slowly available mineral forms.

Retorted shale is expected to undergo a gradual decrease in pH through weathering. Plant-available B is at a minimum at high pH and increases as pH decreases (Prather, 1977). This may indicate that over an extended period of time B will become solubilized and increasingly available to plants.

Table 1. Analysis of boron amended Paraho shale used in plant uptake study.

B added to shale	pH**	EC**	H ₂ O Ext. B		0.01 M CaCl ₂ Ext. B		1 N NH ₄ Ac Ext. B*	
			µg/ml	Recovery	µg/ml	Recovery	µg/ml	Recovery
µg/g				%		%		%
0	8.3	0.64	0.023	-	0.12	-	2.20	-
25	8.1	2.40	0.61	2.4	0.75	3.0	7.50	4.0
50	8.3	2.87	1.43	2.9	1.50	2.8	10.0	20.0
100	8.2	2.70	2.90	2.9	3.20	3.2	20.0	20.0
200	8.3	2.28	6.30	3.2	6.80	3.4	33.8	17.0
400	8.2	1.93	14.0	3.5	15.0	3.8	55.0	13.8

* Solution had a pH of 4.8.

** Analyses were determined on a 1:1 extract (shale to distilled water) paste.

Table 2. Mean of plant uptake of boron and corresponding dry matter yield.

B added to shale	Fourwing Saltbush		Western Wheatgrass		Winterfat *	
	B Uptake	Dry Matter Yield	B Uptake	Dry Matter Yield	B Uptake	Dry Matter Yield
$\mu\text{g/g}$	$\mu\text{g B/g}$	g	$\mu\text{g B/g}$	g	$\mu\text{g B/g}$	g
0	80.5	3.37	58.3	3.89	47	3.59
25	95.3	4.58	236.6	3.15	120	1.12
50	180	3.96	390	2.81	230	0.42
100	357	4.63	573	1.75	450	0.59
200	580	1.61	887	0.77	-	-
400	-	-	-	-	-	-

* These values are not a mean. The three reps were combined to make a sample large enough to analyze.

- No sample.

Table 3. Soluble and available boron levels in boron amended Paraho shale.

Level of B Added to Shale	0.01 M Calcium Chloride Soluble Boron					1 N Ammonium Acetate Soluble Boron				
	Week				% Extracted at 8 Weeks	Week				% Extracted at 8 Weeks
	2	4	6	8		2	4	6	8	
	- - - - - ppm - - - - -					- - - - - ppm - - - - -				
0	0.2	0.11	0.12	0.11	2.10	3.7	3.9	3.6	-	
25	0.69	0.63	0.57	0.53	2.10	8.0	7.75	7.75	6.75	27
50	1.67	1.38	1.24	1.27	2.50	12.0	12.5	11.75	11.0	22
100	4.4	3.68	3.32	3.08	3.08	20	21	19.5	20.5	20.5
200	11.2	10.0	12.2	8.6	4.3	37	37	-	37	18.5
400	26.4	-	22.4	19.6	4.9	80	66	-	66	16.5
TOTAL MEAN					3.4					20.9

Figure 1. Plant uptake of boron of fourwing saltbush as a function of 0.01 M CaCl_2 soluble B in direct retorted Paraho shale.

Figure 2. Plant uptake of boron of western wheatgrass as a function of 0.01 M CaCl_2 soluble B in direct retorted Paraho shale.

Figure 3. Plant uptake of boron of winterfat as a function of 0.01 M CaCl₂ soluble B in direct retorted Paraho shale.

Figure 4. Plant uptake of boron of fourwing saltbush as a function of 1 N NH_4Ac available B in direct retorted Paraho shale.

Figure 5. Plant uptake of boron of western wheatgrass as a function of 1 N NH_4Ac available B in direct retorted Paraho shale.

Figure 6. Plant uptake of boron of winterfat as a function of 1 N NH_4Ac available B in direct retorted Paraho shale.

Figure 7. Dry matter yield of fourwing saltbush as a function of 0.01 M CaCl_2 soluble B in direct retorted Paraho shale.

Figure 8. Dry matter yield of western wheatgrass as a function of 0.01 M CaCl_2 soluble B in direct retorted Paraho shale.

Figure 9. Dry matter yield of winterfat as a function of 0.01 M CaCl_2 soluble B in direct retorted Paraho shale.

Figure 10. Dry matter yield of fourwing saltbush as a function of 1 N NH₄Ac available B in direct retorted Paraflo shale.

Figure 11. Dry matter yield of western wheatgrass as a function of 1 N NH_4Ac available B in direct retorted Paraho shale.

Figure 12. Dry matter yield of winterfat as a function of 1 N NH_4Ac available B in direct retorted Paraho shale.

Figure 13. Dry matter yield of fourwing saltbush as a function of boron uptake by plants growing in direct retorted Paraho shale.

Figure 14. Dry matter yield of western wheatgrass as a function of boron uptake by plants growing in direct retorted Paraho shale.

Figure 15. Dry matter yield of winterfat as a function of boron uptake by plants growing in direct retorted Paraho shale.

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Progress Report 1980-81
THE ANALYTICAL LABORATORY

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The Analytical Laboratory provides analytical service to project investigators. This service includes development of accurate analytical procedures, routine analysis of samples, and data interpretation techniques. Significant progress achieved between February 1980 and February 1981 is summarized below. A brief description of each item is included in the following section.

- 1) Approximately 8000 chemical determinations were performed on 1000 samples during the past year.
- 2) Methods development work and evaluation of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was begun. This technique has been introduced for routine determination of about 20 trace elements in a variety of sample types.
- 3) We have implemented routine Ion Chromatography (IC) procedures for the determination of anion species in aqueous samples.
- 4) The introduction of two new analytical techniques (ICP-AES and IC) have permitted in-house multi-method evaluations of analytical techniques for analysis of shale related materials. A detailed analytical procedures manual is being prepared for distribution to interested parties.

Lab Output

During the past twelve months 8091 determinations have been performed. The principal elements of interest in the past have been Mo, As, Se, B and F. Determination of these species continue to represent approximately forty percent of our analytical output. As other project investigators have refined their experiments they have requested additional elemental determinations. The implementation of two new analytical techniques in our laboratory have permitted the addition of more than 20 other species to our routine analytical repertoire. Routine determination of these species has been requested by other investigators to assist in the interpretation of factors controlling solubility/availability of the five target elements. The addition of automated ICP-AES and IC has permitted the addition of these species to our analytical task with a minimum additional effort. While approximately sixty percent of our analytical determinations are for the non-target elements, they require less than twenty-five percent of our time and effort.

The distribution of sample types submitted to our laboratory remains unchanged over the past year. The complex nature of the oil shale related matrices requires substantial effort in sample preparation prior to analysis. The distribution of analytical effort among sample types is shown below.

Retort/Process waters	15%
Leachates/other aqueous	19
Oil/other miscellaneous	13
Plant tissue	26
Geological/soils/shales	<u>27</u>
	100%

Quality control of accuracy and precision, as described in previous reports, constitutes 12% of our time and effort. The number of samples and determinations devoted to quality control schemes is not included in the numbers reported for lab output.

Implementation of ICP-AES Techniques

With funds obtained from other sources, we have obtained a sequential Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). This instrument is available on a part-time basis for use on this project. We have undertaken extensive testing of the instrumental capabilities with regard to the analysis of oil shale related materials. This effort has included the creation of analytical task files (computerized analytical protocols for automated analyses) for routine analysis of retort/process waters, leachate, plant tissues and geological materials. We have also examined the accuracy and precision of this technique for these matrices. Following a brief description of the instrument operation we will describe several significant features of ICP analysis of shale related materials.

The ICP spectrometer (Applied Research Laboratories Model 35000C) operates under control of a dedicated PDP11/03 computer. The only functions performed by the analyst, after sample preparation, is lighting of the argon torch, loading the automatic sampler and creation of analytical task files. These task files consist of the list of elements to be determined, the appropriate wavelengths for detection, any on-line or off-line correction parameters for interelement interferences or background correction and concentrations of the calibration standards. Correction parameters must be determined for each element in each sample matrix. (Since the proper selection of these parameters determines the accuracy of the final analysis, a careful study of the sample matrix must precede application of this technique to routine work.) Once established, the parameters are stored on magnetic disks for future analyses. Task files were created for determination of approximately twenty elements in geological solid fusion digestates, acid digestates, retort/process waters, spent shale leachates and dilute aqueous samples (natural waters).

Analyses are performed by recalling and executing the appropriate analytical task file. The computer then arranges the selected elements in order of increasing wavelength and begins the execution of the programmed analytical tasks. A set of calibration standards and samples are then placed in the automatic sampler. The computer accepts commands from the analyst to perform the calibration for all elements in the task file. Upon completion of the calibration, the analyst instructs the computer to perform the analysis of the quality control samples and unknowns. The results of the analyses are printed out in real-time and stored on magnetic disk for later presentation of final summary reports.

While the ICP technique is less susceptible to the chemical interferences inherent in other analytical methods, the complex nature of the shale related matrices requires cautious application of sound analytical procedures if accurate results are to be achieved. The high concentration of dissolved inorganic and organic species present in retort waters and aqueous shale leachates presents three significant problems that require analyst attention.

Since the apparent concentration of an element depends upon the rate at which the analyte is delivered to the argon plasma, it is essential that a constant sample uptake rate be maintained. In addition, the uptake rate of sample and calibration standards must be equal. For dilute aqueous samples this requirement is easily achieved. However, the high concentration of dissolved species shale leachates and retort waters leads to a significant reduction in the efficiency of analyte delivery to the plasma. Solution viscosity, density, and surface tension, which control efficiency, are variable among these samples. Therefore, exact matrix matching between calibration standards and samples is difficult. While matrix matching is impractical, the use of this multielement analytical technique permits the use of internal standards to monitor uptake rates and to correct apparent concentration for variations among samples. We have successfully used La or Sc as internal standards for monitoring sample uptake rate. Uptake rate variations of fifteen to forty percent have been observed for a variety of retort waters and spent shale leachates. We strongly recommend the use of internal standards for the analysis of these materials by ICP and flame atomic absorption techniques.

While it is possible to simultaneously determine several elements in a sample using ICP or other multielement techniques, there is a tendency to forget the individual chemical and physical characteristics of the elements that can lead to difficulties. The memory effect of sample delivery systems is one area that requires particular attention in shale related materials. The high dissolved species content and wide variability among samples can lead to significant memory effects. (Memory is the apparent concentration carry-over between samples due to inadequate rinsing.) Since the ICP technique is capable of determining concentrations over several orders of magnitude, failure of the system to return to baseline between samples can lead to serious systematic errors in the analysis of samples having widely varying analyte concentrations. The magnitude of this effect is a function of nebulizer design. While this fact is widely appreciated among ICP users, the fact that each element exhibits a different memory effect is less well known. Figure 1 shows the system memory effect for several elements. Silicon and boron are shown to require significantly longer rinse time for return to baseline. Since samples are often randomized prior to analysis and the samples concentrations vary widely, it is important to be aware of this difficulty. This factor is relevant to oil shale study since boron is one of the elements of interest to several investigators.

The presence of high concentrations of organic and inorganic species in some aqueous shale samples leads to significant alteration in the emission characteristics of the argon plasma. The spectral continuum emission in the vicinity of an analyte peak may be enhanced by concentrations of concomitant

Figure 1.

sample species. We have found that accurate determination of several elements in retort waters and shale leachates requires background (off-peak) correction. Figure 2 shows a wavelength scan of a typical leachate sample in the vicinity of the Mo(2816A⁰) emission. Failure to correct for the enhanced emission (above the blank baseline) in this case would lead to a high bias of 40% in the analysis of Mo. Since each matrix presents different potential effects, careful case-by-case determination of appropriate background correction wavelengths is necessary. Figure 3 shows the effect of reduced continuum emission in the vicinity of the Cu(3247A⁰) line in a retort water sample. This effect (not present in leachates) is probably due to decreased plasma temperature from the presence of organic material. Failure to background correct for this effect in this matrix would lead to a low bias in the analysis of Cu.

The examples of problems encountered in the application of ICP to analysis of shale-related matrices are presented here to illustrate and reinforce the often repeated claim of analysts that shale matrices are different from other sample materials. Continuous efforts to identify these problems are required if accuracy in analysis is to be ensured. Future quality of analysis used in industry will depend upon the careful examination of all the factors that affect the accuracy of instrumental techniques.

The analytical performance of the ICP spectrometer has been monitored on each of six task files over a period of three months. The protocol followed for quality control was described in the last progress report. Briefly, it consists of analyzing two quality control samples (two aliquots of a single composite sample of the representative matrix) within each run of 21 samples. This procedure was repeated over three months in order to obtain an estimate of the within-run and between-run variability of the analytical procedure and instrument performance. It was desirable to determine the short-term (2 hour) and long-term (day-to-day over two months) variation in order to assess the comparability of data obtained over an extended period of time. Representative results of this study are illustrated by the examination of nine trace elements in aqueous media. The mean within-run reproducibility for all constituents over a two hour period was $3.7 \pm 1.6\%$. Between-run (day-to-day) reproducibility was $5.3 \pm 1.7\%$. These observations indicate that we can be confident of detecting systematic differences between samples analyzed over the duration of this project if they are about 10% or more.

In addition to the routine quality control procedures and precision checks described above, we have performed accuracy checks to confirm the validity of the reported analyses. We have conducted accuracy checks using a set of EPA Reference water samples and Omega-9 retort water. While the EPA water standards are not representative of the matrix difficulties associated with leachates, they provide a means of assessing accuracy of instrument calibration. Three EPA samples (Set WP476E) containing 15 trace elements are supplied in concentrate form. The samples were diluted according to instructions to yield three samples ranging from a few ug analyte/liter to several hundred ug/liter. In order to obtain a better estimate of our accuracy over the full range of concentrations observed in actual samples, we prepared a second set of three samples from the EPA concentrates to cover the range from tenths of a mg/liter to 10's of mg/liter. Thus, we obtained a set of 6 samples covering a concentration range of 3 orders of magnitude. The accuracy obtained over the full range of concentrations was better than 7% on Fe, Mn, Cu, Cr, Zn, and V. Lead, Cd, As, and Se do not have sufficiently low detection limits by ICP to make determinations below a few tenths mg/liter. These elements are routinely

Figure 2.

Emission Spectrum around Mo-2816.15 Å

Figure 3.

Emission Spectrum around Cu-3247.54 Å

- Water blank
- Process water

determined by graphite furnace atomic absorption. In the low ug/liter range, our accuracy using this technique was found to be better than 10%. We have performed repeated analyses of Omega-9 retort water in order to establish our accuracy on this more complex matrix type. Results obtained in these tests establish similar accuracy limits for this material.

Implementation of Ion Chromatography (IC) Techniques

While a variety of analytical techniques are available for the determination of inorganic anions, they are subject to severe interferences. In matrices as complex as retort waters these techniques are limited in their ability to provide reliable quantitation of trace species. Several different methods must be used to obtain determinations of different species. Ion Chromatography (developed since 1975) has provided a sensitive and rapid method for determining most anion species on a single sample. The method uses classical ion exchange principles to separate sample species. Ionic charge, size, hydrophobic and Van der Waals forces contribute to the selective interactions that effect separation of various species. The separated species emerging from the ion exchange column are quantitated by their conductivity. Since the species are separated prior to detection, this method is less susceptible to the chemical interferences that plague other analytical techniques. We have recently acquired a Dionex Model 12-S automated Ion Chromatograph and are evaluating its performance in the analysis of shale-related materials. The purpose of this work is:

- to develop a protocol for routine rapid anion analysis of retort and process related waters (F, Cl, NO₃, SO₄, etc.)
- to develop a reliable technique for the determination of sulfur species occurring in these waters, eg., sulfate, sulfite, thio-sulfate, thiocyanate, etc.
- to develop a reliable technique for the determination of sulfide and cyanide using electrochemical detection.

Work in this laboratory and at PNL has already implemented this technique for determination of common anions such as Cl, Br, F, SO₄, and NO₃. Figure 4 illustrates the kind of separations possible with this technique. A standard solution chromatogram (A) is shown for the identification of peaks. Chromatogram (B) was obtained from 100X diluted Omega-9 retort water. Under these eluent conditions thiosulfate and thiocyanate are not observed. Figure 5 shows chromatograms obtained on a standard (A) and 10X dilution of Omega-9 retort water (B) using a stronger eluent solution. The more easily eluted anions, separated well under weak eluent conditions of Figure 4, are not well resolved here. However, thiosulfate and thiocyanate are resolved. (Peak asymmetry may be removed by addition of an organic modifier - not shown.) Figure 6 (B) shows the separations obtained on a 1000X dilution of a Paraho process water using weak eluent. (Sample is NOT representative - shown here for illustration of analytical separation only.) Figure 7 (B) shows the Paraho process water chromatogram obtained using the stronger eluent that permits separation of thiosulfate and thiocyanate. At the dilution factor shown thiocyanate does not appear. However, at lower dilution thiocyanate can be quantitated. These figures illustrate the necessity of performing at least two analyses under separate conditions to obtain complete sulfur speciation.

Figure 4.

Ion Chromatograms

Cal. Std.

Figure 5.

Figure 6.

Figure 7.

We will be evaluating techniques to better quantitate these sulfur species when we obtain an electrochemical detector. This detector will permit the quantitation of cyanide and sulfide not detected by conductivity. Used in series, the conductivity and electrochemical detectors should permit a more complete analysis of anions than presently possible with only conductivity detection.

The progress described in this report is due to the considerable efforts of:

Glenda Swanson
Lynne Taylor
Robert Sistko
Robert McNelly

Without their expertise, dedication and talent, this laboratory would not have been able to perform the analyses requested by the principal investigator.

1980-81 Progress Report
MATHEMATICAL MODELING AND TRANSPORT MECHANISMS FOR
LEACHING OF SPENT OIL SHALE

by

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INTRODUCTION

The general goal of this research is the development of the theoretical and experimental basis for characterizing, predicting, and controlling the soluble pollutants from spent oil shales. There are currently many unanswered questions concerning the effects of *in-situ* and surface retorting of oil shale on ground water quality (Ramirez and Abedi, 1979). Factors which affect leachate compositions include retorting conditions, the porous media properties of the spent shale itself, and the transport rates of pollutants through the spent shale.

The retorting conditions will influence both organic and inorganic leachate compositions. The kinetics of kerogen decomposition determines in a large measure the organic compounds which are leached into ground water. The retorting temperature greatly affects the inorganic elements available for leaching. The original carbonates are converted into water soluble oxides which yield high pH leachates around 600°C. At temperatures over 800°C insoluble silicates begin to form. *In-situ* conversion rates for these high temperature mineralogical reactions are currently unknown (Simth et al, 1978).

Laboratory leaching experiments on surface retorted spent shales have shown definite porous media and mass transport effects (Runnells, 1979; Amy, 1978; Parker, 1976). It has been estimated that 2 to 6 pore volumes of water are needed to remove most leachates; however, there are notable exceptions such as fluorine. Although studies on the levels and environmental impact of contaminants have been performed, little work regarding release mechanisms of these elements in porous media is available.

Since leachate concentrations are likely to be very high in the vicinity of abandoned *in-situ* retorts and surface piles (often exceeding EPA safety limits), it is important to develop an accurate mechanistic understanding of leaching porous media spent shale properties, and mass transport through and near abandoned retorts.

The principal investigator has been conducting research on mass transport in porous media for the past decade. We have studied mass transport through polymeric membranes--as applied to artificial kidney dialysis (Ramirez, Lewis,

1971; Ramirez, 1971; Ramirez, Mickley and Lewis, 1972; Bollenbeck and Ramirez, 1974; Collins and Ramirez, 1979) and the mass transport of surfactants through oil reservoirs for surfactant enhanced oil recovery (Friedman and Ramirez, 1977; Ramirez, Shuler and Friedman, 1979; Ramirez et al, 1980; Ramirez, Friedman and Shuler, 1980).

Our research program on spent oil shale started in June 1980 with the acceptance of our DOE proposal, "Mathematical Modeling and Transport Mechanisms for Leaching of Spent Oil Shale". The major research accomplishments to date (January, 1981) are:

- A characterization of the porous media properties of spent oil shale. Studies have been conducted for Tosco Powders, Paraho Powders, Paraho Consolidated Chunks, and Tosco Pellets made from powdered material. The following properties have been determined:
 - 1) Pore size distributions using mercury porosimetry experiments.
 - 2) Total surface area per gram of material using BET nitrogen adsorption and mercury porosimetry experiments.
 - 3) Visual and chemical analysis by scanning electron microscopy and x-ray elemental spectroscopy.
- Design and construction of an injection controlled dynamic leaching experiment that obtains simultaneously both leachate breakouts as well as tracer breakouts to determine dynamic changes in porous media properties along with pollutant levels.
- Determination of leaching capacity of spent shales by measurement of an Equilibrium Exchange Isotherm for sulphate, carbonate, sodium, calcium, strontium, boron and fluoride.

CHARACTERIZATION OF POROUS MEDIA PROPERTIES OF SPENT SHALE

A complete analysis of porous media properties of spent oil shale is necessary in order to provide fundamental data needed to determine and predict the transport of leachates through surface piles or abandoned modified *in-situ* (MIS) retorts. Studies have been conducted on spent shales from TOSCO II and Paraho retorting processes.

Pore size distributions were determined by mercury intrusion porosimetry, nitrogen adsorption, and scanning electron microscopy (SEM). This distribution is a probability density function giving the distribution of pore volume by a characteristic pore size. It is derived by mercury porosimetry and verified by nitrogen adsorption isotherms and optical analysis. Macropores and some micropores are detected by mercury porosimetry. Micropores and ultra-micropores not observed by porosimetry can be detected by adsorption isotherms.

Specific surface areas were measured using both mercury intrusion porosimetry and BET nitrogen adsorption.

Chemical analysis by x-ray fluorescence spectroscopy was performed at the same time the SEM's were taken.

MERCURY INTRUSION POROSIMETRY

Mercury Porosimetry uses drainage capillary pressure curves to calculate pore size distributions. Pore volume is assigned to the diameter of the entry pores. No information is given for pores accessible through the entry pores. Calculations are based on a "bundle of capillary tubes" model. Distortions arise from assigning the wrong pore volume to the pore diameters. However, the information obtained from mercury porosimetry is quite useful. Resistance offered by pore structure to various transport phenomena is controlled by the entry pores.

Experiment

The Department of Chemical Engineering's AMINCO 15000 PSI mercury porosimeter was used to take data. A sample is placed in a holder and evacuated to 10 microns of mercury. The holder is then filled with a fixed volume of mercury. The holder is pressurized to 15000 PSI and the volume of mercury forced into the sample at various pressures is recorded. Plots of volume versus pressure are used to determine the pore size distribution. As pore diameter decreases, the pressure required for intrusion increases. Any pore accessible through the entry pore will be filled with mercury if its diameter is greater than or equal to that of the entry pore.

Results

Spent oil shale in the form of powders and chunks were analyzed by mercury porosimetry. In particular, spent shale from the Tosco process was used. The mean pore size of the powders was found to be on the order of 10 microns. Under compaction, the pore size decreased to 1 micron. The mean pore size of the consolidated chunks was on the order of 0.5 microns. In all cases, a unimodal distribution was observed. This information makes it possible to model compacted spent oil shale as having a single characteristic pore size. Results are shown in Figures 1 - 3.

The pore volume and the characteristic pore size give the specific surface area of the sample. Values obtained ranged from $0.2 \text{ m}^2/\text{g}$ for powders to $0.4 \text{ m}^2/\text{g}$ for compacted powders to $0.6 \text{ m}^2/\text{g}$ for consolidated chunks.

BET ADSORPTION ISOTHERMS

The presence of pores smaller than those detectable by mercury porosimetry can be determined by adsorption isotherms. BET analysis used adsorption data for relative pressures between 0.05 and 0.3 to obtain specific surface area. Pressure in the sample chamber divided by atmospheric pressure is the relative pressure.

Experiment

A sample is placed in a holder and attached to the Department of Chemical Engineering's BET apparatus. The system is evacuated to less than 10^{-4} millimeters of mercury and the sample is off-gased at 40°C overnight. The sample is then placed in a liquid nitrogen bath (-195°C). Known volumes of purified

Figure 1: Mercury Porosimetry Curve for TOSCO Powder

Figure 2: Mercury Porosimetry Curve for TOSCO Pellet

Figure 3: Mercury Porosimetry Curve for TOSCO Chunk

helium are added to the sample holder section and the resulting pressure is measured using a manometer. Since helium will not adsorb at this temperature, the ideal gas law is used to determine the dead volume of the sample section. The sample is again evacuated and off-gased. The process is repeated with purified nitrogen. For a given volume of nitrogen a lower pressure will result. The difference is due to adsorbed nitrogen.

Results

BET surface area for the TOSCO spent shale samples agrees with surface area calculations from mercury porosimetry. The existence of micropores is not indicated, thus verifying the unimodal pore size distribution found by mercury porosimetry.

SCANNING ELECTRON MICROSCOPY

Visual and chemical analyses were performed using scanning electron microscopy and x-ray fluorescence spectroscopy (XFS).

The SEM's verified the uniform pore properties of the various spent shales found using the analytical techniques as well as providing information on average grain sizes. The surface of the spent shale was observed to be quite crystalline and irregular giving rise to a substantial dead space volume. This indicates that a capacitance type of model is representative of the transport mechanisms involved in the flow of ground water through spent shale. SEM micrographs are given in Figures 4 - 6 for TOSCO powder, TOSCO pellet and TOSCO chunk respectively.

As can be seen in the SEM's the grain sizes are very similar for the three TOSCO spent shale samples. The average grain size is three to four microns. Pores are seen as the space between the grains. The average pore size ranges from 10 to 0.5 microns for powders and consolidated chunks respectively. This is in line with the data from mercury intrusion porosimetry.

The XFS analysis showed large amounts of calcium and silicon and lesser amounts of sodium, aluminum, sulfur, potassium, titanium and iron. Magnesium is present but is masked by the sodium and silicon peaks as they grow during the analysis. The crystalline shape of the grains implies most of the material is in the form of carbonate and silicate crystals.

The XFS for Paraho powder is given in Figure 7. The peaks are labeled and show the presence of sodium (A), aluminum (B), silicon (C), sulfur (D), potassium (E), calcium (F), titanium (G), and iron (H). Two species of calcium and iron are detected. Other elements present cannot be determined from the background levels.

Figure 8 shows a SEM of Colony raw shale that has been through a crushing process. Comparison of SEM's of raw shale and spent shale samples show visually the changes in the structure of the shale due to retorting.

Figure 4: SEM of TOSCO Powder
Scale 2.5mm = 1mm

TOSCO PEL. 2000X MAG. 1MM=357 NM

Figure 5: SEM of Compacted TOSCO
Powder
Scale 2.5mm = 1mm

TOSCO CHUNK 2800X MAG. 1MM=357 NM

Figure 6: SEM of TOSCO Consolidated
Chunk
Scale 2.5mm = 1mm

LK Z=22 TI 0.06 KEV 100 SEC
US= 1K KEVEX 1X10^2 HS=10KEV

Figure 7: XFS of Paraho Spent Shale

COLONY RAW 7000X MAG. 1MM=143 NM

Figure 8: SEM of Raw Shale from
Colony
Scale 2.5mm = 1mm

DYNAMIC LEACHING EXPERIMENTS

There are four major objectives of our dynamic leaching experiments. They are as follows:

- 1) Obtain the porous media properties of a variety of spent shale types. These include permeability, mechanical dispersion, flowing fraction, and mass transfer coefficients.
- 2) Examine the leaching characteristics of the inorganic ions Ca, Na, Sr, Mg, F, SO_4 , B and CO_3 .
- 3) Examine the effects of changes in transport and porous media properties (permeability, porosity, adsorption capabilities, and bulk flow phase velocity) on the leaching characteristics of the aforementioned ions. These changes are those that might be imposed on the system during various retort or spent shale pile abandonment procedures.
- 4) Compare results of an experimental leaching of spent shale with those predicted by the mathematical model and determine the validity and applicability of the model.

An experiment was designed in such a way that all of the above objectives could be achieved simultaneously. To do this, one design had to include all of the components necessary to determine the spent shale properties as well as provide a system that simulates the actual leaching that may take place in abandoned retorts and spent shale piles.

In experimentally determining the mechanical dispersion, dynamic break-out curves for a non-adsorbing, nonleaching species must be obtained. Preliminary studies indicate that sucrose will be an appropriate solute to be used as the tracer. The leachate will be quantitatively analyzed for sucrose with a polarimeter. It has been determined that insignificant amounts of sucrose are adsorbed on the spent shale during leaching and that the spent shale doesn't contain any substances that will interfere with the analysis of the sucrose. In addition to determining the mechanical dispersion, a tracer breakout experiment also gives direct information on flowing fraction and the mass transfer coefficient between flowing and dead space volume. To obtain accurate results in a tracer breakout experiment one must be able to very rapidly switch from the pure leaching fluid (deionized, distilled water) to the tracer solution and vice versa. This must also be done with a minimal amount of mixing of the two fluids prior to entering and after exiting the leaching column. This can be done with the design shown in Figure 9. As an example, to switch from the fluid in reservoir 4 to that in reservoir 5 as the leaching fluid, valve 7 must be closed, valve 8 opened and valve 11 switched from line 1 to line 2. In this configuration the mineral oil is now pumped into reservoir 5 where it applies pressure to the delivery bag which forces fluid out of the reservoir, through back pressure regulator 2 and into the column. The total volume where the two fluids will mix has been minimized to the internal volumes of valve 11 and the fitting at the entrance to the column. The exiting mixing volume is minimized by using 1/16" tubing and locating the fraction collector as close as possible to the exit of the leaching column.

DYNAMIC LEACHING EXPERIMENT DESIGN

Figure 9

A differential pressure transmitter is used to measure the pressure drop over a known length of the spent shale core. This allows one to compute the permeability of the spent shale and to monitor any changes in this porous media property. The amount of dead space in the lines from the pressure taps to the differential pressure transmitter is minimized by using 1/8" tubing and locating the transmitter as close as possible to the column.

To simulate the conditions that might exist in a spent shale pile or a MIS abandoned retort one must be able to vary the flow rate of the leaching fluid and vary the porous media properties of permeability and porosity for one type of spent shale. The flow rate can easily be varied by changing the setting on the pump. The porosity and permeability of the spent shale can be varied by applying different packing pressures when filling the column with shale. By having a top lid that can be adjusted to different spent shale core heights without increasing the exiting mixing volume, the column is designed to accommodate different packing pressures. From Figure 9, the components are as follows:

- 1) Pump (P) - the pump used is a highly accurate Gilson model 301. This pump is capable of delivering a fluid at low flow rates that are typical of those that might be encountered in an abandoned retort or spent shale pile. The flow rates can be easily varied between 0.005 ml/min to 5 ml/min. A pulse dampener (PD) is included to minimize any pulsing that might occur to provide continuous flow. A back pressure regulator (PR) is included on each line to insure that the pump always works against the same pressure, thus preventing any variation in flow rate due to a change in the column pressure.
- 2) Reservoirs (R) - There are two storage reservoirs (R-1, R-2). One contains distilled deionized water and the other contains the tracer solution. The purpose of these reservoirs is to store their respective fluids prior to delivery to their respective delivery reservoirs. They also act as a buffer during refilling operations to prevent the introduction of bubbles to the delivery reservoirs. The fluid is forced into the delivery reservoirs by nitrogen pressure. Nitrogen is used as an inert atmosphere to prevent the growth of aerobic organisms in the storage reservoirs. The storage reservoirs are constructed of plexiglass and have a capacity of 1500 ml. R-3 is the mineral oil storage reservoir. It is capable of holding all of the mineral oil required by this system. It is constructed of plexiglass and has a capacity of 2000 ml. R-4 and R-5 are the delivery reservoirs. They hold the leaching fluids in plastic bags with a capacity of about 750 ml. The bags are sealed against the top lid with a double O-ring system that seals both the inner and outer surfaces of the bag. These reservoirs are also constructed of plexiglass and have a capacity of 750 ml.
- 3) Pressure gauges (PG) - PG-1 and PG-2 are Weiss model 4UGA-2 high accuracy gauges with 0 - 100 psi range and stainless steel fittings. The gauges are necessary to insure that both delivery reservoirs are at the same pressure. This is important during change over from one leaching fluid to the other where a difference in pressure between the

two delivery reservoirs could cause an interruption of flow. This problem is minimized with the presence of the pressure gauges.

- 4) Leaching Column (LC) - The leaching column is constructed of plexiglass and has a length of 36 inches (91.44 cm), an inside diameter of 1 inch (2.54 cm), and holds 450 cm³ of spent shale. A long column is used to minimize end effects and thus provide a more accurate value of the dispersion coefficient. The column has a pressure tap about 15 cm from each end of the column. A differential pressure transmitter (DP) is connected to these taps. The transmitter used is a Taylor Instrument model 3332T with span adjustable between 10 and 80 psi.
- 5) Fraction collector (FC) - The leachate is collected for analysis by a fraction collector capable of collecting by time, drop, or volume increments. The one used is Instrument Specialities Corp model 1200. This instrument is necessary because samples must be collected at equal volume increments during the entire time the experiment is in progress. It is anticipated that samples will be collected every twentieth of a pore volume. Based on an expected porosity of 50% for the spent shale, the sample will be approximately 10 ml in size.
- 6) Valves and fittings - All valves and fittings used have swagelok connections for easy assembly and maintenance. V-1 to V-11 are for 1/4" O.D. tubing with V-11 being a low internal volume valve used to minimize the mixing volume at the inlet to the column. V-12 and V-13 are for 1/8" O.D. tubing. Also included is a pressure relief valve (RV) to prevent high pressures in the system that might damage the delivery reservoirs. The relief valve used may be adjusted to a cracking pressure in a 50-150 psi range.
- 7) Tubing - All tubing used is 316 stainless steel. The tubing from the column outlet to the fraction collector is 1/16" O.D. to minimize mixing. The tubing from the pressure taps to the differential pressure transmitter is 1/8" O.D. The remainder is 1/4" O.D.

LEACHING CAPACITY OF SPENT SHALES

As water invades spent shale, various ions will be solubilized and desorb from the spent shale surface. Leaching capacity is characterized by an equilibrium exchange isotherm. This relates the amount of a given ion released into the water to the bulk concentration. This information is incorporated into a flow model to determine the spacial and temporal leachate compositions. The ions followed in this experiment were fluoride, sulfate, carbonate, calcium, magnesium, sodium, boron, and strontium. Total sulfur and specific conductivity were also determined.

Experiment

The experiments were carried out in polyethylene containers. Fifty grams of TOSCO spent shale were placed in each container with different amounts of distilled water placed in the containers (30 - 500 ml) and sealed. The con-

Figure 10: Bcron Equilibrium Exchange Isotherm

Figure 11: Sodium Equilibrium Exchange Isotherm

tainers were shaken four times daily for thirty days. The leachate was filtered and analyzed.

<u>METHOD</u>	<u>IONS</u>
Ion Chromatography	fluoride, sulfate
Colorimetry	carbonate
Inductively Coupled Plasma (ICP)	calcium, magnesium, sodium, boron, strontium
ICP was also used in the determination of total sulfur.	

Results

A typical equilibrium exchange isotherm is shown in Figure 10 for boron. This behavior is also exhibited by fluoride and carbonate ions. Therefore, two trace ions and one major ion can be calculated directly from these isotherms along with a description of the transport properties of a leaching situation.

However, interactive effects are exhibited in the sodium equilibrium exchange isotherm, Figure 11.

This is also observed in varying degrees for magnesium, strontium and sulfate. The concentration of all other ions in solution. These interactive effects must be understood before these exchange isotherms can be incorporated into a leaching model. The data indicates that some interaction may also be affecting the carbonate exchange capacity. Specific conductivity results also show interactive effects.

Calcium concentration is essentially constant at a level of 1.4 ppm for all samples. This is probably due to the high carbonate concentrations.

Total sulfur analyzed indicates that almost all sulfur is present in the form of sulfate.

MATHEMATICAL MODELING

Based on our spent shale characterization studies conducted this past year, fundamental modeling concepts have been established. Mercury porosimetry studies have shown the existence of a uni-modal pore-size distribution with average pore sizes ranging from 10 microns for Tosco Powders to 1 micron for Tosco Pellets made by compacting powdered material to 5 microns for Paraho Consolidated Chunks. Our SEM studies definitely point to the possibility of significant dead space volume as well as main channel flow regions. The following transport phenomena model is, therefore, suggested for study:

Main Channel Region

Rate of Accumulation	Convective Transport	Dispersive Transport	Transport to Dead Space Volume	Kinetic Rate of Generation
$f \frac{\partial C_m}{\partial t}$	$+ v \frac{\partial C_m}{\partial z}$	$= Df \frac{\partial^2 C_m}{\partial z^2}$	$- k (C_m - C_d)$	$- \frac{A_m}{\phi} \frac{d\Gamma_m}{dt}$

where C_m = main channel leachate composition
 C_d = dead space volume leachate composition
 f = flowing fraction
 v = water phase velocity in porous media
 D = dispersion coefficient
 k = mass transfer coefficient
 A_m = main channel leaching area per volume
 ϕ = porosity of spent shale
 Γ_m = amount of pollutant leached in main channel (given by the Equilibrium Exchange Isotherm)

Dead Space Volume

Rate of Accumulation	Transport to Main Channel	Kinetic Rate of Generation
$(1-f) \frac{\partial C_d}{\partial t}$	$= k (C_m - C_d)$	$- \frac{A_d}{\phi} \frac{d\Gamma_d}{dt}$

where A_d = dead space volume leaching area per volume
 Γ_d = amount of pollutant leached in dead space volume (given by Equilibrium Exchange Isotherm)

The solution of these two partial differential equations yields the pollutant concentration both as a function of time and spatial location in a spent shale pile or *in-situ* rubble.

The model parameters are either porous media properties or transport phenomena properties. The phase velocity, flowing fraction, porosity, and specific leaching areas are all spent shale porous media properties. In contrast, the mass dispersion coefficient, mass transfer coefficient, and release amounts are basic transport leaching properties. For the model to be applicable to different field situations, the transport properties must be determined and correlated with variations in porous media properties.

To date, porosity and specific leaching areas have been determined for Tosco Powders, Tosco Pellets made from compacting powdered material, Paraho Powders, and Paraho Consolidated Chunks. Also, release amounts have been determined by measuring Equilibrium Exchange Isotherms for sulphate, carbonate, sodium, calcium, strontium, boron, and fluorine.

Data gathered from our injection rate controlled dynamic leaching experiment yields information on the remaining model parameters. The tracer breakouts gathered during leaching gives direct information on the mass dispersion, flowing fraction, and mass transfer coefficients. By measuring the pressure drop across the leaching column we can compute the permeability, and therefore, the phase velocity, and monitor any changes in these variables.

With all model parameters determined, the mathematical model can then deterministically predict, without curve fitting, dynamic leachate behavior.

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PROGRESS REPORT 1980 - 1981

Release, Transport, and Fate of Potential Pollutants

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PROFESSIONAL ACTIVITIES DURING THE YEAR 1980

In the Progress Report for 1979-1980 (4) we explained that three manuscripts had been prepared for publication, describing the work done during the preceding few years. Those manuscripts were submitted to reviewed journals during 1980. None of the manuscripts was rejected, and at this time one has been accepted for publication in Chemical Geology (33). After receiving the initial reviews and editorial comments, we rewrote the other two and resubmitted them to Environmental Science and Technology (32,37). We are optimistic that both of the rewritten manuscripts will be accepted. In addition, during 1980 we published one paper in the non-reviewed Proceedings of the 13th Oil Shale Symposium (31).

During 1980 we also gave oral presentations on various aspects of our work at the 13th Annual Oil Shale Symposium in Golden, Colorado (April 16-18), the Eighth International Symposium on Geochemical Exploration, in Hannover, West Germany (April 5-20), and the American Chemical Society Annual Meeting in Las Vegas (August 24-29). A written report on the German meeting was submitted to the Department of Energy, Chicago Operations and Regional Office. During the meeting in Germany we were able to visit the "Posidonia" oil shale deposits at Schandelah, near Braunschweig. On February 6, we gave an oral presentation at the D.O.E. Site Review Meeting in Berkeley, California, and we participated in the Oil Shale Task Force Workshop in Denver on November 6-7, 1980.

Two Ph.D. Dissertations were completed on the Project during 1980, by Ken Stollenwerk and Ola Saether. The laboratory work and manuscript for a Master's Thesis was also completed by Mike Glaze (16), but the final draft of the thesis has not yet been submitted to the university. At this time Esmail Esmaili is a Research Assistant on the Project, working on chemical interactions between oil shale leachates and indigenous geologic substrates from the Piceance Creek Basin.

INTRODUCTION

As the development of a commercial oil shale industry accelerates, many environmental problems need to receive attention. One of the most important of these is the disposal of the waste shale, both fresh and retorted. The potential problem of contamination of surface and subsurface waters due to leaching of the waste shale should be a matter of great concern. Our past efforts have focused chiefly on the chemistry of the leachates that result from interaction of percolating waters with fresh and retorted waste shale. A surface retort, producing about 50,000 barrels of shale oil per day, will also produce about 75,000 cubic meters of waste shale. Even in the modified in-situ method of retorting, about 40% of the shale will be brought to the surface for retorting or disposal. These large amounts of waste shale, whether on the surface or underground, will be susceptible to leaching by percolating natural waters. We have been studying the chemistry of the aqueous leachates that might result from such an interaction.

OBJECTIVES AND PAST WORK

In Figure 1 we present a sketch of the probable nature of a disposal pile for waste shale on the surface of the ground. In constructing such a pile, the operators will probably scrape away the native soil and store it for later reclamation. The first layers of retorted shale will then be super-compacted, to minimize possible percolation of leachate into the underlying strata. Successive layers of shale will be emplaced and the finished pile will be covered with the native soil and revegetated (13). In studying this probable scenario, we can see several possible paths of development and migration of aqueous leachates, as sketched in Figure 2. Figure 2 illustrates that moisture could enter the pile by means of rainfall, snowmelt, or subsurface seepage. Whether or not enough natural precipitation will occur in the region to cause saturation and leaching is a matter of some debate, but it is probable that those disposal sites situated at higher elevations in the Piceance Creek Basin (such as the Colony site) will receive enough precipitation to generate leachates that will be able to move through the piles very slowly (35,37). In fact, because of the long-term nature of the oil shale industry, it may be necessary to consider possible climatic changes and the effect that they will have on the waste shale.

If leachates are generated, both organic and inorganic species will be mobilized and transported. We and other researchers have demonstrated (3,4,22) that aqueous leachates from both fresh and retorted shales are high in many dissolved salts. The leachates usually have an elevated pH and are rich in dissolved sodium and dissolved sulfate, as well as a great many other dissolved chemical species. Our objectives over the past

Figure 1.

Schematic sketch of the probable design of a surface disposal pile of waste shale, showing the different zones of compaction, soil cover, and natural ground.

Figure 2.

Schematic sketch showing potential means of saturation of the waste pile, with generation and movement of leachate to the surrounding environment. Illustrates possible movement of leachate into native soils and into bedrock that underlies the disposal site.

few years have been to investigate the development of such leachates, to characterize their chemistry, and to assess the potential threat that they may pose to the environment (3,4,16,30,31,32,33,35,36,37). Our emphasis has been on the solubility, mobility, and speciation of F, B, Mo, As, Se, S, and TDS. We have found that the solubilities are low for the common heavy metals, such as Pb and Zn, probably because of the precipitation of insoluble hydroxides at the high pH values that obtain in most leachates.

It is clear that the chemistry and behavior of fresh and retorted oil shales vary greatly, depending on the original source, the mode of retorting, the treatment after retorting, and the time of storage of the samples. A large number of empirical studies have been done to better define the range of characteristics of the shales themselves and the resulting leachates. Such information is absolutely essential if we are to make any reasonable predictions of the potential impact of the waste shale on the environment in the distant future (35,37).

OBJECTIVES IN 1980

Most of our experimental work has been conducted on various samples of fresh and retorted Paraho and TOSCO shales. This year we began to work on a new pair of TOSCO shales (identified in our laboratory as SS-4 and OS-4), representing a retorted waste shale and the equivalent fresh feedstock, respectively. We have generated aqueous leachates from these and analyzed them for a wide spectrum of dissolved components. Our reason for going to new samples was the availability of a large amount of the retorted material, necessary for generating the large volumes of leachate that we are using in our studies on the interaction between the leachates and natural soils, rocks, and alluvium from the Piceance Creek Basin.

As can be seen in Figure 2, leachate that may escape from a disposal pile will probably move through soil or bedrock before entering ground water. In some cases the flow may be through fractures in the bedrock, as is probably the case in the Uinta Formation beneath the Colony Development site. It is important to investigate the nature and extent of the chemical reactions that may take place as a result of the contact between the leachates and solid geologic substrates.

Another objective of our recent work has been to investigate the mineralogy, chemistry, and solubility of the capillary salts that develop in abundance on the surface of waste piles of shale. In a commercial operation, the retorted shale will be moistened and compacted in the piles; then, before the next layer of waste shale is added, some evaporation of the moisture will occur. This will almost certainly result in the formation of a thin surface layer of highly soluble capillary salts. Such a layer

will be readily available for leaching and mobilization by downward percolation or by surface runoff from rainstorms and snowmelt. Of equally great concern is the fate and mobility of capillary salts that will probably develop near the surface of the shale piles after the planned reclamation with native soils and vegetation. We have concluded that serious consideration should be given to the emplacement of capillary barriers, such as layers of gravel or broken rock, to prevent the upward migration of salts after reclamation. Even the act of irrigating the piles to aid revegetation could cause these highly soluble substances to leach and move into the environment. During this past year we have investigated the nature and solubility of some of the capillary salts. If the opportunity presents itself during the coming year, we will begin an investigation of the rate and extent of dissolution of the capillary salts by surface runoff.

During the course of other investigations, it has appeared that diffusion may be playing a significant role in the composition and distribution of dissolved salts in columns and piles of waste shale (35). This is caused by a heterogeneity in the salinity of the water in a column of shale, resulting from the dissolution of the most soluble salts by the first increment of water that passes through. We can expect a similar situation to obtain in actual disposal piles in the field as a result of downward percolation of rain and snowmelt. Our results (35,37) show that the first 1/18th of a pore volume of water that passes through a column of TOSCO retorted shale can have a TDS that is more than an order of magnitude higher than later fractions. Such a gradient in chemical potential will cause diffusion to take place in the column of shale, in an attempt to homogenize the distribution of salts. In order to investigate this phenomenon, we have packed columns with retorted shale and allowed them to age for various periods of time up to about 70 days. We plan to take the columns and suddenly immerse them in liquid nitrogen, effectively freezing the interstitial moisture in place and thus immobilizing the salts. We will then cut the frozen columns into sections, allow them to thaw, and analyze the fluids as a function of vertical distribution, comparing the distribution to columns that have not been allowed to age. In this way we should be able to assess the changes in distribution of the salts and of specific ions as a function of time. We hope that this study will allow us to predict the uniformity of the concentrations of dissolved species that we might expect to come out of waste piles in the field if leachate escapes over a period of time. We have just completed the first of these experiments, and we are waiting for the chemical analyses to come back from the laboratory. However, the specific conductances of the fluids from the thawed sections were different between the aged and the fresh columns, in the direction that we would expect to find if diffusion were important. If this approach is successful in defining the concentration gradients, we will attempt to fit the data to known diffusion equations and thus to arrive at the set

of physical parameters that can be used to mathematically predict the extent and rate of diffusive mixing (15,27).

We currently have about 40 columns of shale that have been used in the past work in our laboratory. These represent an important resource for investigating the changes that may occur in the field as the industrial waste piles age. We plan to eventually re-leach these columns, looking for evidence of such processes as self-cementation or dissolution.

We have recently obtained about 100 grams of Lurgi-retorted shale. If the opportunity becomes available, we will leach this shale and compare the chemistry of the leachate with other types of shale that we have investigated over the past five years.

METHODS

Materials

In the past we have used TOSCO II and Paraho retorted shales (SS-1, SS-2, and PSS-1) and fresh TOSCO and Paraho feedstock (OS-1, OS-2, and POS-1) in our leaching studies (3,4,35). A new TOSCO II retorted sample (SS-4) and its equivalent fresh shale (OS-4) are now being used in most of our experiments. The TOSCO Company was very helpful in supplying to us about 300 pounds of retorted material and about 2 pounds of the fresh shale. Both samples are from the Colony Development Site near Grand Valley, Colorado. Sample SS-4 was retorted in the pilot plant of TOSCO, near Golden, in June, 1980.

In August, 1980, seven samples of soils were collected from areas designated as disposal locations near the Colony Development Site. The soils were selected on the basis of being shown as different types on a map published by the U.S. Soil Conservation Service. All of the samples were taken as composites, consisting of a mixture of the obvious horizons revealed in trenches from one to two feet in depth, generally bottoming where channery (pebbles) became dominant. The thin organic layers (O-1 and O-2) were excluded if present. All soils were air-dried in the laboratory, passed through a 2-mm sieve, and stored in plastic bags.

One of the soils, from Davis Gulch, was used in the sorption study described later in this report. The soil was formed on alluvium that was derived chiefly from the Uinta Formation. It falls in the Silas Series on the Soil Conservation Service map, and consists of a dark, grayish-brown, sandy loam. It is from about 5 to 10 feet thick, increasing in thickness toward the stream in the valley. This location is shown on a Colony Development Corporation map as being near the toe of the proposed waste pile; it also underlies the area of the future dam-site in Davis Gulch. Thus, this particular soil will probably be in

contact with any leachate that may escape from the waste pile. It is of great importance that we investigate the chemical reactivity and adsorptive properties of such materials; we wish to know if such materials offer any protection to the underlying ground water and the adjacent stream. We have also generated a "soil leachate" by shaking a slurry of the soil and deionized water in order to determine the concentrations of components that may be leached from the soil by pure water. This background information will be used later to identify the proportion of each species of interest released during experiments on the reversibility of the removal of contaminants from oil shale leachates.

Samples of weathered sandstone, shale, and marlstone were collected from a freshly-excavated trench in the Uinta Formation on the Colony site. The weathered material was collected deliberately from joints and bedding planes in the rock along which escaping leachate might be expected to flow.

Two revegetation plots were visited at the Colony Development site. One is located up-slope near the head of Davis Gulch on the Roan Plateau. The other plot is situated along East Middle Fork, about one mile off the main road to the Colony Plant. According to company personnel, revegetation studies were begun on the Davis Gulch plot in the Spring of 1976. Approximately 400 tons of TOSCO II retorted shale, about one year old, were spread and compacted. The shale covered the site to a depth of about 1.5 to 2 feet. Three strips were developed on the pile; one consisted of a layer of broken rock about two to four inches thick, the second was covered with native soil to a depth of six to ten inches, and the third was simply raw shale with straw worked in at the rate of two tons in the upper six inches. Supplementary water was provided to the strips at approximately two-week intervals. When we visited the site, the strip of raw shale was covered with a white crust of capillary salts. We took a sample of the salt by scraping the surface with a knife blade. We also collected a thin layer of the salts mixed with the immediately underlying shale.

The plot on East Middle Fork Creek was established in June of 1972. It consisted of five strips, with four having soil covers of various thicknesses. The strips were irrigated, but no record is available of the amount or frequency of application. In June, 1972, triple superphosphate was raked in at the rate of 600 pounds per acre. A total of 60 pounds per acre of nitrogen fertilizer was also applied during the summer of 1972. In 1973 an additional 70 pounds/acre of nitrogen was applied. Again, when we visited the site, white capillary salts covered the surface of the strip of raw shale. We collected two samples of the salts and a mixture of the shale plus salts.

Leaching Experiments

Leachates were produced in the laboratory by shaker experiments. In the first set of experiments, samples of OS-4 and SS-4 shales were weighed into 120 ml acid-washed linear polyethylene bottles. Deionized water was added to produce a slurry in a ratio of 1:2.5 shale to water. The bottles were capped and agitated for intervals of 0.25, 1, 2, 5, 10, 17, 31, and 41 days. The slurries were then centrifuged and the extracts filtered through 0.45 micrometer membrane filters. The specific conductance was measured with an ESI Model 250-DE bridge and the pH with a glass electrode calibrated against two buffers. The conductance measurement was checked against standard KCl solution, with a 2% correction for each degree centigrade from 25. All leachates were analyzed for F, B, Mo, Ca, Li, and Sr (Tables A-1 and A-2), except for the 17-day leachates which were analyzed for a total of 37 constituents (Table A-3). The 17-day shaker experiments were duplicated for a better determination of the reproducibility of the studies. Dissolved organic carbon was measured in one sample each of OS-4 and SS-4, using a commercial laboratory.

In a separate set of shaker experiments, four 1:1 slurries were used to generate a large volume of leachate for adsorption studies with soils. The slurries consisted of 1000 grams of shale and 1000 mL of water, shaken for 17 days. This is essentially the same procedure as was used earlier in this laboratory by Glaze (16). The resulting volume of leachate (approximately 2 liters) was filtered through 8.0 and 0.45 micrometer filters. A 100 mL sample was taken from each of the four batches for analysis prior to mixing, and after mixing of the larger volume another four samples were collected. Of these latter four aliquots, one was frozen, one was acidified with nitric acid, and the other two were untreated. All were stored in acid-washed linear polyethylene bottles and submitted for chemical analysis of 37 constituents (Tables A-4 and A-5). We felt that this complete analysis was important to obtain before continuing with later studies using this "standard" leachate.

In a third set of shaker experiments, 80 grams of each sample of a mixture of shale and capillary salts were mixed with 200 mL of water and agitated in a wrist-action shaker for 30 minutes. The capillary salts and shale were collected from the revegetation plots at the Colony site. The agitation was designed to roughly simulate the sudden mixing and leaching that might take place during a heavy rainfall of 30 minutes duration. The leachates were filtered through 0.45 micrometer filters and analyzed for 37 dissolved components (Table A-6).

In an on-going experiment, we have packed one glass and two plastic columns with retorted SS-4. After 50 days of equilibration one of the glass and one of the plastic columns was

leached and the effluent was collected in one-quarter pore volume increments. The pH and conductivity were measured, and the samples have been submitted for complete analysis. The purpose of the column study is to gain a better understanding of the leachate from columns as compared to shakers for SS-4.

Sorption Experiments

Equilibrium batch-type methods were employed for the sorption studies. In three separate sets of experiments, 20 grams each were taken of the air-dried soil from the bottom of Davis Gulch, weathered Uinta Formation, and freshly crushed Uinta Formation shale. Each was weighed into an acid-rinsed plastic centrifuge tube and pre-moistened with 7 mL of water to satisfy the moisture demand. Fifty milliliters of our standard leachate were added to each and they were then shaken for 24 hours on a wrist-action shaker, centrifuged, and filtered through 0.45 micrometer membrane filters. The clay-rich material was scraped off the filters and re-introduced into the slurries. The experiments were then repeated with 50 mL of fresh leachate in the same tube with the same sample of soil. We had intended to repeat this 10 times, following the Harter and Foster method (17) for developing polynomial approximations for adsorption isotherms; unfortunately, during the second run the centrifuge tubes cracked and the experiment was terminated. We intend to repeat the study for all samples in the future, but in this case only the experiment with the soil was redone. The pH and conductivity were measured immediately after filtering, and the samples were analyzed for F, B, Mo, Ca, Al, As, Se, and Na (Table A-7).

Desorption Test

In order to determine the extent to which the adsorbed ions from the previous study would be released to fresh water, the equilibrated soil was mixed with 50 mL of water and agitated for 24 hours. The intent was to simulate the rinsing of a contaminated soil by fresh stream or rain water. However, because of the high concentrations of Na on the exchange sites after contact with the leachate, the soil was completely peptized and it was nearly impossible to clarify the liquid, either by centrifugation or filtration. We even tried passing the liquid through a cascading series of filters of nominal pore sizes 8, 0.8, 0.45, 0.1, and 0.01 micrometers, but the resulting water retained some visible turbidity. This, in itself, tells us that soils that may be impacted by oil shale leachate will become highly peptized, and will have the potential for greatly increasing the turbidity of streams in the area. This probable increase in turbidity should be considered in any environmental control plan. After measurement of pH and specific conductance, the fluid from our last filtration was submitted for analysis for F, B, Mo, As, Se, Al, and Na (Table A-7).

ANALYTICAL METHODS

All of the inorganic components were determined in our Central Analytical Laboratory, directed by Dr. Robert Meglen. Table 1 gives a summary of the methodology, detection limits, and approximate precision for each component. The precision estimates shown as percentages in Table 1 are for high concentrations. The ppm values apply to concentrations near the detection limits. Determination of dissolved organic carbon (DOC) was done by Huffman Laboratories in Denver, using an oxidation step at 950° degrees C, followed by a coulometric determination.

RESULTS AND CONCLUSIONS

Shaker Experiments - pH, TDS, Mo, B, F

In earlier shaker experiments, Stollenwerk (35) determined the leachability of TOSCO and Paraho shales, both fresh and retorted. The results of his studies are included, for comparison with our results, in Figures 3, 4, 5, 6, and 7. The results of our experiments with the new SS-4 and OS-4, given in Tables A-1 and A-2, are also shown in Figures 3 through 7.

As can be seen in Figure 3, the pH of the new TOSCO SS-4 leachate is higher than the previous values seen for SS-1 and SS-2, and all are lower than Paraho leachates. The pH of the SS-4 samples ranges from about 10.5 to 9.4 (Table A-2), with a trend toward lower values with increasing time of shaking. The trend may be due to gradual uptake of carbon dioxide gas from the atmosphere, diffusing through the walls of the plastic containers. The drop in pH could also be due to oxidation of the relatively abundant thiosulfate, with resulting production of sulfuric acid (35).

The pH of fresh OS-4 is also higher than that of the older OS-1, despite the fact that they are both from the Mahogany Zone at the Colony site. The trend toward lower pH values with passing time is not as evident in the results for the fresh shale (pH from 8 to 7.5, Table A-1). The fresh shale seems to achieve a near-constant pH after just one day of shaking.

In Figure 4 the total dissolved solids (TDS) are plotted for all of the samples that have been studied in our laboratory, as a function of time of shaking. The TDS was determined by multiplying the observed conductivities by the empirical conversion factors of Stollenwerk (35), and by new factors determined from the complete chemical analyses obtained for SS-4 and OS-4 (Table A-3). The laboratory results were also multiplied by a factor of 2.5 (weight of water/weight of solid) to convert from mg/L dissolved material in solution to mg/kg shale.

Table 1
Summary list of analytical methods and precision

<u>Species</u>	<u>Method</u>	<u>Precision</u>	
F	Gaseous Diffusion, followed by Calorimetric Alzarín Complex	± .2 ppm	or 15%
As	Graphite Furnace	.005	10
Se	" "	.005	10
As	Atomic Absorption	.2	10
Se	" "	.3	10
K	" "		10
B	Inductively Coupled Plasma Emission Spectrometry (ICP)	.02	10
Mo	ICP	.02	10
Ca	ICP	.0005	10
Sr	ICP	.002	10
Li	ICP	.1	10
Mg	ICP	.3	10
Na	ICP		10
Fe	ICP	.01	10
Al	ICP	.2	10
Mn	ICP	.01	10
U	ICP	.5	10
Ni	ICP	.02	10
Co	ICP	.02	10
Cu	ICP	.01	10
Zn	ICP	.01	10
Sn	ICP	.15	10
Pb	ICP	.1	10
Cr	ICP	.01	10
Ba	ICP		10
Cd	ICP	.02	10
Hg	ICP	.05	10
V	ICP	.02	10
Si	ICP		10

Table 1 (continued)

<u>Species</u>	<u>Method</u>	<u>Precision</u>		
Total S	ICP	±	ppm or	10%
Total C	ICP			10
NH ₄	Ion Selective Electrode	1		10
Cl	Ion Chromatography	1		10
So ₄	" "	1		10
No ₃	" "	1		10
No ₂	" "	.5		10
Po ₄	" "	1		10
Br	" "	1		10
HCO ₃	Calculated from Alkalinity			
Alkalinity	Automated Titration to pH 4.5

Figure 3.

Observed pH of leachates from six retorted and fresh oil shales as a function of time of contact. Sh - type experiments, with ratios 1:2.5 shale to water.

Observed leaching of TDS from six retorted and fresh oil shales as a function of time of contact. Shaker-type experiments, with ratios of 1:2.5 shale to water.

Figure 4

As shown in Figure 4, the retorted SS-4 released much higher concentrations of total dissolved salt than the fresh OS-4, due to changes in mineralogy upon retorting. The same phenomenon was earlier observed with SS-2 and OS-1. The trend in values for OS-4 leachate shows a steady increase with passing time, from about 1600 to 4200 mg/kg shale. This illustrates a slow release from fresh minerals in the rock. The results for OS-4 are quite similar to the older OS-1. The TDS of the new retorted SS-4 is much lower than other TOSCO retorted materials that we have studied, ranging from about 4700 to 6200 mg/kg shale. In fact, the TOSCO SS-4 is releasing approximately the same concentration of dissolved salt as the retorted Paraho PSS-1.

The amounts of Mo released from OS-4 range from about 0.5 to 2.5 mg/kg shale (Figure 5). In general, OS-4 releases less Mo than the previous OS-1. In the shaker studies with retorted SS-4 the Mo ranges from about 4.7 to 11 mg/kg, which is 4 to 14 times higher than the fresh equivalent (Figure 5). The retorting has clearly increased the solubility of Mo. The apparent jump in concentrations at the 31 and 41 days periods in Figure 5 are unexplained and may be due to laboratory or analytical errors. The continually increasing concentrations with time show that neither OS-4 nor SS-4 have come to equilibrium with the water after 41 days of contact; this was also true with the older samples.

Boron follows more or less the same pattern as Mo. The amount of B leached from OS-4 is less than from the older OS-1, whereas the retorted SS-4 falls in between the two previous TOSCO-II retorted shales (Figure 6). Boron concentrations from SS-4 are higher than from the Paraho PSS-1; retorting by the TOSCO process seems to increase the solubility of the boron. The trend shown on Figure 6 indicates that the solution has not yet equilibrated with the shale.

The results of leaching of F in SS-4 are remarkable. As shown in Figure 7, the amount of dissolved F is from 5 to 10 times higher than from any of the other samples, either retorted or fresh. We do not believe that this is an error, as the leachates from fresh OS-4 were treated in the same manner at the same time. In earlier studies, researchers in our group had concluded that surface retorting results in decreased concentrations of F (3,4,30,35,36,37), as indicated by the curves in Figure 7 for OS-1 and SS-2. The reason for this decrease appears to be that the F is in equilibrium with solid fluorite (calcium fluoride), and high concentrations of dissolved calcium in the leachates from retorted shales tend to suppress the conjugate dissolved fluoride; the Ca is probably derived from decomposition of such carbonate minerals as calcite and dolomite in the fresh rock. If the control on F is in fact exerted by Ca, then our results are understandable. As shown in Tables A-1 through A-5, the concentrations of Ca in leachates from SS-4 are very low, but in the leachate from fresh

Figure 5.

Observed leaching of Mo from six retorted and fresh oil shales as a function of time of contact. Shaker-type experiments, with ratios of 1:2.5 shale to water.

Figure 6.

Observed leaching of B from six retorted and fresh oil shales as a function of time of contact shaker-type experiments, with ratios of 1:2.5 shale to wa

Figure 7

Observed leaching of F from six retorted and fresh oil shales as a function of time of contact. Shaker-type experiments, with ratios of 1:2.5 shale to water.

OS-4 the concentration of Ca is higher. If the control on dissolved F is exerted through the solubility of solid fluorite, the low concentrations of dissolved Ca in the leachate from SS-4 would allow a much higher concentration of the conjugate F to be present in solution at equilibrium. We have tested this hypothesis by computer modeling of the chemistry of the leachates, using our program WATEQFC (29), with the complete analyses of Tables A-3 through A-5 as input. The resulting saturation indices from the computer model indicate that the leachates are all saturated with respect to fluorite and calcite, despite the low concentrations of Ca! Correspondingly higher concentrations of dissolved bicarbonate appear to cause the precipitation of calcite, with a corresponding removal of dissolved calcium. The necessary fluoride can dissolve or desorb from the source illitic clay, as suggested by Saether and others (30,31,32). The question of the source of the high concentrations of dissolved bicarbonate must then be addressed. A definite answer would require a specific study which is beyond the scope and purpose of our work. However, the source could be dawsonite in the rock. Smith and others (34) showed that dawsonite decomposes to produce sodium carbonate and carbon dioxide at a temperature as low as 370°C, well below the TOSCO retorting temperatures. If we make the assumption that dawsonite is the only source of the sodium in the leachates, a calculation reveals that less than 2.5% dawsonite in the rock could yield adequate dissolved sodium carbonate and carbon dioxide to account for the high dissolved sodium, high pH, and high dissolved bicarbonate in the leachate. We examined x-ray diffraction tracings of OS-4 and SS-4 for evidence of dawsonite or solid sodium carbonate, but were unable to find either one; this could be because the content was below the minimum of about two weight percent required for detection by x-ray diffraction.

Geochemistry of Shaker-experiment Leachates

Chemical analyses of all major and many minor components of extracts of shaker experiments run for 17 days are given in Tables A-3 through A-5, for solid:liquid ratios of 1:1 and 1:2.5. Table 2 shows the average percentage of the principal components in the extracts with respect to total dissolved solids. The leachate from SS-4 is rich in sodium, sulfate, and bicarbonate, with very low proportions of calcium and magnesium. In OS-4 leachate, sulfate, sodium, and bicarbonate are the most abundant components, but with a significant fraction of dissolved calcium and magnesium. Both leachates contain significant concentrations of fluoride, as discussed earlier.

The chemical analyses also show fairly high concentrations of some trace elements, such as As and Al. The concentration of As in the mixed standard leachate is up to 30 times the EPA Drinking Water Standard of 0.05 mg/L.

Quality control is always a problem in such extensive

Table 2: Percent of principal components in extracts with respect to TDS (from 17 day, 1:1 and 1:2.5, shaker experiments of S-4 and SS-4). The data given here represent averages for each group.

Extracts	Na%	So ₄ %	HCO ₃ %	F%	Cl%	Mg%	Ca%	K%	% in TDS
OS-4, 1:2.5	11	54	12	0.8	0.5	6.8	13	0.9	99.
SS-4, 1:2.5	37	29	28	3.5	1.0	<.005	<.03	<.25	"
Jar 1, 1:1	35	30	31	2.8	0.9	"	"	"	"
Jar 2, 1:1	33	31	32	2.7	0.9	"	"	"	"
Jar 3, 1:1	34	32	29	2.9	1.0	"	"	"	"
Jar 4, 1:1	34	31	30	2.9	0.9	"	"	"	"
Mixed Standard Leachate	34	31	29	2.8	1.0	"	"	"	" 99

studies. We often run duplicates and replicates of our materials, attempting to gain some information on the accuracy and precision. In the case of our new "standard" mixed leachate, we had As analyzed by two different methods at two different times. We analyzed F by the same method, but separated in time by 90 days. In the case of As, by inductively coupled plasma emission spectroscopy, the value was 0.7 mg/L (Table A-5). Reanalyzed 90 days later, by graphite furnace atomic absorption, the value was 1.5 mg/L (Table A-7). Fluorine, analyzed colorimetrically, yielded an initial value of 154 mg/L (Table A-5) and a value of 120 mg/L (Table A-7) 90 days later. We do not know the reason for these differences, but we are at least able to use them as a general guide to the precision that we may expect in our results over a period of time.

As described earlier in this report, we have tested various techniques for storing leachates prior to analysis. Samples which we have frozen and then re-analyzed show no significant changes in the concentrations of any of the components, indicating that freezing is an acceptable means of preserving the samples for the components of importance in our investigations. However, simple acidification with nitric acid did not preserve the original composition. The concentrations of Mo and As fell in the acidified sample, probably as a result of adsorption on a gelatinous precipitate of iron oxide that was present. In contrast, the concentrations of Ni and Cu rose upon acidification; we believe that this was due to leaching of colloidal particles that were present in the leachate. The concentrations of sulfate, ammonium, and silica also went up with acidification. This work has suggested to us that it is not necessary to preserve our leachates over the short period of time that usually passes between collection and analysis. Acidification seems to be worse than no preservation at all. Farrier and others (11) found that waters from the Rock Springs in-situ retort maintained their composition over a long period of time if they were simply filtered and refrigerated at 4° C.

Comparing the compositions of leachates generated with different ratios of SS-4 shale to liquid, we find significant differences between 1:1 and 1:2.5 ratios for F, B, Mo, As, and Al. This is consistent with desorption as a mechanism of release of many of the components, as reported by us earlier on other samples (3,4,35). The data in Tables A-3 through A-5 show a clear and consistent drop as the ratios of shale to water decrease, for a period of shaking of 17 days. If the concentrations were controlled by the dissolution of solid minerals in excess, the ratio would not be significant. Table A-4 shows the excellent agreement that existed between the leachates taken from the four separate experiments that we used to generate the large volume of our "standard" leachate.

Capillary Salts Experiments

Table A-6 summarizes the results of chemical analyses of extracts from 30 minutes of shaking of capillary salts with water. As described earlier, the mixture of shale and capillary salts were scraped from the surface of the waste piles being tested for revegetation at the Colony Development Site. The resulting leachates show very high concentrations of TDS, demonstrating the soluble nature of the capillary materials. The important point to be learned from this is, despite years of rainfall and irrigation, the retorted shale on these plots is still covered with a very highly soluble crust of salt. Such a crust will pose a threat to water resources of the region. Both chemical analysis and x-ray diffraction show that the salt is chiefly sodium sulfate (thenardite).

Concentrations of B and Mo are not very high in the dissolved products of the capillary salts, but F is unusually concentrated. Computer modeling indicates that the leachates are apparently supersaturated with respect to fluorite (calcium fluoride); it is not unusual to have such supersaturation in solutions, resulting from the slow kinetics of nucleation of the solid phases. Other species present at elevated concentrations in the leachates from the salts are Pb (about 0.2 and 0.3 mg/L) and uranium (Table A-6). Arsenic and selenium are both below detection limits.

High concentrations of sodium in this highly soluble crust are a cause for concern. In the final stages of construction, the waste piles will probably be covered with a layer of soil to aid in revegetation. From other studies that we have done on uranium, copper, and zinc tailings, we know that salts will tend to move upward, diminishing the chances for successful revegetation. This will be particularly true when artificial irrigation is terminated. The capillary forces involved moving water upward through a fine-grained material may defeat all attempts to permanently rinse the soluble salts downward. It is our judgement that the disposal of saline and soluble waste oil shale may pose the most difficult environmental problem encountered so far in the energy industry in the United States, including uranium tailings. Uranium tailings, although saline, are composed chiefly of insoluble silicate minerals. In contrast, the oil shale itself is a rock that will continue to dissolve into the foreseeable future, regardless of attempts to irrigate and flush it free of salt. And, of course, the tonnages of waste oil shale will dwarf those of uranium tailings.

As noted above, when the oil shale leachate is allowed to interact with soil from Davis Gulch, the clay-size fraction of the soil is peptized. This will result in a significant decrease in permeability of the soil in the field, and possibly a loss of mechanical strength. The mechanical integrity of the layers of native soil used to cover the abandoned piles may also be

lessened. The resulting hazards from slumping and collapse should be considered if there is any possibility that these saline solutions will escape from the waste piles.

COMPUTER MODELING

As described in earlier reports and publications (3,4,29) our computer model, WATEQFC, is an updated and revised version of WATEQ (27,38) from the U. S. Geological Survey. We have used the several complete chemical analyses that we have of the new leachates (Tables A-3 through A-6) as input to the model. In Table 3 the electrical balances between cations and anions are listed. The results for the mixed leachates from SS-4 and OS-4 are listed as average values for each of the two groups. In theory, for a perfect analysis, the milliequivalents of positive charge in solution must balance the milliequivalents of negative charge. Any deviation from a perfect balance suggests either that an error was made in the analysis or, possibly, that dissolved species present in solution that have not been identified. The differences shown in Table 3 are relatively large in several cases, but within acceptable ranges for such complex and concentrated solutions. We have recently found high concentrations of thiosulfate in the leachates from our shales, but this was not known at the time that the electrical values were calculated for Table 3. It is clear that the anions are too low in all of the leachates from shales in Table 3, and the missing component is probably thiosulfate. On the other hand, the anions are higher than the cations for the leachates from the capillary salts in Table 3, suggesting that we have overlooked a cationic species in the salts. We are now developing layers of capillary salts on trays of shale in the laboratory. We will analyze these later in the year.

Despite the low concentrations of Ca and Mg in the leachates from SS-4, the computer model suggests that they are supersaturated with respect to fluorite. This is a result that we have seen before and have verified in laboratory experiments (4,30,35). The computations also indicate that the leachates are supersaturated with respect to dolomite, calcite, and aragonite.

The output from the computer model indicates that the predominant species of dissolved fluorine in solution is the free fluoride ion (97-99%). Smaller concentrations of aqueous complexes of F are present, chiefly with Na in leachates from retorted SS-4 and with Mg in leachates from fresh OS-4. Again, these results agree with our earlier work on other leachates (30,35). Complexes of F with Al and Ca are present only in small amounts. Our earlier reports on the speciation of dissolved B and Mo (35) apply as well, indicating that the B is present as various hydroxy complexes and Mo chiefly as the free molybdate ion.

Table 3: Differences between meg/L of cations and anions of the leachates of 1:1, 1:2.5 SS-4, 1:2.5 OS-4 and capillary salts. (All units are meg/L)

leachates	cations	anions	(cations-anions)	% of difference with respect to cations
Jar 1	84.4	70.7	13.7	16.2
Jar 2	88.3	78.1	10.2	11.6
Jar 3	79.4	68.2	11.2	14.1
Jar 4	84.7	76.8	7.9	9.4
mix standard (average)	84.1	71.6	12.5	14.9
1:2.5, SS-4 (average)	36.7	27.8	8.9	24.3
1:2.5, OS-4 (average)	19.2	15.5	3.7	19.2
Davis Gulch capillary salts	219.8	241.7	-21.9	-9.9
East Middle Fork capillary salts	721.4	968.2	-246.8	-34.2

No solid minerals of B are indicated as being supersaturated in the leachates, as found earlier. However, for Mo the results are different. In our earlier leachates the computations indicated supersaturation with respect to calcium molybdate (powellite) (4,35,37). In the new leachates there is a state of undersaturation with respect to powellite and other minerals of Mo.

We did not measure the Eh of the leachate from the capillary salts because we had so little sample. However, choosing artificial values over the range from (+) 200 millivolts to (-) 100 millivolts had no significant effect on the computed speciation or saturation indices, with the exception of uranium. In the case of uranium, the lower values of Eh ((-) 100 mv) caused the leachates to become oversaturated with respect to uranium oxide and uranium silicate minerals. This may be helpful in the case of an actual disposal pile, as the Eh should be low within the pile, retarding the movement of the dissolved uranium. Copies of the input and output data for the modeling described here are available from us on request.

INTERACTION OF LEACHATE WITH SOIL AND UINTA FORMATION

The data presented here are the results of the first set of experiments on the interaction between leachate and native soils. We have finished a second set of experimental runs, but the chemical analyses are not yet available. We are now actively engaged in this aspect of our program. At this time we have begun a pedologic characterization of the several soils that were collected in the Piceance Creek Basin.

Table A-7 shows the composition of the leachate that was used in the interaction experiments, before and after contact with the soil. This type of information will be utilized in constructing a computer model for predicting the rate and extent of movement of dissolved species in leachate through the overburden and rocks of the region, modifying the model developed by Harter and Foster (17) for movement of phosphorous through agricultural soils. In each case we will attempt to fit the experimental data on sorption to a polynomial expression that can be incorporated into the computer program. This has already been successfully accomplished by one of our group for the movement of fluorine and boron (16).

Fluoride

Figure 8 shows the adsorption isotherm for fluoride in contact with soil from Davis Gulch, collected from the Colony Development site. As shown in Figure 8, maximum removal of the F had already occurred by the time that the third data point (900 micrograms per gram of soil) was reached. The amount of F removed by this soil was approximately 530 micrograms/gram, with a large inherent error propagated from the analytical procedure. It

Figure 8:

Observed removal of dissolved F from SS-4 leachate in contact with soil (Sample RD11) from Davis Gulch. 24 hours of shaking, with ratio of leachate to soil of 2.5:1.

should be recalled that the same sample of soil was successively transferred from one batch of fresh leachate to the next. It is therefore necessary to carry over the inherent computed error at each step into the results of the new samples, resulting in the progressively larger uncertainties shown in Figure 8. We have chosen to draw a horizontal line through the family of error bars in the diagram.

We began a study of the removal of F upon reaction with crushed shale and weathered material from the Uinta Formation, but the centrifuge flasks cracked and the experiment was terminated after two samples of fluid were collected. The few results that were obtained indicate that these materials also have very high capacities for removal of F from the leachate.

In Figure 8 we have also shown the concentration of Ca in the supernatant solution, after each reaction step. There is a clear relationship between high Ca and low F, again attesting to the control that seems to be exerted by solid fluorite. Because of this relationship, we feel that the removal of F shown in Figure 8 may be a precipitation phenomenon, rather than sorption. The high pH (and resulting competition by hydroxyl ion) may also lessen the extent of sorption of F on the solids. The initially high values of Ca shown in Figure 8 are certainly the result of release from the soil, probably in response to the flooding of surface sorption sites by the high concentrations of Na in the leachate. Some of the Ca could also have come from dissolution of calcium carbonate in the soil.

We also found that a significant amount of the F can later be rinsed from the soil by the distilled water. If verified, the ease of rinse-out could pose an additional hazard to water supplies in the region, with rainfall and snowmelt having the potential to remobilize the fluoride earlier removed by the soils.

Boron

The adsorption isotherm for B in the Davis Gulch soil is shown in Figure 9. The attempt to develop an isotherm for weathered Uinta Formation will be repeated later. As can be seen in Figure 9, the maximum removal of B occurs at the third sample point (Table A-9). After the addition of about 82 micrograms of B per gram of soil (with the estimated error shown), a total of 13 micrograms per gram had been removed. There is apparently some minor desorption of B with continued additions to the solution, but because of the large uncertainty, this is unclear. A similar amount of B had been removed by crushed fresh shale beds of the Uinta Formation at the termination of that experiment, but only about 9 micrograms had been removed by the weathered fraction of the Uinta. Our first experiment on the reversibility of the removal indicates that most of the B can later be remobilized by

Figure 9

Observed removal of dissolved B from SS-4 leachate in contact with soil (Sample RD11) from Davis Gulch. 24 hours of shaking, with ratio of leachate to soil of 2.5:1

distilled water mixed with the soil.

Molybdenum

Figure 10 summarizes the results for Mo in contact with Davis Gulch soil. Early removal is followed by apparent desorption of the Mo, but the cumulative uncertainty of the analytical method is very large. Again, the error bars shown in Figure 10 are the result of computing the maximum cumulative error, carried through all of the steps in the procedure. The actual error is probably much less. After addition of 153 micrograms of Mo per gram of soil, only about 2 micrograms had been removed. This small removal of Mo is in rather sharp contrast to the very large amounts of F removed (Figure 8). The initial experiments on the crushed shale from the Uinta Formation and on the weathered Uinta show very similar small capacities for removal of Mo. A first test shows that much of the Mo can be easily rinsed out of the soil by deionized water.

Arsenic

Figure 11 shows the removal of As by the soil from Davis Gulch. The curve that represents the isotherm has not leveled off, even after nine additions of As to the soil. This is a very different behavior than we saw for F, B, and Mo. The soil seems to have a large capacity for removing As, and this may be quite useful to know in planning the disposal facilities. After addition of a total of about 34 micrograms of As per gram of soil, over 16 micrograms had been removed. An initial test shows that very little of the As can later be rinsed out by deionized water, suggesting that the soil may offer protection from As to water supplies of the region. The materials from the Uinta Formation also show high capacities for removing As from the leachate.

Aluminum

The concentration of Al in the standard leachate is about 18 mg/L (Table A-7). This is an enormously high value for an element that is normally considered to be very insoluble. The reason is that the hydroxyl-complexes of aluminum greatly increase the solubility at the high pH values of the leachates. After interaction with the solid geologic materials, the concentration of Al is below detection limits in all supernatants (<0.2 mg/L). This could be due to either the drop in pH caused by the strong buffering capacity of the solid geologic materials, or to adsorption and precipitation on the surfaces of the mineral grains. In either case, the loss of Al is beneficial in protecting the irrigation waters and the aquatic life in streams of the region from the very toxic effects of dissolved aluminum.

Figure 10

Observed removal of dissolved Mo from SS-4 leachate in contact with soil (Sample RE11) from Davis Gulch. 24 hours of shaking, with ratio of leachate to soil of 2.5:1.

Figure 11.

Observed removal of dissolved As from SS-4 leachate in contact with soil (RD11) from Davis Gulch. 24 hours of shaking, with ratio of leachate to soil of 2.5:1.

SUMMARY

During the past year we have pursued four major areas of investigation. First, we obtained and characterized a new set of shales and corresponding leachates, for the purpose of future studies on the sorption of dissolved contaminants in the leachate on soils and rocks of the Piceance Creek Basin. Second, we began the investigations of the interaction between leachates and a variety of solid geologic substrates from the oil shale region. Third, we identified and began to define the potential danger posed by the layer of capillary salts that forms on the surfaces of the piles of waste shale. And fourth, we devised a new experimental technique and began a study of the importance of diffusion in controlling the chemical composition and homogeneity of leachates from columns of waste shale.

Our computer modeling has continued, with the result that we have a better understanding of the identity of the dissolved species in leachate and the solid compounds that may either precipitate or dissolve in oil shale leachate.

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APPENDIX A

Table A-1: PH, TDS and concentrations ($\mu\text{g/ml}$) of some chemical species in extracts from 1:2.5, OS-4 and water slurry. (In order to convert from $\mu\text{g/ml}$ to mg/Kg of shale, multiply by 2.5)

Days Shaken	PH	TDS	B	Ca	F	Li	Mo	Sr	Al	As	Se
.25	8	640	.71	99.5	9	<.1	.25	.703	-	-	-
1	7.65	780	.97	129	11	<.1	.32	.916	-	-	-
2	7.7	830	1.1	149	11	.3	.34	1.01	-	-	-
5	7.64	990	1.2	189	8.5	.2	.32	1.13	-	-	-
10	7.64	1080	1.4	191	10	.1	.43	1.24	-	-	-
17	7.7	1140	1.6	143	7	.5	.21	1.22	-	-	-
17	7.73	1120	1.6	146	10	.3	.23	1.11	-	-	-
31	7.51	1690	2.1	240	6	-	1.0	-	<.2	<0.01	.04
41	7.7	1220	1.8	190	10	-	.9	-	<.2	0.02	<0.01

Table A-2: Values of pH, TDS and concentrations ($\mu\text{g/ml}$) of some chemical species in extracts from 1:2.5, SS-4 and water slurry. (In order to convert from $\mu\text{g/ml}$ to mg/Kg of shale, multiply by 2.5)

Days Shaken	PH	TDS	B	Ca	F	Li	Mo	Sr	Al	As	Se
.25	10.5	1880	3.4	2.8	42	.2	1.9	.085	-	-	-
1	10.25	2390	4.5	1.7	44	<.1	2.8	.041	-	-	-
2	10.2	2410	4.5	1.3	44	.3	3.0	.038	-	-	-
5	10.42	2430	5	1.6	40	<.1	2.6	.049	-	-	-
10	9.6	2340	4.2	2.1	38	.2	3.6	.063	-	-	-
17	9.8	2110	5.2	1.8	70	<.1	3.5	.076	-	-	-
17	10	2260	5.3	1.3	82	<.1	2.8	.057	-	-	-
31	9.45	2490	4.5	1.9	56	-	4.4	-	2.2	.22	.01
41	9.38	2420	4.4	1.9	52	-	4.3	-	2.1	.16	.03

Table A-3: Values of pH, TDS, Eh, DOC, and concentration ($\mu\text{g/ml}$) of major and minor constituents in extracts from 1:2.5, OS-4 and SS-4 slurry shaken for 17 days. (In order to convert from $\mu\text{g/ml}$ to mg/kg of shale, multiply by 2.5)

	OS-4	OS-4	SS-4	SS-4	Drinking water recommended limits (40)	Crops irrigation water recommended limits (39)
B	1.6	1.6	5.2	5.3	1.0	.75
Ca	143	146	1.85	1.28		
Mo	.21	.23	3.5	2.8		
Sr	1.2	1.0	.076	.057		
Li	.5	.3	<.1	<.1		
Mg	84	71	.4	<.3		
Na	120	120	820	810		
K	11	9	8	9		
Fe	<.01	<.01	<.01	.01	0.3	
Al	<.2	<.2	7.7	7.5		
Mn	<.01	<.01	.01	<.01	.05	
U	<.5	<.5	<.5	<.5		
Ni	.15	.13	<.02	<.02		
Co	<.02	<.02	<.02	<.02		
Cu	<.01	.03	.03	<.01	1.0	
Zn	<.01	<.01	<.01	<.01	5.0	
As	<.2	<.2	<.2	<.2	.05	.1
Se	<.3	<.3	<.3	<.3	.01	.02
Sn	<.15	.22	<.15	<.15		
Pb	<.1	<.1	<.1	<.1	.05	5
Cr	<.01	<.01	<.01	<.01	.05	.1

Table A-3 (continued)

	OS-4	OS-4	SS-4	SS-4	Drinking water recommended limits (40)	Crops irrigation water recommended limits (39)
Ba	.04	.04	.02	.02	1.0	
Cd	<.02	<.02	<.02	<.02	.01	.01
Hg	.08	.05	<.02	<.05	.002	
V	.02	.02	.09	.16		
Si	6.5	5.8	.6	.8		
NH ₄	2	<1	2	<1		
S (total)	250	230	560	500		
C (total)	71	81	95	99		
Cl	4.5	7.5	21	22	250	
Br	<1	<1	<1	<1		
F	7	10	70	82	1.4-2.4	1.0
No ₂	<.5	<.5	<.5	<.5		
No ₃	3	3	<1	3	45	
Po ₄	<1	<1	<1	<1		
So ₄	650	560	620	630	250	
pH	7.7	7.73	9.8	10		
TDS	1140	1120	2110	2260	500	700
Alkalinity as CaCo	80	145	450	560		
DOC (ppm)		16		96		

Table A-4: Values of pH, TDS, Eh and concentration ($\mu\text{g/ml}$) of major and minor constituents in extracts from th jars, 1:1 SS-4 and water slurry shaken for 17 days. (In order to convert from $\mu\text{g/ml}$ to mg/kg of shale, multiply by 1)

	Jar 1	Jar 2	Jar 3	Jar 4	Drinking water recommended limits (40)	Crops irrigation water recommended limits (39)
B	11.5	11.3	11.3	12	1.0	.75
Ca	1.2	1.0	1.0	.95		
Mo	6.1	6.3	6.2	6.6		
Sr	.054	.046	.056	.055		
Li	.1	.2	.3	<.1		
Mg	<.3	<.3	<.3	<.3		
Na	1870	1960	1750	1880		
K	9.5	11	11	11		
Fe	.02	<.01	.01	<.01	0.3	
Al	20	19	24	19		
Mn	<.01	<.01	<.01	<.01	.05	
U	<.5	<.5	<.5	<.5		
Ni	<.02	<.02	<.02	<.02		
Co	<.02	<.02	<.02	<.02		
Cu	<.01	<.01	<.01	<.01	1.0	
Zn	<.01	<.01	<.01	<.01	5.0	
As	.8	.7	.4	.6	.05	.1
Se	<.3	<.3	<.3	<.3	.01	.02
Sn	<.15	.18	<.15	<.15		
Pb	<.1	<.1	<.1	<.1	.05	5
Cr	<.01	<.01	<.01	<.01	.05	.1

Table A-4 (continued)

	Jar 1	Jar 2	Jar 3	Jar 4	Drinking water recommended limits (40)	Crops irrigation water recommended limits (39)
Ba	.014	.014	.020	.019	1.0	
Cd	<.02	<.02	<.02	<.02	.01	.01
Hg	<.05	<.05	.06	<.05	.002	
V	.71	.63	.56	.55		
Si	1.7	1.3	1.2	1.2		
NH ₄	2	1	<1	<1		
S (total)	1500	1300	1300	1200		
C (total)	290	240	180	180		
Cl	50	53	53	52	250	
Br	<1	<1	<1	<1		
F	150	160	150	160	1.4-2.4	1
No ₂	<.5	<.5	<.5	<.5		
No ₃	3	2	3	3	45	
Po ₄	3	3	2	3		
So ₄	1620	1800	1640	1730	250	
pH	10.3	10.35	10.3	10.3		
TDS	5410	5880	5130	5520	500	700
Alkalinity as CaCO ₃	1360	1520	1220	1340		
Eh (volts)	(+) .298	(-) .670	(-) .62	(-) .62		

Table A-5: pH, TDS, Eh, DOC and concentration ($\mu\text{g/ml}$) of major and minor constituents in the mix standard leachate (2 untreated, 1 acidified and 1 frozen), k:1, SS-4 and water slurry shaken for 17 days (In order to convert from $\mu\text{g/ml}$ to mg/kg of shales, multiply by 1)

	untreated	untreated	acidified	frozen	Drinking water recommended limits (40)	Crops irrigation water recommended limits (39)
B	11	11	12	11	1.0	.75
Ca	1.1	1.1	1.4	.73		
Mo	6.2	6.3	4.2	6.4		
Sr	0.05	0.05	0.06	0.03		
Li	<.1	<.1	.2	.1		
Mg	<.3	<.3	.3	<.3		
Na	1880	1860	1850	1850		
K	10	10	12	7.9		
Fe	.01	.01	.05	<.01	0.3	
Al	21	21	22	20		
Mn	<.01	<.01	<.01	<.01	.05	
U	<.5	<.5	<.5	<.5		
Ni	<.02	<.02	.08	<.02		
Co	<.02	<.02	.02	<.02		
Cu	<.01	<.01	.07	<.01	1.0	
Zn	<.01	<.01	.02	<.01	5.0	
As	.8	.7	<.2	.6	.05	.1
Se	<.3	<.3	<.3	<.3	.01	.02
Sn	<.15	.26	<.15	<.15		
Pb	<.1	<.1	<.1	<.1	.05	5
Cr	<.01	<.01	<.01	<.01	.05	.1

Table A-5 (Continued)

	untreated	untreated	acidified	frozen	Drinking water recommended limits (40)	Crops irrigation water recommended limits (39)
Ba	.015	.021	.024	.007	1.0	
Cd	< .02	< .02	< .02	< .02	.01	.01
Hg	< .05	< .05	.06	< .05	.002	
V	.62	.6	.59	.6		
Si	1.3	1.2	3.6	.9		
NH ₄	< 1	< 1	6	< 1		
S (total)	1300	1200	1200	1300		
C (total)	310	170	260	810		
Cl	54	52	63	54	250	
Br	< 1	< 1	< 1	< 1		
F	150	156	146	156	1.4 - 2.4	1.0
No ₂	< .5	< .5	< .5	< .5		
No ₃	9	2		3	45	
Po ₄	2	2		3		
So ₄	1720	1680	2050	1690	250	
pH	10.3	10.3		10.3		
Alkalinity as CaCO ₃	1240	1340		1340		
Eh (volts)	.3279	.3279				
DOC (PPM)	187	187				
TDS	5380	5436		5439	500	700

Table A-6: pH, TDS and Concentration ($\mu\text{g/ml}$) of major and minor constituents in extracts from slurry of 1:2.5 shale and capillary salts and water (In order to convert from $\mu\text{g/ml}$ to mg/Kg of shale, multiply by 2.5)

	Davis Gulch Plot	East Middle Fork Plot	Drinking water recommended limits (40)	Crops irrigation water recommended limits (39)
B	9.1	11.6	1.0	.75
Ca	390	400		
Mo	1.9	6.0		
Sr	7.5	8.7		
Li	1.3	4.6		
Mg	415	1910		
Na	3710	11400		
K	42	230		
Fe	.02	.04	0.3	
Al	< .2	< .2		
Mn	.01	.01	.05	
U	.8	.7		
Ni	.04	< .02		
Co	< .02	< .02		
Cu	.03	.04	1.0	
Zn	.06	.4	5.0	
As	< .2	< .2	.05	.1
Se	< .3	< .3	.01	.02
Sn	< .15	< .15		
Pb	.14	.34	.05	5
Cr	< .01	< .01	.05	.1

Table A-6 (Continued)

Ba	.03	.029	1.0	
Cd	< .02	< .02	.01	.01
Hg	.07	.06	.002	
V	< .02	.03		
Si	1.3	.7		
NH ₄	2	3		
S (Total)	3700	14000		
C (Total)	14	26		
Cl	30	190	250	
Br	< 1	< 1		
F	34	126	1.4 - 2.4	1.0
No ₂	< .5	< .5		
No ₃	60	90	45	
Po ₄	< 1	< 1		
So ₄	11200	43000	250	
PH	8.65	9.06		
TDS	15970	57641	500	700
Alkalinity as CaCo ₃	105	210		

Table A-7 : PH and Concentration ($\mu\text{g/ml}$) of selected constituents in the standard leachate and sorption test supernatants.

	F	B	Ca	Mo	Al	As	Se	Na	PH
Mix standard leachate	120	11	1.1	6.8	18	1.5	.09	1800	10.3
1st run, weathered uinta Fm	20	8.3	67	5.9	<.2	.23	.07	1100	8.13
2nd run, " " "	36	10	70	6.7	.2	.41	.06	1500	8.2
1st run, shale, uinta Fm	16	9.0	130	5.6	<.2	.36	.08	1100	7.95
2nd run, " " "	30	11	48	6.8	<.2	.78	.09	1400	8.07
1st run, Davis Gulch soil	30	6.2	180	5.6	<.2	0.22	.09	1400	8.25
2nd " " " "	40	8.8	120	6.8	<.2	0.49	.06	1200	8.51
1st " , Davis Gulch soil	45	10	210	6.5	<.2	0.21	0.07	1300	8.1
2nd " " " "	40	9.1	44	6.9	<.2	0.53	0.06	1500	8.45
3rd " " " "	70	10	20	7.1	<.2	0.64	0.08	1700	8.67
4th " " " "	120	11	33	6.9	<.2	0.83	0.06	1600	2
5th " " " "	140	11	61	6.8	<.2	0.90	0.10	1700	8.98
6th " " " "	130	11	51	6.8	<.2	0.93	0.08	1700	9.1
7th " " " "	140	11	46	6.9	<.2	0.97	0.08	1700	9.12
8th " " " "	140	12	41	6.7	<.2	1.1	0.07	1700	9.15
9th " " " "	120	12	36	6.8	<.2	.99	0.06	1800	9.14

Table A-8: Sorption data of F in Davis Gulch valley bottom soil (1st and 2nd run), and weathered material and crushed shale of the Uinta Formation

1	2	3	4	5	6	7	8	9	10	11	12	13	14
No. of Equilibrations	µg/ml conc. of F in leachate added	ml of leachate added	gm of geologic material used	Total µg F added	Total µg F added to 1 gm of geologic material	µg/ml conc. of F in supernatant	ml of supernatant	Total µg F in supernatant	Total µg of F sorbed (column 5 - column 9)	Total µg of F sorbed on 1 gm of geologic material	Σ µg F added to 1 gm of geologic material	Σ µg F sorbed on 1 gm of geologic material	Remarks
1	120±18	50	20	6000±900	300±45	30 ± 4.5	50	1500± 225	4500± 927	225±46.3	300± 45	225± 46.3	Davis Gulch valley bottom soil, first run
2	120±18	50	"	"	"	40 ± 6	50	2000± 300	4000± 948	200±47.4	600± 63.6	425± 66.3	
1	120±18	50	20	6000±900	300±45	45 ± 6.7	43	1935± 290	4065± 945	203±47.3	300± 45	203± 47.3	Davis Gulch valley bottom soil 2nd run
2	"	"	"	"	"	40 ± 6	50	2000± 300	4000± 948	200±47.4	600± 63.7	403± 66.9	
3	"	"	"	"	"	70±10.5	"	3500± 525	2500±1041	125±52.1	900± 77.9	528± 84.9	
4	"	"	"	"	"	120±18	"	6000± 900	0±1272	0±63.6	1200± 90	528±106	
5	"	"	"	"	"	140±21	"	7000±1050	-1000±1383	-50±69.2	1500±100.6	478±126.5	
6	"	"	"	"	"	130±19.5	"	6500± 975	- 500±1383	-25±66.4	1800±110.2	453±142.9	
7	"	"	"	"	"	140±21	"	7000±1050	-1000±1383	-50±69.2	2100±119.1	403±158.7	
8	"	"	"	"	"	140±21	"	7000±1050	-1000±1383	-50±69.2	2400±127.3	353±173.2	
9	"	"	"	"	"	120±18	"	6000± 900	0±1272	0±63.6	2700±135	353±184.5	
1	120±18	50	20	6000±900	300±45	20±3	50	1000±150	5000±912	250±45.6	300±45	250±45.6	Weathered material of the Uinta Formation
2	"	"	"	"	"	36±5.4	"	1800±270	4200±939	210±46.9	600±63.6	460±65.4	
1	120±18	50	20	6000±900	300±45	16±2.4	50	800±120	5200±908	260±15.4	300±45	260±45.4	Crushed shale of the Uinta Formation
2	"	"	"	"	"	30±4.5	"	1500±225	4500±927	225±46.4	600±63.6	485±64.9	

Table A-9: Sorption data of B in Davis Gulch Valley bottom soil (first and second run) and weathered material and crushed shale of the Uinta Formation

1	2	3	4	5	6	7	8	9	10	11	12	13	14
No. of Equilibrations	µg/ml conc. of B in leachate added	ml of leachate added	gm of geologic material used	Total µg B added	Total µg B added to 1 gm of geologic material	µg/ml conc. of B in supernatant	ml of supernatant	Total µg B in supernatant	Total µg of B sorbed (column 5 - column 9)	Total µg of B sorbed on 1 gm of geologic material	Σ µg B added to 1 gm of geologic material	Σ µg B sorbed on 1 gm of geologic material	Remarks
1	11±1.1	50	20	550±55	27.5±2.7	6.2±.62	50	310±31	240±31.1	12 ±63.1	27.5±2.7	12 ±63.1	Davis Gulch Valley bottom soil first run
2	"	"	"	"	"	8.8±.88	50	440±44	110±44.1	5.5±70.4	55 ±3.9	17.5±94.6	
1	11±1.1	50	20	550±55	27.5±2.7	10 ±1	43	430±43	120±69.8	6 ±3.5	27.5±2.7	6.0± 3.5	Davis Gulch valley bottom soil 2nd run
2	"	"	"	"	"	9.1± .9	50	455±45	95±71.4	4.7±3.6	55.0±3.9	10.7± 5.0	
3	"	"	"	"	"	10 ±1	"	500±50	50±74.3	2.5±3.7	82.5±4.8	13.2± 6.2	
4	"	"	"	"	"	11 ±1.1	"	550±55	0±77.8	0±3.9	110 ±5.5	13.2± 7.3	
5	"	"	"	"	"	11 ±1.1	"	550±55	0±77.8	0±3.9	137 ±6.1	13.2± 8.3	
6	"	"	"	"	"	11 ±1.1	"	550±55	0±77.8	0±3.9	165 ±6.7	13.2± 9.2	
7	"	"	"	"	"	11 ±1.1	"	550±55	0±77.8	0±3.9	192 ±7.3	13.2± 9.9	
8	"	"	"	"	"	12 ±1.2	"	600±60	-50±81.4	-2.5±4.1	220 ±7.8	10.7±10.8	
9	"	"	"	"	"	12 ±1.2	"	600±60	-50±81.4	-2.5±4.1	247.5±8.3	8.2±11.5	
1	11±1.1	50	20	550±55	27.5±2.7	8.3± .8	50	415±41	135±68.9	6.7±3.4	27.5±2.7	6.7±3.4	Weathered material of the Uinta Formation
2	"	"	"	"	"	10 ±1.0	"	500±50	50±74.3	2.5±3.7	55 ±3.9	9.2±5.1	
1	11±1.1	50	20	550±55	27.5±2.7	9.0± .9	50	450±45	100±71.1	5 ±3.5	27.5±2.7	5±3.5	Crushed shale of the Uinta formation
2	"	"	"	"	"	11 ±1.1	"	550±55	0±77.8	0±3.9	55 ±3.9	5±5.2	

Table A-10: Sorption data of m in Davis Gulch Valley bottom soil (first and second run), and weathered material and crushed shale of the Uinta Formation

1	2	3	4	5	6	7	8	9	10	11	12	13	14
No. of Equilibrations	µg/ml conc. of Mo leachate added	ml of leachate added	gm of geologic material used	Total µg Mo added	Total µg Mo added to 1 gm of geologic material	µg/ml conc. of Mo in supernatant	ml of supernatant	Total µg Mo supernatant	Total µg of Mo sorbed (column 5 - column 9)	Total µg of Mo sorbed on 1 gm of geologic material	Σ µg Mo added to 1 gm of geologic material	Σ µg Mo sorbed on 1 gm of geologic material	Remarks
1	6.8±.68	50	20	340±34	17±1.7	5.6±.56	50	280±28	60±44	3±2.2	17±1.7	3±2.2	Davis Gulch Valley bottom soil first run
2	"	"	"	"	"	6.8±.68	"	340±34	0±48	0±2.4	34±2.4	3±3.25	
1	6.8±.68	50	20	340±34	17±1.7	6.5±.65	43	279.5±27.9	60.5±44	3.03±2.2	17±1.7	3.03±2.2	Davis Gulch valley bottom soil second run
2	"	"	"	"	"	6.9±.69	50	345±34.5	- 5 ±48.5	- .25±2.4	34±2.4	2.77±3.3	
3	"	"	"	"	"	7.1±.71	"	355±35.5	-15 ±49	- .75±2.4	51±2.9	2.03±4.1	
4	"	"	"	"	"	6.9±.69	"	345±34.5	- 5 ±48.5	- .25±2.4	68±3.4	1.78±4.7	
5	"	"	"	"	"	6.8±.68	"	340±34	0 ±48	0±2.4	85±3.8	1.78±5.3	
6	"	"	"	"	"	6.8±.68	"	340±34	0 ±48	0±2.4	102±4.1	1.78±5.8	
7	"	"	"	"	"	6.9±.69	"	345±34	- 5 ±48.5	- .25±2.4	119±4.5	1.52±6.3	
8	"	"	"	"	"	6.7±.67	"	335±33.5	5 ±47.5	.25±2.4	136±4.8	1.78±6.8	
9	"	"	"	"	"	6.8±.68	"	340±34	0 ±48	0±2.4	153±5.1	1.78±7.2	
1	6.8±.68	50	20	340±34	17±1.7	5.9±.59	50	295±29.5	45±45	2.25±2.3	17±1.7	2.25±2.3	Weathered material of the Uinta Foundation
2	"	"	"	"	"	6.7±.67	"	335±33.5	5±47.5	.25±2.4	34±2.4	2.5±3.3	
1	6.8±.68	50	20	340±34	17±1.7	5.6±.56	50	280±28	60±44	3±2.2	17±1.7	3±2.2	Crushed shale of the Uinta Foundation
2	68 .68	"	"	"	"	"	"	340±34	0±48	0±2.4	34±2.4	3±3.3	

Table A-11: Sorption data of AS in Davis Gulch Valley bottom soil (first and second run) and weathered and crushed shale of the Uinta Formation

1	2	3	4	5	6	7	8	9	10	11	12	13	14
No. of Equilibrations	µg/ml conc. of AS in leachate added	ml of leachate added	gm of geologic material used	Total µg AS added	Total µg AS added to 1 gm of geologic material	µg/ml conc. of AS in supernatant	ml of supernatant	Total µg AS in supernatant	Total µg of AS sorbed (column 5 - column 9)	Total µg of AS sorbed on 1 gm of geologic material	Σ µg AS added to 1 gm of geologic material	Σ µg AS sorbed on 1 gm of geologic material	Remarks
1	1.5±1.5	50	20	75±7.5	3.75±.4	.22±.02	50	11 ±1.1	64 ± 7.58	3.2 ± .4	3.7 ± .4	3.20± .4	Davis Gulch valley bottom soil first run
2	"	"	"	"	"	.49±.05	50	24.5±2.4	50.5±7.9	2.52 ±.4	7.5 ± .8	5.73± .5	
1	1.5 ± 1.5	50	20	75±7.5	3.75±.4	.21±.02	43	9.0± .9	65.9±7.5	3.3 ±.4	3.7 ± .4	3.30± .4	Davis Gulch valley bottom soil 2nd run
2	"	"	"	"	"	.53±.05	50	26.5±2.6	48.5±7.9	2.43±.4	7.5 ± .9	5.72± .5	
3	"	"	"	"	"	.64±.06	"	32.0±3.2	43.0±8.1	2.15±.4	11.2± 1.0	7.87± .7	
4	"	"	"	"	"	.83±.08	"	41.5±4.2	33.5±8.6	1.67±.4	15.0± 1.2	9.55± .8	
5	"	"	"	"	"	.90±.09	"	45.0±4.5	30.0±8.7	1.5 ±.4	18.7± 1.4	11.10± .90	
6	"	"	"	"	"	.93±.09	"	46.5±4.6	28.5±8.8	1.42±.4	22.5± 1.5	12.50±1.0	
7	"	"	"	"	"	.97±.10	"	48.5±4.8	26.5±8.9	1.32±.4	26.2± 1.6	13.80±1.1	
8	"	"	"	"	"	1.1 ±.11	"	55.0±5.5	20.0±9.3	1 ±.4	30.0± 1.7	14.80±1.2	
9	"	"	"	"	"	.99±.10	"	49.5±4.9	25.5±9.0	1.27±.4	33.7± 1.8	16.10±1.3	
1	1.5 ± 1.5	50	20	75±7.5	3.75±.4	.23±.02	50	11.5±1.1	63.5±7.6	3.17±.4	3.7± .4	3.17± .4	Weathered material of the Uinta Formation
2	"	"	"	"	"	.41±.04	"	20.5±2.0	54.5±7.8	2.72±.4	7.5± .9	5.90± .5	
1	1.5 ± 1.5	50	20	75±7.5	3.75±.4	.36±.04	50	18 ± 1.8	57 ± 7.7	2.85±.4	3.7 ±.4	2.85±.4	Crushed shale of the Uinta Formation
2	"	"	"	"	"	.78±.08	"	39 ± 3.9	36 ± 8.4	1.8 ±.4	7.5 ±.9	4.65±.6	

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INTRODUCTION

The research completed in the last year has been a continuation of a study of the speciation of trace elements and organic complexing ligands in oil shale wastewaters (1,2)

The importance of determining the presence of complexing ligands in aqueous solution or the existence of stable metallo-organic complexes has been discussed in a review by Jenne and Luoma (3). Lack of information on complexes of organic ligands with trace elements in water, both polluted and unpolluted, is a major limitation in calculating over-all trace element speciation.

Living organisms require the availability of trace elements, even though the margin between adequacy and toxicity for many elements may differ by a factor of two or less (4). Thus any environmental factor that reduces or enhances organismic accumulation of a trace element will have potentially major biological significance. The availability of trace elements to organisms may be influenced by at least four general factors: (1) The physiological and ecological characteristics of the organism; (2) forms of the dissolved trace elements; (3) forms of trace elements in ingested solids and; (4) chemical and physical characteristics of the species dissolved in water. Thus the bioavailability and toxicity of dissolved trace elements is affected by speciation among uncomplexed hydrated forms and among the various organic and inorganic complexes of the various valence states of the trace elements.

The most important complexing agents involve coordination with the metal through oxygen or nitrogen atoms or both. The groups described by Uitert and Fernelius (5,6) as having important co-ordinating functions are, in the order of increasing affinity for metal ions;

-O^- (enolate) > -NH_2 (amine) > -N=N- (azo) >

N (ring N) -COO^- (carboxylate) > -O- (ether)

> -C=O (carbonyl)

The functional groups that have been identified in retort waters include all of the above with the exception of azo and ether moieties (1,7-14). The wastewaters that contain high concentrations of dissolved polar compounds thus have the potential to co-ordinate and complex trace elements in solution, as well as influence the uptake of toxic trace elements from solid phases, such as retorted shale.

The organic ligands that are of greatest concern in the present investigation are the heterocyclic nitrogen compounds and aromatic amines that are found in the basic extracts of crude shale oils. These compounds have also been shown to possess the largest fraction of mutagenic activity in studies undertaken by Oak Ridge National Laboratories (15). These types of compounds have been shown to partition into the retort waters and preliminary investigations of the presence of a few nitrogen base compounds have been reported by Caolo, et al. (1) and Stuber (11).

Investigations of crude shale oil by Caolo, Sievers, and Stanley (2) have shown that the major concentrations of As, Se, Cd, Cr and Pb were fractionated with polar organics of relatively high nitrogen content, but this type of study has not previously been applied to oil shale wastewaters.

The nitrogen base compounds are also of concern because they persist in the environment. Fox (16,17) has reported that the basic fraction of retort water is relatively refractory to microbial action in water purification methods. The need for the identification for the individual basic compounds may be necessary in order to evaluate and develop successful treatment methods for the various waste products.

OBJECTIVES

The objectives of this research were two-fold. 1) The identification of metallo-organic species that may be present in oil shale wastewaters and 2) the separation and identification of complexing ligands, particularly nitrogen bases, that may assist in mobilization of toxic trace elements from waste disposal sites or areas affected by accidental releases or spills.

APPROACH

Several approaches were required to attack these problems due to the complexity of the retort water matrix. Stumm and Brauner (18) have suggested that physical mechanical separations, such as membrane filtration, dialysis, gel chromatography, solvent extraction and chromatography are viable techniques for identifying co-ordinated or complexed species in complex media. Florence and Batley (19) have also discussed the importance of these approaches in a recent review on speciation of trace elements in natural waters. These techniques were combined with trace element analysis via atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry to study trace element-organic ligand interactions. Organic compound analysis was undertaken with high resolution capillary chromatography combined with mass spectrometry, flame ionization, and nitrogen-phosphorous selective detectors for identification of particular types of compounds. Techniques for determining complexing ability of different wastewater systems have been used in conjunction with organic solute fractionation to determine what ligands offer the greatest potential for mobilizing trace elements from disposal areas. Leaching experiments with three different wastewaters were conducted and concentrations of certain trace elements were determined in the leachates. Finally, a discussion of the relative importance of organic ligands identified in this research and other related work is presented.

EXPERIMENTAL

Samples

Oil Shale waste materials used throughout this study are listed in Table I:

Table I. Oil Shale Waste Samples Investigated

<u>Sample</u>	<u>Retort Operation</u>
A. Paraho	Above Ground
Process Water	Direct Mode
Retorted Shale	

<u>Sample</u>	<u>Retort Operation</u>
B. Omega-9 Retort Water	True In-Situ
C. Occidental Oxy-6 Product Water	Modified In-Situ

Thanks for samples are due to R. A. Atwood, R. N. Heistand of Paraho, D. S. Farrier of Laramie Energy Technology Center (LETC), and C. L. Nelson of Pacific Northwest Laboratory.

Two gallons of Paraho retorted shale and one kilogram of retorted shale were collected in September 1978 by R. A. Atwood at the Paraho retort operation near Rifle, Colorado. This retort is an above ground process and is operated by Development Engineering Inc. (DEI) for the Paraho Corporation.

The tank from which the process water was collected is used to separate water from oil generated by the retort process. This tank has been used continuously since operations began in 1977. Oil is drained from the tank every third week and the water is drained once per week. However, the water is never completely removed at any one time and the interfact of water-oil should be a composite of water-oil mixtures from 1977 to September 1978. Thus some of this water may have been generated during the first days of operation.

Wildeman (20) has described the Paraho direct mode and indirect mode of operation and has referred to this sample as an oil storage water with sample designation M-102. Trace element concentrations should compare with results obtained by Wildeman (20) and Fruchter, et al. (21,22).

The Paraho retorted shale was also collected in September 1978 and is representative of the laboratory samples collected from the direct mode operation of the Paraho process. Retorted shale is released from the cylinder and is mechanically crushed. Retorted shale that was less than approximately 60-mesh was obtained.

The Omega-9 water sample is a composite of 12,450 gallons of retort water produced during the last quarter of the Laramie Energy Technology Center (LETC) Rock Springs, Wyo., Site 9, true in-situ oil shale processing experiment that was concluded in November 1976. The retort waters produced were largely diluted with ground-waters intruding into the retorting zone and recovered with the liquid and gaseous products. Because of this dilution, the apparent quality of the Omega-9 sample is somewhat better than that where no ground water intrusion occurs.

Farrier, et al. (23) have presented a complete description of the background, collection, processing and storage of the Omega-9 water sample. This sample has been maintained at 33-40°F since the time that it was produced and has been maintained in that temperature range since it was received from LETC.

The Occidental retort water was received in April 1979 from C. L. Nelson of Pacific Northwest Laboratories. This water was collected in March 1979, and is labeled as OXY-6 Product Water. The water is a field composite of pilot plant condensate produced during March 1979 from Occidental's Retort 6 operation at Logan Wash near Debeque, Colorado. The liquid samples were immediately cooled by refrigeration and returned in sealed, dark Teflon containers to Pacific Northwest Laboratories where the samples were maintained at 4°C. These samples were cooled by ice during shipment to this laboratory and have been maintained at approximately 4°C since that time. These samples were not filtered at the collection site and exhibit considerable amounts of suspended materials. The Oil Shale Task Force (24) has presented a preliminary characterization and assessment of the waste products from the Occidental Retort 6 operation. It should be pointed out at this time that these waste samples might not be indicative of an actual process or technology that will be used to commercially produce shale oil.

Materials and Supplies

All solvents and reagents used in the experimental work were obtained as analytical grade reagents. All glassware and sample vials were cleaned in either a sulfuric acid/No-Chromix^K solution or concentrated nitric acid and were rinsed extensively with distilled, deionized water from a Corning Water Distillation Apparatus, Model # AG-2, with a Barnstead ion exchange column prior to distillation.

Procedure

A. Size Separation:

Separation of Omega-9 retort water was investigated using ultrafiltration. Amicon ultrafiltration membranes XM50, PM30, UM20, UM10, UM2, and UM05 were used in this respective order to fractionate Omega-9 retort water that had previously been filtered through a 0.45 micron cellulose acetate Millipore filter. The Amicon filters were chosen to fractionate molecules of equivalent size for greater than 500 to 50,000 molecular weight units.

Each membrane was flushed extensively with distilled, deionized water prior to use in a 10 mL Amicon stirred filtering unit. Once each membrane was placed in the cell, at least 20 mL of distilled, deionized water was passed through the filter. Twenty milliliter aliquots of the 0.45 micron filtered retort water were then passed through each of the ultrafiltration membranes. Nitrogen pressure was required to force the solution through these membranes of small pore size. Nitrogen pressures were held at values of 15 to 35 psi.

The eluent from the filtering unit was collected in polyethylene bottles and saved for trace element analyses. All sample containers had been previously soaked in concentrated nitric acid and were then rinsed extensively with distilled, deionized water.

Trace element analysis for a number of elements were performed by plasma emission spectrometry. The ARL 36000C Inductively Coupled Plasma (ICP) Spectrometer was used for the determination of Fe, Mo, Zn, Cu, Mn, Si, V, Ba, Sr, Mg, Ca, Cd, and Pb. These analyses were completed at the Environmental Trace Substances Research Program Laboratory, Denver, Colo. As and Se analyses were

performed with the Perkin Elmer 5000 Atomic Absorption Spectrometer equipped with an HGA-500 high Atomic Absorption Spectrometer equipped with an HGA-500 high temperature graphite furnace. A matrix modification technique (25,26) that requires the addition of a 1% nickel solution to each sample was used for both As and Se analysis. The matrix modification promotes the formation of nickel arsenate, nickel arsenite, nickel selenate, etc., that are quantitatively retained in the graphite furnace as compared to the more volatile forms of these elements that might be present in the oil shale wastewaters.

B. Adsorbent Separation:

A final separation of the various wastewaters for the different oil shale technologies was approached by using the organic solute fractionation scheme as developed by Leenheer and Huffman (27-29). Figure 1 is a schematic representation of this procedure that separates retort waters into fractions classified as either hydrophobic or hydrophilic solutes. These can be simplified more by the isolation of the acid, base and neutral subfractions of the major classifications. Hydrophobic bases are isolated by passing the total mixture through the first XAD-8 resin to remove both the hydrophobic base and neutral solutes. The hydrophobic bases are obtained by flushing this column with 0.1 N HCl. The notations DOC 1, DOC 2, etc., in Figure 1 represent the points at which dissolved organic carbon concentration is determined during the separation scheme. The hydrophobic acid organic carbon content is determined by flushing the second XAD-8 column with 0.1 N NaOH.

Amberlite XAD-8 resin (Supelco, Inc., 100-200 mesh) was prepared by rinsing with 0.1 N NaOH followed by 0.1 N HCl solutions to remove adsorbed acidic and basic components and trace elements. This was followed by extraction of the resin with the organic solvents, methanol, acetonitrile, methylene chloride in a Soxhlet extractor for periods of 24 hours each to remove adsorbed neutral solutes. The resin was then rinsed with distilled, deionized water extensively until all detectable methanol had been removed.

One liter of the Omega-9 retort water (pH 8.5) and 500 mL of the Occidental retort water (pH 8.17) were passed through columns of XAD-8 resin (bed volume approximately 20 mL) at the intrinsic pH to remove hydrophobic basic and neutral solutes. The total collected eluent was acidified with concentrated nitric acid to bring the retort water to pH 2. The acidified waters were then passed through the second column of XAD-8 (20 mL volume) resin to remove the hydrophobic acid solutes. Subsequent elution through cation exchange resin AGMP-50 (Biorad Laboratories, Richmond, Ca., hydrogen form, 100-200 mesh, 20 mL volume) and anion exchange resin, AGMP-1 (Biorad Laboratories, 100-200 mesh, 20 mL volume) in the hydroxide form removed hydrophilic bases and acids, respectively. After the water had passed through each column, approximately 60 to 75 mL of the combined effluent was removed for trace element analyses and dissolved organic carbon analysis.

Paraho was also fractionated by this method; however, only 500 mL of this aqueous system was used. This wastewater was diluted to 750 mL with distilled deionized water and was passed at least twice through each of the resins before removing samples for trace element and other analysis. One hundred milliliter volumes of each resin were used to fractionate this specific water.

Trace element analyses were performed for Ba, Sr, Mg, Ca, Cd, Pb, Fe, Mo, An, Cu, Mn, Si, and V by inductively coupled plasma emission spectrometry. As and Se were determined by the matrix modification procedure (25,26) for graphite furnace atomic absorption analysis.

Figure 1. Adsorbent separation scheme as described by Leenheer and Huffman (27).

Source Leenheer, J. A., and Huffman, E. W. D.,
J. Res. U. S. Geol. Surv. (1976) 4 737.

C. Gas Chromatography/Mass Spectrometry Analysis of Nitrogen Bases:

Hydrophobic base compounds were removed from the first XAD-8 resin column for each fractionation series. Dilute hydrochloric acid solution (0.1 N HCl) was eluted through the XAD-8 resin until no color was apparent in the eluent. The columns were then eluted with 50 to 100 mL of additional acid solution. The pH of the acidic eluent was adjusted to pH 9-10 and the nitrogen bases were re-adsorbed onto fresh XAD-8 resin. This allowed the separation of nitrogen bases from neutral organic solutes on the first resin bed. Soxhlet extraction of the air dried resins with methylene chloride yielded relatively pure extracts of the nitrogen base compounds. The resin was further extracted with methanol to completely desorb all organic solutes.

Gas chromatography and gas chromatography/mass spectrometry analysis of these fractions were conducted on the HP 5830A with flame ionization detection, the HP 5730A equipped with nitrogen-phosphorous selective detection, and the HP 5980 GC/MS/DS system. Fused silica columns coated with SE-52 were used for all measurements.

Mass spectral data were used to identify the class of nitrogen compounds present in each sample. Positive identifications in each sample were made by comparison of the retention time and the mass spectrum of each reference compound. Mass spectra obtained from the separated individual compounds in the subfractions were compared with those in reference compilations of the EPA/NIH Mass Spectral Data Base (NSRDS-NBS 63) or with the mass spectra obtained in the present study for pure authentic samples of individual compounds.

D. Dissolved Organic Carbon Analysis:

A Beckman Model 915B Total Organic Carbon Analyzer was used for dissolved organic carbon analysis. Each sample was diluted such that it was in the range of 0-100 μg carbon/mL. The samples were acidified to pH 2 with concentrated phosphoric acid and purged for at least 15 minutes each with a purified nitrogen stream to remove traces of CO_2 .

E. Determination of Complexing Ability of Retort Waters:

Two different procedures were used to assess the complexing ability of retort waters. Both methods were derived from adaptations of work previously described by Manahan, Jones and Kunkel (30-33) concerning determination of strong complexing ligands in natural waters. These techniques involve the complexation of copper at high pH and solubilization of copper from a banded chelating resin.

Solubilization of Copper Hydroxide

The following procedure was used for determination of complexing ability of the various retort wastewaters.

1. 25 mL of each water sample was acidified to pH 2 with nitric acid.
2. Each water sample was filtered through a 0.45 micron Millipore filter.
3. The samples were passed through a small bed of purified Dowex 50-X8 cation exchange resin in the sodium form.
4. One milliliter of $5 \times 10^{-2}\text{M}$ CuSO_4 solution was added to each solution.

5. Sodium hydroxide (1 M) was added with stirring, and the samples were purged with a purified nitrogen stream until the pH was adjusted to 9.8-10.2. If no precipitate was evident at this point additional copper solution was added.
6. The samples were heated to near boiling until the precipitate turned a dark color. The pH was checked periodically at this point to ensure that a pH value of approximately 10 was maintained. Additional sodium hydroxide solution was added if the pH was below 9.8.
7. The samples were cooled and diluted quantitatively to 100 mL.
8. A portion of each sample was filtered through a 0.45 micron Millipore filter and acidified with concentrated nitric acid.
9. The copper content in each sample was determined by flame atomic absorption spectrometry.

Banded Chelex Column Measurements for Complexing Ability.

This procedure is also an adaption of a method presented by Manahan and Jones (32,33). A small stainless column (20 cm in length, 1/8 inch o.d) was prepared as illustrated in Figure 2. The weakly acid cation exchange resin, Chelex 100 (Biorad Laboratories, 100-200 mesh), was used in this analysis. The copper form of the Chelex 100 was prepared by equilibrating sodium form Chelex 100 in a solution of 0.1 M copper chloride. After allowing the suspension to equilibrate for at least one hour, the resin in the copper form was removed by filtration and was washed extensively with distilled deionized water.

The copper form resin and the sodium form resin were then equilibrated in a 0.1 M solution of sodium chloride in a 40% ethanol solution in distilled deionized water. The stainless steel column was packed in the approximate proportions illustrated in Figure 5 by alternating sodium and copper forms of the resin in the column. The lower and middle layers were added by using water aspiration at the exit end of the column to pack the material. The upper layer of the column was added by using a reservoir and pressures of 200-300 psi to pack the resin and to minimize voids in the column.

The prepared column was attached to a Chromatronix nitrogen pressure liquid chromatograph. The mobile phase used in these experiments was 0.1 M sodium chloride in 40% ethanol/distilled deionized water.

A six-port Valco valve was used for sample introduction and sample loops of 50 to 200 microliters were found to be adequate for complexing determinations. Calibrations were performed using standard solutions of disodium ethylenediamine-tetraacetic acid in distilled deionized water. The flow rate through the Chelex column was adjusted to one to two milliliters/minute and was approximately matched with the aspiration rate for the atomic absorption nebulizer.

Flame conditions were optimized for the atomic absorption measurements of copper by aspirating aqueous copper solutions directly before connecting the effluent from the low pressure liquid chromatograph system to the nebulizer.

Figure 2. Banded Chelex column used for determination of complexing abilities of retort waters. Also depicted is the functional characteristic of the Chelex 100 weakly acid cation chelating resin.

F. Gel Chromatography:

A gel chromatography procedure described by Manatoura and Riley (34) for the determination of metal interactions with humic and fulvic acid compounds was followed to determine an approximate molecular weight range for complexing ligands present in Omega-9 retort water.

Biogel P-2 resin (Biorad Laboratories, 200-400 mesh) was equilibrated with a solution of tris-hydroxymethylamino methane (TRIS) buffer. Sodium chloride (0.58 g) was dissolved in 800 mL of distilled deionized water and 1.2. g of TRIS was added. This solution was titrated with 0.5 M HCl to pH 8.5. A sufficient volume of a stock solution of cupric chloride was added to yield a solution that was 10 μg Cu/mL. The mixture was diluted to one liter with distilled, deionized water. This solution was 0.01 M with respect to sodium chloride and TRIS.

The Biogel P-2 Resin equilibrated with this solution was degassed by evacuating with water aspiration. The fines were decanted from the gel and the gel was poured as a slurry into a 100 mL buret equipped with a Teflon stopcock. Ninety five to one hundred milliliters of the gel was held in place by Pyrex glass wool plugs.

One hundred milliliters of the Omega-9 retort water was concentrated by roto-evaporation to approximately 10 mL. Two-milliliter samples of this retort water were equilibrated with equivalent amounts of the metal-Tris buffer and the copper content was adjusted to the concentration in the equilibrated gel. The sample was added to the top of the resin and was allowed to flow into the bed before buffer solution was added. A Harvard Apparatus Model 600-1200 peristaltic pump was used to induce a flow rate of approximately 30 mL/hour through the column. Two milliliter aliquots were collected and each fraction was analyzed for copper content by flame atomic absorption spectrometry. A micro sampling system was used for copper analysis. This required the attachment of a 1 mL pipette tip to the aspirator. One hundred microliter injections of each collected fraction were sufficient to follow the elution of copper from the column. Each collected fraction was diluted one to ten and the absorbance of these solutions was measured at 254 nm on a Cary 219 ultraviolet-visible spectrophotometer to follow the elution of organic compounds from the column.

G. Leaching Experiments.

Initial leaching experiments were conducted with Paraho retorted shale and Paraho process water. Columns defined as "dry packed" were intended to simulate examples of dust control of large disposal piles of spent shale by spraying with wastewater. The columns defined as "wet packed" were prepared to simulate disposal of waste products as mixtures that might be used to layer selected sites. These columns were leached with the Paraho process water to present the worst possible environmental situation and to present the best opportunity for organic ligands to complex trace elements at the surface of the spent shale.

Pyrex glass tubing, 1-cm inside diameter, fitted with ground glass frits was used to prepare the leaching columns. Each column was soaked in concentrated nitric acid overnight and then rinsed extensively with distilled deionized water. All sample vials were treated in a similar manner.

Prior to initiating the leaching studies, the Paraho water that was used was centrifuged at 15,000 rpm at 5°C for 20 minutes to separate insoluble material from the aqueous phase. The middle portion of each centrifuged sample of water was removed for use in the column studies.

The wet packed columns were prepared by mixing the collected centrifuged water with dry, fine-grained retorted shale in a one to five ratio (water/shale) by weight. Approximately 20 g of this mixture was poured into two different glass columns. One pore volume fractions (10 mL) of the leachate were collected until 24 pore volumes had eluted. At this time distilled, deionized water was substituted for the centrifuged process water and leaching was resumed.

The dry packed columns were prepared by adding 10 g of the dry retorted shale to three glass columns. The columns were saturated from the bottom by capillary action with unfiltered, uncentrifuged Paraho process water. The pore volume of the retorted shale in the column was determined to be 5 mL. This void space accounts for approximately 50% of the volume of the column. Paraho process water was added to the top of the column and 10 mL (2 pore volumes) fractions of the leachate were collected. After 30 pore volumes of leachate had been collected over a period of 72 days, distilled, deionized water was added to the top of the column and the leaching was continued.

Short term leaching studies were conducted to compare leaching properties of the three different wastewaters. Columns were prepared with 10 g of Paraho spent shale and were equilibrated with 10 mL of each of the wastewaters or distilled, deionized water. These mixtures were allowed to sit for approximately 48 hours and were then added to separate columns as slurries. Additional water was added to each specific system and the leaching process was initiated. The leachate was collected as approximately 5 mL pore volume fractions. The flow of the leachate solutions was relatively rapid and collection of the leachate was limited to two pore volumes per day until eight to ten pore volumes had been collected from each system.

These leachates and the original waters were analyzed for As, Se, Cd, Cr, Pb, Zn, Co, Cu, Ni, and Mo by flame or graphite furnace atomic absorption spectrometry.

H. Instrumental Methods:

Gas Chromatography

Volatile organic compound characterization of the different samples obtained by liquid-liquid extractions, steam distillations, and adsorbent separations of the wastewaters were obtained using a Hewlett-Packard HP 5830A gas chromatograph equipped with a flame ionization detector (FID).

Glass capillary columns prepared in this laboratory of approximately 24 meters in length, coated statically with either 0.3% SE-30 or SE-52 (poly-(dimethylsiloxane) and poly-(methylphenylsiloxane), respectively, were used in preliminary characterizations and separations of components in the complex mixtures. Both of these capillary columns were previously deactivated by silylation with hexamethyldisilazane following the procedures presented by Grob (35,36). The preliminary analyses were used to determine the conditions needed for gas chromatography/mass spectrometry analyses.

Once tentative identifications of certain types of compounds had been made, fused silica capillary columns were used to make positive identifications with checks of retention times of pure compounds. Fused silica capillary columns

that were used included; Hewlett Packard SP2100 (poly-(dimethylsiloxane), deactivated by Carbowax 20, 30 meters in length, J & W Scientific SE-52 (poly-(methylphenylsiloxane), deactivated by silylation), 30 meters in length, and a HP nondeactivated Carbowax 20M (poly-(ethylene glycol)), 25 meters in length. The SP2100 column and the SE-52 column were used for samples that contained nonpolar and basic compounds. A typical temperature program for these analyses used an initial temperature of 30-40°C, temperature program at 4°C/min., and a final temperature of 270°C. The Carbowax 20M fused silica capillary column was used for samples that contained phenols and free acids. The upper temperature limit for this column was 200°C.

A Hewlett-Packard HP 5730A gas chromatograph equipped with a HP nitrogen-phosphorous selective detector was used to screen samples for the presence of nitrogen-containing compounds. This detector, the HP NPD-18789A, was operated at 300°C with hydrogen flow of 3 mL/minute, and air at 50 mL/minute. Bead voltage for the detector was operated at 16-20 volts.

Gas Chromatography/Mass Spectrometry

Gas chromatography/mass spectrometry analyses were conducted using a Hewlett-Packard HP 5890A/5933A GC/MS/DS system. In most cases, the gas chromatography separations were accomplished using a HP SP2100, meter fused silica column coated with SP 2100 Carbowax deactivator, or a 30 meter J & W Scientific fused silica column coated with SE-54 (1% vinyl in poly-(methylphenylsiloxane), previously deactivated by silylation).

Mass spectra were obtained every 2-3 seconds over the range of 50-400 atomic mass units (amu). Mass spectral data were stored in the computer and later recalled to produce a total ion chromatogram, which is a plot of total ion intensity versus retention time. Specific mass to charge ratios were studied using mass chromatograms to identify the presence of homologous series of compounds containing specific functional characteristics. Mass spectra were interpreted by comparison with the reference compilation of the EPA/NIH Mass Spectral Data Base (NSRDS-NBS 63) or through comparison with the mass spectra of pure compounds.

Atomic Absorption Spectrometry

Trace metal analyses were conducted for liquid-liquid extractions, steam distillations, and leachates with the Perkin Elmer 360 and 5000 atomic absorption spectrometers equipped with the Perkin-Elmer HGA-2100 high temperature graphite furnace. A Perkin-Elmer auto sampling system, AS-1, was used with the PE 5000. Samples that contained high concentrations of particular elements were determined by flame atomic absorption methods. Table II gives the parameters for the elements determined by high temperature graphite furnace techniques. The elements determined by atomic absorption spectrometry included arsenic (As), Selenium (Se), Cadmium (Cd), Chromium (Cr), Lead (Pb), Zinc (Zn), Nickel (Ni), Molybdenum (Mo), and Copper (Cu).

RESULTS AND DISCUSSION

Size Separation

Ultrafiltration membranes offer another unique method for separation of trace elements with organic ligands, although this separation technique is based principally on the differences in size of compounds present in solution. This method has been used previously in comparison with dialysis techniques for

Table II: Operating Conditions for the Atomic Absorption Graphite Furnace Analyses.

Element	Wave Length (nm)	Slit Width (nm)	Sample Size (μ L)	Temperature Program °C **		
				Dry	Ash	Atomize
As*	193.6	0.7	25	100	850	2700
Cd	228.8	0.7	10	100	400	1500
Cr	357.9	0.7	25	100	1350	2700
Cu	324.7	0.7	25	100	1000	2500
Mo	313.3	0.7	25	100	1800	2700
Ni	232.0	0.2	25	100	1200	2500
Pb	283.3	0.7	10	100	550	2000
Se*	196.0	0.7	25	100	850	2700
Zn	213.9	0.7	10	100	500	2000

* Signifies the matrix modification method using 1% nickel solution was used.

** Typical times for temperature programs were: dry (40 sec.), ash (60-90 sec.), atomize (7 sec.).

investigations of complex formation of humic and fulvic acids (37) as well as studying the distribution of trace elements in marine environments (18). This is the first report of using ultrafiltration to study trace element distribution in oil shale wastewaters.

Florence and Balley (19) have recently reviewed the application of ultrafiltration, the importance of determining the size of organic and inorganic complexes of metals in natural value systems. Table III gives information on the possible chemical forms (speciation) of metals that have been studied in natural waters.

Table III
POSSIBLE CHEMICAL FORMS (SPECIATION) OF METALS IN
NATURAL WATERS (19)

Chemical form	Possible examples	Approximate diameter(nm)
Particulate	Retained by 0.45 μ m filter	>450
Simple hydrated metal ion	$Zn(H_2O)_6^{2+}$	0.8
Simple morgame complexes	$Zn(H_2O)Cl$	1
Simple organic complexes	Cu-glycinate	1-2
Stable morganic complexes	PbS, ZnCO	1-2
Stable organic complexes	Cu-fulvate	2-4
Adsorbed on morganic colloids	Cu^{2+} - Fe_2O_3 , Cd^{2+} - MnO_2	10-500
Adsorbed on organic colloids	Pb^{2+} -humic acid Zn^{2+} -organic detritus	10-500

Source: Batley, T. M., Florence, G. E., CRC Critical Reviews in Analytical Chemistry, 1980, 9, 219.

The Amicon ultrafiltration membranes used in this experiment were selected to separate compounds at molecular weight intervals of 500, 1000, 10,000, 20,000, 30,000, and 50,000. These separations are achieved with the membranes UM05, UM2, UM10, UM20, PM30, XM50, respectively. The results from this experiment should not be interpreted as indicating the presence of compounds of this molecular weight range but, rather should be considered as molecules that may pass through membrane pore sizes of less than 5.1 nm to less than 1.0 nm. The Omega-9 water was used for this experiment. It had been previously filtered through a 0.45 micron cellulose acetate Millipore filter prior to introduction into the ultrafiltration cell. The filtered solutions were analyzed for fifteen elements each by inductively coupled plasma emission spectrometry and graphite furnace atomic absorption spectrometry for arsenic and selenium. The results from this experiment are given in Table IV.

There are several different ultrafiltration membranes available as indicated by their notation. The UM ultrafiltration membranes are hydrophilic, exhibit low adsorption, and have few free ionic sites at the surface and maintain a neutral charge. The PM filter is an inert non-ionic polymer, that does not adsorb strong co-ordinated ionic or inorganic solutes, but does adsorb hydrophobic materials. The XM membrane is classified as moderately hydrophilic.

The trace element analysis of the fractionated samples indicates that a large percentage of strontium, magnesium, and iron exist as fairly large molecules or are adsorbed onto particulate matter that cannot pass through the pores of a 0.45 micron Millipore filter. Arsenic and silicon were also noted to decrease in concentration with this filtering step.

Table IV: Distribution of Trace Elements ($\mu\text{g/mL}$) in Omega-9 retort water by size using ultrafiltration membranes.

Element	(M) raw Omega-9	0.45 μ MP	XM50	PM30	UM20	UM10	UM2	UM05	$\sigma(\pm)$
Ba	0.053	0.422	0.400	0.390	0.387	0.357	0.363	0.362	0.024
Sr	1.084	0.898	0.895	0.874	0.874	0.796	0.833	0.819	0.012
Mg	20.06	15.47	17.04	16.56	16.69	15.31	15.98	15.47	0.01
Ca	11.3	12.6	12.9	11.9	12.3	11.5	11.8	11.6	0.2
Cd	0.001	0.016	0.016	0.016	0.015	0.013	0.014	0.012	0.001
Pb	0.012	0.012	0.011	0.010	0.012	0.011	0.012	0.009	0.001
As	0.82	0.69	0.75	0.76	0.73	0.59	0.62	0.53	0.01
Se	0.22	0.16	0.15	0.12	0.12	0.08	0.11	0.08	0.01
Fe	1.09	0.57	0.51	0.50	0.49	0.27	0.19	0.27	0.02
Mo	0.49	0.41	0.37	0.35	0.36	0.33	0.36	0.31	0.04
Zn	0.56	4.32	4.25	4.16	4.22	3.87	4.10	3.67	0.01
Mn	0.06	0.07	0.07	0.08	0.07	0.07	0.07	0.07	0.01
Si	11.3	10.6	9.7	8.4	8.7	8.8	ND	9.1	0.1
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
V	<0.04	<0.04	<0.04	<0.04	<0.02	<0.04	<0.04	<0.02	0.04

ND = not determined

Very little size fractionation was noted for any of the elements studied in this experiment with the exception of iron which did seem to show approximately a 50% difference between the ultrafiltration membrane equivalent to 20,000 molecular weight units and the membrane that allows molecules of less than approximately 10,000 molecular weight units or 1.9 nm in diameter to pass.

Unfortunately, the capabilities for determining dissolved organic carbon content of each of the filtered samples was not available. It was noted, however, that the Omega-9 water that was collected as filtrate from each of the membranes was successively lighter in color as the samples were passed through membranes of smaller pore size. The eluent collected from the membrane of smallest pore size, UM05, was nearly colorless as compared to the original Omega-9 retort water and the strong ammonia odor, characteristic of this water, was evident in all fractions collected.

These results indicate that the majority of trace elements studied in this retort water exist as small, simple ions and do not associate strongly with high molecular weight compounds with the possible exception of iron. Iron, magnesium, silicon and strontium that are removed by a 0.45 micron filter are possibly present as various mineral forms or in the case of iron, as hydrous oxides (38). It is interesting to note that manganese did not show any apparent loss in concentration through the filtration scheme. Manganese is usually associated with manganese dioxide in natural water systems and is important when considering the uptake and transport of heavy metals in the environment (3).

Arsenic and selenium were both noted to decrease in concentration when the Omega-9 water was filtered through the 0.45 micron filter and the membranes of smaller pore size. However, it is difficult to assess a significance to the concentration changes of these elements through this filtration scheme. This is particularly important when considering the values of selenium reported since the changes in concentration are very small. The change in concentration of arsenic was obvious when the raw water was filtered through the Millipore filter. This observation has also been made by Fox (39), and was also evident in the steam distillation experiment where the particulate matter contained 8.0% of the original arsenic concentration for the Omega-9 retort water.

It should also be pointed out that contamination problems for calcium, barium, cadmium and zinc were encountered in the size fractionation procedure. The contamination for these elements evidently arises from the 0.45 micron Millipore filter. The filter used in this study had been rinsed with a 10% nitric acid solution in distilled, deionized water for several hours and then rinsed extensively with several liters of distilled, deionized water. However, it was noted during the course of these experiments that the contaminants are more effectively removed by extending the contact time of the Millipore filter with 10% nitric acid solution for at least 10 to 12 hours.

A final point is that the standard deviation reported for each element analysis was reported from replicate determinations of standards only. The volume of the samples were not sufficient to allow duplicate measurements for these elements.

Adsorbent Separation

Trace Element Analysis:

The previous separation schemes were chosen because they allowed simplification of the oil shale retort water matrix without drastic changes to the aqueous samples. However, these experiments have not really provided a very thorough

characterization of the wastewater system. The adsorbent separation scheme described by Leenheer and Huffman (27) was explored with the purpose of more fully characterizing the constituents of the wastewaters and identifying potential ligands as well as possibly isolating metallo-organic complexes. Leenheer and Huffman (27) have suggested that this method might be useful in separating organic from inorganic solutes in natural and wastewater systems.

The XAD-8 resins are used to remove organic solutes that are not extensively soluble in aqueous solutions and possibly trace element-organic ligand complexes that might be of neutral charge. Skogerboe, et al. (40) have used a similar technique to isolate metal complexes of humic and fulvic materials at various pH values. The requirement for isolation of a metal-organic complex is that the complex must maintain a neutral charge at a given pH.

The first pass through XAD-8 resin at the intrinsic pH of the retort water allows the removal of solutes classified as hydrophobic bases and neutral, (HPO-B, HPO-N), respectively. After the pH has been adjusted to approximately pH 2 and passed through a second column of XAD-8 resin, compounds classified as hydrophobic acids (HPO-A) are removed. Subsequent passage through the cation exchange resin, AGMP-50, and the anion exchange resin, AGMP-1, removes hydrophilic solutes (basic and acidic, HPI-B, HPI-A, respectively) and also trace elements that are present as either cationic or anionic forms. Table V presents the type of organic solute fractionation that might be expected with this procedure.

The Paraho, Occidental, and Omega-9 retort waters were each fractionated by this method. Trace element analyses were completed on a sample of each water after it had passed completely through the particular resin indicated in Tables VI to VIII.

XAD-8 (A) refers to the first resin that the retort water passed through when at its original pH. XAD-8(B) refers to the water that has passed through the second XAD-8 resin following acidification. Each sample that was analyzed was taken from the total volume of the water collected from each resin. The elemental analyses given as AGMP-50 and AGMP-1 refer to trace element concentrations remaining in the waters after eluting from the cation exchange and the anion exchange resins, respectively.

Most of these results were obtained by inductively coupled plasma emission spectrometry. Arsenic and selenium were determined by graphite furnace atomic absorption spectrometry. The results for each element in the Omega-9 retort water were compared to literature values for this sample. All values for these elements compare well with the results reported by LETC.

The largest changes of concentration for most of the trace elements resulted after acidification of the wastewaters and passage through the second XAD-8 resin. Leenheer and Huffman (27) have also observed similar effects in natural water systems and have proposed that trace elements isolated with the organic constituents exist as metal-organic cations and anions adsorbed by the macroreticular resins, although the exchange capacity of the XAD-8 resins are low.

Table V. Compound Class Fractionation That Might Be Expected With The Absorbent Separation Scheme 4.

HPO-B: Aromatic amines except pyridine.

HPO-A: Aliphatic carboxylic acids > five carbons, aromatic carboxylic acids, phenols.

HPO-N: Hydrocarbons, aliphatic alcohols, amides, esters, ketones, and aldehydes of < five carbons, pyrroles, and indoles.

HPI-B: Aliphatic amines, pyridine, amino acids.

HPI-A: Aliphatic acids of $\leq$ five carbons, and polyfunctional acids.

HPI-N: Aliphatic amides, alcohols, aldehydes, esters, and ketones $\geq$ five carbons, polyfunctional alcohols, carbohydrates.

HPO = hydrophobic solutes

HPI = hydrophilic solutes

B = bases, A = acids, N = neutrals

Table VI. Distribution of Trace Elements ($\mu\text{g/mL}$) in Paraho Process Water by Adsorbent Separation

	V	Zn	Ca	Mg	Al	Li	Ba	Ni	As*	Se**
Paraho	<0.02	0.03	37.20	1110	<0.15	4.1	0.579	1.9	5.5	5.77
XAD-8(A)	<0.02	0.09	59.80	1040	<0.15	4.1	0.593	1.7	6.1	5.94
XAD-8(B)	<0.02	<0.01	23.09	408	<0.15	1.4	0.245	0.8	3.3	0.31
AGMP-50	<0.02	<0.01	9.00	341	<0.15	≤ 1.0	0.006	0.8	3.7	0.33
AGMP-1	<0.02	<0.01	9.13	344	<0.15	1.4	<0.002	0.9	3.3	0.19
σ ($\pm$)	0.02	0.01	0.02	0.3	0.15	1.0	0.002	0.1	--	---

* Arsenic values from six separate determinations, $\sigma = \pm 0.30$

** Selenium values from three separate determinations, $\sigma = \pm 0.50(5.94)$ to $0.04(0.19)$.

Standard deviations for all other elements calculated from standards and blanks.

Table VI. (continued)

	Co	Pb	Cd	Mn	Fe	Mo	Si	Cu	B	Cr
Paraho	1.00	<0.02	<0.01	0.221	2.66	0.38	20.9	0.26	56.4	0.07
XAD-8(A)	0.91	<0.02	0.03	0.199	1.93	0.32	18.5	0.28	52.1	0.04
XAD-8(B)	0.31	<0.02	<0.01	0.107	2.23	<0.02	13.3	<0.01	21.0	<0.01
AGMP-50	0.22	<0.02	<0.01	0.068	1.72	<0.02	13.4	0.05	22.5	<0.01
AGMP-1	0.08	<0.02	<0.01	0.081	1.90	<0.02	13.6	<0.01	22.3	<0.01
σ ($\pm$)	0.01	0.02	0.01	0.005	0.01	0.02	0.1	0.01	0.1	0.01

Table VII. Distribution of Trace Elements ($\mu\text{g/mL}$) in Occidental Retort Water by an Adsorbent Separation Scheme.

	V	Zn	Ca	Mg	Al	Ba	Li	Ni	As	Se
Occidental	<0.02	0.02	5.42	108.0	<0.15	0.435	5.7	1.8	1.02	<0.01
XAD-8(A)	<0.02	<0.01	11.52	102.2	<0.15	0.433	6.1	2.0	1.02	<0.01
XAD-8(B)	<0.02	<0.01	5.51	35.9	<0.15	0.214	1.2	0.8	1.30	<0.01
AGMP-50	<0.02	<0.01	<0.02	<0.3	<0.15	<0.002	<1.0	1.0	1.02	<0.01
AGMP-1	<0.02	<0.01	0.03	<0.3	<0.15	0.004	1.3	1.1	0.90	<0.01
σ ($\pm$)*	0.02	0.01	0.02	0.3	0.15	0.002	1.0	0.1	0.01	0.01

* Standard deviations for all elements were determined for standards and blanks only. Reported concentrations were made on one determination for each sample.

Table VII. (continued)

	Co	Pb	Cd	Mn	Fe	Mo	Si	Cu	B	Cr
Occidental	0.16	<0.02	0.02	<0.005	0.07	0.21	17.6	0.04	39.6	0.07
XAD-8(A)	0.14	<0.02	<0.01	<0.005	0.06	0.19	16.9	0.03	38.1	0.04
XAD-8(B)	<0.01	<0.02	<0.01	<0.005	0.18	0.09	16.7	0.03	13.4	<0.01
AGMP-50	<0.01	<0.02	<0.01	<0.005	0.03	0.10	17.6	<0.01	13.3	<0.01
AGMP-1	<0.01	<0.02	<0.01	<0.005	0.06	<0.02	19.5	<0.01	17.1	<0.01
σ ($\pm$)	0.01	0.02	0.01	0.005	0.01	0.02	0.1	<0.01	0.1	0.01

Table VIII. Distribution of Trace Elements (g/mL) in Omega-9 Retort Water by Adsorbent Separation.

	V	Zn	Ca	Mg	Al	Li	Ba	Ni	As	Se
Omega-9	0.04	0.19	11.1	21.8	<0.15	2.0	0.311	0.2	0.73	0.16
XAD-8(A)	0.05	0.21	14.6	26.2	<0.15	3.0	0.480	0.3	0.76	0.12
XAD-8(B)	0.04	0.14	11.1	20.5	<0.15	<1.0	0.100	0.3	0.77	0.03
AGMP-50	0.06	0.08	<0.2	11.8	<0.15	2.0	<0.002	0.3	0.73	0.05
AGMP-1	0.06	0.02	<0.2	14.8	<0.15	3.0	<0.002	0.6	0.06	<0.01
$\sigma(\pm)^*$	0.02	0.01	0.2	0.3	0.15	1.0	0.002	0.1	0.01	0.01

* Standard deviations for all elements were determined for standards and blanks only. Reported concentrations were made on one determination for each sample.

Table VIII. (continued)

	Co	Pb	Cd	Mn	Mo	Fe	Si	Cu	B	Cr
Omega-9	<0.01	<0.02	<0.01	0.042	0.68	0.87	9.9	0.01	24.0	<0.01
XAD-8(A)	0.02	<0.02	<0.01	0.046	0.65	0.88	10.2	0.06	30.1	<0.01
XAD-8(B)	<0.01	<0.02	<0.01	0.058	0.17	0.81	9.5	0.02	22.1	<0.01
AGMB-50	<0.01	<0.02	<0.01	0.012	0.13	1.16	10.3	0.02	21.7	<0.01
AGMP-1	<0.01	<0.02	<0.01	0.011	<0.02	0.21	12.0	<0.01	26.9	<0.01
σ ($\pm$) [*]	0.01	0.02	0.01	0.005	0.02	0.01	0.1	0.01	0.1	0.01

The results from these experiments should not be interpreted as the isolation of metal-organic ligand complexes from the original wastewaters. Acidification of the retort water causes drastic changes in the aqueous chemistry. One of the most obvious changes occurs in the sulfur speciation of the retort waters. Thiosulfate is a major sulfur species in oil shale wastewaters and upon acidification results in the precipitation of copious amounts of elemental sulfur. The organic acids are also precipitated, as evidenced by their removal on the XAD-8 resin, and may possibly act as ion exchange sites at the adsorbent surface. Distinct differences in the concentration of zinc, calcium, magnesium, barium, cobalt, lithium, copper, and manganese were noted at this point of the separation scheme for the different waters. Selenium, boron and molybdenum were also removed by the second XAD-8 column that removes organic solutes, classified as hydrophobic acids. The cation exchange resin, AGMP-50, was effective for removing zinc, calcium, barium, manganese and magnesium from the eluent of the second XAD-8 resin and molybdenum remaining in solution was effectively removed on passage through the AGMP-1 anion exchange resin.

It is also interesting to note that arsenic did not behave the same in the three different water systems. In the Omega-9 retort water, 90% of the arsenic was removed by the final adsorbent column, the AGMP-1 anion exchange resin. Very little difference in arsenic concentration from the Occidental retort water was observed between the original water and the water collected at the end of the total fractionation scheme. The Paraho water shows almost a 50% loss through the second XAD-8 resin after acidification, but greater than 3 µg/mL of arsenic remain in the final solution.

The loss of selenium from the Omega-9 retort water and Paraho process water is also very interesting. Leenheer and Huffman (27) studied a natural water that contained high concentrations of selenium using the adsorbent separation scheme. The selenium in the water was not reduced in concentration until it had passed through the anion exchange resin. However, selenium was reduced significantly in the Omega-9 retort water following acidification and passage of the water through the second XAD-8 adsorbent. Less than 20% of the original selenium concentration was measured at this point. The selenium concentration in the Paraho process water was reduced even more significantly after acidification and passage of the water through the second XAD-8 resin. This suggests that the selenium has changed character upon acidification of the two retort waters. The selenium concentration in the Occidental water was too low in original water to indicate any difference between acidification and separation of the organic solutes.

The observation that some of the trace elements like zinc, calcium, magnesium, barium, cobalt, lithium, copper and manganese were removed from the wastewaters with the hydrophobic acid fraction required additional investigation into the extent of complexation of trace elements in the wastewaters.

The Occidental and Omega-9 retort waters were passed through Chelex 100, a weakly acid chelating resin, and the concentration of a number of trace elements were determined in the eluent. The concentrations in the collected eluents from the Chelex 100 resin are given in Table IX. Most of the trace elements determined have been effectively removed from these two retort waters with this treatment. This procedure has been presented as a means of determining the presence of stable complexes in solutions (45-46). Arsenic, selenium and molybdenum remained at the level of the initial concentrations in each water. These elements are not expected to exchange on a cation chelating resin. These three elements are expected to exist as oxyanionic species in the retort waters and possibly could be removed by anion exchange resins.

Table IX. Removal of Trace Elements with the Weakly Acid Chelating Resin, Chelex 100.

Element	[M] $\mu\text{g/mL}$ Omega-9*	Omega-9 Chelex	[M] $\mu\text{g/mL}$ Occidental**	Occidental Chelex
Ba	0.422	0.024	0.435	<0.002
Sr	0.898	0.014	ND	<0.001
Mg	15.47	0.30	108.0	0.8
Ca	12.6	0.2	5.4	0.1
Cd	0.016	<0.001	0.02	0.01
Pb	<0.01	<0.01	0.02	<0.01
As	0.69	0.84	1.02	1.20
Se	0.16	0.12	<0.01	<0.01
Fe	0.57	0.44	0.07	0.10
Mo	0.41	0.39	0.21	0.18
Zn	4.32	0.11	ND	ND
Mn	0.08	0.01	<0.005	<0.005
Si	10.6	8.4	17.6	16.1
Cu	<0.02	<0.02	0.04	0.03
V	0.04	0.04	<0.02	0.03
Li	ND	ND	57.0	0.7
Co	ND	ND	0.16	<0.01

* This is the same water used for solute size separation experiments with the ultrafiltration membranes.

** These values correspond to those measured for the Occidental retort water used in the adsorbent separation scheme (Table XIV).

ND Not determined

The concentration of iron determined in the exchanged water passed through the Chelex 100 is possibly an indication of the presence of ferrous hydroxides at the pH of the retort water or may be indicative of the presence of some organic complex of iron in solution.

These results suggest that the Chelex-metal complexes formed are more stable than the complexes that might exist in solution. The selectivity of Chelex 100 for divalent over monovalent ions is approximately 5000 to one, and this resin has a very strong attraction for transition elements, even in highly concentrated salt solutions. It is widely used for ultra purification of buffers and ionic reagents since it will scavenge metal contaminants to a high degree of purity without altering the concentration of non-metallic ions.

During the course of this work, Fruchter, et al. (21,22) and Fox (47) have presented information concerning the partitioning of major and minor elements during retort operations. Fruchter (21) classified elements in three categories based on the mobility or partitioning among spent shale, crude oil, retort water, and off gases. The first class of elements included non-volatile mineral phase elements such as Al, Ba, Ca, Cr, Mn, Na, Rb, Si, etc. All of these elements were found to partition less than 0.01% from the raw oil shale into the off-gases, wastewater; and crude oil and it is believed that these elements are redistributed principally as entrained shale fines in shale oil or as dissolved ionic species in the wastewater. Elements that were partitioned from 0.01 to approximately 5% were classified in the second category and included As, B, Co, Fe, Ni, Se, Cu, Zn, Mo and Pb. These elements are believed to be associated with volatile metallic or organometallic compounds that are redistributed primarily into the product shale oil, although significant concentrations of these elements have been found in the wastewaters. The third classification includes those elements of greatest mobility, and consists of C, H, N, S, and Hg.

The results of the mass distribution studies for trace elements in a controlled state retort, as presented by Fox (47) are in good agreement with the investigations of the Paraho process operations. Possible partitioning mechanisms for the elements include mineral decomposition of sulfides, oxides and carbonates, and the reduction of mineral forms to volatile species. Also considered were shale product interactions that might include volatilization of organometallic species like cobalt and nickel porphyrins (48-50), suspension of metal oxides or carbonates released from the oil shale.

Both of these investigations have indicated that levels of trace elements determined in the retort waters are largely a function of the separation time for the oil-water mixtures that are condensed simultaneously in the retort operation. This has been shown in the data provided by Fruchter (21) and indicates that these species are present as ionic forms that can be readily removed from the shale oil, or may exist as polar water soluble organic compounds such as methylarsonic and phenylarsonic acids. However, it is not certain whether these species are the same as those partitioned during pyrolysis or whether they are produced by subsequent chemical reactions or biological activity in the retort water over a period of time.

Dissolved Organic Carbon Fractionation:

The oil shale wastewaters were further characterized by determination of the distribution of the total organic carbon content. Tables X to XII present the data for hydrophobic-hydrophilic solute distribution and a breakdown of each major classification into acid, base and neutral subfractions.

Table X. DOC Fractionation of Retort Waters.
Hydrophobic vs. Hydrophilic Solutes.

	<u>Paraho</u>	<u>Occidental</u>	<u>Omega-9 (74)</u>
Total DOC ($\mu\text{g C/mL}$)	41,900	2300	1000
Percent Hydrophobic Solute	71%	52%	49%
Percent Hydrophilic Solute	29%	48%	51%

Table XI. DOC Fractionation of Oil Shale Wastewaters
Hydrophobic Solutes.

<u>Sample</u>	<u>Acids</u>	<u>Bases</u>	<u>Neutrals</u>
Paraho	21,800 ppm (52.0%)	2280 ppm (5.4%)	5720 ppm (13.7%)
Occidental	630 ppm (26.9%)	70 ppm (3%)	420 ppm (18.3%)
Omega-9 (27)	190 ppm (19%)	130 ppm (13%)	170 ppm (17%)

Values in parentheses represent percentage of total organic carbon in unfractionated water.

Table XII. DOC Fractionation of Oil Shale Wastewaters
Hydrophilic Solutes.

<u>Sample</u>	<u>Acids</u>	<u>Bases</u>	<u>Neutrals</u>
Paraho	1940 ppm (4.6%)	5690 ppm (13.5%)	4770 ppm (11.4%)
Occidental	390 ppm (17%)	<5 ppm (<1%)	8.0 ppm (35%)
Omega-9 (27)	290 ppm (29%)	120 ppm (12%)	100 ppm (10%)

Values in parentheses represent percentage of total organic carbon in unfractionated water.

Total organic carbon content was greatest for the Paraho process water. The higher organic carbon concentration in the Paraho process water was apparent from visual inspection of this wastewater compared with the appearance of the Omega-9 and Occidental retort waters. Compounds classified as hydrophobic were removed by adsorption on XAD-8 resins, while hydrophilic compounds were removed by ion exchange resins.

Hydrophobic and hydrophilic solutes were approximately equally distributed in the Omega-9 and Occidental waters. The Paraho water contained 71% hydrophobic solutes as compared to 29% hydrophilic compounds. This probably has resulted from the fact that this water has had longer contact time with the crude oil in the separating tank. The subfractions of hydrophobic and hydrophilic solute contents were determined for these waters and examination of the data indicates that the acid and neutral solutes comprise the major portions of each water. The hydrophobic acid fraction of Paraho process water is equivalent to 52% of the total organic carbon content. In the Occidental and Omega-9 waters, the hydrophobic acid content exceeds that of the hydrophobic neutral fraction. The total of hydrophobic acids and hydrophobic neutrals in each water show the relative organic carbon content where Paraho > Occidental > Omega-9. This is the same order that was noted for the total organic carbon concentrations of these three waters. However, it should be pointed out that the concentrations of the basic solutes of the hydrophobic fraction decrease in the order, Paraho > Omega-9 > Occidental.

Hydrophilic base solutes also follow this same order and it is interesting to note that Occidental water contains very little detectable hydrophilic bases. The reported value of 5 µg carbon/mL is approximately the detection limit for these waters. This indicates that this water should contain very little pyridine or aliphatic amines. Basic solutes are the major fraction of the hydrophilic components in Paraho process water, and neutrals are in greater abundance than the acids in the Paraho and Occidental wastewaters studied. In Omega-9 retort water, hydrophilic acids are present at three times the concentration of either the basic or neutral components. This demonstrates that different oil shale technologies can produce aqueous wastes that differ markedly in the organic solute concentrations of the general classes.

Gas Chromatography/Mass Spectrometry Identification of Nitrogen Bases:

After the organic solutes from the oil shale wastewaters were separated into subclasses, the fractions were subjected to high resolution gas chromatography with mass spectrometry identification to identify as many individual compounds as possible.

Nitrogen base compounds were recovered from the first XAD-8 resin by elution the column with 0.1 N HCl solution. These eluents were adjusted to pH 10 and the nitrogen bases were readsorbed on clean XAD-8 resin. The resin was air dried and then extracted in a soxhlet apparatus with methylene chloride and methanol, respectively. After reducing the volume of methylene chloride and methanol, gas chromatography analysis of each of the fractions indicated that methylene chloride contained volatile and semi-volatile nitrogen bases, but the methanol extracts contained no detectable volatile compounds.

Identification of the nitrogen base compounds was based upon fragmentation patterns of each peak in the chromatograms and matching of retention times of pure compounds. All identifications by retention times were obtained using a fused silica capillary column. Novotny, et al. (51) have recently reported determination of quinoline derivatives in recycle oil of solvent refined coal, and have pointed out that gas chromatography of nitrogen compounds can often be a difficult task. The difficulties that were noted included irreversible column adsorption and peak asymmetry. These phenomena are especially pronounced in glass capillary gas chromatography. Problems relating to these nitrogen compounds, and particularly, aniline compounds have been observed in this work when working with glass capillary columns. However, the peak shape in Figures 3-9 for the nitrogen base fractions of the oil shale wastewaters indicate no problems with chromatography of these compounds on a fused silica capillary column. The peaks obtained in these chromatograms are symmetrical and do not exhibit tailing.

Figure 3 is a chromatogram of a standard mixture of pyridine, aniline, and quinoline compounds identified by mass spectra in the different wastewater extracts with the exception of aminopyridine. Retention times and compound identification are given in Table XIII. The reproducibility of retention times for these compounds varied from ± 0.10 minutes for pyridine to ± 0.05 minutes for acridine. Retention indices were calculated for each compound with pyridine, quinoline and acridine indices set equal to 100, 200, and 300, respectively. These data were compared to values reported by Novotny, et al. (51), but their results did not compare well enough to use that work as an additional source for identifying individual nitrogen compounds. Retention times relative to $n\text{-C}_{24}\text{H}_{50}$ were also measured for each compound in the samples. Quinoline and isoquinoline are ubiquitous and consequently could be used for relative retention time calculations if so desired.

Figures 4 to 9 present the chromatograms with NPD versus FID detection of each of the different nitrogen base fractions in methylene chloride. The large NPD response indicates that these samples consist principally of nitrogen containing compounds. This is reinforced by the fact that mass spectra for the individual peaks of these samples exhibit odd molecular weight parent ions, which is representative of the presence of an odd number of nitrogen atoms.

The differences in nitrogen base content for the three different wastewaters becomes apparent when the chromatograms in Figures 4 to 9 are compared. Omega-9 retort water (Figures 4-5) has a more evenly distributed ratio of pyridines, anilines, and quinoline compounds. By contrast, more quinoline compounds, than pyridine or aniline analogs were identified for the extract from the Occidental retort water, while the Paraho process water contains substantially greater amounts of substituted pyridines and simple anilines than quinoline derivatives. Paraho process water also appears to contain more high boiling compounds than either the Omega-9 or the Occidental retort waters. Compounds that have been identified by mass spectra and/or retention time in these three samples are given in Tables XIV to XVI.

Each of the wastewaters contains 2,4,6-trimethyl-pyridine, which has been identified positively through mass spectra and retention time. These samples also exhibit similar fragmentation patterns indicating that the other trimethylpyridine isomers are present. Van Meter, et al. (103) have identified the 2,3,5-; 2,3,6-; 2,4,5; and 2,4,6-trimethylpyridine isomers in crude shale oils through distillation and formation of pyridine derivatives. The 2,4-; 2,3-; and 2,5-dimethylpyridine isomers have been identified in Omega-9 and Paraho wastewaters and these plus the 2,6-; 3,4-; and 3,5-dimethyl isomers were also identified in the crude shale oils (52).

Figure 3. FID chromatogram of a standard mixture of pyridine, aniline, and quinoline compounds identified in the various wastewater extracts. This chromatogram was obtained on a J&W Scientific fused silica column, coated with SE-52, 30 meters. Temperature program 30°C, rate 4°C/min., final temperature 270°C, splitless injection, 2μL attn. 1 x 32.

Figure 4. NPD and FID chromatograms of the hydrophobic base fraction of Omega-9 retort water. These chromatograms were obtained on fused silica capillary columns coated with SE-52. Temperature program 30-270°C at 4°/min., splitless injections, 2μL, methylene chloride solvent.

Figure 5. FID chromatogram of the hydrophobic base fraction of the Omega-9 retort water. This chromatogram was obtained on a wide bore fused silica column coated with SE-52. Temperature program 30-270°C at 4°C/min., splitless injection, methylene chloride solution, 2μL, attn. 1 x 32.

Figure 6. NPD and FID chromatograms of the hydrophobic base fraction of Occidental retort water. These chromatograms were obtained on fused silica capillary columns coated with SE-52. Temperature program 30-270°C at 4°/min., splitless injections 2μL methylene chloride solvent.

Figure 7. FID chromatogram of the hydrophobic base fraction of the Occidental retort water. This chromatogram was obtained on a wide bore fused silica capillary column coated with SE-52. Temperature program 30-270°C at 4°C/min., splitless injection 2μL methylene chloride solution, attn. 1 x 32.

Figure 8. NPD and FID chromatograms of the hydrophobic base fraction of Paraho process water. These chromatograms were obtained on fused silica capillary columns coated with SE-52. Temperature program 30-270°C at 4°/min., splitless injections 2 μ L methylene chloride solvent.

Figure 9. PID Chromatogram of the hydrophobic base fraction of the Paraho process water. This chromatogram was obtained on a wide bore fused silica capillary column coated with SE-52. Temperature program 30-270°C at 4°C/min., splitless injection 2μL methylene chloride solvent, attn. 1 x 32.

Table XIII. Nitrogen Base Standard in Methylene Chloride.

Peak #	Retention Index	Conc. ($\mu\text{g/mL}$)	Compound
1	100.00	55	pyridine
2	104.84	170	2-methylpyridine
3	130.65	110/50	3- and 4-methylpyridine
4	146.77	80	2,4-dimethylpyridine
5	150.00	25	2,5-dimethylpyridine
6	154.84	20	2,3-dimethylpyridine
7	159.68	30	aniline
8	161.29	200	2,4,6-trimethylpyridine
9	164.52	100	2-aminopyridine
10	175.81	80	N-methylaniline
11	179.03	60	N,N-dimethylaniline
12	185.48	40	N-ethylaniline
13	190.32	60	2,4-dimethylaniline
14	198.39	80	N,N-diethylaniline
15	200.00	150	quinoline
16	203.85	50	isoquinoline
17	219.23	100	2-methylquinoline
18	226.92	40	7-methylquinoline
19	230.77	50	3-methylquinoline
20	242.31	30/50	2,6 and 2,7 dimethylquinoline
21	246.15	40	2,4-dimethylquinoline
22	300.00	50	acridine

Table XIV. Nitrogen Base Compounds Identified in Omega-9 Retort Water.

Peak #	Retention Time (min)	Compound	Identification	
			RT	Mass Spectra
1	5.83	2-methylpyridine	X	
2	8.33	3-and/or 4-methylpyridine	X	X
3	10.55	2,4-dimethylpyridine	X	X
4	11.01	2,5-dimethylpyridine	X	X
5	11.83	2,3-dimethylpyridine	X	X
6	12.53	aniline	X	X
7	12.97	2,4,6-trimethylpyridine	X	X
8	16.70	N,N-dimethylaniline	X	
9	18.23	N-ethylaniline	X	
10	19.60	2,4-dimethylaniline	X	X

Table XIV. (continued)

<u>Peak #</u>	<u>Retention Time (min)</u>	<u>Compound</u>	<u>Identification</u>	
			<u>RT</u>	<u>Mass Spectra</u>
11	21.96	N,N-diethylaniline	X	X
12	22.37	quinoline	X	X
13	23.07	isoquinoline	X	X
14	24.92	2-methylquinoline	X	X
15	26.39	7-methylquinoline	X	X
16	26.61	3-methylquinoline	X	X
17	28.84	2,6-and/or 2,7-dimethyl- quinoline	X	X
18	29.56	2,4-dimethylquinoline	X	X

Table XV. Nitrogen Bases Identified in Occidental Retort Water.

<u>Peak #</u>	<u>Compound</u>	<u>Identification</u>	
		<u>RT(min)</u>	<u>Mass Spectra</u>
1	aniline	X	X
2	2,4-6-trimethylpyridine	X	X
3	N,N-diethylaniline	X	X
4	quinoline	X	X
5	isoquinoline	X	X
6	2-methylquinoline	X	X
7	7-methylquinoline	X	X
8	3-methylquinoline	X	X
9	2,4-dimethylquinoline	X	X

Table XVI. Nitrogen Base Compounds Identified in Paraho Process Water.

Peak #	Retention Time (min)	Compound	Identification	
			RT(min)	Mass Spectra
1	5.33	pyridine	X	
2	7.02	2-methylpyridine	X	
3	8.33	3-and/or 4-methylpyridine	X	X
4	10.52	2,4-dimethylpyridine	X	X
5	10.93	2,5-dimethylpyridine	X	X
6	12.46	aniline	X	X
7	12.86	2,4,6-trimethylpyridine	X	X
8	15.83	N-methylaniline	X	X
9	16.65	N,N-dimethylaniline	X	X
10	18.23	N-ethylaniline	X	X
11	19.54	2,4-dimethylaniline	X	X
12	21.85	N,N-diethylaniline	X	X
13	22.19	quinoline	X	
14	22.99	isoquinoline	X	X

Table XVI. (continued)

<u>Peak #</u>	<u>Retention Time (min)</u>	<u>Compound</u>	<u>Identification</u>	
			<u>RT(min)</u>	<u>Mass Spectra</u>
15	24.77	2-methylquinoline	X	X
16	26.39	7-methylquinoline	X	X
17	26.55	3-methylquinoline	X	X
18	28.83	2,6-and/or 2,7-dimethylquinoline	X	X
19	29.55	2,4-dimethylquinoline	X	X
20	40.51	acridine	X	X

More extensively alkylated isomers of pyridines have also been identified (C_4 - C_5 -alkyl substituted). The mass spectra of these compounds exhibit molecular ions of 100% abundance or fragment ions at $M-15^+$ indicating that these compounds are either tetramethyl; dimethyl, ethyl; ethyl,ethyl; etc. types of isomers. Alkyl substituted isomers, such as those with propyl, butyl, or pentyl groups have been reported (53) to be present in crude shale oils, but have not been identified by mass spectrometry in the aqueous waste.

Aniline compounds have been previously reported to be present in crude shale oils by Brown, et al. (53). The extraction of these nitrogen compounds with XAD-8 resin from retort waters has been presented by Stuber (11), who used HPLC techniques to identify several simple isomers.

Figure 10 is a mass chromatogram for the nitrogen base fraction of Occidental retort water. Mass to charge ratios of 129, 143, 157 are representative of quinoline, isoquinoline, and the methyl and C_2 -alkyl isomers of these parent compounds. Mass chromatograms that were very similar were generated for the nitrogen base fractions obtained from the other waters, also. This indicates that particular compounds appear to be formed during the retorting and partitioning processes. For example, m/e 143 shows at least 8 distinct major peaks for methyl quinolines and isoquinolines in the mass chromatograms. The pattern for m/e 143 is the same for all waters and it should be pointed out that there are only 14 possible isomers. There are 56 possible isomers for the C_2 -alkyl-substituted quinolines and isoquinolines, but only 4 or 5 peaks are distinct for this mass value (m/e 157) and this pattern is also the same for all aqueous samples studied, regardless of the separation method (e.g. liquid-liquid extraction, steam distillation, or adsorbent separation).

The identification of acridine in the hydrophobic base fraction of the Paraho water has serious implications since this compound is a known mutagen (54). The bioaccumulation potential and toxicity of aza-arenes have been shown to increase from isoquinoline to acridine to benz(a)acridine (54). Stuber (11) has reported investigations of the presence of the larger cyclic aza-arenes in Omega-9, Geokinetics, and the 150-ton retort waters, but has not positively identified any of these compounds. The Omega-9 and Occidental concentrates of basic components do not show evidence for the presence of aza-arenes larger than the dimethyl quinolines. The peak labeled as acridine in the Paraho water has been identified by matching of retention time using flame ionization detection and nitrogen selective detection. This compound is also distinguished by an intense molecular ion at an m/e value of 179. This particular sample was then spiked with acridine and an increase in peak area was noted in the mass chromatogram. This supports the identification of this compound.

Stuber (11) has reported that contact of crude shale oil with surface waters can result in the solubilization of high molecular weight nitrogen bases. The Paraho process water has been described as a composite of water from an oil separator tank from operations of at least one year. This has allowed sufficient time for solubilization of acridine in this wastewater. The concentration of acridine in the Paraho process water is less than one nanogram per milliliter based on the results of the experiments in this work. Stuber (11) has calculated that acridine could be present at concentrations of 0.3 ng/mL in a water that has been in contact with a crude oil shale that contains 6 ng acridine/mL.

The nitrogen base compounds can also be isolated from the retort waters by using a steam distillation technique. This procedure was described in a previous progress report (1) using a modified Nielsen-Kuyger steam distillation apparatus. The retort waters were brought to reflux for 48 hours and the steam distillate was condensed and extracted with organic solvents. The organic solvents were removed after 48 hours of distillation. Those solvents included

**MASS CHROMATOGRAM OF NITROGEN BASES
OCCIDENTAL RETORT WATER**

Figure 10. Mass chromatogram of the hydrophobic base fraction of Occidental retort water. The m/e values 129, 143, 157 illustrate the presence of quinoline, isoquinoline, and the methyl and C₂-alkyl isomers of these parent compounds.

hexane, toluene, and ethyl acetate, respectively. The Omega-9 and Occidental retort waters were steam distilled and these two waters plus the Paraho process water were also liquid-liquid extracted in a Strodty type liquid-liquid continuous extractor.

Gas chromatography/mass spectrometry analyses of the fractions obtained for the liquid-liquid extractions and steam distillations of the retort waters were conducted to determine the presence of volatile complexing or coordinating organic ligands present in the retort waters. Mass chromatograms of specific mass to charge ratios (m/e values) were generated for each sample to determine the presence of specific classes of compounds. This procedure was followed in order to evaluate the fractionation achieved with the techniques of continuous liquid-liquid extraction and steam distillation and to allow a comparison of organic compounds present in the different oil shale wastewaters.

The classes of compounds that were evident and appear to be the major extractable solutes from each of the three waters included substituted pyridines, anilines, and quinolines or isoquinolines, which were most generally found in the hexane extracts from the steam distillation procedures for Omega-9 and Occidental retort waters. Hexane was the first solvent used in the steam distillation procedures for Omega-9 and Occidental retort waters. Hexane was the first solvent used in the steam distillation method for both waters. Phenol, ortho-, meta-, and para-cresol, as well as dimethyl phenols were found in the toluene fraction from this technique and volatile fatty acids from C_8 - C_{12} were noted in the chloroform and ethyl acetate extracts of the steam distillations. These solvents were used in this respective order after the hexane fraction had been removed from the apparatus.

The liquid-liquid extractions also exhibited a similar fractionation extraction, but the samples were considerably more complex. The hexane fractions from liquid-liquid extractions indicated the presence of normal hydrocarbons, C_7 - C_{17} , substituted benzenes and naphthalene isomers, as well as the pyridine, aniline, and quinoline compounds. The hydrocarbons and substituted aromatic compounds were more prominent in the extracts from the Paraho process water than in extracts from the Omega-9 and Occidental retort waters. This is probably due to the longer contact time of the Paraho water with the crude shale oil product. The more polar solvents in the liquid-liquid extractions (e.g., toluene, chloroform, ethyl acetate) contained the phenolic and acidic compounds.

The condition of the glass injection port inserts was noted to affect the chromatography of these samples after several injections of the concentrated liquid-liquid extracts. Examination of the inserts revealed that pyrolysis of the non-volatile materials had created a residue on the insert walls. Injection of the samples collected from the steam distillations did not show this effect. The best practice when working with these environmental samples, however, is to replace the injection port insert frequently.

Figures 11 to 14 and Tables XVII to XIX are representative of the kinds of polar organic ligands present in the oil shale wastewaters. It should be pointed out that a class fractionation has been achieved using the steam distillation method. Separations of the hexane fractions with principally nitrogen bases is noted in Figures 11 and 12. The loss of the volatile base compounds (3.g., pyridines, anilines, quinolines, and ammonia) from the retort water was accompanied by a change in pH from approximately 8.5 to neutral pH as mentioned earlier. These volatile basic compounds were collected in the hexane solvent. The change in pH allowed the distillation of the phenolic compounds and the carboxylic acids, which were observed to occur as a movement of crystalline material through the Nielsen-Kryger steam distillation apparatus.

Table XVII. Compounds tentatively identified in the Biller Biemann Reduced Total Ion Chromatograph of the hexane extract of steam distilled Omega-9 retort water.

<u>Figure 7 Peak #</u>	<u>Parent Ion</u>	<u>Formula</u>	<u>Compound</u>
1	107	C ₇ H ₉ N	C ₂ -alkylpyridine
2	107	C ₇ H ₉ N	C ₂ -alkylpyridine
3	107	C ₇ H ₉ N	C ₂ -alkylpyridine
4	107	C ₇ H ₉ N	C ₂ -alkylpyridine
5	121	C ₈ H ₁₁ N	C ₃ -alkylpyridine (trimethyl)
6	121	C ₈ H ₁₁ N	C ₃ -alkylpyridine (trimethyl)
7	121	C ₈ H ₁₁ N	C ₃ -alkylpyridine (trimethyl)
8	93	C ₆ H ₇ N	aniline
9	121	C ₈ H ₁₁ N	2,4,6-trimethylpyridine
10	121	C ₈ H ₁₁ N	C ₃ -alkylpyridine (trimethyl)
11	135	C ₉ H ₁₃ N	C ₄ -alkylpyridine/C ₃ -alkylaniline
12	121	C ₈ H ₁₁ N	C ₃ -alkylpyridine (trimethyl)
13	135	C ₉ H ₁₃ N	C ₄ -alkylpyridine/C ₃ -alkylaniline
14	135	C ₉ H ₁₃ N	C ₄ -alkylpyridine/C ₃ -alkylaniline
15	135	C ₉ H ₁₃ N	C ₄ -alkylpyridine/C ₃ -alkylaniline
16	135	C ₉ H ₁₃ N	C ₄ -alkylpyridine/C ₃ -alkylaniline
17	135	C ₉ H ₁₃ N	C ₄ -alkylpyridine/C ₃ -alkylaniline
18	149	C ₁₀ H ₁₅ N	C ₄ -alkylpyridine/C ₃ -alkylaniline
19	149	C ₁₀ H ₁₅ N	C ₄ -alkylpyridine/C ₃ -alkylaniline
20	108	C ₇ H ₈ O	methylphenol

Table XVII. (continued)

<u>Figure 7 Peak #</u>	<u>Parent Ion</u>	<u>Formula</u>	<u>Compound</u>
21	149	$C_{10}H_{15}N$	C_5 -alkylpyridine/ C_4 -alkylaniline
22	149	$C_{10}H_{15}N$	C_5 -alkylpyridine/ C_4 -alkylaniline
23	129	C_9H_7N	quinoline
24	129	C_9H_7N	isoquinoline
25	143	$C_{10}H_9N$	2-methylquinoline
26	143	$C_{10}H_9N$	3-methylquinoline
27	143	$C_{10}H_9N$	methylquinoline/isoquinoline
28	163	$C_{11}H_{17}N$	C_6 -alkylpyridine/ C_5 -alkylaniline
29	143	$C_{10}H_9N$	methylquinoline/isoquinoline
30	143	$C_{10}H_9N$	methylquinoline/isoquinoline
31	157	$C_{11}H_{11}N$	dimethylquinoline/isoquinoline
32	157	$C_{11}H_{11}N$	2,6-and/or 2,7-dimethylquinoline
33	157	$C_{11}H_{11}H$	2,4-dimethylquinoline

Compounds referred to as pyridine/aniline means the compound is either a pyridine or an aniline isomer.

Table XVIII. Compounds positively identified in the toluene fraction of steam distilled Occidental retort water.

Peak #	Compound	Identification	
		RT(min)	Mass Spectra
1	phenol (C_6H_6O)	X	X
2	o-cresol (C_7H_8O)	X	X
3	p-cresol (C_7H_8O)	X	X
4	m-cresol (C_7H_8O)	X	X
5	C_2 -alkylphenol ($C_8H_{10}O$)		X
6	3,5-dimethylphenol ($C_8H_{10}O$)	X	X

Table XIX. Compounds positively identified in the ethyl acetate fraction of steam distilled Occidental retort water.

Peak =	Compound	Identification	
		RT(min)	Mass Spectra
1	Hexanoic acid ($C_6H_{12}O_2$)	X	X
2	Heptanoic acid ($C_7H_{14}O_2$)	X	X
3	Phenol (C_6H_6O) + o-cresol (C_7H_8O)	X	X
4	Octanoic acid ($C_8H_{16}O_2$)	X	X
5	p-Cresol (C_7H_8O)	X	X
6	m-Cresol (C_7H_8O)	X	X
7	C_2 -Alkylphenol ($C_8H_{10}O$)		X
8	3,5-Dimethylphenol ($C_8H_{10}O$)	X	X
9	Nonanoic acid ($C_9H_{18}O_2$)	X	X
10	Decanoic acid ($C_{10}H_{20}O_2$)	X	X
11	Undecanoic acid ($C_{11}H_{22}O_2$)	X	X
12	Dodecanoic acid ($C_{12}H_{24}O_2$)	X	

The comparison of flame ionization detection with nitrogen selective detection (Figure 11) indicates that the hexane fraction of Omega-9 steam distillate consists almost entirely of nitrogen containing compounds. Preliminary identification of these compounds were made by gas chromatography/mass spectrometry and positive identifications were made by matching retention times and mass spectra of the pure compounds. Figure 12 is a representation of a Biller-Biemann reduced total ion chromatogram (73). This is the only chromatogram presented in this thesis that has been subjected to dynamic data reduction. All other chromatograms presented are reproduced from the raw data. Almost all of the peaks shown in the total ion chromatogram exhibit a molecular ion of odd m/e value indicating the presence of an odd number of nitrogen atoms in the molecule (56). Mass to charge ratios of 107, 121, 135, and 149 are indicative of alkyl substituted pyridines (C_2-C_5) or alkyl substituted anilines (C_1-C_4). These m/e values represent the molecular ions of these compounds. Quinoline, isoquinoline, and alkyl-substituted quinolines and isoquinolines were recognized by their simple fragmentation patterns and the intense molecular ions at m/e values of 129, 143, and 157 (57-59).

Substituted aniline compounds are apparent from base peak fragments at $[M-1]^+$ values and also appear to be simple alkyl-substituted compounds, or nitrogen substituted compounds that show base peak ions at m/e values $[M-15]^+$ (60).

Figure 13 is the representation of the toluene fraction of the steam distillation for the Occidental retort water. Toluene was used to replace the first solvent, hexane, in the apparatus after 48 hours of steam distillation. The presence of phenols was determined by mass chromatograms with m/e values of 94 (phenol), 108 (o-, m-, p-cresols), and 122 (dimethyl or C_2 -alkyl substituted phenolic compounds) (60). The fragmentation patterns are characteristic for each of these isomers, but it was necessary to match chromatographic retention times for positive identification (Table XVIII). The same phenols were determined to be present in the toluene fraction of the Omega-9 steam distilled water and also in the liquid-liquid extractions of all three waters.

Figure 14 is the reproduced chromatogram of the ethyl acetate steam distilled fraction of Occidental retort water and exhibits the presence of straight chained carboxylic acids in the range of C_6-C_{12} . Ethyl acetate was used to replace the toluene solvent after 48 hours of steam distillation. Also present in this sample are the isomers of the phenols that were detected in the toluene sample (Table XIX).

An m/e value of 60, corresponding to the fragment ion $C_2H_4O_2^+$ (60), was used to determine the presence of these carboxylic acids in different extracts. Tailing peak shapes of ions at m/e 60 were also indicative of acid functional groups. Poor peak shape was noted in GC/MS using a fused silica capillary column coated with SP 2100 and also for glass capillary columns coated with SE-52. The chromatogram shown in Figure 14 exhibits excellent peak shape and demonstrates the superiority of the nondeactivated fused silica capillary column coated with Carbowax 20M. This column exhibits no serious problems with active sites at the surface of the fused silica unlike the glass capillary columns that were prepared in this laboratory or the SP 2100 fused silica column that was deactivated with Carbowax 20M.

Figure 11. NPD and FID chromatograms of the hexane fraction of the Omega-9 retort water steam distillation, splitless injection, 2 μ L.

Figure 12. Biller-Biemann Reduced Total Ion chromatogram of the hexane fraction of Omega-9 retort water steam distillation. This chromatogram was obtained on a 12 meter SP2100 fused silica capillary column.

Figure 13. FID chromatogram of the toluene fraction of Occidental retort water steam distillation. This chromatogram was obtained on an HP fused silica capillary column, coated with Carbowax 20M, 25 meters. Temperature program was initially 60°C, rate 4°C/min., final temperature 200°C, 30 min., splitless injection, 2μL, attn. 1 x 32.

Figure 14. FID chromatogram of the ethyl acetate fraction of Occidental retort water from steam distillation. This chromatogram was obtained on a HP fused silica column, coated with Carbowax 20M, 25 meters. Temperature program was initially 60°C, rate 4°C/min., final temperature 200°C, 30 min., splitless injection, attn. 1 x 32.

This is the first report of the ability to chromatograph the free acids (underivatized) in oil shale wastewater extracts. Other investigations (12,14) have concentrated on determining organic acids in this matrix with derivatization methods to facilitate chromatographic separation of these compounds.

The organic acids were found in Occidental and Paraho wastewater extractions and Occidental water steam distillation. The carboxylic acids were not identified in this work for Omega-9 retort water, but have been reported in a recent article (14).

The results from the steam distillation experiments are particularly interesting since steam stripping is one of the proposed methods for upgrading wastewaters from the oil shale industry.

Complexing Ability of Oil Shale Wastewaters

Complexing ability determinations have been presented as a means of estimating the capacity of a water to complex and potentially mobilize trace elements in environmental situations. The two different procedures used to assess complexing ability of the oil shale wastewaters were based on 1.) solubilization of copper hydroxide and 2.) the competition of organic ligands in aqueous solution for copper bound by a chelating resin.

Copper is not a trace element of environmental concern in oil shale waste materials, but does preferentially bind to nitrogen containing ligands in aqueous solutions (107) and has been used as a matter of convenience in these experiments.

Both of the methods above were adaptations of procedures described by Manahan, Jones and Kunkel (30-33) for the determination of strong complexing ligands in natural waters. The first technique, the solubilization of copper at high pH is based on the following equations.

Equation (1) signifies that the addition of Cu(II) at high pH results in the precipitation of cupric hydroxide. At pH 10, the concentration of uncomplexed cupric ion in equilibrium with cupric hydroxide may be calculated as follows.

$$K_{sp} = [\text{Cu}^{2+}] [\text{OH}^-]^2 = 3 \times 10^{-20} \quad (2)$$

$$[\text{Cu}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{3 \times 10^{-20}}{[1 \times 10^{-4}]^2} = 3 \times 10^{-12} \text{M} \quad (3)$$

From these calculations it is evident that the solubility of cupric ion at pH 10 is extremely low and is near the detection limit for flame atomic absorption spectrometry.

The presence of a strong complexing ligand at pH 10 keeps some of the copper in solution as a copper complex. The solubilization of Cu(II) in the basic media enables a determination for good complexing ligands. For a strong complexing ligand, L^{x-} , the following equation is responsible for copper solubilization.

Excess Cu(II) added to the solution is precipitated as the hydroxide as illustrated by equation (1). This method was originally presented as a means of measuring strong complexing ligands, such as EDTA, in natural waters but has also been applied for the analysis of complexing ability of brine solutions from oil wells (30).

Interferences to the determination of the complexing ability of dissolved organic ligands by this procedure result from the presence of high concentrations of divalent or trivalent cations, dissolved carbon as carbonate, and the presence of ammonium salts or dissolved ammonia. These possible interferences are noted at high concentrations in all retort waters. Acidification and purging of the retort waters are necessary to remove inorganic carbon from solution. The water must also be passed through a cation exchange resin to remove high concentrations of divalent cations such as Mg, Ca, etc., that might interfere. Heating of the sample is necessary to avoid interference problems resulting from ammonium salts and dissolved ammonia.

After the copper solution has been added and the pH adjusted to 10, a light blue flocculent precipitate is noted to form. This precipitate, $Cu(OH)_2$ is converted to less soluble cupric oxide by heating and this is observed as the conversion to a fine dark-colored precipitate. The effect of high concentrations of ammonia and ammonium salts, when solutions are not heated, has been demonstrated by Kunkel and Manahan (30). Before copper content was determined for any of the treated waters the pH was checked to ensure that a pH of approximately 10 was maintained. All three retort waters required readjustment of pH after varying times of heating, indicating that dissolved ammonia in the solutions was being liberated. This was confirmed by the color change of wet litmus held over the hot solutions. The pH of the solutions was monitored until a value was maintained at pH 9.8-10.2.

The results obtained for the measurements of complexing ability by solubilization of copper hydroxide are presented in Table XX.

The second procedure for determining complexing ability is based on the competition of complexing ligands in solution with the weakly acid chelating ligands in solution with the weakly acid chelating resin, Chelex 100, that has Cu(II) bound at the surface. Initial experiments were conducted using large columns of the chelating resin in the copper form entirely. This procedure was abandoned because it required large sample volumes and the copper form resin tended to give high results because of the instability of the resin toward the retort water. This was indicated by changes in the swelling of the resin, which created large void spaces in the column material and substantially reduced the flow of the solution through the resin.

Table XX. Complexing Ability of Oil Shale Wastewaters Expressed as Uptake of Copper.

<u>Sample</u>	<u>Solubilization of Cu(OH)₂</u>	<u>Banded Chelex Column</u>
Omega-9	42 ± 2.1 µg/mL	38.9 ± 1.0 µg/mL
Occidental	8.6 ± 0.4 µg/mL	2.6 ± 0.1 µg/mL
Paraho	570 ± 30 µg/mL	750 ± 200 µg/mL

The copper resin was more stable towards retort water when the resin had been equilibrated first with sodium chloride solutions of 0.1 to 1.0 M. The resin was washed extensively with distilled, deionized water and then equilibrated with the solution used as mobile phase in the banded Chelex column, before packing this column with the slurry mixtures.

The sodium form resin layered above the copper resin in the banded Chelex column allowed removal of possible interfering cations that could displace the copper. The lower sodium resin prevents the elution of copper that is not strongly complexed. Calibration standards of Na_2EDTA were prepared and working curves equivalent to 0-100 $\mu\text{g Cu/mL}$ were used for the determination of the complexing ability of the different retort waters. Standards that are copper-EDTA elute as very nice sharp peaks, but the copper complexes eluted after the addition of the retort waters tended to tail slightly. This effect was more apparent with the Occidental retort water with low concentrations of complexing ligands than with the Paraho or Omega-9 waters, which contained higher concentrations of complexing ligands. The results obtained by this method are presented in Table XX together with the results from the solubilization of cupric hydroxide. The values shown are the average of duplicate measurements for each sample.

The values are in good agreement for both the Omega-9 and the Occidental retort waters. The Omega-9 water sample complexes and mobilizes approximately 40 $\mu\text{g Cu/mL}$ in each method, while Occidental retort water shows a complexing ability of less than 10 $\mu\text{g Cu/mL}$. The Paraho process water gives much higher values for the uptake of copper than either the Omega-9 or Occidental samples. The solubilization of copper hydroxide gives a more reproducible value than the banded Chelex column technique for this particular sample.

If these complexing ability measurements are compared with total organic carbon analyses for the three waters there is no apparent correlation. The total organic carbon content (Table XVII) is in the order of Paraho >> Occidental > Omega-9, while complexing ability is in the order Paraho >> Omega-9 > Occidental. If the dissolved organic carbon concentrations of the neutral, dissolved organic carbon concentrations of the neutral, acid, and base subfractions of the retort waters are compared (Tables XVIII and XIX) it becomes evident that the basic fraction of both the hydrophobic and hydrophilic solutes corresponds to the same order as found for the complexing abilities. This is what might be expected because the complexing measurements are based on interactions of ligands with Cu(II) , and the nitrogen bases are known to form complexes with this ion. The acidic and neutral components of the hydrophobic and hydrophilic solutes are of the same order as total organic carbon and show no correlation to the complexing ability.

Several compounds were spiked separately into aliquots of the Omega-9 retort water and the relative complexing abilities were compared with that of the original Omega-9 water by the banded Chelex column technique. Compounds that did not exhibit any enhanced mobilization of copper from the banded Chelex column resin included carboxylic acids ($\text{C}_6\text{-C}_{22}$), dicarboxylic acids ($\text{C}_3\text{-C}_{11}$), adipamide, succinamide, and oxamide. Quinoline and isoquinoline were also added at high concentrations but did not induce any increase of copper mobilization into the flame. Phenol, ortho, meta, and para-cresol, p-methoxyphenol, and o-methoxybenzoic acid did not show complexation greater than that observed for the Omega-9 water by itself.

The compounds that did demonstrate enhanced complexing ability by the banded Chelex column method included pyridine, 2-methyl, 3-methyl, and 4-methylpyridine, 2,4-dimethylpyridine, and 2,4,6-trimethylpyridine. Ortho- and meta-phenylenediamine and p-aminophenol were also spiked into small volumes of the Omega-9 retort water and showed increases of copper concentration eluting from the column. These compounds have not been identified in retort water, but were added as a means to study the effects of multifunctional solutes. Catechol and resorcinol, the 1,2-dihydroxy and 1,3-dihydroxybenzenes, respectively, were added to Omega-9 water. These compounds have been used as models in studying complexation of humic and fulvic acids (37). The solution spiked with catechol produced a great increase in mobilized copper as indicated by copper absorption in the flame. Subsequent injections of Omega-9 retort water showed that this compound had been retained to a large extent by the column material. This was noted by elution of large concentrations of copper with each subsequent injection of Omega-9 water. It was necessary to prepare a new column at this point. Resorcinol showed some mobilization of copper, while the solution spiked with catechol at approximately the same concentration gave a very large response on the same column.

The banded Chelex column method was used as a quantitative method. However, this method is very dependent on the preparation and handling of the copper and sodium form resins. The copper form resin is stable from pH 4 to 9, but it is necessary to prepare this directly as received from the manufacturer (32). It is also necessary to equilibrate the resin at salt concentrations near that of the retort water, followed by extensive rinsing with distilled deionized water. The major limitation of this procedure is that the column has a finite lifetime, since the copper resin is depleted in the analysis. This method does offer qualitative information from experiments like spiking solutions with standard compounds.

The Omega-9 retort water that was fractionated by ultrafiltration membranes was studied with the banded Chelex column. This experiment yielded qualitative information only. The results indicate that there are different size ranges of organic solutes that complex with copper in the resin. Approximately a 50% difference was noted for the solutions fractionated by the PM 30 membrane (30,000 MW) and the UM10, UM2, and UM05 filters (10,000-500 MW). The solutions that were separated by the XM50 (50,000 MW) and UM20 (20,000 MW) membranes had developed a reddish color and both gave large off-scale peaks, indicating contamination from the filters.

A gel chromatography experiment was designed to determine whether there was actually a size difference in the complexing ligands in retort water. Figure 15 presents the results from this experiment. The upper trace is a chromatogram of the elution of compounds that absorb at 254 nm. Each of the 2 mL fractions was diluted one to ten for this measurement. The exclusion limits for the gel (Biogel P-2) are 1800-100 molecular weight units. The first peak that appears at approximately 40 mL of eluent represents the void volume of the column at which point material of greater than 1800 molecular weight units pass. The last peak at 100-120 mL of eluent corresponds to small molecular weight compounds. The lower trace represents elution of copper in the eluent. The dashed line represents the copper concentration present in the buffer solution (10 µg Cu/mL) used for elution of the components.

The positive deviations in the curve represent the elution of copper complexes from the resin. Negative deviations are indicative of deficiencies of copper in the eluent created by complexation. There are three peaks where complexation of copper has occurred. The first peak corresponds to elution of compounds at the void volume of the column and indicates that a

Figure 15. Elution profiles for ultraviolet absorbing compounds and copper concentration from the gel chromatography column.

large amount of complexing material is present. This is followed by a trough or negative deviation showing the deficiency of copper that has complexed with these solutes. Positive deviations from the background are noted at 80-100 mL of eluent, indicating further complexation of copper by smaller molecular weight organic molecules, possibly hydrophobic or hydrophilic base solutes. This is followed by a deficiency of copper before returning to the concentration in the buffer solution. As expected, the areas under the positive peaks and the troughs representing copper deficiency are approximately the same.

In the original experiment, particulate material was observed to elute with the void volume. Particulate matter is often associated with the uptake of trace elements in natural systems (61) and this possibility was investigated. The concentrated Omega-9 water was filtered through a 0.45 micron Millipore filter and the experiment was repeated, demonstrating that complexation was occurring with dissolved organic solutes of high molecular weight rather than copper being bound to the particulate matter. The experiment was repeated a number of times at copper concentrations of 3 and 10 $\mu\text{g Cu/mL}$ in the buffer. The results from each investigation gave the same elution profiles for copper concentration with the three intervals of copper uptake.

This type of experiment should be considered for investigating interactions of any particular trace element with organic ligands in the retort waters. Considerably more information could be generated by pre-separation of the retort water by the Leenheer, Huffman (27) adsorbent method and studying the fractions by this gel chromatography technique. The distribution and reactivity of certain classes of organic compounds, particularly the hydrophobic and hydrophilic bases, could be studied more effectively with the combined techniques.

Metal-Ligand Interactions

Metal-ligand interactions are examples of Lewis acid-base behavior, and the preference of a particular ligand for binding certain metal ions can be correlated with the concept of hard and soft acids and bases. Lewis acids and bases can be ranked according to an empirical property of hardness or softness, which is determined by such factors as size, charge, polarizability, and the nature of the electrons participating in the interaction. A hard acid is small with a high positive charge and not readily polarizable, while a soft acid is large with a small or no positive charge and electrons in orbitals that are readily influenced by other atoms. Hard bases are small, with high electronegativity, while soft bases are large with easily distorted electron clouds.

The utility of the hard-soft concept is simply the rule that like prefers like. That is, interaction among species of similar hardness or softness is preferred over interactions involving a large difference in hard-soft properties. This is not to say that complexing between hard and soft species will not take place, but that the interaction is normally less strong than between like species.

In any aqueous system, water is the most abundant ligand. Distortion of the electron distribution on a water molecule as a result of coordination causes the protons to be more readily ionizable. The result may be the formation of metal hydroxo (OH^-) or oxo (O^{2-}) complexes. The aquo complex may thus be partially or even completely deprotonated, depending on the nature of the metal ion and the pH.

The extent of hydrolysis reactions can be correlated roughly with the size and the charge of the metal ion. Hydrolysis is more extensive for smaller and more highly charged ions at a given pH. In general, ions with a +1 charge form simple aquo complexes over most of the pH range. Aquo complexes of +2 ions predominate in acidic media, but hydroxo species exist under alkaline conditions. Metals with +3 charge are present as hydroxo species at pH values normally encountered in natural waters and in oil shale retort waters. While 4+ ions form hydroxo or oxo species in all but highly acidic solutions.

The formation of a complex in solution is part of an equilibrium process that can be represented by a series of steps, each described by its own equilibrium constant. A large value for the formation constant means that the formation equilibrium lies far to the right and the complex is quite stable. Complexes in solution normally undergo continuous breaking and remaking of the metal-ligand bonds. If the bond breaking is fast, and ligand exchange is rapid, the complex is referred to as labile. However, if the ligand exchange interactions are slow, the complex is said to be inert. Many metal ions complexed by unidentate ligands (e.g., pyridine, Cl^- , etc.) will undergo complete exchange within a time of fractions of a second, although some complexes might be much slower with complete exchange requiring hours to days. These complexes are inert and are associated with particular electronic configurations of the metal ion. It is also known that exchange rates are slower for multidentate ligands and that the inert complexes in particular have properties different from both the free metal ion and the ligands.

The complex stability can be correlated with several properties of the metal ion and ligand. These properties include the size and oxidation state of the metal. Small size and higher positive charge lead to stronger complexing. The complex stability is also dependent on both entropy and enthalpy changes of the reaction. For example, when unidentate ligands are replaced by polydentate ligands a larger number of independent molecules exists. This results in a positive contribution to the entropy change of the system and a larger negative free energy change than the exchange of one unidentate ligand for another. The complex stability is also highly dependent on the hard-soft match of the metal-ligand as previously mentioned. Table XXI gives the classifications of hard and soft Lewis acids and bases that are of interest when considering the formation of metal organic complexes in oil shale wastewaters. Previously, organic compounds in oil shale wastewaters that are potential ligands have been reported, but no discussion has been offered of the specific interactions that might occur with the various trace elements.

Table XXI. Classification of Lewis Acids and Bases(62,63).

<u>Hard Acids</u>	<u>Soft Acids</u>
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+
$Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}$	$Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}$
$Al^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}$	
<u>Borderline</u>	
$Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}$	
<u>Hard Bases</u>	<u>Soft Bases</u>
H_2O, OH^-, F^-, RCO_2^-	$RSH, RS^-, SCN^-, S_2O_3^{2-}$
$SO_4^{2-}, Cl^-, CO_3^{2-}, NO_3^-$	
$ROH, RO^-, R_2O, NH_3, RNH_2$	
<u>Borderline</u>	
C_6H_5N (pyridine), $C_6H_5NH_2$ (aniline)	

It is apparent that the speciation of the elements magnesium, calcium, strontium, manganese, iron, cobalt and chromium should be strongly controlled by the high concentrations of sulfate, carbonate, ammonia, carboxylic acids, phenols, and possibly amines. These ligands are in competition with water and hydrolysis reaction products favoring hydroxide and oxide formation in solution. Of particular importance in the case of manganese, iron, and chromium is the formation of hydrous oxides.

The forms of those elements classified as borderline Lewis acids (i.e., nickel, copper, zinc, lead, etc.) are influenced by the presence of these ligands as well as the presence of pyridine, aniline, and the quinoline compounds in the aqueous wastes. The speciation of each of these elements is also affected by the formation of hydrolysis products or hydroxides at the pH values encountered in oil shale wastewaters.

Sillen and Martell (64) have compiled an extensive number of conditional stability constants for a number of organic ligands and trace elements. A comparison of the reported stability constants for copper complexes of carboxylic acids versus the nitrogen heterocyclic pyridine isomers illustrates the preference of copper to bond with the more basic nitrogen compounds. In considering bond strength as a function of the basicity of the organic ligand, it is known that the alkyl pyridines are stronger bases than pyridine (65). This phenomenon is noted in the formation of complexes that are more stable than those with pyridine. This has been attributed to hyperconjugative and inductive effects from the alkyl substituents (114). It is known that the 2- and 4-alkyl substituted pyridines are stronger bases than the 3-alkyl substituted pyridines (66). Examination of the formation constants for copper complexes reveals that the 2-methyl and 4-methylpyridines have greater stability constants than the 3-methylpyridine and pyridine. The log of the formation constant for the formation of a complex, CuL^{2+} , for pyridine, 3-methyl and 4-methylpyridine has been reported as 2.52, 2.70, 2.83, respectively (107).

The basicity of pyridine is increased by increasing the numbers of substituted alkyl groups. However, this effect is not additive when both positions alpha to the heterocyclic nitrogen are occupied. This is indicated more pointedly in the decreasing basicity with increasing branching of the 2-alkylpyridines, the lower basicity of a 2-alkyl as compared to a 4-alkylpyridine, and the weak basicity exhibited by 2,6-di-*t*-butylpyridine (65). Steric effects probably play an important part in the formation of stable metal-ligand complexes. Brown and Cahn (67) have shown steric effects lower the stability of complexes formed by the reaction of alkyl halides with alkyl pyridines. However, if the compounds tentatively identified as methyl substituted pyridines in retort water are present rather than substituted propyl, butyl, or pentyl isomers, the stability of the metal ligand complex should not be greatly effected, although Tanaka (68) has shown that the log of the formation constants for the 2,6- versus the 3,4-dimethylpyridine for the species, CuL^{2+} , are 1.78 and 3.11, respectively.

Examination of the literature shows that pyridine bases have been removed from coal tars and petroleums by forming complexes with metal salts such as ZnCl_2 , HgCl_2 , and CuSO_4 (65,69,70). Zinc chloride has been used to separate pyridines from pyrrole and is known to readily form complexes with the methyl-substituted pyridines (69,71). Quinoline and aniline compounds are also expected to form coordination complexes with trace elements such as zinc, nickel, or copper, but the stability of these complexes should be less than complexes with pyridine based on the differences in the basicities of the ligands. The log of the base dissociation constants for pyridine, quinoline, and aniline are 8.7, 9.1, and 9.4, respectively.

In the consideration of the relative stabilities of transition metal complexes with any of these ligands, the Irving-Williams order is applicable (72).

The major features of arsenic and selenium chemistry that affect their movement, toxicity, and deficiency in environmental matrices are associated with changes in their oxidation states and the resulting differences in chemical properties (73,76). Arsenic is known to exist in oxidation states of -3, 0, +3, and +5, while selenium can exist in the -2, 0, +4, and +6 oxidation states. Examination of the oxidation-reduction potentials versus pH for these two elements indicates that the predominant forms of arsenic and selenium in the wastewaters (pH 8) should be the +5, +3, +6 and +4 oxidation states, respectively.

The effect of the presence of various organic ligands in wastewaters has not previously been considered in evaluating the speciation of arsenic and selenium. Extensive literature exists for the reaction and behavior of arsenic and selenium organo-metallic compounds. A literature review indicates that aniline, substituted anilines, and aliphatic amines may have more interaction with arsenic and selenium by coordination with the nitrogen atom than do pyridine or quinoline. However, Masaguer, et al. (77) have recently reported formation of adducts of pyridine oxides with trivalent and pentavalent halides of arsenic, and Couch, et al. (78) have reported the coordination of selenium halides with pyridine and related compounds.

Arsenic in the trivalent form, as the halide, can form arsenic-nitrogen bonds when it undergoes reaction with primary amines or ammonia (79-81). These reactions can be controlled to give diarsino- and triarsino amines $((\text{R}_2\text{As})_2\text{NR}')$ or $(\text{R}_2\text{N})_3\text{As}$. Kober (82) has also shown that the dimethylarsine derivatives with pyrrole, pyrrolidine and piperidine substituents can also be prepared from trivalent arsenic compounds.

Investigations of arsenic chemistry as early as 1920 were conducted by Schmidt (83), who reacted AsCl_3 with aniline in heptane to yield the reported hydrochloride, $\text{As}[\text{NH}(\text{HCl})\text{C}_6\text{H}_5]$. However, this compound was noted to decompose on addition of water.

Paterno (84) in 1922, reported that the addition of arsenic acid (H_3AsO_4) to aniline in any proportions resulted in the formation of the arsenate of aniline in a ratio of 1:2. and Boon and Ogilvie reported (85) that the addition of arsenic acid to naphthylamine resulted in the formation of a substituted arsonic acid. The pyridine and quinoline compounds are also reported to be readily arsonated in similar reactions (75), although these compounds do not involve arsenic-nitrogen bonds. Ivanov and Todorva (86) have used high molecular weight amines to aid in the extraction of heteropoly arsenomolybdates ($\text{H}_3\text{AsMo}_{12}\text{O}_{40}$) from aqueous solutions. The high molecular weight amines used for the extraction included 2-ethylexylamine, dinonylamine, and di-iso-octylamine in 1,2-dichloroethane.

Other ligands that have been reported to form complexes with arsenic species include polyhydroxy compounds. Englund (87) reports that alpha aliphatic glycols form esters with arsenic acid more readily than with the beta or gamma glycols. Reactions of catechol with arsenic acid to form esters of the arsenic acid, $\text{AsO}(\text{OR})_3$, where $\text{R} = \text{OC}_6\text{H}_4\text{OH}$, have been reported by Weinland and Heinzlen (88). Christiansen (89) has also studied the arsonation of ortho- and meta-cresol and has reported the formation of the products, 3,4- and 2,4- $\text{CH}_3(\text{OH})\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$, respectively.

The formation of many of these compounds in aqueous solution is impeded or prevented due to competing hydrolysis reactions. As mentioned at the beginning of this discussion, the forms of arsenic compounds present in solution are highly dependent on the pH and oxidation-reduction potential. Kary (90) has reported that there is a relationship between the strength of organic nitrogen bases and the solubility of arsenic trioxide. The data interpreted by Kary (90) indicated that the presence of weak bases such as aniline, pyridine, or urea (PK_b 9.4, 8.9, and 13.8, respectively) should have no effect on the dissolution of arsenic trioxide. However, Kary (90) points out that organic bases with K_b greater than 10^{-8} (aliphatic amines, ethanolamines) are effective in dissolving the arsenic trioxide and may possibly lead to the formation of organic nitrogen base-arsenite complexes. The details of experiments leading to these conclusions are lacking and the products of new arsenic compounds proposed by Kary (90) have not been reported in more recent compilations of reactions of arsenic and its organometallic compounds.

Selenium, also occurs in a variety of forms and can act as either an acceptor or as part of a donor ligand (76). Selenium dioxide has been reported to form addition compounds with pyridine, quinoline, and isoquinoline (65,91). Couch, et al. (78) have reported that selenium halides ionize very little in dimethylformamide, unless this solvent contains species with electron donating properties such as pyridines and other related compounds. Hsi, et al. (92) have reported formation of aniline adducts with divalent metal selenates at room temperature. These compounds have the formula $\text{M}^{++}\text{SeO}_4 \cdot 2\text{H}_2\text{O}$. Selenium compounds with nitrogen-selenium bonds form upon reaction of selenite with diamines like ortho-phenylenediamine. These compounds have been used as analytical reagents for the complexation and volatilization of selenium for gas chromatographic analysis. The reaction for the formation of this type of complex is depicted below (106-109).

$\text{X} = \text{NO}_2, \text{Cl}^-, \text{etc.}$

The aqueous chemistry of selenium should favor the presence of oxidized Se(VI) in solution and this species should predominate as selenate, although selenite might also exist at the conditions presented in oil shale wastewaters (i.e., pH 8-9 and oxidizing conditions).

Arsenic and selenium that are present in the retort waters are probably present as the oxyanions and thus these species may function as ligands for metal ions. This behavior is used to the advantage of the atomic absorption spectrometry technique using matrix modification (25,26) with a 1% nickel solution. The addition of nickel promotes the formation of the less volatile nickel arsenates, nickel selenates, etc., during the ashing and atomization steps. However, the form of arsenic and selenium in the retort waters may be influenced by aromatic amines, ammonia or polyhydroxy compounds that might be present in retort waters as indicated by the previous discussions.

Leaching Studies

Leaching of the retorted or spent shale that is produced during the oil shale recovery operations may present a very significant potential environmental problem. The concern of the possible contamination of ground and surface water supplies by toxic elements from the spent shale through leaching processes has been investigated by a number of researchers (93-96). However, these leaching studies have not considered the effect that organic ligands might have on the solubilization and mobilization of the toxic elements. The results from complexing ability determinations in this study have indicated that constituents of the retort water can complex copper and possibly a number of other elements. Therefore, it was necessary to investigate potential mobilization of trace elements in situations in which retorted shale and retort waters may be co-disposed, or events in which large volumes of wastewaters may be accidentally released and come in contact with retorted shale.

The trace-element organic ligand interactions that might be expected between oil shale wastewaters can be visualized in Figure 16. This consideration of the interactions of organic ligands and trace elements and the uptake of individual or complexed species by hydrous oxides in aqueous systems has previously been presented by Davis and Leckie (97).

The trace element-organic ligand interactions with retort water and retorted shale may include: adsorption of trace elements or organic ligands from the waste water on the spent shale surface, formation of metal-organic ligand complexes at the surface of the spent shale, or the interactions of trace elements at the surface of the spent shale with organic ligands in the wastewater or leachate to form soluble metal-organic ligand complexes that may be mobilized from the retorted shale. The last interaction is the leaching process that was studied in this laboratory experiment.

Fruchter, et al. (21,22) have determined the trace element concentration in Paraho retorted shale and have shown that concentrations of many of the toxic trace elements considered in this study are in the range of approximately 1 to 100 $\mu\text{g/g}$. The concentrations of most of the elements in retorted shale are higher in comparison to the concentrations found in the raw oil shale (21,22,98-100).

Leaching studies that used Paraho spent shale and the three different wastewaters did not show any apparent mobilization of trace elements that could be related to the formation and solubilization of metal complexes. The trace elements in the leachates studied included lead, cadmium, chromium, nickel, copper and zinc. The analyses of the leachates indicated that there are not significant concentrations of any of these elements in the leachates. The concentrations of each of these elements were at the very low ng/mL concentration in the leachates. The concentrations of these elements in the original wastewaters are listed in Tables XIII-XV. A percolate resulting from mixing Paraho spent shale with an aqueous solution of 0.04 M Na_2EDTA , a complexing agent that is known to form strong complexes with these trace elements, exhibited little or no mobilization of these elements. The concentrations of these elements were very close to the detection limits of graphite furnace atomic absorption spectrometry (ng/mL).

Figure 16. Major reaction pathways for trace element and organic ligand transport in aqueous systems.

Source: Davis, J.A., and Leckie, J.D., Env. Sci. Tech., 1978, 12, 1309.

The only element that did show considerable mobilization in all leaching experiments was molybdenum. This element has been shown to be leached from both retorted and unretorted shale in previous work by Stollenwerk, et al. (94,95,101). The original concentration of molybdenum in each of the three wastewaters was less than one $\mu\text{g/mL}$. Molybdenum was determined to elute at concentrations of approximately 5 $\mu\text{g/mL}$ in the first pore volume of each of the short term experiments (i.e., Paraho, Occidental, Omega-9 retort waters, and distilled deionized water). The concentration of this element dropped in subsequent pore volumes to a value of less than one $\mu\text{g/mL}$ after seven pore volumes.

The behavior of arsenic in the Paraho process water constituted one of the most significant results in the percolation studies. Arsenic was noted to decrease in concentration from the wastewaters when brought in contact with the spent shale. The arsenic concentration in the original Paraho process water was determined as 5.1 $\mu\text{g/mL}$. The concentration of arsenic in the percolates collected was approximately 0.3 $\mu\text{g/mL}$ (Figure 17). The percolation was carried out for more than 20 pore volumes for the Paraho process water-Paraho spent shale systems and no increases in the concentrations of arsenic were observed. The concentration of arsenic was not determined in the percolates from Omega-9 and Occidental retort waters. The concentration of arsenic in the percolates collected from distilled, deionized water was found to be less than or equal to 0.1 $\mu\text{g/mL}$ and is in good agreement with previous leaching studies of Paraho spent shale (101).

This phenomenon of arsenic removal may be useful to the oil shale industry in the treatment and disposal of their wastewaters. Preliminary studies have been done to evaluate the capacity of the spent shale for arsenic adsorption. Also various organoarsenic compounds were introduced to spent shale to determine whether the adsorption mechanism is effective for organic forms of arsenic. Figure 18 is a plot of the percent of arsenic removed from a standard solution by spent shale vs. the concentration of arsenic initially added to the spent shale. It may be seen that the arsonic acid is essentially completely removed from solution by the spent shale. Capacity studies have shown that 0.99 mg As (as H_3AsO_4) per gram of spent shale can be adsorbed and the full capacity has not yet been reached. On the other hand, methyl arsonic acid, which has been identified by Fish in retort water (110), is not completely removed from solution upon short term contact with the spent shale. Continued investigation of this arsenic removal phenomenon is needed to evaluate the mechanism and reversibility upon exposure to rain.

Selenium, on the other hand, was found at approximately 6 $\mu\text{g/mL}$ in the Paraho process water. The concentration of selenium in the first pore volume collected was significantly reduced, but a value of about 6 $\mu\text{g/mL}$ was noted after collection of four to five pore volumes of leachate from two different columns. This indicates that some adsorption of selenium occurred initially. (See Figure 19.) The concentrations of selenium in the leachate collected when distilled, deionized water, Occidental, and Omega-9 retort waters were used for leaching was less than or equal to 0.1 $\mu\text{g/mL}$ in up to ten pore volumes of leachates from each of these columns. The concentration of selenium in the Omega-9 retort water was initially 0.16 $\mu\text{g/mL}$, and the initial concentration of selenium in the Occidental retort water was less than 0.01 $\mu\text{g/mL}$.

Figure 17. Arsenic from Paraho Process Water by Paraho Spent Shale.

Figure 18. Arsenic removed from aqueous standards by Paraho spent shale.
(Conditions: 10 mL of arsenic standard per 10 grams of spent shale.)

Figure 19. Selenium concentration from leachates collected the Paraho spent shale-Paraho process water system.
(Conditions: 20 grams of spent shale leached with 10 mL pore volumes of retort water.)

The determination of selenium in the raw Paraho process water presented the most serious analytical problem encountered in the entire study. Initial experiments with the Paraho water indicated that the selenium concentration was approximately one $\mu\text{g/mL}$ when this water was injected undiluted into the graphite furnace assembly and compared with aqueous standards of selenium. The selenium concentration in the Omega-9 retort water was measured with the same set of standards and samples and a value that was very close to that reported by LETC (50-52) was obtained. This indicated no apparent discrepancies in the analysis of selenium in the Paraho process water. However, when the percolates were injected into the graphite furnace undiluted, very large absorbances were recorded indicating much higher concentrations of selenium. Dilution of these samples was necessary before the concentrations could be determined effectively (approximately 6 $\mu\text{g/mL}$). The concentration of selenium in Paraho retorted shale has an average concentration of 2-3 $\mu\text{g/g}$ (20,48) and it was noted in extended percolating studies (greater than 20 pore volumes) the selenium concentration did not drop significantly in concentration. Close examination of the data indicated that a high concentration of selenium was apparently being eluted compared with what was known to be present in the shale and thought to be present in the process water before leaching. This anomaly prompted a more extensive study to determine the true concentration of selenium in the original Paraho wastewater. By measurements of selenium in diluted Paraho process water, it was shown that matrix effects were responsible for the reported (1) lower concentrations of selenium. The responsible matrix effect is apparently eliminated when the retort water is passed through the spent shale.

The leachates from the Omega-9 and Occidental retort waters were significantly reduced in color and odor relative to the original samples. The first pore volume collected from each of these systems was almost colorless in appearance and the odor characteristic of retort waters was not apparent. Subsequent pore volumes of Occidental leachate had an odor similar to phenol. The strong amine odor usually associated with retort waters was not apparent until after the seventh pore volume in both of these systems.

The color and odor of the Paraho process water leachate were not noticeably altered in the first pore volume collected. This can probably be attributed to the higher concentrations of organic carbon in the Paraho water.

The adsorption of the organic carbon onto retorted shale has been studied by Stuber and Leenheer (41), and Fox and Jackson (16). The results of these studies have indicated that the passing the retort water through beds of the retorted shale might be effectively used for removing certain constituents of the water. These studies included measurements of dissolved inorganic carbon concentrations in the retort waters and the leachates, and water that had been equilibrated in batch studies with the retorted shale. The dissolved inorganic carbon content was reduced significantly for retorted shales that had been at high temperatures ($> 800^{\circ}\text{C}$). This may be due to the fact that phase transitions have altered the surface of the spent shale such that it is a good adsorbent surface for inorganic materials.

The retorted shale that was used in the present investigations was produced by a direct mode retort operation. The upper temperature limit for this process is approximately 750°C and mineral phase transformations to silicates are possible (96,102,103). Stollenwerk (101) has demonstrated that the

leachability of spent shale from the Paraho process is low compared to that of Tosco spent shale.

Fruchter, et al. (21,22) have determined the trace element concentration in Paraho retorted shale and have shown that the concentrations of many of the toxic trace elements considered in this study are in the range of 1 to 100 $\mu\text{g/g}$. The low leachability of the trace elements from this retorted shale may very well be due to the incorporation of the elements into the insoluble crystal lattices.

Leenheer, Stuber and Noyes (104,105) have conducted leaching studies with Omega-9 retort water and soil obtained near the Rock Springs, Wyoming, Site-9, retort operation. This study was conducted to evaluate the effect of the accidental release of retort water on surrounding soil. The concentrations of trace elements and the distribution of hydrophobic and hydrophilic organic solutes in the leachates were determined. This study allowed comparison of the breakthrough volumes of acidic, basic, and neutral solutes with trace element profiles. The results reported by Leenheer, et al. (104,105) indicated a strong correlation between the elution profile for copper and the breakthrough volumes of both the hydrophobic and hydrophilic base solutes. Although this finding is not conclusive, it does present evidence that the basic compounds in oil shale wastewaters can potentially mobilize trace elements in the environment.

SUMMARY AND CONCLUSIONS

The wastewaters from oil shale retorting operations studied in this research are complex mixtures of hydrophobic and hydrophilic organic solutes, inorganic salts, and trace elements. Following adsorbent separations of the organic constituents, measurements of dissolved organic carbon showed the proportions of acid, base, and neutral subfractions that comprise the hydrophobic and hydrophilic solutes are very different for three different processes and sources of oil shale wastewaters. The organic compounds that have been identified by high resolution fused silica capillary chromatography included phenol, alkyl-substituted phenols, n-C₆-C₁₂ carboxylic acids, methylpyridines, dimethylpyridines, trimethylpyridines, aniline, substituted anilines, quinoline, isoquinoline, methyl-, and dimethyl-substituted quinolines. The use of fused silica capillary columns provided separations with high resolution and excellent peak shapes for polar compounds like underivatized carboxylic acids and the aromatic amines. Many of the organic compounds identified are good complexing ligands. Independent measurements of the abilities of the compounds in the oil shale wastewaters to form complexes with a model cation, Cu(II), were made. The complexing ability of the three wastewaters does not correlate with the dissolved organic carbon concentration, but does compare well with the dissolved organic carbon concentration of the hydrophobic and hydrophilic base subfractions of the wastewaters. The complexing ability of the wastewaters decreases in the order, above-ground retort is much greater than a true in-situ, which is greater than a retort water from a modified in-situ operation. The complexing ligands are also distributed by size, as demonstrated by gel chromatography measurements of the constituents of the true in-situ retort water.

Studies using wastewater and retorted shale from an above-ground process indicated that arsenic can be removed effectively from the wastewater by

percolating it through the retorted shale. The retorted shale was also effective in reducing color and odor from the retort waters obtained from true in-situ operations. Selenium, initially present at relatively high concentrations in the wastewater from an above-ground process, was not adsorbed. Molybdenum was leached from the spent shale with all three wastewaters and with distilled, deionized water, irrespective of the concentrations of total dissolved organic carbon.

Adsorbent separation, liquid-liquid extraction, and steam distillation provide class fractionation of the organic solutes in the wastewaters. Steam distillation produces extracts that are readily amenable to gas chromatography, while organic solvent concentrates from liquid-liquid extraction contain considerable amounts of non-volatile materials. Adsorption on polymeric material (XAD-8) and ion exchange resins allows the concentration of organic solutes from large volumes of water.

Size fractionation and ion exchange experiments indicated that the majority of trace elements in a true in-situ retort water are present as small hydrated ions or as labile organic or inorganic complexes. This type of procedure should be applied to wastewaters that contain relatively high concentrations of particular toxic trace elements since toxicity is greatly increased for the small solvated ions or labile complexes as compared to stable complexes.

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AWARDS

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Progress Report: 1980-1981

Chemical Analysis of Inputs and Outputs of Oil Shale Retorts

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INTRODUCTION

This is a summary of the accomplishments that have been made in 1980 in the research program on the Chemical Analysis of Inputs and Outputs of Oil Shale Retorts. The project is headed by Thomas Wildeman from the Department of Chemistry/Geochemistry at the Colorado School of Mines. Co-investigators are Daniel Melchior and Alice Laffoon, who are students at CSM.

This year two research objectives were actively pursued. The most important objective is to finish the research on the Paraho Retort by June 1, 1981. The other research objective is to start to study the mineralogy of raw and spent shales. Both objectives are being met. This report provides a detailed discussion on the iron mineralogy of raw and spent shale as determined by Mössbauer spectroscopy. The research on the Paraho Retort is summarized in this report and the final report on Paraho should be available in June 1981.

PARAHO STUDIES

The research program on the Paraho Retort has covered three years because so many samples of different types were secured in 1977 (1). In the first year of the program, the solids were analyzed; in 1979, the waters were analyzed; in 1980, the oils were analyzed. In addition to the analysis of the oils, this year's program objectives are to complete a Paraho Data Catalog early in 1981 and to prepare a final report by June 1981. The Data Catalog should be available in the office of the Center for Environmental Studies in February 1981. The final correlation studies of the analytical results are now being done. So, the June deadline for the final report should be met.

Paraho Data Catalog

The Data Catalog will contain the major and trace element analytical results for almost 200 samples. The sample types include raw shales, spent shales, crusher fines, baghouse dusts, product waters, recycle condensates, process waters, and shale oils. Certainly, not everyone is interested in the individual analytical results so the catalog will not be generally distributed. However, copies are available on request from the Center for Environmental Studies. Summaries of the raw and

spent shale analyses are found in the 1978-1979 Progress Report (2). A summary of the water analyses is in the 1979-1980 Progress Report (3). Also, reports on the sampling scheme (4), the raw and spent shale analyses (5), and the analyses for the major constituents in the water (6) have already been published.

Oil Analyses

The shale oils were analyzed for C, H, N, and S by Huffman Laboratories in Denver and for trace elements by Energy Dispersive X-ray Fluorescence (7). The results will be summarized in the final report on the Paraho Retort.

MÖSSBAUER STUDIES

The original objective of the Mössbauer studies was to determine how much pyrite was contained in raw and spent shales so that the speciation of sulfur in these materials could be established. We have satisfied this objective and also found that the reactivity of pyrite strongly depends on the retorting conditions. In addition, we have discovered that the other iron minerals found in spent shales are important indicators of the temperature and the oxidizing-reducing conditions of the system. We now think that the analysis of the iron minerals along with an analysis of major minerals will be key tests to determine the efficiency of a retort and to assess how spent shale will react with waters that happen upon it. Our proposal for this year is to continue studies in this area.

So far the Mössbauer studies have been reported in two presentations (8, 9), one publication (10), and one thesis (11). The publication (10), which was included in the Proceedings of the 13th Oil Shale, is reprinted in this report. Copies of the thesis (11) are available on request from the Center for Environmental Studies. One more publication on the Mössbauer studies is in preparation (12) and a presentation of the petrology of spent shale is planned for the 14th Oil Shale Symposium.

PROFESSIONAL ACTIVITIES

During 1980, three presentations were made at national and regional meetings (8, 9, 14), five papers were published (4, 10, 14, 15, 16), one thesis was published (11), and three papers are in publication (6, 12, 17).

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CHANGES IN IRON MINERALS DURING OIL-SHALE RETORTING

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INTRODUCTION

The problems of trace element mobility during retorting of oil shale have been previously studied by several researchers (Fox and others, 1977; Kuo and others, 1979; Wildeman and Heistand, 1979; Wildeman and Meglen, 1978). To this date, no studies have been presented on the fate of the iron minerals in oil shale during retorting. Mineralogical studies of oil shale in the past have been done using various microprobe, scanning electron microscope, and X-ray techniques (Brobst and Tucker, 1973; Desborough and Pitman, 1974). The use of Mössbauer spectroscopy on unretorted oil shale was first advanced by Cole and others (1978) with successful identification of seven iron bearing phases in the Green River Formation. These seven phases can be grouped into two different mineralogical categories, sulfides and carbonates. This paper will investigate questions about the fate of the iron sulfides and iron carbonates in oil shale during retorting. These questions include: (i) What are the products that result from iron minerals during retort? (ii) Are the iron mineral changes a result of typical thermal reactions or special reactions within the retort? (iii) Does the iron in this shale matrix react with other minerals? (iv) What are the environmental implications of the changes of the iron minerals? Mössbauer spectroscopy for the ^{57}Fe transition will be used to determine the iron minerals in raw oil shales and the fate of these minerals when the shale is retorted by various methods.

The Mössbauer effect is an analytical tool that can be used to study various properties of solids. The effect is a phenomenon based on a resonant, recoilless, interaction between the nucleus of an atom and a gamma ray. This resonance for the ^{57}Fe isotope is well documented and has often been used in studies of naturally occurring iron phases (for example see Morice and others, 1969; Bancroft, 1973, 1979; Huffman and Huggins, 1978; Montano, 1979). Mössbauer spectra can provide valuable information on the iron phases present in a complicated material such as oil shale. The parameters that are available to characterize the phases present are the isomer shift, quadrupole splitting, and magnetic splitting. The isomer shift is a result of electrostatic interactions between the nucleus and electrons. Quadrupole splitting occurs when an inhomogeneous electric field acts on a

Figure 1. Mössbauer spectrum of pure pyrite showing the isomer shift (δ) relative to metallic Fe and quadrupole splitting (Δ). The zero velocity corresponds to the center of metallic Fe. The solid line passing through the data is generated by the computer fitting program discussed in the text.

Figure 2. Mössbauer spectrum of pure hematite showing the magnetic splitting (H) into six lines.

non-spherical nucleus. The inhomogeneity in the electric field is caused when the iron atom is in a crystallographic site which has non-cubic symmetry. Figure 1 shows the isomer shift and quadrupole splitting in pyrite. Magnetic splitting is due to the interactions of the nuclear dipole moment with a magnetic field created by the electrons. Figure 2 shows the magnetic splitting in hematite. In addition to using the above parameters to identify the various iron phases, Mössbauer spectroscopy can also yield quantitative data on the amount of Fe present in each of the phases. This is obtained from the resonance area (linewidth x intensity) associated with each phase. For recent applications to quantitative analysis see Huffman and Huggins (1978) and Williamson and others (1980). More detailed discussions of the principles of Mössbauer spectroscopy are available for example in Gibb (1976), Bancroft (1973), and Cohen (1976).

Retorting of oil shale is a thermal process which pyrolyzes the kerogen and bitumen from the rock. Several processes are in practice and have had varying degrees of success. This paper will concern itself with three retorts that will each alter the oil shale matrix differently. The Lawrence Livermore Laboratory's 125 Kg retort is a pilot scale modified in-situ process. It may be operated with internal combustion of carbon on the spent shale or with an externally-heated gas (Hall, 1977). This study has used samples from the externally-heated gas mode. The Paraho oil shale retort involves the direct combustion of residual carbon on the retorted shale in the retort to supply the retorting energy. The temperature within the retort is controlled by the gas streams fed to the sets of distribution ports and by adjusting the composition of the recycled gas return. Jones (1976) gives a detailed illustration and an in-depth discussion of the process that takes place within the retort. The Tosco II process uses heated ceramic balls for heating the shale as opposed to the heated gases used in the other processes (Kilburn, and others, 1974). This process has the advantage that it allows better control of the retort temperature than in the other processes. The feed stock is crushed to smaller sizes than for the other processes, and it is subjected to further crushing by the heated balls in the pyrolysis drum. From an organic recovery standpoint, the Tosco II process appears to give better yields than the other two processes (Wildeman and Meglen, 1978). Table 1 is a summary of the various retorting processes that are studied in this paper.

EXPERIMENTAL

The oil shale samples used in this study were obtained from different sources. The Tosco II shales were the subject of previous studies by Wildeman (1977) and Wildeman and Meglen (1978); the Paraho samples are the subject of current studies by our research group (Wildeman and Heistand, 1979); and the modified in-situ samples from the Lawrence Livermore Laboratory were provided by Dr. J.P. Fox of the Lawrence Berkeley Laboratory (Fox and others, 1977).

Each sample was ground to 200 mesh and finer, and homogenized

Table 1. Retorting conditions for the oil shale samples used in this study.

	Type	Heating Mode	Max. Temp.	Atmosphere	Reference
Tosco II	Above Ground	Indirect	482°C	Pyrolysis Gases	Kilburn and others (1974) Wildeman and Meglen (1978)
Fischer Assay	Laboratory	Indirect	500°C	Pyrolysis Gases	Goodfellow and Atwood (1974) Wildeman (1977)
Paraho	Above Ground	Direct	600°C	Air + Combustion Derived CO ₂	Jones (1976)
Lawrence Livermore Laboratory	Modified In-Situ	Indirect	Variable	Variable	Fox, and others (1977)
	S-7	Indirect	750°C	Air + N ₂ (7.6%O ₂)	"
	S-9	Indirect	510°C	H	"
	S-10	Indirect	935°C	Air + Recycled Gas (10.5%O ₂)	"
	S-11	Indirect	1030°C	Air (21% O ₂)	"

according to procedures outlined by Wildeman (1975). The homogenized samples were then split into three groups to provide a more random sampling profile. From each split, 1.000 gram was weighed and separately placed in a 2.54-cm diameter pelletizer. Sufficient pressure was then applied to yield a pellet that held its shape. Each pellet had a thickness of about 1.5 mm.

The Mössbauer analysis was performed using a constant acceleration spectrometer with either a $^{57}\text{Co}/\text{Pd}$ or a $^{57}\text{Co}/\text{Rh}$ source. The spectrum for each split was run at room temperature of 298K until statistically significant results were obtained. Liquid nitrogen temperature runs were made on two samples to aid in their characterization.

The spectra obtained were each fit through a computer program which used a least squares Lorentzian algorithm. Mössbauer parameters were calculated from the fit spectra and then compared with iron compound parameters published in other papers. Figures 3, 4 and 5 are Mössbauer spectra of raw and retorted shales.

RESULTS

Table 2 summarizes the iron mineral phases found in each sample. Some of these shales were run several times to test reproducibility and to improve precision. The spectrum parameters and the relative areas of absorption were deduced from the Lorentzian fitting program. The percentages in Table 2 are the fractions of the total Mössbauer absorption area. Experimental uncertainties are given in parentheses and represent an estimated error based on counting statistics and problems caused by computer decomposition of overlapping resonance lines. In the calculations, it is assumed that the recoilless fractions of the phases observed are equal and the resonance area is directly proportional to iron concentration. The latter assumption is reasonable because of the low concentration of iron in these samples. Thus the percentages given in Table 2 are approximately equal to the fractional amounts of iron present as that mineral.

Abundances of iron and sulfur for several of the raw and retorted shales have been previously determined (Fox and others, 1980; Wildeman, 1980). These results coupled with the observations from the Mössbauer data allow the weight percentages of iron to be divided among the phases. For the sulfides, pyrite and pyrrhotite, the formulas for the minerals can be described as FeS_2 and Fe_7S_8 (Morice and others, 1969). Using these formulas, the amount of sulfur combined in the iron sulfides can be calculated and compared to the total amount of sulfur in the samples. The results of these calculations are given in Table 3.

DISCUSSION

Raw Oil Shales

The distinctive mineralogy of oil shale from the Mahogany zone has been studied in several articles. Smith and Robb (1966) recognized that ankerite is a persistent carbonate mineral in the kerogen rich zone.

TABLE 2. Fractional amount (in percent) of iron present in each phase in the oil shale samples studied. The uncertainty in the last significant figure is given in parentheses.

	Pyrite	Ankerite	Hematite	Magnetite	Pyrrhotite
Tosco II Raw	40(1)	60(1)			
Tosco II Retorted	24(3)	61(3)			15(3)
Fischer Assay Spent Shale	12(3)	53(3)			35(3)
Paraho Raw Shale	20(3)	75(2)			5(2)
Paraho Retorted Shale	19(5)	37(5)	33(5) ^a	Unknown 6(5)	5(5)
Lawrence In-Situ Raw 1B	19(3)	76(3)			5(3)
SOS 7	21(3)	17(3)	24(3)	38(3)	
SOS 9	13(3)	66(3)			21(3)
SOS 10			39(5) ^b	61(5)	
SOS 11B			42(5) ^b	50(5)	

^a Combination of hematite and magnetite.

^b The fraction includes superparamagnetic hematite.

Figure 3. The Mössbauer spectrum of Tosco raw shale OS-1. The resonances for ankerite (ank) and pyrite (py) are designated.

Ankerite is an iron containing carbonate that has the rhombohedral structure of dolomite and is noted chemically as $\text{Ca}(\text{Mg}, \text{Fe})(\text{CO}_3)_2$ (Dasgupta, 1965). Smith and Robb (1966) reported an average composition of $\text{Ca}(\text{Mg}_{0.85}\text{Fe}_{0.15})(\text{CO}_3)_2$ for ankerite in the mahogany zone. The Mössbauer parameters for ankerite are known and are similar to those of siderite, FeCO_3 (Lefelhocz and others, 1967). However the smaller quadrupole splitting for ankerite allows it to be distinguished from siderite.

Previous studies of iron and sulfur in oil shale have indicated the presence of iron sulfides such as pyrite, marcasite and pyrrhotite (Cole and others, 1978). The chemical formula of cubic pyrite is FeS_2 ; marcasite is also FeS_2 but structurally is orthorhombic and pyrrhotite occurs as Fe_{1-x}S where x varies from 0 to 0.125. The Mössbauer parameters of these three minerals in the pure state are well documented (Huffman and Huggins, 1978; Morice and others, 1969) and have been confirmed on iron sulfide studies in our laboratory. Because of the similarity of the Mössbauer parameters of pyrite and marcasite it is difficult to distinguish the one mineral in a large amount of the other (Montano, 1979; Williamson and others, 1980). Our parameters are closer to those of pyrite, but a small amount of marcasite may be present. Consequently the pyrite column in Table 2 should not be considered as pure pyrite.

Within the raw shales studied, three iron minerals were found. In two of the three raw shales two paramagnetic species and a third magnetic phase were found, while the third raw shale contained only two paramagnetic phases. The phases found and their relative fractions are listed in Table 2. The two paramagnetic phases observed in all three shales had parameters typical of pyrite and ankerite. A pyrrhotite-like material was identified in the Raw 1B from Anvil Points and the Paraho raw shale from Anvil Points. These conclusions are consistent with the results of other studies (Desborough, 1978; Milton and Eugster, 1959) that identified these minerals as present in oil shale. All three of the oil shales are from the Mahogany zone of the Green River Formation.

Tosco II Retort

In the Tosco II retorting process, a significant change in the pyrite was observed. The FeS_2 was selectively degraded over the ankerite to yield a magnetic pyrrhotite-like material. The relative amounts of ankerite indicate that this mineral was left unchanged by the Tosco process (shown in Table 2).

During Fischer assay, the changes in iron minerals were similar to those for the Tosco II process. The raw shale that was the feed-stock for this experiment was a split from OS-1 which contained the FeS_2 and ankerite. In the Fischer retort, the FeS_2 underwent changes to a magnetic pyrrhotite-like component. The ankerite also appears to have undergone slight decomposition but the small differences in fractions between the raw shale and Fischer assay spent shale may not be statistically significant.

Figure 4. The Mössbauer spectrum of Lawrence Livermore spent shale SOS-9 from Run S-9. The resonances for ankerite (ank), pyrite (py), and pyrrhotite (pyh) are designated.

Paraho Retort

The Paraho retort was run in the direct mode at the time the samples were taken. The feedstock which entered the retort contained three separate iron phases: FeS_2 , ankerite, and a small amount of magnetic sulfide similar to pyrrhotite. During retorting, a portion of the ankerite was decomposed to a mixture of magnetic oxides and a compound which may be a superparamagnetic oxide (see Table 2). In the Paraho process, changes in the carbonate occurred while the FeS_2 compound remained unchanged within experimental error. The fate of the pyrrhotite is not clear since the large resonance of the magnetic oxide component overlaps the small area of the pyrrhotite phase.

LLL Retort

The modified in-situ retort at the Lawrence Livermore Laboratory was run under four different sets of conditions ranging from a H_2 atmosphere to an atmosphere of 21% O_2 . The retorting conditions for each sample are listed in Table 1. The feedstock placed into the 125 Kg retort was observed to contain three distinct iron phases which included the two paramagnetic phases and a magnetic phase. The magnetic phase had parameters of pyrrhotite, while the two paramagnetic species are pyrite and ankerite. The relative fractions of each phase are presented in Table 2 along with the results observed in the spent shales.

Run S-9 yielded a spent shale (SOS-9) in which the pyrite was decomposed to pyrrhotite. The ankerite apparently decreased in Run S-9, but the small differences in the fractions of ankerite in the raw and spent shale may not be statistically significant. Spent shale SOS-9 from Run S-7 is the least complex of in-situ samples in that only the ankerite phase changed during retorting. The products of the ankerite decomposition have Mössbauer parameters that are similar to those of hematite (Fe_2O_3) and magnetite (Fe_3O_4). The assignment of the one magnetic component as magnetite is somewhat uncertain. As seen in Figure 5, the peaks for this phase are broad and the average magnetic field splitting is smaller than that of pure Fe_3O_4 . There are other magnetic oxides such as $\text{Ca}_2\text{Fe}_2\text{O}_5$ which have Mössbauer parameters similar to those found here (Whitfield, 1967).

The last two in-situ samples were run at similar conditions with S-11 using an atmosphere of twice as much oxygen as S-10, and maintaining a retort temperature of 1030°C , which was 95°C higher than that of S-10. At these conditions, there was a complete decomposition of the original iron phases pyrite, ankerite and pyrrhotite. They were converted to magnetic oxides much like what was observed in SOS-7. The supplementary liquid nitrogen measurements of SOS-10 and SOS-11B demonstrated the presence of small superparamagnetic particles of Fe_2O_3 and confirmed the Fe_2O_3 identification since a reversal of sign in the quadrupole splitting was observed (Kündig and Bömmel, 1966).

Mineral Decomposition Products

Recent studies have considered the decomposition of minerals during

Figure 5. The Mössbauer spectrum of Lawrence Livermore spent shale SOS-7 from Run S-7. The resonances for ankerite (ank), pyrite (py), pyrrhotite (pyh), hematite (hem), and magnetite (mag) are designated.

retorting and reactions of the decomposition products to form igneous-rock silicate minerals (Kuo and others, 1979; Smith and others, 1978). These studies show the formation of pyroxenes, olivines, and feldspars at about 800°C and these silicate minerals should be capable of including iron into their structures. The decomposition products of the iron minerals during retorting have been shown to be oxides such as hematite and magnetite. The temperatures for formation of the oxides range from 600°C in the Paraho retort to 1030°C in the Lawrence Livermore retort. These temperatures bound the 800°C for formation of silicates which was found in the other two studies. Within the uncertainties in Table 2, none of the iron has reacted to form silicate minerals in the samples studied.

The two recent studies on the formation of igneous silicates pointed out that the formation of these minerals should help to minimize the environmental consequences of in-situ retorting because cations will be incorporated in a relatively inert silicate matrix (Smith and others, 1978; Kuo and others, 1979). In fact, the one study showed the decrease in concentration of cations leached from shales retorted at temperatures above 800°C because of silicate mineral formation (Kuo and others, 1979). However, the inability of iron minerals to form silicates in these samples means that the iron from pyrite may not be bound into a less reactive matrix during in-situ retorting. Other trace elements such as molybdenum, arsenic, cadmium, zinc, lead and copper are also suspected of being associated with the pyrite in oil shale (Desborough and others, 1976; Wildeman, 1979). If the iron is not bound, then these trace elements may not be bound in the silicates either. Consequently, the formation of silicate minerals during retorting at temperatures greater than 800°C does insure that a large fraction of the major cations such as Mg, Ca, Na, and K are bound in silicate minerals, but this does not imply that trace metals from pyrite and other sulfide minerals are similarly bound.

Sulfur Reactions During Retorting

A secondary reason for studying the changes in iron phases during retorting was to try to determine the fate of the iron sulfides present. In the conversion of coal to generate power, the decomposition of iron sulfides have created a specific set of economic and environmental problems. Before full scale exploitation of oil shale occurs, questions about the fate of sulfur need to be investigated.

In the Green River Mahogany zone, a significant portion of the iron is directly related to sulfides. As seen in Table 2, over 20% of the iron is in sulfides in the Paraho and Raw 1B shales while the Tosco II raw shale has about 40% of the iron bonded as a sulfide. For the raw shales Tosco OS-1 and Paraho, the total abundance of sulfur has been determined and the results in Table 3 show that the majority of S in the shales is bonded as iron sulfides, with little in other phases.

When OS-1 was retorted in the Tosco II retort it is observed that almost 90 percent of the sulfur in the resultant spent shale was

TABLE 3. Weight percent of iron contained in the various minerals in the oil shale samples.

	Total Wt.% Fe ^(a)	Ankerite	Weight Pyrite	Percent of Iron as Mineral			Wt.% S in Sulfides	Wt.% S ^(b) Total Minerals	%S as Fe
				Pyrrhotite	Hematite	Magnetite			
Tosco II Raw	1.87 0.04	1.22	.075	--	--	--	.086	1.12	77
Tosco II Retorted	2.45 0.08	1.50	0.59	0.36	--	--	0.91	1.04	88
Fischer Assay Spent Shale	2.31 0.04	1.22	0.28	0.81	--	--	0.85	0.84	99
Paraho Raw	2.13 0.04	1.60	0.43	0.11	--	--	0.56	0.60	93
Paraho Retorted	2.31 0.04	0.85	0.44	0.12	0.90	--	0.58	0.58	100
Lawrence Livermore Raw 1B	2.18 0.04	1.66	0.41	0.11	--	--	0.54	--	--
SOS 7	2.70 0.13	0.46	0.57	--	0.65	1.03	0.66	--	--
SOS 9	2.35 0.15	1.55	.30	0.49	--	--	0.67	--	--
SOS 10	3.05 0.13	--	--	--	1.19 ^(c)	1.86	0	--	0
SOS 11B	3.13 0.15	--	--	--	1.32 ^(c)	1.82	0	--	0

(a) From Fox and others, 1980. (b) From Wildeman, 1980. (c) Including superparamagnetic Fe₂O₃.

in the form of iron sulfide. Smith (1962) reported that about 75 percent of the raw shale sulfur was retained while the non-condensable gas contained about 17 percent available sulfur H_2S . The sulfur balances on the Fischer assay retorted shale and the Paraho retorted shale also show that almost all of the sulfur in the sample can be accounted for in the iron sulfides. Consequently, it can be concluded that, at lower retorting temperature, before the iron sulfides completely decompose, the majority of the sulfur in the retorted shale is associated with the iron sulfide minerals. When pyrite does completely decompose during retorting, Smith and others (1978) suggest that the sulfur in the retorted shale is in the form of anhydrite ($CaSO_4$).

Even though the majority of the sulfur is retained in the spent shale in all of the lower temperature retorts, it can be seen in Tables 2 and 3 that in some cases pyrite definitely reacted to pyrrhotite. A comparison of when pyrite did break down with when it did not provides interesting observations. In an inert environment pyrite should be stable up to $750^{\circ}C$ where it incongruently melts into pyrrhotite and liquid sulfur (Kullerud, 1967). In three retorting situations (Tosco II, Fischer Assay, and Lawrence Livermore with H_2 gas) pyrite has definitely partially decomposed to pyrrhotite at temperatures below $750^{\circ}C$. In all three cases, oxygen is not introduced into the retort. In the Paraho process and in Lawrence Livermore Run S-7, pyrite has not appeared to decompose. It is important to note that Run S-7 was made at $750^{\circ}C$ - the decomposition temperature of pyrite (Kullerud, 1967). In both these cases, the ankerite decomposed instead of the pyrite. In the samples studied, oxygen introduced into the retort apparently retards the decomposition of pyrite up to the pyrite decomposition temperature of $750^{\circ}C$. This observation may be quite important for the reduction of sulfur emissions in oil shale retorts. In the previous section it was noted that pyrite probably has other toxic trace elements associated with it. If the breakdown of pyrite is retarded, the mobilization of these trace elements may also be retarded.

For two of the retorted shales that were studied, the retorting temperatures did exceed the pyrite decomposition temperature of $750^{\circ}C$. In Lawrence Livermore Run S-10 the temperature reached $935^{\circ}C$ and in Run S-11 the temperature reached $1030^{\circ}C$. In both retorts oxygen was added. In both retorted shales, pyrite, pyrrhotite and ankerite have decomposed to iron oxides. Nothing can be said about the fate of sulfur in these two situations except that the sulfur is no longer bound to any iron phases.

CONCLUSIONS

From the Mössbauer studies on these samples the following conclusions can be made:

1. The iron minerals found in the raw shales are ankerite and pyrite and minor amounts of pyrrhotite.

2. In the Tosco II, Fischer Assay, and Lawrence Livermore Run S-9 processes, where the retorting was done in the absence of oxygen, pyrite decomposes to form pyrrhotite but the ankerite remains unchanged. This decomposition reaction occurs at temperatures below the normal decomposition temperature of 750°C.

3. In the Paraho retort and in Lawrence Livermore Run S-7, where oxygen was introduced into the retorting, the decomposition of the pyrite was retarded but the ankerite decomposed to iron oxides.

4. In the two retorting processes where the temperatures exceeded 750°C, pyrite, pyrrhotite, and ankerite have all been decomposed to iron oxides.

5. The iron was not found in silicate minerals in any of retorted shales. In these samples, the decomposition products are iron oxides and these oxides do not react with quartz to form silicates.

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IWG Corp Report

OIL SHALE RISK ANALYSIS PROGRESS REPORT

INTRODUCTION

This progress report summarizes the effort to date of the first year of the Oil Shale Risk Analysis (OSRA) conducted by the Center for Environmental Sciences, University of Colorado at Denver and IWG Corp. of San Diego. This effort is part of the DOE Oil Shale R,D and D program.

The objective of this project is to perform an analysis of potential risks to human health and the environmental impact associated with an oil shale industry capable of supplying a significant fraction of the United States' energy demand. The information contained in this project will be reported and disseminated in a HEED (Health and Environmental Effects Document). The HEED will include a qualitative and quantitative description of knowledge and uncertainty regarding potential health and ecosystem impacts of an oil shale industry. It will provide information to aid in the reduction of human health and environmental hazards.

The overall oil shale risk analysis process is shown in Figure 1. The nature of the risk analysis process is iterative because of the mutual interdependence among its key elements and the need to refine the results. The first year's effort is a "broadbrush" approach to the entire analysis. Key elements of the oil shale risk are the result of a highly interactive process of (1) the exposure resulting from source terms (as characterized by the probability of exposure), (2) the health effects (as characterized by the conditional probability of effect given the exposure), and (3) the population at risk.

The risk is the expectation of population effects under the exposures considered. In mathematical terms, this relationship (simplified) is

$$\langle r \rangle = \int_{\text{all } y} y p(y/x) p(x) dy$$

where y accounts for the actual population at risk, $p(x)$ represents the exposure probability and $p(y/x)$ is the conditional probability of health effect y given exposure x .

The major objective of the first year's effort was the establishment of the maximum relative risk terms. However, the following were also considered key objectives:

Figure 1.

RISK ANALYSIS PROCESS

- Establishment of the significant (e.g., large magnitude or critical from a toxicity or chronic effect) exposure.
- Establishment of the significant probabilities for the relevant exposures.
- Establishment of the critical uncertainties for the risk analysis.

A necessary process in risk analysis is the continual data gathering. Table 1 indicates the data categories. At the time of the analysis, a "horizontal sweep" through the data categories occurs to perform the analysis. This is repeated in an iterative mode as (1) identified data needs are filled, (2) uncertainties are resolved, and (3) relative priorities are established.

The overall analysis strategy is described in the subsequent section as well as the associated progress, the source term characterization, the scenario, the environmental transport and transformation, the ecosystem risk, and the health effects analysis. Two additional sections describe the conceptualization and the workshop conducted as a part of the first year's effort.

SOURCE TERM CHARACTERIZATION

One of the important steps in the process of developing a successful risk analysis is the proper identification of the various source terms. The source terms description is a process which identifies the emission sources for the stages in the oil shale fuel cycle. The major requirements for proper identification of these emission sources are:

- Detailed characterization of the processes and the effluents of each step and waste stream
- The specific site of the plant, such as the plant being located in a canyon or on a ridge.

There are many processes for retorting oil shale, each having different effluent characteristics. The characterization effort considers the source terms for seven different processes. The selection of these processes is based primarily on data availability and representation of different categories of retorting. The processes were broken down into an oil shale fuel cycle flow chart, Figure 2, which shows the steps involved in taking raw oil shale and refining it into oil or gas. Each part of the different processes has associated environmental and health issues. A guide, in the form of a matrix, determines the major concerns in the steps of the oil shale fuel cycle. This matrix, presented in Table 2, outlines specific steps in the fuel cycle and the possible environmental and health issues.

In the matrix, the pollutant issues have been divided into categories, such as air, liquid, and solid. The compiled source terms have been subdivided whenever possible, mainly in the liquid effluent category. In

Table 1.

DATA CATEGORIES

COMPONENT	HAZARD SOURCE	POLLUTANT	PATHWAY	ENTRY	SYSTEM	HEALTH EFFECT	GROUP
EXTRACT	PRODUCT	ORGANIC	WATER	INGEST	RESPIRATORY	SYSTEMIC	OCCUPATIONAL
RETORT	OIL	COMPOUNDS	AIR	INHALE	CIRCULATORY	POISONING	PUBLIC
RECOVER	PRODUCT	INORGANIC	LAND	ABSORB	NEUROLOGIC	ORGAN	LOCAL
UPGRADE	GAS	COMPOUND	BIOLOGIES		REPRODUCTIVE	DYSFUNCTION	STATE
TRANSPORT	PRODUCT	TRACE ELEMENTS	CONTACT		GASTROINTESTINAL	CARCINOGENIC	U.S.
REFINE	WATER	PARTICULATES			IMMUNOLOGIC	TERATOGENIC	WORLD
CONVERT	WASTE	NOISE			DERMAL	PSYCHOLOGICAL	
	SPENT SHALE	OTHER			SKELETAL		
	ACCIDENTS				ENDOCRINE		
					MUSCULAR		
					HEPATIC		

Figure 2.

OIL SHALE FUEL CYCLE ANALYSIS FLOW CHART

Figure 2 (cont.).

OIL SHALE FUEL CYCLE ANALYSIS FLOW CHART (Cont.)

Table 2.

OIL SHALE FUEL CYCLE ISSUES

OIL SHALE PROCESS				ISSUES								COMMENTS
FUEL CYCLE PARTS	PROCESS STEPS	PROCESS STEPS	STEP TECHNOLOGY	AIR	LIQUID	SOLID	NOISE	OTHER	ECOSYSTEM	PUBLIC HEALTH	OCCUP. H&S	
EXTRACTION & RETORTING	SURFACE	MINING	UNDERGROUND									
			SURFACE									
		CRUSH & SIZE		NA					NA			
	MIS	RETORTING	INDIRECT									
			DIRECT									
		MINING										
		FRAC & RUB.			NA				NA			
		RETORTING			NA							
		CRUSH & SIZE		NA					NA			
	IN-SITU	RETORTING	INDIRECT									
			DIRECT									
		FRACTURE			NA				NA			
		IGNITION			NA				NA			
PRODUCT RECOVERY & UPGRADING	OIL	UPGRADING	Thermal									
			Catalytic									
			Chemical									
	GAS	UPGRADING	Clean-up									
REFINING & CONVERSION			Onsite E/H									
			Offsite E									
			Conv. Oil Ref.									
USES			Bldg. H&C		NA			NA				
			Industry Proc. H		NA							
			Misc.									
			C&F									
			Transportation		NA							

addition, the raw shale, product oil, product water, and product gas are described, when feasible. To facilitate comparison, the generated wastes and products were normalized to a general oil shale yield of 25 g/T and a plant production level of 50,000 bbl/d.

The following is a list of the seven processes and the inputs, waste-streams, and products that have been compiled for each process.

TOSCO: Air emissions
Water effluents
Effluent constituents
Solid waste
Product water
Retorted shale
Product oil

PARAHO: Raw oil shale
Air emissions
Water effluents
Effluent constituents
Solid waste
Product water
Retorted shale
Product oil
Product gas

OCCIDENTAL: Raw oil shale
Air emissions
Water effluents
Effluent constituents
Solid waste
Product water
Retorted shale
Product oil
Product gas

TRUE-IN-SITU: Air emissions
Effluent constituents

RIO BLANCO: Raw oil shale
Air emissions
Water effluents
Effluent constituents
Solid waste

UNION "B": Air emissions
Effluent constituents
Solid waste

SUPERIOR: Air emissions
Retort water and its constituents
Solid waste

As an example, the TOSCO wastestreams and products are presented in Tables 3 through 6.

SCENARIO

The million barrel per day scenario (10^6 bbl/d) presented in Table 7 was prepared for the oil shale risk analysis. The scenario approach was used to evaluate the impact of a full-scale industry. The selection of a proper scenario for the risk analysis is all-important because the environmental effect of the industry is dependent upon several crucial variables; the location of the plant, the process, and its production level. The data presented in the scenario is consistent with the perceived trends of the federal government and the stated commitments of the private companies.

The important features of the selected scenario are:

- The extraction and retorting process above ground account for 47% of the total and most, if not all, are indirect processes. Twenty-seven percent of the processes are in situ and the remaining are unknown at the present time.
- The product recovery and upgrading will be 30% on-site.
- The transportation will be primarily by pipeline except for 5% of the total, which will be transported by rail.
- The refining and conversion will be off-site.

TRANSPORT AND TRANSFORMATION

A major effort of the risk analysis determines the parameters in the transport and transformation of oil shale pollutants. This area is necessary for estimating human exposures and health effects. The effort has proceeded along the following major exposure routes: air, water, solid waste and food chain.

Air

A workable data base was gathered on air transport processes, dispersion modeling, and transformation mechanisms applicable to oil shale industry location and source characteristics.

Development of the data base led to an analysis strategy which incorporates dispersion modeling, empirical studies, and theoretical considerations. To estimate public exposure the results from Gaussian dispersion modeling were used. To calculate occupational exposures a simplified box model was reproduced. Particle and aerosol deposition were estimated by assuming gravitational settling as the dominant removal mechanism. Atmospheric reaction rate and product came from empirical studies in the literature. These results were used as a screening procedure to select pollutant constituents as candidates for more detailed analysis.

Table 3

Air Emissions - TOSCO (kg/bbl)*

	Part.	SO ₂	NO _x	HC	CO	H ₂ S	CO ₂
Mining (R&P)	0.32	0	0.054	0.011	0.096	--	--
Shale Preparation	3.47	0	0	0	0	--	--
Retorting	2.49	0.033	0.311	0.011	0.013	1.3	46
Spent Shale Treatment & Disposal	0.30	0	0.028	0.0022	0	--	--
Upgrading	trace	0.0022	0.0044	0.0022	trace	--	--
NH ₃ and S Recovery	0	7.0	0	0	0	--	--
Product Storage	0	0	0	0.033	0	--	--
H Production	0.002	0.0065	0.017	trace	0.0022	--	--
Total	6.6	7.1	0.42	0.059	0.11	1.3	46

*kg/bbl: kilograms per barrel of oil produced

Table 4

Water Effluents-Aboveground-Indirect (g/bbl)*
(e.g. TOSCO)

Step	Quantity	Pollutants	Control	Efficiency (%)
Mine Drainage	---	Suspended Solids	Filtration	95
		Dissolved Inorganics	Distillation	99
Cooling Tower	23-37	Suspended Solids	Filtration	95
		Dissolved Organics	Chemical Oxidation	90
Boiler Blowdown	6.6-7.2			
Boiler Feedwater Treatment Wastes	3.4-3.8			
Gas Washing Condensate	---			
Gas Condensate (net)	13-14	Trace Organics	Chemical Oxidation	90
		Trace Metals	Distillation	99
		Dissolved Organics	Chemical Oxidation	90
		Dissolved Inorganics	Distillation	99
		Dissolved Gases	Steam Stripping	95
		Oil & Grease	Coalescing Filter	99
		Suspended Solids	Filtration	95
Retort Condensate	---	Trace Organics	Chemical Oxidation	90
		Trace Metals	Distillation	99
		Dissolved Organics	Chemical Oxidation	90
		Dissolved Inorganics	Distillation	99
		Dissolved Gases	Steam Stripping	95
		Oil & Grease	Coalescing Filter	99
		Dissolved Organics	Chemical Oxidation	90
Coker Condensate	1.1	Dissolved Gases	Steam Stripping	95
		Oil & Grease	Coalescing Filter	99
Hydrotreater Wash Condensate	16			
Net Hydro-treater Condensate (Upgrading)	0.71	Trace Organics	Chemical Oxidation	90
		Dissolved Organics	Chemical Oxidation	90

g/bbl: gallons per barrel of oil produced

Table 5

Effluent Constituents: Aboveground-Indirect*
(kg/bbl)(e.g. TOSCO)

	Mine Drainage Treatment	Cooling Tower Blowdown	Boiler Treatment Wastes	Gas Condensates	Retort Condensate	Coker Condensate	Upgrading Condensate
As	--	--	--	--	67E-6	--	--
B	--	0	0	0	3E-5	0	0
BOD	0	0	0	.5171	.1297	.041	.027
Ca	--	.025	.013	0	.013	0	0
Cl	0	.070	.032	0	.0404	0	0
Co	--	--	--	--	15E-8	--	--
CO ₂	0	0	0	.3	--	.025	--
CO ₃ ⁼ +HCO ₃ ⁻	--	0	0	0	.4380	0	0
F	--	0	0	0	.00002	0	0
Fe	--	--	--	--	.0001	--	--
H ₂ S	0	0	0	.042	.0030**	.0033	1.1
K	--	0	0	--	.0005	0	0
Li	--	--	--	0	.4E-6	--	--
Mg	--	.0069	.0035	--	.0005	0	0
Mo	--	--	--	0	.4E-6	--	--
Na	--	.53	.013	.27	.03	0	0
NH	0	0	0	--	.5235	.021	2.4
Rb	--	--	--	0	31E-7	--	--
S	--	.096	.028	0	.288	0	0
Si	--	0	0	--	84E-6	0	0
Sn	--	--	--	--	77E-8	--	--
Ti	--	--	--	--	14E-6	--	--
V	--	--	--	--	15E-8	--	--

*It is assumed that Hydrotreated Condensate is the same as Upgraded Condensate
**Sulfide

Table 6
Solid Waste-Aboveground (kg/bbl) (e.g. TOSCO)

		Spent Shale	1800
		Raw Shale Dust	46
		Spent Shale Dust	4
		Green Coke	2
		Non-Shale Solids	0.08
Constituent	Wt. %	Spent Shale (kg/bbl)	Spent Shale Dust (kg/bbl)
SiO ₂	33.00	594	1.32
CaO	15.80	284	.63
MgO	5.31	96	.21
Al ₂ O ₃	6.80	122	.27
Fe ₂ O ₃	2.52	45	.10
Na ₂ O	8.68	156	.35
K ₂ O	3.28	59	.13
SO ₃	2.63	47	.11
P ₂ O ₅	0	0	0
Mineral CO ₂	5.71	103	.23
Org. C	4.49	81	.18
Inorg. C	5.71	103	.23
Other	5.07	109	.24

TABLE 7
Million Barrel Per Day Scenario for the Oil Shale Industry

Tract/Group	Process	Production (BPD)
Surface Induced		
Long Ridge (Union Oil Co.)	Union "B"/Union SGR*	150,000
Superior (Superior Oil Co.) ^a	Superior Circular Grate	46,000
Dow (Colony, CDO)	TOSCO II*	47,000
Sandwash, Utah (TOSCO)	TOSCO II	50,000
U-a, U-b (Combined White River Project)	Paraho (Indirect)/ Union B	100,000
Paraho (Utah, Uinta County)	Paraho (Indirect)	30,000
Chevron (So. Piceance/ Parachute)	Unknown	100,000
Mobil (E. Parachute Creek)	Unknown	100,000
Getty (Parachute Creek)	Unknown	50,000
NOSR-1 (Garfield County, CO)	Unknown (Paraho ?)*	100,000
NOSR-3		
In-Situ Induced		
C-a (Rio Blanco)	Mod LLL RISE/Lurgi	100,000 ^b
C-b (Oxy/Tenneco)	Oxy (MIS)/Lurgi	100,000
Multi Minerals (Federal Lease) ^a	IIS (Integrated)	50,000
Equity (Colorado)	BX Pure/Stream	20,000
Geokinetics (Uinta County, Utah)	LOFRECO In Situ	

* Potential Upgrading/Refining Facilities on site.

a) Mineral co-product production (Soda-Ash, Alumina and Nacholite).

b) Surface Processing (Lurgi).

Water

The water transport and transformation data base was broken down into categories of effluent characteristics, surface water characteristics, transport mechanisms, and transformation reactions, which may be applied to conditions in the Uinta and Piceance Basins. Surface water transport of accidental discharges was estimated assuming complete mixing and instantaneous release. This assumption was used as a bound to estimate the maximum concentration. Water transformation reactions were examined to qualitatively determine effects on downstream concentrations.

Solid Waste

Leachate transport and transformation data were broken down into categories of leachate composition, leachate transport, leachate transformation, and aquifer characteristics. The leachate concentration was estimated by assuming constant leachate concentration, constant leaching rate, and mainly macropore contribution. These assumptions were necessary to allow an initial estimate of leachate concentrations. Leachates were immediately "transported" to surface and groundwater without benefit of dispersion or transformation.

Food Chain

Literature on food chain transport and transformation was organized in categories of bioaccumulation of pollutants in organisms at various trophic levels, transformation in various organisms, ingestion rates, and excretion rates. Bioaccumulation factors were found for most generic pollutants currently expected from the oil shale industry. Input to the food chain results from deposition of air pollutants and absorption of water pollutants. Estimates were prepared for the constituents stored in each trophic level from bioaccumulation factors and animal ingestion rates. Human exposure estimates were calculated by assuming an ingestion scenario based on consumption of agricultural products and game species.

ECOSYSTEM RISK

The initial effort in determining ecosystem risk includes an evaluation of alternative methodologies for quantifying the risk to ecosystems. The major result was a definition of ecosystem risk consistent with the stochastic nature of the usual risk concept. Ecosystem risk was defined as the change in community diversity resulting from oil shale development. Community diversity is a concept which can either be predicted mathematically or measured in the field. A decline in community diversity implies a simpler community composition resulting from changes in species populations. Simpler communities are found to be more unstable, more susceptible to predation and disease, and may result in local extinction of rarer species.

The impact on community diversity, resulting from a one million bbl/day oil shale industry in the Piceance Basin, was estimated by predicting terrestrial and aquatic animal populations. Changes in terrestrial animal populations were based on habitat preferences. Aquatic population changes due to increased salinity were also examined.

HEALTH EFFECTS

Current health effects data was reviewed and a risk analysis base compiled. Two data areas necessary to support the proposed analysis are:

- 1) The toxicology and epidemiology data of the pollutants expected from oil shale effluents. These data include air pollutants, trace elements and organics. Data was also collected on absorption rates, body burden, metabolism and excretion.
- 2) Specific oil shale data including the results of current toxicologic testing of oil shale, shale oils, oil shale wastes as well as epidemiologic data from U.S., Estonian and Scottish oil shale industries.

Strategy

To determine public exposure risk, each pollutant was assessed separately. Oil shale characterizations were studied to determine the pollutants of health significance. However, since this list consisted of over twenty-five compounds, trace elements and organic classes, it was necessary to rapidly screen out the pollutants found at concentrations far below levels of adverse health effects. The remaining "priority" pollutants were individually examined to find dose response relationships to be used in the risk analysis. Combining the dose response with the exposure data resulted in estimates of health risk.

Occupational health risk analysis must include calculations of risk due to direct exposure to industry materials, products, and effluents. Using the oil shale-specific data base, estimates of occupationally related health effects are determined. Epidemiologic data from Estonia has relative risk estimates that can be converted to absolute risk. Toxicologic data can be converted to human risk. Both methods require extensive caveats and assumptions. Nonetheless, due to the lack of detailed occupational exposure data, this strategy is the only viable alternative methodology.

Priority Pollutants

To establish the pollutants of potential health importance, or the priority pollutants, from the remaining ones, a rough estimate of exposure was needed. Using the available shale characterization and the air dispersion model results, ambient air concentrations were calculated for each pollutant. Comparing the resulting estimates with promulgated Occupational Safety Standards determined the priority pollutants. If the estimates were within two orders of magnitude of the standards, priority status was assigned. One major exception to this rule was the assignment of priority to all pollutants having carcinogenic effects. The results of the screening are presented in Table 8. This table indicates which pollutants were assigned priority status. Pollutants marked by a question mark indicate that priority status may be given if future work shows these pollutants have a significant impact on human health.

Table 8. Results of Screening with Important Health Effects

Pollutant	Conclusion of Screening	Health Effects	Priority
SO _x and Particulates	Without controls, air concentrations near plant may exceed morbidity thresholds.	Suspected co-carcinogen increase URT infections, nasopharyngitis, exacerbation of chronic bronchitis.	X
NO _x	Release is at same order of magnitude (10 mg/m ³) as promulgated TWAs.	Decreased vital capacity and pulmonary dysfunction in animals, heart, kidney and liver damage secondary to lung.	X
CO	Estimated release well below federal standards as well as effect thresholds.	Hypoxia is noted effect with acute exposure. Chronic exposure causes myocardial alteration in persons with restricted coronary blood flow.	
O ₃	Inconclusive. Exposure is a function of photo-activity and NO _x . Needs special attention.	Eye and deep lung irritation. Acute exposure: pulmonary edema, slowing of heart neurologic effects. Animals: suppression of AHH activity.	X
NH ₃	Most processes propose NH ₃ recovery. Environmental exposures will be very small. Occupational exposure needs work.	Eye and respiratory irritation. Direct contact causes burns. Headache.	
H ₂ S	May be a hazard in the mines. Public annoyance factor due to bad odor.	Acute: histotoxic hypoxia. Chronic: conjunctivitis pulmonary edema.	
Arsenic	Exposure is in mg/m ³ range but non-threshold effect gives this pollutant priority.	Lung cancer (skin CA suspect). Peripheral neural effects renal, hepatic and GI effects with ingested As.	X
Boron	Exposure negligible.	Mucous membrane changes CNS depressant. Cattle show GI effects.	
Barium	Exposure negligible and effects minimal.	Pneumoconiosis; barite occup. exp. Acute exposure: CNS effect, GI effects, and muscle paralysis.	
Beryllium	No estimate made. Lack of data.	Suspect carcinogen. Pulmonary granulomatous pneumonitis, cardiovascular, renal and hepatic fibrosis. Gastrointestinal effects in animals.	?
Cadmium	Exposure estimate matched 8 hr TLV standard (0.2 mg/m ³). May be very important.	Suspected carcinogen. Proteinuria. Respiratory irritant. Hypertension, cirrhosis of liver, and GI effects related.	X

Table 3. (Continued)

Pollutant	Conclusion of Screening	Health Effects	Priority
Chromium	Very little air release. Leaching to water supplies may be important.	Bronchogenic carcinoma (Cr VI). Acute exposure: respiratory inflammation, dermatitis, perforation of nasal septum.	X
Copper	Insignificant release.	GI effects with acute exposure. No evidence of chronic exposure effects.	
Fluoride	Unable to present estimate. Water release may increase local water supply concentrations.	Osteosclerosis, mottled dental enamel, hematologic changes, alteration of kidney and thyroid function.	?
Iron	Release would not greatly increase background exposure.	Siderosis (inhaled), hemochromatosis (excessive dietary). Increased risk of lung CA in hematite miners.	
Lead	Estimate is an order of magnitude below level at which blood lead levels do not increase $2-3 \text{ mg/m}^3$. While inhaled may not be important, ingested Pb may. More environmental transport work needed.	Anemia. Renal damage. Neurologic effects. GI effects.	?
Mercury	Most of Hg is volatilized in retorting. Calculation did not use 10^{-4} dust release. Nonetheless, very little is released.	Acute: pneumonitis and bronchitis. Ingested Hg causes GI inflammation. Chronic: tremors, fatigue and erethism, proteinuria.	
Molybdenum	Insignificant release.	Animal toxicity only. No evidence for human effects acute or chronic.	
Nickel	Estimate surpassed NIOSH TWA (15 mg/m^3).	Health effects unclear. Epidemiology links NiCO_4 to lung CA. Dermatitis, pneumonitis. Animal: cardiovascular, renal, hepatic involvement.	X
Selenium	Very small release. Several orders of magnitude below standards.	Evidence of carcinogenicity and anti-carcinogenicity. Liver damage. Pulmonary irritation. Neurologic effects. Dental caries.	X
Strontium	Large release but no standards for comparison. Only of importance concerning radioactivity.	^{90}Sr : bone marrow CA.	
Vanadium	Very small release. Several orders of magnitude below standards.	Bronchitis and broncho-pneumonia (acute exposure). Depression. Skin irritation. Renal damage.	
Zinc	Release adds little to background concentrations.	Respiratory, dermal, gastrointestinal irritation.	
Organic hydrocarbons (PAHs and aza-arenes)	Large quantities in oil and product water. No estimate can be made. Environmental behavior under investigation.	Some PAHs are highly carcinogenic in animals. No threshold assumed. Human data supports carcinogenic hypothesis.	X

Dose-Effect Modeling

A fundamental decision was made concerning threshold levels for health effects. A threshold is the largest dose of a pollutant at which there is no adverse effect. For the purpose of this analysis, carcinogenic effects were assumed to have no threshold, however, all other effects were assumed to have thresholds. The latter assumption implies that background levels of these pollutants must be estimated before oil shale related effects can be calculated.

Carcinogenic pollutants of oil shale are arsenic, chromium (VI), selenium, and polycyclic organic matter (i.e., PAHs and aza-arenes). Dose-effect models have been developed for arsenic and PAHs. Curves for selenium and chromium can be estimated from toxicologic data. These curves yield risk estimates for different exposure levels.

Non-threshold pollutants relate to a variety of effects, many of which have only been observed in occupational settings. The risk analysis identifies the most sensitive effect for each priority pollutant, that is, the effect manifested at the lowest dose above threshold. The threshold levels are available in the literature. The dose-effect relationship for the most sensitive effect is best estimated from epidemiologic data or, when not available, toxicologic data.

Effects and dose-response relationships are sometimes modified by host factors, such as smoking, disease, age and others. Where possible, special thresholds and dose-effects are determined for sensitive groups.

THE CONCEPTUALIZATION

In the first month of the analysis effort a methodology was compiled and documented as the "Oil Shale Risk Analysis Conceptualization." This working document described in detail the methods and concepts which IWG intends to use in the coming years. The overall structure of the analysis was presented with two examples to demonstrate the quantitative procedures. An analysis of arsenic, with a no threshold level, linear dose-effect curve and an approach for mercury, with a non-linear, threshold dose-effect curve were done to demonstrate prescribed methods. Despite the document's rapid preparation, the effect and associated review comments were of great value for the ensuing analysis.

WORKSHOP

On January 8 and 9, 1981, in San Diego, a workshop on the health and environmental risk analysis was conducted to discuss current problems and issues. The attendees included project staff, consultants, selected members of the Oil Shale Task Force, and other interested parties. The workshop was divided into a health effects group and a source term/ecosystem group. It addressed questions, prepared before the workshop, in all areas of the

analysis. The results of the discussion on these questions are presented in the workshop proceedings.² The workshop's goals were achieved, allowing a useful exchange of ideas and results leading to a positive impact on the oil shale risk analysis.

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