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TRACE ELEMENTS IN OIL SHALE

Progress Report for 1979-1980

By
Willard R. Chappell

Work Performed Under Contract No. AC02-79EV10298

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

U. S. DEPARTMENT OF ENERGY

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TRACE ELEMENTS IN OIL SHALE

Progress Report 1979 - 1980
DOE Contract #EV-10298

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PROGRESS REPORT: 1979 - 1980

Introduction and Summary of Research

Willard R. Chappell
Center for Environmental Sciences
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The purpose of this research program is to understand the potential impact of an oil shale industry on environmental levels of trace contaminants in the region. The program involves a comprehensive study of the sources, release mechanisms, transport, fate, and effects of toxic trace chemicals, 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.

The program is a part of the Environmental Trace Substances Research Program (ETSRP) which is one of the programs under the Center for Environmental Sciences at the University of Colorado at Denver. The Principal Investigator is Dr. Willard R. Chappell, Professor of Physics and Director of the Center for Environmental Sciences, University of Colorado at Denver. The other Senior Investigators are:

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The present report describes the progress of the fourth year of funding as of February 15, 1980.

The overall 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. Wherever 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 120 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 three 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" methods or by development of new methods. This is a highly significant result because the "standard" methods tend to be used in many environmental assessments.

Recent results have included:

- A sampling manual written for the environmental scientist and practicing engineer with specific application to sample design for geochemical baseline studies of surficial materials in the oil shale country is in draft form and has been reviewed by a number of specialists.
- 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 concomitant side reactions of pH decline and possible pollutant solubilization.
- Other microbial research indicates that microbiological 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.

The program consists of seven interrelated research projects which are briefly described below (the following sections give a more detailed description by the individual investigators):

Trace Element Reconnaissance

(R. Klusman, Colorado School of Mines)

One of the most difficult problems in environmental research is determining whether the environment has been altered from its previous state. These difficulties highlight the importance of reliable and reproducible baseline data. In many cases, baseline data is collected in a manner that has little connection, if any, with the variability (spatial or temporal) of the parameters measured. In recent years, considerable progress has been made in the development of techniques for deriving reproducible trace element maps covering large regions. These maps have been shown to be of tremendous value in the analysis of environmental impacts.

Dr. Klusman has been collecting surficial materials in the Piceance Creek Basin since the project began. An initial regional reconnaissance conducted partly with funding from the Colorado Energy Research Institute with the cooperation of the U.S. Geological Survey (before the ERDA/DOE funding became available) was used to establish appropriate intervals for subsequent grid sampling in the

vicinities of lease tracts C-a and C-b, and the Anvil Points site. These regional surveys showed that As, B, Mo, and Se tend to be elevated in the soils of the Piceance Basin. Dr. Klusman also found that Zn, Cu, Li, and F have a significant regional trend with increasing concentrations from north to south. The data also revealed that Mo and As are elevated in stream sediment. Significant differences have been found between streams in terms of the concentrations of several elements. Stable geochemical maps have been constructed for several elements in both soils and plants for tracts C-a and C-b.

Because it was possible to construct trace element maps for some constituents, it will be possible to detect changes due to releases from production facilities, if these releases are large enough to give rise to significant differences. Preliminary calculations have been made of the time required to detect contamination. Because of the limited data available, there is considerable uncertainty in the results. For example, using the figures for particulates and mercury emissions given in the revised Detailed Development Plan for C-b, and assuming uniform dispersal over 45 square miles, the contamination due to Mo release could be detected in 236 years, while that due to Hg would be detected in less than a year (assuming quantitative adsorption of Hg by the surface soils). Clearly, these numbers could be greatly changed when better data becomes available or by a more sophisticated dispersal calculation allowing for the directional effects due to prevailing winds.

We believe the data being developed by Dr. Klusman will provide an extremely valuable baseline for this region and will establish the value of this approach for other types of development.

Chemical Characterization of Oil Shale Effluents

(T. Wildeman, Colorado School of Mines)

While the purpose of the study by Dr. Klusman is to establish a baseline for later comparison, the work being done by Dr. Wildeman has as its purpose the examination of the potential sources of change. In recent years researchers have become increasingly concerned about trace element emissions from coal-fired power plants. Recent work has shown, for example, that certain elements such as As, Cd, and Se have higher concentrations on smaller particles. Although oil shale retorting processes are quite different in character from the combustion of coal, they will handle solids at a rate which will greatly exceed most coal-fired power plants.

Dr. Wildeman has been conducting a study of the input and output streams of various retorts. This work began with an extensive study of the Fischer Assay as a model retort. Subsequent studies have involved TOSCO II materials and Paraho materials. Dr. Wildeman found that the Fischer Assay is a good model of the TOSCO II process and the substantial releases of the Hg into the gaseous phase occurred (as determined by a mass balance). The Paraho study involved

a carefully designed sampling of the liquid and solid materials that is giving a very thorough picture of the temporal behavior of the process. These studies indicate a loss of Zn into the gaseous phase. Of great interest is the apparently great homogeneity in time in the solid materials. The data indicate that the best sampling plan would involve infrequent sampling with a relatively thorough analysis. Because of the considerable analytical problems involved with these materials, Dr. Wildeman has been involved with Pacific Northwest Laboratory and Lawrence Berkeley Laboratory in an extensive interlaboratory comparison. This comparison has shown that there is a good consistency in the analyses of solid samples.

Dr. Wildeman's results on Paraho materials show that the bag house dust contains significantly higher concentrations of Ni, Cu, As, Mo, and Pb than the materials going into the retorted shale pile. On the other hand, raw shale dust (consisting of the crusher fines) does not differ in trace element content from larger raw shale particles.

The Release, Transport, and Fate of Some Potential Pollutants in Oil Shale

(D. Runnells, University of Colorado)

It is well known that many factors play a role in determining the behavior of trace elements. While it is important to determine total concentrations of trace elements in the various effluents, the ultimate fate and effects of these materials depend on the chemical environment present, the chemical form of the elements, and other factors. If we could determine all of the parameters required (such as chemical form) and if we had a sufficient understanding of the behavior of these substances and their effects, we could predict ultimate impact. Unfortunately, there are not methods, the understanding, the time, nor the money to take this approach.

Dr. Runnells and his students are studying the potential for the release of trace elements by the leaching of processed and raw shales. They have performed leaching experiments on many materials including raw shales and shales retorted by several processes (TOSCO II, Paraho and Geokinetics). They have also collected leachates from lysimeters installed for reclamation studies. Their results show that in terms of leaching the primary elements of concern are F, B, and Mo. They have also found very high concentrations of S, existing in several valence states in leachates. Their results show that raw shale releases significant amounts of F and B and in fact, releases somewhat more F than retorted shales. This result has considerable significance with regard to the large amounts of raw shale that will be stored or disposed of on the surface.

They have found that the amounts of trace elements released differ with the process. For example, Paraho shale leachates contain significantly less Mo, B, and F than TOSCO II leachates. The

Geokinetics leachates (an in situ process) are very similar to the Paraho leachates except for containing slightly lower TDS.

Very low concentrations of As and Se have been found in most leachates, although there is some evidence that repeated wetting and drying may cause more Se to be released. But, the concentrations of F, B, and Mo are significant when compared to various water quality recommendations or standards. A result of considerable importance involves the very high concentrations of reduced sulfur species. Upon oxidation of these compounds a considerable drop in pH is observed. This drop in pH could mobilize additional elements (such as Cu and Zn) which are not present in the initially alkaline leachates. Very good comparison has been observed between the field samples obtained from the lysimeters and the laboratory shaker and column data.

Of considerable interest is the observation that, as opposed to TDS and Mo, which are rapidly flushed from retorted shales, F stays constant in the leachate after very long leaching periods (more than 20 pore volumes). Considerable progress has been made by Dr. Runnells and his students in understanding this phenomenon.

Work has begun on the ability of the soils in the oil shale area to sorb trace elements from leachates. These soils have also been leached to determine their ability to release trace elements. These results show that the soil leachates contain significantly lower B and F but about the same TDS as from retorted oil shales. These leachates also contain high concentrations of Ca which may help control the F levels by precipitation as CaF_2 .

The Availability of Trace Elements to Plants

(W. Lindsay, Colorado State University)

While the work of Dr. Runnells addresses the question of potential contamination of ground and surface waters by leachates, it does not address the potential for uptake by plants growing on either raw or processed shale piles. Since reclamation plans involve either covering these materials with soil which is then vegetated or establishing plant life directly on these materials, it is important to establish whether trace elements can be taken up into these plants at concentrations that will either be toxic to the plants (and thus affect the viability of the plant life) or to the animals which graze the plants.

Dr. Lindsay and his students have been conducting greenhouse experiments and studying revegetation sites in order to understand the bioavailability of these materials. They have found that a number of factors influence the uptake of trace elements by plants. These factors include the retorting process used, the depth of soil cover, the aspect, the elevations, the precipitation, and the species of plant. Greatly increased concentrations (compared to controls) of B have been observed in western wheatgrass growing on TOSCO II retorted shales covered by varying amount of soil. These levels are as high as 15-20 times those in control plants. Plants differ

considerably in their susceptibility to B toxicity, but these levels (as high as 190 ppm) may be causing a chronic B toxicity. These increased B levels are not observed with shales retorted by the USBM method. On the other hand, greatly increased concentrations of Mo have been found in fourwing saltbush growing in USBM shales covered with varying depth of soil and in alfalfa growing on Paraho shales. These levels (20-30 ppm) coupled with relatively normal Cu concentrations (5-7 ppm) could lead to Mo toxicity in livestock grazing these plants.

In general, the uptake decreases with increasing soil cover. Arsenic, F, and Se are not observed to be taken up in significant quantities. The work on As and Se provides a very good example of the cost-effectiveness of coupling various projects together, as is this case with this total program. Arsenic and Se analyses present very difficult analytical problems, particularly in plants. At a very early stage in the investigations the work by Runnells indicated that As and Se were present in relatively insoluble forms in raw and retorted shales because of the low concentrations in leachates; this indicated that these elements would probably not be readily available to plants. As a result, we designed an analytical scheme to determine the range of As and Se concentrations in the plant samples in a manner that minimized the number of analyses. Upon verification that the concentrations were not elevated, we terminated further analyses for these elements in plants. As a result, we were able to devote more resources to the investigation of the other elements which were observed to be elevated in some cases.

The Role of Organics in Mobility of Trace Elements

(R. Sievers, University of Colorado)

There are many examples of organic complexation or chelation playing an important role in the mobility and/or toxicity of trace elements. Probably the most famous is that of mercury. Since the organic content of retort waters and leachates can be quite high, there is the potential for such phenomena to play an important role in the transport, fate, and effects of trace elements associated with oil shale materials.

Dr. Sievers and his colleagues have recently begun an extensive study of this subject. They are applying a variety of techniques such as liquid-liquid extraction and GC/MS analysis to determine which organic compounds are present that could play a role and whether some of the trace elements are associated with such compounds.

Their results show that there is a tendency for some elements such as Cd, Se, Cr, and Zn to associate with specific organic fractions. For example, most of the Cd, Se, and Cr in shale oil is associated with the organic fraction containing the majority of nitrogen-containing compounds.

Analytical Chemistry

(R. Meglen, University of Colorado)

The analytical chemistry facility is central to all the work involved in the program. The laboratory has had over nine years of experience with similar programs and during this period has performed more than 70,000 analyses. While some analyses are performed by the individual investigators when this is deemed to be cost-effective, the central laboratory has the dual responsibilities of developing and refining analytical methods and performing most of the analyses. The laboratory specializes in the development and implementation of analytical methods that are inexpensive, fast, and do not require instrumentation that is unavailable to most laboratories (e.g., neutron activation analysis). Thus, the development work has considerable potential for technology transfer to industrial and government laboratories and indeed, methods developed in our laboratory are being used in several other laboratories.

During the past few years we have significantly upgraded the capabilities of the laboratory. A new atomic absorption spectrophotometer was installed which has greatly increased sample flow. In addition, a used Technicon Auto Analyzer was installed and is being used to automate the colorimetric methods (e.g., boron). An extensive automated analytical system has been designed and funds obtained from other sources to acquire a data handling and acquisition system. More recently a new graphite furnace was obtained.

Microbial Investigations

(C. Brierley and J. Brierley, New Mexico Institute of Mining and Technology.

D. Klein, Colorado State University)

It is well known that microorganisms can play an important role in determining the solubility and ultimate fate of trace elements. Indeed, the discovery of the methylation of mercury by bacterial was one of the major events which catapulted heavy metal environmental research into the prominent position it holds today. Other types of chemical alterations by bacteria also exist and these biological mechanisms need to be understood before a long term strategy for dealing with the solid waste and waste water issues can be devised.

For these reasons a new subproject was developed last year which involves three well-known microbiologists who are focusing on two major issues:

- can soil bacteria which exists in the spent shale piles transform toxic elements such as As and Se, which are presently quite immobile, into more soluble or volatile compounds?
- do sulfur oxidizing bacteria play a key role in determining the rate at which the high amounts of reduced species found in leachates and retort waters are oxidized?

A number of experiments are presently being carried out. The data obtained, so far indicates a partial yes to both of the above questions. Namely, the data indicates that bacterial growth in spent shale together with soil and nutrients does increase the solubility of As in the spent shale. Moreover, thiobacilli have been tentatively identified in oil shale material, and laboratory research has demonstrated the ability of oil shale materials to support the growth of such microbes.

The results of the research described above are described in detail in the following sections.

PROGRESS REPORT -- JUNE 1978 - MAY 1980

U.S. Department of Energy

THE OIL SHALE TASK FORCE

Project #EV - 10298

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INTRODUCTION

The Oil Shale Task Force, formerly the DOE/EV Modified in Situ (MIS) Task Force, was formed in June 1978 in response to a letter from Governor Lamm of Colorado to Secretary Schlensinger. This letter (Fig. 1) asked for the assistance of DOE in developing a research program to investigate the environmental and health effects of MIS processes with a particular focus on the operation by Occidental Oil Shale, Inc. (OXY) at the Logan Wash, Colorado site. The first major progress report on this research effort was recently published and addresses work in the area of leaching, characterization, and health effects studies. Since the inception of the Task Force, the scope of responsibilities has been broadened to include other MIS processes (e.g., Rio Blanco Oil Shale Co.) and surface retorting.

Dr. Willard R. Chappell was appointed chairman of the Task Force to provide planning, field coordination, and management assistance for DOE/ASEV sponsored oil shale research. More recently, as part of the RD & D plan, Dr. Chappell has been named coordinator for the Data Base Development Subactivity, with the Task Force serving as the coordinating tool for that subactivity.

PLANNING ACTIVITIES

During the summer of 1978 the Task Force met three times to discuss the research activities that would be required and to develop an initial plan for the research.¹ This plan was reviewed by DOE during two sets of briefings in August 1978.

Since September 1978 the Task Force has met seven times to further develop research plans, strategize implementation of the plans, and report on progress of the research.

- September 1978 in Grand Junction. The Task Force was briefed by DOE/LETC and OXY representatives on the environmental activities relating to the Logan Wash site. On the basis of these briefings, a specific research plan for Logan Wash² (Appendix B) was developed.

- November 1979 in Denver. The Task Force met to update the original research plan and Appendix B. Rio Blanco Oil Shale Co. (RBOSC) representatives attended the meeting and discussed their comments on the basic research plan and RBOSC's future participation.
- February 1979 in Denver. The Task Force met to update Appendix B and to prepare a list of specific sampling instructions for the team of DOE and Task Force members who would visit OXY's Retort 6 site on February 6, 1979. Also, further discussions on oil shale and related research projects were presented.
- April 1979 in Denver. The Task Force meeting was dedicated to discussion of OXY sampling efforts and division of the OXY Retort 3E samples. In addition, updated reports on a variety of oil shale operations were reported (e.g., RBOSC, Geokinetics).
- July 1979 in Denver. The Task Force and other researchers working on Task Force efforts met for the purpose of drafting the first progress report on Task Force research. Three primary areas of research were discussed (Characterization, Leaching, Health Effects) and preliminary reports written.
- October 1979 in Santa Fe. The Task Force met to complete the progress report and to outline future Task Force activities. A RBOSC representative attended the meeting and briefed the Task Force on RBOSC's progress and planning for tract C-a.
- February 1980 in Denver. The Task Force was briefed by representatives from RBOSC on the updated plans for tract C-a, their environmental programs and research the Task Force could perform to assist them. Based on the briefing, an outline for a proposed research plan was developed, and a specific plan is being written.

Implementation will begin when RBOSC ignites Retort 0 in July 1980.

Another Task Force meeting is scheduled for May 1 and 2, 1980 in Laramie to finalize the RBOSC research plans and sampling efforts.

In addition, two public meetings have been scheduled to communicate the planning and research efforts of the Task Force and other DOE sponsored oil shale environmental programs. This is a major effort (co-sponsored by League of Women Voters and Club 20) to encourage public participation in DOE research activities

and has been structured to maximize information transference. The same meeting will be conducted on the west and east slopes of Colorado (Grand Junction and Denver, respectively) to reach the widest audience. A panel discussion has been planned whereby the panelists will address some of the most frequently asked questions about oil shale. The areas to be covered are technologies and their differences, health effects--both worker and public, ground and surface water related problems, air pollution--control systems and the capacity of the region to accept industrial development, reclamation, socio-economic impacts and water availability. In addition, poster sessions will be set up illustrating the research efforts in the areas of industrial hygiene and safety, biological studies and industrial health, reclamation, the varying technologies, characterization, analytical methods, geochemical baseline studies, and intended wildlife studies. The tentative participants in the panel and the poster sessions are listed in Table 1. Ms. Nancy Dick, Lieutenant Governor, State of Colorado, will be the keynote speaker at the Grand Junction meeting.

Over 900 brochures announcing the meeting have been mailed to industry; environmental groups; local, state and federal agencies (including Wyoming and Utah); universities; and interested citizens.

A summary of the meetings will be written and published as a Task Force document, and distributed to all attendees and other interested individuals.

Other activities which have transpired related to planning efforts include:

- The chairman has had several meetings with representatives from RBOSC, Union Oil Shale Co., Geokinetics, state agencies, and environmental groups to discuss Task Force activities.
- The initial planning of a major symposium on oil shale research in the environmental area to (1) realize DOE's commitment to develop a set of review papers, annually, (2) to summarize progress over the year, and (3) set the stage for program planning.
- EPA Oil Shale Tour. On August 7 and 8, 1979, Dr. Chappell participated in the annual EPA tour of oil shale country. This two-day tour involved visits to tracts C-a and C-b, Logan Wash, the Equity site, and Anvil Points.
- On November 20, 1979 a subgroup of the Task Force met to discuss the disposition of the spent shale core samples obtained from Retort 3E.

TABLE 1

Tentative Panelists and Poster Session Participants
April 10 and 12, 1980 Public Meetings

Panel

Art Hartstein (Technologies)
U.S. Department of Energy

L. M. Holland (Health Effects)
Los Alamos National Laboratory

Carol Nieuwenhuis (Ground Water)
University of Colorado

Ray Wildung (Surface Water)
Battelle-Pacific Northwest Laboratories

Dave Sheesley (Air)
Laramie Energy Technology Center

Sumner Barr (Air)
Los Alamos National Laboratory

Ed Redente (Reclamation)
Colorado State University

Eric Stenehjem (Socio-economic)
Denver Research Institute

Bill McDonald (Water Availability)
Colorado Department of Natural Resources

Poster Sessions

Harold Ettinger (Industrial Hygiene and Occupational Medicine)
Marvin Tillery
Los Alamos National Laboratory

L. M. Holland (Biology and Toxicology)
Los Alamos National Laboratory

Wayne Cook (Reclamation)
Colorado State University

Bill Little (Technologies)
Laramie Energy Technology Center

Jon Fruchter (Characterization)
Battelle-Pacific Northwest Laboratories

TABLE 1
(continued)

Robert Meglen (Analytical Methods)
University of Colorado

Ron Klusman (Geochemical Baselines)
Colorado School of Mines

Gary White (Wildlife)
Tom Hakonson
Los Alamos National Laboratory

FIELD COORDINATION

In September 1979 two cores were obtained from Retort 3E at Logan Wash in a joint Task Force/OXY effort.

In December 1979 a staff scientist, Ms Carol Nieuwenhuis was hired to assist the Chairman in similar field coordination efforts. Since that time the efforts have resulted in the lithologic and structural logging of a raw shale core from Occidental Oil Shale, Inc.'s (OXY) Logan Wash site. The core was obtained by OXY for mine stability and Fischer Assay studies. The Task Force was represented by Carol Nieuwenhuis during the core loggings to assure that it was obtained and packaged in a manner which would suit future research needs. The core spanned the interval encompassing Retorts 7 and 8 and will serve as a baseline material for purposes of comparison with retorted shale upon completion of the burn. Negotiations in early March 1979 will determine core distribution decisions. It is the desire of the Laramie Energy Technology Center and the Task Force to obtain two equal vertical splits of the core. The portion assigned to the Task Force will be archived by Dr. Jonathan Fruchter of Battelle-Pacific Northwest Laboratories and thence apportioned to researchers interested in performing solid characterization and leaching studies. Dr. Paul Wagner of Los Alamos Scientific Laboratory, Dr. John Zachara of Battelle-Pacific Northwest Laboratories and Dr. Fruchter have expressed interest in obtaining portions of the core.

Further field coordination efforts will be undertaken at the Rio Blanco Oil Shale Co.'s Modular Development site at tract C-a. A small retort, Retort 0, will be burned in July 1980 and the Task Force will undertake a comprehensive sampling program of oils, waters, and emissions. Ms. Nieuwenhuis will serve as technical liaison during the sampling effort which is being coordinated by Dr. Jon Fruchter and Rosielea Gash of RBOSC.

Data Management

The feasibility of a "decision support system" of data management is being investigated. Members of the Task Force at each of the national laboratories have been contacted regarding their data management needs. A first step would be to trace all samples with uniform coding procedures through storage in a centralized computer, preferably at the University of Colorado, Denver. The system presently under evaluation is that devised by Dr. Kenneth Cowser at Oak Ridge National Laboratory for environmental data. Sample location, type, person responsible, manpower and financial requirements, dates of sampling, and dates of analysis would comprise the initial output. Data would be collated into the system at some later date. The system should be on line prior to the RBOSC sampling effort in July 1980. In the meantime, efforts will concentrate on coding previously obtained data to be compatible with the proposed system.

MANAGEMENT ASSISTANCE

Recently, the Chairman of the Task Force was appointed a member of DOE's management team for DOE's environmental activity in oil shale research as manager of the data base development 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:

- One of the most significant activities of this type was the creation of a liaison group to facilitate communication with various interest groups. This twelve-person group contains three representatives from the oil shale industry, two from environmental groups, one from a union, a member of the Colorado Legislature, and representative from USGS, EPA and NIOSH. The group has met twice to be briefed on the program of the Task Force.
- The Chairman has met frequently with individuals in the Colorado Department of Health and the Colorado Department of Natural Resources to keep them informed of the Task Force's progress.
- Several briefings have been held:
 - On December 8, 1979 Ralph Franklin, Willard Chappell and Robert Siek (then the Colorado Department of Natural Resources representative on the Task Force) briefed Ruth Clusen, Assistant Secretary of the Environment on (1) oil shale technological processes, (2) activities of various federal agencies, (3) the major environmental issues related to oil shale development, (4) activities of the Task Force, and (5) some of the concerns of the State of Colorado.
 - On July 25, 1979 Dr. Chappell briefed the Department of Interior's Oil Shale Environmental Advisory Panel on the background and activities of the Task Force.
 - January 22, 1980 Dr. Chappell briefed Harris Sherman, Director of the Colorado Department of Natural Resources, on the Task Force.
- The Chairman has presented papers on the work of the Task Force.
 - 12th Annual Oil Shale Symposium in Golden, Colorado in April 1979. This paper is published in the Proceedings.

--In September 1979 Dr. Chappell served on a panel on oil shale sponsored by the Colorado League of Women Voters Natural Resources Workshop.

- On August 20, 1979 Lydna Brothers (Deputy Assistant Secretary), Carol Jolly (Special Assistant to the Assistant Secretary for Environment), and Helen McCammom (Director of the Division of Ecological Research) attended a meeting with the liaison group and met with the Governor's Environmental Assistant, several representatives of environmental groups, and a representative of EPA to discuss the activities of the Task Force. The following day the Chairman took this group, and Ralph Franklin and Andrew Decora of DOE on a tour of several oil shale facilities on the western slope.
- Oil Shale Management Meetings. Dr. Chappell has participated in two meetings of the Oil Shale Management Team. These were held in Denver on November 15 and 16, 1979 and on February 27 and 28, 1980 in Las Vegas.
- RD & D Planning. Dr. Chappell and other members of the Task Force participated in a two day planning effort in Washington, D.C. on December 10 and 11, 1979.
- On August 28 and 29, 1979 the Chairman attended an EPA sponsored meeting to discuss the draft of the Pollution Control Guidance for oil shale development.
- In January 1980 Dr. Chappell visited the Scottish oil shale area near Edinburgh. This tour revealed an opportunity to obtain valuable information from the Scottish experience.
- The Task Force has published three newsletters which were distributed to over 100 individuals informing them of our activities.

SUMMARY

Since the formation of The Oil Shale Task Force the chairman has been involved in a variety of activities assisting the Department of Energy in the areas of planning, field coordination, and management assistance for DOE/EV sponsored oil shale programs. Recently, Dr. Chappell was appointed a member of DOE's management team as coordinator of the data base development subactivity under the major environmental activity.

Two professional full-time staff members have been added to the staff--Ms. Kathy Petersen, Assistant to the Chairman and Ms. Carol Nieuwenhuis, Staff Scientist--and the level of activities in all the above-named areas has increased substantially as the Task Force's involvement in environmentally-related oil shale research develops.

REFERENCES

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PROGRESS REPORT 1979-1980

The Analytical Laboratory

Robert R. Meglen

The Analytical Laboratory provides analytical service to the project investigators. This service includes development of accurate analytical procedures, routine analysis of samples, and data interpretation techniques. Significant progress achieved between February 1979 and February 1980 is summarized below. Brief descriptions of each item is included in the following section.

1. Over seven thousand chemical analyses have been performed during the past 12 months.
2. Significant improvement in the analysis of arsenic and selenium in aqueous matrices has been achieved with the adaptation of graphite furnace atomic absorption.
3. The method developed for fluoride analysis has been improved with respect to speed and reproducibility.
4. Automation of atomic absorption and colorimetric analyses begun in April of 1979 has been completed. The automation has doubled the rate at which analyses can be done.
5. A significant increase in the number of multi elemental analyses requested has required implementation of sequential multi element procedures.

LAB OUTPUT

During the past twelve months over seven thousand analyses have been performed. The percentages of the laboratory output by element are listed below.

Fluoride	30%	
Boron	15	
Arsenic, Selenium	15	
Magnesium, Calcium	15	
Other	25	
	<hr/>	
TOTAL	100%	(7318 analyses)

The principal elements of interest in the past have been Mo, As, Se, B and F. In the past year we have experienced an increased number of requests for analyses other than these target elements. The reason for the increased interest in these elements is that as the other principal investigators have refined their experiments it has become clear that adequate understanding of factors controlling solubility/availability of the target elements, requires information regarding other species which may be present in solution. With automated analytical techniques it has been possible to supply the additional analyses requested without increasing technician staff. In the work planned for the coming year the principal investigators have proposed work which would require an additional doubling of analytical rate. This will be accomplished through the use of automated methods already mentioned and new instrumentation obtained this past month. Methods of analysis using inductively coupled plasma emission spectrometry (ICP) are currently being validated and should be available for routine work soon.

ANALYSES FOR ARSENIC AND SELENIUM

We have improved our ability to provide accurate analyses of arsenic and selenium at the sub mg/mL level in aqueous solution. Prior to this development we were limited to using the time consuming and tedious hydride generation - atomic absorption technique. The improved technique utilized automated sampling and our newly purchased Perkin-Elmer Model 500 graphite furnace. This system represents a significant improvement in reproducibility. Since reproducibility at low concentrations determines the detection limit we have obtained a factor of five improvement in detection limit for these elements and sensitivity has been doubled. The enhanced sensitivity and reproducibility has been necessary to supply valid analyses to the professors Klein and Sievers, whose work depends upon accurate analyses of these elements at low levels. The details of the procedure are described in an addendum to this section.

FLUORIDE ANALYSIS

In previous reports we have described improved techniques for the separation and detection of fluoride in complex matrices. The colorimetric detection method for fluoride is much more rapid than the atomic absorption technique described in earlier reports. Because the colorimetric method and ion-selective electrode technique are extremely susceptible to chemical interferences the rapid method of gaseous diffusion separation described in previous reports has been adapted to use with either colorimetric or ion selective electrode detection of fluoride. The details of this technique are also included in the addendum to this section.

QUALITY ASSURANCE

A total quality assurance program for chemical analysis requires two separate stages. First the validity of the chosen analytical technique must be established. Secondly, a continuous surveillance of the sampling, treatment, preparation and analysis must be maintained.

While it is impossible to determine absolute accuracy it is possible to obtain an estimate by using several techniques. Table I shows the principal techniques available for estimation of accuracy and precision of analytical results. All of these results have been used in this laboratory to establish the validity of the chosen analytical procedures. Because there is no certified reference standard for oil shale materials we have relied upon the analysis by independent methods such as x-ray fluorescence, neutron activation, atomic absorption, etc. and collaborative testing with other laboratories.

The persistent problem of quality control during routine analyses requires continuous monitoring of analyses to determine the onset of systematic errors and the sudden appearance of large random errors which affect precision. Research being performed in this project has spanned several years. It is essential that results obtained during early phases of the project be comparable to those obtained at later stages. We have therefore employed the quality control procedure described in detail below.

There are two types of errors associated with any chemical analysis; systematic (determinate) and random (indeterminate). Inaccurate results which occur due to systematic errors are always higher or lower than the "true" value. That is, they tend to have the same algebraic sign. These errors, are the result of erroneous calibration, instrumental drift, loss of analyte or contamination during sample treatment, failure to account for blank or background effects, etc. Through adequate testing procedures it is possible to determine the magnitude of this type of error (hence the known determinate error.) The validation phase of any analytical methods development is designed to eliminate this source of error. Occasionally systematic errors suddenly appear after the methods have been in use for some time. An effective quality control scheme should permit the rapid identification of the appearance of these systematic errors.

Random or indeterminate errors have a frequency of occurrence which is symmetrical. Small positive or negative errors have the highest probability of occurrence while very large positive or negative deviations are less probable. These errors are inherent in any measurement technique which is based upon a continuous interval scale such as reading peak heights, analog scales, masses, etc. While careful control of experimental variables can minimize the magnitude of these errors; they are always present. These errors establish the precision of the measurements and the ability to detect sudden changes in the magnitude of these errors is essential to a quality control scheme.

The ability to distinguish between random and systematic error in measurement is important for the diagnosis of problems within the analytical procedure. The technique described in this discussion is based upon the method described by W. J. Youden. The Youden treatment is designed for the separation and identification of systematic and random errors which occur among laboratories participating in interlaboratory tests. The present modification is

TABLE I

Techniques for Estimation
of Accuracy and Precision

	<u>Method Used to Estimate Accuracy*</u>	<u>Method Used to Estimate Precision**</u>
Primary:	1. Analysis of certified stds.	Replicates
	2. Independent methods	Replicates
	3. Collaborative tests (other labs)	Replicates
Secondary:	1. Secondary (in house) stds.	Replicates
	2. Spike Recovery Tests (inferential only)	

* Accuracy: Measure of closeness to "true" result or agreed upon value.

** Precision: Measure of reproducibility of a given result.

designed for use within a single laboratory. The results obtained from day-to-day are treated like the analyses performed in separate laboratories. Two different plotting techniques are used to monitor daily performance. A description of these graphical methods will be provided after a brief mathematical treatment of the technique has been presented.

Assume that a single sample is split into two portions labeled A and B. Analysis should yield the "true" value X plus any systematic error and random error.

$$A = X + S + R$$

$$B = X + S + R^1$$

Where S is the systematic error (same algebraic sign and magnitude for each split), and R and R¹ are the random errors (Positive and negative signs are equally probable. The magnitude of these errors follow a normal distribution function). The sum T of the results obtained for both splits will yield a result which is double the systematic error of one analysis.

$$T = A + B = 2X + 2S + R + R^1$$

Since the random errors come from a symmetrical frequency distribution with both algebraic signs these two terms will, on average, cancel each other after many analyses.

When the difference D between D between the results A and B is computed the systematic errors which have the same magnitude and sign will cancel leaving the sum of the two random error components.

$$D = A - B = R - R^1$$

By plotting the A and B sums T and differences D in time ordered sequence the variation of these two sources of error can be monitored from analytical run to analytical run.

The procedure used for day-to-day monitoring utilizes a single real sample (usually a large composite of previously analyzed samples) is split into two aliquots labeled A and B. These samples are carried through the analytical procedure together with the unknown samples. The results of the sum T, and difference, D, are plotted in time ordered sequence.

The results of such a plot are shown in Figure I which covers a five month span consisting of 26 analytical runs. The long term mean with plus and minus one standard deviation are designated on the T plot. Similarly the mean of all differences should be zero as shown and the plus/minus standard deviation in the mean is also designated. Large deviations of T from the mean with small or no deviation in D indicates systematic errors dominate, (eg results of 2/6/79 and 4/19/79). Conversely, large deviations in D with small deviation in T such as on 5/14/79 and 6/1/79 are indications that reproducibility is poor. Obvious difficulties showing both poor precision and accuracy were observed on 5/3/79 and 6/6/79.

TIME ORDERED ANALYTICAL RUNS

Figure 1. Quality control charts for sums (T) and differences (D) vs. time.

These plots are used to establish quality control criteria. When either plot shows that a given analytical run produces results outside of the control limit the method is reviewed for sources of error, the analyses for that day are discarded and new analyses are performed. The appearance of various patterns in these plots can be used to isolate and identify potential sources of difficulty in the analytical procedure. Eight basic patterns have been identified, and their characteristics and possible causes have been catalogued for quick diagnosis of problems.

The second type of graphical representation which has been used to separate systematic and random errors is the quadrant plot. The result of analysis on split A is plotted against the result obtained on split B. If no systematic error were present and only random errors prevailed there would be four possible outcomes:

<u>A</u>	<u>B</u>	
+	+	Both higher than true
-	-	Both lower than true
-	+	One higher and one
+	-	lower than true.

Each outcome is equally probable. The plot of these results would show a circular distribution of points. By drawing horizontal and vertical axes to designate the mean values of A and B four quadrants are defined.

Similarly if NO random errors were present and only systematic high (++) and systematic low (--) errors existed, a linear distribution of points would appear spanning quadrants I and III at 45° from the horizontal. In real situations one obtains distributions somewhere between these two extremes. By connecting the points with straight line segments in time ordered sequence one can monitor the day-to-day performance of the analytical method. Lines with negative slopes

indicate changes in systematic error between analytical runs. The lengths of the connecting line segments are proportioned to the magnitude of the changes. A control limit circle with radius equal to one or two standard deviations may be used for rejection criteria. Figure II shows the quadrant plot of the same data shown in Figure I.

Both of the graphical methods described above provide the same information. They provide alternate ways of recognizing the occurrence of changing dominance of systematic and random errors in day-to-day analytical performance. In this laboratory both techniques are used daily to assess performance for possible data rejection. In addition the long term occurrence of patterns within the time ordered T and D plots is used to help in the diagnosis of analytical errors. The technique is easily implemented with either mineral preparation of quality control charts or through daily computer generated plots such as those included here. The primary concerns with any quality control scheme are rapidity with which problems are detected and the efficiency of its implementation. This scheme has advantages in both regards. It is particularly efficient since it requires a small number of additional analyses (two per analytical run). This small addition to the analytical sample load provides a rigorous statistical basis for establishing rejection criteria.

Figure 2. Quadrant plot used for monitoring systematic and random errors. (Points connected in time ordered sequence.)

Analysis of As and Se by
Graphite Furnace A.A.

Reagent: 1% Ni prepared by dissolving
99.99% pure Ni with reagent
grade Nitric acid. Final solution
is 1% Ni in 10% v HNO₃

Graphite Furnace: Perkin-Elmer Model 500

	<u>Step Number</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
TEMP (°C)	110	1000	2700	30
RAMP (sec)	15	15	0*	1
HOLD (sec)	20	15	8	30
Recorder (sec)	-	-	-5	-
Read	-	-	-2	-
Baseline	-	-	-5	-
AR flow (mL/min)	300	300	30	300

20 ml injection consisting of 50:50
Sample plus 1% Ni Reagent

Atomic Absorption Spectrophotometer: Perkin-Elmer Model 5000

	<u>Se</u>	<u>As</u>
Wavelength	196.0	193.7
Lamp	EDL 6 watts	EDL 8 watts
AA-BG	Background D ₂	Background D ₂
Slit (nm)	0.7 H	0.7 H
Mode	peak height	peak height
Absorb Scale	1.0	1.0

Standards:

Low Range: 0, 10, 30, 50 mg/L
High Range: 0, 100, 200, 300 mg/L

Typical absorbance: 10 mg/L - 0.2 Abs.

RAPID ANALYSIS OF FLUORIDE BY GAS DIFFUSION SEPARATION with COLORIMETRIC ANALYSIS

Reagents:

- 1) Diffusion Reactant: 6 M HCl saturated with hexamethyl disiloxane.
- 2) Trapping Solution : 0.1 M Na_2CO_3

The analysis of F is accomplished by the isolation of the ion by gas diffusion, the formation of alizarin-fluoride and the subsequent detection of the species by molecular absorption.

Diffusion Separation

Ten mL of standard or acidified sample are pipetted into a plastic specimen cup. A plastic microbeaker containing 1.0 mL of 0.1 M Na_2CO_3 is floated on the sample solution. A 0.5 mL of 6 M HCl saturated with hexamethyldisiloxane is carefully added to the sample avoiding contact with the carbonate solution in the microbeaker. The specimen cup is immediately capped tightly and the diffusion process is allowed to proceed for approximately 20 hours. After that period of time the microbeaker, into which the F has diffused, is removed and the contents are diluted to 10 mL.

Colorimetric Detection

Reagent: Alizarin Complexone:

Dissolve 0.0479 g alizarin complexone in 0.1 mL conc. aqueous NH and 1.0 mL 20% w/v ammonium acetate and a few mL water. Filter through Whatman #1 into 200 mL vol. flask containing 8.2 g anhydrous sodium acetate, 6.0 mL glacial acetic acid, and sufficient water to dissolve the solids. Wash the filter paper with a small amount of water and slowly add 100 mL acetone. Dissolve 0.0408 g La_2O_3 in 2.5 mL 2M HCl. Warm gently and add it to the acetone buffer mixture. Dilute to 200 mL. Allow the stand for 30 minutes before using. The reagent has a shelf life of about one month.

Procedure:

Use plastic ware throughout preparation.

1. Pipet 2.0 mL sample which has been previously separated from interferences by gaseous diffusion.
2. Add 1.0 mL alizarin complexone-buffer solution.
3. Dilute with 1.0 mL deionized water.
4. Swirl and allow to stand for 30 minutes.
5. Read the absorbance of stds. and unknowns at 622 nm.

Aqueous NaF standards 2.0 mL in the range 0-3.0 mg/mL are used for preparing the calibration curve. The colored fluoride complex is stable for up to 3 hours.

Progress Report: 1979 -1980

Microbial Affect on the Quality of Water in Oil Shale Retorting

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INTRODUCTION

The Department of Energy has recognized the magnitude of the water problem associated with the in situ leaching of oil shale (Farrier et al., 1978). 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 are generally very alkaline and contain high concentrations of dissolved organic and inorganic constituents. One of the major inorganic species is thiosulfate (1).

A potential problem that may result as a consequence of the presence of thiosulfate in water is a microbially-catalyzed oxidation of the thiosulfate to sulfate, sulfur or polythionates. Subsequently, this could further degrade water quality through leaching of toxic metals from mineral substrates.

A number of microorganisms can oxidize thiosulfate. These microbes include species of the genus Thiobacillus which are widely distributed in nature and are capable of thiosulfate-oxidation in various physico-chemical conditions. Some characteristics of this genus are presented in Table 1 (2). The reactions catalyzed by these microorganisms, which are of potential concern for systems containing thiosulfate, include the following (3):

The species T. thioparus, T. denitrificans and T. novellus are not particularly acid tolerant. However, they could oxidize the thiosulfate producing enough sulfuric acid to decrease the pH to the point where acidophilic microbes, such as T. thiooxidans and T. ferrooxidans, could succeed them and further oxidize sulfur compounds producing more sulfuric acid. Of greater concern are the species of T. neapolitanus, T. intermedius and T. perometabolis which are themselves capable of sulfur compound oxidation over a wide range of pH. The latter two of this group grow best if organic matter is present with thiosulfate, and T. perometabolis has a requirement for organic matter (e.g., yeast extract, fructose, arabinose, ribose, or xylose). All of these microbes, with the exception of T. denitrificans, require oxygen for growth. Only T. denitrificans can utilize nitrate as an alternate terminal electron acceptor and grow under anaerobic conditions. Anaerobic growth usually does not result in a pH decline, since thiosulfate is generally oxidized only to tetrathionate.

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

Species	pH range for growth	Products of thiosulfate oxidation	Metabolism
<u>I. thioparus</u>	4.5 - 7.8	$\text{SO}_4^{=}$, S, polythionates	autotrophic
<u>I. denitrificans</u>	6.0 - 8.0	polythionates	autotrophic
<u>I. neapolitanus</u>	3.0 - 8.0	$\text{SO}_4^{=}$, S, polythionates	autotrophic
<u>I. thiooxidans</u>	1.0 - 3.5	$\text{SO}_4^{=}$	autotrophic
<u>I. ferrooxidans</u>	2.5 - 5.8	$\text{SO}_4^{=}$	autotrophic
<u>I. novellus</u>	5.0 - 9.2	$\text{SO}_4^{=}$	facultative autotrophic
<u>I. intermedius</u>	1.9 - 7.0	$\text{SO}_4^{=}$	mixotrophic
<u>I. perometabolis</u>	2.8 - 6.8	$\text{SO}_4^{=}$	obligate mixotrophic

Sulfur and polythionates are also oxidized to sulfate by heterotrophic bacteria (microbes requiring reduced organic compounds for synthesis of cell structure and oxidation for energy) found in the soil environment. Two heterotrophic microbes, believed to be Micrococcus, have been isolated from soil: one oxidized thiosulfate, the second oxidized sulfur, each producing "significant" amounts of sulfate (4). Optimum oxidation occurred when the soil was supplemented with glucose at a soil pH range between 5.6 and 9.6 and at 25°C to 35°C. These authors suggested that nonacidophilic microorganisms may be important in the oxidation of sulfur compounds in neutral to alkaline soils, and they might be the primary oxidizers of sulfur until the pH is decreased and secondary oxidation by thiobacilli occurs. It has been suggested that heterotrophic microbes may play the dominant role in the oxidation of sulfur compounds in soils (5). Other heterotrophic microbes, Pseudomonas aeruginosa, Pseudomonas fluorescens and Archromobacter stutzeri oxidize thiosulfate to tetrathionate (6). The thiosulfate-oxidation has no effect on the growth rate or cell yield of the microbes. Sulfur compound oxidation by heterotrophic bacteria has not yet been shown to have any physiological role, but it might have considerable effect on the sulfur cycle in nature (7).

The Department of Energy has recognized the potential for microbial alteration of components in the aqueous effluents from in situ oil shale processing, and have identified a microbe as the agent responsible for chemical instability in stored retort water samples (1; Phillips, personal communication). Samples of oil shale retort waters containing high concentrations of thiosulfate, stored in the Geological Sciences laboratory at the University of Colorado, were observed over a period of one year to decrease in thiosulfate concentration and lower in pH from 11 to 3. Enrichment culturing for microorganisms using S_2O_3 as the sole energy source were positive in a sample which had experienced a decrease, indicating the presence of thiosulfate-oxidizing, chemolithotrophic bacteria.

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 (1). Although oxygen may not be abundant in the actual retort area, contact of the leachate waters with the atmosphere would create an ideal environment for development of the heterotrophic and chemolithotrophic microbes. T. denitrificans could be active within the retort zone if nitrate was present. Russian scientists have evaluated stratal waters associated with oil fields for T. thioparus and have found these organisms in waters of open deposits and in wells flooded for secondary oil recovery. The organism was not found in closed deposits (8). The presence of tetrathionate and sulfate in aqueous effluents from retort areas (1) may signify the activity of microbes in in situ leaching areas.

The production of sulfuric acid by microbial oxidation of reduced sulfur compounds could result in increased solubilization of the elements associated with oil shale (9), resulting in a further degradation of water quality. There is considerable volume of data available to support the role of bacteria in the mobilization of inorganic elements (10).

The report of the microbiological portion of the study is for research conducted from August through December, 1979. This portion of the project was initiated during that period.

OBJECTIVES

Listed below are the objectives of the microbiological research phase. These objectives will provide information necessary for evaluation of a system's potential for generation of acid pollution and mobilization of toxic elements by biological processes.

- The potential for acid production can be determined by demonstration of the presence of sulfur- and polysulfide-oxidizing bacteria associated with the oil shale project system. Various locations will be sampled in order to determine if sulfur- and thiosulfate-oxidation bacteria are present, their distribution throughout the system, and the relative abundance of autotrophic and heterotrophic sulfur-oxidizing bacteria. Locations to be considered shall include: (1) the oil shale leachate which has a high concentration of thiosulfate, (2) the shales, (3) ground water of the area, and (4) "downstream" samples from the effluent discharge point.

- A systematic laboratory study will be conducted in order to determine the physico-chemical conditions which affect microbial oxidation of sulfur compounds associated with the oil shale project environment. From this study, the kinetics of sulfur-compound oxidation in laboratory-simulated field conditions can be defined, and the characteristics and succession of microbes leading to an acidified environment will be followed. This information will establish the conditions favoring an acid pollution problem.

METHODS

Thirty samples, including oil shale, retorted oil shale, column leached shale, leachates from laboratory columns, and soil from the Piceance Basin were provided by Mr. Kenneth Stollenwerk of the University of Colorado. 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 (11) for thiosulfate-oxidizing bacteria consisted of (g l⁻¹): Na₂HPO₄, 1.2; KH₂PO₄, 1.8; MgSO₄·7H₂O, 0.1; (NH₄)₂SO₄, 0.1; CaCl₂, 0.03; FeCl₃, 0.02 g; MnSO₄, 0.02; and Na₂S₂O₃, 10.0, for aerobic bacteria and the following were added for culture of anaerobic bacteria (g l⁻¹): NaHCO₃, 0.5; and KNO₃, 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* (5), Na₂S₂O₃·7H₂O, 10.0; K₂HPO₄, 2.0; KH₂PO₄, 2.0; MgSO₄, 0.8; NH₄SO₄, 0.4; and 5.0 ml of trace metals solution; for *T. intermedius* (11), Na₂S₂O₃·5H₂O, 10.0; NH₄Cl, 1.0; MgSO₄, 0.5; K₂HPO₄, 0.6; KH₂PO₄, 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 (11): A, Na₂S₂O₃·5H₂O, 5.0g; NH₄Cl, 1.0g; KNO₃, 2.0g; and 250 ml distilled water; B, KH₂PO₄, 2.0g; and 250 ml distilled water; C, NaHCO₃, 2.0g; and 250 ml distilled water; D, MgSO₄·7H₂O, 0.8g; 2.0 ml of trace metals solution, and 250 ml distilled water. The four solutions were combined aseptically following sterilization. The pH of all media was adjusted to 6.9 to 7.0.

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

Thiosulfate-oxidation was followed by determination of the thiosulfate remaining in the cultures compared with uninoculated controls after incubation. An iodometric titration was used (12).

RESULTS AND CONCLUSIONS

A brief description of the samples used to determine if thiosulfate-oxidizing bacteria are present in oil shales, leachates, and soils is presented in Table 2. Only the numerical designation for each sample will be used in following tables presenting results of microbiological analyses. Although the number of samples used was limited, a diverse representation of various conditions in which thiosulfate-oxidizing microbes may be found was analyzed in this series.

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 in the presence of nitrate, the organism will grow aerobically if oxygen is present. The oxidation of thiosulfate in anaerobic 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 soil 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 preliminary results indicate that thiosulfate-containing waters exposed to aerobic conditions have potential for microbial thiosulfate-oxidation and acid production.

Selected shale, leachate and soil samples placed in enrichment culture were inoculated with cultures of T. denitrificans, (incubated anaerobically),

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

Sample Designation	Sample	Description
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:	Solum 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

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
80	8.7	23.3	7.2	25.2

¹ incubated for 38 days² incubated for 55 days

T. neapolitanus and T. intermedius (incubated aerobically). The samples were inoculated in order to determine if some inherent quality prevented growth of particular 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). The results are presented in Table 4. The T. denitrificans did grow in the presence of samples 6, 10, 15, 21, 23 and 28 which previously had negative results (Table 3). No microbial growth was observed with samples 16, 19, 22, 25 and 26--Paraho and Rio Blanco column leached shale and leachate. This suggests that some substance, inhibitory to the test microbes, may be present in these samples. Neither the aerobic T. neapolitanus nor the T. intermedius grew in samples 10 and 17--Oxidental core samples and Paraho column leached shale. These microbes did not grow in samples 15 (Paraho retorted shale), 21 and 23 (leachates from Paraho column leached shale). These samples were previously found to have aerobic microbial thiosulfate-oxidizing bacteria, apparently not due to T. neapolitanus or T. intermedius.

Media which favor the growth of particular species of thiobacilli, but do not necessarily preclude the development of others, were inoculated with transfers from the original enrichment cultures. This was done in order to obtain preliminary information regarding the types of thiobacilli which might be present in the samples (Table 5). The aerobic transfers were incubated for 54 days; the anaerobic cultures were incubated for 68 days. Evidence of growth consisted of appearance of microbial cells in the media and decrease in pH. Most aerobic cultures 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 2) had suggested that T. thioparus is a likely microorganism to be present. The anaerobic cultures indicated presence of T. denitrificans. Transfers were made from these cultures to solidified media to observe colonial characteristics of the microbes. Diverse colony types were obtained from each sample indicating a heterogenous microbial flora. No colonies characteristic of thiobacilli have been observed at this time. However, work is continuing to define what types of microbes are present which oxidize the thiosulfate.

Since several types of microbes were observed, work is in progress to establish if heterotrophic microbes might be responsible for thiosulfate oxidation.

Although specific thiosulfate-oxidizing microbes have not yet been identified, and it is not absolutely certain of the source of the thiosulfate-oxidizing bacteria, it is clearly evident that potential exists for microbial thiosulfate oxidation and the concomittant side reactions of pH decline and possible pollutant solubilization. Although preliminary, these results do indicate that treatment of process waters for thiosulfate removal may be necessary to prevent microbially-mediated acid production.

Table 4. Growth or acid production by thiosulfate-oxidizing bacteria inoculated into media containing samples

Sample	Microorganisms		
	<u>T. denitrificans</u>	<u>T. neapolitanus</u>	<u>T. intermedius</u>
6	+	-	+
8	+	+	+
10	+	-	-
15	+	-	-
16	-	ND ²	ND
17	± ¹	-	-
19	-	ND	ND
21	+	-	-
22	-	ND	ND
23	+	-	-
25	-	ND	ND
26	-	ND	ND
27	-	ND	ND
28	+	-	+

¹ ± : inconclusive results

² ND: not determined

Table 5. Growth of thiosulfate-oxidizing microbes on transfer from presumptive enrichment cultures to selective enrichment cultures

Sample	Media		
	<u>T. intermedius</u> ¹	<u>T. thioparus</u> ¹ <u>T. neapolitanus</u>	<u>T. denitrificans</u> ²
2	+	+	+
3			+
4	+	+	+
5	+	+	
7	+		
8		+	+
11		+	
12		+	+
13	+	+	+
14		+	+
18	+		
19	+	+	
20		+	
21	+	+	
23		+	
24		+	+
25	+	+	+
26		+	
27		+	

1 aerobic incubation

2 anaerobic incubation

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PROGRESS REPORT 1979-1980

Nutrient Effects on Microbial Mobilization of Arsenic
and Selenium from Retorted Oil Shale

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INTRODUCTION

Microorganisms are known to carry out important functions in the global cycles for arsenic and selenium (1,6,9,10,14,16,17). Both of these metals are common constituents in soils, plant materials and higher organisms (5), and arsenic 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 and selenium which are found in this material, with values in the range of 60 and 14.6 $\mu\text{g/gm}$, respectively, having been reported (12). During the retorting process, the major portion of the arsenic and selenium found in shales appears to remain in the residual solid materials, and only minor amounts will be released to the retort waters (12), making disposal and reclamation of the retorted shale of particular interest for managing the possible release of these metals to the environment.

In developing strategies for the revegetation and reclamation of areas where retorted oil shale materials may be stored on the soil surface, available information suggests that revegetation will be more effective when a surface soil layer is used, which will allow more efficient establishment of plant communities. Studies which have been completed to date in the Piceance Basin, where surface soil at varying depths have been placed over retorted shale, suggest that microbiological activities in surface soils will be sensitive to the presence of underlying retorted shales (13). Generally, soils located directly over oil shale had lower microbiological activities than controls or soils placed over capillary barriers. With plant growth into the surface soil-shale interface, organic matter may be released as a result of plant growth, which can result in a marked stimulation of 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 and selenium.

Another source of organic substrates which can influence possible mobilization and solubilization of arsenic and selenium in retorted oil shales may involve 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 the retorted shale materials.

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 these metalloids. Possible effects of microorganisms on the solubilization, oxidation, reduction or alkylation of arsenic and selenium have been documented (1,2,6,10,14,16,17). 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 (2) showed that microorganisms in water-logged soils produced gaseous arsenial products from arsenate, arsenite, and mono- and di-methyl arsenate. This was only detectable when urea and glucose were added to soil slurries.

The present studies were carried out to provide initial information on possible effects of microbial growth in the presence of added nutrients on supernatant arsenic and selenium levels after microbial growth on retorted shale-soil mixtures.

OBJECTIVES

This study was carried out to meet the following objectives:

1. To determine the effects of microbial growth on retorted oil shale and soil-shale mixtures with added glucose plus protein or glucose and mineral nitrogen on the levels of arsenic and selenium in supernatants.
2. To determine if microbial growth which might lead to increased availability of arsenic, selenium or mercury from retorted shale could lead to the development of increased metal resistance in microbial populations.

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.

EXPERIMENTAL MIXTURE PREPARATION

In all experiments 250 ml Erlenmyer Flasks were used, and 5.0 g of retorted oil shale, or 5.0 g of oil shale with either 100 mg or 5 g of soil were added to the flasks. To each flask, 130 ml of a sterile modified Bushnell-Haas medium was added, modified to eliminate nitrogen or iron additions. This medium consisted of: 0.2 g MgSO_4 , 0.02 g CaCl_2 , 1.0 g KH_2PO_4 , and 1000 ml of deionized water.

For the flasks where a complex proteinaceous substrate was added, Difco peptone was made up in a 100x concentrated solution, sterilized, and added to give a final concentration of 0.2% w/v peptone. Glucose was also added to give a final concentration of 0.1 % w/v..

For the carbon, nitrogen or carbon plus nitrogen experiments, soil and shale samples were mixed in the following manner: 5.0 g shale; 5.0 g shale + 5.0 g soil, or 5.0 g soil + 100 mg 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 NH_4NO_3 were prepared and filter sterilized through sterile Morton glass 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 glu, 0.1 w/v glu, 0.1 w/v N, and 0.8 w/v glu + 0.1 w/v N. A sterile control with 0.8 w/v glu + 0.1 w/v N was also prepared and treated in the same manner as test samples.

SAMPLE INCUBATION

All flasks were weighed and shaken at 210 rpm on a New Brunswick Gyrorotary 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 distilled water.

ENUMERATION OF MICROORGANISMS

Fungi were enumerated using Rose Bengal Agar plates consisting of 10 g of dextrose, 5 g peptone, 1 g KH_2PO_4 , 0.5 g $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$, 0.033

g of rose bengal, 20 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 procedures of Martin (7).

The actinomycetes and bacteria were enumerated with sodium caseinate agar and Gy agar. The sodium caseinate agar consisted of 0.2 g sodium caseinate, 5 g K_2HPO_4 , 0.2 g $MgSO_4 \cdot 7H_2O$, 0.01 g $MgCl_2$, 15 g agar, and 1000 ml of deionized water (4). The Gy agar consisted of 2.0 g glucose, 5.0 g casamino acids, 1.0 g yeast extract, 15.0 g agar, 5.45 g KH_2PO_4 , 5.68 g Na_2HPO_4 , 0.2 g $MgSO_4$, 0.02 g $CaCl_2$, and 1000 ml deionized water. The samples were diluted using phosphate buffer dilution blanks, and plates were inoculated and spread using an alcohol-flamed curved glass rod, using 0.1 ml inocula. Plates were incubated for one week at 25°C. The fungi were counted on Rose Bengal agar, and the bacteria and actinomycetes were counted differentially 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 ANALYSES

For the analysis of metals in the supernatant solutions, 30 grams of the incubation slurry were centrifuged for 30 min at 10,000 rpm at 5°C. Using a sterile pipette, 20 ml of supernatant were removed with a pipette and placed in 30 ml Sybron/Nalge bottles with 0.1 ml of 3X distilled concentrated 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 and selenium levels by Dr. R. R. Meglen of the Environmental Trace Substances Laboratory, University of Colorado.

MONITORING OF METAL RESISTANCE

To evaluate potential changes in the metal resistance patterns of organisms growing with or without added nutrients in the presence of retorted shale, selected representative colonies were isolated at zero time and at three and six weeks of incubation, and purified by growth on Gy agar. Between 8-10 colonies were selected from each slurry type at each of these sampling times. After checking for uniformity, the organisms were streaked on master plates in a spoke pattern to allow multiple inoculation. The multiple inoculations were carried out using a multipoint inculator which was alcohol-sterilized before use. The organisms were transferred to Gy medium containing the following levels of the particular metals, in $\mu g/ml$:

Metal	Form	Conc. $\mu\text{g/ml}$
Hg	HgCl_2	5
		10
		20
As	Na_2HAsO_4	10
		100
		400
Se	SeO_2	10
		100
		400

These levels were chosen based on recommendations by Nakahara, et al. (8) and Timoney et al. (15).

After inoculation of the final plate in any of the series, a control plate was again inoculated to determine if all plates had received a proper inoculum. If all of the test cultures did not carry across through the entire inoculation sequence, the entire run was discarded and repeated.

Each of the test organisms was also checked for Gram reaction and basic cellular morphology, to determine if particular organisms might predominate, based on the varied shale, soil mixture and nutrient amendments used in the study.

RESULTS

GLUCOSE PLUS PROTEIN AMENDMENTS

After addition of glucose and protein to shale and soil-shale mixtures, significant increases in the levels of bacteria, actinomycetes and fungi were observed. Typical responses are shown in Figures 1 and 2, which illustrate results from the retorted shale samples. With the addition of glucose and protein, within the first week of incubation a 4-log unit increase in the viable population of bacteria and actinomycetes was evident (Figure 1). For the fungi (Figure 2), a lesser increase was noted, being approximately a two log unit increase in the viable count. By the third week of incubation, distinct decreases in the viable counts of the bacteria, actinomycetes and fungi occurred.

The pH and supernatant arsenic levels in the shale experiment are shown in Figure 3. Without added nutrients, the supernatant arsenic levels increased steadily over the six-week experiment

Figure 1. Effects of glucose plus protein additions on the viable bacterial and actinomycete populations of a retorted shale slurry.

Figure 2. Effects of glucose plus protein additions on the viable fungal population of a retorted shale slurry.

Figure 3. The effects of added glucose and protein on the pH (3a) and supernatant arsenic levels (3b) of retorted shale slurries incubated for a six-week period. For the arsenic values, $\sigma = \pm 0.020 \mu\text{g}/\text{ml}$.

period, from approximately 0.16 $\mu\text{g/ml}$ to 0.37 $\mu\text{g/ml}$ at the end of the six-week experimental period. During this time, there was only a gradual increase in the solution pH, shifting from approximately 7.5 to 8.0. With the addition of nutrients, a markedly different pattern of pH-supernatant metal responses was observed. By the third week of incubation, a distinct increase in the solution pH occurred, reached pH 8.62, and a trend to a slightly higher supernatant arsenic level was detectable. By the fourth week of incubation, the solution pH had shifted to the 7.3-7.5 range, and the supernatant arsenic level was approximately 0.5 to 1 $\mu\text{g/ml}$ higher than found in the non-nutrient controls. In this experiment, the increase in supernatant arsenic levels began prior to the major pH shift, suggesting that there might not be a rigid relationship between solution pH and supernatant levels of this metal.

In addition to the experiments which were carried out using only retorted shale, parallel experiments were carried out where soil was added, either as an inoculum (100 mg) or in a concentration (5 g) equal to that used for the shale. In both of these situations, similar pH-supernatant arsenic relationships were observed, although the times where the pH-supernatant arsenic shift occurred varied. For the samples with equal amounts of soil and shale, the pH shift occurred one week earlier than with the shale alone (Figure 4), while with a small soil inoculum, the pH shift was delayed and less accentuated (Figure 5). In both of these experiments, without added nutrients, the supernatant arsenic increased to levels found in the plain shale systems. Similar trends of bacterial, actinomycete and fungal responses were observed.

Soil controls had supernatant arsenic levels in the range of 0.016-0.022 $\mu\text{g/ml}$. No particular shifts in supernatant arsenic values were noted over the six-week incubation time, suggesting that the soils were not making significant contributions to the available arsenic.

During the course of the experiment, approximately 8-10 bacterial colonies were isolated from each test culture at the three and six week samplings, and tested for their growth on media containing selected levels of mercury, arsenic or selenium in ionic forms. Between 88 and 100% of the colonies from slurries with and without nutrients grew in the presence of 400 $\mu\text{g/ml}$ of arsenic. A trend towards a lower percent resistance with added soil present was observed in the non-nutrient samples. However, no particular trend could be identified which would suggest that with increased levels of arsenic in supernatants, that microorganisms with greater resistance to arsenic presence would be selected for.

A routine examination of the Gram reactions and morphology of bacterial isolates grown on the Gy medium from the various test systems was also carried out, to determine if Gram-positive cocci might be predominant, as previously reported by Rogers and McNair

Figure 4. The effects of added glucose and protein on the pH (4a) and supernatant arsenic levels (4b) of 130 ml slurries made up with 5 g shale and 5 g soil. For the arsenic values, $\sigma = \pm 0.020 \mu\text{g/ml}$.

Figure 5. The effects of added glucose and protein on the pH (5a) and supernatant arsenic levels (5b) of 130 ml slurries made up with 5 g shale and 100 mg soil. For the arsenic values, $\sigma = \pm 0.020 \mu\text{g}/\text{ml}$.

(11). No particular trends toward the predominance of this type of organism were noted, with a wide range of cocci and rods being present. Over the entire experimental period, of the isolates which were examined (52 cultures), 35, or approximately two-thirds, were Gram-positive, and these organisms varied widely in their morphology.

In the course of these experiments, the selenium in supernatants was also monitored. Generally, 7 to 15 $\mu\text{g/l}$ was present, and although similar nutrient and growth effect trends were noted as observed with arsenic, the selenium level changes were generally within the range of analytical variability.

CARBON, NITROGEN OR CARBON PLUS NITROGEN EXPERIMENTS

Based on the previous studies, where possible effects of nutrients and microbial growth on the supernatant levels of arsenic were indicated, additional experiments were completed in which specific carbon and/or nitrogen sources were added. Glucose and ammonium ion were added to evaluate possible effects of either of these components on arsenic and/or selenium mobilization from retorted shale. 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. In this set of experiments, soil controls were not used.

The responses of the bacteria and actinomycetes to the addition of various nutrients to shale are shown in Figure 6. 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 ammonium ion nitrogen, essentially no increases in viable counts were observed. This material appears to serve to some degree as a nitrogen source, due to responses shown after the addition of glucose at final concentrations of 0.1 and 0.8% w/v. With both of these amendments, essentially similar increases in bacterial and actinomycete numbers occurred, suggesting that another factor was limiting microbial growth on this material, which can be assumed to be nitrogen. This was confirmed in the experiments where glucose and nitrogen additions were made, where the bacterial and actinomycete populations increased to 10^8 - $10^9/\text{ml}$.

The microbial responses to similar amendments with a shale-soil mixture are shown in Figure 7. Under these conditions, the soil served as a source of carbon or nitrogen to supplement possible deficiencies in the retorted shale materials. In this experiment, much more erratic changes in viable counts were observed, with no particularly distinct responses being observed with the presence of the additional soil materials. Similar results were observed when 100 mg of soil was present with the 5.0 g of retorted shale.

The related pH and supernatant arsenic values for the retorted shale slurries are shown in Figure 8. With the control and amended

Figure 6. The effects of glucose and/or ammonium ion additions on bacterial and actinomycete viable populations in a retorted oil shale slurry.

Figure 7. The effects of glucose and/or ammonium ion additions on bacterial and actinomycete viable populations in a retorted oil shale-soil slurry.

Figure 8. The effects of glucose and/or ammonium ion additions on the pH (8a) and supernatant arsenic levels (8b) in re-torted shale slurries. For the arsenic values, $\sigma = \pm 0.020\mu\text{g}/\text{ml}^{-1}$.

flasks, a gradual shift to higher pH values occurred. This was most pronounced with the carbon and nitrogen-amended soil, while in contrast, the nitrogen or glucose-amended soils appeared to have slightly lower relative pH values. The supernatant arsenic and pH changes showed particularly interesting trends, which were different from those found in the protein amendment experiment. With the shale slurries, higher supernatant arsenic levels, in the range of 0.46 $\mu\text{g/ml}$, were found with the carbon plus nitrogen amendments, which showed the highest pH value, 8.48, at the end of the experiment. In contrast, the control shale slurry with distilled water had a pH value of 8.2 and a supernatant arsenic value of approximately 0.4 $\mu\text{g/ml}$.

Of especial interest in this experiment was the effect of added mineral nitrogen on the pH and supernatant arsenic levels. With the mineral nitrogen additions, as noted in Figure 6, the microbial populations showed only slight increases over those shown for the controls. In spite of this minor viable count shift and essentially no change in the pH value, these samples showed the highest supernatant arsenic levels at the end of the experiment, 0.49 $\mu\text{g/ml}$, in comparison with a control value of 0.41 $\mu\text{g/ml}$.

A similar set of trends was seen in the samples which contained equal amounts of soil plus shale (Figure 9). With these samples, some decreases in solution pH values were noted at the three-week sampling, but these were not reflected in the corresponding supernatant arsenic values. By the end of the experiment, the carbon plus nitrogen-amended samples did show an increased relative pH, which occurred at the same time as a decrease in the supernatant arsenic level was evident.

With mineral nitrogen added to the soil-shale mixture, a similar trend of increased supernatant arsenic levels was observed as noted with the shale slurries. At the second week, the supernatant arsenic levels for the control and nitrogen treatments were essentially similar, approximately 0.35 to 0.36 $\mu\text{g/ml}$. During the third and fourth weeks the supernatant arsenic levels in the nitrogen-amended slurries increased at a constant rate, reaching a final value of 0.55 $\mu\text{g/ml}$, while in the control samples the final arsenic level was 0.4 $\mu\text{g/ml}$.

Similar results were observed in slurries where 5.0 g of re-torted shale were mixed with 100 mg of soil.

During the course of this experiment, random bacterial colonies were subcultured to evaluate the Gram reaction and morphology of organisms from these test systems. Results for the shale cultures without soil amendments suggest that the majority of the organisms which were growing on this material were Gram positive, but that these did not have a predominantly coccal morphology (Table 1). This is in contrast to the work of Rogers and McNair (11) at Batelle Pacific Northwest laboratories, where the Gram positive cocci were

Figure 9. The effects of glucose and/or ammonium ion additions on the pH (9a) and supernatant arsenic levels (9b) in re-torted shale-soil slurries. For the arsenic values, $\sigma = \pm 0.020 \mu\text{g/ml}$.

found to be the dominant group of organisms found to be growing in retorted shale materials without added amendments.

The present studies, which were carried out to determine if microbial growth in the presence of various nutrients might influence supernatant arsenic and selenium levels, suggest that microbial growth may make these metals more available for movement in waters. In comparing the two experiments, where proteins were added, a possible pH decrease-supernatant arsenic increase relationship was observed, while in the second group of experiments, where separate carbon and nitrogen amendments were made, no particular relationship between pH shifts and supernatant arsenic levels was observed.

When shale samples were amended with mineral nitrogen, a particularly unique phenomenon appears to have taken place. Under these conditions, only minimal increases in the microbial populations occurred, most likely due to the inability of the retorted shale to serve as a carbon source. However, in spite of this, potentially significant increases in supernatant arsenic levels were observed.

These results suggest that in an extremely carbon-stressed growth environment, (1) the carbon fractions which could have been used by the microorganisms made the bound arsenic more available, or (2) in the presence of excess nitrogen, amine- or ammonia nitrogen-containing arsenic compounds were formed, which could have greater solubility or mobility.

It should be emphasized that the arsenic and selenium forms monitored in these studies remained in centrifuged supernatant liquids derived from shaken, aerated cultures. With the well-known ability of soil microorganisms to synthesize a variety of volatile organometallic compounds of both arsenic and selenium (1,2,10,14,17), it is possible that the increases in these metals monitored in this study represent only a minor portion of the arsenic being made more mobile as a result of nutrient additions and subsequent microbial growth. For this reason, in future experiments it would appear to be appropriate to monitor a broader range of volatile arsenic forms which may be formed as a result of microbial activities.

This information will make it possible to more fully assess the potential for transport and mobilization of pollutants contained in oil shale materials, as recommended in objective A33 of the Oil Shale R, D and D Program Management Plan (3).

CONCLUSIONS

Microbial growth in the presence of nutrients appears to have the following effects on the supernatant levels of arsenic and selenium released from retorted shale and soil-shale mixtures:

1. With protein substrate additions, increases in supernatant arsenic levels are observed, which may be accentuated by pH decreases which occur during the latter part of a six-week incubation period.
2. No evidence could be obtained to suggest that the increased levels of supernatant arsenic which were observed might be related to a greater level of arsenic resistance in the organisms found in the test systems.
3. 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.
4. With nitrogen additions, no major increases in microbial populations occurred, indicating that retorted shale is a particularly poor source of carbon for microbial growth.
5. Ammonia nitrogen additions appear to be related to increased levels of supernatant arsenic, which reached a peak of approximately 0.55 $\mu\text{g/ml}$ in the soil-shale mixtures. Control values were in the range of 0.40 $\mu\text{g/ml}$.
6. The organisms recovered from the retorted shale test systems appeared to be predominantly (77%) Gram-positive forms, of which only approximately 29% were cocci, based on a limited sample size.
7. Addition of nutrients and microbial growth on retorted shale and shale-soil mixtures did not lead to marked increases in supernatant selenium levels, with most values being in the range of 0.008 to 0.015 $\mu\text{g/ml}$.

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PROGRESS REPORT 1979 - 1980

Trace Element Reconnaissance in the Oil Shale Region
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INTRODUCTION

Studies are continuing on the trace element baseline studies of surficial materials in the Piceance Creek Basin of Colorado. The initial studies by Ringrose and others (1) and Ringrose (2) on surface soils and stream sediments, respectively, provided the basis for the subsequent studies. Subsequent studies have focused on smaller areas in and around sites considered for early development. Plant materials were also added to the collection in the more detailed studies. Candito (3) developed baseline data for the Colorado oil shale Tract C-a and vicinity and Zuccaro (4) completed a similar study for Tract C-b and vicinity. The bulk of this report will outline the results for work completed at Anvil Points and vicinity, the site of the past U.S. Bureau of Mines retorting research and the recent Paraho experimentation (Rutherford, (5)).

The oil shales of the Piceance Creek Basin were deposited under unusually alkaline conditions. This alkaline character affects the mobility of the trace elements, resulting in a particular suite of elements being present in the oil shale at high concentration. The same set of elements has the potential for mobilization during processing and disposal of spent shale. In addition, several other elements have potential for volatilization and atmospheric dispersal during the reducing conditions of retorting. The elements of prime interest include: Mo, B, F, Hg with As, Se, Cd, Zn of secondary interest. Generally, pH and organic carbon were also determined in soils and stream sediments because of the relationship to the possible chemical form of the elements and their subsequent mobility.

OBJECTIVES

The Anvil Points study of Rutherford (5) had the following objectives:

- 1) Determine the means and ranges in concentration for Mo, B, and F in soils, stream sediments, and the three species of plants; Big sagebrush, Indian ricegrass, and Western wheatgrass. For soils and stream sediments, the

parameters Hg, pH, and organic carbon were also determined.

- 2) Determine the geographic scale of variance for the constituents in each medium sampled.

Additional objectives for which preliminary results will be reported include:

- 3) Determination of the rate of adsorption of Hg by native soils of the Piceance Creek Basin.
- 4) Estimate the time required for significant environmental impact to occur in selected areas of the basin utilizing estimates of gas and particulate dispersion from oil shale operations.

MATERIALS AND METHODS

MATERIALS

A variety of surficial materials were collected as part of the baseline studies for the Anvil Points area. Soil samples were a composite of the top two centimeters taken over an area at least 10 meters in radius. They were sieved through a 4 mesh stainless steel sieve and stored in stream sediment bags. A separate split was sieved to -80 mesh and stored in sealed plastic vials for later Hg analysis. Stream sediments were collected in an analogous way for general analysis and for Hg analysis. Stream sediment samples were a composite over at least 10 meters of stream channel. The -4 mesh samples intended for general analysis were split to 12-15 g and ground to -200 mesh in tungsten carbide. The -80 mesh sample was not ground prior to Hg analysis as this may result in loss of Hg.

The plant materials sampled included: Big sage (Artemisia tridentata), Indian ricegrass (Oryzopsis hymenoides), and Western wheatgrass (Agropyron smithii). The collection of plant materials is a composite from the same area as the soil collection. The Big sage collection was primarily of new growth with a minimum of woody material, collected high enough above the ground to avoid rainsplash. The grasses were clipped near ground level, air dried, and stored in paper sacks. Since the grasses did have considerable rainsplashed soil material, the samples were washed with distilled water in an ultrasonic bath. After drying, the grasses were chopped in a blender. The sage was not washed in the ultrasonic bath as the leafy material tended to disintegrate during the process and proper sample recovery was not possible. The sage samples were also chopped in the blender after drying.

SAMPLE DESIGN

Three sample designs were used in the Anvil Points study. A hierarchical analysis of variance design was used as a first stage design to assess the geochemical variability within the study area. This design is analogous to that used by Candito (3) and Zuccaro (4) and described in some detail by Miesch (6). The purpose of this sample design is to determine the effect of sample spacing on geochemical variability and determine the sample density necessary to produce a reproducible chemical map.

The second stage designs consisted of collecting soil and plant samples on a grid system and collecting stream sediment samples on 1/2 mile intervals along stream channels. The objective of the second stage sample design is to collect samples in order to calculate baseline concentrations and outline areas of possible anomalous concentrations.

The selection of sample sites for soils and plant samples involved gridding the 36 mi.² study area on 1/2 mile intervals and locating the sample site at the grid line intersections. Figure 1 shows the resulting sample pattern and sample location numbers superimposed on the geology of the area. This type of sample design was used since an objective of the study is to obtain baseline data for the area as a whole. This results in the number of samples per geologic unit being proportional to the amount of surface area exposed.

Plant samples were collected when the species of interest was present at the sample site. Big sage was fairly evenly distributed over the study area with 125 out of the 171 possible sample sites having sage present. The distribution of Indian ricegrass and Western wheatgrass was more dependent on topographic aspect and climate. The area has about 4000 feet of relief, resulting in considerable variation in climate and character of plant cover.

Stream sediment samples were collected on 1/2 mile intervals on all clearly defined stream channels within and immediately adjacent to the study area (Figure 2). These sites included both flowing and dry channels and totaled 161 locations.

ANALYTICAL METHODS

The samples from the Anvil Points study were analyzed at the Colorado School of Mines and the central analytical facility at the University of Colorado. Molybdenum, B, and F were determined by the methods described by Meglen in this report.

Mercury was analyzed at the Colorado School of Mines utilizing a Jerome Model 301 Hg analyzer. This method is based upon the change in electrical resistance during amalgamation of a Au film. Organic carbon is determined by the wet-oxidation

Figure 1: Sample Location Key

Walkley-Black method (7) on the ground soil sample. The pH is determined by the saturation paste method on unground -4 mesh soil or stream sediment material.

RESULTS AND CONCLUSIONS

ANVIL POINTS STUDY

Soils and Plants

The interpretation of the results of the Anvil Points work is made more complex by the large stratigraphic interval exposed in the area. The primary purpose of the hierarchical analysis of variance design is to estimate the distribution of variance with geographic distance or sample spacing. Because of the stratigraphic interval exposed in the area, the hierarchical design has a geologic component of variance as well as the geographic component. If the geochemistry of the rock unit varies significantly, then the usefulness of the hierarchical results is in question.

To test for this, a model for examining this possibility is developed using the grid samples described in the section on sample design. The model for examining the variance in soils and plants reflecting the underlying geologic unit is:

$$X_{ijk} = \mu + A_i + B_{ij} + C_{ijk}$$

where μ is the grand mean for the study area, A is the variation caused by differences between underlying geologic units, B is the variation caused by differences within a geologic unit, and C is the analytical variation. This is a three level analysis of variance model and the complete results are shown in Table 1.

Focusing attention on the columns labeled "F-Value" and "Percent of Total Variance", it can be seen that the underlying geologic unit has a significant effect on the compositional variability of the overlying soil and plant material. This indicates that sampling designs must consider geologic effects on surface material as well as the contribution of sample spacing.

The analysis of variance results were recalculated using only the three sections which were entirely on one geologic formation, namely the Wasatch Formation shown on Figure 1. These results indicate that none of the soil parameters measured can be reliably mapped within the Wasatch Formation, but the plant compositions can be mapped. The most important results of the soils and plants study at Anvil Points, besides establishing means and ranges, is that the basic sample design must be different for geologically complex areas than for homogeneous areas such as Tract C-b. This conclusion is confirmed by

Table 1: Analysis of Variance Results Gridded and First Stage Samples Broken Down by Geologic Unit.

<u>Rock Unit</u>	<u>Source of Variation</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Value</u>	<u>% of Total Variance</u>	<u>Estimated Variance Component</u>
<u>Soil</u>							
pH	Between						
	Rock Unit	29.22	4	7.305	54.99***	65.96	.2317
	Within						
	Rock Unit	26.17	197	.1328	51.59***	33.31	.1170
	Analytical	.05922	23	.002575		.73	.002575
OC	Between						
	Rock Units	11.44	4	2.860	41.98***	59.52	.09822
	Within						
	Rock Units	13.42	197	.06814	146.6***	40.46	.06677
	Analytical	.000186	4	.0004649			.0004649
Hg	Between						
	Rock Units	.9346	4	.2336	5.285***	11.42	.00518
	Within						
	Rock Units	8.709	197	.04421	1.238	14.69	.007097
	Analytical	1.464	41	.03571		73.90	.03571
Mo	Between						
	Rock Units	.5185	4	.1296	2.711*	5.62	.002613
	Within						
	Rock Units	9.420	197	.04782	30.90***	91.06	.04236
	Analytical	.02941	19	.001548		3.33	.001548
B	Between						
	Rock Units	.3145	4	.07862	6.634***	15.61	.002062
	Within						
	Rock Unit	2.335	197	.01185	2.077**	41.19	.005441
	Analytical	.1540	27	.005705		43.20	.005705

Table 1: Continued

<u>Rock Unit</u>	<u>Source of Variation</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Value</u>	<u>% of Total Variance</u>	<u>Estimated Variance Component</u>
<u>Soil</u>							
F	Between						
	Rock Units	.4337	4	.1084	6.415***	16.50	.003121
	Within						
	Rock Units	3.329	197	.01690	19.73***	78.97	.01493
	Analytical	.01285	15	.0008567		4.53	.0008567
<u>Sage</u>							
Mo	Between						
	Rock Unit	2.988	4	.7470	18.82***	.04177	52.02
	Within						
	Rock Unit	6.034	152		18.97***	.03644	45.38
	Analytical	.01046	5	.002092		2.61	.002092
B	Between						
	Rock Unit	.2237	4	.05592	5.917***	22.89	.002695
	Within						
	Rock Unit	1.436	152	.009451	12.44***	70.66	.008320
	Analytical	.005319	7	.0007598		6.45	.007598
F	Between						
	Rock Units	10.49	4	2.621	26.08***	61.70	.1374
	Within						
	Rock Units	15.28	152	.1005	16.31***	35.53	.07914
	Analytical	.1848	30	.006162		2.77	.006162

Table 1: Continued

<u>Rock Unit</u>	<u>Source of Variation</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Value</u>	<u>% of Total Variance</u>	<u>Estimated Variance Component</u>
<u>Ricegrass</u>							
Mo	Between						
	Rock Units	.4633	3	.1544	9.082***	1.23	.01006
	Within						
	Rock Units	2.211	130	.01701	.02105	0.00	0.000
	Analytical	4.037	5	.8073		98.77	.8073
B	Between						
	Rock Units	.05043	3	.01681	.7066	0.00	0.00
	Within						
	Rock Units	3.093	130	.02379	19.97***	94.33	.01983
	Analytical	.02383	20	.001191		5.67	.001191
<u>Wheatgrass</u>							
Mo	Between						
	Rock Units	.3837	3	.1279	2.243	9.13	.005530
	Within						
	Rock Units	3.820	67	.05702	6.165	75.61	.04582
	Analytical	.02775	3	.009250		15.26	.009250
B	Between						
	Rock Units	.02036	3	.006787	.1589	0.00	0.000
	Within						
	Rock Units	1.2862	67	.04271	36.88***	96.58	.03271
	Analytical	.02316	20	.001158		3.42	.001158

* Significant at .05
 ** Significant at .025
 *** Significant at .01

considering the soils and plants on different geologic units as different populations and applying the student t-test to them.

Some unexpected variations in soil and plant composition occur in the Anvil Points area. The F in surface soils exhibits only a moderate contrast between geologic units (Figure 3). The F in Big sage has a very strong contrast, depending on the geologic unit upon which it is growing (Figure 4). The trace element Mo exhibits a similar but less pronounced contrast. The reason for this is not known, but soil pH variation is suspect. Soil pH also has a strong contrast which will affect trace element availability to plants.

Stream Sediments

The earlier work by Ringrose (2) and McNeal and others (8) demonstrated there were significant differences in sediments from different streams, as well as within streams. This information was used to formulate the sampling and statistical analysis of the stream sediment data, the results of which support the conclusions of Ringrose (2) and McNeal and others (8). Table 2 is the analysis of variance results considering between and within stream variability. All six parameters measured have significant variation at the between stream level.

Also of interest for the Anvil Points area is the effect of the underlying geologic unit on stream sediment geochemistry. Table 3 contains the results of considering the geologic unit as a factor in controlling stream sediment composition. Because of the sample distribution, it is possible that the variability between streams and the variability between geologic unit is confounded. Some of the drainages are entirely within one geologic unit, a few in two or more. To separate these effects, a two way analysis of variance was computed, the results of which are shown in Table 4. This data indicates that except for Hg, both between stream variance and between geologic unit variance are significant. Again, this provides important information about sample design for stream sediment surveys in geologically complex areas.

MERCURY ADSORPTION

The adsorption of Hg by soils from Tracts C-a, C-b, and Anvil Points is being determined with a long term experiment under field conditions. Field conditions are more appropriate than a laboratory experiment because of the sensitivity of Hg adsorption processes to temperature, humidity, and sunlight exposure. The DDP for C-b (11) estimates ground level concentrations of Hg at $0.16 \mu\text{g}/\text{m}^3$ at ground level near the boiler exhaust if fired by in-situ process off-gas. Fox and others (9) suggest relatively high concentrations of Hg vapor may exist underground and on the surface near retort or exhaust operations. The short term atmospheric concentrations may be

Figure 3

Table 2: Stream Sediments
Analysis of Variance by Stream

	<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Probability</u>
pH	Between	4.6361	12	.3861	6.16	0.0000
	Within	9.2825	148	.06212		
	Total	13.9186	160			
OC	Between	230.8355	12	19.24	23.07	0.0000
	Within	123.4243	148	.8339		
	Total	354.2598	160			
Hg	Between	18.8763	12	7.573	7.683	0.0000
	Within	30.3005	148	.2047		
	Total	49.1768	160			
Mo	Between	5.5516	12	.4626	4.468	0.0000
	Within	15.3240	148	.1035		
	Total	20.8756	160			
F	Between	12.9586	12	1.080	14.38	0.0000
	Within	11.1122	148	.07508		
	Total	24.0709	160			
B	Between	82.9916	12	6.916	17.40	0.0000
	Within	58.8283	148	.3975		
	Total	141.8198	160			

Table 3: Stream Sediments
Analysis of Variance by Geologic Unit

	<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Probability</u>
pH	Between	3.9042	4	.9760	15.21	0.0000
	Within	10.0137	156	.06419		
	Total	13.9179	160			
OC	Between	181.037	4	45.26	40.76	0.0000
	Within	173.223	156	1.110		
	Total	345.260	160			
Hg	Between	18.8409	4	4.710	24.22	0.0000
	Within	30.3360	156	.1945		
	Total	49.1769	160			
Mo	Between	2.6238	4	.6560	5.607	0.0000
	Within	18.2518	156	.1170		
	Total	20.8756	160			
F	Between	9.5173	4	2.379	25.50	0.0000
	Within	14.5534	156	.09329		
	Total	24.0707	160			
B	Between	59.4179	4	14.85	28.12	0.0000
	Within	82.4020	156	.5282		
	Total	141.8199	160			

Table 4 : Stream Sediments

Two-way Analysis of Variance - Geologic Unit and Stream

	<u>Source</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Probability</u>
pH	G.U. elim. St.	1.04	4	.26	4.31	.0026
	St. elim. G.U.	1.77	12	.15	2.45	.0063
	Interactions	.14	9	.02	.27	.9822
	Within Cells	8.10	135	.06		
OC	G.U. elim. St.	11.73	4	2.93	3.66	.0073
	St. elim. G.U.	61.53	12	5.13	6.39	0.0000
	Interactions	3.40	9	.38	.47	.8921
	Within Cells	108.29	135	.40		
Hg	G.U. elim. St.	3.39	4	.85	4.67	.0015
	St. elim. G.U.	3.43	12	.29	1.56	.1068
	Interactions	2.38	9	.26	1.45	.1721
	Within Cells	24.53	135	.18		
Mo	G.U. elim. St.	.96	4	.24	2.68	.0392
	St. elim. G.U.	3.89	12	.32	3.62	.0001
	Interactions	2.30	9	.26	2.85	.0041
	Within Cells	12.07	135	.09		
F	G.U. elim. St.	.75	4	.19	2.79	.0287
	St. elim. G.U.	4.19	12	.35	5.20	.0000
	Interactions	1.29	9	.14	2.13	.0307
	Within Cells	9.07	135	.07		
B	G.U. elim. St.	8.01	4	2.00	5.52	.0004
	St. elim. G.U.	31.59	12	2.63	7.25	.0000
	Interactions	1.81	9	.20	.55	.8322
	Within Cells	49.00	135	.36		

St. = Between Stream effects

G.U. = Between Geologic Unit effects

controlled by adequate technology but the long term adsorption of Hg by surface soils is an unknown factor. The soil baseline concentrations of Hg are quite low (1,3,4,5) averaging $1/3 - 1/2$ of a world-wide average for soils.

Six large samples of soil were collected from ridge tops and valley floors on Tracts C-a, C-b, and the Anvil Points area, thoroughly mixed and split. One gram aliquots of each of the six soil samples were loaded into 180 shallow vials for exposure under five conditions, totaling 1080 samples. The five conditions include: ambient conditions at a field site and exposure to elemental Hg vapors, HgO vapor, control (no exposure), laboratory exposure to Hg vapor and HgO vapor. Sufficient samples are set up and being exposed to allow analysis in triplicate of each soil, under each of the five conditions, at 12 times of exposure. The first set of samples were removed for analysis after two months of exposure. Adsorption levels are shown in Table 5.

It is obvious that significant adsorption of Hg occurs whether the soils are exposed to Hg or HgO. The adsorption is less under ambient conditions, which mimics the fall-winter climate, than in the laboratory environment. The adsorption of Hg by the ridge top soils is much higher than the adjacent valley floor soils, no matter which geographic area they are from. The reason for this is not known yet, though is likely related to grain size distribution and/or mineralogy.

The field site is in a climate similar to the Piceance Creek Basin with a wide range of temperature and humidity. These parameters are being continuously monitored at the field site. Exposure to elemental Hg vapor results in a partial pressure that is likely too high for the expected exposure level. A continuous, lower level of exposure is maintained using HgO which results in an equilibrium atmospheric concentration of $< 0.1 - 10 \mu\text{g}/\text{m}^3$, depending on temperature and humidity. This is 3-4 orders of magnitude below the elemental Hg vapor pressure. Additional samples will be removed and analyzed after longer periods of exposure. Possible desorption of Hg exposed soils under strong sunlight conditions will be determined in the summer of 1980.

CULTIVATED SOIL COMPOSITION

Approximately 90 additional samples of soils and plants have been collected from the cultivated alluvial valleys to complement the existing baseline data. In the baseline studies, cultivated areas were specifically avoided as these soils may not be at baseline values. This additional data will allow determination of whether cultivated soils are chemically the same as the baseline soils or not. Since trace element impact may be concentrated in valley floors, the composition of these cultivated soils will be determined and compared with the

TABLE 5. MERCURY CONCENTRATIONS IN SOILS EXPOSED FOR 64 DAYS IN LABORATORY AND FIELD CONDITIONS

(October 13, 1979 to December 15, 1979)

	<u>Control</u> ppb	<u>Field Ambient Conditions</u>		<u>Laboratory Conditions</u>	
		<u>HgO</u> ppb	<u>Hg</u> ppb	<u>HgO</u> ppb	<u>Hg</u> ppb
C-a Ridge Top	29	88	1400	1900	74,000
C-a Valley Floor	30	56	310	670	17,000
C-b Ridge Top	32	320	2200	1600	47,000
C-b Valley Floor	50	130	170	340	17,000
Anvil Points Ridge Top	18	480	4300	3000	82,000
Anvil Points Valley Floor	42	260	560	650	32,000

baseline soil composition. This data will also be used in the "trace element impact" study and modeling of dispersal.

TRACE ELEMENT IMPACT

A number of studies have been made on the atmospheric dispersal of contaminants on Tracts C-a and C-b (10,11,12,13). The gas and particulate dispersion have been modeled for both C-a and C-b using the EPA Valley model for dispersion of a plume. The model has problems in adequately predicting the dispersion in mountainous terrain (14). Subsequently, tracer studies were done using SF₆ on both tracts to determine the validity of the model in these situations. The tracer studies were done at a time of stable atmospheric conditions which result in the released tracer gas being carried into adjacent valleys.

The primary difficulties with modeling the contaminant dispersal in the Piceance Creek Basin is the strong terrain influence on local meteorological conditions. Koch and others (15) discuss plume dispersal in complex terrain. A common situation will be the development of a strong shear and turbulence at some point up to several hundred meters above ground level. In the lower layer, terrain dominated air flow will develop under stable atmospheric conditions which will persist a significant portion of the time. Under these conditions a gentle down-valley flow and inversion will develop during the night. At some point in the early morning, as the sun heats the ground level air, the flow will reverse. The up-valley flow will continue until the shear layer is destroyed and the synoptic flow established dominance.

The synoptic flow is generally from the southwest and will result in a wide dispersal of pollutants from Tract C-a. On Tract C-b there will also be a wider dispersal, but the synoptic flow may result in impingement of the plume on the hills to the north of Piceance Creek. The time of the day when the synoptic flow will establish predominance will vary from season to season. During the peak of the summer, it will be relatively early in the day due to rapid ground heating. In the winter, during snow cover, synoptic flow near ground level may not be established at all on many days. If one assumes uniform dispersion of estimated contaminants over a large area, trace element impact does not seem severe except for Hg (Klusman, work in progress). The DDP for C-b (11) estimates particulate emission at 133 lbs/hr. for full scale operation. Utilizing data from Zuccaro (4) on baseline concentrations, and a raw shale Mo content of 20 ppm, and the emission rate, one can estimate time required for significant contamination. A simple calculation assuming uniform dispersal over the 45 sq. mi. sampled, the contamination increment can be detected with 95% certainty in 236 years. For Hg in the off-gas, with an estimated loss of 48 lb/hr., a raw shale composition of 0.43 ppm, the time is less than one year, assuming quantitative adsorption of the Hg by the

surface soils. The DDP for C-a (10) estimates the particulate emission at 576 lb/hr. An analogous calculation with the soil baseline data of Candito (3), results in detectable contamination in 87 years.

These calculations are quite simple but indicate there is potential for significant impact in much shorter time when dispersal is non-uniform. The two day tracer studies done on Tracts C-a and C-b (12,13) confirm non-uniform dispersal. The approach currently underway is to model dispersion using a number of variables. For Tract C-b, these variables include: proportion of impacted area in the heavily impacted Piceance Creek Valley floor, proportion of area in less impacted adjacent valley floors, proportion of area in ridge tops, composition and amount of contaminant, baseline composition, thickness, and density of affected soil layer, proportion of time in each of five general atmospheric conditions. By varying these parameters within realistic limits, some estimate of trace element impact can be made over the simply classified areas. Although these estimates may have considerable uncertainty, the degree of sensitivity of each parameter can be determined. Preliminary computer results indicate trace element impact will be most sensitive to the relative areas in the impacted region and the prevalence of the various general meteorological conditions. This effort will be modified with the advice of atmospheric specialists to approach a realistic or best situation.

SAMPLING MANUAL

A manual written for the environmental scientist and practicing engineers with specific application to sample design for baseline studies of surficial materials in the oil shale region was completed in draft form (16). Copies of the draft manual were distributed to a wide range of specialists with interests in the oil shale industry with a request for critical review. These scientists, engineers, and research groups include:

Don Runnells - University of Colorado
Ralph Franklin - Office of Environment, DOE
Ian Thornton - Royal School of Mines, London
Ray Wilding, John Zachara - PNL, Battelle
Joe Kubota - USDA
Glenn Miller, Miles LaHue, Bob Elderkin - AOSO, Grand Junction
Willard Lindsay - CSU
Walter Dean, Al Miesch - Branch of Regional Geochemistry, USGS
Staff - LETC
Staff - Project Rio Blanco
Staff - Occidental Oil Shale Corp.

Excellent comments and suggestions have been received and the manual will undergo extensive revision with a final draft ready for printing by June, 1980.

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UPTAKE OF CHEMICAL ELEMENTS BY
PLANTS GROWING ON SPENT SHALE

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INTRODUCTION

Revegetation of spent oil shales is presently considered the best method of reclaiming the massive amounts of waste produced by the processing of oil shale. Returning this material to natural vegetation will reduce the risk of erosion and minimize the overall impact of mining the shale. However, there are potential hazards involved in the revegetation process. Spent shales are known to contain high levels of elements which are usually present in trace quantities. Some of these elements are toxic to plants and animals. Before widespread reclamation of these industrial wastes is attempted, it must be proven that the revegetation procedures will limit the uptake of toxic elements.

The usefulness of placing topsoil over spent shale was tested to determine if such techniques are effective in reducing hazards. The treatments were investigated with the objective to examine plant uptake of a broad scope of elements affected by soil cover.

MATERIALS AND METHODS

SOIL TREATMENTS

Five soil-shale treatments at the Intensive Revegetation Site of C.W. Cook et al. (1) were examined in this study. As illustrated in Fig. 1, the treatments consisted of 30.5 cm, 61 cm, and 91.5 cm of topsoil over spent shale; 61 cm of topsoil plus 30.5 cm of gravel over spent (Paraho) shale; and indigenous subsoil. The topsoil covers were to function as a buffer region between plants and shale. The addition of gravel was used to provide a physical and capillary barrier between soil and shale. The subsoil acted as a control. Plants seeded directly into the spent shale with no soil cover (fig. 1 "Panel 1") did not survive and could not be sampled. All treatment plots were replicated three times and were fertilized with 56 kg N/ha and 28 kg P/ha and seeded with a native mixture of shrubs, forbs, and grasses (Mixture B) in June, 1977.

PLANT SAMPLES

In June of 1979, six plant species were sampled in each rep. The common and scientific names of these plants are listed in Table 1. The samples were immediately placed in a cooler with dry ice and transported to Colorado State University. The plants were washed with phosphate-free detergent and distilled water to remove surface contaminants and placed in a forced air oven at 70°C for 48 hours. The plants were then ground in a stainless-steel mill to pass a 20 mesh sieve.

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

<u>Common Name</u>	<u>Scientific Name</u>
Rosana western wheatgrass	Agropyron smithii
Indian ricegrass	Aryzopsis hymenoides
Utah Sweetvetch	Hedysarum boreale utahensis
Fourwing saltbrush	Atriplex canescens
Winterfat	Ceratoides lanata
Sherman big bluegrass	Poa Ampla

PLANT ANALYSIS

Dried, ground plant samples were sent to the analytical laboratory in Boulder, Colorado. These samples were analyzed for B, Mo, and F.

The same samples were also analyzed at Colorado State University. One gram of sample was digested in 4:1 $\text{HNO}_3:\text{HClO}_4$ and diluted to 50 ml. The samples were then taken to the CSU Soil Testing Laboratory for analysis by ICP-OES. The elements P, K, Ca, Mg, Na, Zn, Mn, Cu, Ni, Ti, Cd, Ba, B, Mo, Cr, Pb, Co, and Al were analyzed by conventional aspiration methods, and Hg, As, and Se were analyzed by vapor-hydride methods.

STATISTICAL ANALYSIS

The plant uptake of each element was analyzed as a split-plot factorial design. The computer program STAT 41V assisted in numerical analyses. The 3 rep means of each soil treatment were compared within each plant species if there was significant soil treatment and plant species. The means were broken into non-significant groups using Bayes LSD (5). The mean Cu:Mo ratios were also compared. In Figures 2-18, non-significant groupings of treatment means for each plant species contain the same letter in their labels. For example, treatments within a given species labeled a, ab, and abc are not significantly different. Treatments within a species labeled a and b are significantly different.

RESULTS AND DISCUSSION

The analyses of Cd, Co, and Pb by ICP-OES were not sensitive enough to detect these elements in the plant tissues. All Cd and Co levels were below 1.0 ppm, and all Pb levels were below 5.0 ppm in the plant. This does not reveal any major conclusions except that Pb, Cd, and Co are not accumulating in the vegetation.

Leaching studies by Runnels et al. (2) suggested that F may be potentially hazardous in oil shale revegetation. Our analyses revealed that many of the fluorine levels were below the detection limit of 1.4 ppm, and none of the plants levels exceeded 5 ppm. Because plants from some of the treatments were below the detection level, analysis was impossible, but the results show that F levels were significantly low to be of no concern.

The Cr and Hg analyses were obscured by the combination of low levels and intermittent contamination.

The essential nutrients P, K, Ca, and Mg (Fig. 2-5) and the non-essential element Na (Fig. 6) show statistically significant differences between plant species and some differences between treatments within species. However, these differences follow no particular trend and are of little practical significance. The same is true for the trace elements Zn, Fe, Mn, Ni, Ti, and Ba (Fig. 6-12). These elements show no differences in uptake as a function of soil cover and do not exhibit unusually high or low levels of accumulation.

The elements boron, selenium, arsenic, molybdenum, and copper are of environmental importance. High levels of boron found in spent shales are potentially phytotoxic if accumulated in large quantities. If grasses accumulate greater than 50-60 ppm B, injury may occur to the plant (3). Klusman (4) reported mean

B levels of 8 ppm in western wheatgrass grown on the soils within the Federal Oil Shale tract, C-a, in the Piceance Basin of Colorado. The increased boron content in dicots has been observed earlier (6), and does not necessarily indicate boron tolerance.

Figure 13 illustrates the mean boron uptake by the six plant species grown on the five shale treatments. As discussed, the grasses contained far less boron than the dicots. The mean boron levels for winterfat, fourwing saltbush, and Utah sweetvetch were 31, 50, and 54 ppm, respectively. These concentrations are approaching phytotoxicity levels. Unfortunately, the presence of topsoil has no significant effect on B concentrations. The revegetation of spent shales with dicots could encounter some problems due to elevated boron levels.

Selenium levels in spent shales (7) are 20 times lighter than normal soil levels for the region (4). However, Fig. 14 illustrates that Se uptake by plants were well below the 4-5 ppm hazard level (8) and were unaffected by soil cover. This confirms previous findings by Kilkelly (9).

Arsenic analyses of plant samples provided little more information than obtained in 1978 (10). Most of the arsenic in the shale was apparently not available to plants. In this study (Fig. 15) it was observed that grasses were much more efficient at extracting arsenic than dicots. Grasses contained as much as ten times the As as dicots. However, these relatively elevated levels should not pose serious problems.

Previous leaching studies (2) indicated that molybdenum has the potential for accumulation by plants and toxicity to grazing wildlife. Miltimore and Mason (11) reported that a Cu:Mo ratio less than two could result in molybdenosis. Kilkelly (6) observed high levels of Mo coupled with low Cu in plants growing on USBM and TOSCO spent shales. The presence of small depths of topsoil (less than

31 cm) did not affect the Cu:Mo ration. This years's data on Paraho shale partially supports these findings. Figures 16 and 17 show the trends for Mo and Cu uptake on the various soil treatments. Molybdenum was very low in the grasses and thus exhibited no significant trends. In the dicots, molybdenum was much higher and showed highly significant decreases with increasing soil cover. Vlek and Lindsay (12) showed that Mo solubility increases with increasing pH. Since the pH of spent shales is often greater than 12, high molybdenum solubility was expected. Since the Cu:Mo ratio is critical to grazing animals, Fig. 18 was prepared. The dotted lines represent a ratio of 2. With all plants, except Utah sweetvetch, the Cu:Mo ratio increased from near or below two to a safe level. In Utah sweetvetch none of the treatments displayed a ratio significantly greater than two. Barshad (13) and Kubota et al. (14) suggest that because Mo is assoicated with N₂-fixing enzymes, legumes such as Utah sweetvetch tend to accumulate higher levels of Mo than non-legumes.

Comparing Fig. 16, 17, and 18, one sees that the increases in Cu:Mo is due mostly to the decreases in Mo and only partially due to increases in Cu. It is possible that root penetration through deeper layers of soil and gravel is not yet great enough to accumulate available Mo from the shale. It is, therefore, advised that the sampling of these plots be continued for a least one more year. Although deeper soil covers have seemingly corrected the Mo toxicity problem, this could be temporary.

SUMMARY

Plants were sampled from the Intensive Oil Shale Revegetation Site in the Piceance Basin of Colorado to test the affects of soil cover on plant uptake of several elements. The uptake of the majority of elements showed no response

to soil cover. The elements F, Cd, Pb, and Co were generally at or below analytical detection limits, indicating that there is no danger of high accumulation of these elements. Uptake of As and Se was below toxicity limits, supporting the previous year's data. Dicots grown on these plots were high in boron (>30 ppm). Although plants vary in their susceptibility to boron toxicity, the accumulation of boron in these plants could create difficulties in revegetation projects. The accumulation of Mo and the ratio of Cu:Mo were both significantly affected by soil cover. With 30.5 cm of soil over shale, the Cu:Mo ratio was below two for all plants, indicating possible danger of molybdenosis for grazing animals. The plants growing on 61 cm of soil plus 30.5 cm of gravel over shale had Cu:Mo ratios significantly greater than two for all plants except winterfat. Another year's sampling and Cu-Mo analysis is recommended to monitor the effect of time on these results.

Figure 1: Soil-treatment profiles for the Retorted Shale Successional Study using Paraho retorted shale.

Figure 2: Phosphorus concentrations in the plants as function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil. Bayes-LSD = 0.063.

Figure 3: Potassium concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil. Bayes-LSD = 0.31.

Figure 4: Calcium concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 0.019.

Figure 5: Magnesium concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 3.05 cm gravel, S is subsoil, Bayes-LSD = 0.18

Figure 6: Sodium concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 0.064

ZINC

Figure 7: Zinc concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 7.20

Figure 8: Iron concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 42.

Figure 9: Manganese concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 43.

Figure 10: Nickel concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 gravel, S is subsoil, Bayes-LSD = 3.68

Figure 11: Titanium concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 1.52

Figure 12: Barium concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 13.6

Figure 13: Boron concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 7.1

Figure 14: Selenium concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 0.415

Figure 15: Arsenic concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 0.028

Figure 16: Molybdenum concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 4.17

Figure 17: Copper concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil, 2G is 61 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 3.02

COPPER TO MOLYBDENUM RATIO

Figure 18: The ratio of copper to molybdenum concentration in the plants as a function of treatment: 1 is 30.5 cm soil, 2 is 61 cm of soil, 3 is 91.5 cm of soil plus 30.5 cm gravel, S is subsoil, Bayes-LSD = 4.7

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Progress Report: 1979-1980

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 1979 in the research program on the Chemical Analysis of Inputs and Outputs on Oil Shale Retorts. The project is headed by Thomas Wildeman from the Department of Chemistry/Geochemistry of the Colorado School of Mines. Co-investigators on the project are Alice Laffoon, Kenneth Dahlin, Douglas Ramsey, and Steven Halvorson, who are all students at the Colorado School of Mines. This year the primary emphasis of the research has been on retort waters from the Paraho operation. Initial analyses on the major constituents in these waters showed that standard analyses for the major constituents worked satisfactorily except for sulfur analyses (1). Sulfur species have already proved to be of great interest in leachates from spent shale (2, 3). Thus the total amount of sulfur as well as the amounts of different sulfur species are of interest. Also, a program for the analysis of trace elements in the water was carried out. These analyses used an energy dispersive x-ray fluorescence (EDXRF) technique that had been developed for liquid samples (4). The trace element of greatest interest which cannot be detected by EDXRF is mercury, so development work on a method of analysis for mercury in the retort waters was also necessary. Finally, the indicative tests of Eh, pH, and conductivity on the waters appeared to be good measures of the chemical state of the water. It was decided to do studies which would relate these tests to chemical parameters such as total dissolved solids, the acid buffering capacity of the water, and the reducing capacity of the waters. The next section shows how these activities fit into the overall objectives of the project.

OVERVIEW AND GENERAL OBJECTIVES

The evolution of the objectives for this project were described in last year's progress report (5). Originally, the objectives of this project emphasized obtaining a mass balance for each element between the original oil shale and final products. This objective has changed to the analysis of oil shale materials to uncover the chemical relations in the raw shale and see if any of these relationships change during retorting in such a way that unusual concentrations of elements occur in the products. This approach to the question of redistribution and release of elements during oil shale retorting is also seen in recent papers by Dr. Phyllis Fox (6) and Dr. Jon Fruchter (7). The emphasis in these papers and in our original paper on mass balances on Fisher assay analyses (8) is to analyze the products to find what has been mobilized and released from the raw shale into other products. For example, in all three studies just mentioned (6, 7, 8), all the As in the raw-shale can be accounted for in the retorted shale to within an uncertainty of $\pm 10\%$. However, hidden in this uncertainty is the fact that all three studies show that arsenic is mobilized from the raw shale and released to the oil and retort water so that the levels may be harmful to the workers or to the surrounding environment. This condition of relatively small releases of elements during retorting still causing concentrations of potential harm in the products and by-products changes the methods of study for the environmental effects of oil shale retorting. Now, the objectives logically turn to determining the relation of arsenic in the water and oil to other elements in these materials. If trends can be established, then the detection of high levels of one species in water may signal high concentrations of other species. Another important objective is now to find if there is a relation between arsenic in the oil and water and arsenic or some other constituent in the raw shale. A third objective is to see if certain retorting conditions will change the amount of arsenic released to the products. Finally, there is the objective of determining whether special treatment methods will be needed to eliminate harmful constituents from the products.

This development of objectives used arsenic as an example, but there are other elements and species that are of interest to this project. The constituents that are of most interest include boron, fluorine, sulfur, zinc, selenium, molybdenum, cadmium, mercury, and lead. Dr. Fox (6) reports that H, N, S, Cd, Hg, C, Se, Ni, As, and Co have a mobility of one percent or more during oil shale retorting. Dr. Fruchter (7) reports that H, C, N, S, As, Co, Hg, Ni, and Se are redistributed to an extent greater than one percent during the operation of the Paraho retort. The question of which elements to study can be broken down into four categories:

1. Those species that do show mobility, such as those mentioned above.
2. Those species that are chemically related to the mobile elements. For example, Cd and Hg show mobility and Zn is closely related to these two elements so its behavior is of interest.
3. Those species which other research groups consider to be of interest. This group includes B, F, and Mo.
4. Those species which may be the key to uncovering why specific species are mobile and others are not. Presently our research group is concentrating on sulfur to see if it is the key.

There is an important procedural objective that has to be employed to achieve the research objectives stated above. If trends and relationships are to be established, then it is necessary to analyze a suite of samples and not just one set of samples obtained under one set of retort conditions. One has to have variety in the composition of the samples or in the retort conditions so that variety will appear in the composition of the products. Presently, this research project is studying a suite of samples secured from the Paraho Retort in the Summer of 1977. The suite includes matched samples of raw shale feedstock, retorted shale, oil, and product water (9, 10). The virtue of this procedure of studying a suite of samples can be seen in the results found in the raw and retorted shales from the Paraho Retort (5, 10). Statistical analysis of the results of the suite of samples showed that there was an organic portion to oil shale that was not related to the other elements; a sulfide portion that contained Cu, Ni, Pb, As, and Mo; and a lithophite phase that contains Ca, Fe, Mn, Rb, Si, Y, Ba, Ga, and Nb. The capability of performing statistical tests on a suite of samples allows these conclusions to be made.

THIS YEAR'S OBJECTIVES

The primary subject of study this year was the Paraho retort waters and the general objectives stated above dictate how the study was made. The analyses were performed on a suite of samples. In this case, two different suites of water were analyzed and they represent different points of collection on the retort. The analyses included the use of EDXRF as a multi-element technique so that possible elemental relationships could be uncovered. The preliminary analyses of Paraho waters showed that the major constituents were uniform in composition, and so a study was undertaken to see how the indicative tests of Eh, pH and conductivity could be related to these major constituents. Sulfur analyses on the waters proved to be interesting but also difficult. Therefore, a method for the analysis of total sulfur in oil shale materials was developed and used for the analysis of retort waters.

Along with the primary objective of analysis of waters, two other tasks have been undertaken this year. It is important that the capability for analysis of mercury be developed in our project, and so the development of a method was started this year. The interest in sulfur in oil shales and how it is mobilized during retorting lead to the Mössbauer analysis of a suite of raw and retorted oil shales.

All of these activities are discussed in this report except for the Mössbauer study. It is planned that the results of the Mössbauer study will be given at the 13th Oil Shale Symposium in April 1980 (11). The sections of the report include:

1. CHARACTERISTICS AND MAJOR CONSTITUENTS IN PARAHO WATERS
2. COMPARATIVE METHODS FOR DETERMINING SULFUR IN OIL SHALES
3. ANALYTICAL RESULTS ON RETORT WATERS
4. THE ANALYSIS OF SULFUR IN RETORT WATERS
5. TRACE ELEMENTS IN RETORT WATERS
6. ANALYSIS OF MERCURY IN OIL SHALE MATERIALS
7. INDICATIVE TESTS ON RETORT WATERS.

PROFESSIONAL ACTIVITIES

There were many talks presented and papers written in 1979, since this year marked the close of the first grant period for the ETSRP oil shale project. During 1979 four presentations were made at regional and national meetings (12, 13, 14, 15) and four papers were submitted to journals or symposium proceedings (1, 10, 16, 17).

CHARACTERISTICS AND MAJOR CONSTITUENTS IN PARAHO WATERS

In the summer of 1977, members of the Environmental Trace Substances Research Program (ERSRP) were given the opportunity to do environmental studies on the Paraho Retort under a grant from the Department of Energy. This retort is an above-ground operation located at Anvil Points near Rifle, Colorado and is operated by Development Engineering Inc. (DEI) for the Paraho Corp. One of the studies which was conducted was a program to characterize as well as possible the inputs and outputs of the retort. For this program extensive sampling of solids and liquids was performed (9). Among the samples were waters collected from eight different sites associated with the retort operations. This report describes the retort, the locations of the sampling sites, and the general differences among the waters collected at each site. Then the analyses of the major constituents in the waters are

Figure 1. A schematic diagram of the Paraho Retort for the direct heated mode. The three sites where water samples were taken are shown in the diagram.

described and the results presented. Finally, the measurement of conductivity of the waters and the analysis of sulfur in water is discussed.

PARAHO RETORT OPERATIONS

General Description

A schematic diagram of the 10½ foot O.D. Semi-Works retort is shown in Figure 1 (18, 19). The Direct Mode operation, where combustion occurs within the retort to provide necessary heat, is portrayed in this schematic diagram. Operations are continuous and flows are countercurrent. Gases flow upward. The downward flow of shale is controlled by a hydraulically-operated grate mechanism. Shale is distributed evenly across the top of the bed by a rotating distributor. Here, the shale is preheated by rising hot gases in the mist formation zone. Next, the preheated shale passes through the retorting zone where the organic kerogen is decomposed into oil, gas, and coke. The coke remaining on the retorted shale serves as fuel in the combustion zone. Air is distributed evenly across the bed in an air-gas mixture in this zone. In the lower section of the retort, the shale is cooled by bottom recycle gas and this gas, in turn, is preheated before entering the combustion zone. The oil, as a stable mist, is carried out the top of the retort through the off-gas collector and is separated from the gas in a coalescer-electrostatic precipitator system.

In the Indirect Mode operation, the gas blower is replaced by an external heater. The middle and upper recycle gas is passed through this heater to provide heat needed for retorting. In this mode, the product gas is not diluted with products of combustion and nitrogen from the air, and the carbon remaining on the retorted shale is not utilized. All of the sampling was done while the retort was operating in the Direct Mode.

Water Sampling Sites

The numbers in the title of each subsection refer to the actual samples of water associated with each site.

Retort Waters (LPW-116, RC-139, RC-141)--

Water can be collected from at least three places on the retort. These are shown as sites A, B, and C in Figure 1. Site A on the retort is the first place where water is condensed from the gases which leave the retort column and sites B and C are successively later sites where condensate can be extracted from the gas recycle line. At site A the oil and a small amount of water is separated from the gas in a coalescer-electrostatic precipitator system. This liquid

can be directed into an eight hour shale-oil storage tank. The sample LPW-116 is actually collected at the storage tank and has been in contact with product oil for eight hours or more. Nevertheless, this site represents the first place where it is reasonably possible to collect condensate that has come from the retorting column. Site B is at the blowers on the recycle gas line. The blowers compress the gas after it has left the oil-gas separator unit and this causes condensation of more liquid. At this site the condensate is mostly water rather than organic liquids. Sample RC-139 is this blower condensate. Site C is a recycle gas sampling line whose diversion point is after the discharge side of the blowers. It is possible to collect condensate from the recycle line by sending the vapor through gas washing bottles that are cooled in an ice bath. This recycle condensate is RC-141.

Oil Storage Waters (M-102, M-103)--

During normal operations, liquid product is allowed to sit in a 1000 bbl holding tank for 1-3 days to obtain a maximum separation of water. Then the water is drained from the holding tank and the oil is pumped to the Navy storage tanks. Portions of the water in this settling tank are possibly from the first day of operation because the water is never completely drained. This holding tank sample is M-102.

The liquids from the drainage of the recycle gas blowers and the other miscellaneous retort discharges are accumulated in a settling tank and labeled as process water. The relation of the process water to the product water is unknown because there is no control over what may be a miscellaneous discharge. For example, often the blowers and other portions of the gas recycle line are steam cleaned and the condensate from this cleaning would probably end up in the process water settling tank. The process waste water sample is M-103.

Evaporation Pond Waters (M-107, M-108, M-109)--

An evaporation pond for the Anvil Points retort operations lies in an arroyo about 200 feet below the retort. There are two water streams which discharge into the pond. Waste water from general operations as well as the process and product water tanks discharge into the pond. This discharge accounts for the majority of the water in the pond. Sample M-107 is the discharge into the pond from retort operations. The pile of retorted shale from Anvil Points operations lies along the banks of the arroyo just upstream from the evaporation pond. Meteoric or surface waters which may leach through the retorted shale pile are diverted by channels into the evaporation

pond. At one of the sampling times, there just happened to be water flowing in these channels. Sample M-109 is water taken from the channel at the discharge point into the pond. The pond water itself was taken as a grab sample from the middle of the pond. It is sample M-108.

EXPERIMENTAL PROCEDURES

Handling, Preparation and Storage

Previous encounters with handling retort waters experienced by this group (8, 14) and others (20, 21, 22) have shown that the collection and preparation of these samples is not routine and uniform procedures are not available. This group as well as other research groups have recently discussed the various aspects of sampling, handling, and quality assurance of oil shale materials at an EPA symposium in Denver in March 1979 (14). The proceedings of that symposium should be available soon. A detailed description of handling and storage procedures for these samples is available (9).

In general, the philosophy on handling and storage was that complete preservation of the samples is impossible and furthermore a universal water sample is also impossible. Consequently, the sample was split into specimens which have been handled and stored in different ways. An objective of this procedure is to see how much of a difference handling and storage procedures can make.

For samples LPW-116, RC-139, M-102, and M-103, the samples were filtered by gravity through cotton to adsorb oil globs. Then specimens were prepared and stored in eight 1-ounce polyethylene bottles by each of the following methods: refrigeration, freezing, N₂ gas bubbling and refrigeration, N₂ gas bubbling and freezing. None of the specimens were acidified. For the pond waters M-107, M-108, and M-109, the samples were filtered through 0.45µm filters. Then, specimens were prepared and stored in eight 1-ounce polyethylene bottles by each of the following methods: acidified with 0.5 ml of 1:1 HNO₃ per 100 ml of water and frozen, acidified and refrigerated, unacidified and frozen, unacidified and refrigerated. None of the specimens were bubbled with N₂ gas.

On-Site Tests

The on-site tests made on the waters are the typical field tests which can be performed immediately upon collection. The results are presented in Table 1. The tests are described below.

pH--

The pH of the waters was determined immediately upon

TABLE 1. Characteristics and concentrations of some major constituents in Paraho water.

Sample No.	Analysis Date	Handling & Storage	pH	Eh mV	Cond millimho cm	Alkalinity				NH ₃ in mg/mL	S ₂ O ₃ ⁼ mgS/mL	Total S mgS/mL
						high pH	meq/mL	low pH	meq/mL			
LPW-116	9/77	Initial	8.88	-66	---	--	--	--	--	---	--	--
	6/78	R	9.16	89	164	7.70	0.080	3.65	0.720	23.1	9.25	27.1
	7/78	R	8.86	19	234	7.62	0.105	3.75	0.703	22.3	6.80	31.4
	6/78	N ₂ ,R	9.15	79	164	7.70	0.090	3.70	0.720	23.5	9.25	30.9
	7/78	N ₂ ,R	8.63	132	224	7.58	0.112	3.65	0.705	22.7	7.17	29.2
	6/78	F	8.78	44	123	7.70	0.092	3.75	0.726	19.5	7.28	31.1
	7/78	F	8.64	34	230	7.92	0.038	3.65	0.730	21.6	7.17	27.8
	6/78	N ₂ ,F	8.75	19	123	7.70	0.092	3.70	0.762	23.7	7.28	30.3
	7/78	N ₂ ,F	8.54	34	226	7.65	0.082	3.87	0.705	22.7	7.02	27.1
RC-139	9/77	Initial	8.95	-176	32.5	--	--	--	--	---	--	--
	6/78	N ₂ ,R	9.20	202	39.6	7.65	0.110	4.40	0.408	7.35	2.19	--
	7/78	N ₂ ,R	8.94	214	50.0	7.85	0.113	4.55	0.413	7.35	1.96	0.1
RC-141	9/77	Initial	8.70	-166	--	--	--	--	--	---	--	--
	6/78	N ₂ ,R	8.56	246	126	7.60	0.430	4.55	1.71	25.1	0.130	=0
	7/78	N ₂ ,R	8.76	266	194	7.75	0.395	4.25	1.73	23.5	0.151	0.2
M-102	9/77	Initial	8.80	-6	--	--	--	--	--	---	--	--
	6/78	R	8.97	94	190	5.74	0.333	3.57	0.618	30.0	23.3	42.5
	7/78	R	8.60	62	314	7.25	0.119	3.55	0.594	28.8	21.2	41.7
	6/78	N ₂ ,R	9.07	104	298	5.74	0.280	3.42	0.568	28.2	22.9	41.2
	7/78	N ₂ ,R	8.80	64	253	7.25	0.118	3.60	0.615	29.4	21.4	42.8
	6/78	F	8.63	29	149	5.74	0.296	3.72	0.528	23.6	9.7	45.4
	7/78	F	8.60	104	173	--	--	--	--	29.8	26.0	--
	6/78	N ₂ ,F	8.68	14	172	5.74	0.368	3.57	0.656	29.3	22.7	45.0
	7/78	N ₂ ,F	8.68	106	316	--	--	--	--	29.5	19.8	34.0
M-103	9/77	Initial	9.40	144	--	--	--	--	--	--	--	--
	6/78	N ₂ ,R	8.93	219	45.8	7.23	0.071	4.06	0.217	7.60	4.87	1.1
	7/78	N ₂ ,R	8.83	214	68.2	7.30	0.075	4.00	0.223	6.72	3.80	6.5
M-107	9/77	Initial	7.70	279	2.00	--	--	--	--	--	--	--
	6/78	R	7.50	354	2.56	5.80	0.0022	4.75	0.0039	=0	=0	=0
	7/78	R	7.65	384	3.52	--	--	5.20	0.0035	0.03	0.01	=0
M-108	9/77	Initial	3.13	234	2.500	--	--	--	--	--	--	--
	6/78	F	3.56	294	3.60	--	--	5.08	0.0053	=0	0.045	=0
	7/78	F	3.68	334	4.80	--	--	5.35	0.0062	0.10	0.039	0.1
M-109	9/77	Initial	3.00	284	1.61	--	--	--	--	--	--	--
	6/78	R	7.36	394	2.74	--	--	4.32	0.0029	0.09	0.092	=0
	7/78	R	7.26	424	3.20	--	--	5.20	0.0026	0.08	0.083	0.3

collection in accordance with ASTM Test for pH of Water and Wastewater (D 1293-65) (23). A Leeds-Northrup Model 7417 meter was used; this is a Type I meter. A combination glass electrode with a Ag/AgCl reference provided stable readings.

Eh (Oxidation-Reduction Potential)--

The Eh or Oxidation-Reduction potential of the water was determined immediately upon collection in accordance with ASTM Practice for Oxidation-Reduction Potential of Water (D-1498-76) (23). A Leeds-Northrup Model 7417 meter was used; this is a Type I meter. A separate electrode system consisting of a platinum button for the inert electrode and a saturated calomel electrode for the reference gave reliable results. This group has had little success using combination redox electrodes. Since many of the measurements were made in the field, the indirect calibration procedure was used and the reference cell value for the calomel electrode of +.0244 volts was added to the field readings (24). In accordance with the geochemical literature, the values are reported in millivolts and termed Eh.

Conductivity--

Measurements of the conductivity of the waters were attempted in accordance with ASTM Test for Electrical Conductivity and Resistivity of Water (D-1125-77) (23). A YSI Model 33 dip-type portable conductivity meter which had a cell with a constant of 5.0 cm^{-1} was used. This meter extends to readings of 50 millimhos/cm and most of the retort waters had conductivities above that limit. The conductivity values for the pond waters were within the range of the conductivity meter. For these readings and subsequent readings, the temperatures of the solutions were maintained at $25 \pm 2^\circ \text{C}$.

Tests in the Laboratory

The tests made on the waters in the laboratory were performed almost one year after collection. The results are presented in Table 1. One objective of the study was to find out how collection and storage affected the concentrations of the major constituents. To test this, 1-ounce bottles were opened in June 1978 and a small portion taken for analysis. Then, the bottle was returned to the refrigerator and taken out for duplicate analyses in July, 1978. The correlation of results from different splits and different analysis times gives a good measure of the precision of the analyses. The tests which were routine are described below. The tests for conductivity and total sulfur were not routine and will be described later.

pH and Eh--

These tests were performed in the same manner as for the on-site tests.

Alkalinity--

Measurements of alkalinity were made in accordance with ASTM Test for Acidity or Alkalinity of Water (D 1067-70) (23). The electrometric titration (Method A) was used. For these samples, two inflection points in the pH curve were encountered. The high pH inflection ranged from 7.7 to 5.7; the low pH inflection ranged from 4.7 to 3.4. Different splits of the same sample showed consistent pH values for the inflections but the pH values varied considerably from sample to sample.

Ammonia--

Measurements of NH_3 in the water samples were made in accordance with ASTM Test for Ammonia Nitrogen in Water (D 1426-74) (23). The distillation method followed by titration with sulfuric acid was used for the analysis. The end point of the titration was determined electrometrically.

Thiosulfate--

Thiosulfate ($\text{S}_2\text{O}_3^{2-}$) was determined by a colorimetric method which was originally developed for soil determinations (25). In the procedure $\text{S}_2\text{O}_3^{2-}$ is reacted with cyanide (CN^-) to form the thiocyanate ion (SCN^-), excess ferric ion (Fe^{3+}) is added and the ferric thiocyanate complex formed determines the amount of $\text{S}_2\text{O}_3^{2-}$ in the sample. The procedure has been readily adapted to waters and the results are reasonably precise. The relative standard deviation of duplicate samples is 3%. The method can also be adapted for the analysis of tetrathionate ($\text{S}_4\text{O}_6^{2-}$), but no determinations of $\text{S}_2\text{O}_3^{2-}$ were made on these samples.

CONDUCTIVITY TESTS

The measurement of the conductance of water is a useful guide to the total ion concentration of the solution. With the design of modern conductivity meters, the measurement is simple, rapid, and straight-forward. However, the conductivity of aqueous solutions increases by about 2% for every one degree Centigrade increase in the temperature of the solution (26, 27). This makes it difficult to achieve standard results especially if the measurements are made in the field. Nevertheless, differences in the conductivity of water samples measured under similar conditions give the easiest measurement of differences in ion concentration. Consequently, the test is quite useful.

When an attempt was made to measure the conductivity of the retort waters the high concentration of ions caused the upper limit of the meter to be exceeded. Fortunately, a method which proved quite acceptable was devised to overcome the problem. An aliquot of the water sample was diluted by

a factor of 100 so that the value read on the conductivity meter was no more than 5,000 $\mu\text{mho/cm}$. Then this value, multiplied by 100, was used as the conductivity. In this manner the conductivity could be measured without having to purchase a new meter or probe. The conductivity values listed in Table 1 were measured by this procedure.

This dilution procedure has theoretical merits which perhaps make it preferable to a measurement of the actual solution. The usefulness of a conductivity measurement is to assess the concentration of ions. Some of the retort water samples listed in Table 1 have conductivities exceeding 100,000 $\mu\text{mho/cm}$. The concentration of ions in these solutions exceeds one equivalent per liter. At this high a concentration, conductivity measurements are affected by ion pair formations and solvent sphere interactions as well as ion concentrations (26). Dilution of the solution down to 0.01 equiv/liter eliminates the side effects and allows a better measure of the ion concentration. Typically, there will be a straight line relation between concentration and conductivity up to about 5,000 $\mu\text{mho/cm}$ (27). Consequently, dilution of the sample so that the conductivity reading is in the range of 100 $\mu\text{mho/cm}$ may be the best way to proceed.

TOTAL SULFUR TESTS

The measurement of total sulfur in the retort waters has been difficult to perform. The results presented in Table 1 may be inaccurate even though they appear to be precise. All of the methods which we have used rely on a barium sulfate (BaSO_4) precipitation. The problem is that small variations in the method of preparing the water sample prior to analysis have caused inexplicable variations in the results. The methods used are summarized below:

Precipitation Methods

Method A--

A suitable aliquot of sample was diluted to 50 ml with H_2O . A 40 g portion of cation exchange resin in the Na^+ form was added to the solution, stirred, and then left to sit for $\frac{1}{2}$ hour. The resin was filtered from the mixture and washed three times so that the volume of the filtrate was 150 ml. This solution was evaporated down to 25 ml, 6 ml of HCl and 2 ml of HNO_3 were added, and the solution was heated to just below boiling on a hot plate for 1 hr. The volume of the solution was adjusted to 50 ml and the BaSO_4 precipitate was formed in accordance with ASTM Test for Sulfate Ion in Water and Wastewater (D-516-68) (23).

Method B--

The method proceeds in the same way as Method A through the resin step. After the resin step the same quantities of HCl and HNO₃ were immediately added to the filtrate and the solution was warmed to just below boiling for 1 hr. Then the BaSO₄ precipitate was formed.

Method C--

The 6 ml of HCl and 2 ml of HNO₃ were added immediately to a suitable amount of sample. The solution was evaporated almost to dryness on a hot plate. Then it was diluted with 50 ml of water and 4 m of NaOH was added to the solution until it was neutral. Then, the resin step was performed. The filtrate from the resin separation was warmed and the BaSO₄ precipitate was formed in the usual manner.

Discussion of the Sulfur Results

All of the total sulfur results reported in Table 1 were done by Method A. This was chosen because it gave the highest value. In Table 2 the weight in grams of BaSO₄ precipitated per milliliter of retort water is presented for various specimens analyzed by various methods. The results in Table 2 were so disturbing that it was decided to try Methods A and C on various mixtures of solutions of Na₂SO₄ and Na₂S₂O₃ in which the concentration of total sulfur was 25.0 mg S/ml. The results of the analyses on the SO₄²⁻ and S₂O₃²⁻ solutions are presented in Table 3. In addition to all of these experiments, a procedure was tried which uses Br₂ in CCl₄ for the oxidation of sulfur species in solution. It also gave unreliable results.

Study of the results presented in Tables 2 and 3 makes it clear that none of the three preparation methods are reliable. Method A was reported in Table 1 because it appears the other methods do a poorer job of converting reduced sulfur species to sulfate. However, the results in Table 3 imply that Method A doesn't even completely convert S₂O₃²⁻ to SO₄²⁻. If one cannot determine the amount of total sulfur in the water then a sulfur balance cannot reliably be made. If a sulfur balance cannot be made then the relative amounts of the various sulfur species in the water are uncertain. Reduced sulfur species such as S₂O₃²⁻, SO₃²⁻, and S₄O₆²⁻ will definitely play important roles in determining how retort waste waters should be treated (22, 28, 29). An accurate and precise method for the analysis of total sulfur in waters of this type is urgently needed.

DISCUSSION OF THE RESULTS

In general, the major constituents in the retort water

TABLE 2---Weight of BaSO₄ in grams precipitated from retort waters using different methods of sample preparation.

Water Sample	Handling & Storage	Analysis Date	Gram of BaSO ₄ Preparation Methods		
			A	B	C
M-102	R	6/78	0.309		0.246
			0.298		0.246
			0.273		
M-102	R	7/78	0.304		0.257
M-102	N ₂ , R	6/78	0.299	0.252	
			0.300	0.232	
M-102	N ₂ , R	7/78	0.312		0.272
LPW-116	F	6/78	0.226	0.152	
LPW-116	F	7/78	0.202		0.148
LPW-116	N ₂ , F	6/78	0.221	0.136	
LPW-116	N ₂ , F	7/78	0.197		0.157

TABLE 3---Percent of sulfur precipitated from mixtures of Na₂SO₄ and Na₂S₂O₃ solutions. The total amount of sulfur is 25 mg.

Percent of S as Na ₂ SO ₄	100	75	25	0
Percent of S as Na ₂ S ₂ O ₃	0	25	75	100
Percent of S Recovered by Method A	107	95.3	72.5	71.3
Percent of S Recovered by Method C	100	90.0	76.5	67.3

samples were not affected by the method of preparation and storage or by aging for one month. There are some aberrant results for M-102 and RC-139, but these appear to be the exception. The values for the pH, Eh and conductivity do appear to be affected by preparation, handling, and aging. The trends in most cases are to lower values of pH, higher values for conductivity, and to higher values for Eh. Based on a comparison of initial values of pH and Eh for M-102 and LPW-116, it appears that freezing the samples preserves the original values better than does refrigeration. However, after the samples have been opened for one month there is little difference in any values of Eh, pH, and conductivity among the four methods of preparation and storage.

The measurement of Eh and the values generated deserve special comment. The on-site tests for Eh gave reproducible and consistent results for the waters collected from site A on the retort. Thirteen waters were tested and the values ranged from -95 mV to +34 mV. The consistency leads one to believe that these waters contain an oxidation-reduction couple that is responsive to a platinum electrode. Examination of the literature on sulfur species in waters would suggest that the couple $\text{SO}_3^{=}/\text{S}_2\text{O}_3^{=}$ is a likely candidate (29). Indeed, equimolar solutions of $\text{SO}_3^{=}$ and $\text{S}_2\text{O}_4^{=}$ have Eh values of -60 mV at pH=8 and -120 mV at pH=9 (30). Whether the $\text{SO}_3^{=}/\text{S}_2\text{O}_3^{=}$ couple reacts reversibly at a platinum electrode will need to be checked by experiment. In any case the possibility of a reactive oxidation-reduction couple in retort waters is quite important. This couple is capable of intrinsically stabilizing the water sample so that reduced species will not be subjected to a disequilibrium environment which causes oxidation. Also, if the oxidizing capacity of a retort water can be established, then theoretical calculations can be made on what species of trace constituents are possible in the water. Specifically, this would be important to the determination of which species of arsenic, selenium, and molybdenum should be the major constituent in retort waters.

The water samples from the evaporation pond are quite different from the retort waters. The low values of NH_3 and $\text{S}_2\text{O}_3^{=}$ in the sample from the operations discharge (M-107) imply that either these two species have been eliminated from the product and process waters (M-102 and M-103) or that this discharge is diluted with large amounts of water from the general operations. The discovery of thiosulfate in the leachate from the retorted shale pile (M-108) is significant. Thiosulfate is a constituent of leachates from retorted shale investigations tried in the laboratory (2, 3). This is perhaps the first report of $\text{S}_2\text{O}_3^{=}$ occurring in water leached from an actual pile of retorted shale. The occurrence of this species in waters makes the chemistry of that system quite unlike typical natural waters (2, 3, 27, 28, 29, 30).

COMPARATIVE METHODS FOR DETERMINING SULFUR IN OIL SHALES

Oil shale, in addition to its hydrocarbon components, contains nitrogen, oxygen, and sulfur compounds which cause refining problems (37). These problems are related to the actual retorting process where oil shale solids are heated to temperatures near 500°C. Heat allows the transfer of elements from the solids to the crude oil products. However, the analysis of these elements presents many problems resulting from a complicated oil shale matrix composed of silicates, organics, pyrite, and a variety of other minerals (32).

Determining the total sulfur content of oil shales is an example of such an analytical problem. The total sulfur content is desirable for material-balance studies; however, two problems hinder the analysis. One is the wide variety of sulfur forms, including pyrite and organic sulfur compounds, found in oil shales. This combination of sulfur forms requires a method of analysis in which all sulfur compounds are either oxidized to the sulfate form or reduced to the sulfide form. A second problem, further complicating the analysis, is the high organic content of the oil shales which prevents the use of conventional digestion procedures without the possible loss of volatiles.

No methods exist for analyzing total sulfur in oil shales making it necessary to adapt methods for similar materials, such as coal and fuel oil, to the analysis of oil shales. This study provides a comparison of several methods that can be adapted for oil shale analysis and determines whether there is a practical in-lab method which yields reliable results. This study encompasses the American Society for Testing and Materials (ASTM) method D-3177, several different fusions, a Leco sulfur analysis and a Fisher sulfur analysis.

EXPERIMENTAL

In this study, both retorted and unretorted oil shales were analyzed by several methods. The ASTM D-3177 method and several different fusions were chosen for the in-lab methods. Analyses on a Leco Sulfur Analyzer and on a Fisher Sulfur Analyzer were conducted for comparison. Experimental procedures were as follows.

Collection Methods

The samples used in this study were collected from a Fisher Assay retort and from a TOSCO Modified Fisher Assay (8). The spent shales from the Fisher Assay and both raw shales and spent shales from the TOSCO Assay comprised the samples used in this study.

The original oil shale was acquired from the Dow Mine of the Colony Development Company at the head of Parachute Creek in the Piceance Creek Basin, Colorado. Pulverizing was carried out in a shatter box with hardened steel or tungsten carbide grinding chambers, to minimize contamination. At the completion of grinding and splitting, samples were stored in a refrigerator (8).

ASTM D-3177 Method

Described in the 1977 Annual Book of ASTM Standards (33), the ASTM method for total sulfur analysis was followed closely, with the exception of a few minor variations. The first variation was that the samples were retained in the muffle furnace at 800°C for 2 hours as opposed to the recommended 1½ hours. In addition, the Methyl Orange indicator solution, prepared as directed, was not concentrated enough to hold its color in solution with the oil shales. As an alternative, a saturated solution of Methyl Orange in distilled water was used with satisfactory results. Another variation in the standard procedure involved filtering the BaSO₄ precipitate. In opposition to the conventional filtration with ashless filter paper, followed by ignition of the paper in a muffle furnace, the BaSO₄ precipitate was filtered with a pre-weighed millipore filter and dried in a desiccator with Drierite desiccant. Except for these alterations, the ASTM D-3177 procedure was followed closely.

Fusion Methods

Three different fusions were attempted. The first involved the fusion of a mixture of 0.5 grams of oil shale sample and approximately 3.0 grams of Na₂O₂. Another method attempted was the fusion of 0.5 grams of oil shale mixed with about 0.5 grams of Na₂CO₃ and approximately 2.5 grams of Na₂O₂. The last of the fusion methods involved a mixture of 0.5 grams of oil shale, about 0.5 grams of LiBO₂, and approximately 2.5 grams of Na₂O₂. All fusions were carried out in zirconium crucibles.

Leco Sulfur-Analysis Method

A Leco sulfur analyzer, a product of Leco Corporation, was used in determining total sulfur in the oil shale samples. The induction furnace used was a Leco Model 521, equipped with "L" modification on the combustion chamber. Titration of the products was accomplished on a Leco Semi-Automatic Titrator Model 518. The procedure of analysis for this study is detailed in the instruction manual for the Leco Model 521, available from Leco Corporation. Standardization was accomplished through use of a National Bureau of Standards (NBS) fuel oil standard, NBS-1621. Figure 2 illustrates the features of the furnace on the Leco sulfur analyzer (36).

Figure 2: The induction furnace on the Leco Sulfur Analyzer

Fisher Sulfur-Analysis Method

Analyses of the oil shale samples, on a Fisher Model 470 sulfur analyzer, were conducted by Huffman Laboratories, Inc., in Wheatridge, Colorado. Total sulfur analyses were completed by the procedure described by the instruction manual for the apparatus. According to Dr. Edward Huffman, a variety of organic and inorganic standards were used to standardize the sulfur analyzer. Figure 3 describes the basic elements of the Fisher sulfur analyzer (35).

RESULTS AND DISCUSSION

All results of the study are available in Table 4, where a comparison of methods may be made. Discussions of the results for each method follow.

ASTM D-3177 Method

Results from the ASTM method were very close to those obtained through the use of the Fisher sulfur analyzer. The close comparison of the results indicates that the Leco method is a reliable in-lab method that compares favorably with the type of mechanical analysis most often used in analytical labs. However, as illustrated in Table 5, the ASTM method failed to give reliable results for the analysis of various standards. Here, accuracy was a problem, with the ASTM method results considerably lower than the results obtained with the Fisher sulfur analyzer.

A possible explanation for the low-standard results of the ASTM method may be the oxidation process itself. In the ASTM method, oxidation is accomplished through the use of a sintering material in an open crucible. The heat may have caused the volatilization of some of the standards, allowing the resulting gases to escape from the open crucible before they were oxidized. These results seem to favor closed systems such as the Leco and Fisher sulfur analyzers. However, the close results of the open-system ASTM procedure and the closed-system Fisher sulfur analyzer also indicate that for the analysis of total sulfur in oil shales, a small amount, if any, of the volatiles are lost. This consideration makes the ASTM method an adequate procedure for the determination of total sulfur in oil shales.

Fusion Methods

All of the fusions attempted were dismissed as unacceptable procedures for two reasons. The first is the extreme difficulty of a quantitative transfer of the molten fusion. When the molten samples were poured into distilled water, excessive splattering resulted in the mechanical loss of material. The

Figure 3: A block diagram of the Fisher Sulfur Analyzer

TABLE 4---Results of Analysis of Total Sulfur on Oil Shales:
(wt/wt) % Total Sulfur.

Sample	ASTM D-3177 Method	Leco Method	Fisher Method
TOSCO-Unretorted			
OS-1	0.99	1.26	1.11
split 18	1.10	1.21	-
OS-1	1.12	1.20	1.13
split 24	1.14	1.25	-
OS-1	1.13	1.23	1.11
split 10	1.12	1.18	-
TOSCO-Retorted			
SS-2	1.06	1.13	1.06
split 13	1.02	1.30	-
SS-2	1.04	1.20	-
split 10	1.04	1.19	-
SS-2	1.03	1.17	1.01
split 16	1.03	1.18	-
Fisher-Retorted			
FASS	0.80	0.91	0.84
split 19	0.83	0.95	-
FASS	0.84	0.98	-
split 13	0.89	-	-
FASS	0.83	0.91	0.82
split 2	0.83	0.97	-

TABLE 5---Analysis of Standards (wt/wt) % Total Sulfur.

Sample	ASTM D-3177 Method	Leco Method	Fisher Method
2% Sulfur	1.67	2.28	2.01
(S, Al ₂ O ₃)	1.61	2.18	-
2% Sulfur	1.38	2.26	1.90
(Thioacetamide, Al ₂ O ₃)	1.46	2.24	-
2% Sulfur	1.61	2.35	1.91
(Thiourea, Al ₂ O ₃)	1.60	2.16	-

second is the possible loss of volatiles at such high temperatures. Problems dealing with fusions of oil shales are expressed by T.R. Wildeman and R.R. Meglen (8):

"The high organic content of these shales complicate the conventional basic salt-fusion techniques which are supposed to render the silicates soluble. The temperatures required for these fusions are so high that the organic constituents and volatile trace elements are lost during the heating process. This occurs at a temperature below the nominal fusion temperature."

In addition, fusions have a problem where the flux "introduces a large quantity of alkali salts into the solution and therefore gives greater coprecipitation errors" (34). As a result of these problems, fusions were discarded as possible methods for determining total sulfur in oil shales.

Leco Sulfur-Analysis Method

Results of the analysis of the oil shale samples on a Leco sulfur analyzer appear to be considerably higher than the results from the other methods. Even the results of the analyses of the standards, Table 5, indicate higher values. The high values are possibly due to the problems encountered in standardization. The Leco sulfur analyzer is first calibrated with a standard of known sulfur content. For the calibration to be valid, a standard very similar to the samples, in terms of matrix, must be chosen. However, a close standard-sample correlation is impossible since there are no oil shale standards available. Because the oil shale matrix is complex, composed of a wide variety of materials, creating a standard oil shale is difficult. The calibration of the Leco sulfur analyzer is a very important part of the determination because a calibration factor is introduced into the calculation of the total amount of sulfur in the sample. The ASTM Committee D-5 also found the Leco or induction furnace method unsatisfactory for total sulfur determinations (31).

Fisher Sulfur-Analysis Method

Results of this method of analysis are very typical of those results obtained with the ASTM method. However, the results of this closed-system method are considerably different from the results obtained with the other closed-system method, the Leco sulfur analyzer. According to Dr. Edward Huffman, of Huffman Laboratories, Inc. (1979), the Fisher sulfur analyzer appears not to have the same standardization problem encountered with a Leco sulfur analyzer. Dr. Huffman contends that a difference in the methods of combustion probably accounts for this variation in calibration requirements between

the two methods.

In the Leco sulfur analyzer, an induction furnace produces SO_2 gas at temperatures of approximately 1300°C . However, some of the sample may not be combusted at 1300°C if the sample leaves the sample cup before complete combustion. If combustion of parts of the sample occurs much lower than approximately 1000°C , SO_3 is produced. Since SO_3 is not titrated in the titrating vessel, the resulting determination of total sulfur is inaccurate. In a Fisher analyzer, because a tube furnace is used instead of an induction furnace, not only the sample but also its surroundings are at temperatures close to 1300°C . Therefore, the sample is totally combusted at 1300°C , and all sulfur is converted to SO_3 .

The Leco combustion method demands that standard and sample have the same matrix because all samples will be combusted differently, some producing more SO_3 than others. Effectively, the Leco would not be determining the total amount of sulfur, but rather only a percentage of the total amount. The procedure relies on a standardization factor to predict the total sulfur content. However, in the Fisher analyzer, the combustion method aims at a total-sulfur content value, no matter what the sample. Therefore, the Fisher analyzer is not dependent on a standard for predicting the total-sulfur content.

CONCLUSIONS

On the basis of the findings of this study, both the ASTM D-3177 method and the Fisher sulfur-analysis method are adequate for determining total sulfur in oil shales. The ASTM method has the advantage of being an in-lab process, allowing more control over the determination. However, because the ASTM method seems to involve a possible loss of highly volatile sulfur compounds, it should be monitored by a second method.

Both the Leco sulfur-analysis method and the fusion methods are unsatisfactory procedures for determining total sulfur in oil shales. The Leco sulfur analyzer is inadequate because of its combustion method. The combustion procedure requires an impossible standardization because of the lack of oil shale standards. Fusions of the oil shale samples made analysis difficult because of splattering and loss of volatiles at the high-fusion temperatures.

ANALYTICAL RESULTS ON RETORT WATERS

The following tables contain all the results of analyses done on Paraho waters as of January 31, 1980. The locations for collection of the waters were described in the section on

PARAHO WATERS. The methods of collection, preparation and storage are also explained in that section of this report. Two complete suites of samples have been analyzed. They are:

1. The product waters which were collected at Site A in Figure 1.
2. The condensates from the blowers on the recycle gas line collected at Site B in Figure 1.

For the other sites, only selected samples from the complete suite have been analyzed so far. For the complete suite of water samples, the results are arranged according to the retort day. The results for each day are contained in Tables 6-11. For product water LPW-116 and blower condensate RC-139, a number of splits and duplicate samples were analyzed; these results are contained in Tables 12 and 13. The results on those process waters that have been analyzed are contained in Table 14. Table 15 contains the results on the pond waters that have been analyzed.

NOTES ON THE TABLES

Shift

The shifts for each day correspond to the following times (9):

Shift 1	0000-0800 hr.
Shift 2	0800-1600 hr.
Shift 3	1600-2400 hr.

For the product waters, the sample represents the water that was produced over the full eight hours. For the blower condensates the sample is a grab sample taken during the shift and is part of what was accumulated during the eight hours. The blowers are a seven stage configuration, but condensation accumulates primarily in the first stage and sometimes in the second. When a sample from stage 2 was collected, it is noted next to the shift number.

Preparation

The methods for preparation and storage are fully explained in the PARAHO WATERS section. The different methods are:

R	Refrigerated.
N ₂ R	Bubbled with nitrogen at collection time and refrigerated.
F	Frozen.
N ₂ F	Bubbled with nitrogen at collection time and frozen.

Whenever two or more samples of the same number were analyzed, an average was taken. The relative standard deviation (RSD) is the standard deviation divided by the average. The RSD is expressed as a percent.

Conductivity, Eh, pH

The methods of analysis for these three parameters are explained in the PARAHO WATERS section. The units for conductivity are millimho/cm; note that this is 1000 times the usual unit of micromho/cm. The units of Eh are millivolts. A large positive number represents an oxidizing condition for the water (27, 30). The values in the table columns represent the result of the analysis at the time the bottle was taken from storage. For the samples in Tables 6-11 this was during the Summer of 1979. For many of the samples these parameters were measured when the sample was collected. The values at the time of collection are recorded in the footnotes at the bottom of the Tables.

Alkalinity and NH_3

Analyses on alkalinity and NH_3 were performed in the Summer of 1978 on the samples that were used in the preliminary study. The analyses are described in the PARAHO WATERS section, and the results were listed in Table 1. For convenience, the results have also been included in Tables 12-15. The units for alkalinity are milliequivalents per milliliter (meq/mL). The units for NH_3 are milligrams per milliliter (mg/mL).

SCN^- , $\text{S}_2\text{O}_3^{2-}$, Total S

The analysis for $\text{S}_2\text{O}_3^{2-}$ was described in the PARAHO WATERS section and it relies on the reaction of $\text{S}_2\text{O}_3^{2-}$ with CN^- to form SCN^- . Dr. Leenheer of the U.S. Geological Survey suggested to our research group that SCN^- may be already in the waters (28). So an analysis for this sulfur species was made that skipped the addition of the CN^- . For both SCN^- and $\text{S}_2\text{O}_3^{2-}$ the units for the results are milligrams of sulfur per milliliter (mgS/mL).

Element Results (Fe-F)

Boron (B) and fluorine (F) were analyzed by the methods developed by Dr. Meglen of the ETSRP group. The procedures are described in the 1979 progress report (38). The analyses for the other trace elements were performed by the EDXRF method (4). In all cases the units for the results are parts-per-million (ppm) or milligrams per liter (mg/L).

INTERLABORATORY COMPARISON

The research group from Battelle Pacific Northwest Laboratory (PNL) was collecting samples on August 24, 1977 through August 26, 1977 (7). Some of the water samples that they collected were the same as this group's samples. The Process

TABLE 6.

Day 2		Product Waters and Recycle Waters						8/23/77	
Sample	LPW-101 ^a	LPW-101			LPW-102	LPW-102			
Shift	1	1			2	2			
Preparation	N ₂ R	R	Avg.	RSD	F	F	Avg.	RSD	
Conductivity	195	210	202	5	194	-	-	-	-
Eh	137	103	120	20	106	-	-	-	-
pH	8.41	8.42	8.41	1	8.42	-	-	-	-
SCN ⁻	0.423	0.443	0.43	3	0.445	-	-	-	-
S ₂ O ₃ ²⁻	13.7	12.8	13.2	5	12.3	-	-	-	-
Total S	40.2	40.7	40.4	1	37.93	-	-	-	-
Fe	4.57	4.60	4.59	1	8.26	5.21	6.74	32	-
Ni	0.70	0.41	0.56	37	0.50	0.31	0.41	33	-
Cu	-	0.11	0.11	-	5.69	5.67	5.68	1	-
Zn	1.59	1.59	1.59	1	18.6	18.4	18.5	1	-
As	4.11	3.91	4.01	4	10.4	10.0	10.2	2	-
Se	6.04	6.31	6.18	3	6.32	6.39	6.36	1	-
Br	0.12	0.21	0.17	39	0.15	0.15	0.15	1	-
Rb	0.21	0.16	0.19	19	0.17	0.17	0.17	1	-
Sr	0.71	0.68	0.70	3	0.67	0.63	0.65	4	-
Zr	-	-	-	-	-	-	-	-	-
Mo	0.17	0.20	0.19	11	0.36	0.35	0.36	2	-
Hg	0.23	0.46	0.35	47	0.15	-	0.15	-	-
Pb	-	0.22	0.22	-	-	-	-	-	-
B	0.9	1.1	1.0	10	-	-	-	-	-
F	2.5	2.5	2.5	1	-	-	-	-	-

Sample	RC-107 ^b	RC-109 ^b	RC-110	RC-112	RC-112		
Shift	1	2-Stage 1	2-Stage 2	3	3		
Preparation	F	F	F	F	F	Avg.	RSD
Conductivity	165	120	83	132	-	132	-
Eh	175	176	192	167	-	167	-
pH	8.25	8.62	8.41	8.42	-	8.42	-
SCN ⁻	0.925	0.840	0.625	0.810	-	0.810	-
S ₂ O ₃ ²⁻	14.0	11.0	12.7	12.8	-	12.8	-
Total S	34.6	24.6	16.2	28.5	-	28.5	-
Fe	250	110.3	9.5	8.20	18.1	13.1	53
Ni	5.9	-	0.15	-	-	-	-
Cu	27.2	7.5	2.50	4.48	6.02	5.25	21
Zn	9.31	11.0	1.63	4.77	17.0	10.9	80
As	8.3	5.1	3.31	1.92	2.04	1.98	4
Se	0.50	6.3	1.10	3.52	8.88	6.2	61
Br	2.05	1.41	0.28	0.31	0.19	0.25	34
Rb	-	-	-	-	0.05	0.05	-
Sr	2.59	2.89	0.43	2.14	1.45	1.8	27
Zr	0.15	0.29	-	-	-	-	-
Mo	0.79	-	-	-	-	-	-
Hg	4.88	1.63	0.34	-	-	-	-
Pb	5.16	2.67	0.61	0.49	0.49	0.49	1
B	2.8	5.5	2.4	8.6	8.5	8.6	1
F	<0.2	<0.2	0.6	<0.2	-	<0.2	-

^a For LPW-101, on 8/23/77, pH = 8.4, Eh = -6

^b For RC-107, Sn is 3.3 µg/ml; for RC-109, Sn is 0.7 µg/ml.

TABLE 7.

Day 3 Product Waters and Recycle Waters 8/24/77									
Sample	LPW-103 ^a		LPW-103		LPW-104 ^b		LPW-104		LPW-105 ^c
Shift	1	1			2	2			3
Preparation	N ₂ R	R	Avg.	RSD	R	R	Avg.	RSD	R
Conductivity	204	205	204	1	229	-	-	-	142
Eh	85	70	77	14	135	-	-	-	114
pH	8.34	8.34	8.34	-	8.41	-	-	-	8.55
SCN	0.413	0.423	0.42	2	0.420	0.425	0.42	1	0.240
S ₂ O ₃ ²⁻	12.0	11.7	11.8	2	15.1	15.1	15.1	1	12.5
Total S	40.5	40.0	40.2	1	43.9	-	43.9	-	25.2
Fe	2.39	3.04	2.72	17	3.55	3.73	3.64	3	3.39
Ni	0.33	0.36	0.35	6	0.35	0.41	0.38	11	0.54
Cu	0.38	0.16	0.27	58	0.32	0.24	0.28	20	1.09
Zn	1.16	0.81	.99	25	0.69	0.81	0.75	11	0.34
As	4.94	4.41	4.68	8	3.95	3.86	3.91	2	2.81
Se	7.76	7.13	7.45	6	8.07	8.16	8.12	1	2.28
Br	0.16	0.16	0.16	10	0.15	0.16	0.16	5	0.11
Rb	0.13	0.11	0.12	12	0.10	0.13	0.12	18	0.04
Sr	0.59	0.54	0.57	6	0.61	0.59	0.60	2	0.30
Zr	-	0.03	0.03	-	-	0.01	0.01	-	0.01
Mo	0.16	0.16	0.16	10	0.14	0.21	0.18	28	0.08
Hg	0.35	0.18	0.27	45	0.22	0.27	0.25	14	0.20
Pb	-	-	-	-	3.19	0.21	1.70	124	0.04
B	1.4	1.2	1.3	11	.6	-	0.6	-	13
F	2.1	1.8	1.9	11	1.9	-	1.9	-	-

Sample	RC-115	RC-117	RC-118	RC-118			RC-120
Shift	1	2-Stage 1	2-Stage 2	2-Stage 2			3
Preparation	F	F	F	F	Avg.	RSD	F
Conductivity	226	185	140	-	140	-	100
Eh	155	138	147	-	147	-	6
pH	7.50	8.35	8.49	-	8.49	-	8.62
SCN	2.13	1.81	1.24	-	1.24	-	0.720
S ₂ O ₃ ²⁻	23.7	13.4	13.0	-	13.0	-	6.5
Total S	50.7	36.9	25.1	-	25.1	-	16.2
Fe	147	13.1	13.9	124	69.1	113	19.1
Ni	-	0.24	-	-	-	-	0.13
Cu	3.69	0.90	1.38	1.67	1.53	13	0.57
Zn	8.8	1.15	1.05	14.7	7.8	123	1.10
As	18.7	8.85	11.40	8.97	10.19	17	1.22
Se	65	2.95	1.8	19.5	10.6	118	0.94
Br	1.27	0.61	0.45	1.52	0.99	77	0.37
Rb	-	-	-	-	-	-	-
Sr	41	2.46	0.60	0.59	0.60	1	0.92
Zr	-	-	0.01	0.34	0.18	133	0.05
Mo	-	-	-	-	-	-	-
Hg	-	1.17	1.47	3.87	2.67	64	0.75
Pb	4.39	0.67	0.21	1.30	0.76	102	0.98
B	13	8.6	2.1	-	2.1	-	-
F	<0.2	<0.2	<0.2	-	<0.2	-	-

^a For LPW-103, on 8/24/77, pH = 8.45, Eh = 24.

^b For LPW-104, on 8/24/77, pH = 9.1, Eh = -66.

^c For LPW-105, on 8/24/77, pH = 8.75, Eh = -46.

TABLE 8.

Day 6

Product Waters and Recycle Waters

8/27/77

Sample	LPW-106 ^a	LPW-106			LPW-107 ^b	LPW-107		
Shift	1	1			2	2		
Preparation	N ₂ R	R	Avg.	RSD	R	R	Avg.	RSD
Conductivity	165	160	162	2	152	-	152	-
Eh-	88	89	88	1	120	-	120	-
pH	8.62	8.55	8.59	1	8.56	-	8.56	-
SCN ⁻	0.248	0.250	0.25	1	0.235	-	0.23	-
S ₂ O ₃ ²⁻	7.6	8.2	7.9	5	7.0	-	7.0	-
Total S	29.5	28.9	29.2	1	26.9	-	26.9	-
Fe	2.41	2.40	2.41	1	4.84	6.86	5.85	24
Ni	0.43	0.32	0.38	21	0.31	0.35	0.31	1
Cu	0.45	0.24	0.35	43	0.13	0.94	0.54	10
Zn	1.09	1.05	1.07	3	0.52	1.24	0.88	58
As	4.70	5.57	5.14	12	6.02	4.41	5.22	22
Se	7.07	7.72	7.40	6	7.38	6.97	7.18	4
Br	0.14	0.15	0.15	5	0.11	0.25	0.18	55
Rb	0.12	0.13	0.13	6	0.12	0.13	0.13	6
Sr	0.49	0.56	0.53	9	0.49	0.45	0.47	6
Zn	0.03	-	0.03	-	0.02	0.25	0.14	120
Mo	0.04	0.10	0.07	61	0.09	0.33	0.21	81
Hg	0.23	0.25	0.24	6	0.26	0.25	0.26	3
Pb	0.15	-	0.15	-	0.18	0.33	0.26	42
B	2.4	2.4	2.4	1	1.5	-	1.5	-
F	0.9	1.2	1.0	20	1.7	-	1.7	-

Sample	RC-121	RC-124	RC-124			RC-125
Shift	1	2-Stage 1	2-Stage 1			2-Stage 2
Preparation	F	F	F	Avg.	RSD	F
Conductivity	48	38	-	38	-	35
Eh	243	251	-	251	-	207
pH	8.65	8.62	-	8.62	-	8.96
SCN ₂	0.360	0.205	-	0.205	-	0.360
S ₂ O ₃	0.6	0.6	-	0.6	-	1.4
Total S	1.44	1.10	-	1.10	-	2.95
Fe	5.50	4.09	4.22	4.16	2	11.4
Ni	0.08	0.16	-	0.16	-	0.52
Cu	0.35	0.59	0.24	0.42	60	0.74
Zn	0.30	0.21	0.33	0.27	31	0.83
As	0.96	1.42	0.65	1.04	53	2.13
Se	0.13	0.25	0.16	0.21	31	0.46
Br	0.16	0.15	0.10	0.13	28	0.25
Rb	-	-	-	-	-	-
Sr	0.06	0.05	0.03	0.04	35	0.13
Zr	0.03	0.03	0.02	0.03	28	0.05
Mo	-	-	-	-	-	0.03
Hg	0.45	0.53	0.18	0.36	70	0.53
Pb	0.50	0.26	0.19	0.23	22	0.76
B	0.8	0.9	-	0.9	-	1.2
F	<0.2	<0.2	-	<0.2	-	0.5

^a For LPW-106, on 8/27/77, pH = 8.60, Eh = -46.

^b For LPW-107, on 8/27/77, pH = 8.80, Eh = -86.

TABLE 9.

Day 17	Product Waters and Recycle Waters					9/7/77
Sample	LPW-108 ^a	LPW-110	LPW-110			LPW-109
Shift	1	2	2			3
Preparation	R	F	F	Avg.	RSD	F
Conductivity	221	243	-	243	-	200
Eh	99	82	-	82	-	111
pH	8.35	7.70	-	7.70	-	8.25
SCN ⁻	0.620	0.583	-	0.58	-	0.483
S ₂ O ₃ ²⁻	13.2	12.9	-	12.9	-	14.0
Total S	45.2	58.1	-	58.1	-	39.3
Fe	19.0	5.50	10.7	8.17	46	4.85
Ni	0.68	0.27	0.51	0.39	44	0.23
Cu	2.62	4.05	5.01	4.53	15	5.48
Zn	6.32	5.41	6.77	6.09	16	4.14
As	4.63	7.54	7.75	7.65	2	5.60
Se	8.23	6.04	6.93	6.49	10	5.95
Br	0.26	0.20	0.41	0.31	49	0.28
Rb	0.18	0.18	0.17	0.18	4	0.17
Sr	0.76	0.87	1.03	0.95	12	0.77
Zr	0.02	-	0.02	0.02	-	-
Mo	0.22	0.27	0.36	0.32	20	0.23
Hg	0.51	0.33	0.79	0.56	58	0.55
Pb	0.40	0.17	0.59	0.38	78	0.24
B	0.7	-	-	-	-	34
F	2.4	-	-	-	-	-

Sample	RC-127	RC-128	RC-130	RC-130		
Shift	1	2	3	3		
Preparation	F	F	F	F	Avg.	RSD
Conductivity	69	65	47	-	47	-
Eh	200	201	227	-	227	-
pH	8.64	8.72	8.65	-	8.65	-
SCN ⁻	0.735	0.660	0.405	-	0.40	-
S ₂ O ₃ ²⁻	2.9	2.6	1.9	-	1.9	-
Total S	9.83	8.78	6.32	-	6.32	-
Fe	12.9	13.9	8.73	12.1	10.4	23
Ni	0.26	-	-	-	-	-
Cu	0.68	1.09	1.10	1.10	1.10	1
Zn	0.84	1.21	1.17	1.38	1.28	12
As	5.64	3.90	1.38	2.24	1.81	34
Se	0.31	0.92	0.41	0.62	0.52	29
Br	0.33	0.22	0.31	0.19	0.25	34
Rb	-	-	-	-	-	-
Sr	0.36	0.55	0.06	0.17	0.12	68
Zr	0.02	0.05	0.07	0.07	0.07	1
Mo	-	-	-	-	-	-
Hg	0.74	0.29	0.26	0.25	0.26	2
Pb	0.54	0.50	0.19	0.41	0.30	52
B	4.8	3.5	2.3	-	2.3	-
F	1	0.7	0.5	-	0.5	-

^a For LPW-108, on 9/7/77, pH = 8.40, Eh = -6.

TABLE 10.

Day 25		Product Waters and Recycle Waters				9/15/77			
Sample	LPW-111 ^a	LPW-111			LPW-112 ^b	LPW-113 ^c	LPW-113		
Shift	1	1			2	3	3		
Preparation	N ₂ R	R	Avg.	RSD	R	R	R	Avg.	RSD
Conductivity	194	225	210	10	135	305	-	305	-
Eh	56	56	56	1	213	96	-	96	-
pH	8.30	8.38	8.34	1	8.26	8.22	-	8.22	-
SCN ⁻	0.388	0.370	0.38	3	0.355	0.603	-	0.603	-
S ₂ O ₃ ²⁻	12.5	13.4	13.0	5	9.9	28.2	-	28.2	-
Total S	39.1	41.1	40.1	4	24.5	61.0	-	61.0	-
Fe	4.07	3.00	3.54	21	11.6	19.1	8.54	13.8	54
Ni	0.34	-	0.34	-	0.25	0.32	0.31	0.32	2
Cu	0.80	0.59	0.70	21	0.45	0.09	0.24	0.17	64
Zn	5.89	6.33	6.11	5	1.58	1.20	1.06	1.13	9
As	3.74	3.14	3.44	12	4.24	7.82	6.98	7.40	8
Se	5.99	6.54	6.27	6	3.08	10.6	9.9	10.3	11
Br	0.13	0.12	0.13	6	0.21	0.18	0.14	0.16	18
Rb	0.11	0.10	0.11	7	0.09	0.26	0.22	0.24	12
Sr	0.59	0.52	0.56	9	0.70	0.98	0.85	0.92	10
Zr	-	0.01	0.01	-	-	0.07	0.02	0.05	79
Mo	0.14	0.10	0.12	24	0.16	0.24	0.23	0.24	3
Hg	0.35	0.28	0.32	16	0.23	-	0.38	0.38	-
Pb	0.29	0.14	0.22	49	0.28	-	-	-	-
B	1.7	1.8	1.7	6	23	24	-	24	-
F	1.6	1.8	1.7	6	-	1.8	-	1.8	-

Sample	RC-132	RC-133	RC-135	RC-135			RC-137
Shift	1-Stage 1	1-Stage 2	2	2	Avg.	RSD	3
Preparation	F	F	F	F			F
Conductivity	47	70	69	-	69	-	84
Eh	256	220	263	-	263	-	206
pH	8.60	8.84	8.61	-	8.61	-	8.65
SCN ⁻	0.110	0.610	0.335	0.325	0.33	2	0.253
S ₂ O ₃ ²⁻	0.8	3.6	3.0	2.4	2.7	16	5.3
Total S	2.08	12.5	7.86	-	7.86	-	12.8
Fe	4.38	3.11	4.33	5.60	4.97	18	5.49
Ni	0.09	-	-	-	-	-	-
Cu	0.80	7.16	4.14	1.93	3.04	51	0.28
Zn	3.41	1.95	0.70	1.31	1.01	43	0.35
As	0.81	4.40	4.24	0.81	2.53	96	0.43
Se	0.18	0.84	0.20	0.15	0.18	20	0.51
Br	0.54	0.27	0.17	0.10	0.14	37	0.04
Rb	0.05	-	-	-	-	-	-
Sr	0.10	0.71	0.42	0.22	0.32	44	0.08
Zr	0.03	0.01	0.03	0.03	0.03	1	0.03
Mo	-	-	-	-	-	-	-
Hg	0.22	0.45	0.21	0.23	0.22	6	0.16
Pb	0.61	0.24	0.24	0.19	0.22	16	0.16
B	1.2	2.5	-	-	-	-	2.1
F	<0.2	0.8	-	-	-	-	<0.2

^a For LPW-111, on 9/15/77, pH = 8.30, Eh = 14.

^b For LPW-112, on 9/15/77, pH = 8.05, Eh = 34.

^c For LPW-113, on 9/15/77, pH = 8.30, Eh = 4.

TABLE 11.

Day 30		Product Waters and Recycle Waters				9/20/77	
Sample	LPW-114 ^a	LPW-114			LPW-115 ^b	LPW-116 ^c	
Shift	1	1			2	3	
Preparation	N ₂ R	R	Avg.	RSD	R	Avg.	RSD
Conductivity	161	162	162	1	171	185	23
Eh	70	84	77	13	36	53	67
pH	8.40	8.42	8.41	1	8.45	8.73	3
SCN ⁻	0.385	0.385	0.38	1	0.305	0.43	1
S ₂ O ₃ ²⁻	8.7	8.4	8.6	2	6.7	7.7	11
Total S	29.0	29.0	29.0	1	29.3	29.8	6
Fe	6.08	7.23	6.66	12	4.78	9.4	59
Ni	0.43	0.50	0.47	11	0.46	0.9	49
Cu	0.15	0.85	0.50	99	0.07	0.3	66
Zn	0.39	1.17	0.78	71	0.58	0.7	51
As	2.68	2.69	2.69	1	3.88	4.6	29
Se	4.94	4.49	4.72	7	5.09	7.2	39
Br	0.59	0.36	0.48	34	0.10	0.3	67
Rb	0.10	0.10	0.10	1	0.10	0.2	65
Sr	0.39	0.56	0.48	25	0.54	0.7	29
Zr	-	0.02	0.02	-	-	1.0	100
Mo	0.14	0.16	0.15	9	0.13	0.22	52
Hg	0.30	1.00	0.65	76	-	0.33	32
Pb	0.16	0.79	0.48	94	-	0.25	68
B	1.5	2	1.7	20	.4	0.8	15
F	1.3	1.8	1.6	23	1.7	2.0	5

Sample	RC-139 ^d		RC-140	RC-142	RC-144
Shift	1-Stage 1		1-Stage 2	2	3
Preparation	Avg.	RSD	F	F	F
Conductivity	46	7	63	46	45
Eh	231	8	213	217	236
pH	8.88	2	8.51	8.71	8.62
SCN ⁻	0.33	1	0.890	0.310	0.258
S ₂ O ₃ ²⁻	1.9	7	2.7	1.5	1.2
Total S	3.17	2	9.50	2.68	2.06
Fe	15	54	6.15	6.07	7.27
Ni	0.2	57	0.09	-	0.04
Cu	0.57	42	3.07	0.49	0.33
Zn	0.77	88	0.95	0.45	0.29
As	3.03	28	10.39	1.48	2.23
Se	0.7	27	1.39	0.69	0.23
Br	0.1	67	0.06	0.03	0.04
Rb	0.02	50	0.03	0.01	0.01
Sr	0.2	87	0.54	0.21	0.12
Zr	0.05	62	-	0.04	0.02
Mo	0.02	100	0.10	0.01	-
Hg	0.9	47	0.55	0.28	0.24
Pb	0.36	100	0.41	0.40	0.90
B	1.6	15	2.7	1.9	1.4
F	<0.2	-	0.8	<0.2	<0.2

a

For LPW-114, on 9/20/77, pH = 8.62, Eh = -6.

b

For LPW-115, on 9/20/77, pH = 8.43, Eh = -95.

c

For LPW-116, the average is for the 13 values on the following page.

d

For RC-139, the average is for the 10 values on the following page.

TABLE 12.

	LPW-116					Product Waters					Day 30					LPW-116					9/20/77					Shift 3					LPW-116				
Preparation	F	N ₂ F	N ₂ F	R	N ₂ R	F	N ₂ F	R	R	N ₂ R	N ₂ R	R	R			F	N ₂ F	R	R	N ₂ R	N ₂ R	R	R			F	N ₂ F	R	R	N ₂ R	N ₂ R	R	R		
Analysis Date	6/78	6/78	6/78	6/78	6/78	7/78	7/78	7/78	7/78	7/78	6/79	6/79	6/79			7/78	7/78	7/78	7/78	7/78	6/79	6/79	6/79			7/78	7/78	7/78	7/78	7/78	6/79	6/79	6/79		
Conductivity	123	123	-	164	164	230	226	234	-	224	185	178	-			230	226	234	-	224	185	178	-			230	226	234	-	224	185	178	-		
Eh	44	19	-	89	79	34	34	19	-	132	40	43	-			34	34	19	-	132	40	43	-			34	34	19	-	132	40	43	-		
pH	8.78	8.75	-	9.16	9.15	8.64	8.54	8.86	-	8.63	8.40	8.43	-			8.64	8.54	8.86	-	8.63	8.40	8.43	-			8.64	8.54	8.86	-	8.63	8.40	8.43	-		
Alkalinity	0.726	0.762	-	0.720	0.720	0.730	0.705	0.703	-	0.705	-	-	-			0.730	0.705	0.703	-	0.705	-	-	-			0.730	0.705	0.703	-	0.705	-	-	-		
NH ₃	19.5	23.7	-	23.1	23.5	21.6	22.7	22.3	-	22.7	-	-	-			21.6	22.7	22.3	-	22.7	-	-	-			21.6	22.7	22.3	-	22.7	-	-	-		
SCN	-	-	-	-	-	-	-	-	-	-	-	-	-			-	-	-	-	-	-	-	-			-	-	-	-	-	-	-	-		
S ₂ O ₃ ²⁻	7.28	7.28	-	9.25	9.25	7.17	7.02	6.80	-	7.17	7.8	7.7	-			7.17	7.02	6.80	-	7.17	7.8	7.7	-			7.17	7.02	6.80	-	7.17	7.8	7.7	-		
Total S	31.1	30.3	-	27.1	30.9	27.8	27.1	31.4	-	29.2	31.5	31.4	-			27.8	27.1	31.4	-	29.2	31.5	31.4	-			27.8	27.1	31.4	-	29.2	31.5	31.4	-		
Fe	14.7	11.7	14.6	7.75	8.83	7.43	22.9	5.19	11.0	3.46	5.59	4.03	5.16			7.43	22.9	5.19	11.0	3.46	5.59	4.03	5.16			7.43	22.9	5.19	11.0	3.46	5.59	4.03	5.16		
Ni	1.34	1.27	1.79	0.79	0.70	0.41	1.42	0.61	1.16	0.50	0.84	0.51	0.47			0.41	1.42	0.61	1.16	0.50	0.84	0.51	0.47			0.41	1.42	0.61	1.16	0.50	0.84	0.51	0.47		
Cu	-	0.38	-	0.15	0.11	0.67	0.50	0.36	0.37	0.06	0.16	0.12	0.29			0.67	0.50	0.36	0.37	0.06	0.16	0.12	0.29			0.67	0.50	0.36	0.37	0.06	0.16	0.12	0.29		
Zn	1.14	1.34	1.35	0.67	0.75	0.61	0.66	0.32	0.38	0.25	0.90	0.33	0.73			0.61	0.66	0.32	0.38	0.25	0.90	0.33	0.73			0.61	0.66	0.32	0.38	0.25	0.90	0.33	0.73		
As	5.53	7.09	6.69	5.39	5.55	3.41	3.57	3.19	3.59	3.41	4.74	3.83	3.93			3.41	3.57	3.19	3.59	3.41	4.74	3.83	3.93			3.41	3.57	3.19	3.59	3.41	4.74	3.83	3.93		
Se	12.8	11.1	11.4	7.38	8.08	5.11	5.79	4.06	4.90	5.73	6.76	5.32	5.63			5.11	5.79	4.06	4.90	5.73	6.76	5.32	5.63			5.11	5.79	4.06	4.90	5.73	6.76	5.32	5.63		
Br	0.57	0.62	0.72	0.41	0.59	0.22	0.17	0.20	0.10	0.23	0.16	0.10	0.19			0.22	0.17	0.20	0.10	0.23	0.16	0.10	0.19			0.22	0.17	0.20	0.10	0.23	0.16	0.10	0.19		
Rb	0.40	0.28	0.49	0.16	0.21	0.13	0.12	0.12	0.09	0.11	0.13	0.14	0.11			0.13	0.12	0.12	0.09	0.11	0.13	0.14	0.11			0.13	0.12	0.12	0.09	0.11	0.13	0.14	0.11		
Sr	1.07	1.05	1.01	0.78	0.86	0.51	0.70	0.52	0.61	0.53	0.66	0.56	0.59			0.51	0.70	0.52	0.61	0.53	0.66	0.56	0.59			0.51	0.70	0.52	0.61	0.53	0.66	0.56	0.59		
Zr	6.01	3.88	0.22	0.44	1.22	0.14	0.17	0.15	0.24	0.23	0.03	0.01	0.03			0.14	0.17	0.15	0.24	0.23	0.03	0.01	0.03			0.14	0.17	0.15	0.24	0.23	0.03	0.01	0.03		
Mo	0.17	0.33	0.49	0.22	0.24	0.12	0.15	0.16	0.42	0.16	0.18	0.12	0.15			0.12	0.15	0.16	0.42	0.16	0.18	0.12	0.15			0.12	0.15	0.16	0.42	0.16	0.18	0.12	0.15		
Sn	-	-	-	-	-	-	1.64	-	2.09	-	-	-	-			-	1.64	-	2.09	-	-	-	-			-	1.64	-	2.09	-	-	-	-		
Hg	-	-	-	-	-	-	-	-	-	-	0.29	0.25	0.45			-	-	-	-	-	0.29	0.25	0.45			-	-	-	-	-	0.29	0.25	0.45		
Pb	0.21	-	0.59	0.44	0.15	0.10	0.41	0.07	0.21	-	0.09	-	0.27			0.10	0.41	0.07	0.21	-	0.09	-	0.27			0.10	0.41	0.07	0.21	-	0.09	-	0.27		
B	-	-	-	-	-	-	-	-	-	-	0.8	0.9	-			-	-	-	-	-	0.8	0.9	-	-			-	-	-	-	0.8	0.9	-		
F	-	-	-	-	-	-	-	-	-	-	2	2.1	-			-	-	-	-	-	2	2.1	-	-			-	-	-	-	2	2.1	-		

Note: For LPW-116 on 9/20/77, pH = 8.88, Eh = -66.

TABLE 13.

RC-139	Recycle Condensate					Day 30	RC-139	9/20/77	Shift 1	RC-139
Preparation	F	N ₂ F	N ₂ R	N ₂ R	N ₂ R	R	N ₂ R	N ₂ R	N ₂ R	N ₂ R
Analysis Date	6/79	5/79	6/79	6/79	6/79	6/79	7/78	7/78	6/78	6/78
Conductivity	46	46	46	-	-	46	50	-	40	-
Eh	232	247	247	-	-	247	214	-	202	-
pH	8.78	8.76	8.78	-	-	8.80	8.94	-	9.20	-
Alkalinity	-	-	-	-	-	-	0.413	-	0.408	-
NH ₃	-	-	-	-	-	-	7.35	-	-	-
SCN ⁻	0.333	0.330	0.333	-	-	0.340	-	-	-	-
S ₂ O ₃ ²⁻	1.9	1.8	1.9	-	-	1.9	1.96	-	2.19	-
Total S	3.26	3.11	3.16	-	-	3.15	-	-	-	-
Fe	20.6	21.3	24.7	28.5	11.8	9.58	10.0	7.77	8.06	6.36
Ni	0.11	0.09	-	0.17	-	-	0.32	0.12	-	-
Cu	0.77	0.73	0.70	1.06	0.35	0.57	0.43	0.44	0.32	0.35
Zn	1.21	2.13	0.71	1.70	0.38	0.32	0.26	0.33	0.29	0.38
As	4.02	3.43	2.33	2.84	2.78	3.03	3.63	2.59	4.24	1.38
Se	1.09	0.85	0.53	0.84	0.70	0.59	0.46	0.56	0.73	0.59
Br	0.07	0.07	0.10	0.11	0.05	0.05	0.29	0.16	0.11	-
Rb	0.01	0.04	0.02	-	0.01	-	-	-	-	0.01
Sr	0.57	0.44	0.19	0.43	0.09	0.16	0.14	0.10	0.05	0.02
Zr	0.07	0.04	0.03	0.07	0.03	0.02	0.06	0.10	0.01	0.11
Mo	-	-	0.04	-	-	0.01	0.01	0.05	0.01	0.02
Sn	-	-	-	-	-	-	0.41	-	-	-
Hg	1.17	0.83	1.21	1.55	0.96	0.89	-	0.25	0.75	0.33
Pb	0.28	1.24	0.51	0.49	0.06	0.17	0.21	0.12	-	0.12
B	1.6	1.9	1.3	-	-	1.6	-	-	-	-
F	0.2	<0.2	<0.2	-	-	<0.2	-	-	-	-
Cd	-	-	-	0.49	-	-	-	-	-	-

Note: On 9/20/77, for RC-139, pH = 8.95, Eh = -176.

TABLE 14.

	Day 5				Process Waters				8/26/77 No Special Shift			
Sample	M-102	M-112	M-102	M-102	M-102	M-102	M-102	M-102	M-102	M-102	M-103 ^a	M-103 ^b
Preparation	F	N ₂ F	N ₂ F	R	N ₂ R	F	N ₂ F	R	R	N ₂ R	N ₂ R	N ₂ R
Analysis date	6/78	6/78	6/78	6/78	6/78	7/78	7/78	7/78	7/78	7/78	6/78	7/78
Conductivity	149	172	-	190	298	173	316	314	-	253	46	68
Eh	29	14	-	94	104	104	106	62	-	64	219	214
pH	8.63	8.68	-	8.97	9.07	8.60	8.68	8.60	-	8.80	8.93	8.83
Alkalinity	0.528	0.686	-	0.618	0.568	-	-	0.594	-	0.615	0.217	0.223
NH ₃	23.6	29.3	-	30.0	28.2	29.8	29.5	28.8	-	29.4	7.60	6.72
SCN ⁻	-	-	-	-	-	-	-	-	-	-	-	-
S ₂ O ₃ ²⁻	9.7	22.7	-	23.3	22.9	26.0	19.8	21.2	-	21.4	4.87	3.80
Total S	45.4	45.0	-	42.5	41.2	-	34.0	41.7	-	42.8	1.1	6.5
Fe	7.24	25.46	9.59	5.92	5.55	17.30	3.41	17.38	1.83	18.90	5.56	7.89
Ni	-	2.13	0.84	0.36	1.01	-	-	-	-	-	0.16	0.51
Cu	0.30	-	0.30	1.24	1.19	1.38	0.70	4.12	0.51	0.96	0.76	0.94
Zn	0.22	1.27	0.86	1.08	1.18	1.13	0.71	1.04	0.40	0.70	0.54	0.47
As	3.10	4.74	6.43	14.98	12.84	7.63	11.78	3.17	5.61	5.48	1.60	1.37
Se	0.98	13.16	8.81	11.05	10.51	7.93	5.55	3.54	4.41	7.66	1.89	0.90
Br	0.09	0.80	0.58	0.97	1.09	0.50	0.51	0.68	0.50	0.48	0.23	0.20
Rb	-	0.36	0.21	0.87	1.03	0.57	0.38	0.96	0.27	0.69	0.02	-
Sr	0.02	1.71	1.09	1.90	2.43	1.17	1.05	0.74	0.83	0.80	1.49	0.76
Zr	0.04	-	0.05	0.31	-	0.07	0.03	0.39	-	0.33	0.07	0.06
Mo	-	0.22	0.25	0.82	0.76	0.49	0.47	0.30	0.37	0.42	-	0.68
Hg	0.48	-	-	-	-	-	-	-	-	-	-	-
Pb	0.06	0.34	-	0.26	-	0.22	-	0.47	0.14	0.55	0.11	0.13

^a For this sample, Tungsten = 0.2 ppm.

^b For this sample, Tin = 0.5 ppm.

Note: For M-102, on 8/27/77, pH = 8.80, Eh = -6.

For M-103, on 8/27/77, pH = 9.40, Eh = 144.

TABLE 15..

	Day 25		Pond Waters		9/15/77	Collection Time: 1530			
Sample	M-107 ^a	M-107 ^a	M-108	M-108	M-108	M-109 ^b	M-109 ^b	M-109 ^b	M-109 ^b
Site	Retort	Retort	Pond	Pond	Pond	Leachate ^b	Leachate	Leachate	Leachate
Preparation	R	R	F	F	F	R	R	R	R
Analysis Date	6/78	7/73	6/78	7/78	7/78	6/78	6/78	7/78	7/78
Conductivity	2.56	3.52	3.60	4.80	-	2.74	-	3.20	-
Eh	354	384	294	334	-	394	-	424	-
pH	7.5	7.65	8.56	8.68	-	7.36	-	7.26	-
Alkalinity	0.0039	0.0035	0.0053	0.0026	-	0.0029	-	0.0026	-
NH ₃	=0	0.03	=0	0.08	-	0.09	-	0.08	-
SCN	-	-	-	-	-	-	-	-	-
S ₂ O ₃ ²⁻	=0	0.01	0.045	0.083	-	0.092	-	0.083	-
Total S	=0	=0	=0	0.3	-	=0	-	0.3	-
Fe	1.02	2.97	0.56	1.86	3.47	5.73	0.42	0.42	1.08
Ni	0.49	0.30	-	0.09	0.32	0.48	-	-	0.05
Cu	0.32	0.58	0.05	0.17	0.28	0.71	0.38	0.04	0.14
Zn	0.68	0.36	0.07	0.18	0.23	0.45	0.03	0.19	0.07
As	0.28	0.04	0.53	0.44	0.56	0.38	0.34	0.04	0.04
Se	0.10	0.02	0.03	0.01	-	0.19	0.26	0.03	0.02
Br	0.77	0.32	0.29	0.22	0.21	0.42	0.46	0.14	0.15
Rb	0.02	-	0.05	0.03	0.04	0.08	0.08	0.01	-
Sr	5.82	1.75	1.66	0.97	1.32	4.10	4.39	0.52	0.30
Zr	-	0.05	0.02	0.03	0.05	0.58	-	0	0.02
Mo	0.17	0.11	0.03	0.02	0.03	0.84	0.79	0.10	0.06
Sn	-	0.43	-	0.15	-	0.25	-	-	-
Hg	-	-	-	-	0.06	-	-	0.21	0.38
Pb	0.15	0.16	0.04	0.14	0.18	0.76	-	0.05	0.07
K	-	-	-	-	-	71	67	-	-
Ca	-	-	-	-	-	248	258	-	-
Mn	-	-	0.39	-	-	-	-	-	-

^a This water is the discharge from plant operations.

^b This water leachate from the spent shale pile.

Note: For M-107, on 9/15/77, pH = 7.70, Eh = 279, conductivity = 2.0

For M-108, on 9/15/77, pH = 8.13, Eh = 234, conductivity = 2.5

For M-109, on 9/15/77, pH = 8.00, Eh = 284, conductivity = 1.61

TABLE 16---Comparison of Analytical Results on Retort Waters Analyzed in this Study and by Batelle Pacific Northwest Laboratory (7).

Date	Product Waters		Process Waters	
	ETSRP ^a 8-24-77	PNL 8-24-77	ETSRP ^b 8-26-77	PNL 8-26-77
Total S	36.4	39	41.8	51
Fe	3.3	1.5	11.3	4.2
Ni	0.42	0.54	1.0	0.41
Cu	0.55	0.7	1.2	21
Zn	0.69	0.41	0.86	5.0
As	3.8	5.7	7.6	10.9
Se	6.0	9.8	7.4	6.4
Rb	0.09	0.14	0.59	0.41
Sr	0.49	0.85	1.2	1.1
Mo	0.14	0.15	0.46	0.53
Hg	0.24	0.023	0.48	<0.5
Pb	0.87	<0.4	0.29	<0.3
B	5.0	43	-	41

^a Average of LPW-103, LPW-104, and LPW-105 from Day 3.

^b Average of M-102 results from Table 14.

Water M-102 is the same as PNL settling tank water of 8-26-77. The average of product waters LPW-103, LPW-104, and LPW-105 is comparable to PNL gauging tank water of 8-24-77. Table 16 is a comparison of the results of PNL and this group on those two waters from the Paraho retort.

THE ANALYSIS OF SULFUR IN RETORT WATERS

In order to determine the amount of sulfur in retort waters it was first necessary to develop an analytical method that would give accurate and consistent results. Several different methods were evaluated and the evaluation procedure is described in the COMPARATIVE METHODS section. The results of this evaluation showed that for the purposes of this investigation, a modified Eschka analysis or a Fisher instrumental technique could give satisfactory sulfur values.

When it was necessary to decide which analysis was to be used for the oil shale retort waters, economics was the deciding factor. The Eschka analysis could be performed on campus at CSM by students hired for that purpose. Samples analyzed by the Fisher method had to be sent to Huffman Laboratories for analysis. Once there they had to be run on a Fisher model 470 sulfur analyzer by a specially trained technician. The cost for a Fisher analysis is fourteen dollars per sample. Consequently the Eschka method for the analysis of these waters was chosen.

Once an analysis method was chosen, it was necessary to make sure that it was applicable to liquid samples and not just solid oil shale. This was done by preparing aqueous standards that had precisely known concentrations of sulfur. The standards prepared were sodium sulfate, sodium sulfite and sodium thiosulfate. Two analyses of each of these standards were performed by two different analysts seven months apart. The results of these standards analyses appear in Table 17.

TABLE 17---Sulfur Concentrations in mgS/mL of Standards Using the Eschka Method.

Standard Compound	Standard Sulfur Concentration	Analyst 1 Results	Analyst 2 Results
Na ₂ SO ₄	25.0	24.35	25.15
Na ₂ SO ₃	25.0	25.4	24.74
Na ₂ S ₂ O ₃	50.0	49.2	49.7

These results indicate that the Eschka method does work well for liquid samples and can give closely agreeing results with different analysts.

A further test of this method for liquid samples was done by replicate analysis of a single product water sample seven times. The product water sample was LPW-116-R; the analytical results in mg/mL sulfur were 31.33, 31.53, 31.30, 31.22, 31.24, 30.54, and 31.94. The standard deviation is 0.42 and the relative standard deviation (RSD) is 1.34%. This degree of reproducibility was well within the desired precision limits for this study. Interlaboratory results can be compared by investigating retort waters that were analyzed by PNL and this group. The values for total sulfur are contained in Table 16. For the PNL water samples, total sulfur was analyzed by instrumental neutron activation analysis (7).

RESULTS AND DISCUSSION

The reagents and procedure used in the Eschka analysis of the Paraho waters are described at the end of this section.

A complete listing of all analytical results appears in Tables 6-15 of this report. This section of the report will just be concerned with general observations of the results.

It appears that the Eschka analysis is reproducible for retort waters. Table 18 below lists a few typical results.

TABLE 18---Selected Sulfur Concentrations in mgS/ml for Paraho waters.

Sample	Sulfur Concentration	Avg.	σ	RSD(%)
LPW-104-R	44.16, 43.60	43.88	0.40	0.90
LPW-106-R	28.67, 29.08	28.88	0.29	1.00
LPW-111-R	40.89, 41.49	41.19	0.42	1.03
RC-110-F	16.15, 16.20	16.17	0.03	0.22
RC-112-F	28.77, 29.20	28.48	0.40	1.41
RC-121-F	1.47, 1.41	1.44	0.04	2.95
RC-128-F	8.91, 8.64	8.78	0.19	2.18
RC-144-F	2.04, 2.07	2.06	0.02	1.03

It can be seen that if the concentration of sulfur in the sample is above 10-15 mg/ml, one can expect a relative standard deviation (RSD) of 1.5% or less. Lower concentrations of sulfur tend to raise the RSD to about 3%. It should be pointed out that standard waters containing sulfate and sulfite were run at the same time as the samples as a quality control check.

Sample preparation and storage is an important question for oil shale waters (14). In the preliminary analysis of the Paraho waters it appeared that the concentration of total sulfur and of sulfur species did not change when the preparation and storage was changed (1). A study of the results in Tables 6-15 confirms that this preliminary conclusion of no change in total sulfur nor in the sulfur species analyzed is upheld. In all cases where analyses were made on the same sample but different methods of preparation and storage the RSD on the average is within 5% for SCN^- , $\text{S}_2\text{O}_3^{=}$ and total S. For RC-139, splits from the four methods were extensively analyzed in 1979. The results are contained in Table 19. There is no significant difference between any of the splits for any of the sulfur concentrations.

TABLE 19---Concentrations of Sulfur Species in Different Splits of Blower Condensate RC-139. Values are in mg of S/mL.

Sample Split	SCN^-	$\text{S}_2\text{O}_3^{=}$	Total S
RC-139, R	0.340	2.2	3.15
RC-139, R, N_2	0.333	2.2	3.16
RC-139, F	0.333	2.2	3.26
RC-139, R, N_2	0.330	2.3	3.11

It is not surprising that the total amount of sulfur in the waters has not changed. A change in the total would require a phase separation and this has not been observed for these waters. However, a change in the amount of $\text{S}_2\text{O}_3^{=}$ or SCN^- is easily possible, especially after two years of storage. That this does not happen for the sulfur species in the water implies that when the water is isolated from the surroundings, it is quite stable.

Other observations on sulfur species in the Paraho waters can be made. First, it is apparent that the recycle condensates are generally lower in sulfur content than the product waters. There can be anywhere from 1.5 to 10 times as much sulfur in the product waters as there is in the condensates. A possible explanation for this is that the electrostatic precipitator that is used to coalesce the oil-water mist from the retort may act as a scrubber for the retort gases. This scrubbing action would reduce the amount of sulfur in the gases that pass through the precipitator and consequently reduce the sulfur found in the blower condensates. This trend in sulfur concentration also appears when one examines the data on SCN^- and $\text{S}_2\text{O}_3^{=}$ concentrations in the Paraho waters in Tables 6-11. With a few minor exceptions, all the recycle condensate SCN^- and $\text{S}_2\text{O}_3^{=}$ values are less than their product water counterparts. This is especially true with the $\text{S}_2\text{O}_3^{=}$ species, whose condensate values are generally half that of

the corresponding product water results.

Another observation that can be made is that if the sulfur content in the product water is high, the condensate values are also high. Although the data supporting this statement is much less clear than in the previous conclusion, there are some definite trends visible. For instance, on 8-17-77, the product water sulfur values range from 27-29 mg/ml and condensates are around 1 to 3 mg/ml sulfur. On 9-7-77 the product water samples are up to 40 to 50 mg/ml sulfur and the recycle samples have climbed to 6 to 10 mg/ml sulfur. When the product water values go back down to 30 mg/ml as on 9-20-77, the recycle condensates fall back to 2 to 3 mg/ml.

This observation might be expected when one considers that the product waters may be in equilibrium with the recycle gases. If this is the case, one would expect to see this correlation in the sulfur values between the recycle condensates and the product waters.

Sulfur Analyses by the Eschka Method

Reagents--

Barium chloride solution---Dissolve 100 grams of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in 2 liter of distilled water.

Eschka mixture---Thoroughly mix 2 parts by weight of magnesium oxide (MgO) with 1 part of anhydrous sodium carbonate (Na_2CO_3). Both materials should be as free as possible from sulfur.

Hydrochloric acid (1:1)---Mix equal volumes of hydrochloric acid (HCl) and distilled water.

Hydrochloric Acid (1:9)---Mix 1 volume hydrochloric acid with 9 volumes distilled water.

Methyl orange indicator---Prepare a saturated solution in distilled water. For 100 mL of water, this is about 0.2 g of methyl orange.

Sodium hydroxide solution---Dissolve 100 grams of sodium hydroxide (NaOH) in 1 liter of distilled water.

Saturated bromine water---Add an excess of bromine to distilled water.

Procedure---

(1) Thoroughly mix approximately 1 gram of the solid sample (1 mL of water sample) and 3 grams of Eschka mixture in a porcelain crucible. Cover all of this with 1 gram of the

Eschka mixture to totally cover the contents of the crucible. Be sure to cover completely to prevent the loss of $\text{SO}_2(\text{g})$.

(2) Place the crucible in a muffle furnace and raise the temperature gradually to $800 \pm 25^\circ\text{C}$ over a period of about an hour. Maintain this temperature for 2 hours.

(3) Remove crucible from furnace, allow to cool, and quantitatively transfer sample to a 250 mL beaker.

(4) Digest the sample with about 100 mL of hot distilled water for $\frac{1}{2}$ to $\frac{3}{4}$ of an hour.

(5) Filter and wash by decantation. Transfer insoluble matter to the filter and wash 5 times, keeping the mixture well agitated. Whatman 40 is a suitable paper for this process.

(6) Treat the filtrate, about 250 mL, with 10-20 mL of saturated bromine water and make slightly acidic with (1:1) HCl. Boil to expel liberated bromine. The solution will usually appear a dark yellow at the addition of the HCl.

(7) Add methyl orange indicator solution until a constant color is observed. Adjust the pH until the solution is just neutral to the indicator, by adding 10% NaOH solution or 1:1 HCl as needed. Methyl orange is red in acid and yellow in base.

(8) Add 10 mL of 10% BaCl_2 solution to the hot solution, stirring constantly.

(9) Digest the solution, with the BaSO_4 ppt, for at least 1 hour and let stand overnight. Cover with a water glass to prevent contamination.

(10) Filter solution through a preweighed millipore filter.

(11) Let filter dry overnight in a desiccator.

(12) Reweigh and calculate % sulfur in sample.

Calculations---

$$S = (\text{grams BaSO}_4 \text{ in samp.}) - (\text{grams BaSO}_4 \text{ blank}) \times$$

$$\frac{\text{M.W.S. (32.006)}}{\text{M.W. BaSO}_4 (233.426)}$$

$$\% \text{ Sulfur in sample} = \frac{S}{\text{sample wt.}} \times 100$$

TRACE ELEMENTS IN RETORT WATERS

This section contains the conclusions that can be drawn from the results of the trace element analyses on the Paraho waters listed in Tables 6-15. The methods of analysis for B and F were developed by Dr. Meglen (38); the other results were obtained by EDXRF (4).

PRECISION AND ACCURACY

The most obvious and disturbing feature of the results is the wide scatter in duplicate analyses for the EDXRF results. The RSDs for the average of the 13 LPW samples range from 29% to 100%. The RSDs for the average of the 10 RC-139 samples range from 27% to 100%. For B and F the RSDs range from 5 to 15 %. The precision of EDXRF results can only be considered to be semi-quantitative. The question now has to be asked if the imprecision of the results is caused by the EDXRF method or by a difficult matrix. The answer appears to be that both reasons cause scatter in the analytical results.

With respect to the EDXRF method, there are a number of factors that cause scatter. When the value of the concentration is below 0.5 ppm, the x-ray peak is small enough that the error in the counts is 10%. This of course increases until the counting error for concentrations of less than 0.1 ppm is typically 30%. Another factor that generates scatter is that the x-ray background is high for elements of atomic number from 20 through 28 and becomes lower until it is at a minimum at molybdenum (atomic number 42) (4). The result of this change in the background can be seen in the precision of the results. For Fe, the EDXRF results have large RSDs even though the concentration of iron in the waters is higher than most of the other elements. For As and Se the RSDs are around 25% or less because the x-ray peak is strong and the background is low (4). It should be kept in mind that the EDXRF results for solid oil shale samples are precise and accurate (9, 10, 17). For example, the analytical RSDs for the averages of the Paraho raw shale samples were typically lower than 10 percent (17).

If precise EDXRF analyses are possible on solids and not on liquids, then the matrix of retort water must be difficult to analyze. This idea is somewhat supported by a study of the trace element concentrations in Paraho waters which were generated by PNL (7). In that study, the PNL group analyzed fewer samples but concentrated on obtaining precise results. The key to the precision was to use a multitechnique approach for the analysis of the samples. Generally, the scatter in the results by different techniques is higher for water samples than for solid samples. It also should be noted that the scatter in results between techniques is less than the 25-100% that is the case in this study. So, more precise results of analysis can be obtained on retort waters, but the precision probably will not be as good as that obtained for oil shale solids and obtaining more precise results on waters takes great analytical expertise and resources.

This conclusion, that one needs great analytical expertise in order to analyse oil-shale retort waters, has disturbing practical consequences. Obviously, analyses will have to be made on oil shale waters, for EPA criteria pollutants such as As, Se, Pb and Hg. In this case, the analyses for these constituents is not going to be as easy as it is for other aqueous effluents such as acid mine drainages (39). A special quality control program and verification of laboratory procedures may have to be devised for retort waters. This conclusion of caution in the procedures for the analysis of oil shale waters is not new. The results of the inter-laboratory analytical program on the Omega-9 water brought about similar conclusions (22).

ENVIRONMENTAL ASSESSMENT

There are two other factors about the retort waters which raise environmental concerns. First, it appears that for some of those inorganic constituents where the EPA has set maximum contaminant levels for aqueous effluents, the retort waters exceed the limits. This means that if the product water or blower water were released from the retort property before treatment, that this would constitute a discharge of a hazardous waste. It must be kept in mind, that in that plans that industries have for commercial surface retorts, that this product water and blower condensate would be retained, treated, and eventually reused in the process. Thus, the industry is already responding to this potential hazard. The elements arsenic, selenium, lead, and mercury are typically considered to be pollutants upon which concentration limits are always imposed (41). In the product water and blower condensate, these elements exceed the concentration limits that are usually imposed on aqueous effluents.

Another factor which is disturbing and which will definitely affect environmental planning and assessment is the great variability of the trace constituents in these waters. Table 20 gives the values for the average concentrations in product waters. The relative standard deviations (RSD) are all 20 percent or more. For example, the RSD for the arsenic in product waters range from 3 to 10 ppm. The range of concentrations values for arsenic in blower condensates is 1 to 19 ppm. These are large ranges in concentrations, especially when they are compared to the ranges in concentration in the raw oil shale feedstock (5, 10, 16). As of now, one cannot be sure whether the wide ranges are due primarily to analytical problems or actual differences in the waters.

ELEMENT RELATIONSHIPS

Statistical modeling of the retort waters has not yet been attempted; averages, correlation coefficients, and

levels of variance are not available. However, some things can be pointed out after studying the data contained in Tables 6-11. The variability in the results surely diminishes the clarity by which trends and relationships can be seen. Consequently, the conclusions stated here should be considered to be tentative until statistical tests confirm them.

It appears that both in the product waters and blower condensates the siderophile elements such as Cu, Zn, As, Se, Pb, and Hg increase and decrease as a group and that total sulfur increases and decreases with them. It is true that the waters that are highest in sulfur such as RC-107, RC-115, LPW-110, and LPW-113 have generally high concentrations of all the other siderophile elements. It is also true that those waters which are low in total sulfur such as RC-121, RC-124, LPW-105 and LPW-107 are generally low in the other siderophile elements. However, there is much scatter in the middle values which clouds the relationships. For example, it is not clear that iron concentrations in the waters are strongly related to total sulfur levels.

Even though this relation between total sulfur and the siderophile elements is not strong, it does have important practical significance. The total sulfur analysis of retort waters is not complex and is capable of providing results that are precise and reasonably accurate. Consequently, a high total sulfur value is a good indication that toxic trace elements are also in high concentrations in product waters. The problem is that a low sulfur value does not necessarily imply that the same toxic elements are in low concentrations in product waters.

Element mobility is an important concept in the study of chemical relations in oil shale retorts (6, 7). The INTRODUCTION section of this report explained how a small release of an element from the raw shale can still result in a significant concentration of that element in the oil or water. Mobilities are usually expressed as the percent of a constituent that has been transferred from the raw shale to the products. In this study, the percentage of an element that has been transferred to the water can be estimated by using the average elemental abundances in the raw shale feedstock for Paraho that were reported last year (7). An additional piece of information that is necessary for the calculation is the amount of water produced in the Paraho retort per amount of raw shale feedstock. The Paraho report by the PNL group gives that value as 3.9 g of water produced per 1 kg of raw shale feedstock. The mobilities of the elements expressed as percent transferred to the water are listed in Table 20. The values for mobilities

TABLE 20---Amount of Elements Transferred from Feedstock to Product Water. All concentrations are in ppm.

	Product Water		Raw Shale ^a Feedstock		Percent ^b Transferred
	Average	RSD	Average	RSD	
Se	6.4	31	1.5	17	1.6
As	5.0	40	44	13	0.044
Cu	2.1	100	35	10	0.023
B	7.6	100	140	14	0.021
Zn	3.2	100	83	29	0.015
Pb	0.4	100	24	13	0.0062
Ni	0.4	39	32	9	0.0052
Mo	0.2	20	23	11	0.0033
Rb	0.15	34	89	7	0.00072
F	1.8	22	1340	12	0.00052
Sr	0.64	26	770	9	0.00032
Fe	6.9	66	21300	10	0.00012

^a Averages taken from last year's report (5)

^b Values calculated by using the PNL value of water produced as 3.9 g water per 1 kg of raw shale (7).

are similar to those of the PNL group for the Paraho retort (7).

The small amount of water that is produced by a surface retort such as the Paraho operation leads to two interesting conclusions about the trace element concentrations in the water. First, the mobilization of even a small amount of a toxic element such as arsenic can result in an appreciable concentration of that element in the retort water. In that regard, mobilization of even small fractions of toxic elements can pose a problem during surface retorting. On the other hand a second conclusion can be made that the small amounts of toxic elements that are released during retorting are incorporated in the product water which comprises only a small fraction of the total volume produced and can be easily recovered for treatment. This conclusion implies that emissions of toxic elements from surface retorts can be controlled by recovery and treatment of the by-products. However, one question remains before this conclusion can be accepted. That is, are all the toxic elements trapped by the water and oil, or do some remain in the product gas which may escape from the retort?

The PNL group addressed this question of escape into the product gas in their study of the Paraho retort. By special methods of collection and analysis, they were able to detect As and Hg in the recycle gas that is returned to the retort and in the thermal oxidizer gas which is released from the retort (7). For all other elements, the concentrations in the gases were below detection limits. This question can be studied by methods other than direct observation. If condensates can be taken at places along the recycle gas line and the concentrations of species in these condensates compared with the product water, then the tendency for an element to persist in the gas stream beyond the point where product oil is taken off can be evaluated. This analysis can be made in this study by comparing the product waters with the blower condensates.

Element ratios of the product water to the blower condensates were calculated on a shift-by-shift basis using the results in Tables 6-11. An average ratio was calculated for each element and these averages are shown in Figure 4. A ratio of one or less implies that the element persists in the recycle line, whereas a ratio far above one implies that the element is trapped in the product water. Figure 1 shows the positions where the product water and blower condensate were collected on the retort.

The ratios in Figure 4 cluster into three groups: those with a ratio less than two, those with a ratio of about six, and those with a ratio greater than 10. A high ratio implies

Figure 4: Ratios of elements in the product water to those in the blower condensate.

TABLE 21---Average Ratios of Elements in By-Products of the Paraho Retort.

	<u>Product Water</u> Blower Condensate	<u>Retorted Shale Dust</u> Retorted Shale
SCN ⁻	1.0	-
S ₂ O ₃ ⁼	5.8	-
Total S	8.6	-
Fe	0.8	1.16
Ni	6.0	1.40
Cu	1.2	1.50
Zn	2.0	1.29
As	2.3	1.92
Se	15.4	1.00
Br	1.4	-
Rb	<16	1.09
Sr	6.9	1.02
Mo	<16	1.45
Hg	0.9	-
Pb	0.7	1.28
B	2.0	-
F	8.8	-
Zr	-	1.03
Nb	-	1.07
Ba	-	0.87
Y	-	0.85

the constituent is incorporated in the liquid products and probably doesn't escape. Selenium, with a ratio of about 15, is taken out in the liquid products and its release by escape of the product gas may not be a problem. A low ratio implies that the constituent is not taken out with the liquid products and may escape with the product gas. Arsenic and mercury may escape and the results from the PNL group show that they are detected in the thermal oxidizer gas.

Another type of sample from the Paraho retort where enrichments of siderophile elements were found is the dust from the bag house which collects the retorted shale dust. It is interesting to compare the ratios of retorted shale dust to retorted shale, and product water to blower condensate. This is done in Table 21. Those elements which are enriched in the retorted shale dust are also persisting along the recycle gas line. For example, copper, zinc, arsenic and lead have high ratios of retorted shale dust to retorted shale and low ratios of product water to blower condensate. It is curious that selenium is not enriched in retorted shale dust and also has a high ratio for product water over blower condensate. Molybdenum is one element which is enriched in the retorted shale dust but also seems not to be found in the blower condensates. Based on the values of the ratios in Table 21, it appears that iron, copper, zinc, arsenic, and lead are definitely exhibiting some mobility in the Paraho retort.

ANALYSIS OF MERCURY IN OIL SHALE MATERIALS

In our analysis of the mercury content of oil shale, we attempted 5 different methods of analysis: direct combustion of solid samples using a Jerome #301 Gold-Film mercury detector; an acid digestion of the solid samples analyzed with the Jerome Instrument; direct atomization of solid samples with flameless atomic absorption spectrometry; direct atomization of oil shale retort waters; and direct combustion of solid samples in a double gold amalgamation train with cold vapor atomic absorption spectrometry. We found that double gold amalgamation is the easiest and most reproducible technique.

GOLD FILM METHOD

The first method of analysis attempted was the use of a Jerome #301 gold film mercury detector. Using this instrument, a sample is heated in a quartz combustion bulb with a bunsen burner. The mercury and whatever impurities were in the sample are passed over a piece of gold plated nichrome wire, to form an amalgam and remove the mercury. The rest

of the air stream is vented. The Nichrome wire is then heated to drive off the mercury. The air stream carrying the mercury is filtered with Malcasorb to remove hydrogen sulfide, and is then split into two equal streams. One stream is filtered with paladium chloride to remove the mercury, and is then passed over a gold collector. This is the control stream. The second air stream is passed over a second gold collector. The two collectors are legs in a Wheatstone bridge. The collector that absorbed mercury will undergo an increase in resistance. This increased resistance is proportional to the amount of mercury that was in the sample. The instrument is standardized with mercury vapor.

For the analysis of inorganic material, the Jerome Instrument gives fairly reproducible results. For a Fisher assay spent shale, a result of 0.061 ± 0.035 ppm was obtained. The Battelle Pacific Northwest Laboratory found that the Fisher assay spent shale contained $0.041 \pm .001$ ppm Hg. The Lawrence Berkeley Laboratory found that this sample contained $.0045 \text{ ppm} \pm .005$.

The Jerome Instrument proved to be ineffective in analyzing organic material, particularly unretorted oil shales. When unretorted oil shale samples were run, the Wheatstone bridge of Jerome Instrument went off scale. If only mercury caused this change in resistance, the unretorted oil shale must contain over 1 ppm of mercury. It is unreasonable to assume that there is this much mercury in the oil shale as most samples contain only 0.200 ppm Hg (5, 6, 7, 17).

Apparently there is another compound chemisorbing with the gold collectors which causes a change in resistance. Since the problem didn't exist with the retorted oil shale, the compound is probably organic. The values for the retorted shale were higher than those obtained by other laboratories, and it is possible that there was a smaller interference occurring with these samples.

DIGESTION TECHNIQUES

The next method attempted was to digest the unretorted oil shale with a nitric-sulfuric-perchloric acid mixture, to oxidize the organic material. The digestion was carried out in an areation flask, which was connected to the Jerome instrument. A few drops of SnCl_2 were added to reduce the mercury and cause it to vaporize. The mercury vapor was then run on the Jerome Instrument.

We found that the acid digestion method was unsuitable for the Jerome Instrument. There was a large blank in the

acids which was about 10 times as great as the amount of mercury in the sample (assuming the raw oil shale has 140 ppb Hg). This made it impossible to even run the samples accurately on the Jerome, as the upper limit of its linear working range is around 30 nanograms.

If extremely mercury-free grades of acid were obtained, this method would become more feasible, but acid digestion is still not the best choice of a method of analysis. In a perchloric acid digestion, explosive organic perchlorates can form, which raises questions of safety about this technique. A digestion is also a time consuming procedure. In addition, a large amount of glassware must be used, which increases the potential for contamination or loss of mercury during the analysis. Methods of analysis that do not require sample pretreatment will eliminate some of these problems.

Because of the narrow working range of the Jerome instrument, an acid digestion is probably more suited to flameless atomic absorption spectrometry.

DIRECT ATOMIZATION OF SOLID SAMPLES

The Instrumentation Laboratories #555 Controlled Temperature Furnace Atomizer allows solid samples to be atomized directly, without any pretreatment. Solid samples are preweighed into a graphite microboat, which fits into a square graphite cuvette. With the IL555 there is the capability of setting up highly reproducible time-temperature profiles. The primary absorption line for mercury is 253.7nm, which unfortunately is a wavelength in which aromatic hydrocarbons absorb. This creates interference in the analysis of oil shales. The IL951 Atomic Absorption Spectrometer has a deuterium lamp for background correction. If too many aromatic molecules are in the light path at once, the deuterium corrector can become saturated, and precise numerical measurements cannot be made.

Our hope was that by manipulating the time-temperature profile of the furnace, the mercury could be driven out of the sample before or after the interfering aromatics are vaporized. We manipulated the time-temperature profile using maximum temperature ranges varying between 400°C and 1200°C and could never eliminate the strong background interference. This technique does not, therefore, appear to be viable for oil shale.

DIRECT ATOMIZATION OF LIQUID SAMPLES

Direct injection of liquid into a graphite cuvette is a much more common method of analyzing samples in flameless atomic absorption spectrometry, and it is the method we

attempted to use in the analysis of oil shale retort water. We prepared the samples by adding enough $K_2Cr_2O_7$ to make a 00.05% solution and added enough HNO_3 to make a 2% solution. The mercury in the sample should combine with oxygen at $300^\circ C$, and remains in the sample. The HgO then decomposes at $500^\circ C$ and the mercury is analyzed. This allows the liquid to be pyrolyzed at $250^\circ C$, without vaporizing any of the mercury.

We first checked this method using standards prepared by ASTM methods, in ultrapure water. Fairly reproducible results can be obtained down to 5ppb. The analysis of the retort waters proved to be much more difficult as there is a great deal of organic carbon in the samples (7). Also, the retort waters contain approximately 1 ppb Hg. To obtain accurate results at this concentration, one must use a peak area integration. When the retort water was analyzed, carbon was deposited out onto the inside of the graphite cuvette. This physically blocked part of the light beam from the mercury lamp, which caused a large amount of background drift in the atomic absorption spectrophotometer. After every 5 or 6 samples were run, we had to take apart the furnace and scrape out the excess carbon from the graphite cuvette. Under these conditions, it was impossible to obtain precise results. By preparing spikes of 10 ppb Hg of retort water, we found that it is possible to tell the difference between the spiked and unspiked samples by looking at the analyte peak on the video screen of the atomic adsorption spectrophotometer. However, a precise analysis of retort water for mercury has not been possible by direct atomization in a graphite furnace.

DOUBLE GOLD AMALGAMATION

Double gold amalgamation has proved to be the easiest and most accurate technique employed to date. It requires no sample pretreatment, and it takes about 5 minutes to analyze each sample. In this technique, a sample is heated to $650^\circ C$ in a quartz tube furnace through which a stream of oxygen flows at 0.4 l/min. The vaporized portion of the sample is passed over heated silver wool, which oxidizes organic compounds that were in the sample and could potentially interfere with the analysis. The air stream is then passed over 2 gold amalgamators and vented. The mercury should be entirely absorbed by the first amalgamator. The first amalgamator is then heated to $400^\circ C$, and the mercury is driven off to the second amalgamator. Any organo-mercury compounds in the sample should have been decomposed to elemental mercury when they were driven off the first amalgamator. The second amalgamator is heated and the mercury is run through a cold vapor absorption cell where it is analyzed. The system is standardized by withdrawing

vapor from a Dewar flask which has a drop of elemental mercury in it. This vapor is injected through a septum that is right before the first amalgamator. It is important that a reproducible procedure is used.

Procedure

For the generation of a standard curve, withdraw 1.0 mL of vapor from the Dewar flask and inject it into the amalgamation train before the first amalgamator. Record the temperature in the Dewar flask. Allow 15 sec. for the sample to form an amalgam. Then heat the first amalgamator for exactly 40 seconds. Then heat the second amalgamator to send the mercury to the atomic absorption spectrophotometer (A.A.). After the analyte peak is recorded from the A.A., turn the second amalgamator off and allow the amalgamation train to cool for three minutes and 30 seconds. Then repeat this procedure for 0.4, 0.5, 0.6, and 0.8 mL of mercury laden vapor. From vapor pressure data one can calculate the nanograms of mercury per mL of air. A calibration curve can be plotted which should be a straight line.

To analyze the sample, weigh out about 50 milligrams of sample into a quartz boat. Insert the boat into the tube furnace and heat it for 2 minutes. Open the valve after the second amalgamator to vent the waste gases. Close the valve and heat the amalgamators the same way as for the standards. Allow two minutes cooling between samples.

For inorganic substances, the amalgamation train is fairly accurate and reproducible. For NBS1633 coal fly ash which is rated at .14 ppm, we found mercury concentrations of $.135 \text{ ppm} \pm .008$. For spent shale-1 we get a value of $.054 \text{ ppm} \pm .007$. Battelle P.N.L. reports a value of $.058 \pm .004$, and the Lawrence Berkeley Laboratory reports a value of $.053 \pm .005$.

For raw oil shale (OS-1) we found mercury concentrations of $.212 \text{ ppm} \pm .024$, which is higher than the values obtained by Battelle and Berkeley ($.14 \pm .007$ and $.16 \pm .02$ respectively). It is possible that organic compounds are interfering at the surface of the gold amalgamator and giving artificially high results.

FUTURE WORK

With our amalgamation train, we can begin analysis of retorted oil shales. For raw shale, more data must be taken to ensure the validity of the technique. An additional filter can be added to the amalgamation train, possibly

heated alumina support, to filter out organics. We would also like to develop a method for the analysis of oil shale retort water in the amalgamation train. It may be possible to analyze it by directly combusting it in the tube furnace.

INDICATIVE TESTS ON RETORT WATERS

CONDUCTIVITY

Instrumentation

The conductance measurements were all done using a Yellow Springs Conductivity Meter model 33. The cell used was the 3300 series probe made by Yellow Springs. The cell constant of the probe was equal to 5.0 cm^{-1} . This was the cell constant for which the meter was designed. The cell required constant cleaning and checking against a standard potassium chloride solution. The retort waters are quite corrosive to the electrodes.

Temperature

A feature of the probe used was that a thermocouple allowed the temperature to be easily monitored. Although no direct measurements were done on a standard solution to observe the temperature dependence of the conductivity, it was observed to be very dependent. A temperature of 25°C was used consistently throughout the experiments. Water baths were used to maintain a constant temperature. The temperature error in the retort samples is $\pm 1^{\circ}\text{C}$. Although the retort samples were not placed in a water bath, the water used to make the dilution and the room temperature were both $25^{\circ}\pm 1^{\circ}\text{C}$. The temperature of each solution was checked before the actual conductivity measurements were made.

Ammonium Carbonate Solutions and Sample Measurements

Solutions of both $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)\text{HCO}_3$ from concentrations of 0.001M to 1.00M were prepared in volumetric flasks for conductivity and pH measurements. Upon dissolution of the solid carbonate or bicarbonate, a gas was evolved. The smell of ammonia was obvious but not overpowering. A simple test on the gas was performed using lime water. The gas was bubbled through the lime water and indeed, the water turned cloudy. This indicated that the gas was probably a mixture of carbon dioxide and ammonia.

Measurements of the conductivities of these ammonium

carbonate solutions were done in a water bath to assure uniform temperature. The conductivity reading of a freshly prepared solution was unstable with time. After the solution was poured from the stoppered volumetric flask, and the conductivity measured, the same solution would give higher readings after each two-minute interval. Stable and reproducible readings could be obtained only after about seven to eight minutes.

Measurements of the retort water were done carefully because species in the waters had previously destroyed the platinum black of the cells. Only 1:100 dilutions were measured. A series of measurements on a diluted sample showed no time dependence on the readings. The probe was periodically checked with the standard KCl solution to assure the cell constant was still 5.0 cm^{-1} .

Table 22 and Figure 5 summarize the data taken on the carbonate solutions. Note the line is almost linear even at higher concentrations. One would expect ion-ion interactions to start to flatten out the curve. This occurs to a small extent for $(\text{NH}_4)_2\text{CO}_3$.

PH

Instrumentation

Three different instruments were tried to obtain reproducible pH readings: a Sargent-Welch PAX system, an Orion 701 meter, and a Leeds and Northrup meter. A glass electrode with a saturated calomel reference was used. Only the Leeds and Northrup meter gave reproducible results with both buffer solutions and ammonium carbonate solutions. The other two meters were digital and would take minutes to obtain a constant reading. The Leeds and Northrup instrument was a meter-type and worked very well.

Ammonium Carbonate Solutions and Retort Waters

Problems with obtaining a reproducible pH reading were particularly troublesome for both standard ammonium carbonate solutions. It took at least 30 seconds for the meter to stabilize and the more concentrated the solution, the worse the problem became. The readings for the retort waters were all fairly stable and reproducible. The retort water pH was taken by pouring the water into a 50mL teflon beaker and the pH electrode was placed directly in the water. Between measurements the electrode was rinsed thoroughly with distilled water. Occasionally between sets of measurements a buffer solution acted as a check on the pH electrode.

Figure 5: Conductance of ammonium carbonate and ammonium bicarbonate solutions.

TABLE 22---Conductance Measurements of Ammonium Carbonate Solution.

$(\text{NH}_4)_2\text{CO}_3$		$(\text{NH}_4)\text{HCO}_3$	
Molarity	Conductance μmho	Molarity	Conductance μmho
.500	43100	.500	20000
.450	40400	.400	16750
.400	36700	.300	13150
.350	33000	.200	9100
.300	29300	.100	4745
.250	26000	.050	2750
.200	22020	.010	535
.150	16800	.005	280
.100	11900	.001	63
.075	8740		
.050	5980		
.025	2736		
.005	712		
.002	355		
.001	151

Figure 6: The change in pH of ammonium bicarbonate solutions after 24 hours.

The reproducibility of the pH readings of both ammonium carbonate solutions was poor. The plot of pH against $(\text{NH}_4)\text{HCO}_3$ concentration is shown in Figure 6. It shows a change of about 0.25 pH units when the solution is allowed to remain for 24 hours in beakers covered with watchglasses. Even after one hour, the readings would change by 0.1 pH unit.

The pH measurements of the retort waters were consistent and reproducible. The correlation of the pH of the retort water to either ammonium carbonate solution is difficult to define. The average LPW water pH value is 8.4. This seemed to fall halfway between the $(\text{NH}_4)_2\text{CO}_3$ and the $(\text{NH}_4)\text{HCO}_3$ solutions at low concentrations. The pH of the RC waters averages about 8.6 to 8.7. This falls into the $(\text{NH}_4)_2\text{CO}_3$ region for the low concentration values.

EH MEASUREMENT

The Eh measurements of the retort waters were done using an Orion Model 170 meter, a saturated calomel electrode and a platinum button reference electrode. A Zobell reference solution was prepared to standardize the system (24, 27). The apparatus was calibrated and checked periodically. There was some concern that the constituents in the retort water might damage the electrodes. Since a saturated calomel electrode was used, a correction factor of .24453 volts was added to each measured value.

Each retort water was analyzed by directly placing the two electrodes into the sample. This was done immediately after the pH reading was taken. There was a problem of a stable reading. The initial reading would usually be high and then it would decrease. A six-minute waiting period gave reasonably stable readings. In general, the LPW waters were less stable than the RC waters. The RC waters would stabilize within two minutes and all Eh values were recorded at the end of four minutes.

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PROGRESS REPORT 1979 - 1980

Geochemistry of Oil Shale Leachates

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INTRODUCTION

During the past year we have approached the completion of several of the research tasks that we established during the preceding three years. Based on this work, we have prepared three manuscripts for submittal to major scientific journals. Our Progress Report, which follows, is essentially comprised of three manuscripts. In view of the editing and rewriting that has gone into these manuscripts, we feel that they offer the best possible vehicle for presenting our work in this Progress Report. In addition to the three manuscripts, there is one additional section concerning our work on the sorption and removal of fluorine and boron from leachates by native soils of the Piceance Creek Basin.

In the first manuscript, Stollenwerk and Runnells summarize the results of the leaching studies. We have investigated a number of fresh and retorted shales, and the results of the leaching experiments allow us to make some reasonable predictions about the possible impact of surface disposal of such materials in the oil shale region. Of particular interest in this work is the result of experiments to test the effect of aging on the solubility of the shales, and some rather surprising results have been observed. Our efforts at computer modeling of the aqueous chemistry of the leachates are also summarized in the first section of the Report.

The second and third sections of the Report consist of two manuscripts prepared by Saether and Runnells on the geochemistry of fluorine in oil shale. Early in our research, we recognized that fluorine is one of the most important and potentially hazardous contaminants in aqueous leachates from oil shale. These two manuscripts describe the intensive and rather novel approaches that we have employed to identify the mineralogical residence of the fluorine in the shales, and to define and understand its behavior upon leaching with water.

The fourth and final section of our Progress Report summarized the work being conducted by Glaze and Runnells on the sorption and retardation of fluorine and boron from aqueous leachates upon passage through the native soils of the region. We have found that the nature of the reaction between the dissolved contaminants and the soils depends strongly upon the initial pH of the leachate. At elevated values of pH the leachates absorb carbon dioxide from the air, resulting in rapid precipitation of calcium carbonate. This precipitate of calcium carbonate tends to plug the pore spaces in the soil and to strongly reduce the flow to the leachates. Such a reaction might offer a useful method for reducing the movement of fluids out of piles of waste shale, either on the surface or underground.

During the year we have given three talks on our work at national scientific meetings, as well as three talks at gatherings of researchers in the field of oil shale.

Geochemistry of Leaching of Trace Elements of Oil Shale

K. Stollenwerk and D. Runnells

INTRODUCTION

Development of a commercial oil shale industry in the United States appears very likely. The largest known deposits of oil shale are located in the Green River Formation of Wyoming, Utah, and Colorado (Figure 1), where an estimated 600 billion barrels of oil exist in deposits at least 3 m thick and averaging .6 barrels/ton (105 L/tonne (2)). Of the approximately 80 billion barrels that may be recoverable using existing technology, 75% is contained in the Piceance Creek Basin of northwestern Colorado.

Oil shale is a fine-grained sedimentary rock containing a significant amount of kerogen, a type of organic matter largely insoluble in organic solvents, which yields oil and gas upon pyrolysis. Extraction of oil is accomplished by heating the shale to temperatures in excess of 500° C by any one of a number of methods, including above-ground (surface) and underground (in-situ) processes (3,4). The most common minerals found in the inorganic fraction of oil shale are listed in Table I. In addition to these, hundreds of other minerals are present locally in small amounts (4-12). Several investigators have discussed the geologic origin of the Green River Formation (11, 13-20).

Perhaps the largest problem facing the oil shale industry is the disposal of the solid wastes. After retorting by surface methods, the retorted shale occupies a volume roughly 20% greater than the raw shale in place (21). This means that for a 500,000 bbl/day shale oil industry, approximately 75,000 m³/day of waste will be generated in excess of that returned to the mine. Current plans are to dispose of this waste by filling canyons in the area. Even if production of shale oil were accomplished by the "modified in-situ" method (22), approximately 20% of the rock would be mined and brought to the surface. The 20% removed will be retorted on the surface and disposed of above-ground. In addition to waste from retorted oil shale, both above and below ground, significant quantities of waste unretorted oil shale may be generated as by-products and will also have to be disposed on the surface.

OBJECTIVES

One important aspect of the development of this industry concerns the potential problem of contamination of groundwater and surface water by toxic materials resulting from leaching of the waste oil shale by percolating waters. The percolating water might consist of rainfall or snow melt, or, in the case of in-situ extraction of oil, the water might be groundwater that percolates through abandoned underground chambers. If such waters pick up significant quantities of toxic contaminants, they could carry these contaminants into valuable ground and surface water resources of the region. In a semi-arid region such as the Piceance Creek Basin of western Colorado, any potential threat to existing water resources must be investigated.

EXPLANATION

Area Underlain by the Green River Formation in Which the Oil Shale is Unappraised of Low Grade

Area Underlain by Oil Shale More Than 10 Feet Thick, Which Yields 25 Gallons or More Oil Per Ton of Shale

Figure 1

TABLE 1

Major Minerals in Oil ShaleDominant

Quartz	SiO_2
Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Calcite	CaCO_3
Albite	$\text{NaAlSi}_3\text{O}_8$

Locally Abundant

K-Feldspar	KAlSi_3O_8
Dawsonite	$\text{NaAl}(\text{OH})_2\text{CO}_3$
Analcime	$\text{NaAlSi}_2\text{O}_6\text{H}_2\text{O}$
Nahcolite	NaHCO_3
Illite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
Pyrite	FeS_2
Siderite	FeCO_3

This study is chiefly concerned with the release and mobility of certain inorganic components of oil shale which are potentially toxic, namely, those elements which form anionic dissolved species in water. Boron, fluoride, molybdenum, arsenic, and selenium were chosen because of their known toxic effects on plants and animals, and because they may exhibit increased solubility and mobility at the elevated values of pH that result from the interaction between oil shale and water. This projected chemical behavior is in sharp contrast to that of some other trace species, such as lead, copper, zinc, and mercury, which form relatively insoluble hydroxides at elevated pH (23). Values of pH ranging from 7.3 to 11.7 have been reported in leachates from fresh and spent oil shale (24, 25) and various published analyses show the presence of significant quantities of the five elements of interest in oil shale (26-29).

The toxicity of As is a well known fact (30). Selenium, which is an essential trace element in man and animals, is also toxic at high concentrations (31,32). Maximum allowable concentrations for As and Se in drinking water are .05 and .01 mg/L respectively (33). Small concentrations of B are essential for growth in higher plants, but some species are very sensitive to an excess of B. Irrigation water containing more than 1.25 mg/L B is unacceptable for many fruit trees including peach, apple, and pear (34,35). High levels of B have also been associated with gastrointestinal and pulmonary disorders in lambs (36). Excessive F can cause fluorosis in animals and man as well as mottling of teeth (37); and the U.S. Environmental Protection Agency has set a limit of 2 mg/L in drinking water for humans. Molybdenosis in ruminants is perhaps the most serious disease caused by excessive Mo. The state of New Mexico has now set a standard of 1.0 mg/L for dissolved Mo in irrigation water (38) because of the danger of molybdenosis to grazing animals.

During the course of our investigations, high concentrations of reduced sulfur species, principally thiosulfate ($S_2O_3^{2-}$), were found in leachates from retorted oil shale (25). Reduced species of sulfur may have significant effects on the environment should such leachate ever escape into natural waters. For example, Audus and Quastel (39) have shown that thiosulfate in concentrations ranging from 450 to 4,600 mg/L inhibits seed germination in several types of plants. In addition, in Canada it has been found that reduced species of dissolved sulfur in aqueous effluent from metallurgical mills may later oxidize to produce sulfuric acid in the rivers which receive the discharge.

METHODS

Materials. Most leaching experiments were conducted using four different types of oil shale. Two of the shales, OS-1 and SS-2, were characterized and supplied to us by Dr. Thomas Wildeman of the Colorado School of Mines, collected from TOSCO (The Oil Shale Corporation); these shales were mined from the Mahogany Zone at the Colony Development site near Grant Valley, Colorado (40). Sample OS-1 was collected from feedstock which was used in the TOSCO II above-ground retorting process, while SS-2 represents the retorted equivalent of fresh shale OS-1. By comparing fresh shale to the retorted equivalent, we can measure the effect of retorting on the solubility of the elements of interest.

Sample PSS01 is an oil shale retorted by the Paraho surface process at Anvil Points, Colorado. As a result of the larger size of the Paraho feedstock, the shale oil gases in the interior of the particle must force passages through the rest of the shale fragment, resulting in a retorted fragment that is porous (41). We collected this particular sample from two large lysimeters which were constructed in the field at Anvil Points by Drs. Trey Harbert and William Berg of Colorado State University, for the purpose of determining the best methods of revegetating and stabilizing retorted Paraho oil shale (41). The samples offer us an opportunity to determine how closely our leachates generated in the laboratory simulate field conditions. Spent shale taken directly from the Paraho retort is about the same size as the initial feedstock (.6-7.6 cm). During compaction in disposal piles, the size of fragments is significantly reduced; based on sieve analyses in our laboratory, approximately 18% are larger than 18 mm, 42% range from 2 to 18 mm, and 40% are <2 mm. Only the fraction <2 mm in size was used in the laboratory columns due to the scaled down nature of the experiments. One major difference between the field site and samples used in the laboratory is the size of the fragments of shale.

Sample POS-1, also collected by Dr. Wildeman (42) represents fresh oil shale which had been crushed too small to be fed into the Paraho retort. Current estimates indicate that up to 10% of the oil shale that is mined for the Paraho process could be lost during the crushing process. This fine material will probably be disposed along with the spent shale (43). Sample POS-1 of our classification corresponds to Wildeman's sample designation of M104.

Leaching Experiments. Leachates were generated in the laboratory by packing approximately 200 g of shale into boro-silicate glass columns 30 cm high and 2.8 cm inside diameter. Nylon mesh was used as a plug to contain the shale. Earlier experiments indicated that neither loss of F nor gain of B was significant because of the limited contact between the solutions and the inside surfaces of the glass columns (44). Columns were initially saturated from the bottom to allow air bubbles to escape. Once saturated, the columns were sealed and allowed to stand for various periods of time before leaching in order to determine the length of time required for oil shale and water to equilibrate. Leaching was carried out by adding de-ionized water on top of the columns and collecting the leachate in increments of 1/3 of a pore volume, one pore volume being equal to the total porosity of the column of shale. Preliminary tests were conducted in order to determine if filtering of the leachates would be necessary. Results showed no difference in dissolved constituents between 0.45 micron filtered samples and non-filtered replicates; therefore, the filtering step was omitted in the small column set of experiments.

Table II gives the bulk density, porosity, and hydraulic conductivity of the four shales in the column equilibrium experiments. Paraho spent shale in the columns was compacted to about 60 to 65% of the density Paraho expects to achieve in the field, and TOSCO II retorted shale to about 75-85% (Table II). As a result of the lower bulk densities of retorted shale in the columns, porosities are higher than would be expected in an actual disposal pile.

TABLE II

BULK DENSITY, POROSITY, AND HYDRAULIC CONDUCTIVITY
OF OIL SHALE IN COLUMNS

Oil Shale	Bulk Density g/cm ^{3c}		Porosity %		Hydraulic Conductivity cm/sec.	
	Ave.	Range	Ave.	Range	Ave.	Range
POS-1 ^a	1.36	1.21-1.41	28.9	27.3-32.6	1.8x10 ⁻⁴	8.8x10 ⁻⁵ -7.1x10 ⁻⁴
PSS-1 ^a	1.03	1.01-1.04	48.7	48.0-49.3	8.6x10 ⁻⁴	5.4x10 ⁻⁴ -1.0x10 ⁻³
OS-1 ^b	1.07	1.06-1.10	38.0	37.0-39.0	1.3x10 ⁻⁴	7.3x10 ⁻⁵ -1.6x10 ⁻⁴
SS-2 ^b	1.15	1.14-1.16	43.6	42.4-44.7	1.4x10 ⁻⁴	1.2x10 ⁻⁴ -1.6x10 ⁻⁴

^aBased on results from five columns. ^bBased on results from 3 columns.

^cThe expected bulk density of shale compacted in actual disposal piles for Paraho retorted shale = 1.60-1.68 g/cm³ (45); and for TOSCO retorted shale = 1.36-1.52 (46).

A separate leaching experiment on four large columns was carried out for the purpose of obtaining enough aqueous leachate for a complete inorganic chemical analysis. The data were used as input to a computer program, modified WATEQF (47,48), used for modelling the chemistry of natural waters. The large columns (30 cm high by 8.4 cm inside diameter) were packed with about 1500 g of shale; four of these columns were used for each type of shale to insure adequate volumes of leachate. Each set of columns was treated in an identical fashion; the columns were saturated by inverting and saturating from the bottom up to allow as much air as possible to escape. The direction of water movement during saturation corresponds to the direction of flow during leaching. After 46 days of equilibration, leachate was collected in 1/4 pore volume fractions (125 ml); the equivalent fractions from each of the four columns were then combined into one sample for analysis. Measurements of specific conductance on each fraction indicated homogeneity between columns of the same shale and pore volume fraction. Bulk density, porosity and hydraulic conductivity values were all similar to those measured in the experiments with smaller columns. Both POS-1 and PSS-1 were used; however, there was an insufficient amount of OS-1 and SS-2, so another of TOSCO II re-torted shale (SS-3) was used; this sample was virtually identical to SS-2 in grain size and chemical response. The fourth shale used in the large columns, INOS-1, was collected from Federal Oil Shale Lease Tract C-a, where the Rio Blanco Oil Shale Project is currently underway. Production of shale oil at this site will be by the modified in-situ process, which requires that 20% of the shale be brought to the surface in order to create enough room for fracturing of shale and retorting (22). Sample INOS-1 was collected from a disposal pile on the surface at the site of the mine; it allows us to gather information on the range of leaching characteristics one might expect from fresh oil shale. Table III lists the distribution of particle sizes of the six shales, including the surface areas as measured by the B.E.T. nitrogen saturation method (49). Table IV gives the concentration of B, F, Mo, As, and Se in the solid shales; samples SS-3 and INOS-1 are missing from Table IV because they have not yet been analyzed.

Specific conductance (S.C.), total alkalinity, pH, and reduced sulfur species were measured immediately after collection, followed by complete evaporation and preparation of targets of the residue for analysis by x-ray fluorescence. The remaining sample of liquid was analyzed for Mo, B, and F within a few days of collection, followed by analysis of the remaining constituents.

Values of TDS were determined from S.C. using empirical conversion factors. The conversion factors are dependent both on the type of ionic species present and the concentration, as shown in Figure 2. The factors shown in Figure 2 were determined by analyzing for the principle components in leachate and then making up synthetic solutions containing the correct proportions of each major component. Then, by successive dilution of these solutions, we were able to construct a characteristic curve for each leachate, thus allowing us to use the best empirical factor to convert the measured S.C. to the corresponding TDS. The solid lines in Figure 2 are curves for the artificial solutions and the dashed lines represent the first four one-quarter fractions of actual leachates from the large column experiments.

TABLE III

Particle Size Distribution of Shales Used in Experiments

<u>Oil Shale</u>	<u>%Clay</u>	<u>%Silt</u>	<u>%Sand</u>	<u>%2-6 mm</u>	<u>Surface area (cm²/gm)^d</u>
OS-1 (fresh)	4	17	79	0	1.8
SS-2 ^a (retorted)	4	86	10	0	6.1
POS-1 (fresh)	2	10	75	13	1.2
PSS-1 ^{b,c} (retorted)	2	18	80	0	14.5
INOS-1 (fresh)	1	9	90	0	-
SS-3 ^a (retorted)	3	56	41	0	-

^aContains 4-5% residual carbon. ^bContains 2-3% residual carbon.

^cBased on less than 2 mm size fraction. ^dSurface area determined by B.E.T. nitrogen saturation method (49) after samples was heated to 150° for approximately 18 hours.

TABLE IV

Concentration of B, F, Mo, As, and Se in Oil Shale^a

Oil Shale	B $\pm 10\%$	F $\pm 10\%$	mg/kg		
			Mo $\pm 10\%$	As $\pm 15\%$	Se $\pm 15\%$
POS-1	175	1,500	20	27	1.7
PSS-1	160	1,500	28	54	2.0
OS-1 ^b	110	1,020	28	70	4.1
SS-2 ^b	146	1,490	36	82	4.9

^aThe shale samples were fused with a 50-50 mixture of Na_2CO_3 - K_2CO_3 at 1000°C for .5 hours, dissolved, and analyzed for B and F. Another portion of the shale samples were digested in a mixture of HF , HNO_3 , and H_2SO_4 , followed by analysis for Mo. The techniques for B, F, and Mo analysis are described under analytical methods. Arsenic and selenium were analyzed by x-ray fluorescence. ^bReference, 29, p.82.

ANALYTICAL METHODS

Leachates were analyzed by the following procedures: 1) fluoride was determined by a molecular absorption technique developed by Dr. Robert Meglen of our central analytical laboratory (50); 2) boron was determined by the azomethine-H colorimetric method; 3) molybdenum by a colorimetric procedure using the thiocyanate complex (51); 4) arsenic and selenium by x-ray fluorescence. Molybdenum was also determined in some of the leachates by x-ray fluorescence as a check on the accuracy of the colorimetric method. Analytical precision for these five elements in leachate is the same as that reported for the solids (Table IV). Total sulfate in solution was determined after oxidizing the leachate with 30% H_2O_2 , followed by titration with nitrochromeazo (52). Determination of thiosulfate ($\text{S}_2\text{O}_3^{2-}$), trithionate ($\text{S}_3\text{O}_6^{2-}$), and the other polythionates ($\text{S}_4\text{O}_6^{2-}$, $\text{S}_5\text{O}_6^{2-}$, and $\text{S}_6\text{O}_6^{2-}$), was based on the conversion to SCN^- under different reaction conditions, followed by the measurement of the ferric thiocyanate color complex (53,54). Thiocyanate in the leachates was determined by measuring the intensity of absorption of light by the ferric thiocyanate complex, without any other chemical preparation. Atomic absorption spectroscopy was used to determine K, Ca, Mg, and Na, while the argentometric titration method was used for Cl (47), and alkalinity was measured by titration with HCl to pH 4.5 (47). The oxidation-reduction potential (Eh) was determined by immersing several platinum electrodes, at different depths; within columns packed with saturated oil shale.

RESULTS AND CONCLUSIONS

SMALL COLUMN LEACHING EXPERIMENTS

Figures 3,5,7,9, and 11, show the relationships between the length of time of contact between water and shale, the pH, and the concentration of total dissolved solids (TDS), Mo, B, and F. Saturated columns of all four types of shale were allowed to equilibrate for 0.3, 7, and 13 months before leaching was initiated; columns of shales POS-1 and PSS-1 were also allowed to equilibrate for 1.5 and 18 months. Figures 4,6,8, 10 and 12 show how the composition of the leachate varies with the amount of water passed through the shale.

As can be seen from Figure 3, there is little difference in pH between leachate from fresh oil shales OS-1 and POS-1, and from the spent shale retorted by the TOSCO II process (SS-2 in Figure 3). Retorting by the Paraho process (sample PSS-1 in Figure 3), however, results in an increase in pH to 9.6 in the laboratory leachates. We measured values as high as 11.7 in leachates collected from spent Paraho shale in the field lysimeters installed by Berg and Harbert of Colorado State University. The lower pH values measured in the laboratory leachates appear to be a result of aging, possibly caused by the uptake of atmospheric carbon dioxide gas (re-carbonation) by the solid samples; over 1.5 years elapsed between collection of the Paraho retorted shale and the column experiments. Independent shaker experiments with Paraho spent shale immediately after collection in the field resulted in much higher pH values, of about 11 (25).

Figure 2

Figure 3

Such high pH values are clearly the result of partial loss of carbon dioxide and decomposition of carbonate minerals into their respective oxides with resulting hydrolysis reactions between the calcined oxides and water.

The length of time that water and shale are in contact in the laboratory generally does not appear to have any major effect on pH, except for the Paraho shale, where 10 days is insufficient time for equilibration. This may be due to the carbonaceous coating on the particles of shale. Figure 4 shows that the pH remains relatively constant for up to 15 successive pore volumes of leachate.

Figure 5 shows the change in total dissolved solids in the leachates with time. It is evident that higher concentrations of dissolved solids are released from retorted shale than from unretorted shale. This is especially noticeable when comparing the TOSCO II retorted shale (SS-2), to its unretorted equivalent (OS-1). After 13 months of water-shale contact, leachate from SS-2 contained 29,700 mg/L of dissolved solids compared to 7,100 mg/L in OS-1 leachate. Part of the reason for this increase is probably due to the greater surface area of the predominantly silt-size SS-2 ($6.1 \text{ cm}^2/\text{g}$), compared to the predominantly sand-size OS-1 ($1.8 \text{ cm}^2/\text{g}$). Also importantly, chemical reactions take place during retorting which increase the solubility to sulfates, resulting in highly soluble minerals being exposed to percolating waters.

As shown in Figure 5, leachate from oil shale retorted by the Paraho process (PSS-1) contains only half the dissolved solids of leachate from shale retorted by the TOSCO II process (SS-2), despite the greater surface area of PSS-1 (Table III). Because of the higher temperature of retorting, sample PSS-1 probably contains less highly soluble salt than SS-2, or possibly, the water percolating through the columns is simply not contacting all of the surfaces reached by the nitrogen gas in the B.E.T. measurement of surface area.

Leachate from fresh shale (POS-1) collected from the Paraho plant contains nearly 90% more TDS than does leachate from the fresh shale (OS-1) from the TOSCO process, in spite of the larger surface area of OS-1 (Table III). Differences in mineralogy are probably involved; leachate from POS-1 is predominantly Na-HCO_3 , while leachate from PSS-1, OS-1, and SS-2 contains mostly Na-SO_4 . Also, there is probably more kerogenous material on the surfaces of mineral particles in sample OS-1 (140 L/tonne) than in POS-1 (95 L/tonne). Figure 5 shows that the TDS continues to rise in all leachates, from both fresh and retorted shales, up to a period of at least 13 months. After 18 months, the TDS levels off in leachates from the column of sample POS-1 (fresh Paraho shale); unfortunately, we did not have sufficient sample to extend all experiments to 18 months.

Figure 6 shows how the concentration of dissolved solids varies with the amount of water percolated through the shale. It can be seen that there is a rapid exponential drop in TDS over the first few pore volumes, followed by a gradual leveling off towards some baseline concentration. This exponential decrease indicates that the TDS concentration in the first few pore volumes of leachate is principally controlled by the rinsing out of the readily soluble salts. After these free salts are gone, slow dissolution of the less soluble minerals becomes the controlling factor in the concentration of TDS, as is evident from the flatter portion of the curves.

Figure 4

Figure 5

Figure 6

Leachates from SS-2, POS-1, and OS-1, all have similar curves; leachate from PSS-1, however, behaves in a different manner. In the curve for PSS-1, a break occurs in the exponential decrease of TDS between pore volume 3 and 12. The uniform concentrations between pore volumes 3 and 12 may be due to the diffusion of salts from the interstices of the porous oil shale particles. After the salts have been diffused out of the interior of the oil shale particles, bulk concentrations again decrease rapidly until reaching some baseline which is controlled by less soluble minerals.

Other results (not presented here) also indicate that termination of the active leaching after four of five pore volumes, followed by equilibration for one year, does not result in any significant increase in TDS when leaching is eventually resumed.

Figure 7 shows that concentrations of Mo in leachate from retorted oil shale (PSS-1 and SS-2) are largely independent of the time of contact between water and shale; however, there is clearly a decrease with time in the concentration of Mo in leachates from fresh POS-1, far in excess of the estimated analytical error of $\pm 10\%$ of the reported concentration. This trend may be leveling off near 8 mg/L Mo for POS-1 in Figure 7. The difference in total concentration of Mo between the fresh POS-1 and OS-1 reflects the difference in TDS leached from these two shales (Figure 5), and is clearly due to differences in mineralogy, even though the concentrations of total Mo in the shales are similar (Table IV).

One can also see from Figure 7 that retorted SS-2 releases more Mo to water than the fresh equivalent, OS-1. This difference can be partially attributed to the difference in particle sizes, and probably to higher concentrations of Mo present in the more soluble surface coatings in SS-2. Oil shale retorted by the Paraho process releases the lowest amount of Mo, approximately 1 to 2 mg/L (Figure 7).

Concentrations of Mo in leachate from all shale samples are greatly reduced by the third pore volume (Figure 8), down to values near or below the New Mexico State standard of 1.0 mg/L (38). The exponential rate of decrease for each leachate is similar to that observed for TDS, indicating a similar mechanism of release.

There is considerable variation in the amount of B released to water from the different shales. As shown in Figure 9, as much as 2.8 mg/L were found in leachate which had equilibrated with fresh POS-1 for 13 months, compared to a maximum concentration of 2.6 mg/L in leachate from the retorted PSS-1, despite the fact that both solid samples contain approximately the same total concentration of B (Table IV). The lower equivalent values of 20 mg/L for 1.5 and 18 months (POS-1) do not fit any readily discernible pattern, and may be analytical error; the equilibrium concentration therefore appears to be between 20 and 28 mg/L. The same holds true for OS-1 and the equilibrium value will be between 13 and 17 mg/L. A decreasing rate of increase in B with time is evident in leachate from SS-2, the retorted equivalent of OS-1. The rate of increase appears to be leveling off after 13 months, and it is likely that the equilibrium concentration can be extrapolated to about 15 mg/L from Figure 9.

The dramatic drop in the concentration of B in leachate from PSS-1 compared to leachate from unretorted POS-1 is probably a function of the high retorting temperature (approximately 650°C) attained in the Paraho process. As the retorting temperature increases, the original minerals present in oil shale begin to alter to minerals characteristic of higher temperatures (55,56). It is likely that B has become locked up in new, relatively insoluble silicate minerals; these minerals have not yet begun to form in the lower temperature TOSCO II process.

Figure 7

Figure 8.

Figure 9

Figure 10 shows that B is rapidly rinsed out of shale samples POS-1 and OS-1, following the pattern exhibited by TDS and Mo. This is not the case for leachate from PSS-1 and SS-2; the fact that B is not rapidly rinsed out of the first few pore volumes probably reflects a slower rate of release from newly formed silicate minerals.

Fluoride (figure 11) in the first pore volume of leachate from both samples of fresh shales (POS-1 and OS-1) decreases as the time of contact increases between shale and water. Allowing shale and water to equilibrate for less than 1.5 months resulted in concentrations greater than 50 mg/L in the first pore volume of leachate from POS-1; however, after 18 months of equilibration F was only about 16 mg/L. There is little change in F between 13 and 18 months, indicating that 16 mg/L is probably a reasonable equilibrium concentration for F in POS-1. Sample OS-1 may also be at equilibrium at a value near 15 mg/L after 13 months.

In contrast to fresh oil shale, Figure 11 shows that retorted oil shale releases more F to water as the length of contact time increases. This striking contrast in behavior is surely related to changes in the mineralogy of the shales resulting from retorting, but we have not studied the character of such change.

Figure 12 shows how the concentration of F in leachate varies as a function of the number of pore volumes of water passed through the columns. In contrast to the concentrations of TDS, Mo, and B, which decrease after passage of one or two pore volumes of water, F remains at an elevated level. Leachate from POS-1 actually exhibits a significant increase in F between the first and second pore volume, going from 17 to 36 mg/L, which is a change well beyond analytical error. Some of the apparently erratic nature of the curves in Figure 12 is due to periods where leaching was discontinued from a few days to a few weeks; however, the concentration of F in the leachate from PSS-1 remains about the same through 30 pore volumes, despite interruptions in leaching. The high and constant concentrations of F in successive pore volumes of leachate clearly mean that there is a solid reservoir of F in the shale that is capable of replenishing and restoring F to percolating water. This behavior obviously has major implications to any plan of reclamation which includes the "rinsing out" of contaminants from waste shales. Most contaminants can indeed be rinsed out, but F poses a special hazard in leachates from both fresh and retorted shales. A detailed study of the mineralogic residence and leaching of F is currently being conducted by others in our research group.

Concentrations of As and Se in oil shale leachates are generally low (table V). The highest concentrations of As are in leachates from oil shale associated with the Paraho process; the concentrations decrease with time and number of pore volumes. The highest values for Se are associated with unretorted oil shale. It would appear that As and Se do not pose any significant threat to water quality under the leaching conditions used in our experiments.

COMPUTER MODELING

Our computer program, WATEQF, is a major modification of the original WATEQ program (57); it calculates the equilibrium distribution of inorganic aqueous species, of the major and many minor

TABLE V

Variation in As and Se Concentration in Oil Shale with Time
Values are for the First Pore

Volume Shale	As (mg/L)			Se (mg/L)		
	Months Equilibrated			Months Equilibrated		
	<u>.3</u>	<u>7</u>	<u>13</u>	<u>.3</u>	<u>7</u>	<u>13</u>
POS-1	.102	.030	.027	.095	.057	.085
PSS-1	.072	.019	.034	.033	.026	.082
OS-1	.017	.016	.009	.116	.010	.040
SS-2	.018	.022	.021	.020	.022	.036

Figure 10

Figure 11

Figure 12

elements in natural waters, as well as calculating the apparent state of saturation of these species with respect to solid phases. Input into the computer program consists of the elemental analysis, temperature, pH, and Eh.

Table VI lists the concentrations of Mo, B, F, and the major elements measured in the first pore volume of leachate from the experiments involving large columns. Sulfate (SO_4^{2-}) is the predominant anion in all leachates except POS-1, where HCO_3^- dominates. Sodium is by far the major cation, but Mg is present in relatively high concentrations in SS-3. Total dissolved solids, pH, Mo, B, and F concentrations for POS-1, PSS-1, and SS-3 agree very well with concentrations measured in the smaller column experiments (Figures 3, 5, 7, 9, and 11). One exception, however, is the lower concentration of Mo (3.9 mg/L) in SS-3 (Table VI) leachate compared to about 10 mg/L for SS-2 (Figure 7). Although SS-2 and SS-3 release comparable amounts of TDS, SS-3 apparently contains less soluble Mo than SS-2, demonstrating that variations can certainly occur in leachates from shale retorted by the same process. The F concentration of POS-1 (82 mg/L) is also higher than any values found in the small column experiments (Figure 11).

Table VII shows the cation-anion balance for the same four leachates. Ideally, the total milliequivalents/L (meq/L) of anions in solution should equal the total milliequivalents/L of cations, any differences resulting from incomplete or inaccurate analysis. As can be seen from Table VII, there is a relatively good balance between the total meq of cations and the total meq of anions for each leachate. The number of elements that we were able to input into WATEQF comprise 96.6 to 99.9% of the total concentration of dissolved solids which were determined (Table VII).

The distribution of species of B, F, and Mo for the first pore volume of leachate from the large columns, as calculated by WATEQF, is presented in Table VIII. More than 99% of the aqueous Mo in leachates from oil shale appears as the free molybdate ion, MoO_4^{2-} . The Mo concentration appears to be controlled by the mineral powellite (CaMoO_4) in leachates from PSS-1, SS-3, and INOS-1, in which computed saturation indices (48) range from (+)0.3 to (+)0.6 (Table IX) indicating supersaturation of the leachates with respect to powellite. Only leachate from POS-1 is slightly undersaturated with respect to this mineral. These observations seem to explain the observed decrease in Mo with time noted in Figure 7, which correlates with an increase in TDS (Figure 5), and hence, with increased concentrations of dissolved Ca in the leachates. Apparently, dissolved Ca in leachate from POS-1 has not yet reached a concentration high enough to precipitate powellite. The rapid "rinse-out" of Mo in the first few pore volumes (Figure 8), reflects the dissolution of powellite from the exposed surface of the oil shale particles.

The dominant aqueous species of B in oil shale leachates are B(OH)_3 and B(OH)_4^- , with the ratio controlled by pH. At pH values above 9, B(OH)_4^- will predominate. The charges on the dissolved species of B will be important in any consideration of sorption of dissolved B by solid geologic materials.

TABLE VI

Concentrations of Major Elements and Mo, B,
and F in First Pore Volume of Leachate from
Large Column, 46 Day Equilibration Experiment

<u>Concentration mg/L^a</u>				
Element	POS-1	INOS-1	PSS-1	SS-3
SO ₄ ²⁻	1,260	3,560	8,620	15,730
Cl ⁻	15	8.9	220	230
HCO ₃ ⁻	2,830	350	80	390
Ca ²⁺	5.6	560	480	470
Mg ²⁺	7.6	640	33	1,740
Na ⁺	1,660	310	4,000	4,730
K ⁺	11	16	640	77
Mo	19	1.5	1.5	3.9
B	23	.8	.6	10
F	82	3.4	6.4	26
pH	8.4	7.4	9.5	8.0
TDS ^b	6,140	5,580	14,225	23,640

^aAll values $\pm 10\%$; ^bIncludes elements not listed in Table, except pH, $\pm 1\%$, and TDS 5%.

TABLE VII

Analytical Balance Between Anions and Cations
in Leachates from Large Column Experiment

<u>Measured Concentration in Leachate (meq/L) ^a</u>				
	<u>POS-1</u>	<u>INOS-1</u>	<u>PSS-1</u>	<u>SS-3</u>
Cations	74	96	220	384
Anions	78	82	192	352
Difference	5	15	13	8
<u>Proportion of TDS Entered into WATEQF (%) ^b</u>				
	<u>POS-1</u>	<u>INOS-1</u>	<u>PSS-1</u>	<u>SS-3</u>
	96.6	98.5	99.9	99.7

^aThe meq values were determined from the total concentration of each element entered in WATEQF, i.e., SO_4^{2-} , Cl^- , Ca^{2+} , Na^+ , etc.

^bTDS entered into WATEQF.
TDA analyzed

$$\text{Equation 1: meq/L} = \text{mg/L} \left(\frac{\text{charge}}{\text{formula weight}} \right)$$

Boron is not supersaturated with respect to either of the two minerals of B in the computer model ($B(OH)_3$ and CaB_4O_7). It has been suggested that the mineralogical residence of B in oil shale may be in authigenic k-feldspar (6); however, the association of B with clay minerals has also been well documented (58-62) and it seems likely that some of the B may be associated with illite as well.

The free fluoride anion is computed to be the predominant dissolved form present in leachates from all types of oil shale studied. Magnesium forms an important fluoride complex when present in sufficient concentrations as is evident in SS-3 (Table VIII), whereas the NaF^0 , CaF^0 , and other complexes not shown in Table VIII are far less important. As is shown in Table IX, all leachates are supersaturated with respect to fluorapatite ($Ca_5(PO_4)_3F$) by several orders of magnitude.^{6,7} The thermodynamic equilibrium constant for fluorapatite is 1.6×10^{-67} moles/L. This would limit the concentration of F in solution to approximately 1 ug/L; however, data presented in Table VIII shows much higher F concentrations. Clearly, fluorapatite can not be the major factor controlling the release of F to the leachate. Instead, it appears that fluorite (CaF_2) is exerting influence over the solubility of F; leachates from POS-1, PSS-1, and SS-3, are only slightly supersaturated with respect to fluorite, and INOS-1 leachate is slightly undersaturated (Table IX). The solubility of fluorite is obviously related to the activity of Ca, and the activities of both Ca and F are modified by the composition and concentration of TDS.

LEACHING DYNAMICS OF OIL SHALE

From the data presented here, we can predict that water percolating through a disposal pile of oil shale will be characterized by high TDS in the initial portion of leachate, followed by steadily decreasing concentrations in subsequent fractions. This behavior is due in part to the presence of highly soluble minerals in oil shale which are readily dissolved by the slowly moving saturation front. Table X shows the concentration of TDS in the first and last quarter fractions of the first pore volume for each of four shales in the large column experiment. Total dissolved solids in the first quarter of the initial pore volume from both unretorted oil shale leachates (POS-1 and INOS-1) are twice the concentration measured in the last quarter. In contrast, the first quarter pore volume from both retorted shales (PSS-1 and SS-3) contained five times as much TDS as the last quarter, clearly reflecting the abundance of soluble salts in the retorted equivalents. This phenomenon has been reported previously (24) in a study using TOSCO retorted shale, in which the first 1/18 pore volume was found to have a S.C. of 78,100 umhos/cm corresponding to approximately 136,000 mg/L; the last 1/18 had a S.C. of less than 3,000 umhos/cm and the average for the entire first pore volume was approximately 17,200 umhos/cm. We duplicated this particular experiment on a smaller scale in order to see if the TOSCO spent shale we were using behaved in a similar manner. Figure 13 shows the S.C. for one column that was rapidly leached, with no time allowed for complete equilibration (simulating the published study (24)), and another column where water and shale were allowed to equilibrate for 10 days before leaching. Specific conductance was measured for every 1/18 pore volume. The first 1/18 pore volume from the non-equilibrated column has a S.C.

Table VIII. Computed Speciation of Mo, B, and F in Oil Shale Leachated, Using Modified WATEQF (48).

<u>Concentration (mmoles/L)</u>				
<u>Specie</u>	<u>POS-1</u>	<u>INOS-1</u>	<u>PSS-1</u>	<u>SS-3</u>
MoO_4^{2-}	.20	.02	.02	.04
(total Mo)	(.20)	(.02)	(.02)	(.04)
B(OH)_3^0	1.8	.07	.02	.89
B(OH)_4^-	.3	.001	.04	.08
(total B)	(2.1)	(.07)	(.06)	(1.0)
F^-	4.2	.12	.32	.80
MgF^+	.02	.05	.005	.55
CaF^+	.001	.004	.005	.01
NaF^0	.10	-	.02	.04
(total F)	(4.3)	(.18)	(.34)	(1.4)
Observed pH	8.4	7.4	9.5	8.0

Table IX. Computed Saturation Indices-log of the Ratio of Ion Activity Product (IAP) to Thermodynamic Equilibrium Constant (KT) (48).

$$SI^a = \log (IAP/KT)$$

<u>Shale</u>	<u>CaMoO₄</u>	<u>Ca₅(PO₄)₃F</u>	<u>CaF₂</u>
POS-1	-.2	7	1
PSS-1	.3	14	.5
SS-3	.6	11	1.2
INOS-1	.6	10	-.03

^aValues greater than zero indicate supersaturation.

Table X. Comparison of the First and Last Quarter of the First Pore Volume from the Large Column Experiment.

<u>Shale</u>	TDS mg/l		B mg/l		F mg/l		Mo mg/l	
	<u>1st$\frac{1}{4}$</u>	<u>4th$\frac{1}{4}$</u>	<u>1st$\frac{1}{4}$</u>	<u>4th$\frac{1}{4}$</u>	<u>1st$\frac{1}{4}$</u>	<u>4th$\frac{1}{4}$</u>	<u>1st$\frac{1}{4}$</u>	<u>4th$\frac{1}{4}$</u>
PSS-1	27,700	5,900	.8	.6	7.9	5.1	2.5	.7
SS-3	44,300	8,500	13	7.8	49	46	5.5	2.3
POS-1	8,700	3,600	30	13	115	59	31	7.4
INOS-1	7,600	3,700	1.1	.5	3.8	3.5	2.1	1.0

of 71,000 umhos/cm; comparable to the 78,100 umhos/cm value found previously. Allowing the water and shale to be in contact for 10 days before leaching resulted in a first 1/18 pore volume S.C. of only 60,100 umhos/cm. If one makes the reasonable assumption that the highly soluble solids in each column were initially distributed equally, then the difference resulting from 10 days of water-shale contact must be due to the diffusion of these ions away from the more concentrated front, towards the more dilute fractions. This is evident from Figure 13 where concentrations in the 10 day equilibration column surpass those for the zero day column by the 2/18 fraction.

This behavior raises an important question concerning the actual concentration of any leachate which may escape from a disposal pile. Due to the low rainfall in the Piceance Creek Basin (ranging from about 300 to 510 mm per year (2)), many years will be required for water to move through surface piles of waste oil shale. If the rate of movement is sufficiently slow, diffusion could reduce the gradient in TDS, resulting in leachate that approximates the concentrations of whole pore volumes reported in Table VI, rather than the range shown in TABLE X. It is difficult to estimate the proportion of annual precipitation that will infiltrate into, and eventually through, a disposal pile of oil shale. The maximum possible rate of infiltration would occur if the entire precipitation for a year were to infiltrate the disposal pile. Assuming an average shale height of 100 m, and an available water holding capacity of 35% by volume, a particle of water would take between 70 and 120 years to migrate from the top of the shale pile to the bottom (at an annual precipitation rate from 300 to 510 mm). At this rate, leachate from the first one-quarter pore volume would take 18 to 30 years to rinse out of the disposal pile. Under actual field conditions, however, it is doubtful whether any of the 300 mm per year precipitation will infiltrate into the shale pile; leachate produced from 510 mm per year of precipitation will take hundreds of years to percolate through a disposal pile of oil shale.

COMPARISON OF LABORATORY AND FIELD DATA

Both of the Harbert-Berg field lysimeters (at the Paraho site) were filled with spent shale transported directly from the Paraho retort in early spring of 1977. Each lysimeter, one for simulation of precipitation at low elevation disposal sites and the other to simulate precipitation at high elevation sites, was divided into six treatments, including: spent shale, spent shale with four different depths of soil cover, and a pure soil control. The plots containing only retorted shale and the plots with 20 cm soil cover were irrigated with a sprinkler system in June, 1977 in order to leach the readily soluble salts from the upper layers of shale prior to seeding. Some water was added to the lysimeters during shale compaction for dust control; this water resided in the shale for about two months, and the time of equilibration of water and shale is therefore comparable to that used in our laboratory columns. Table XI show the composite results of 29 leachate samples collected from the irrigated plots in June, 1977, together with data for comparison from the large column laboratory experiment. It is clear that leachates collected from the lysimeters at Anvil Points, Colorado, are similar in composition to the leachates generated from the same shale in our laboratory. This gives us some assurance that our experimental studies are meaningful when applied to situations in the field.

Figure 13

Table XI. Comparison of Leachates Generated in the Field and Laboratory Using Oil Shale Retorted by the Paraho Process (PSS-1).

<u>Lysimeter^a</u>			<u>Laboratory Column</u>	
<u>Parameter</u>	<u>Average</u>	<u>Range</u>	<u>First Quarter</u>	<u>First Pore Volume</u>
pH	11.0 ^b	8.2-11.7	9.6	9.5
TDS	18,200	11,100-34,100	27,700	14,220
Mo	4.1	2.5-8.3	2.5	1.5
B	1.9	1.4-3.2	.8	.6
F	8.8	4.1-13.6	7.9	6.4

^a Average of 29 Values.

^b Arithmetic average of the negative log of the hydrogen ion activity.

The average lysimeter pH of 11 is reasonable for Paraho retorted oil shale leached shortly after retorting. However, the lower value (8.2) and laboratory pH (9.5) are probably more realistic for leachate which may take years to escape from any disposal pile and has therefore had an opportunity to equilibrate with carbon dioxide gas and organic matter. The upper range of TDS in lysimeter leachates (34,000 mg/L) represents the first small fraction (approximately 1/100) of a pore volume to pass through the shale and is therefore higher than the first quarter of a pore volume collected from the column. Likewise, the average lysimeter TDS (18,200 mg/L), which represents less than one pore volume of leachate, is higher than the TDS for the entire first pore volume from the column (14,200 mg/L). Concentrations of Mo, B, and F, could be discussed in similar fashion.

SULFUR

A particularly interesting aspect of the chemistry of oil shale and of the aqueous leachates is the behavior of sulfur. The total concentration of sulfur in Colorado oil shale ranges from 0.56 to 1.94% by weight (4). Of the total, 19-37% occurs as organic sulfur, 63-79% as inorganic sulfides, principally pyrite, and up to 4% as sulfate (4). Much of this total sulfur is subject to alteration and mobilization during retorting, as indicated by the high concentrations and variety of sulfur species found in various retort products. Stuber and others (63) have measured 2,300 mg/L total dissolved sulfur in water from the Omega-9 retort (Laramie Energy Technology Center) with 30% as SO_4^{2-} , 55% as $\text{S}_2\text{O}_3^{2-}$, 4% as $\text{S}_4\text{O}_6^{2-}$, and 3% as SCN^- . We have similarly found reduced species of dissolved sulfur in leachate collected from the retorted Paraho shale in the field lysimeters during the initial irrigation of the shale in June, 1977 (25). Unfortunately, at the time of collection we did not have methods for analyzing the leachates for reduced species of sulfur. After collection, the bottles of leachate were stored on laboratory shelves. We found that the pH of the leachates had dropped significantly after only three weeks of storage, in some cases dropping from a pH of 10.5 to as low as 3.5. Accompanying the decrease in pH, a white to slightly yellowish precipitate formed in the bottles; x-ray diffraction shows the precipitate to be native sulfur. Qualitatively, the largest amounts of precipitate are found in the leachates that show the greatest drop in pH. It is clear that oxidation of the reduced species of sulfur has taken place, with the production of sulfuric acid and sulfur. A similar phenomenon has been noted by other researchers (46) using leachate derived from lysimeters of TOSCO retorted shale. Because thiosulfate is the major reduced form of sulfur in retort waters (63), it seems likely to also be predominant in leachate from retorted shale, although tetrathionate and thiocyanate may also be significant. Any $\text{S}_2\text{O}_3^{2-}$ that might have still been preserved in our leachates was measured in November of 1978, almost a year and a half after they were collected. Table XII gives the $\text{S}_2\text{O}_3^{2-}$ concentration and shows the pH change with time for five of the leachates which are representative of all of the 29 samples collected from the lysimeters in June, 1977. Also given is the concentration of $\text{S}_2\text{O}_3^{2-}$ in one sample of leachate (RW 5364) collected from the lysimeters in May, 1978. Concentrations of $\text{S}_2\text{O}_3^{2-}$ in laboratory leachates are also shown in Table XII. Tetrathionate ($\text{S}_4\text{O}_6^{2-}$) and thiocyanate (SCN^-) were also detected in leachates, but

Table XII. Thiosulfate ($S_2O_3^{2-}$) in Leachates from Retorted Oil Shale (mg/L)

<u>Leachate</u>	<u>Date Collected</u>	<u>Initial pH</u>	<u>pH on 11/22/78</u>	<u>mg/L remaining 11/22/78</u>
RW5279	6/8/77	10.2	3.6	3,800
RW5292	6/13/77	11.0	7.3	2,200
RW5295	6/13/77	10.7	7.3	900
RW5298	6/13/77	11.7	7.7	1,290
RW5307	6/14/77	11.1	7.7	2,580
RW5364	5/10/78	8.5	-	40

<u>Shale</u>	<u>Column Experiment</u>	<u>mg/L 1st Pore Volume</u>
PSS-1	Large	80
PSS-1	7 month	15
PSS-1	13 month	120
PSS-1	18 month	0
SS-2	7 month	1,940
SS-2	13 month	0
SS-3	Large	130

were present in only a few of the samples, at relatively low concentrations, and are not listed in Table XII.

From Table XII, it is seen that all leachates from the laboratory experiments contain significantly lower concentrations of $S_2O_3^{2-}$ than the initial lysimeter leachates, with the exception of SS-2 (7 months). This absence of $S_2O_3^{2-}$ in laboratory leachates was unexpected because PSS-1 was collected from the same lysimeters which produced the leachates rich in $S_2O_3^{2-}$ in Table XII. It is apparent that a mechanism is operating which destroys $S_2O_3^{2-}$ with time, both in leachate and in oil shale. Thiosulfate is almost completely gone in leachate collected from the lysimeters a year later, and it is gone from TOSCO retorted shale (SS-2, Table XII) after 13 months of water-shale contact.

Although $S_2O_3^{2-}$ is thermodynamically unstable in water, it may persist for a long time if a pH greater than 7 is maintained, and microorganisms, oxygen, and sunlight are excluded (64). Decomposition into S and SO_4^{2-} should not occur at the elevated pH values associated with spent shale leachate unless catalyzed by some agent, bacteria being the most likely (64). In order to test whether bacteria might be responsible for the behavior observed in the lysimeter leachates, aliquots of RW5279 and RW5292 (Table XII) were sent to Ms. Corale Brierley, a chemical microbiologist with the New Mexico State Bureau of Mines and Mineral Resources in Socorro, New Mexico. Ms. Brierley adjusted the environment of both samples to promote bacterial growth. After a period of time, RW5279 was found to be devoid of bacteria; however, in RW5292, *Thiobacillus thiooxidans* and *Thiobacillus thioparus* were found. *T. thioparus* is a thiosulfate-oxidizing bacteria which can grow between pH 4.5-10.0, although its optimum range is from 6.6-7.2. Investigators (65,66) have shown that the end products of thiosulfate oxidation are SO_4^{2-} and S. Although there may be short-lived intermediate products, the net reaction is $5Na_2S_2O_3 + H_2O + 4O_2 \rightarrow 5Na_2SO_4 + H_2SO_4 + 4S$ (67). The presence of *T. thioparus* in the lysimeter leachates thus offers the most plausible explanation for the behavior of $S_2O_3^{2-}$. *T. thiooxidans* is a sulfur-oxidizing bacteria having a growth range from pH 0.5-6, the optimum being between 2.0-3.5. Thus, *T. thioparus* can generate an environment favorable for growth of *T. thiooxidans* by producing acid and sulfur. *T. thiooxidans* can then in turn oxidize the sulfur to sulfate with the production of even more acid, according to the following net reaction: $2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$ (67). This could lead to serious acid pollution problems in natural environments having a low buffering capacity; however, the abundant carbonates and buffering capacity of the Green River Formation should be able to neutralize any acid generated by oxidation of sulfur compounds. Problems due to leachate acidification might arise only where the leachate enters surface water directly, with little contact with carbonate rocks; in such a case the buffering capacity of the surface waters might not be sufficient to immediately neutralize the acid. Any acid produced by the oxidation of $S_2O_3^{2-}$ within the disposal piles would most likely be neutralized by the carbonate minerals in the shale. Our experience with $S_2O_3^{2-}$ leads us to conclude that adverse effects due to the chemistry of sulfur will not be an environmental problem associated with leachate from oil shale in the majority of circumstances.

Table XIII summarized the range in concentration of TDS, F, Mo, and B that could be expected in leachate escaping from disposal piles composed of the different oil shale types used in this study. The lower limit assumes that infiltration of water into a disposal pile will occur at a slow rate, allowing diffusion of ions away from the saturation front and resulting in uniform concentrations for the entire first pore volume of leachate percolating out of the disposal pile. A more realistic appraisal of initial leachate composition may be given by the higher values, which are based on the first quarter pore volume from the large column experiments of duration 1.5 months. These values have been adjusted so that they approximate equilibrium concentrations, by using the results from the 13 month column equilibrium experiment. For example, the first quarter pore volume of leachate from SS-3 contained 44,260 mg/L TDS; if the water and shale had equilibrated for 13 months instead of only 1.5 months, and assuming no diffusion, the first quarter pore volume would contain 55,300 mg/L. The composition of leachate can be expected to vary even from shale retorted by the same process; mineralogical variations exist stratigraphically and throughout the basin. Differences in leachate can also be expected depending on the type of retorting method used and the exact conditions of retorting at any given time. In addition to spent shale, surface disposal piles will contain a variety of other materials, including unretorted shale fines (10% of the disposal pile for Paraho and 3% for TOSCO (68)), water treatment sludge, flue gas, retort water, scrubber sludge, and in general, any waste product which can be disposed with the shale. With two possible exceptions, these wastes will probably be minor in comparison with the large quantities of retorted oil shale which can be expected to control leachate composition. The first exception would be the use of retort water (separated from the oil and gas) to control dust and aid in compaction, as described in current proposals. Unfortunately, retort water contains large concentrations of TDS and dissolved organics (69) and may contribute to the toxicity of leachate. A second exception might occur if saline groundwater, having its own chemical characteristics, were to contribute to leaching of surface disposal piles.

Published data is limited concerning the composition of leachate migrating from abandoned chambers of in-situ retorted shale. Ideally, the shale is retorted at a higher temperature (up to 1200°C) and for a longer time than is surface processes (500-750°C (55)), resulting in a partial mineralogical transformation to more insoluble minerals, such as akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), diopside ($\text{CaMgSi}_2\text{O}_6$), augite ($(\text{Ca}, \text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Ti}, \text{Al})_2(\text{Si}, \text{Al})_2\text{O}_6$), and melilite ($(\text{Ca}, \text{Na}, \text{K})_2(\text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}, \text{Si})_3\text{O}_7$) (55,56). In tests to date, however, only partial retorting has been accomplished (approximately 65% (69)), in part because of the difficulty in obtaining a uniform particle size and maintaining a uniform and complete retorting zone. This results in a composition of spent shale ranging from the relatively insoluble silicate minerals to almost unretorted raw oil shale. In addition, we should probably never expect complete mineralogical transformation to insoluble silicates; it would be amazing indeed to find exactly the stoichiometric proportions of carbonates and silicates initially present in the raw oil shale to be ultimately transformed into an exact mixture of insoluble silicates, with no residue of soluble oxides and sulfates. The composition of in-situ leachate will

Table XIII. Range of Concentrations Expected in Leachate from Surface Disposal Piles of Retorted and Unretorted Oil Shale, Assuming Various Conditions Discussed in the Text.

<u>Parameter</u>	<u>Fresh POS-1</u>	<u>PSS-1</u>	<u>Retorted SS-3^a</u>	<u>In-situ^b</u>
TDS	5,600-18,400	13,300-27,700	29,700-55,300	4,000-30,000
Mo	1.0-8.7	1.9-3.2	8.6	
B	.8-32	2.1-2.8	14-18	
F	3.5-16	7.7-9.5	19	

^aAdjusted using SS-2, 13 month equilibrium value. ^bReferences (56) and (68).

ultimately depend upon the initial mineralogy of the raw shale, the degree of retorting achieved, the composition of ground water moving through the retort, and the extent of contact between the more soluble, partially retorted oil shale and water. The range of TDS measured in in-site leachate and presented in Table XIII is based on very limited data and should be used with caution. It is doubtful that the average first pore volume concentration of leachate from an abandoned in-situ retort will be as low as 4,000 mg/l; however, a realistic upper limit cannot yet be estimated from the limited data available.

PROJECTED ENVIRONMENTAL IMPACT

The amount of leachate that might escape from a disposal pile of oil shale will depend primarily on the annual precipitation, which can range from 300-510 mm/yr (2). The following estimate contrasts the quantity of leachate that might escape from a high elevation disposal site (410 mm/yr) compared with a low elevation site (290 mm/yr).

High Elevation Site

Colony Development Corporation plans to dispose of its TOSCO retorted oil shale in Davis Gulch, a tributary to Parachute Creek. Most of the 16 km² drainage area of Davis Gulch lies between 2260-2500 m in elevation (61) and receives an annual precipitation estimated to average from 410 mm (62) to 460 mm (63). The Colony disposal pile will cover approximately 20% (761 acres) of the drainage basin of Davis Gulch and will be located in valleys tributary to the main channel (61).

To make an estimate of the average quantity of leachate that might percolate from the shale pile in Davis Gulch on an annual basis, one must determine the amount of water that is currently infiltrating the area. Wymore (63) calculated a water balance for Davis Gulch, taking into account precipitation, evapotranspiration, available soil water storage capacity, runoff, and deep percolation; he concluded that the combined surface runoff plus deep percolation for present conditions on the proposed shale disposal area is equal to 65 acre-ft/yr (AFY). A base flow from Davis Gulch of 6-8 L/sec during the non-snow melt period of the year has been noted. This base flow results from inflow from the alluvium and from springs from the bed-rock aquifer. Since this water is recharged locally, the base flow can be considered to represent the quantity of water that percolates through the geologic cover of Davis Gulch. Using an average value of 7 L/sec, the annual base flow from the proposed shale disposal area amounts to 35 AFY. In addition to the 35 AFY which infiltrates and emerges as surface flow, a certain quantity of water enters the bed-rock aquifer system through fractures and leaves the area as sub-surface flow. Calculations based on data from Metcalf and Eddy (62) indicate that this could amount to an additional 18 AFY. Thus, it is estimated that as much as 53 AFY of water could conceivably percolate through a shale pile in Davis Gulch. This amounts to an average net infiltration rate of 20 mm/yr over the entire surface area of the pile.

Approximately 20% of the volume of a completed disposal pile will be empty pore space (64). At an infiltration rate of 20 mm/yr, ten years will be required to saturate one meter of shale. Thus, about 1000 years will be required for initial precipitation to percolate through the average shale pile thickness of 100 m. However, minor leachate will begin migrating from the thin edges (2 m thick) of the shale pile within 20 years. Any leachate produced during the lifetime of the Colony operation will probably be prevented by the operators from leaving the site. Should the site be abandoned after production ceases, conditions will return to some natural state and leachate could then enter the surface runoff from Davis Gulch.

Table XIV presents the potential impact on surface water quality downstream from Davis Gulch. Assumptions are that 35 AFY of leachate will leave the shale pile every year to become surface runoff in Davis Creek, and the concentration of TDS, Mo, B, and F in the leachate will approximate the first one quarter pore volume values for TOSCO retorted oil shale in Table XIII. Infiltration of leachate to the bedrock aquifer system was ignored in the calculations due to uncertainties in the hydrology. All components can be expected to slowly decrease with time with the possible exception of F. Fluoride in leachate will remain at about 19 mg/L for many pore volumes. Table XIV clearly shows that the greatest danger to plant and animal life from TDS, Mo, F, and B lies in the drainage area of Parachute Creek between Davis Gulch and the Colorado River.

Low Elevation Site

The low elevation site that was investigated in this study is Rinky Dink Gulch on Tract C-a. The Rio Blanco Oil Shale Project will use the modified in-situ method to retort the shale, which means that 20% of the original volume of shale must be brought to the surface. The Rio Blanco consortium currently plans (65) to retort this shale on the surface by the Lurghi process (4); some of the Lurghi retorted material will be slurried into the abandoned underground retort chambers where it is hoped that it will form a cement, thereby sealing the chambers from groundwater. The excess material will be disposed in Rinky Dink Gulch. Lurghi retorted shale is similar to TOSCO material in size, but it is nearly all decarbonized. For the purpose of this evaluation we will assume the leachate from Lurghi retorted oil shale is similar to leachate from TOSCO retorted oil shale.

Rinky Dink Gulch covers 6 km², lies at an elevation between 2130-2260 m and flows into Yellow Creek, a tributary to the White River. The average discharge measured at the mouth of Rinky Dink Gulch was 1 AFY, ranging from 0.3-2.3 AFY for the four-year period of record. The percent which migrates through the alluvium before emerging as discharge is not known, nor is the quantity of water flowing through the alluvium beneath the gaging station known. We have used 1 AFY as a reasonable estimate of the average net quantity of water that may infiltrate a shale disposal pile in Rinky Dink Gulch. Assuming that the shale pile occupies 880 acres (66) of Rinky Dink Gulch, the annual net infiltration would amount to 0.8 mm. The average depth of the shale pile will be approximately 90 m. Assuming 20% empty pore space, 240 centuries would be required for water to percolate through 90 m of retorted oil shale at Rinky Dink Gulch; however, small volumes of leachate will probably

Table XIV. Increase in Concentration of TDS, Mo, B, and F Expected from Leachate Migrating from Davis Gulch

<u>Location</u>	<u>TDS</u>	<u>Concentration (mg/l)</u>			<u>Discharge (a.f./yr)</u>
		<u>B</u>	<u>F</u>	<u>Mo</u>	
Concentration in leachate ^a	55,000	18	19	9	35
1.3 miles downstream from mouth of Davis Gulch	1600	0.5	0.6	0.3	1,200
Parachute Creek at Grand Valley	90	0.03	0.03	0.02	2,760,000
Colorado River at Lees Ferry	.2	0.001	0.001	0.001	12,400,000

^aValues from which rest of table was calculated. Values are from Table XIII.

begin to percolate through the thinner edge much earlier. Assuming that 1 AFY of leachate containing 55,000 mg/L TDS escapes, the increase in TDS at the mouth of Yellow Creek would amount to 30 mg/L and the increase in TDS at Lees Ferry would be 0.004 mg/l.

The capacity of surface streams in the area for diluting any leachate depends on the volume of leachate and its quantity. Leachate may migrate through alluvium before entering surface water, and chemical and physical reactions could occur to increase or decrease the concentration of various contaminants. The greatest hazard is to the Piceance Creek Basin, where many of the salts leached out of oil shale may precipitate in the floodplains of the local creeks. The two disposal cases considered above represent approximately 100,000 bbl/day of production. The most recent plans are to ultimately produce at least one million bbl/day of shale oil. Although some of this development will occur in Utah and possibly Wyoming, most will take place in Colorado. This could result in several surface disposal sites for retorted and/or unretorted oil shale. In order to minimize the impact on surface water quality, these surface piles of retorted oil shale should be located in small drainage areas with low precipitation. Disposal of retorted shale at the mouth of a large drainage area should be avoided, since the runoff from the entire drainage area must then travel over or through the shale, thereby increasing the volume of leachate.

The calculations presented above serve to point out that a leachate problem may exist and should be anticipated. Should actual field data show that significant quantities of leachate will migrate from a particular disposal site, plans must be made to prevent this leachate from contaminating downstream water supplies. It should be recognized that mitigation measures may have to be instituted for hundreds of years.

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Appendix Table A-1. Measured Concentration of Dissolved Constituents in the first pore volume of leachate from the large column (1.5 month) equilibrium experiment.

	<u>Mg/L</u>				<u>Analytical Precision</u>
	<u>POS-1</u>	<u>PSS-1</u>	<u>INOS-1</u>	<u>SS-3</u>	
Total Dissolved Solids	6,140	14,225	5,580	23,640	+15%
HCO ₃	2,830	80	350	390	+10%
SO ₄	1,260	8,620	3,560	15,730	+10%
Ca	5.6	480	560	470	+10%
K	11	640	16	77	+10%
Na	1,660	4,000	310	4,730	+10%
Mg	7.6	33	640	1,740	+10%
D.O.C.	210	24	36	73	+10%
NH ₄	3.2	1.4	11	7.7	+15%
Fe	.12	.08	.06	.24	+25%
Ni	.02	<.02	.20	<.04	+30%
Cu	.02	.04	.03	.08	+40%
Zn	.05	<.02	.17	.03	+20%
As	.290	.045	.009	.020	+15%
Se	.014	.069	.024	.019	+15%
Br	.06	.16	.06	1.3	+15%
Rb	.02	2.2	.06	.18	+15%
Sr	.17	6.8	8.4	9.8	+15%
Zr	.10	N.O.	.10	N.O.	+15%
Sn	.02	<.02	<.02	<.02	+45%
Pb	<.01	<.01	<.01	<.02	-
U	.02	N.O.	.16	N.O.	+35%
Mo	19	1.5	1.5	3.9	+10%
F	82	6.4	3.4	26	+10%
B	23	.6	.8	10	+10%
Cl	15	220	8.9	230	+15%
Si	7.0	9.4	14	6.4	+10%
PO ₄	.28	.09	.14	.18	+10%
Al	≤.1	≤.1	≤.1	≤.1	-
NO ₃	1.9	<.2	60	<.2	+15%
NO ₂	<2	.36	.16	<.13	+15%
Cr	.02	.06	.05	.12	+15%
Mn	≤.01	<.01	.49	.42	+15%
S ₂ O ₃	0	77	0	130	+10%
SCN	0	22	0	0	+20%
S ₄ O ₆	0	0	0	6	+25%
pH	8.4	9.5	7.4	8.0	+1%
Eh(volts)	-.212	-.154	-.200	-.065	+50%

APPENDIX A

Partial Example of WATEQF Output;
only the first two pages of output
are presented here.

INDS-1
1ST PORE VOLUME, CUMULATIVE
EM=-.2

INITIAL SOLUTION

TEMPERATURE = 25.00 DEGREES C PH = 7.400 ANALYTICAL EPICAT = 95.341 ANALYTICAL EPMAN = 81.712

*** OXIDATION - REDUCTION ***
DISSOLVED OXYGEN = 0 MG/L
EM MEASURED WITH CALOMEL = 9.9000 VOLTS
MEASURED EM OF ZOBELL SOLUTION = 9.9000 VOLTS
CORRECTED EM = -.2000 VOLTS
PE COMPUTED FROM CORRECTED EM = -3.381

*** TOTAL CONCENTRATIONS OF INPUT SPECIES ***

SPECIES	TOTAL MOLALITY	LOG TOTAL MOLALITY	TOTAL MG/LITRE
CA 2+	1.405010E-02	-1.8523	5.600300E+02
MG 2+	2.647195E-02	-1.5772	6.400000E+02
NA +	1.355000E-02	-1.6578	3.100000E+02
K +	4.114744E-04	-3.3857	1.600000E+01
CL -	2.524404E-04	-3.5970	8.900000E+00
SO4 2-	3.726679E-02	-1.4287	3.560000E+03
HCO3 -	5.768154E-03	-2.2390	3.500000E+02
SI02 TOTAL	5.012439E-04	-3.2999	2.005000E+01
FE 2+	1.040372E-05	-5.9864	6.000000E-02
PO4 3-	1.482371E-06	-5.8290	1.400000E-01
SR 2+	9.640482E-05	-4.0159	8.400000E+00
F -	1.795532E-04	-3.7446	3.400000E+00
NH4 +	8.132104E-04	-3.2124	1.100000E+01
NO3 -	9.730795E-04	-3.0119	6.000000E+01
FORON	7.441939E-05	-4.1283	8.000000E-01
BR -	7.550323E-07	-6.1223	6.000000E-02
BN 2+	8.950011E-06	-5.0473	4.000000E-01
MOLYBDENUM	1.572229E-05	-4.8035	1.500000E+00
URANIUM	6.759451E-07	-6.1701	1.600000E-01

*** CONVERGENCE ITERATIONS ***

ITERATION	S1-ANALCO3	S2-SO4TOT	S3-FTOT	S4-PTOT	S5-CLTOT
1	4.603984E-04	3.042330E-02	4.918196E-05	2.844942E-06	5.550441E-08
2	3.687571E-04	9.232607E-03	3.555264E-05	8.447676E-07	8.541274E-09
3	1.970057E-05	3.421929E-04	1.770494E-05	2.306773E-08	-1.395393E-10
4	4.958061E-05	6.018110E-05	4.204170E-07	5.667474E-09	-7.778700E-11
5	1.266312E-06	2.052393E-05	1.120001E-07	1.421119E-09	-2.134195E-11

THE REQUESTED CONVERGENCE TOLERANCES FOR THIS JOB WERE AS FOLLOWS

5.764125E-06	3.726679E-05	1.795632E-07	1.482371E-09	2.524404E-07	(REAL TOLERANCE)
.0010000000	.0010000000	.0010000000	.0010000000	.0010000000	(FRACTIONAL TOL.)

DESCRIPTION OF SOLUTION

ANALYTICAL	COMPUTED	PH	ACTIVITY H2O = .9986
EPICAT 95.841	65.449	7.400	PCO2 = 1.033094E-02
EPMAN 81.712	51.412		LOG PCO2 = -1.9859
		TEMPERATURE	PO2 = 9.045917E-60
		25.00 DEG C	PCM4 = 6.090461E-12
EM = -.2000 PE = -3.381			CO2 TOT = .604839E-02
PE CALC S = 100.000		IONIC STRENGTH	DENSITY = 1.0000
PE CALC DOX = 100.000		1.058000E-01	TDS = 5500.9MG/L
PE SATO DOX = 100.000			

INCS-1

IN COMPUTING THE DISTRIBUTION OF SPECIES, PE = -3.301 EQUIVALENT EH = -.200 VOLTS
 THE VALUES OF THE DEBYE-HUCKEL SOLVENT CONSTANTS ARE, A = .5108 AND B = .3286
 CORALN = 0 FEALC = 1 FLAG = 3 IGO = 1 THE ALKALINITY CORRECTION = 4.029274E-08

DISTRIBUTION OF SPECIES

I SPECIES	PFM	MOLALITY	LOG MOL	ACTIVITY	LOG ACT	ACT. COEFF.	LOG A COF
6 SO4 2-	2.11725E+03	2.21638E-02	-1.6544	8.09302E-03	-2.0918	3.65182E-01	-.4375
2 MG 2+	4.65874E+02	1.67877E-02	-1.7750	6.72206E-03	-2.1725	4.00415E-01	-.3975
3 NA +	2.96007E+02	1.29826E-02	-1.8906	1.01129E-02	-1.9951	7.78960E-01	-.1085
23 H2SO4	1.09945E+03	9.18474E-03	-2.0369	9.41143E-03	-2.0263	1.02468E+00	.0106
1 CA 2+	3.41045E+02	8.59662E-03	-2.0677	3.26491E-03	-2.4035	3.83859E-01	-.4150
32 CASO4	7.15577E+02	5.28551E-03	-2.2769	5.41597E-03	-2.2563	1.02468E+00	.0106
7 HCO3 -	3.06694E+02	5.04380E-03	-2.2973	3.95857E-03	-2.4027	7.84555E-01	-.1054
85 HNO3 -	6.06660E+01	9.73077E-04	-3.0119	7.53757E-04	-3.1210	7.77695E-01	-.1092
44 H2SO4 -	6.53633E+01	5.52356E-04	-3.2578	4.29366E-04	-3.3670	7.77695E-01	-.1092
39 NH4 +	9.86254E+00	5.49304E-04	-3.2598	4.27580E-04	-3.3590	7.77695E-01	-.1092
24 H4SiO4	4.77238E+01	4.99302E-04	-3.3016	5.11626E-04	-3.2910	1.02468E+00	.0106
22 H2HCO3 +	3.37479E+01	3.97713E-04	-3.4004	3.09299E-04	-3.5096	7.77695E-01	-.1092
4 K +	1.51553E+01	3.83778E-04	-3.4092	2.96100E-04	-3.5286	7.59682E-01	-.1194
86 H2CO3	2.12501E+01	3.44520E-04	-3.4628	3.53479E-04	-3.4516	1.02600E+00	.0111
5 CL -	8.89310E+00	2.52309E-04	-3.5979	1.91735E-04	-3.7173	7.59582E-01	-.1194
30 CANCO3 +	1.74132E+01	1.73205E-04	-3.7614	1.34701E-04	-3.8706	7.77695E-01	-.1092
62 F -	2.30157E+00	1.21823E-04	-3.9143	9.47411E-05	-4.0235	7.77695E-01	-.1092
88 SR 2+	6.39959E+00	9.64045E-05	-4.0159	3.52642E-05	-4.4527	3.65794E-01	-.4368
36 B(OH)3	4.49050E+00	7.30209E-05	-4.1365	7.48324E-05	-4.1259	1.02468E+00	.0106
92 NH4SO4 -	6.50468E+00	5.73272E-05	-4.2416	4.45831E-05	-4.3528	7.77695E-01	-.1092
20 HGF +	2.33025E+00	5.41043E-05	-4.2658	4.20766E-05	-4.3760	7.77695E-01	-.1092
21 H2CO3	2.44751E+00	2.91337E-05	-4.5356	2.98058E-05	-4.5250	1.02468E+00	.0106
40 H2HCO3	1.83307E+00	2.15507E-05	-4.6594	2.25607E-05	-4.6478	1.02468E+00	.0106
46 KSO4 -	2.91399E+00	2.16572E-05	-4.6644	1.68427E-05	-4.7738	7.77695E-01	-.1092
31 CACO3	2.10390E+00	2.11981E-05	-4.6737	2.17213E-05	-4.6631	1.02468E+00	.0106
117 HCO3 2-	2.49595E+00	1.56920E-05	-4.8043	5.74032E-06	-5.2411	3.65794E-01	-.4368
18 CO3 2-	7.32244E-01	1.22816E-05	-4.9107	4.65324E-06	-5.3322	3.78873E-01	-.4215
101 MN 2+	3.93434E-01	7.20257E-06	-5.1425	2.63466E-06	-5.5793	3.65794E-01	-.4368
38 NH3	1.01230E-01	9.97144E-06	-5.2235	6.12497E-06	-5.2129	1.02468E+00	.0106
49 CAF +	2.04787E-01	3.42540E-06	-5.4577	2.71057E-06	-5.5669	7.77695E-01	-.1092
25 H3SiO4 -	1.04142E-01	1.94897E-06	-5.7106	1.51415E-06	-5.8198	7.77695E-01	-.1092
225 B(OH)4 -	1.08507E-01	1.30805E-06	-5.8573	1.08010E-06	-5.9665	7.77695E-01	-.1092
42 HACO3 -	9.25710E-02	1.12156E-06	-5.9502	8.72232E-07	-6.0594	7.77695E-01	-.1092
109 MN:O4	1.59526E-01	1.06240E-06	-5.9737	1.08862E-06	-5.9631	1.02468E+00	.0106
98 BR -	6.00000E-02	7.55653E-07	-6.1220	5.87201E-07	-6.2312	7.77695E-01	-.1092
8 FE 2+	4.03350E-02	7.37635E-07	-6.1372	2.69322E-07	-6.5680	3.65794E-01	-.4368
111 H2HCO3 +	8.03715E-02	6.97602E-07	-6.1558	5.42655E-07	-6.2660	7.77695E-01	-.1092
140 U(OH)5 -	2.16378E-01	6.74440E-07	-6.1711	5.24513E-07	-6.2302	7.77695E-01	-.1092
73 H2HPO4	7.65316E-02	6.58914E-07	-6.1845	6.73128E-07	-6.1719	1.02468E+00	.0106
97 HAF	2.26429E-02	5.42783E-07	-6.2658	5.55067E-07	-6.2552	1.02468E+00	.0106
47 HPO4 2-	3.52464E-02	3.69282E-07	-6.4326	1.35501E-07	-6.5694	3.65794E-01	-.4368
19 HCO3H +	1.46290E-02	3.56327E-07	-6.4485	2.78850E-07	-6.5577	7.77695E-01	-.1092
34 FCCO4	5.10273E-02	3.37786E-07	-6.4714	3.46124E-07	-6.4508	1.02468E+00	.0106
27 OH -	5.45302E-03	3.24015E-07	-6.4894	2.51885E-07	-6.5586	7.77695E-01	-.1092
74 H2HPO4	3.21244E-02	2.37420E-07	-6.6245	2.43286E-07	-6.6139	1.02468E+00	.0106
48 H2PO4 -	1.07115E-02	1.11374E-07	-6.9532	8.66154E-08	-7.0524	7.77695E-01	-.1092
40 H2HPO4 -	6.09760E-03	5.13202E-06	-7.2007	3.99114E-08	-7.3989	7.77695E-01	-.1092
64 H +	5.13133E-05	5.11507E-08	-7.2938	3.98107E-08	-7.4000	7.77695E-01	-.1092
94 NaCl	2.74979E-03	4.73140E-08	-7.3250	4.84818E-08	-7.3144	1.02468E+00	.0106

PSS-1
1ST FORT VOLUME CUMULATIVE
EH=-.154

INITIAL SOLUTION

TEMPERATURE = 25.00 DEGREES C PH = 9.500 ANALYTICAL EPNCAT = 220.392 ANALYTICAL EPMAN = 191.804

*** OXIDATION - REDUCTION ***
DISSOLVED OXYGEN = 0 MG/L
EH MEASURED WITH CALOMEL = 9.9000 VOLTS
MEASURED EH OF ZOBELL SOLUTION = 9.9000 VOLTS
CORRECTED EH = -.1540 VOLTS
PE COMPUTED FROM CORRECTED EH = -2.603

*** TOTAL CONCENTRATIONS OF INPUT SPECIES ***

SPECIES	TOTAL MOLALITY	LOG TOTAL MOLALITY	TOTAL MG/LITRE
CA 2+	1.214807E-02	-1.9155	4.800000E+02
MG 2+	1.376910E-03	-2.8611	3.300000E+01
NA +	1.764001E-01	-.7533	4.600000E+03
K +	1.660337E-02	-1.7798	6.400000E+02
CL -	8.294840E-03	-2.2910	2.200000E+02
SO4 2-	9.102751E-02	-1.0408	8.620000E+03
HCO3 -	1.339002E-03	-2.8761	8.000000E+01
SIO2 TOTAL	3.395010E-04	-3.4692	2.010903E+01
FE 2+	1.453103E-08	-5.8377	8.000000E-02
PO4 3-	9.613131E-07	-6.0171	9.000000E-02
SR 2+	7.972649E-05	-4.1039	6.800000E+00
F -	3.417261E-04	-3.4663	6.400000E+00
NH4 +	7.873007E-05	-4.1039	1.400000E+00
BCOON	5.630420E-05	-4.2455	6.000000E-01
BF -	2.031130E-06	-5.6923	1.600000E-01
ACLYBODENUM	1.506013E-05	-4.7997	1.500000E+00
S2O3 2-	6.956743E-04	-3.1570	7.700000E+01
SCN -	3.842600E-04	-3.4154	2.200000E+01

*** CONVERGENCE ITERATIONS ***

ITERATION	S1-ANALCO3	S2-SO4TOT	S3-FYOT	S4-FYOT	S5-CLTOT
1	1.171177E-03	7.372149E-02	2.005749E-05	4.218381E-06	1.374605E-05
2	2.628559E-04	9.378641E-03	1.077996E-05	1.013909E-06	3.704279E-06
3	1.970232E-07	1.002533E-05	-1.800001E-08	4.908503E-09	-7.953072E-08
4	2.253534E-06	8.027883E-05	9.643000E-08	6.401869E-09	1.329205E-08
5	2.635443E-07	9.411282E-05	1.121452E-08	7.677276E-10	1.194975E-09

THE REQUESTED CONVERGENCE TOLERANCES FOR THIS JOB WERE AS FOLLOWS

1.124989E-06	9.102751E-05	3.417261E-07	9.613131E-10	6.294843E-06	(REAL TOLERANCE)
.0010000000	.0010000000	.0010000000	.0010000000	.0010000000	(FRACTIONAL TOL.)

DESCRIPTION OF SOLUTION

ANALYTICAL	COMPUTED	PH	ACTIVITY H2O = .9952
EPNCAT 220.392	189.332	9.500	PCO2 = 5.650513E-06
EPMAN 191.804	100.031		LOG PCO2 = -5.2479
		TEMPERATURE	PO2 = 2.909357E-56
		25.00 DEG C	PCM4 = 3.213800E-38
EH = -.1540 PE = -2.603			CO2 TOT = .766003E-03
PE CALC S = 100.000		IONIC STRENGTH	DENSITY = 1.0000
PE CALC DOX = 100.000		2.498002E-01	TDS = 14209.1MG/L
PE SATO DOX = 100.000			

IN COMPUTING THE DISTRIBUTION OF SPECIES, PE = -2.603 EQUIVALENT EM = -.154 VOLTS
 THE VALUES OF THE DEBYE-HUCKEL SOLVENT CONSTANTS ARE, A = .5108 AND B = .3286
 CURALK = 0 PECALC = 1 FLAG = 3 IGO = 1 THE ALKALINITY CORRECTION = 2.050127E-04

 DISTRIBUTION OF SPECIES

I SPECIES	PPM	MOLALITY	LOG MOL	ACTIVITY	LOG ACT	ACT. COEFF.	LOG A COF
3 NA +	3.55250E+03	1.61165E-01	-1.7927	1.10011E-01	-.9281	7.32240E-01	-.1353
6 SO4 2-	6.36925E+03	6.72490E-02	-1.1723	1.80698E-02	-1.7430	2.68700E-01	-.5707
44 NA2SO4 -	1.77970E+03	1.51645E-02	-1.8192	1.11912E-02	-1.9511	7.37906E-01	-.1320
4 K +	5.71629E+02	1.48296E-02	-1.8259	1.02982E-02	-1.9872	6.94433E-01	-.1584
5 CL -	2.19537E+02	3.28159E-03	-2.2019	4.36214E-03	-2.3603	6.94433E-01	-.1584
32 CASO4	8.57627E+02	8.16679E-03	-2.2019	6.53189E-03	-2.1850	1.05920E+00	.0250
1 CA 2+	2.51911E+02	5.83962E-03	-2.2314	1.77454E-03	-2.7509	3.02327E-01	-.5195
46 KSO4 -	2.56114E+02	1.77205E-03	-2.7515	1.30775E-03	-2.8035	7.37966E-01	-.1320
207 S2O3 2-	7.70000E+01	6.93074E-04	-3.1570	2.06644E-04	-3.6048	2.96615E-01	-.5278
2 MG 2+	1.66221E+01	8.93555E-04	-3.1539	2.26201E-04	-3.6155	3.26143E-01	-.4866
23 H2SO4	7.92107E+01	6.67525E-04	-3.1755	7.07046E-04	-3.1506	1.05920E+00	.0250
214 SCN -	2.70000E+01	3.84261E-04	-3.4154	2.83579E-04	-3.5473	7.37986E-01	-.1320
7 HCO3 -	2.23774E+01	3.72024E-04	-3.4234	2.72438E-04	-3.5647	7.32312E-01	-.1353
62 F -	5.93644E+00	3.16974E-04	-3.4930	2.33923E-04	-3.6309	7.37986E-01	-.1320
24 H2SiO4	2.08424E+01	2.19373E-04	-3.6576	2.32936E-04	-3.6327	1.05920E+00	.0250
18 CO3 2-	8.29766E+00	1.40235E-04	-3.6531	4.03370E-05	-4.3943	2.87597E-01	-.5412
42 NaCO3 -	9.78223E+00	1.13559E-04	-3.9224	8.02323E-05	-4.0544	7.37986E-01	-.1320
25 H2SiO4 -	1.10285E+01	1.17029E-04	-3.9295	8.66039E-05	-4.0614	7.37956E-01	-.1320
31 CaCO3	9.47521E+00	9.60224E-05	-4.0176	1.01718E-04	-3.9926	1.05920E+00	.0250
88 SR 2+	6.79943E+00	7.87199E-05	-4.1039	2.33495E-05	-4.6317	2.96615E-01	-.5278
27 OH -	7.18262E-01	4.20410E-05	-4.3331	3.16161E-05	-4.5001	7.37986E-01	-.1320
225 B(OH)4 -	3.15109E+00	4.05447E-05	-4.3921	2.99214E-05	-4.5243	7.37986E-01	-.1320
38 NH3	6.67155E-01	3.97305E-05	-4.4009	4.28913E-05	-4.3758	1.05920E+00	.0250
39 NH4 +	5.62305E-01	3.16205E-05	-4.4919	2.33402E-05	-4.6319	7.37956E-01	-.1320
43 NH4CO3	1.41320E+00	1.70691E-05	-4.7618	1.80797E-05	-4.7429	1.05920E+00	.0250
117 MgO4 2-	2.50055E+00	1.58553E-05	-4.7957	4.70429E-06	-5.3275	2.96615E-01	-.5278
36 B(OH)3	9.50024E-01	1.55988E-05	-4.8059	1.65274E-05	-4.7819	1.05920E+00	.0250
97 NAF	6.25645E-01	1.51153E-05	-4.8206	1.60102E-05	-4.7956	1.05920E+00	.0250
84 NaCl	7.03099E-01	1.21519E-05	-4.9154	1.29713E-05	-4.8904	1.05920E+00	.0250
21 MgCO3	6.10339E-01	8.22140E-06	-5.0351	8.70015E-06	-5.0691	1.05920E+00	.0250
92 NH4SO4 -	8.26096E-01	7.36223E-06	-5.1330	5.43323E-06	-5.2649	7.37986E-01	-.1320
30 CaHCO3 +	6.70610E-01	6.72493E-06	-5.1622	5.01051E-06	-5.3201	7.37986E-01	-.1320
49 CAF +	2.25311E-01	4.89402E-06	-5.3019	3.61542E-06	-5.4418	7.37956E-01	-.1320
20 HGF +	2.02083E-01	4.73717E-06	-5.3245	3.43597E-06	-5.4584	7.37956E-01	-.1320
90 BR -	1.66600E-01	2.03114E-06	-5.6923	1.49395E-06	-5.8242	7.37986E-01	-.1320
29 CAOH +	1.07467E-01	1.96963E-06	-5.7131	1.40920E-06	-5.8510	7.37956E-01	-.1320
26 H2SiO4 2-	1.76163E-01	1.80902E-06	-5.7215	5.63255E-07	-6.2493	2.96615E-01	-.5278
19 MgOH +	6.45229E-02	1.58495E-06	-5.8032	1.16901E-06	-5.9322	7.37986E-01	-.1320
95 KCl	8.10481E-02	1.10276E-06	-5.9575	1.10635E-06	-5.9325	1.05920E+00	.0250
22 MgHCO3 +	0.16373E-02	9.71117E-07	-6.0127	7.16371E-07	-6.1447	7.37986E-01	-.1320
75 CaPO4 -	7.76836E-02	5.78395E-07	-6.2373	4.27292E-07	-6.3693	7.37956E-01	-.1320
79 FE(OH)4 -	5.90214E-02	4.33232E-07	-6.3158	3.56485E-07	-6.4477	7.37956E-01	-.1320
8 FE 2+	2.11976E-02	3.85036E-07	-6.4145	1.14207E-07	-6.9423	2.96615E-01	-.5278
34 FESO4	4.62410E-02	3.08793E-07	-6.5103	3.27075E-07	-6.4854	1.05920E+00	.0250
11 FEOM +	1.67802E-02	2.33644E-07	-6.6314	1.72426E-07	-6.7634	7.37956E-01	-.1320
47 HFO1 2-	1.87245E-02	1.97901E-07	-6.7036	5.97093E-08	-7.2314	2.96615E-01	-.5278
86 H2CO3	1.11310E-02	1.62059E-07	-6.7398	1.93335E-07	-6.7137	1.06194E+00	.0261
226 B(OH)5 2-	1.50355E-02	1.59110E-07	-6.7983	4.71844E-08	-7.3231	2.96615E-01	-.5278
40 MgPO4 -	1.17072E-02	9.92804E-08	-7.0019	7.34742E-08	-7.1339	7.37956E-01	-.1320
74 CAMPO4	7.23202E-03	5.53193E-08	-7.2683	5.71118E-08	-7.2433	1.05920E+00	.0250

POS-1
1ST PORE VOLUME - CUMULATIVE
EH = -.212

INITIAL SOLUTION

TEMPERATURE = 25.00 DEGREES C PH = 8.400 ANALYTICAL EPMCAT = 74.022 ANALYTICAL EPMAN = 77.849

*** OXIDATION - REDUCTION ***
DISSOLVED OXYGEN = 0 MG/L
EH MEASURED WITH CALOMEL = 9.9000 VOLTS
MEASURED EH OF ZOBELL SOLUTION = 9.9000 VOLTS
CORRECTED EH = -.2120 VOLTS
PE COMPUTED FROM CORRECTED EH = -3.583

*** TOTAL CONCENTRATIONS OF INPUT SPECIES ***

SPECIES	TOTAL MOLALITY	LOG TOTAL MOLALITY	TOTAL MG/LITRE
CA 2+	1.403547E-04	-3.8522	5.600000E+00
MG 2+	3.144000E-04	-3.5024	7.600000E+00
NA +	7.263698E-02	-1.1388	1.660000E+03
K +	2.881403E-04	-3.5404	1.120000E+01
CL -	4.199462E-04	-3.3768	1.480000E+01
SO4 2-	1.319400E-02	-1.8796	1.260000E+03
HCC3 -	4.665717E-02	-1.3311	2.830000E+03
SIC2 TOTAL	2.507189E-04	-3.6008	1.497500E+01
FE 2+	2.161555E-06	-5.6652	1.200000E-01
PO4 3-	2.965876E-06	-5.5278	2.000000E-01
SR 2+	1.951779E-06	-5.7096	1.700000E-01
F -	4.341919E-03	-2.3623	8.200000E+01
NH4 +	1.784564E-04	-3.7485	3.200000E+00
NO3 -	3.033895E-05	-4.5180	1.870000E+00
BOFON	2.140361E-03	-2.6695	2.500000E+01
BR -	7.553385E-07	-6.1219	6.000000E-02
MOLYBDENUM	2.034160E-04	-3.6916	1.940000E+01
URANIUM	8.452497E-08	-7.0730	2.000000E-02

*** CONVERGENCE ITERATIONS ***

ITERATION	S1-ANALCO3	S2-SO4TOT	S3-FTOT	S4-PTOT	S5-CLTOT
1	3.102691E-03	4.797137E-03	1.493417E-04	6.055235E-07	5.371207E-07
2	1.502715E-04	1.086379E-04	1.250920E-05	4.803536E-08	2.443795E-08
3	-2.823465E-06	-1.107516E-06	-3.094647E-07	-7.546690E-10	-9.155347E-10
4	4.844906E-07	3.576440E-07	4.209199E-08	1.880537E-10	5.953761E-11
5	7.137505E-10	3.683750E-09	-1.349348E-10	1.419215E-12	-1.705492E-12

THE REQUESTED CONVERGENCE TOLERANCES FOR THIS JOB WERE AS FOLLOWS

4.630047E-05	1.319489E-05	4.341319E-06	2.965856E-09	4.199462E-07	(REAL TOLERANCE)
.0010000000	.0010000000	.0010000000	.0010000000	.0010000000	(FRACTIONAL TOL.)

*** DESCRIPTION OF SOLUTION ***

ANALYTICAL	COMPUTED	PH	ACTIVITY H2O = .9977
EPMCAT 74.022	70.384	8.400	PCO2 = 8.780895E-03
EPMAN 77.849	74.630		LOG PCO2 = -2.0565
		TEMPERATURE	PO2 = 1.394337E-64
		25.00 DEG C	PCN4 = 2.177711E-18
EH = -.2120 PE = -3.593		IONIC STRENGTH	CO2 TOT = .450690E-01
PE CALC S = 100.000		8.540185E-02	DENSITY = 1.0000
PE CALC DOX = 100.000			TDS = 5934.3MG/L
PE SATO DOX = 100.000			

IN COMPUTING THE DISTRIBUTION OF SPECIES, PE = -3.503 EQUIVALENT EM = -.212 VOLTS
 THE VALUES OF THE DEBYE-HUCKEL SOLVENT CONSTANTS ARE, A = .5103 AND B = .3206
 CORALR = 0 PECALC = 1 FLAG = 3 IGI = 1 THE ALKALINITY CORRECTION = 3.507002E-04

DISTRIBUTION OF SPECIES

I SPECIES	PPM	MOLALITY	LOG MOL	ACTIVITY	LOG ACT	ACT. COEFF.	LOG A COF
3 NA +	1.58526E+03 ✓	8.93665E-02	-1.1588	5.49165E-02	-1.2603	7.91686E-01	-.1014
7 HCO3 -	2.55793E+03 ✓	4.21717E-02	-1.3750	3.36293E-02	-1.4733	7.97438E-01	-.0983
6 SO4 2-	1.09379E+03 ✓	1.14543E-02	-1.9410	4.40894E-03	-2.3479	3.91893E-01	-.4068
62 F -	7.56166E+01 ✓	4.21587E-03	-2.3751	3.33005E-03	-2.4775	7.89884E-01	-.1024
35 U(OH)3	1.10001E+02 ✓	1.00205E-03	-2.7441	1.83346E-03	-2.7355	1.01926E+00	.0035
44 H2PO4 -	1.93131E+02 ✓	1.03755E-03	-2.7857	1.23371E-03	-2.8932	7.89884E-01	-.1024
43 HPO4 2-	8.50214E+01 ✓	1.01831E-03	-2.9921	1.03354E-03	-2.9936	1.01986E+00	.0085
18 CO3 2-	5.03440E+01 ✓	9.78061E-04	-3.0096	3.95507E-04	-3.4028	4.04379E-01	-.3932
42 HCO3 -	4.20517E+01 ✓	5.09675E-04	-3.2927	4.02505E-04	-3.3951	7.89884E-01	-.1024
5 Cl -	1.47015E+01 ✓	4.19508E-04	-3.3773	3.25305E-04	-3.4877	7.75448E-01	-.1104
225 U(OH)4 -	2.63005E+01 ✓	3.35050E-04	-3.4741	2.65125E-04	-3.5765	7.89884E-01	-.1024
86 H2CO3	1.81440E+01 ✓	2.94290E-04	-3.5312	3.00443E-04	-3.5222	1.02094E+00	.0090
4 K +	1.08035E+01 ✓	2.79432E-04	-3.5536	2.10724E-04	-3.6341	7.75448E-01	-.1104
24 H2SiO4	2.30724E+01 ✓	2.41482E-04	-3.6171	2.40278E-04	-3.6086	1.01986E+00	.0085
117 HPO4 2-	3.23251E+01 ✓	2.03377E-04	-3.6917	7.91689E-05	-4.1014	3.89272E-01	-.4037
2 HS 2+	4.20566E+00 ✓	1.74061E-04	-3.7593	7.35276E-05	-4.1330	4.23000E-01	-.3737
39 H2A +	2.73791E+00 ✓	1.52687E-04	-3.8162	1.20505E-04	-3.9186	7.89884E-01	-.1024
97 HAF	4.34065E+00 ✓	1.03255E-04	-3.9830	1.06061E-04	-3.9744	1.01986E+00	.0085
1 CA 2+	3.13523E+00 ✓	7.80924E-05	-4.1041	3.21076E-05	-4.4934	4.08014E-01	-.3893
25 H2SO4	6.70703E+00 ✓	5.50570E-05	-4.2514	5.71710E-05	-4.2428	1.01986E+00	.0085
22 H2CO3 +	3.09700E+00 ✓	3.64540E-05	-4.4392	2.87350E-05	-4.5407	7.89884E-01	-.1024
85 H2S -	1.87000E+00 ✓	3.03330E-05	-4.5100	2.30842E-05	-4.6204	7.89884E-01	-.1024
32 CASO4	3.89500E+00 ✓	2.87874E-05	-4.5408	2.93000E-05	-4.5323	1.01986E+00	.0085
21 H2CO3	2.20421E+00 ✓	2.72510E-05	-4.5646	2.77922E-05	-4.5561	1.01986E+00	.0085
20 H2F +	6.82951E-01 ✓	2.05003E-05	-4.6851	1.61982E-05	-4.7905	7.89884E-01	-.1024
31 CA CO3	1.70240E+00 ✓	1.76942E-05	-4.7522	1.80150E-05	-4.7436	1.01986E+00	.0085
38 NH3	2.46725E-01 ✓	1.60392E-05	-4.7711	1.72763E-05	-4.7625	1.01986E+00	.0085
30 CAHCO3 +	1.42379E+00 ✓	1.41674E-05	-4.8487	1.11506E-05	-4.9511	7.89884E-01	-.1024
25 H2SiO4 -	8.72302E-01 ✓	9.22735E-06	-5.0319	7.29853E-06	-5.1374	7.89884E-01	-.1024
92 H2MSO4 -	1.00147E+00 ✓	8.82940E-06	-5.0541	6.97427E-06	-5.1565	7.89884E-01	-.1024
46 KSO4 -	1.10233E+00 ✓	8.65543E-06	-5.0627	6.03670E-06	-5.1651	7.89884E-01	-.1024
27 OH -	5.33873E-02 ✓	3.18138E-06	-5.4956	2.51766E-06	-5.5990	7.89884E-01	-.1024
47 HPO4 2-	2.49386E-01 ✓	2.61384E-06	-5.5927	1.01749E-06	-5.9925	3.89272E-01	-.4037
88 SR 2+	1.00205E-01 ✓	1.95176E-06	-5.7096	7.50706E-07	-6.1193	3.83272E-01	-.4097
8 FE 2+	9.00535E-02 ✓	1.62222E-06	-5.7899	6.31404E-07	-6.1993	3.89272E-01	-.4037
49 CAF +	6.02371E-02 ✓	1.17990E-06	-5.9295	9.31203E-07	-6.0009	7.89884E-01	-.1024
98 DR -	6.00030E-02 ✓	7.55330E-07	-6.1219	5.94300E-07	-6.2243	7.89884E-01	-.1024
232 H2O(OH)5 -	6.27250E-02 ✓	5.14451E-07	-6.2907	4.03300E-07	-6.3911	7.89884E-01	-.1024
34 FESO4	6.65203E-02 ✓	4.40511E-07	-6.3560	4.49259E-07	-6.3475	1.01986E+00	.0085
94 NaCl	2.54449E-02 ✓	4.37980E-07	-6.3595	4.46678E-07	-6.3500	1.01986E+00	.0085
231 BF(OH)3 -	2.74366E-02 ✓	3.41461E-07	-6.4607	2.69715E-07	-6.5691	7.89884E-01	-.1024
233 B(OH)3(OH)4 -	2.92903E-02 ✓	1.90520E-07	-6.7022	1.86000E-07	-6.0040	7.89884E-01	-.1024
50 H2HPO4 -	1.63125E-02 ✓	1.37234E-07	-6.8633	1.01000E-07	-6.5009	7.89884E-01	-.1024
11 FE OH +	6.90007E-03 ✓	9.01161E-09	-7.0172	7.89884E-09	-7.1150	7.89884E-01	-.1024
226 B(OH)5 2-	8.15053E-03 ✓	8.55450E-08	-7.6678	3.39400E-08	-7.4776	3.89272E-01	-.4097
48 H2PO4 -	7.96339E-03 ✓	8.25977E-08	-7.8930	6.52400E-08	-7.1855	7.89884E-01	-.1024
121 UO2(CO3)3 4-	3.47865E-02 ✓	7.7553E-08	-7.1093	1.78542E-09	-8.7483	2.29620E-02	-1.6390
73 H2HPO4	6.51151E-03 ✓	5.44543E-08	-7.2640	5.55357E-08	-7.2554	1.01986E+00	.0085
40 H2PO4 -	4.94316E-03 ✓	4.16878E-08	-7.3820	3.29285E-08	-7.4024	7.89884E-01	-.1024
116 H2O4 -	6.32400E-03 ✓	3.99017E-08	-7.3990	3.15177E-08	-7.5014	7.89884E-01	-.1024

SS-3
1ST PORE VOLUME CUMULATIVE MMH
EM = -.065, LOW P

INITIAL SOLUTION

TEMPERATURE = 25.00 DEGREES C PH = 8.000 ANALYTICAL EPMCAT = 384.031 ANALYTICAL EPMAN = 352.300

*** OXIDATION - REDUCTION ***
DISSOLVED OXYGEN = 0 MG/L
EM MEASURED WITH CALOMEL = 9.9000 VOLTS
MEASURED EM OF ZOBELL SOLUTION = 9.9000 VOLTS
CORRECTED EM = -.0650 VOLTS
PE COMPUTED FROM CORRECTED EM = -1.099

*** TOTAL CONCENTRATIONS OF INPUT SPECIES ***

SPECIES	TOTAL MOLALITY	LOG TOTAL MOLALITY	TOTAL MG/LITRE
CA 2+	1.200962E-02	-1.9205	4.700000E+02
MG 2+	7.329728E-02	-1.1349	1.740000E+03
NA +	2.107100E-01	-.6763	4.730000E+03
K +	2.016745E-03	-2.6953	7.700000E+01
CL -	6.528520E-03	-2.1852	2.260000E+02
SO4 2-	1.677020E-01	-.7755	1.573000E+04
HCC3 -	6.545923E-03	-2.1840	3.900000E+02
SIO2 TOTAL	2.333789E-04	-3.6319	1.389200E+01
FE 2+	4.401196E-06	-5.3564	2.400000E-01
PO4 3-	1.941060E-06	-5.7120	1.800000E-01
SR 2+	1.145406E-04	-3.9410	9.800000E+00
F -	1.401573E-03	-2.8534	2.600000E+01
NH4 +	4.371666E-04	-3.2594	7.700000E+00
BORON	9.663495E-04	-3.0149	1.020000E+01
BR -	1.666123E-05	-4.7783	1.300000E+00
MN 2+	7.829531E-06	-5.1063	4.200000E-01
MOLYBDENUM	4.163170E-05	-4.3806	3.900000E+00
S2O3 2-	1.169212E-03	-2.9321	1.280000E+02
S4O6 2-	2.968707E-05	-4.5274	6.500000E+00

*** CONVERGENCE ITERATIONS ***

ITERATION	S1-ANALCO3	S2-SO4TOT	S3-FTOT	S4-PTOT	S5-CLTOT
1	9.090705E-04	1.715944E-01	3.800842E-04	4.508886E-06	1.155519E-05
2	9.431415E-04	4.540545E-02	5.909955E-04	2.336691E-06	5.327452E-06
3	6.322132E-05	2.811657E-03	3.509933E-05	8.548998E-08	1.008576E-07
4	1.446052E-05	6.252747E-04	7.822336E-06	1.879441E-08	1.989579E-08
5	3.304107E-06	1.445225E-04	1.833606E-06	4.342750E-09	4.317563E-09
6	7.953350E-07	3.415415E-05	4.319242E-07	1.026347E-09	1.002232E-09

THE REQUESTED CONVERGENCE TOLERANCES FOR THIS JOB WERE AS FOLLOWS

6.463634E-06	1.677020E-04	1.401573E-06	1.941060E-09	6.528520E-06	(REAL TOLERANCE)
.0010000000	.0010000000	.0010000000	.0010000000	.0010000000	(FRACTIONAL TOL.)

DESCRIPTION OF SOLUTION

ANALYTICAL	COMPUTED	PH	ACTIVITY H2O = .9929
EPMCAT 384.031	272.283	8.000	PCO2 = 2.293331E-03
EPMAN 352.300	240.688		LOG PCO2 = -2.6395
		TEMPERATURE	PD2 = 3.013724E-56
		25.00 DEG C	PCN4 = 1.211818E-35
EM = -.0650 PE = -1.099			CO2 TOT = .624312E-02
PE CALC S = 100.000		IONIC STRENGTH	DENSITY = 1.0000
PF CALC DIX = 100.000			

PE SA'D BOX= 100.000

3.995E-01

TDS = 23570.9MG/L

IN COMPUTING THE DISTRIBUTION OF SPECIES, PE = -1.099 EQUIVALENT EM = -.065 VOLTS
 THE VALUES OF THE DEBYE-HUCKEL SOLVENT CONSTANTS ARE, A = .5108 AND B = .3286
 CORALN = 0 PECALC = 1 FLAG = 3 ICD = 1 THE ALKALINITY CORRECTION = 8.223976E-05

DISTRIBUTION OF SPECIES

I SPECIES	PPM	MOLALITY	LOG MOL	ACTIVITY	LOG ACT	ACT. COEFF.	LOG A COF
3 NA +	4.22784E+03 ✓	1.83340E-01	-.7251	1.34445E-01	-.8715	7.13843E-01	-.1484
6 SO4 2-	9.53345E+03 ✓	1.01630E-01	-.9939	2.27756E-02	-1.6425	2.24024E-01	-.6496
23 MGSO4	4.39004E+03 ✓	3.73505E-02	-1.4277	4.09511E-02	-1.3877	1.09640E+00	.0400
2 MG 2+	8.22625E+02 ✓	3.43530E-02	-1.4603	1.03913E-02	-1.9832	2.99954E-01	-.5229
44 HASO4 -	2.55050E+03 ✓	2.20104E-02	-1.6574	1.69700E-02	-1.7940	7.30110E-01	-.1366
5 CL -	2.25530E+03 ✓	6.51572E-03	-2.1891	4.29177E-03	-2.3671	6.59193E-01	-.1810
32 CASO4	8.13771E+02 ✓	6.34730E-03	-2.1974	6.90327E-03	-2.1574	1.09640E+00	.0400
1 CA 2+	2.18220E+02 ✓	5.54392E-03	-2.2543	1.50001E-03	-2.8239	2.70512E-01	-.5677
7 HCC3 -	2.95750E+02 ✓	4.96412E-03	-2.3042	3.43650E-03	-2.4564	7.04374E-01	-.1522
4 K +	6.72765E+01 ✓	1.76192E-03	-2.7540	1.16114E-03	-2.9350	6.59193E-01	-.1810
201 S2O3 2-	1.28000E+02 ✓	1.16921E-03	-2.9321	3.32235E-04	-3.4786	2.84153E-01	-.5464
36 B(OH)3	5.37218E+01 ✓	8.89793E-04	-3.0507	9.75569E-04	-3.0107	1.09640E+00	.0400
62 F -	1.48419E+01 ✓	8.00077E-04	-3.0939	5.84144E-04	-3.2335	7.30110E-01	-.1366
22 MHCOC3 +	4.82333E+01 ✓	5.70010E-04	-3.2374	4.22359E-04	-3.3740	7.30110E-01	-.1366
20 MGF +	2.32333E+01 ✓	5.48330E-04	-3.2611	4.01153E-04	-3.3957	7.30110E-01	-.1366
39 MHA +	5.78330E+00 ✓	3.28330E-04	-3.4897	2.39717E-04	-3.6203	7.30110E-01	-.1366
46 KSO4 -	3.36040E+01 ✓	2.94610E-04	-3.5311	1.85900E-04	-3.7307	7.30110E-01	-.1366
43 NACOC3	1.97740E+01 ✓	2.41110E-04	-3.6178	2.64357E-04	-3.5778	1.09640E+00	.0400
24 HASO4	2.15216E+01 ✓	2.29319E-04	-3.6376	2.51426E-04	-3.5996	1.09640E+00	.0400
21 MCO3	1.21059E+01 ✓	1.48128E-04	-3.8294	1.62407E-04	-3.7894	1.09640E+00	.0400
60 SR 2+	9.79397E+00 ✓	1.14546E-04	-3.9410	3.25457E-05	-4.4875	2.84153E-01	-.5464
62 NMSO4 -	1.07327E+01 ✓	9.63340E-05	-4.0182	7.03315E-05	-4.1528	7.30110E-01	-.1366
225 S(OH)4 -	5.37730E-00 ✓	7.62475E-05	-4.1172	5.57401E-05	-4.2538	7.30110E-01	-.1366
39 CAMCO3 +	7.34032E+00 ✓	7.44325E-05	-4.1241	5.43205E-05	-4.2647	7.30110E-01	-.1366
68 HCCO3	4.31990E+00 ✓	7.13291E-05	-4.1467	7.84676E-05	-4.1053	1.10008E+00	.0414
18 CO3 2-	3.89630E+00 ✓	6.65072E-05	-4.1771	1.63713E-05	-4.7859	2.46159E-01	-.6088
42 NACO3 -	4.52930E+00 ✓	5.58778E-05	-4.2528	4.07369E-05	-4.3894	7.30110E-01	-.1366
117 MCO3 2-	6.49910E+00 ✓	4.16155E-05	-4.3907	1.18252E-05	-4.9272	2.84153E-01	-.5464
97 MAF	1.70310E+00 ✓	4.15122E-05	-4.3815	4.55475E-05	-4.3415	1.09640E+00	.0400
31 CACOC3	3.11058E+00 ✓	3.15204E-05	-4.4972	3.45657E-05	-4.4572	1.09640E+00	.0400
215 S4O6 2-	6.50000E+00 ✓	2.93371E-05	-4.5274	8.43367E-06	-5.0739	2.84153E-01	-.5464
98 BA -	1.30000E+00 ✓	1.69012E-05	-4.7793	1.21645E-05	-4.9149	7.30110E-01	-.1366
94 MACL	7.51330E-01 ✓	1.31375E-05	-4.8815	1.44373E-05	-4.8405	1.09640E+00	.0400
38 NH3	2.07342E-01 ✓	1.24690E-05	-4.9042	1.36705E-05	-4.8642	1.09640E+00	.0400
49 CAF +	6.82063E-01 ✓	1.04526E-05	-4.9815	7.63155E-06	-5.1174	7.30110E-01	-.1366
101 HN 2+	3.82033E-01 ✓	5.60503E-06	-5.2496	1.61020E-06	-5.7931	2.84153E-01	-.5464
25 HSSO4 -	3.15704E-01 ✓	4.05700E-06	-5.3913	2.96227E-06	-5.5254	7.30110E-01	-.1366
19 MSHO +	9.26571E-02 ✓	2.32138E-06	-5.6343	1.69486E-06	-5.7709	7.30110E-01	-.1366
8 FE 2+	1.22700E-01 ✓	2.25167E-06	-5.6445	6.29311E-07	-6.1939	2.84153E-01	-.5464
34 FMSO4	3.12480E-01 ✓	2.19310E-06	-5.6574	2.30010E-06	-5.6385	1.09640E+00	.0400
109 MMSO4	2.51770E-01 ✓	1.70707E-06	-5.7813	1.87223E-06	-5.7276	1.09640E+00	.0400
27 OH -	2.26692E-02 ✓	1.33692E-06	-5.8815	9.97528E-07	-6.0011	7.30110E-01	-.1366
73 MGHPO4	1.08021E-01 ✓	9.26485E-07	-6.0332	1.01580E-06	-5.9932	1.09640E+00	.0400
47 HPO4 2-	4.34703E-02 ✓	4.60937E-07	-6.3335	1.31829E-07	-6.8800	2.84153E-01	-.5464
111 MMSO3 +	4.54037E-02 ✓	4.01015E-07	-6.3916	2.92735E-07	-6.5335	7.30110E-01	-.1366
40 MMSO4 -	3.02807E-02 ✓	3.05412E-07	-6.5140	2.39777E-07	-6.6202	7.30110E-01	-.1366
95 NCL	8.61152E-03 ✓	1.18233E-07	-6.9240	1.29100E-07	-6.8871	1.09640E+00	.0400
74 CAMPO4	1.31372E-02 ✓	9.00803E-08	-7.0049	1.03419E-07	-6.9649	1.09640E+00	.0400

Trace Elements in Rich Oil Shales of the Mahogany Zone
Concentrated by Differential Density Centrifugation

Presented at Geological Society of America, Annual Meeting
San Diego, Ca. November 1979

Saether, O.M., Runnells, D.D., and Meglen, R.R.
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ABSTRACT

A new combination of techniques which makes it possible to separate the minerals in oil shale into different density fractions is presented. The procedure involves low-temperature ashing and high-speed centrifugation in a discontinuous density gradient. Mineralogical and quantitative chemical analysis of trace metals and fluorine using a variety of analytical techniques gave the distribution of nine potentially toxic elements as a function of density. A maximum enrichment factor is calculated for Ni, Cu, Zn, Pb, As, Se, Mo, Cd, and F. The results are treated statistically and a paired hierarchical cluster dendrogram is drawn based from the correlation matrix.

The trace metals are concentrated from 3.6 to 208 times in the heavier than 2.9 g/cm^3 density fraction, where sulfides and iron-rich carbonates are present. Fluorine is most concentrated in the 2.4 g/cm^3 and 2.5 g/cm^3 density fractions which contain the micaeous clay minerals.

Application of this combination of analytical techniques to four oil shale samples demonstrates the feasibility of separating micron-sized mineral grains held tightly together by carbonate cement and organic matter. The results may be useful in the design processes to remove potentially toxic trace elements from retort waters and solid oil shale waste, prior to disposal.

INTRODUCTION

Information on the residence of potentially toxic trace elements in sediments and sedimentary rocks is valuable when possible release of such elements to the environment is to be evaluated. Particular interest is attached to the chemical forms of trace elements in fine-grained rocks, such as coal and oil shale, which are raw materials for production of synthetic fuels. During burning of such materials, various trace elements can be released in the form of gases or particulates via smoke stacks, waste waters, or solid wastes. Assessment of how each element is released to water in contact with waste material depends on knowledge of its mobility in the aquatic environment, which can best be predicted if the residence is known for the element of concern.

This study focusses on the residence of fluorine in the oil shales of the Green River Formation, Piceance Creek Basin, northwestern Colorado. A combination of low-temperature ashing and high-speed centrifugation in a discontinuous density gradient was performed on samples of oil shale from the rich Mahogany Zone. Subsequent mineralogical and chemical analysis of 26 elements were performed on samples weighing less than 1 mg. This paper describes the methods used and discusses the results obtained with respect to nickel, copper, zinc, lead, arsenic, selenium, molybdenum, cadmium, and fluorine in four oil shale samples selected at different depths within the Mahogany Zone.

The Green River oil shales are stratified marlstones of Eocene age. They are composed of micron-sized grains of minerals, surrounded by a cement of carbonate minerals and kerogenous organic matter (Fig. 1). The composition of a typical Mahogany Zone oil shale from Colorado is given in Table 1 (1).

The principal previous investigation which discusses the mineralogical residence of trace elements in Green River oil shales is a report by Desborough and others (2); they used a combination of petrographic and electron microprobe methods to study several samples of rich oil shale from Colorado and Utah. By comparing the ratios of 34 major, minor and trace elements obtained in the quantitative spot analysis by electron microprobe, the mineralogical residence of 24 of these elements was suggested (2). Conclusive evidence for assigning Zn, As, and Cd to sulfide minerals, and F to anhydrous grains of fluorite (CaF_2) and cryolite (Na_3AlF_6) was established by using the petrographic microscope. The mineralogical residence of Se, Mo, and Pb could not be established.

Elemental analyses with the electron microprobe on bulk samples of oil shale are restricted by the small size of grains of the minerals present. Under ideal conditions, the electron beam should impinge upon a chemically homogeneous target which is at least 10 micrometers in diameter. This relationship between the size of target and beam will eliminate interference from neighboring mineral phases. In the case of oil shale, if a separation of the different mineralogical components could be made, valuable information regarding trace element residence could be obtained by means of the electron microprobe; such a separation of the inorganic fraction from the ubiquitous kerogen was done by Tisot and Murphy (3), but the thermal treatment (400°C) and subsequent water or acid treatment (6N HCl), almost certainly caused breakdown of some sulfide and carbonate minerals, thus altering the distribution of trace elements to an unknown extent. Complete removal of the cementing organic matter in oil shale, leaving unaltered micron-sized grains of minerals, would be the ideal preparation of material on which to perform chemical analyses. The present study utilized low-temperature ashing and high-speed centrifugation to separate the grains. Our technique of separation is simpler and more direct than previous applications to mineralogical separations of soils and sediments (4-6).

10 μ m

Figure 1

Photomicrograph of oil shale from the Mahogany Zone under crossed nicols. The picture shows the size range of rhombohedral dolomite crystals embedded in organic matter.

MAHOGANY ZONE OIL SHALE, COLORADO

INORGANIC PORTION	WT. %
DOLOMITE	32
CALCITE	16
QUARTZ	15
ILLITE	19
ALBITE	10
MICROCLINE	6
PYRITE	1
ANALCIME	<u>1</u>
	<u>100</u>

(SMITH, 1969)

Table 1. Composition of typical oil shale sample from Colorado (inorganic fraction only).

MATERIALS AND METHODS

Sample Preparation

Eleven samples of raw oil shale from the Mahogany Zone were selected from different depths in the U.S. Bureau of Mines drill-core 01-A, taken from the central part of the Piceance Creek Basin (Sec. 29, T1S, R97W, Rio Blanco County), northwestern Colorado. The wafer-shaped samples (4 x 2 x 0.5 cm) were exposed to activated oxygen (activated by radio frequency fields, 13.6 MHz) at reduced pressure in a low-temperature plasma ashing oven (Tracerlab, Model LTA 600) (7-8). This treatment removed organic matter from a thin surface layer of each sample wafer. At intervals of 24 hours, the ashed surface of the sample was gently brushed off and collected as a powder in a sample bottle. The temperature remains below 200°C during the ashing. The temperature increases during the ashing as a result of exothermic reactions associated with oxidation of kerogen, but the overall temperature stays well below the melting point for the carbonate, sulfide, and silicate minerals in the oil shale.

Centrifugation

A discontinuous density gradient ranging from 2.0 to 2.9 g/cm³ was made by mixing different ratios of 1,1,2,2-tetrabromoethane (TBE) and 99% ethanol (ETOH). The densities of these end-member liquids are 2.96 and 0.82 g/cm³, respectively. The density gradient was made by laying 1 mL each of ten mixtures of TBE and ETOH, starting with the heaviest at the bottom and the lightest on top in a 16 x 95 mm polypropylene tube. An organic solute, polyvinylpyrrolidone (PVP K-30, molecular weight of 40,000), was used as a dispersant on a 10% weight basis in the ETOH phase. In an extensive study, Bonner and others (9) concluded that this combination of liquids gave the best density gradient for separation of soils. The ashed oil shale sample (100 mg) was dispersed ultrasonically for 5 minutes in 3 mL of ETOH s/PVP before it was carefully laid on top of the density gradient.

The samples were centrifuged in a Sorvall RC-2B Model high-speed centrifuge with a HB-4 rotor head at a thermostatically controlled 25°C. The centrifugation time was 24 hours at 10,000 rpm. The G-values varied from 9,500 at the top of the sample to 15,000 at the bottom of the tube. Studies by Francis and others (4) on sedimentation time as a function of particle diameter and density showed that after 200,000 G-hours, 0.05 micrometer particles of density 2.0 g/cm³ should have settled to their isopycnic point in the gradient. Assuming that retardation at the interfaces in our step-wise density gradient is negligible, the period of centrifugation that we employed should be adequate for all particles to reach their isopycnic point.

After the period of centrifugation was completed, five to eight discrete bands of particles were observed in each container. The distance of each band from the bottom was observed, and the density was determined from the compartment in which the fraction was located. Ten one-milliliter layers of the density medium were easily recognized because of refraction of light at the interfaces. In a test run, measurements of refractive indices on the ten layers confirmed that the densities of the fluids remained constant during centrifugation.

LIGHT MINERALS (density less than 2.9 g/cm ³)		
Mineral	Formula	Density (g/cm ³)
Analcime	NaAlSi ₂ O ₆ H ₂ O	2.27
Illite	K ₂ Al ₆ Si ₆ O ₂₀ (OH) ₄	2.5-2.6
Othroclase	KAlSi ₃ O ₈	2.57
Albite	NaAlSi ₃ O ₈	2.62
Quartz	SiO ₂	2.65
Calcite	CaCO ₃	2.71
Villiaumite	NaF	2.80
Dolomite	CaMg(CO ₃) ₂	2.85
HEAVY MINERALS (density greater than 2.9 g/cm ³)		
Mineral	Formula	Density (g/cm ³)
Cryolite	Na ₃ AlF ₆	2.97
Magnesite	MgCO ₃	3.0-3.2
Fluorite	CaF ₂	3.18
Fluorapatite	Ca ₅ (PO ₄) ₃ (F,OH)	3.1-3.2
Siderite	FeCO ₃	3.96
Marcasite	FeS ₂	4.89
Pyrite	FeS ₂	5.02

Table 2. Density of minerals in oil shale from the Green River Formation.

The bands were removed using a one-milliliter pipette with disposable plastic tip, and the sample from each band was washed three times with 25 mL ETOH aided by ultrasonic dispersion.

Analytical Chemical Methods

The samples were analyzed for 26 elements (atomic number higher than 18) by a custom-built x-ray fluorescence unit. Because of the very small mass of sample (5-10 mg) available from each density fraction, analysis for fluorine by wet chemical methods was not feasible. The same 300 ug targets used for XRF analysis for the 26 heavy elements were later analyzed by the method of Nuclear Inelastic Scattering (10) using equipment at the University of Colorado Cyclotron. In the method of Nuclear Inelastic Scattering, the samples are exposed for approximately 15 minutes to a beam of protons of 5.9 meV. The first (110 keV) and second (197 keV) excited states of the ^{19}F nucleus are populated by inelastic scattering of the protons. The gamma rays emitted by a hyper-pure germanium (HPGe) detector. The number of these X-rays observed is proportional to the amount of fluorine present in the sample. A more detailed description of the analytical set-up measuring fluorine in this study is presented elsewhere (10, 13).

Mineralogical identification of the sample fractions was made by x-ray diffraction of 0.1 mg. samples mounted on collodion, using a Philips Norelco unit (35 kV, 18 mA, Cu-K α filter with 1 $^\circ$ slit opening). Scanning electron microscope studies were performed on a Cambridge Model SM4 with an energy-dispersive Kevex^R fluorescence attachment, Model 5500. In addition, the exact mineralogical residence of fluorine was verified by using an ARL (Applied Research Laboratories) electron microprobe, Model SM, at the U.S. Geological Survey Laboratories in Denver, Colorado. This electron microprobe is calibrated for quantitative analysis of fluorine using different types of micas as standards (A. Gunow, analyst).

RESULTS AND DISCUSSION

Density

An evaluation of the specific gravity of minerals that have been detected in oil shales of the Green River Formation (Table 2) reveals that each mineral has a unique density, and the density is generally at least 0.1 g/cm³ different from that of other major minerals present. Consequently the gradient selected in this study ranges from 2.0 to 2.9 g/cm³, with a 0.1 g/cm³ hiatus between each density step. Four of the eleven samples were used in the study are discussed in this paper; it was these four samples that the physical separation was most successful with respect to concentration of trace elements.

Mineralogy

Minerals identified by x-ray diffraction confirm the physical separation achieved during centrifugation; these results are presented in Table 3. The x-ray diffractograms of the density fraction are simple and easy to interpret when compared to that of the bulk sample. The relative peak-height of the primary peaks for the different minerals can only be used semi-quantitatively when com-

paring their relative abundance within one sample, since different amounts of sample were used from each density fraction. The 2.9 g/cm³ fraction contains primarily Mg- or Fe- rich carbonates, which are separated from dolomite (CaMg(CO₃)₂), the predominant mineral of fraction 2.8 g/cm³. The density separation of the carbonate minerals yielded separations as a function of the degree of solid substitution of Ca by Mg and Fe, underscoring how refined this method of separation can be when applied to fine-grained materials.

In density samples No. 2-1 and 9-1 (Table 3) pyrite was present in large enough quantities to be detected by x-ray diffraction. The pyrite occurs as discrete euhedral crystals of 5-10 micrometers diameter. Quartz and feldspar first appear in fractions of density 2.7 g/cm³, and these are the dominant minerals of the 2.6 g/cm³ fractions. Illite first appears with quartz and K-feldspar in the 2.5 g/cm³ fraction and is the only mineral, other than quartz, which is present in the lightest 2.4 g/cm³ fraction. The presence of minerals such as magnesite, pyrite, and illite would not have been verified by x-ray analysis of the bulk sample alone. The isolation of a monomineralic density fraction was not obtained because of the heterogeneous mineral assemblages with composite densities different from that of pure minerals. However, the distribution of minerals among the density fractions is consistent among the samples centrifuged.

When examined under the scanning electron microscope, each density fraction appears as aggregates of grains, with one or two minerals dominating the fraction. Flocculation of the particles in each density fraction occurred after centrifugation was complete, during washing of the sample with ethanol.

Distribution of Major Elements

Knowing the mineralogy of each density fraction provides for a consistent and reasonable interpretation of the distribution of the major elements Fe, Ca, and K (Fig. 2). Iron reaches its maximum concentration in the heaviest fraction where it resides in Fe-rich carbonates and sulfides. The gradual decrease in iron-concentration with decreasing density is explained by decreased iron-content of the carbonate minerals present. Calcium makes up 24-30 weight percent of the 2.8 g/cm³ fraction, where dolomite is the predominant mineral. The concentration of potassium reaches maximum levels in the 2.5 and 2.4 g/cm³ fractions, which contain illite.

Distribution of Trace Elements

The concentrations of the trace elements Ni, Cu, Zn, Pb, As, Se, Mo, Cd, and F in each density fraction, are presented in Table 4. The distribution of the elements within the various density fractions is fairly consistent among the four oil shale samples. It is interesting to observe that most of the metals are concentrated in the heaviest density fraction. This fraction contains the highest amount of iron due to the presence of iron-rich carbonates and sulfides. Only in exceptional cases, such as Mo in samples No. 1 and 11, is the maximum concentration of the trace metal present in the

lighter fractions. In this case Mo probably occurs in the clay minerals. Calculation of the maximum enrichment factor for each element (the ratio between the concentration of the element in the most concentrated fraction after centrifugation and the bulk sample before centrifugation (Table 5)) gives values which range from 3.6 for Mo to 12.3 for Pb. Cadmium has a very high maximum enrichment factor of 208. The results of these calculations confirm that an isolation of the primary source for each element has been accomplished. X-ray fluorescence analysis of the heaviest density fraction of sample No. 9, under the scanning electron microscope, did not lead to verification of Zn, As, and Cd being associated with sulfides; this is probably because the detection limit for the Kevex^R, Model 5500, is too high with respect to these elements. The highest concentrations of these elements were indeed detected in samples that exhibit good peaks for pyrite. Further, based on a statistical correlation, one can use this assumption and infer the residence of elements that show a strong positive correlation with Zn, As, and Cd, e.g. Ni, Pb, Cu, Se, and Mo.

In a statistical treatment of our data, a correlation matrix was calculated for the concentrations of the different trace elements in the various density fractions. The matrix of correlations was used as a measure of similarity for the preparation of a paired hierarchical cluster dendrogram. (Fig. 3) (11). The excellent correlation between the concentration of Cu and As is used as indirect evidence for assigning Cu to the sulfide minerals. A similar, but slightly less convincing argument is used for the residence of Ni and Pb in the sulfides. These four trace elements all correlate well with the concentrations of iron (Correlation of 0.82, Fig. 6). The grouping of these elements is consistent with the Goldschmidt (14) classification of chalcophile elements.

The elements Se and Mo correlate well ($r=0.72$ Fig. 3) and a common residence of these two elements is probable. Selenium and molybdenum have a correlation coefficient, $r = 0.65$, with Fe and associated elements. These latter heavy elements could reside either in an iron-rich carbonate or pyrite, so no firm inference can be made of their mineralogical residence. However, because Zn, As, and Fe are included in the same branch of the dendrogram, it is possible that all of the elements discussed so far reside primarily in sulfides. It is well known that in highly reducing sedimentary environments molybdenum first coprecipitates as molybdenum sulfide with FeS or other metal sulfides. The second stage is the fixation of Mo by adsorption, reduction and other mechanisms on clay minerals or in the organic fraction (112).

Selenium is located under sulfur in the periodic system, and the Se^{2-} -ion is the predominant selenium species in highly reducing and alkaline aqueous environments. The primary occurrence of selenium in coals is commonly diagenetic pyrites (13). As a result of the extremely large relative variations observed in Cd-concentrations, cadmium does not exhibit a significant correlation with these elements.

Figure 2: Distribution of Fe, K, and Ca as function of density in samples No. 1, 2, 9 and 11.

Fraction	$\rho(\text{g/cm}^3)$	Sample			
		1	2	9	11
6	2.4	Illite Quartz	Illite Quartz Dolomite	Illite	Quartz Illite
5	2.5	Quartz K-feldspar Illite	Illite Quartz K-feldspar	Quartz Illite	Quartz K-spar Illite
4	2.6	Quartz K-feldspar Dolomite	Quartz K-feldspar Dolomite	Quartz K-feldspar Dolomite	Dolomite Quartz K-spar
3	2.7	Dolomite Quartz K-feldspar	Dolomite Quartz K-feldspar	Dolomite Quartz K-feldspar	Dolomite K-spar
2	2.8	Dolomite	Dolomite Quartz	Dolomite Quartz	Dolomite
1	≥ 2.9	Magnesite Dolomite	Dolomite Magnesite Pyrite	Pyrite Dolomite Quartz	Dolomite Magnesite

Table 3. Minerals identified in density fractions after centrifugation. Minerals are listed in order of decreasing height of primary x-ray diffraction peak.

Table 4. Concentration (g/g) of Ni, Cu, Zn, Pb, As, Se, Mo, Cd, and F as a function of mineral density.

No.1 $\rho(\text{g/cm}^3)$	Ni	Cu	Zn	Pb	As	Se	Mo	Cd	F
2.4	65	79	116	52	26	4.3	75	3.6	11522
2.5	37	40	85	31	22	2.2	41	3.2	2677
2.6	24	29	121	19	20	1.2	18	1.6	2095
2.7	44	49	114	44	36	2.9	28	2.1	2767
2.8	45	27	62	28	33	3.4	16	<d.1	1288
>2.9	223	214	152	382	341	10	34	1.5	987
<hr/>									
*Bulk	44	46	129	46	50	2.1	48	4.2	2600
No.2 $\rho(\text{g/cm}^3)$	Ni	Cu	Zn	Pb	As	Se	Mo	Cd	F
*2.3	34	52	115	30	6.4	2.3	36	1.7	2423
2.4	36	53	97	9.6	13	1.7	51	2.4	5232
2.5	21	26	73	7	9.5	1.3	24	1.4	2221
2.6	20	20	68	5	11	0.7	15	<d.1.	1453
2.7	24	30	74	12	23	1.9	15	<d.1.	1620
2.8	32	26	44	17	24	2.6	9.3	<d.1.	1605
>2.9	210	552	227	417	515	37	91	416	1497
<hr/>									
*Bulk	36	46	88	34	47	3.9	36	2.0	1600

<d.1. Below detection limit of 1.0 $\mu\text{g/g}$

*Not used in correlation matrix

Table 4. (cont.)

No. 9 $\rho(\text{g}/\text{cm}^3)$	Ni	Cu	Zn	Pb	As	Se	Mo	Cd	F
2.4	66	55	105	43	16	6.3	62	2.1	1329
2.5	32	32	75	10.4	48	2.1	50	<d.1.	1813
2.6	28	39	888	21	75	2.2	34	1.3	1027
2.7	51	81	186	40	142	3.3	43	1.9	1325
2.8	51	96	153	52	164	4.0	41	3.4	1982
>2.9	330	1122	875	754	1844	53	304	17	917
<u>*Bulk</u>	59	138	231	77	240	6.0	85	3.1	1300
No. 11 $\rho(\text{g}/\text{cm}^3)$	Ni	Cu	Zn	Pb	As	Se	Mo	Cd	F**
2.3									*1439
2.4	55	71	55	79	d.1.	7.8	116	1.3	*1305
2.5	41	46	58	43	19	6.7	112	1.0	*12834
2.6	27	28	61	21	17	3.9	53	1.1	
									*1325
2.7	42	39	122	20	27	4.0	58	3.7	
2.8	28	17	48	3.7	11	1.9	24	<d.1.	
									*1357
>2.9	174	338	1585	281	305	20	88	21	
<u>*Bulk</u>	40	40	137	41	32	3.8	95	3.5	1400

<d.1. Below detection limit of 1.0 $\mu\text{g}/\text{g}$

* Not used in correlation matrix

** Fluorine concentration measured on density separates from replicate run

Table 5. Maximum concentration of trace elements in density fractions of samples 1, 2, 9, and 11.

Sample		1		2		9		11	
Element		PPM	E_F	PPM	E_F	PPM	E_F	PPM	E_F
Ni	A	223	5.1	210	5.8	330	5.6	173	4.3
	B	44		36		59		40	
Cu	A	214	4.7	557	12.0	1122	8.1	338	8.5
	B	46		46		138		40	
Zn	A	152	2.1	226	2.6	875	3.8	1584	11.6
	B	129		88		231		137	
Pb	A	382	8.3	417	12.3	754	9.8	281	6.9
	B	46		34		77		41	
As	A	341	6.8	514	10.9	1844	7.8	304	9.5
	B	50		47		240		32	
Se	A	10	5.0	37	9.7	53	8.8	21	5.4
	B	2		4		6		3	
Mo	A	75	1.6	91	2.5	304	3.6	116	1.2
	B	47		36		85		95	
Cd	A	3.6	0.9	416	208.0	17	5.5	21	6.0
	B	4.2		2.0		3.1		3.5	
F	A	11963	4.6	5232	3.3	1813	1.4	12834	9.2
	B	2600		1600		1300		1400	

A = Concentration of element in density fraction

B = Concentration of element in bulk ashed sample

$E_F = A/B$ = Enrichment factor for element

DENDROGRAM FOR ELEMENTAL CONCENTRATION IN DENSITY FRACTIONS OF SAMPLES No. 1, 2, 9, AND 11

Figure 3: Results of cluster analysis presented as a paired hierarchical cluster dendrogram. Cophenetic correlation coefficient is 0.910. Concentrations of fluorine in sample No.11 was not available on the same targets as the trace elements and has a concentration of 0.26 with K based on data from samples No.1, 2 and 9.

The concentration of fluorine in the lighter density fractions of samples No. 1, 2 and 11, is very interesting, since its mineralogical residence in oil shales of the Mahogany Zone has earlier been reported (2) as being in the heavy minerals fluorite and cryolite. Because the concentration of fluorine in density fraction sample No. 11, were not available on the exact same targets on which the other trace elements were analyzed only the results of F-analysis of density fraction samples No. 1, 2, and 9 were used in the statistical treatment. The positive correlation between the concentration of K and F, and the negative correlation of these elements with Ca, suggest that illite is the primary residence for fluorine in these oil shale samples. Conclusive evidence for fluorine being associated with micaceous clay minerals in the 2.4 g/cm³ density fraction, has been obtained from electron microprobe analysis of clay platelets in sample No. 1-6 (15).

CONCLUSIONS

By combining the techniques of low-temperature ashing, high-speed density centrifugation, x-ray diffraction, scanning electron microscopy, x-ray fluorescence, nuclear inelastic scattering, and statistical cluster analysis, insight has been obtained into the distribution of trace elements in oil shale as a function of density. Less than 1 mg material was used for mineralogical and quantitative elemental analysis of each density fraction obtained after centrifugation.

The trace heavy metals of rich oil shales are concentrated in minerals of specific gravity greater than 2.9 g/cm³. It is probable that the principal mineralogical residences of Ni, Cu, and Pb are sulfides, although conclusive evidence for this remains to be established. No significant enrichment of trace metals was found in the clay minerals of the oil shale, except for Mo which was most concentrated in the lighter 2.4 g/cm³ fraction in two samples. Selenium also correlates well with Mo and a common source for the two elements in diagenetic sulfides of the oil shale is likely. We have determined that fluorine is concentrated in the lighter density fractions and most likely substitutes for hydroxyl ions in illitic clay minerals or is sorbed on the surface.

The centrifugation procedure described in this paper is a feasible alternative to the more difficult and expensive method of Zonal Centrifugation (4). The yield of material is adequate for elemental analysis using x-ray fluorescence and nuclear inelastic scattering.

The overall conclusion of this study is that trace heavy metals in oil shale are chiefly concentrated in the fraction with the highest density. Fluorine, on the other hand, resides in the lighter fractions of oil shales from the Mahogany Zone. Possible development of technology aimed at removing these potential contaminants, and preventing their release to the environment, should take these factors into consideration.

FIGURE CAPTIONS

- Fig. 1 Thin-section of oil shale in B&W.
- Fig. 2 Distribution of Fe, K, and Ca as function of density in samples 1, 2, 9 and 11.
- Fig. 3 Dendrogram for elemental concentration in density fractions of samples No. 1, 2, 9 and 11. Cophenetic correlation coefficient is 0,910.
- Table 1 Composition of typical oil shale sample from Colorado
- Table 2 Density of minerals in oil shale from the Green River Formation
- Table 3 Minerals identified in density fractions after centrifugation.
- Table 4 Concentration mg/g of Ni, Cu, Zn, Pb, As, Se, Mo, Cd, and F as a function of mineral density.
- Table 5 Maximum concentration of trace elements in density fractions of samples 1, 2, 9 and 11.

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Fluorine: Its Mineralogical Residence in the Mahogany Zone
of the Green River Formation, Piceance Creek Basin, Colorado

Presented at Soils Science Society of America
Fort Collins, Co. August 1979

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ABSTRACT

The Eocene oil shales of northwestern Colorado comprise one of the major resources of hydrocarbons in the United States. Oil shales of the Mahogany Zone (Parachute Creek Member, Green River Formation) contain up to 2100 mg/kg fluorine. The content of fluorine changes rapidly within short stratigraphic intervals, and, although not organically bound, correlates positively with the organic content of the rock.

Studies of the mineralogical residence of fluorine in oil shale were made possible by combining the methods of low-temperature ashing, high-speed centrifugation in a liquid with a density gradient, x-ray diffraction, x-ray fluorescence, nuclear inelastic scattering, and electron microscopy. A major portion of the fluorine in the Mahogany Zone appears to be associated with the ubiquitous micaceous clay minerals, especially illite. Other fluorine-bearing minerals, such as fluorite (CaF_2), cryolite (Na_3AlF_6), and fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) were not detected in the eleven samples studied. However, this does not exclude the possible presence of discrete crystals or aggregates of these minerals in other portions of the Mahogany Zone.

INTRODUCTION

Commercial extraction of oil from oil shales (kerogen-rich dolomitic marlstones) in Colorado, Utah and Wyoming, will yield large amounts of crushed raw and retorted oil shale (Fig. 1) (1). These solid wastes will be left in abandoned underground retorts or disposed of in canyons in the region. It has been estimated that a medium-sized retort operation will produce 7,000 m³ of spent shale, in excess of that returned to the mine, per 50,000 bbls of oil extracted (2). *In Situ* retort methods will leave both retorted and residual raw oil shale in abandoned retort chambers. Chemical interaction between natural waters and the waste shales may influence the quality of ground water. In a semi-arid region, such as northwestern Colorado, any threat to existing water resources must be considered before large-scale contamination of unpredictable consequence has taken place.

Approximately 80% of the oil shale resources of the Green River Formation are located in the Piceance Creek Basin of northwestern Colorado (3). The first target for the developing oil shale industry

is the Mahogany Zone (approximately 70 meters thick) in the Parachute Creek Member of the Green River Formation (Eocene in age) (Fig. 2) (4).

This unit is composed almost entirely of oil shale yielding more than 25 gallons of oil per ton of rock. The Mahogany Zone acts as an aquiclude between the fairly fresh water of the Upper Aquifer and the saline water of the Lower Aquifer of the Piceance Creek Basin (5). The direction of flow of water across this interface changes in short distances. It is therefore difficult to predict the consequences of disrupting the geohydrological behavior of this important stratigraphic unit.

Fluorine is the most abundant halogen in sedimentary rock (6). In oil shale it is present in concentrations up to ten times those found in average coal (7-8). Experiments in which deionized water is passed through columns of various types of raw or processed shale yield leachates of pH 8 to 13, with fluoride concentrations that exceed the current EPA standard for drinking water of 0.8 to 1.7 mg/L (USPHS, 1962) by over one order of magnitude (9). The fluoride concentration remains high in experimental leachates from some varieties of shale even after passage of 40 pore volumes; this behavior is quite different from that of other anionic trace elements such as As, Se, Mo, and B, which are rapidly rinsed out of the shale (9). An understanding of the mechanism of release and chemical speciation of fluorine in the waters is imperative if proper control and efficient reclamation of contaminated waters are to be carried out. The first step towards this understanding is knowledge of how fluorine is chemically bound in the oil shale. The physical properties of the Green River oil shales make such a study difficult; these rocks consist of micron-sized grains of carbonates and silicates, held together by kerogen and cements of carbonate minerals.

Several fluorine-bearing minerals have been reported from the Green River Formation by other researchers (Table 1). Trudell (pers. comm., 1977) detected fluorite (CaF_2) by x-ray diffraction of samples from the A-groove, and just below the tuffs of the B-groove below the Mahogany Zone (Fig. 3). Cryolite (Na_3AlF_6) was also reported as being present in samples from the R-4 zone (Fig. 2) (Trudell, pers. comm., 1977). Milton and Eugster (10) reported authigenic fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) and neighborite (NaMgF_3). The latter has only been found at the contact between nahcolite (NaHCO_3) and the enclosing oil shale in Utah. Desborough and others (11) obtain permissive evidence for assigning fluorine in oil shale to anhedral grains of fluorite and cryolite, 1 to 10 micrometers in diameter.

Because fluorine is ubiquitous in samples from the Mahogany Zone, we have concluded that fluorine in the Mahogany Zone must be present in one or more of the following: 1) the organic (kerogen) fraction, 2) a minor mineral, or 3) as a trace element in one of the major minerals in oil shale.

Studies of the mass balance on trace elements from test samples of oil shale retorted in the Fisher Assay show that there is no

EXPLANATION

Area Underlain by the Green River Formation in Which the Oil Shale is Unappraised of Low Grade

Area Underlain by Oil Shale More Than 10 Feet Thick, Which Yields 25 Gallons or More Oil Per Ton of Shale

Figure 1: Oil shale areas in Colorado, Utah and Wyoming

FM	MEMBER	OIL SHALE MEASURES	
GREEN RIVER FORMATION	PARACHUTE CREEK ~500m		UPPER OIL-SHALE ZONE
		MAHOGANY	
		R-6	
		R-5	
		R-4	
		R-3	
		R-2	LOWER AND MIDDLE OIL-SHALE ZONE
	GARDEN GULCH ~250m	R-1	
		R-0	
	DOUGLAS CREEK ~250m		

Figure 2: Stratigraphic chart of the Green River Formation, Piceance Creek Basin, Colorado

TABLE 1

FLUORINE-BEARING MINERALS
REPORTED FROM GREEN RIVER FORMATION

Mineral	Formula	Wt. % F
Cryolite	Na_3AlF_6	54.3
Fluorite	CaF_2	48.7
Fluorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	3.8
Neighborhood	NaMgF_3	54.8
Villiaumite	NaF	45.2

Figure 3: Concentration of fluorine and the yield of oil in gallons per ton of rock versus depth below the surface

significant loss of fluorine from the solid fraction during retorting (12). Nor does fluorine seem to be lost systematically when the organic matter is oxidized during low-temperature ashing. Based on these observations, we tentatively conclude that fluorine in oil shales is largely inorganically bound. Additionally, we present evidence below for association of fluorine with micaceous clay minerals in the samples which we studied from the Mahogany Zone of the Green River Formation.

MATERIALS AND METHODS

Prior to selecting samples for this study, the total fluorine concentration was measured on 136 composite samples from different depths and stratigraphic positions in the U.S. Bureau of Mines corehole 01-A, in the central part of the Piceance Creek Basin of northwestern Colorado, U.S.A. (Fig. 1). The samples were analyzed for fluorine using the ion-selective method for rocks (12). The thickness of the Mahogany Zone is 70 meters at this location. Each sample represents stratigraphic intervals of 30 to 90 cm. The mineralogic composition of splits of these samples had also been studied by x-ray diffraction and Fisher Assay at the U.S. Department of Energy Laramie Energy Technology Center, Laramie, Wyoming. New analyses of 12 samples using the fluoride method for coal did not yield significantly different results. In addition, 30 samples were analysed for fluorine in our laboratory by a new molecular absorption method, using an atomic absorption spectrophotometer and a graphite furnace (14). The results from the three methods are very consistent.

Eleven of the 136 samples from corehole 01-A were selected for low-temperature ashing at reduced pressure (Tracerlab low-temperature ashing oven, Model LTA 600) to remove the organic material. Each ashed sample was laid on top of a discontinuous density gradient made by mixing 1,1,2,2,-tetrabromoethane (TBE) and 99% ethanol (ETOH) with 10 weight percent polyvinylpyrrolidone (PVP K-30) as dispersant, and centrifuged for a minimum of 200,000 gravity hours at 25°C. After centrifugation was completed, mineralogical identification by x-ray diffraction and chemical analysis by x-ray fluorescence for 26 elements were performed on each of the several density fractions obtained from each sample. The details of the analytical techniques and results are discussed in Saether and others (15).

Because the mass of each density fraction was too small for standard wet-chemical analysis for fluorine, the relatively new analytical technique of nuclear inelastic scattering was employed. This method is discussed in detail in an earlier publication (16). The samples, which weighed only 300 µg and consisted of the density fractions obtained from the bulk samples, were irradiated by a beam of 5.9 MeV protons from the University of Colorado cyclotron. An approximately uniform flux of protons was obtained by diffusing the beam by small angle Coulomb scattering in a 2 mg/cm aluminum foil located 35 cm upstream from the sample position. This uniform flux irradiated the entire sample, thus tolerating non-uniformity in the sample areal density and greatly simplifying sample preparation.

Interaction of the protons with the nuclei of fluorine atoms in the sample sometimes excites them to the first or second excited states at 110 keV or 197 keV. These excited states then rapidly decay by gamma-ray emission back to the ground state. By detecting these gamma rays and measuring their energies accurately with a hyper-pure germanium gamma-ray detector (ORTEC Model 1113-16300), the presence of fluorine in the sample can be unambiguously determined. An example of the spectra obtained by this method with the detector located about 5 cm from the sample is presented in Figure 4. An aluminum absorber, 4mm thick, was placed between the sample and detector to reduce the high counting rate due to x-rays at the lower end of the energy spectrum. The method is made quantitative by use of calibration samples which we made from NaF for the fluorine mass range of 80 to 1280 ng and from CaF for the range of 74 to 296 μg . This calibration is shown in Figure 5 for the 110 keV gamma ray. The method was found to be linear, with no indication of a zero offset, over four orders of magnitude; this range includes the fluorine content of all samples considered in this paper. The results for the 197 keV gamma ray are not shown in this figure because the analysis involving this gamma ray, is not as straightforward as for the 110 keV gamma ray due to the much longer half-life of the 197 keV state. This is because the fluorine nuclei can be driven out of the sample by the proton collisions which produce the nuclear excitations. In the case of the much more prompt 110keV transition, the gamma emission takes place before the target nucleus moves significantly from its original position, but for the longer-lived 197 keV state, the target nucleus may actually leave the field of view of the gamma ray detector before the gamma emission occurs. This effect will obviously reduce the number of 197 keV gamma rays reaching the detector. The probability of the recoiling nuclei in the 197 keV excited state escaping from the target before gamma emission depends on the sample mass. The recoiling excited nucleus will most probably be brought to a stop in a thick sample whereas a thinner sample will tend to allow it to escape from the detector's field of view. Thus, for the 197 keV gamma ray, the probability of gamma-ray detection per nuclear interaction is a function of sample mass. In the case at hand, all sample masses were approximately 300 μg so a calibration appropriate to this sample mass was employed. The calibration for the 110 keV gamma ray is independent of sample mass.

It is interesting to compare the results obtained on bulk oil shale samples by this nuclear technique and by a new molecular absorption technique (14). A comparison for six samples is shown in Figure 6. The nuclear method was applied to 300 μg splits from the much larger samples analyzed by the chemical method. While the values obtained by the two methods are seen to be linearly related, the least squares straight line fit to these data displays a zero offset of 310 $\mu\text{g/g}$ and a slope of 0.65, substantially different than the slope of 1.0 expected for a perfect correlation. The non-zero intercept may be due to the fact that the lowest fluorine values shown in Figure 6 were near the limits of detection for the molecular absorption method. The calibration of the nuclear method shown in Figure 5 indicates that the method yields results in strict

Figure 4: Semilogarithmic plot of gamma-ray spectra obtained in the nuclear method of fluorine analysis.

Figure 5: Calibration and linearity check of the nuclear inelastic scattering method of measuring fluorine.

Figure 6: Comparison of two methods of fluorine analysis: molecular absorption and nuclear inelastic scattering.

proportion to the amount of fluorine present in the sample, and we therefore believe that the method of nuclear inelastic scattering is the more reliable method in this case. The method of molecular absorption requires a difficult step of wet digestion of the oil shale, and this step is avoided in the analysis by nuclear inelastic scattering.

RESULTS AND DISCUSSION

Analysis of the 136 samples from the U.S. Bureau of Mines corehole 01-A gave a range of fluorine concentration from 200 to 2100 ppm (Fig. 3). There is a weak positive correlation between the gallons of oil yielded per ton of rock and the concentration of fluorine (Fig. 7). Particularly distinct (Fig. 3) is the transition from the oil-lean A-groove to the oil-rich Mahogany Zone. From the toluene extractions mentioned above, it appears that most of the fluorine in these samples of oil shale is inorganically bound. The correlation between content of fluorine and yield of oil must therefore be indirect, with both factors being stratigraphically controlled, probably as a result of the conditions that existed during original deposition or diagenesis of this sediment. In connection with possible future development of an oil shale industry, this suggests that shales which yield the highest amount of oil may leave residual waste with the highest concentrations of fluorine.

The fluorine concentrations in the separated density fractions, as determined by the nuclear method, are preserved in Figure 8. These values are the averages of results from analysis of the 110 keV gamma ray yield and the 197 keV gamma ray yield. From checks on internal consistency and analysis of counting statistics we estimate that these average values are accurate to about ten percent. In only three (No. 1, 2, and 11) of the six samples was a fluorine-rich fraction isolated. Two of these three density fractions are from the samples which contained the highest amount of fluorine before the density fractionation was made (Table 2). Fluorine in samples 3, 5, and 9 is more or less evenly distributed among the different density fractions, probably as a result of the lighter minerals of fluorine adhering to surfaces of forming parts of aggregates of heavier minerals present in the oil shale.

Fluorine is concentrated in density fraction 2.4 g/cm^3 of samples No. 1 and 2, and density fraction 2.5 g/cm^3 of sample No. 11. These density fractions contain from 0.5 to 1.2 weight percent fluorine. This is a factor of 3.3 to 9.2 times the concentration of fluorine in the bulk sample, after the organic matter has been removed. X-ray diffractograms of the three sub-samples verified the presence of micaceous minerals, appearing to be illitic clays. A photomicrograph taken of the clay minerals present in density fraction 2.4 g/cm^3 of sample No. 1 is shown in Fig. 9a. Semi-quantitative analysis by energy-dispersive x-ray analysis (Kevex, Model 5500) at the twelve points marked in Fig. 9b gave responses only to K, Al, Si, and Fe. Fluorine lies in the soft x-ray region and cannot be detected with this system.

Figure 7: Fluorine concentration of 136 composite samples from U.S. Bureau of Mines Corehole 01-A versus gallons of oil yielded per ton of rock.

CONCENTRATION OF FLUORINE IN DENSITY FRACTIONS

Figure 8: Concentration of fluorine in the density fractions of samples 1, 2, 3, 5, 9, and 11 determined by nuclear inelastic scattering.

TABLE 2

Concentration of F in Eleven Oil Shale Samples Before and After Low-Temperature Ashing

I	II	III	IV	V	VI
Sample depth ¹⁾ interval (feet below surface)	LETC ²⁾ Sample Number	ug/g F ³⁾ Raw Sample	Sample depth ⁴⁾ location (ft. below surface)	Sample no. ⁵⁾ (this study)	ug/g F ⁶⁾ lta'd Sample
901.3-902.3	5108	1425	901.8	1*	2600
902.3-904.0	5109	1375	903.8	2*	1600
904.0-905.3	5110	1175	904.6	3*	1500
7)	7)	7)	965.0	5*	1500
906.2-907.3	5111	1400	907.0	6	1000
940.3-941.6	5136	1200	941.0	7	900
941.6-943.6	5137	980	943.0	8	990
955.7-956.7	5148	515	956.4	9*	1300
955.7-956.7	5148	515	955.7	10	1100
957.8-959.0	5150	1125	958.5	11*	1400
1065.0-1066.0	5221	1500	1065.0	12	560

- 1) Composite samples from Fisher Assay. Low-temperature ashed sample wafers collected from these intervals.
- 2) Laramie Energy Technology Center
- 3) Determined by Graphite Furnace Molecular Absorption
- 4) Exact location of 2.5x5.0 cm wafers used for low-temperature ashing
- 5) Density fractions of samples marked with asterix were analyzed for fluorine by nuclear scattering method.
- 6) F-concentration in low-temperature ashed material (i.e. bulk sample before centrifugation) determined by molecular absorption.
- 7) Not available as composite sample from LETC

Figure 9a: Scanning electron micrograph of micaceous clay minerals in the 2.4 g/cm³ density fraction of sample No. 1

Figure 9b: Scanning electron micrograph as shown in Fig. 9a. Twelve gridpoints marks location of areas that were analyzed by energy dispersive x-rays.

The illitic aggregates were analyzed with an ARL electron microprobe (Model SM) at the U.S. Geological Survey Laboratories in Denver, Colorado (A. Gunow, analyst). Aluminum, Si, K, Ti, and Fe were analyzed with the energy dispersive system and F was analyzed using the wave-length dispersive system. Feldspar and micas were used as calibration standards. The analysis verifies that fluorine is associated primarily with K, Al, Si, and Fe. The results of three microprobe analyses and their average values (Table 3) are low because none of the sample targets analyzed was large enough to cover the 100 square micrometers of the electron beam. However, when the SiO_2 content is normalized to that of a theoretical illite, the results add up to 95.4% (H_2O and Mg not taken in consideration). The apparently high values obtained for Fe are reasonable and acceptable when one considers the high concentrations of iron present in oil shales of the Mahogany Zone. The weight percent of Ca is lower in all three cases than the weight percent fluorine, thus excluding the possibility of CaF_2 (fluorite) being the source for fluoride in these samples.

The variation of F in the illites which we studied varies considerably, and ranges from 0.85 to 2.9 weight percent (8500 to 29,000 ppm). Quantitatively, these values are minimum values, and because a factor of 2.19 was required to normalize the analyses to the SiO_2 content of a theoretical illite they are probably approximately half of the actual fluorine content of the illite. Assuming conservatively that the average content of fluorine in the illites is 1.5 weight percent, the 2.4 g/cm³ density fraction of sample No. 1 must contain 80% illite. Because bulk sample No. 1 contained 2600 ppm fluorine after removal of the organic matter, it must have contained approximately 17 weight percent illite. This value compares well with the value of 19 weight percent given by Smith (12) for the content of illite in the Mahogany Zone oil shales.

The assignment of fluorine in oil shales of the Mahogany Zone to illitic clay minerals also corresponds well with the positive correlation found between fluorine concentration and oil yielded per ton of shale. It was confirmed by Robb and Smith (18) that the dark, organic-rich laminae in the oil shales primarily consist of silicate minerals, whereas the organic-poor, light-colored laminae consist primarily of carbonates.

An evaluation of the specific gravities of the fluorine-bearing minerals which have been reported earlier from the Green River Formation (Table 1) suggest that these should have been concentrated in the heaviest fraction, except for villiaumite, which has a density of 2.80 g/cm³. None of these heavy minerals was detected during studies of the x-ray diffractograms obtained from each density fraction. However, this does not exclude the possibility that fluorite, cryolite, and fluorapatite could be present as discrete crystals or crystal assemblages in other geographic areas and stratigraphic sections of the Mahogany Zone and thus may have been missed when samples were obtained for this study.

TABLE 3

Results of Electron Microprobe Analysis of Sample No. 1-6

Oxide	Analysis 1	Analysis 2	Analysis 2	Average three samples	Normalized*
SiO ₂	24.5	25.8	22.7	24.3	53.2
Al ₂ O ₃	6.5	6.2	6.3	6.3	13.8
Fe ₂ O ₃	5.4	6.5	6.7	6.2	13.6
CaO	0.09	0.20	0.17	0.15	0.33
K ₂ O	5.0	4.2	4.3	4.5	9.9
TiO ₂	0.94	0.36	0.54	0.61	1.3
F	2.9	0.85	0.86	1.5	3.3
Total					95.4

*Each oxide multiplied by 2.19, which is required to give SiO₂ in theoretical illite.

CONCLUSIONS

Fluorine in three samples from the Mahogany Zone of the Green River Formation is associated with the ubiquitous illitic clay minerals of the oil shale. It is probable the fluorine substitutes for hydroxyl ions in the illite lattice or is adsorbed on the surface by ion-exchange. Similar residency is commonly observed for fluorine in sediments and soils, and fluorine-bearing micas are common in igneous rocks (6). The possibility of non-oxidized organic matter containing fluorine and being adsorbed on the clay platelets cannot be totally excluded on the basis of our work, however, because the correlation between the concentration of fluorine was not significantly extractable by toluene and is not lost from the oil shale during retorting.

This study excludes fluorite and cryolite from being the major source for fluorine in the six samples studied. However, these minerals may be present as discrete crystal or crystal aggregates in other portions of the Mahogany Zone (11).

In connection with future development of an oil shale industry, it appears that shales which yield the highest amount of oil will leave residual waste shale with the highest concentrations of fluorine.

FIGURE CAPTIONS

- Fig. 1 Oil shale areas in Colorado, Utah and Wyoming, United States Bureau of Mines Corehole 01-A, from which samples used in this study were taken, is located at sec. 29, T15S, R97W, in the Piceance Creek Basin (1).
- Fig. 2 Simplified stratigraphic chart of the Green River Formation, Piceance Creek Basin, Colorado. (Cashion and Donnell, 1974).
- Fig. 3 Concentration of fluorine and the yield of oil in gallons per ton of rock is plotted versus depth below the surface in U.S. Bureau of Mines Corehole 01-A. The stratigraphical intervals (1-3 feet) from which the 136 composite samples were taken, are marked with thick vertical bars in the first column. Exact location of eleven samples that were ashed at low temperatures and centrifuged, are indicated by sample number (see corresponding numbers in Table 2, column IV). The density fractions of the six samples circled were analyzed for fluorine by the nuclear scattering method.
- Fig. 4 Semilogarithmic plot of gamma-ray spectra obtained in the nuclear method of fluorine analysis. The channel number is proportional to gamma-ray energy. The lower spectrum was obtained from a calibration sample known to contain 640 ng of fluorine as sodium fluoride. The upper spectrum is from a typical oil shale sample. The running time for this sample was approximately five minutes at a proton beam current of 50 nA. The sample was found to contain 735 ng at a concentration of 2213 ppm by weight. The fluorine 110 keV and 197 keV peaks are labelled; the other peaks are due to elements other than fluorine in the sample and in the beam collimation apparatus. The counts near channel 100 are from x-rays produced by proton interactions in the sample.
- Fig. 5 Calibration and linearity check of the nuclear inelastic scattering method of measuring fluorine. The number of counts in the 110 keV gamma-ray peak per microcoulomb of proton beam per square centimeter at the target location is plotted as a function of the mass of fluorine in each calibration sample. The log-log plot covers approximately four decades, from 80 ng to 296 mg. The straight line corresponds to the adopted calibration of 1.79×10^8 counts per microcoulomb per gram of fluorine.
- Fig. 6 A comparison of two methods of fluorine analysis: molecular absorption and nuclear inelastic scattering. Two values are shown for the nuclear analysis of each of the six samples, one obtained from the 110 keV gamma ray, the other

from the 197 keV gamma ray. The split of the sample used for the nuclear method consisted of about 300 μg . The straight line, a linear least squares fit to the twelve data points, indicates that the two methods give results linearly related by $y = 310 + 0.65 x$ where y is the chemical and x the nuclear result, both in $\mu\text{g/g}$. The two sigma (95% confidence level) experimental uncertainty for each data point is estimated independently for the molecular absorption $\pm 200 \mu\text{g/g}$ and $\pm 10\%$ for the nuclear inelastic scattering method.

- Fig. 7 The fluorine concentration of 136 composite samples from U.S. Bureau of Mines Corehole 01-A is plotted versus gallons of oil yielded per ton of rock. Correlation coefficient is 0.48.
- Fig. 8 Concentration of fluorine in the density fractions of samples 1,2,3,5,9, and 11 determined by nuclear inelastic scattering. Average values of fluorine ($\mu\text{g/g}$) determined from the 110 keV and 197 keV peaks are plotted versus specific gravity (g/cm^3). Anomalously high concentrations of fluorine were observed in sample No. 1 (2.4 g/cm^3), No. 2 (2.4 g/cm^3), and No. 11 (2.5 g/cm^3). X-ray diffractograms of these three fractions exhibit a prominent asymmetric peak at $10^\circ 2\theta$. In sample No. 11 density fractions 2.6 and 2.7, and 2.8 and $\geq 2.9 \text{ g/cm}^3$, were combined for F-analysis.
- Fig. 9a. Scanning electron micrograph of micaceous clay minerals in the 2.4 g/cm^3 density fraction of sample No 1.
- Fig. 9b. Same scanning electron micrograph as shown in Fig. 9a. Twelve gridpoints marks location of areas that were analyzed by energy dispersive x-rays.

AKCNOLEDGEMENTS

Financial support for this study was provided by Grants No. EY-76-S-02-4017 and EY-76-6-02-0535 from the U.S. Department of Energy. The kind help of P. Patterson, and A. Gunow, Department of Geological Sciences, University of Colorado, C. Crouch, Nuclear Physics Laboratory, University of Colorado, and H. Neuman, U.S. Geological Survey, in connection with sample preparation and analysis is greatly appreciated. J. Widows of the U.S. Bureau of Mines, J. Dyni, U.S. Geological Survey, and J. W. Smith, Laramie Energy and Technology Center assisted in making the core samples available.

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THE INTERACTION OF LEACHATES WITH SOILS

By Michael Glaze & Donald D. Runnells

OBJECTIVES

This work deals with the capability of soils from the Piceance Creek Basin to remove boron and fluoride which are dissolved in leachates from retorted oil shale. Solid wastes from the retorting process which are stored on the surface will be subject to leaching by precipitation and industrial waters. The ability of soils to attenuate boron and fluoride represents a natural means for preventing the movement of aqueous species of these two elements into the underlying aquifers. Boron and fluoride are considered important because they will be leached from the shale piles in amounts that could possibly be harmful to plants and animals. A comparison of the change in the retentive capacity of the soils with a change in the pH is considered in the experiments.

The soils used in this study were collected from locations which have been designated as areas for the disposal of retorted oil shale. Solutions similar to leachates obtained from the disposal piles were prepared by shaking deionized water with shale retorted by the Paraho process. The leachates were passed over columns of soils to determine the capacity of the soils to remove boron and fluoride. This experimental model was designed to simulate the possible movement of leachates in the field out of disposal piles into the soils. This type of movement might occur for example, at the toes of the disposal piles.

Results from the column experiments were interpreted to produce a series of adsorption isotherms for which polynomial expressions were derived. With the aid of an existing computer program¹, the rate of movement of a substance through a column of soil can be estimated. This information should be useful in predicting the amount of time before boron and fluoride pass through various soils and enter the groundwater.

METHODS

Leachates

The leachates were prepared by shaking a slurry of deionized water and oil shale. A ratio of 1:1 by weight of water to shale was used. Typically, 1,000 grams of shale were slurried with 1,000 ml of water. Work described in previous progress reports (1978, 1979) showed that equilibrium with respect to boron and fluoride was reached after agitation on the shaker table for a period of five days. After shaking, the solutions were decanted from the shale and filtered through Whatman #50 filter paper. Usually only about 50 percent of the water could be recovered by filtration because the fine-grained particles of shale held the water tenaciously.

The solutions were stored in plastic Nalgene^C bottles. Solutions were used in experiments within five days of filtration. Two sets of experiments were conducted using leachates with pH values of 7 and 12. If the pH of the solution was to be maintained at its original value of 12, the solution was stored open to the atmosphere via a tube filled with Ascarite^C, which adsorbed carbon dioxide. This prevented the lowering of the pH by the precipitation of calcium carbonate. For some of the experiments, the pH of the solution was adjusted to pH 7 using dilute sulfuric acid and was stored in closed containers.

Soils

The soils used in the columns were collected from areas which have been pre-designated as sites for the disposal of waste shale. These sites are gulches in the Piceance Creek Basin which will be cleared of the present vegetation and topsoil, filled with either spent shale from surface retorts or raw shale taken from the chambers for in-situ retorting, and recovered with topsoil and vegetation. The sites from which the soils in this study were collected are:

Rinky Dink Gulch	Federally leased Tract C-a, Piceance Creek Basin, Colorado
Cottonwood Gulch	Federally leased Tract C-b, Piceance Creek Basin, Colorado
Balzac Gulch	Naval Oil Shale Reserve, Anvil Points, Colorado

All of the soils were collected in the valley bottoms. On Tract C-a, the soils in the valley floors belong predominately to the Glen-dive Series. These soils are well-drained. They have formed in the alluvium which has weathered from the bedrock Uinta Formation. The soils were collected as two sets of samples because they appeared visually different in the field. The soils from the upper western end of Rinky Dink Gulch (RDGU) contained 7.2 percent CaCO_3 and the soil from the lower end of Rinky Dink Gulch (RDGL) contained 24 percent CaCO_3 . Sample RDGU had a porosity of 48.8 percent and RDGL had a porosity of 52.5 percent.

On Tract C-b, the soils which have formed in the gulches are Rentsac channeries (soil which contains fractured parent material). The Rentsac Series is formed in the residuum on the broad uplands. The parent material is the fractured sandstone of the Uinta Formation which is present as pebbles in the soil. The content of CaCO_3 in the soil is 3.4 percent. The porosity is 49.8 percent.

The soil from Balzac Gulch is developed on the badlands and is very immature. It can be classified as a Torriorthent, which is generally clayey to loamy and contains variable amounts of gravel, cobbles, and stones derived from the Wasatch and Green River Formations. In most places the soil was collected in a flat area of the gulch. The CaCO_3 content of the soil is 6.3 percent. It has a porosity of 58 percent.

All of the soils which were collected for the study can be classified texturally as loams. The slurry pH values were between 7.5 and 8.0, reflecting the presence of calcium carbonate. The hydraulic conductivities of these soils were in the vicinity of 10^{-4} cm/sec. These values are low, but they are in the range expected for silty sands.

Description of Column Studies

" The material used for the column casting was a plastic Nalgene^C Buchner funnel. This plastic column was chosen because fluoride can be sorbed by glass and borates can be leached from glass.

" The Buchner funnel was lined on the bottom with Whatman^C #50 filter paper to prevent the soil from falling through the pores. Twenty-five grams of the soil were weighed into the funnel and compacted with a plunger. Water was added to the soil dropwise, using a buret filled with deionized water. The soil was considered to be saturated when the surface glistened. An additional increment of water was then added. The volume of water was recorded, and the column was sealed and fitted into a test tube with a rubber stopper to stand overnight to drain. The amount of water collected in the bottom of the test tube was measured and subtracted from the total amount of water initially added to the soil. This procedure allowed the pore volume of the soil to be determined after gravity drainage.

The diameter of the soil columns was 55 mm, and the depth of soils in the column was 10 mm. For the purposes of computer modeling, this small volume of soil can be considered a unit cell of a larger soil column.

A solution of leachate was siphoned from a storage bottle onto the column of soil and flow was regulated out of the column by a screw-clamp on the hose. The head of solution was maintained between 0 and 2 cm. The solution leaving the column was collected in a 10 ml bulb with a siphon attached. The aliquots were delivered to plastic test tubes in a fraction collector, and the volume of each fraction was measured to determine the corresponding number of the pore volume. The solutions were then stored for analysis.

A comparison was made of the influence of the pH on the ability of the soils to remove boron and fluoride from leachates. In one set of experiments, the pH of the leachate was maintained at the original value of 12. The leachate was applied steadily to the column and flow through the column was uninterrupted. This case simulated movement of a leachate through a disposal pile directly into a soil. Such a case may occur at the toe of the disposal pile or beneath the pile if the soil is not removed prior to disposal. This may also be the case if a debris flow should breach the area of containment for the disposal pile and flow onto the land.

In a second set of experiments, the pH of the solution was adjusted to 7. This solution was allowed to flow through the soil uninterrupted. In this case, the solution would represent a leachate which had aged open to the atmosphere. In the aging process, the

precipitation of calcium carbonate or the oxidation of reduced sulfur species in the solution may lower the pH of the leachate. This has, in fact, been noticed in leachates of retorted oil shales after a season of weathering². Leachates which are collected in catchment basins will probably become more acidic as the constituents react with atmospheric carbon dioxide and oxygen.

Another set of experiments examined the effect of non-continuous flow and time of contact between the soil and solution. An aliquot of the leachate at pH 12, equal in volume to the pore volume, was put on the soil column to displace the water which originally saturated the column. The solution and soil were then allowed to age for five days. New leachate was added every five days, displacing the previous pore volume.

All of the solutions which were collected were analysed for pH, specific conductance, boron, fluoride, and calcium.

The concentrations of these species in each pore volume were compared to their original concentrations in the leachates. The ratio of the concentrations (C/C_0) versus the number of pore volumes was used to construct breakthrough curves for boron, fluoride, and calcium. Curves for adsorption isotherms were also prepared for each element by comparing the summation of the number of micrograms of the substance entering the soil to the summation of the number of micrograms of the substance removed in the soil. Polynomial expressions for the adsorption isotherms were derived using the program, CURVFIT II, provided by Dr. Robert Meglen of The ETSRP Central Analytical Facilities. The program allows the order of the equation to be chosen which will provide the best and most realistic fit of the data.

Because the adsorption isotherms were empirically derived, they cannot be extrapolated beyond the experimental data. When determining the capacity of the soils to retain substances, the prediction cannot be carried further than the number of pore volumes reached in the experiment.

The equations of the adsorption isotherms will be input into a computer model developed by Harter and Foster (1976). Other data to be supplied to the program includes the number of micrograms of substance in each pore volume, the number of unit cells of soil in the column, and the number of pore volumes passing through the column. The ultimate goal of the modeling program is to predict the capacity of columns of native soils for removing boron and fluoride.

RESULTS

The interpretation of the results is not complete at this time. Only the data obtained using the soil from the upper Rinky Dink (RDGU) are presented here.

Fluoride: The soil (sample RDGU, in this example) has some ability to remove fluoride. Figure 1 shows that the breakthrough of fluoride was reached after 45 pore volumes for a leachate with pH 7. Breakthrough is defined as the point at which the concentration of a substance in solution leaving the soil is equal to the concentration of that substance in solution entering the soil. When the pH of the leachate is 12, the curve (Figure 1) indicates that fluoride does not reach breakthrough, but seems to reach an equilibrium concentration at 80 percent of its initial concentration in the leachate after 40 pore volumes.

The calculated adsorption isotherms for fluoride at pH 7 and pH 12 in RDGU are shown in Figure 2. At pH 7, the maximum amount of fluoride sorbed by the soil is 2,000 ug in twenty-five grams of soil (80 ug/g soil). At pH 12, the amount of fluoride being removed is increasing at a steady rate. The shape of this curve might suggest that the process of removal is adsorption, except for the fact that the equilibrium concentration of fluoride levels off at 80 percent of breakthrough.

Boron: Figure 3 shows that the breakthrough of boron occurred after thirty pore volumes when the leachate was at pH 7. However, the boron concentration reached only 70 percent of its initial concentration in the leachate when the pH was 12, showing that some process other than adsorption was occurring. In Figure 4 the adsorption isotherms are dramatically different in the degree of removal of boron from the leachates for the values of pH 7 versus pH 12. At pH 7, the maximum removal of boron was reached at 100 ug of boron in 25 grams of soil (4 ug/g soil). At pH 12, however, the removal of boron was increasing even after sixty pore volumes.

Calcium: As shown in Figure 5, at pH 7, calcium was initially rapidly removed from the soil. At pH 12, the breakthrough curve for calcium is erratic.

During the experiments using leachates with a pH of 12, a precipitate formed in the free water column above the soil. This precipitate was collected and identified by analysis with x-ray diffraction to be aragonite (CaCO_3). The precipitation of aragonite is probably the cause of the fluctuation of the calcium breakthrough curve, as well as the reason that the breakthrough curve for calcium did not reach 100 percent of its original concentration. As long as the solution was stored in the absence of gaseous carbon dioxide, the calcium remained in solution. Once exposed to the atmosphere, carbon dioxide was absorbed and the precipitation of aragonite was very rapid.

When the leachate was allowed to be in contact with the soil during the experiments of interrupted flow, the concentration of calcium was found to decrease in each successive pore volume. Finally, after six pore volumes (30 days of contact time), flow of the solution through the column of soil was obstructed by the precipitation of calcium carbonate (Figure 6). The precipitate had filled the interstices in the soil, making the soil impermeable.

Figure 1: Breakthrough curves for fluoride in soil from upper Rinky Dink Gulch using leachates at pH 12 and pH 7 and continuous flow.

Figure 2: Adsorption Isotherms for fluoride in soil from upper Rinky Dink Gulch for leachates at pH 12 and pH 7 and continuous flow.

Figure 3: Breakthrough curves for boron in soil from upper Rinky Dink Gulch using leachates at pH 12 and pH 7 and continuous flow.

Figure 4: Adsorption isotherms for boron in soil from upper Rinky Dink Gulch for leachates at pH 12 and pH 7 and continuous flow.

Figure 5: Breakthrough curves for calcium in soil from upper Rinky Dink Gulch using leachates at pH 12 and pH 7 and continuous flow.

Figure 6: Breakthrough curve for calcium in soil from upper Rinky Dink Gulch using leachate at pH 12 and a contact time of five days between each pore volume.

CONCLUSIONS

From these studies, it is apparent that soils from the Piceance Creek Basin remove more boron and fluoride from solution at pH 12 than at pH 7. When all of the studies have been completed, a comparison will be made of the adsorptive capabilities of the soils for boron and fluoride.

At pH 12, some mechanism other than adsorption seems to be operating to remove boron and fluoride from the leachates. The possibility that adsorption is contributing in some way in removing boron and fluoride cannot be ruled out. However, if adsorption were the predominant mechanism for retaining these two anions, the breakthrough curves would eventually reach 100 percent of the initial concentrations of the species in the leachates. At this point of saturation of the exchange sites, the concentrations of boron and fluoride in the solution leaving the soil would be equal to the concentrations in the corresponding influent.

It is not possible to identify the mechanism by which boron and fluoride are removed from the leachates at pH 12, but the shape of the breakthrough curves for boron and fluoride suggests that precipitation is important in removing these anions.

Fluoride may also be removed from the leachate by precipitation of either fluorite or fluorapatite. Computer studies with our version of WATEQF show that the leachates are supersaturated with respect to both of these minerals. However, this cannot fully explain the removal of fluoride because precipitation of the minerals does not occur at pH 7, even though more calcium is available in solution.

It is not likely that boron is being removed from solution as precipitates of borate salts. Boric acid must polymerize to form borate salts, and Ingri (1957) calculated that the total concentration of boron must exceed 270 mg/L in the pH range of 6 to 11 for polyborate species to be of any importance. However, other precipitates of boron could possibly occur.

The precipitation of calcium carbonate in the interstices of the soil represents a possible mechanism for the control of the movement of leachates. This precipitate could form a hardpan in the soil which would be impermeable to further flow, thus hindering the movement of boron and fluoride into the underlying aquifers.

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PROGRESS REPORT 1979-1980

INVESTIGATION OF TRACE ORGANIC COMPOUNDS IN OIL SHALE WASTES

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INTRODUCTION

Recent action by The President and Congress has placed high priority upon the development of shale oil technology. Since more than 200,000 barrels per day of shale oil production by 1987 is anticipated, there is concern regarding the environmental impact on water quality. Large quantities of water are consumed for cooling, adding moisture to retorted shale, reclamation, hydro-treating crude shale oil for upgrading and other purposes depending on the process, resulting in the increased usage of precious water supplies. At the same time, large amounts of wastewater are produced in various stages of shale oil recovery. The sources of water emissions from these operations are summarized in Table 1 (1). In addition, solid wastes will be generated in enormous quantities. The ex-situ and modified in situ processes will deposit the retorted shale on the surface where it will be exposed to leaching by rain and snow. The in-situ retorting process will yield retorted shale underground, which may interact with and contaminate ground water. Of particular concern is the possible mobilization, through complexation or chelation, of toxic trace elements present in the retorted shale, such as arsenic, selenium, cadmium, chromium, and lead. These complexes are important since they may be more toxic than the simple inorganic species and a "solubilization effect" is frequently exhibited (2). A comparison of the levels of these elements in raw and retorted shale is shown in Figure 1 (3). Most of each of these trace elements is retained in the retorted shale and therefore may be susceptible to possible subsequent mobilization facilitated by complex formation with organic ligands.

OBJECTIVES

This study was conducted to determine the speciation of selected metal ions and the identification of associated organic ligands in water samples (process water, retort water, and leachates) arising from oil shale recovery operations.

EXPERIMENTAL METHODS

Samples of leachates, ex-situ, modified in-situ and in situ retort waters were investigated using the techniques of column chromatography, liquid-liquid extraction, steam distillation, gas chromatography (GC), gas chromatography/mass spectrometry/data system (GC/MS/DS), and atomic absorption spectrometry analysis. The types of samples obtained and/or investigated during these studies are given in Table 2.

Table 1. Water Emissions from Oil Shale Operations

Process Step	Activity	Water Emissions
1. Site Preparation	Leveling and Grading	Surface Runoff due to Land Disturbance
2. Retort Preparation	Drilling and Fracturing ^{1,2}	Contaminants to Groundwater
3. Retorting and Product Recovery	Combustion of Shale, Separation of Oil and Water, Fuel Combustion ³	Large Quantity of Highly Saline Retort Water
4. Site Restoration	Plugging Boreholes Revegetation	Surface Runoff
5. Air Pollution Control	SO ₂ Particles and other Pollutants Removal	Wastewater
Water Pollution Control	Retention, Evaporation, Treatment and Reuse	Oily Residuals-Groundwater Leachate from Retention Pond
Solid Waste Disposal	Land Filling and Revegetation	Surface Runoff Groundwater Leachate
6. Support Facilities Operation	Power Plant	Thermal Discharge or Blowdown Sanitary Wastes

¹In Situ Retorting Process²Modified In Situ Retorting Process³Surface Retorting Process

Ref: Proceedings of the Second Pacific Chem. Eng. Congress (PACHEC '77)
August 28-31, 1977, Denver, Colorado. Vol.I, p. 456.

Figure 1. Trace Metal Concentrations in Raw and Retorted Shale.

Table 2. Samples Investigated and Obtained*

A. PARAHO

Process Water	4L
Retorted Shale	5.6 Kg
Column leachates from D. Runnells	

B. OMEGA-9

Retort Water	8L
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C. OCCIDENTAL

Retort Water	4L
Oil	0.5L

*Our thanks are due to R.A. Atwood and R.N. Heistand of Paraho, D.S. Farrier of LETC, C.L. Nelson of Occidental, and D. Runnells, University of Colorado, for supplying our laboratory with water samples.

LIQUID-LIQUID EXTRACTION

Extraction of retort water samples was carried out in Apparatus A (Figure 2), a continuous liquid-liquid extractor that is adaptable for use with solvents of specific gravity above and below that of water. Samples of the retort waters (100 mL) were extracted successively with approximately 500 mL of solvents of increasing polarity (hexane, toluene, chloroform, and/or dichloromethane, and ethyl acetate). After a given period of extraction, 1-8 days (Table 3), each solvent was removed from the apparatus and was reduced by roto-evaporation to approximately 10 mL. One milliliter aliquots were set aside for gas chromatography and mass spectrometry investigations, while the remaining solution was subjected to atomic absorption spectrometric analyses for selected trace elements. Blanks for gas chromatography and atomic absorption analyses were prepared by treating pure solvents in a similar manner.

STEAM DISTILLATION

Steam distillation of Omega 9 and Occidental retort waters was carried out in a modified Nielsen-Kryger type apparatus (Figure 3) (4). The experimental conditions for each sample are listed in Table 4. Reduction of solvent volume and splitting of sample for atomic absorption and gas chromatography/mass spectrometry analyses were handled in a manner similar to that for the liquid-liquid extracts.

During the steam distillation process a fine particulate matter began to form in the aqueous phase. This material was removed by filtration through a 0.45 micron Millipore filter upon completion of the steam distillation and cooling of the retort water. When air dried, the residue exhibited considerable amounts of highly colored crystalline particles. The residues were weighed (Table 4) and subjected to atomic absorption analyses for the selected trace elements along with the extracts of the organic solvents.

PARAHO SHALE AND PROCESS WATER LEACHATE STUDIES

Leaching studies of Paraho retorted shale with Paraho process water have been conducted in five columns intended to imitate proposed methods of disposal of retorted shale and waste water. Columns, which are defined as dry packed columns, were intended to simulate examples of dust control of large disposal piles of dry spent shale by spraying with wastewater. The columns defined as "wet packed" imitate disposal of the waste products as a mixture which may be used to layer selected disposal sites. These columns were then leached extensively with a wastewater for a given period of time.

Pyrex glass tubing, 1 cm inside diameter, fitted with ground glass frits was used to prepare the spent shale columns. Each empty glass column was soaked overnight in a 3% EDTA solution, rinsed with distilled, de-ionized water, and soaked in concentrated nitric acid before rinsing extensively with distilled, de-ionized water to remove trace element impurities on surface. All sample collection vials were washed in the same way.

STRODTZ TYPE LIQUID-LIQUID EXTRACTOR

Figure 2. Strodtz Type Liquid-Liquid Extraction Apparatus (A)

Table 3. Experimental Conditions for liquid-liquid extraction of retort water on Apparatus Type A.

Solvent	Time (days)				
	Hexanes	Toluene	Chloroform	Methylene Chloride	Ethyl Acetate
Paraho Process Water	1	1	1	-	1
Paraho Centrifuged Process Water	1	1	1	-	1
Omega-9 Retort Water	1	1	1	-	1
Occidental Retort Water	8	4	4	3	4

NIELSEN-KRYGER TYPE EXTRACTOR

Figure 3. Nielsen-Kryger Type Extraction Apparatus (B)

Table 4. Experimental Conditions for the Steam Distillation of Retort Waters using Apparatus B.

Time (days) (Volume (ml))							
	Volume Distilled (ml)	Hexanes	Toluene	Chloroform	Methylene Chloride	Ethyl Acetate	Residue*
Omega-9 Retort Water	250	2 (50 ml)	2 (50 ml)	2 (30 ml)	-	4 (50 ml)	0.4490 g
Occidental Retort Water Run #1	200	2 (50 ml)	2 (50 ml)	2 (25 ml)	2 (40 ml)	2 (50 ml)	0.1300 g
Occidental Retort Water Run #2	100 (plus 150 ml distilled deionized water)	2 (50 ml)	2 (50 ml)	2 (30 ml)	-	2 (50 ml)	0.3327 g
Occidental Retort Water Run #3	150 (plus 100 ml distilled deionized water)	2 (50 ml)	2 (50 ml)	2 (30 ml)	-	4 (50 ml)	0.5078 g

* Particulate material present in water after steam distillation which was removed by filtration through a 0.45 micron Millipore Filter.

The Paraho process water that was used in these leaching studies was centrifuged at 15000 RPM at 5°C for 20 minutes. 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 then poured into two different glass columns. Leaching was initiated by the addition of the centrifuged process water to the head of the column. One pore volume fractions (10 mL) of the leachate were collected until 24 pore volumes had eluted. At this time distilled, de-ionized water was substituted for the centrifuged process water and collection of the leachate was continued.

The "dry packed" columns were prepared by adding 10 g of the dry retorted shale to three different glass columns. The columns were then 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 45% of the volume of the column. Paraho process water was then 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, de-ionized water was added to the top of the column and the leaching was continued.

The collected leachates from both the dry packed columns and the wet packed columns were analyzed for the specific trace elements with atomic absorption spectrometry methods.

INSTRUMENTAL METHODS

Gas Chromatography

Volatile organic compound characterization of the different samples that were obtained from liquid-liquid extractions and steam distillations of the wastewaters were obtained using a Hewlett-Packard HP 5830A equipped with a flame ionization detector (FID).

Capillary columns of approximately 24 meters in length, coated statically with either 0.3% SE-30 or 0.3% SE-52, were used to achieve separation of components in the complex mixtures. These analyses were used to determine conditions needed for gas chromatography/mass spectrometry analyses. Operating conditions varied as a function of sample and solvent used, but a representative set of conditions are: column temperature, initially 40°C, then increased to 270°C at 4°C per minute; helium carrier gas flow rate at 1 mL/minute with 10 psig inlet pressure; hydrogen, 40psig, 30 mL/minute; air, 40 psig, 240 mL/minute; injection temperature, 250°C, detector temperature, 350°C.

Gas Chromatography/Mass Spectrometry

Gas chromatography/mass spectrometry analyses were conducted using the Hewlett-Packard HP 5980/5933A GC/MS/DS. In most cases, the gas chromatography separations were accomplished using a 12-meter fused silica column coated with SP 2100. As the components were eluted from the GC column, mass spectra were acquired over the desired mass range every 2-3 seconds. The enormous quantity of mass spectral data obtained was stored in the 5933A computer data system. The mass spectral data were then recalled to produce a reconstructed gas chromatogram, which is a plot of total ion intensity versus retention time. This type of plot is described as a Total Ion Chromatogram (TI or TIC). A computer program was used to resolve further the chromatographic data on the basis of the slopes of m/e intensity values as they change with time. The program determines which m/e values maximize as a function of time and generates a spectrum based on these mass resolved data. The Total Ion Chromatograms resulting from mass resolved spectra are referred to in this report as a Biller-Biemann Total Ion Chromatogram(5). Mass spectra were interpreted by comparison with reference compilations when available or by manual (non-computer) literature search and interpretation procedures.

Atomic Absorption Spectrometry

Trace Metal analyses were conducted with the Perkin Elmer 360 and 5000 atomic absorption spectrometers equipped with a high temperature graphite furnace, the Perkin Elmer HGA 2100. A Perkin-Elmer Auto Sampling System, AS-1, was used with the PE 5000. Parameters for the operation of the atomic absorption graphite furnace are shown in Table 5. Samples that were high in zinc and chromium were analyzed by flame absorption spectrometry. A standard air-acetylene flame head was used with fuel-lean conditions for zinc analyses and fuel-rich for the chromium analyses.

Each of the various fractions from the liquid-liquid extractions and the steam distillations of the retort waters was taken to dryness by evaporation at room temperature and weighed (Table 6). A minimum volume of fuming nitric acid was added to each of the fraction residues and allowed to react. To ensure the complete oxidation of the material, a minimum volume of 30% hydrogen peroxide was added. The extracts from the steam distillations were completely digested, while the liquid-liquid extracts formed a white precipitate. Each sample was then diluted to 10 or 25 mL with distilled de-ionized water and the resulting solutions were analysed for the following elements: arsenic (As), selenium (Se), cadmium (Cd), chromium (Cr), lead (Pb), and zinc (Zn).

Particulate matter filtered from the aqueous phase of the steam distillations was digested in the same manner as the organic residues. The leachate samples were analyzed directly without any sample preparation.

Table 5. Operating Conditions for the Atomic Absorption Graphite Furnace.

Metal	Lamp	Wave Length (nm)	Slit Width (nm)	Sample size (ul)	Temperature Program °C***		
					Dry	Char	Atomize
As	EDL*	193.6	0.7	20	110	850	2500
Cd	HC**	228.8	0.7	10	110	400	1500
Cr	HC	357.9	0.7	20	110	1350	2700
Pb	HC	283.3	0.7	10	110	550	2000
Se	EDL	196.0	0.7	20	110	850	2500
Zn	HC	213.9	0.7	10	110	500	2000

*Electrodeless Discharge Lamp

**Hollow Cathode Lamp

***Typical times for temperature programs are: dry (40 sec.), char (30 sec.), and atomize (7 sec.)

Table 6. Residue weights (g) of extracts from the liquid-liquid extractions and steam distillations of retort waters.

Liquid-liquid extractions	Hexane	Toluene	Chloroform	Dichloromethane	Ethyl Acetate	Particulate*
Paraho centrifuged process water	0.1753	0.7252	0.6190	NA	1.6203	NA
Omega-9 retort water	-	0.0151	0.0047	NA	0.0364	NA
Occidental retort water	0.0924	0.0859	0.0667	0.0600	0.1819	NA
Steam distillations						
Omega-9 retort water	0.0141	-	0.0002	NA	0.0047	0.4490
Occidental retort water, run #1	0.0264	0.0185	0.0107	0.0052	0.0819	0.1300
Occidental retort water, run #2	0.0081	0.0071	0.0074	NA	0.0151	0.3327
Occidental retort water, run #3	0.0091	0.0046	0.0093	NA	0.0364	0.5078

*particulate material present in water after distillation that was removed by filtration through a 0.45 micron Millipore filter.

NA-not applicable

RESULTS

Paraho Shale and Process Water Leachate Studies

Leachability of selected trace elements from laboratory columns of Paraho retorted shale and Paraho process water has been studied. Centrifuged Paraho process water was added by gravity feed to the tops of three dry packed and two wet packed columns of retorted shale intended to simulate different waste disposal methods. All leachates that were collected retained the characteristic color and odor of the original process water, but contained no particulate matter. The fractions that were collected after distilled, de-ionized water had been added to the head of the column exhibited a light yellow or straw color.

All leachate samples collected were analyzed for arsenic, selenium, chromium, and zinc by high temperature graphite furnace and flame atomic absorption methods. Arsenic and selenium were selected because of their toxicity and because these two elements have relatively high abundance in retorted shale. Other groups have commented on the possible mobilization of these elements during the retorting process (6, 7). Chromium and zinc were chosen because their chemistries are representative of other trace elements present in retorted shale and the retort waters.

The data obtained for these elements is presented in Table 7-8, and Figures 4-10 illustrate the concentration versus pore volume of the collected leachate for each specific element. A comparison of the results for the wet packed and dry packed columns indicates that the metal concentration varied with pore volume in an analogous manner in both systems.

After the process water had been passed through the columns for an average of 61 days, distilled, de-ionized water was added to the head of the columns. It was noted throughout the leaching studies that the flow through the column dropped steadily, and after the distilled, de-ionized water had been added little leachate was collected. In the dry packed columns, flow gradually decreased and ceased entirely after a time period of 75 days.

In the columns in which distilled, de-ionized water was used for leaching, metal concentrations were generally below detection limits. The metal concentrations in process water leachates, on the other hand, were well above detection limits and exhibited considerable variability. Table 9 shows the concentrations of the selected metals in the original process water. Selenium concentrations in leachate from both wet and dry packed columns were high, ranging from 6-17 $\mu\text{g/mL}$ compared with a concentration of 0.84 $\mu\text{g/mL}$ for the initial process water before it contacted the spent shale (Table 7-8). Effluents from the dry packed columns show a sharp rise in selenium concentration in the fourth pore volume becoming nearly constant at approximately 9.5 $\mu\text{g/mL}$ (Figure 4). The selenium in the leachate from wet packed columns on the other hand, had an initial concentration of approximately 13.0 $\mu\text{g/mL}$, and this remained fairly constant at an average of 12 $\mu\text{g/mL}$ (Figure 5). The concentration levels of arsenic in all samples collected were below that of this element in the process water used for leaching (5.1 $\mu\text{g/mL}$). This seems to indicate that some of the arsenic in the water was retained by the surface of the retorted shale. One column

Table 7. Metal concentration ($\mu\text{g/ml}$) of leachates from the dry-packed columns of Paraho retorted shale and Paraho process water.

Pore Volume #	Column #1				Column #2				Column #3			
	Cr	Zn	Se	As	Cr	Zn	Se	As	Cr	Zn	Se	As
2	<0.20	4.5	6.0	0.30	0.2	4.4	6.7	0.34	0.20	4.6	7.3	0.34
4	<0.20	11.2	17.1	0.35	0.2	6.8	14.0	0.31	0.20	4.2	12.9	0.40
6	0.15	1.4	11.3	0.50	0.16	1.0	11.2	0.47	0.20	2.4	10.6	0.64
8	0.13	0.9	9.6	0.52	0.15	0.43	10.1	0.67	0.15	.47	10.2	0.64
10	0.13	1.0	9.7	0.56	0.12	0.36	8.5	0.58	0.14	1.2	10.7	0.65
12	0.13	0.48	8.7	0.50	0.12	0.36	8.5	0.61	0.16	1	10.9	0.61
14	0.15	0.47	9.6	0.54	0.16	0.38	8.9	0.63	0.14	.58	9.2	0.56
16	0.15	0.53	8.7	0.66	0.13	0.34	8.3	0.69	0.14	.54	10.8	0.57
18	0.14	0.45	8.5	0.55	0.15	0.43	9.7	0.77	0.14	.52	8.9	0.63
20	0.13	0.46	8.7	0.58	0.13	0.41	8.7	0.75	0.17	.48	7.1	0.58
22	0.13	0.43	8.1	0.63	0.13	0.34	8.4	0.98	0.15	2	9.0	0.68
24	0.13	0.42	9.1	0.63	0.14	0.35	9.2	1.27	0.12	.04	8.8	0.68
26	0.12	1.1	10.6	0.67	0.12	0.41	9.1	1.93	0.02	<0.02d	<0.5d	0.20d
28	-	-	-	-	0.15	0.32	8.8	2.42	<0.02	<0.02d	0.2d	0.10d
30	-	-	-	-	0.12	0.38	7.8	1.55	-	-	-	-
32	-	-	-	-	0.13	0.37	9.0	0.65d	-	-	-	-

d denotes leachate from distilled de-ionized water.

- denotes no leachate collected.

Table 8. Metal concentration ($\mu\text{g/ml}$) of leachate from wet-packed columns of Paraho retorted shale and Paraho process water (centrifuged)

Pore Volume#	<u>Column #1</u>				<u>Column #2</u>			
	Cr	Zn	Se	As	Cr	Zn	Se	As
1	0.10	2.7	12.8	0.32	0.02	4.2	13.4	0.38
2	0.10	1.6	12.1	0.32	0.09	2.2	13.8	0.36
3	0.14	1.5	13.4	0.35	0.09	1.5	13	0.36
4	0.12	1.4	14.3	0.33	0.12	1.6	11.6	0.34
5	0.1	1.0	11.5	0.3	0.12	1.5	11.8	0.35
6	0.1	1.0	12.8	0.36	0.14	1.2	13.8	0.32
7	0.13	1.0	11.8	0.41	0.13	1.2	12.6	0.40
8	0.14	1.2	12.9	0.58	0.12	1.5	13.6	0.48
9	0.15	0.8	11.5	0.52	0.13	1.2	10.3	0.46
10	0.14	0.8	12.3	0.51	0.14	1.1	12.1	0.45
11	0.13	1.0	09.7	0.57	0.13	1.4	11.3	0.46
12	0.13	1.1	10.9	1.03	0.14	1.0	11.3	0.44
13	0.11	1.2	13.0	0.54	0.14	2.5	12.8	0.39
14	0.14	1.0	11.9	0.52	0.13	3.6	10.3	0.45
15	0.12	1.8	11.4	0.56	0.02d	0.14d	1.0d	0.21d
16	0.12	1.5	10.6	0.55				
17	0.15	3.9	10.3	0.59				
18	0.15	3.8	13.4	0.54				
19	0.12d	1.6d	8.8d	0.34d				
20	0.02d	0.02d	12.8d	0.09d				
21	0.02d	0.02d	11.3d	0.07d				
22	0.02d	0.02d	11.5d	0.06d				
23	0.02d	0.02d	0.08d	0.08d				
24	0.02d	0.02d	1.0d	--				

d-denotes leachate from distilled, de-ionized water

Figure 4. Pore volume versus selenium concentration ($\mu\text{g}/\text{ml}$) for leachates from Paraho dry packed retorted shale columns and process water.

Figure 5. Pore volume versus selenium concentration ($\mu\text{g}/\text{ml}$) for leachates from Paraho wet packed retorted shale columns and process water.

Figure 6. Pore volumes versus arsenic concentration ($\mu\text{g/ml}$) for leachates from Paraho dry packed retorted shale columns and process water.

Figure 7. Pore volumes versus arsenic concentration ($\mu\text{g}/\text{ml}$) for leachates from Paraho wet packed retorted shale columns and process water.

Figure 8. Pore volume versus chromium concentration ($\mu\text{g/ml}$) for leachates from (A) Paraho dry packed and (B) wet packed retorted shale columns and process water.

Figure 9. Pore volume versus zinc concentration ($\mu\text{g}/\text{ml}$) for leachates from Paraho dry packed retorted shale columns and process water

Figure 10. Pore volume versus zinc concentration for leachates from Paraho wet packed retorted shale columns and process water.

from each of the wet and dry packed series showed an increase in arsenic levels in the later pore volumes (Figures 6-7). The cause for this variation is not known presently. Chromium levels in the leachates show negligible deviation from those in the original process water (0.10 $\mu\text{g/mL}$). This might indicate little interaction between the process water and the retorted shale with regard to the leachability of chromium (Figure 8).

The concentrations of zinc in the first pore volumes were approximately twice as high as in the original process water and might be attributed to soluble species in the solvent front. These values dropped and became constant at concentrations close to those of the original process water (2.0 $\mu\text{g/mL}$). (Figures 9-10). However, in the later pore volumes, the concentration of zinc increased to levels above those in the process water. Since a change to distilled water was made at this time, it is not known whether the zinc levels would have continued to rise if use of the process water was maintained. Column studies using distilled, de-ionized water and Paraho retorted shale have been conducted by Runnells, et al (8). A comparison of their results with those from these studies is shown in Table 9. It can be seen that the concentrations of all four elements were higher in the leachates from process water than from the distilled, de-ionized water leachates (8). However, when process water was passed through the retorted shale, the levels of zinc and selenium in the leachates were considerably higher than those in the original process water or in the leachates from distilled, de-ionized water. The organic ligand content and the pH of the process water leachates are factors that will be investigated more fully with respect to the leachability of these elements from retorted shale. Also, the concentrations of other trace metals of environmental importance (e.g. Cd and Pb) are presently being determined in these leachates.

RETORT WATER FRACTIONATIONS

Gas Chromatography Analyses

The fractions obtained from liquid-liquid extraction and steam distillation of the various retort waters have been analyzed by gas chromatography. A typical set of GC-FID chromatograms is shown in Figures 11-14 for the liquid-liquid extraction of Paraho process water. The use of high resolution glass capillary columns allowed the separation and the detection of many individual components in these complex mixtures. Temperature programs and conditions for these experiments were used for the mass spectral analyses.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

GC/MS analyses of the fractions obtained for the liquid-liquid extractions and steam distillations of the retort waters have been conducted (Figures 15-35). A systematic analysis of approximately one-third of the fractions for selected classes of compounds (hydrocarbons, alkyl-benzenes, fused aromatics, phenols, pyridines, quinolines, piperidines, and acids) has been completed. These compounds were chosen for preliminary mass spectral analyses for several reasons:

Table 9. Comparison of trace metal concentration ($\mu\text{g/mL}$) in Paraho process water and in leachates from columns using distilled, de-ionized (8) versus process water.

<u>Element</u>	<u>Paraho process water</u>	<u>*Columns using distilled de- ionized water</u>	<u>*Columns using process water ($\mu\text{g/mL}$)</u>				
			<u>Dry-packed</u>			<u>Wet-packed</u>	
			<u>#1</u>	<u>#2</u>	<u>#3</u>	<u>#1</u>	<u>#2</u>
Chromium	$0.1 \pm 0.05 \mu\text{g/mL}$	-	0.07	0.08	0.08	0.15	0.15
Zinc	$2.0 \mu\text{g/mL}$	$0.05 \mu\text{g/mL}$	5.60	3.4	-	3.9	4.2
Selenium	$0.84 \pm 0.04 \mu\text{g/mL}$	$0.08 \mu\text{g/mL}$	8.60	5.6	6.4	14.3	13.8
Arsenic	$5.1 \pm 0.1 \mu\text{g/mL}$	$0.07 \mu\text{g/mL}$	0.33	1.21	0.39	1.03	0.48

Runnells, D., Glaze, M., Saether, O., Stollenwerk, K., Release, Transport and Fate of Some Potential Pollutants in Water Associated with Oil Shale. In Trace Elements in Oil Shale Progress Report, Contract # EY-76-S-02-4017, Department of Energy, 1979.

*The metal concentrations shown for the leachates are the highest values obtained for one pore volume.

Figure 11. FID chromatogram of the hexane fraction from the liquid-liquid extraction of Paraho process water on a 24m. SE 52 glass capillary column. Conditions: splitless injection, 2 minutes at 40°C, 2°C/min. to 15 min., 4°C/min. to 25 min., 8°C/min. to 310°C.

Figure 12. FID chromatogram of the toluene fraction from the liquid-liquid extraction of Omega-9 retort water on a 24m SE-52 glass capillary column. Conditions: splitless injection, 2 minutes at 90°C, 4°C/minute to 310°C.

PARAHO PROCESS WATER (CHCl₃ EXTRACT)

Figure 13. FID Chromatogram of the chloroform fraction from the liquid-liquid extraction of the Paraho process water on a 24 m SE-52 glass capillary column. Conditions: splitless injection, 2 minutes at 40°C, 2°C/min. to 15 minutes, 4°C/min. to 25 minutes, 8°C/min. to 310°C.

Figure 14. FID chromatogram of the ethyl acetate fraction from the liquid-liquid extraction of the Paraho process water on a 24 m. SE-52 glass capillary column. Conditions: splitless injection, 50°C, 4°C/min. to 310°C.

Figure 15. Biller Biemann Total Ion Chromatogram (12 m. fused silica column SP2100, 4°C to 270°C at 4°C/min. m/e 50-350) of the hexane fraction from the liquid-liquid extraction of Paraho process water.

Figure 16. Biller-Biemann Total Ion Chromatogram (12 m. SP2100 fused silica column, 75°C to 270°C at 4°C/min., m/e 50-300) of toluene extract from the liquid-liquid extraction of Paraho process water.

Figure 17. Biller-Biemann Total Ion Chromatogram (12 m. SP2100 fused silica column, 50 °C to 270 °C at 4 °C/min., m/e 50-400) of the chloroform fraction from the liquid-liquid extraction of Paraho process water.

Figure 18. Biller-Biemann Total Ion chromatogram (8 m SE-52 glass capillary column, 40° C/min., m/e 50-400) of the ethyl acetate fraction from the liquid-liquid extraction of Paraho process water.

Figure 19. Biller-Biemann Total Ion chromatogram (12 m SP2100 fused silica column, 40°C to 270°C at 4°C/min., m/e 50-350) of the hexane fraction from the liquid-liquid extraction of Occidental retort water.

Figure 20. Eiller-Biemann Total Ion Chromatogram (12 m SP2100 fused silica column, 4 minutes at 75°C, 2°C/min. to 140°C, 4°C/min. to 270°C, m/e 50-350) of the toluene fraction from the liquid-liquid extraction of Occidental retort water.

Figure 21. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica column, 40°C to 270°C at 4°C.min., m/e 50-350) of the chloroform fraction from the liquid-liquid extraction of Occidental retort water.

Figure 22. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica column, 40°C to 270°C at 4°C/min., m/e 50-350) of the methylene chloride fraction from the liquid-liquid extraction of Occidental retort water.

Figure 23. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica, 40°C to 270°C at 4°C/min., m/e 40-350) of the ethyl acetate fraction from the liquid-liquid extraction of Occidental retort water.

Figure 24. Biller-Biemann Total Ion Chromatogram (8m SE-52 glass capillary column, 40°C to 270°C at 4°C/min., m/e 50-350) of the hexane fraction from the liquid-liquid extraction of Omega-9 retort water.

Figure 25. Biller-Biemann Total Ion Chromatogram (8m SE52 glass capillary column, 40°C to 250°C at 4°C/min., m/e 10-300) of the toluene fraction from the liquid-liquid extraction of Omega-9 retort water.

Figure 26. Biller Biemann Total Ion Chromatogram (8m SE52 glass capillary column, 2 minutes at 50°C, 8°C/min. to 250°C, m/e 30-300) of the ethyl acetate fraction from the liquid-liquid extraction of Omega-9 retort water.

Figure 27. Biller-Bienmann Total Ion Chromatogram (12m SP2100 fused silica column, 40°C to 270°C at 4°C/min., m/e 50-350) of the hexane fraction from the steam distillation of Occidental retort water.

Figure 28. Biller-Biemann Total Ion Chromatogram (12m SP 2100 fused silica column, 75°C to 270°C at 4°C/min., m/e 50-400) of the toluene fraction from the steam distillation of the Occidental retort waters.

Figure 29. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica column, 40°C to 270°C at 4°C/min., m/e 40-400 of the chloroform extract from the steam distillation of Occidental retort water.

Figure 30. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica column, 40°C to 270°C at 4°C/min., m/e 50-400) of the methylene chloride fraction from the steam distillation of Occidental retort water.

Figure 31. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica column, 40°C to 270°C at 4°C/min., m/e 50-400) of the ethyl acetate fraction from the steam distillation of Occidental retort water.

Figure 32. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica column, 40°C to 270°C at 4°C/min., m/e 40-400) of the hexane fraction from the steam distillation of Omega-9 retort water.

Figure 33. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica column, 75°C to 270°C at 4°C/min., m/e 40-400) of the toluene fraction from the steam distillation of Omega-9 retort water.

Figure 34. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica column, 40°C to 270°C at 4°C/min., m/e 50-400) of the chloroform fraction from the steam distillation of Omega-9 retort water.

Figure 35. Biller-Biemann Total Ion Chromatogram (12m SP2100 fused silica column, 40°C to 270°C at 4°C/min., m/e 50-400) of the ethyl acetate fraction from the steam distillation of Omega-9 retort water.

1. to evaluate the fractionation achieved with the techniques of liquid-liquid extraction and steam distillation.
2. to enable ready comparison among the different water samples
3. to determine whether correlations exist between the trace metal concentration of each fraction with the types of organic compounds present.

The results of this component analysis are shown in Tables 10-12.

In general, for steam distillation and liquid-liquid extraction using solvents of increasing polarity, there was not as clear-cut a separation of compound classes, as was achieved with the same solvents in alumina column studies with shale oil (7). Specifically, saturated hydrocarbons, fused aromatics and quinolines were found in the hexane extracts. Alkyl aromatics and straight chain acids were distributed between the hexane and toluene extracts. Pyrrolidines were present in the toluene fraction, while piperidines were scattered throughout the hexane, toluene, and the chloroform fractions. The behavior of phenols was anomalous, these were found in both the non-polar hexane and the polar ethyl acetate fractions.

Overall, the extracts of the three waters showed little variation in content for the selected compounds. Since each extract is still a complex mixture, further compound class fractionation by column chromatography is needed before high resolution gas chromatography to obtain better separation for mass spectral studies.

It should be noted that after extraction and steam distillation, the water samples retained considerable color, characteristic of the retort water. However, the odor of the extracted and steam distilled waters had been largely removed which should coincide with the loss of volatile compounds during the fractionation schemes. Also, the Occidental retort water that was subjected to liquid-liquid extraction for periods of longer than 24 hours, indicated higher concentrations of extracted components than the other fractionation schemes.

TRACE ELEMENT ANALYSES OF THE RETORT WATER EXTRACTS

After the liquid-liquid extractions and steam distillations of the Paraho, Omega-9, and Occidental retort waters had been completed, metal analyses were performed to determine whether there were tendencies for relatively high concentrations of the individual elements to be associated with specific classes of organic compounds. The solvent was allowed to evaporate from each of the concentrated samples and the resulting residues were weighed. These residues were digested in a minimum volume of fuming nitric acid and enough 30% hydrogen peroxide to maintain a sufficient oxidizing environment.

Table 10. Compounds identified in the liquid-liquid extractions of the retort waters with hexane.

Compound	mw	Paraho	Occidental	Omega-9
n-C ₉ H ₂₀	128	X	X	X
n-C ₁₀ H ₂₂	142	X	X	X
n-C ₁₁ H ₂₄	156	X	X	
n-C ₁₂ H ₂₆	170	X	X	X
n-C ₁₃ H ₂₈	184	X	X	X
n-C ₁₄ H ₃₀	198	X		
n-C ₁₅ H ₃₂	212	X		
n-C ₁₆ H ₃₄	226	X		
n-C ₁₇ H ₃₆	240	X		
C ₂ alkyl benzene	106	X	X	
C ₃ alkyl benzene	120	X	X	X
C ₄ alkyl benzene	134	X	X	X
C ₅ alkyl benzene	148	X	X	X
C ₆ alkyl benzene	162	X		
indan	118	X	X	
methyl indan	132	X	X	
C ₂ alkyl indan	146	X	X	
Napthalene	128	X	X	X
methyl napthalene	142	X	X	X
C ₂ alkyl napthalene	156	X	X	X
C ₃ alkyl napthalene	170	X	X	
C ₄ alkyl napthalene	184	X		
C ₂ alkyl pyridine	107	X	X	
C ₃ alkyl pyridine	121		X	X
quinoline	129		X	
methyl quinoline	143	X	X	
C ₂ alkyl quinoline	157	X	X	
C ₃ alkyl quinoline	171		X	
C ₅ acid (C ₅ H ₁₀ O ₂)	102	X		-
C ₆ acid (C ₆ H ₁₂ O ₂)	116	X	X	-
C ₇ acid (C ₇ H ₁₄ O ₂)	130	X	X	-
C ₈ acid (C ₈ H ₁₆ O ₂)	144	X	X	-
C ₉ acid (C ₉ H ₁₈ O ₂)	158	X	X	-
C ₁₀ acid (C ₁₀ H ₂₀ O ₂)	172	X	X	-
C ₁₁ acid (C ₁₁ H ₂₂ O ₂)	184	-	X	-
Phenol	94	X	X	
methyl phenol	108		X	
C ₂ alkyl phenol	122		X	
C ₃ alkyl phenol	136		X	

X-denotes positive identification of a particular compound

- denotes that a particular compound is definitely not present

Table 11. Compounds identified in the toluene fractions of the liquid-liquid extractions of the retort waters.

Compound	mw	Paraho	Occidental	Omega-9
C ₅ acid (C ₅ H ₁₀ O ₂)	102	X	-	-
C ₆ acid (C ₆ H ₁₂ O ₂)	116	X	X	-
C ₇ acid (C ₇ H ₁₄ O ₂)	130	X	X	-
C ₈ acid (C ₈ H ₁₆ O ₂)	144	X	X	-
C ₉ acid (C ₉ H ₁₈ O ₂)	158	X	X	-
C ₁₀ acid (C ₁₀ H ₂₀ O ₂)	172	-	X	-
Pyrrolidinel (1-butenyl)		X		
C ₈ H ₁₅ N	125			
C ₈ H ₁₇ N	127			
C ₇ H ₁₅ N	113			
n-C ₉ H ₂₀ -n C ₁₇ H ₃₆		-	-	-
quinolines		-	-	-

X denotes positive identification of a particular compound

- denotes that a particular compound is definitely not present

Table 12. Compounds identified in the steam distillation experiments.

Compound	mw	Occidental hexane extract	Omega-9 chloroform extract	Omega-9 ethyl acetate extract
Phenol	94		X	X
methyl phenol	108			X
C ₂ alkyl phenol	122	X	X	X
C ₃ alkyl phenol	136	X		X
C ₅ -C ₁₀ acids		-	-	-
methyl pyridine	93	-	X	-
C ₂ alkyl pyridine	107	-	X	-
C ₃ alkyl pyridine	121	-	-	-
Benzaldehyde	106		X	
C ₂ alkyl benzene	106	X		X
C ₃ alkyl benzene	120	X		
C ₄ -C ₆ alkyl benzene		-	-	-
Napthalene	128	X		
quinoline	129	X		
methyl quinoline	143	X		X

X denotes positive identification of a particular compound

- denotes that a particular compound is definitely not present

The residues from the steam distillation extract were completely dissolved, while the digests of the liquid-liquid extracts contained an insoluble white precipitate. This precipitate was also noted in digestions of the particulate matter that was filtered from the aqueous phase of the steam distilled samples. Each sample was then diluted volumetrically to 10 or 25 mL. Reagent blanks for the organic solvents and distilled, de-ionized water were also carried through this process.

Trace element analyses of these samples for As, Se, Cd, Cr, Pb, and Zn were performed using atomic absorption flame and graphite furnace methods. The results from these experiments are given in Tables 13-17.

These analyses indicate that only a very small percentage of As, Se, Cr, and Pb were transferred to the organic phase in the liquid-liquid extractions, and that the degree of mobilization for these elements occurred to an even lesser extent in the steam distillation experiments. Significant concentrations of zinc were determined in the extracts from the Paraho and the Occidental retort waters. A comparison of the percentage distribution of the metals indicates that in the steam distilled waters most of the zinc that had been fractionated was found in the filtered particulate matter. This pattern was observed for all elements studied with the exception of selenium, which only showed transfer into the organic extracts from the Omega-9 water.

In most cases for mass balance determinations there appeared to be good agreement between the initial values of elemental compositions of fractions from each of the separations. However, the mass balance for selenium is somewhat low for the Occidental retort water showing a recovery of 70 percent, indicating that some of the selenium may have been lost as a very volatile species. Considerably more cadmium was measured in the fractions than was originally found in the retort water suggesting some contamination problems.

As and Zn appeared to be fractionated in the liquid-liquid extraction scheme, similar to that observed in the alumina-column fractionation of the Paraho shale oil (9). These patterns are not nearly as distinct as were found for the Paraho shale oil, but this may be attributed to a less specific class fractionation by the liquid-liquid extraction and steam distillation methods. Zinc was concentrated in the hexane and the toluene fractions of the liquid-liquid extractions of Occidental retort water, while the zinc from the Paraho shale oil was concentrated in the toluene fraction (Table 18). Arsenic that was extracted into the organic solvents from the retort water appeared to be concentrated mainly in chloroform, the solvent in which most of the arsenic was found in the column investigation of Paraho shale oil (9). It should be pointed out that the fractions from the liquid-liquid extraction of the Occidental retort water contained higher concentrations of all elements studied, with the exception of selenium, than extracts of other water samples. This may be due in part to the longer extraction times used for the Occidental retort water sample.

Table 13. Concentration of arsenic ($\mu\text{g/mL}$) in the retort water extracts

Liquid-liquid extractions	Hexane	Toluene	Chloroform	Methylene Chloride	Ethyl acetate	Particulate	Extracted water
Paraho centrifuged process water	0.14 (0.2) *	0.12 (0.2)	0.25 (1.2)	NA	0.30 (0.6)	NA	ND
Omega-9 retort water	-	-	-	NA	-	NA	ND
Occidental retort water	<0.01 (0.2)	0.10 (0.9)	1.15 (10.1)	-	0.85 (7.5)	NA	0.85 (74.6)
Steam distillations							
Omega-9 retort water	0.02 (0.1)	0.02 (0.1)	-	NA	0.11 (0.1)	51.0 (7.9)	1.00 (87.0)
Occidental retort water, run #1	<0.01 (0.1)	<0.01 (0.1)	<0.01 (0.1)	-	0.04 (0.4)	13.0 (0.7)	1.01 (88.6)
Occidental retort water, run #2	<0.01 (0.1)	-	<0.01 (0.1)	NA	<0.01 (0.1)	4.3 (1.9)	1.03 (90.4)
Occidental retort water, run #3	0.02 (0.2)	0.02 (0.1)	<0.01 (0.1)	NA	0.02 (0.2)	(0.3)	1.00 (104.4)

Paraho process water $5.1 \pm 0.1 \mu\text{g/mL}$ ^(a)

Occidental retort water $1.14 \pm 0.11 \mu\text{g/mL}$ ^(a)

Omega-9 retort water $1.15 \pm 0.12 \mu\text{g/mL}$, $1.0 \pm 0.2 \mu\text{g/mL}$ ^(b)

^(a) Value from this work

^(b) Value from LETC¹⁰

NA- Not applicable

ND- Not determined

*Values in parentheses indicate the percentage of total metal found in a particular fractionation scheme as compared to the original water value.

Table 14. Concentration of selenium ($\mu\text{g/mL}$) in the retort water extracts

Liquid-liquid extractions	Hexane	Toluene	Chloroform	Methylene Chloride	Ethyl acetate	Particulate	Extracted water
Paraho centrifuged process water	-	-	-	NA	-	NA	ND
Omega-9 retort water	-	-	0.54 (17.0) *	NA	0.06 (13.5)	NA	ND
Occidental retort water	-	-	-	-	-	NA	<0.01 (70)
Steam distillations							
Omega-9 retort water	0.01 (0.4)	-	0.005 (2.4)	NA	<0.02 (≤ 0.3)	0.93 (61.7)	0.03 (22)
Occidental retort water, run #1	-	-	-	-	-	-	<0.01 (70)
Occidental retort water, run #2	-	-	-	NA	-	-	<0.01 (70)
Occidental retort water, run #3	-	-	-	NA	-	-	<0.01 (70)

Paraho process water $0.84 \pm 0.04 \mu\text{g/mL}$ ^(a)

Occidental retort water $0.14 \pm 0.2 \mu\text{g/mL}$

Omega-9 retort water $0.15 \pm 0.02 \mu\text{g/mL}$ ^(a), $0.21 \pm 0.11 \mu\text{g/mL}$ ^(b)

^(a) Values from the work

^(b) Values from LETC¹⁰

NA- Not applicable

ND- Not determined

*Values in parentheses indicate the percentage of total metal found in a particular fractionation scheme as compared to original water value.

Table 15. Concentration of chromium ($\mu\text{g/mL}$) in the retort water extracts

Liquid-liquid extractions	Hexane	Toluene	Chloroform	Methylene Chloride	Ethyl acetate	Particulate	Extracted water
Paraho centrifuged process water	0.20 (10) *	-	0.20 (10)	NA	-	NA	ND
Omega-9 retort water	-	<0.10 (<10)	<0.10 (<10)	NA	<0.10 (<10)	NA	ND
Occidental retort water	-	0.008 (10.0)	0.011 (22.0)	0.013 (27.0)	0.017 (35.0)	NA	0.009 (73.7)
Steam distillations							
Omega-9 retort water	-	-	-	-	0.055 (11.1)	0.034 (17.1)	0.009 (43.0)
Occidental retort water, run #1	-	0.018 (7.5)	-	0.011 (4.5)	0.001 (1.1)	0.043 (45.6)	0.003 (23.7)
Occidental retort water, run #2	-	-	0.017 (14.6)	NA	-	0.013 (28.2)	0.007 (55.1)
Occidental retort water, run #3	-	-	-	NA	-	0.032 (45.5)	0.004 (31.4)

Paraho process water $0.10 \pm 0.05 \mu\text{g/mL}$ ^(a)Occidental retort water $0.012 \pm 0.001 \mu\text{g/mL}$ ^(a)Omega-9 retort water 0.020 ± 0.001 ^(a), $0.02 \pm 0.01 \mu\text{g/mL}$ ^(b)^(a) Values from this work^(b) Values from LETC¹⁰NA- Not applicable
ND- Not determined

*Values in parentheses indicate the percentage of total metal found in a particular extraction scheme as compared to the original value.

Table 16. Concentration of lead (µg/mL) in the retort water extracts

Liquid-liquid extractions	Hexane	Toluene	Chloroform	Methylene chloride	Ethyl acetate	Particulate	Extracted water
Paraho centrifuged process water	-	-	-	NA	-	NA	ND
Omega-9 retort water	-	-	-	NA	-	NA	ND
Occidental retort water	0.02 (0.4) *	0.025 (0.5)	0.01 (0.2)	-	0.01 (0.2)	NA	0.13 (64)
Steam distillations							
Omega-9 retort water	<0.01 (0.1)	<0.01 (0.1)	0.02 (0.2)	NA	<0.01 (0.1)	-	0.19 (70.7)
Occidental retort water, run #1	-	-	0.01 (15.8)	0.02 (31.6)	0.02 (52.6)	3.6 (1.2)	0.17 (85)
Occidental retort water, run #2	-	-	-	NA	-	-	-
Occidental retort water, run #3	0.02 (0.4)	0.02 (0.4)	-	NA	0.02 (0.4)	8.9 (15.1)	0.19 (85)

Paraho Process Water 0.010 ± 0.005 µg/mL ^(a)

Occidental retort water 0.20 ± 0.02 µg/mL ^(a)

Omega-9 retort water 0.011 ± 0.006 µg/mL ^(a), $0.005-0.02$ µg/mL ^(b)

^(a)Values for this work

^(b)Values from LETC¹⁰

NA- Not applicable

ND- Not determined

*Values in parentheses indicate the percentage of total metal found in a particular fractionation scheme as compared to the original water value.

Table 17. Concentration of zinc ($\mu\text{g/mL}$) in the retort water extracts

Liquid-liquid extractions	Hexane	Toluene	Chloroform	Methylene chloride	Ethyl acetate	Particulate	Extracted water
Paraho centrifuged process water	2.9 (14.5) *	0.8 (4.0)	-	NA	1.2 (15)	NA	ND
Omega-9 retort water	-	>5.0 (25.0)	-	-	0.5 (7.1)	NA	ND
Occidental retort water	1.8 (75)	2.1 (35)	1.1 (18)	-	-	NA	-
Steam distillations							
Omega-9 retort water	1.7 (10.0)	-	-	NA	-	1.3 (18.6)	-
Occidental retort water, run #1	2.1 (17.5)	2.2 (18.3)	0.6 (5.0)	3.4 (28.0)	2.5 (52.0)	2.6 (54.2)	0.1 (16.7)
Occidental retort water, run #2	1.2 (20.0)	0.8 (13.3)	0.4 (6.7)	NA	0.4 (6.7)	0.8 (33.3)	0.2 (33.3)
Occidental retort water, run #3	-	-	-	NA	-	1.7 (47.2)	0.2 (33.3)

Paraho process water 2.0 $\mu\text{g/mL}$ ^(a)Occidental retort water 0.60 $\pm$ 0.02 $\mu\text{g/mL}$ ^(a)Omega-9 retort water 0.31 $\pm$ 0.04 $\mu\text{g/mL}$ ^(b)^(a) Values from this work^(b) Values from LETC¹⁰

NA- Not applicable

ND- Not determined

*Values in parentheses indicate the percentage of total metal found in a particular extraction scheme as compared to the original water value.

Table 18.. Elemental Concentrations ($\mu\text{g/mL}$) of a Shale Oil Sample Being Eluted from an Alumina Column by Solvents with Increasing Polarity (9).

Fraction	Cd	Pb	Cr	As	Zn	Se
1. hexane	0.11 ± 0.01	0.2	4.0 ± 0.2	0.1	0.7	0.2
2. toluene	0.18 ± 0.02	3.2 ± 0.4	19.6 ± 0.4	1.6	58.0 ± 2.4 (74.9%)	0.4
3. CHCl ₃ (three fractions combined)	0.13 ± 0.01 (52.2%)	3.5 ± 0.4	6.8 ± 0.2 (36.4%)	1.5 (37.1%)	2.3 ± 0.1	0.3 (46.4%)
4. THF/ETOH	0.09 ± 0.02	4.6 ± 0.2 (68.2%)	18.0 ± 0.4	2.7 ± 1.5	7.5 ± 0.2	0.5 ± 0.4
5. MeCH	0.15 ± 0.06	6.0 ± 1.1	34.0 ± 1.1	18.0 ± 4.5 (32.3%)	9.5 ± 0.7	1.5 ± 1.1

*Numbers in parentheses refer to the percentage of an element in the principal fraction containing that element.

CONCLUSIONS

Leachate studies involving Paraho retorted shale and Paraho process water have shown mobilization of higher concentrations of selenium and zinc. The phenomena has not been observed on other investigations that have involved the leaching of raw and retorted shales with distilled, de-ionized water. The selenium concentration of the initial process water was on the order of 1 $\mu\text{g/mL}$, while the leachates collected from the columns gave values ranging from 10 - 14 $\mu\text{g/mL}$ when the Paraho process water was in contact with the retorted shale. These values are in considerable excess of the naturally occurring levels of selenium in practically all water resources which are generally well below 0.1 $\mu\text{g/mL}$. It is not clear at this time whether the increase in selenium concentration is due primarily to the interaction of the retorted shale with the highly buffered alkaline process water or a combined effect of high pH values and the presence of large amounts of organic compounds in the water that may complex with available selenium.

Although zinc showed relatively high concentrations in the leachate from these experiments, it is expected that these levels should not present a large environmental problem. However, the significance of this result implies that trace elements of more toxic nature and having chemistry similar to zinc (e.g. Pb and Cd) should also be examined in the leachates from wastewater and retorted shales.

These results should be considered in instances where retorted shale and wastewaters are mixed for waste disposal purposes, especially when leaching processes from continued contact with wastewaters or natural water is expected. This data also implies the need to consider trace metal concentrations of wastewaters that have been passed through columns of retorted shale in attempts to remove organic material.

Wastewater from the Paraho, Occidental and Omega-9 processes have been studied using techniques of solvent extraction, steam distillation, gas chromatography, mass spectrometry, and atomic absorption spectrometry.

Results from these experiments indicate that the different wastewaters contain a large number of organic compounds that are similar to one another. Specifically, saturated hydrocarbon, alkyl benzenes, indans, fused aromatic pyridines, quinolines, phenols and acids.

Trace metal analyses of the fractions obtained from liquid-liquid extractions and steam distillation show that only a very small percentage of the trace metals appear to be associated with the organics extracted from the wastewater. However, zinc did exhibit considerable fractionation, especially in the liquid-liquid extraction of the Occidental retorted water. Zinc was found in the more non-polar solvents of the extraction process. This is also where the major portion of zinc was found in earlier studies of column fractionation of Paraho shale oil.

Arsenic, also fractionated similar to its behavior in the column separation of the shale oil. In both instances, the arsenic fractionated was found principally in the more polar solvents.

Finally, it should be noted that considerable non-extractable organic material remains in the aqueous phase during the different extraction processes and that the organic compounds in this phase are yet to be determined and evaluated for their association with trace elements.

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