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TRACE ELEMENTS

IN

OIL SHALE

Progress Report: 1976 - 1979
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Progress Report: 1976 - 1979

Introduction and Summary of Research
Willard R. Chappell

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.

✓ This program is a part of the Environmental Trace Substances Research Program (ETSRP) at the University of Colorado. The Principal Investigator is Dr. Willard R. Chappell, Professor of Physics, University of Colorado at Denver. The other Senior Investigators are:

Dr. Ronald W. Klusman
Department of Chemistry-Geochemistry
Colorado School of Mines

Dr. Willard L. Lindsay
Department of Agronomy
Colorado State University

Dr. Robert R. Meglen
Analytical Facility
Environmental Trace Substances
Research Program
University of Colorado, Boulder

Dr. Donald D. Runnells
Geological Sciences
University of Colorado, Boulder

Dr. Robert E. Sievers
Department of Chemistry
University of Colorado, Boulder

Dr. Thomas R. Wildeman
Department of Chemistry-Geochemistry
Colorado School of Mines

All inquiries regarding this program should be addressed to:

Dr. Willard R. Chappell
Environmental Trace Substances
Research Program
Campus Box 215
University of Colorado
Boulder, Colorado 80309
(303) 492-7588

The present report describes the progress of the third year of funding as of February 15, 1978, and also reviews the progress since funding was initiated on June 1, 1976.

The overall objective of the program is to evaluate the environmental and health consequences of the release of toxic trace elements by shale 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 processes 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.

	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 past 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.

The program consists of six 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 use 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 that 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 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.

Within the last few months Dr. Meglen has written computer programs to perform pattern recognition analysis on the trace element data. This analysis shows a clustering of most elements in raw and retorted shales into lithophile and siderophile elements. However, Zn, oil, and water are found to correlate with none of the other elements analyzed nor with each other. This result adds reinforcement to other data on the Paraho materials, indicating that Zn is behaving peculiarly and deserves further study.

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 elevation, 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 amounts 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 on 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 just this year 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 initial 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. There is data from Oak Ridge National Laboratory which indicate that that fraction has the highest mutagenic activity.

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 eight years of experience with

similar programs and during this period has performed more than 50,000 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 year 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.

Numerous new methods have been developed to deal with the special problems of oil shale-related materials. A single fusion method for boron and fluorine analyses was developed, replacing separate time-consuming methods previously used. A new analytical procedure for F has been developed which is rapid, reliable, and capable of automation.

In addition to AA and colorimetric methods, we have an x-ray fluorescence capability through the Nuclear Physics Laboratory which has long been associated with our program. While most of our samples are processed by other techniques, we do process a limited number of samples by this procedure when we are in need of multielement analyses or when we are working with very small sample sizes. The total analytical output during the past year for the Central Analytical Laboratory and the x-ray fluorescence was approximately 5,000 analyses.

In addition to the analytical work, Dr. Meglen and Dr. Donald Denney have begun applying a very powerful statistical tool - pattern recognition - to the interpretation of the analytical data. These methods allow for the investigation of complex relationships between large numbers of variables. Drs. Meglen and Denney have written computer programs to perform these analyses and have applied them to Dr. Wildeman's data. They were also asked to analyze some GC data acquired by the Laramie Energy Technology Center on some in situ cores. This later analysis revealed several unsuspected relationships.

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

Progress Report: 1976 - 1979

Trace Element Reconnaissance in the Oil Shale Region
Ronald W. Klusman
Department of Chemistry and Geochemistry
Colorado School of Mines

INTRODUCTION

Renewed interest in the oil shale resources, particularly in Colorado, has generated concern in the potential environmental impact of surface and in situ retorting of oil shale. The alkaline character of the raw and spent shale and the reducing conditions of retorting raise the possibility of mobilizing several trace elements, some of which can be toxic. The chemistry of soils, plants, and stream sediments are being studied to establish baseline concentrations. The data will be used to determine if unusual concentrations exist at present, for predicting the impact of an industry, and for future reference in monitoring the effects of an oil shale industry.

The unusual alkaline geochemical conditions prevailing at the time of deposition make the deposits unique (1). Most organic rich shales are deposited under less alkaline marine conditions and may be acidic below the water sediment interface. Since the oil shales in this area were deposited under alkaline conditions, the mobilities of trace elements will be affected. In alkaline environments, anionic elements such as Mo, B, As, Se, F, and the cation Li are mobilized and may be a potential pollution hazard. In addition, As, Se, Zn, and Hg may be volatilized under the reducing conditions of retorting, increasing the possibility of atmospheric dispersal (2). The extensive loss of Hg during retorting has been confirmed by Fox and others (3).

Geologically, the Piceance Creek basin is a major structural feature of the Colorado Plateau physiographic province (Figure 1). The majority of the exposed rocks in the basin are Eocene in age. The lowest unit commonly seen is the varicolored mudstone and siltstone of the Wasatch formation. The Green River formation consists of the Douglas Creek and Garden Gulch members and the kerogen-rich Parachute Creek member. In the vicinity of Rifle, the Douglas Creek and Garden Gulch members are named the Anvil Points member. The unit at the top and exposed over most of the interior of the basin is the sandy Uinta formation.

JUSTIFICATION OF BASELINE STUDIES AND OBJECTIVES

To the casual observer, the Piceance Creek basin appears to be geologically and physically homogeneous, and the baseline studies can be minimal. The area does exhibit considerable variability, natural regional trends, and confirms that certain elements may pose more of a hazard than others. The primary reasons for baseline studies can be summarized as:

- 1) Establish means and ranges in concentration for selected elements in various media.
- 2) Confirm existence of geochemical trends prior to development.
- 3) Relate surficial material composition to geology of the area.

Figure 1. Simplified geologic map of the Colorado portion of the oil area.

- 4) Identify and quantify potential problems so that appropriate environmental controls can be designed in.
- 5) Allow the prediction of, and at a later date, the actual magnitude of geochemical impact.

The efforts of the past three years have concentrated on the first three categories. Recently, crude attempts have been made on the fourth item. As more and better information accumulates on atmospheric dispersal of contaminants, this can be better quantified. Sufficient data is on hand to qualitatively identify the most likely trace element problems. Proposed work will move into the area of quantifying the problems of the fourth item and the prediction aspect of item five.

MATERIALS AND METHODS

MATERIALS

A variety of surficial materials were collected on part of the baseline studies. Initial collections over the entire Piceance Creek basin were of surface soil and stream sediments. As the studies focused in on areas of prime potential for development, plants were added to the collections. The plant materials sampled included; Big sage (Artemisia tridentata), subspecies tridentata and wyomingensis, Indian ricegrass (Oryzopsis hymenoides), and Western wheatgrass (Agropyron smithii).

Soil samples were a composite of the top one inch 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. Stream sediments from the regional study were collected at one location from a bar away from overhanging banks. In the more localized studies, stream sediments were composited over at least 10 m of stream channel. All samples were field sieved to -4 mesh and stored in stream sediment bags. The samples were split to 12-15 g and ground to -200 mesh in tungsten carbide for trace element analysis.

The collection of plant materials was 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 of soil material. 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.

ANALYTICAL METHODS

The analytical work for the regional soil study was done by the U.S. Geological Survey (6). The major elements Al, Si, Ca, Ti, Fe, K and the trace elements Sn, Sb, Ge, As, and Se were analyzed by X-ray fluorescence.

Magnesium, Na, Li, Zn and Rb were determined by atomic absorption spectrometry. Fluorine was determined by specific ion electrode. Mercury was determined by wet oxidation followed by flameless atomic absorption. Total carbon was determined by combustion. The remaining trace elements (B, Ba, Be, Co, Cr, Cu, Ga, Mn, Mo, Nb, Ni, Pb, Sc, Sr, V, Y, Yb and Zn) were all determined by optical emission spectrometry.

The analytical work for the regional stream sediments was done at the Colorado School of Mines and the central analytical facility for the project at the University of Colorado. Mercury, As, Cd, and Zn were analyzed by atomic absorption, organic carbon by wet oxidation, and pH by electrode. The pH determination was made on unground sample by the saturation paste technique. Molybdenum was determined by the methods described by Meglen in this report.

The samples for the local studies were analyzed at the Colorado School of Mines and the central analytical facility at the University of Colorado. Zinc, Hg, Li were determined by atomic absorption, organic carbon by wet oxidation, and pH by electrode. Mercury in the Anvil Points area is being determined by the resistance in an amalgamated gold film method. Molybdenum, B, and F were determined by the methods described by Meglen in this report.

SAMPLE DESIGN

For purposes of these studies, a baseline is defined to be a reference that not only describes the means and limits of concentration inherent in nature, but also quantifies the geographical scale of variability. The most effective way of expressing a baseline is with a geochemical map. If the variability is local, too many samples will be required to develop a stable or reproducible geochemical map. If the variation is local, an expected range is an appropriate means of expressing a baseline. Constructing a contour map when the majority of the variance is at local geographic scales results in a map that appears satisfactory but is an artifact of the samples and may not be reproducible.

Regional Soils

The sampling design for the study of the soils in the Piceance Creek basin is a partially unbalanced rested analysis of variance design described in detail by Miesch of the U.S. Geological Survey (4,5). The regional study was considered reconnaissance in nature, with objectives of ascertaining the general chemical character of the soils, regional trends if any, and develop guidelines for sampling design in more localized studies (6). The sampling localities are shown diagrammatically in Figure 2. The initial sampling design, as used in the field, was balanced. Within each of 36 townships, two sections were chosen at random. Within each section, two samples of surface soil were collected 100 meters apart. All four samples within a given township were collected either from ridge tops or valley bottoms. Four townships were grouped into "supertownships". Ridge tops and valley bottom sampling alternated according to a checkerboard design. By eliminating one sample from one section in each township, a slightly unbalanced design resulted in a reduction of analytical load of 25 percent. These samples were analyzed by the U.S. Geological Survey prior to initialization of the ERDA supported research.

Figure 2. Index map (top) showing location of study area, lease tracts C-a and C-b and soil sampling localities. Map (bottom) showing soil sampling design and number of samples at each locality.

Level 1 (the top level) was designed to examine geochemical differences between soils on ridge tops and those in valley bottoms; level 2 was designed to examine geochemical differences at geographic scales greater than 19 km (between supertownships); level 3 examines differences at scales from 3 to 19 km (between townships); level 4 examines differences at scales from 0.1 to 3 km (between sections); level 5 examines differences at a scale of 100 m (between samples); level 6 measures analytical precision and includes errors due to sample inhomogeneity, sample preparation, and analysis.

Regional Stream Sediments

As in the case of the regional soils study, the initial stream sediment studies were of a reconnaissance nature (7). These were two components to the regional stream sediment study; one to determine if anomalous drainages or areas existed, and the other an analysis of variable design to quantify geographic variability and enable planning of the more localized studies to follow.

The sampling plan for determining which streams in the basin contain anomalous trace element concentrations in sediments was to collect two 200 g samples 10 m apart at the mouths or junctions of most of the named streams in the basin (Figure 3). Approximately 100 stream junctions were sampled in the basin. To keep the analytical load at a feasible level only one of the two samples was analyzed. If a sample was thought to be abnormally high, the other sample could be analyzed to substantiate the first determination.

When locality is used in the discussion of stream junction sampling, it will represent the stream channel above the junction. Random sampling within the length of the stream channel will not express an anomalous locality as effectively as will sampling on the downstream end of the stream or tributary. Of course, this assumption is dependent on the nature of the dispersion train from the anomalous source. If an anomalous source is located at the head of a typical sampled stream, a dispersion halo of 10 km or longer may be required for detection at the mouth of the stream. Thus only strong anomalies or relatively large size targets will be detected by this sampling approach.

An estimate of the natural variability in five major drainages was determined using the hierarchical analysis of variance design of Miesch (4,5) but modified to fit a one-dimensional stream channel (7). Figure 4 illustrates the various geographic scales in the stream channel sampling which partition the variance in a 10 km stream channel segment. Within each of these 2 km segments, two 200 meter segments were picked at random, one within each 1 km segment. Then within each 200 m segment, two 20 m segments were picked at random, one within each 100 meter segment. Finally within each 20 m segment, two samples were collected over a distance of one meter, one within each 10 m segment.

One of the hierarchical stream sediment sampling models is randomly placed in each of the five major streams of the basin as shown in Figure 5. The dashed lines across the streams show the predefined limits of the main stem that will possibly be in the 10 km segment to be sampled. The dashed boxes show the actual position of the randomly placed 10 km hierarchical model in the individual stream drainages.

Figure 4. Details of stream sediment analysis of variance sample design.

Figure 5. Locations of stream sediment analysis of variance sample design.

Local Studies

The data from the regional soils study (6) and the regional stream sediment study (7) were used in planning the sampling for more localized studies. At this time initial ERDA funding became available and the localized studies were stipulated to include plant materials as described under the section on materials. Stream sediments were collected at the same time as soils and associated plants but generally have not been analyzed because of analytical capacity. The collection of the stream sediments at the same time as soils and plants adds very little to field costs and are available for future baseline studies. The local studies were carried out on Tract C-a and vicinity, Tract C-b and vicinity, and the Anvil Points area.

Analysis of Variance Design--

The analysis of variance design for the local studies served to confirm the results of the regional studies when applied to areas in the 40-50 sq. mile range. At each sample locality, surface soils and the three plant species were collected. The design consisted of randomly selecting four sections (1 sq. mi.) in the study area and collecting according to Figure 6. The sampling was designed to analyze the variability shown in five separate levels (Figure 7). The levels are: variance at the greater than 1.6 km level, variance at the 0.4 km level, variance at the 0.1 km level, variance between samples at the 50 m level, and error in the chemical analysis. The model is defined as:

$$X_{ijklm} = u + a_i + b_{ij} + c_{ijk} + d_{ijkl} + e_{ijklm} \quad (1)$$

where u is the mean of all the nested samples, a_i is the regional component (>1.6 km), b_{ij} is the 0.4 km segment, c_{ijk} is the 0.1 km segment, d_{ijkl} is the 50 m segment, and e_{ijklm} is the analysis. The population variance is divided as follows:

$$\sigma_x^2 = \sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2 + \sigma_e^2 \quad (2)$$

and is calculated as the sample variance:

$$S_x^2 = S_a^2 + S_b^2 + S_c^2 + S_d^2 + S_e^2 \quad (3)$$

In the interpretation of the analysis of variance design, ratios of the variances at different levels of the sampling model are examined. The variance ratio (V) is the ratio of the variance between sections (>1.6 km) and the sum of the variance at the other levels of the model (0.4 km, 0.1 km, 50 m, and analytical error). The larger the variance ratio the greater the probability that the component in question displays a regional component of variation. In the context of local studies, regional implies a trend across the area being studied which in these studies ranged from 36-48 sq. miles.

The variance mean ratio (V_m) is similar to the variance ratio but incorporates the nested design of the sampling model used. The maximum acceptable error variance for a balanced sampling design (E_r) and the error variance for a hierarchical design (E_s) are used to determine the stability of a geochemical map (5). If the variance observed in a nested design (E_s) is less than the maximum permissible error variance for a balanced design (E_r), then the model produces an accurate representation of the variance shown by the particular component (4).

Figure 6. Schematic analysis of variance design used in local soil sampling studies.

Figure 7. Nested analysis of variance design used in local soil sampling studies.

TABLE 1. ANALYSIS OF VARIANCE OF SURFACE SOIL CHEMISTRY, PICEANCE CREEK BASIN, COLORADO.

Element	Total Logarithmic Variance	Variance components as percentage of total variance					Analytical Error
		Between Ridge Tops and Valley Bottoms	Between Super- townships (>19 km)	Between Townships (3-19 km)	Between Sections (0.1-3 km)	Between Samples (0-100m)	
Al	.0044	0	18	0	58*	14*	10
Ca	.1596	0	28*	15*	48*	9	0
Fe	.0080	0	27*	0	38*	2	33
Mg	.0291	0	28*	3	57*	1	11
K	.0075	2	7	0	80*	6*	5
Si	.0038	0	22*	0	46*	22*	10
Na	.0473	0	4	41*	46*	6*	3
Ti	.0064	1	28*	0	54*	9*	8
Total-C	.0535	1	14	26*	19	31*	10
As	.0914	0	0	0	81*	6	13
B	.0173	0	18*	0	57*	5	21
Ba	.0313	0	0	0	35*	6	58
Be	.0264	0	24*	0	37*	0	39
Co	.0624	0	12	0	33*	0	55
Cr	.0452	0	17*	0	37*	0	46
Cu	.0821	0	28*	0	18*	1	52
F	.0331	3	7	0	15	34*	41
Ga	.0677	0	10*	0	59*	0	32
Ge	.1378	0	0	11	0	27	62
Hg	.1631	2	10	36*	31*	4	17
Li	.0363	5	23*	0	58*	10*	5
Mn	.0476	0	0	8	4	0	88
Mo	.0976	0	11	0	48*	7	33
Nb	.1055	0	1	0	17	0	82
Ni	.0694	0	10	0	24	36*	30
Pb	.1029	0	6	0	39*	0	55
Rb	.0127	0	6	0	77*	6	11
Sb	.1867	1	2	0	0	10	86
Sc	.0491	0	5	0	37*	0	59
Se	.0947	1	0	15	0	25	59
Sn	.3488	0	2	0	0	33	65
Sr	.0350	1	19	18*	31*	5	27
V	.0396	0	7	0	52*	0	41
Y	.0330	0	9*	0	42*	0	49
Yb	.0986	0	8*	0	38*	0	54
Zn	.0083	1	31*	12	32*	19*	5
Zr	.0359	2	1	0	28	2	66

* Indicates component is significantly different from zero at the 0.05 probability level.

Grid Design--

Based on the regional soil study (6) and an evaluation of analytical capability and capacity, sampling of the soils and plants on the 36-48 sq. mile local areas at $\frac{1}{2}$ mile intervals was carried out. The number of samples collected was then adequate to obtain a stable estimate of means and ranges for constituents. If the analysis of variance results allowed, stable geochemical maps showing general trends could be constructed using the grid data.

Stream Sediments--

Stream sediments were also collected in the local studies. Based on the regional study (7) an interval of $\frac{1}{2}$ mile (0.8 km) of stream channel length was selected as an appropriate interval. Samples were composited over at least 10 m of channel to eliminate the very small scale variance. The stream sediment sampling covered the same area as the grid plus considerable areas downstream. To date, stream sediments collected in the local studies have not been analyzed but are available for further baseline studies as the need arises.

RESULTS AND CONCLUSIONS

REGIONAL SOILS

Logarithmic variance components for 37 elements in surface soils from Piceance Creek Basin (Table 1) shows that most of the geographic variation for most elements occurs between sections (0.1 to 3 km). This conclusion supports analysis of variance results for soils from other areas which indicate that most of the variability in soil composition occurs at local scales (8).

Of the 37 elements listed in Table 1, 27 have significant variance components at the section level (Al, Ca, Fe, Mg, K, Si, Na, Ti, As, B, Ba, Be, Co, Cr, Cu, Ga, Hg, Li, Mo, Pb, Rb, Sc, Sr, V, Y, Yb, and Zn).

Only 10 elements (Al, K, Si, Na, Ti, F, Li, Ni, Zn and total C) have significant variance components at the sample level (100-meter distance) and only five elements (Ca, Na, Hg, Sr, and total C) have significant variance components at the township level (3-19 km). More than one-third of the elements listed in Table 1 (14 of 37) have significant variability between supertownships (>19 km). These 14 elements include Ca, Fe, Mg, Si, Ti, B, Be, Cr, Cu, Ga, Li, Y, Yb, and Zn. Although soil development and characteristic vegetation on ridge tops visibly differ from than in bottom valleys, we were surprised to find that there were no significant elemental differences between soil samples collected on ridge tops and those collected in valley bottoms. This means that the ridge top and valley bottom samples can be viewed as part of the same population. It was expected that there would be differences between ridge tops and valley bottoms due to differences in soil development and vegetative cover.

By a quantitative examination of the distribution of the variance it can be determined that the sampling was adequate to describe the variability for

five elements (Fe, Be, Cu, Li, and Zn) in a map form. If most of the variance is at the upper geographic scales, a relatively limited number of samples will produce a stable (reproducible) geochemical map. If the variance is concentrated at local scales as is the case for As, only small scale sampling will allow a map representation of the As concentrations in soils. In this case, sampling and analytical costs restrict the description of the basin-wide data to a mean, range and deviation.

All five elements for which stable geochemical maps can be made show higher concentrations in the southern part of the basin and three (Cu, Li, and Zn) exhibit well-defined trends in that direction. Concentrations of soil Zn increase from 68 ppm in the northeastern part of the basin to almost 100 ppm in the southwestern part. Figure 8 illustrates the Zn distribution. A more detailed discussion of the results of the first phase soil studies is published (6).

The five elements (As, B, F, Mo, and Se) previously discussed as a potential environmental hazard are elevated in concentration in the soils of the Piceance Creek Basin. A possible exception is fluorine. Fluorine is elevated in the parent material but is not particularly elevated in surface soils. Table 2 summarizes the geometric mean, geometric deviation, and observed range in concentration of 37 elements in the surface soils of the Piceance Creek Basin.

REGIONAL STREAM SEDIMENTS

The objectives of this portion of the study are twofold: 1) to determine if there exist any significant trace element anomalies in the stream sediments of the Piceance Creek Basin, and to determine the geochemical variation of five major streams (Roan, Black Sulfur, Parachute, Piceance, and Yellow Creeks) for the purposes of establishing practical baselines. A knowledge of any existing anomalous stream sediment geochemistry will be important for making recommendations for any future oil shale plant sites. The details of the design were discussed previously.

The streams in the Roan Plateau area dissect the Uinta sandstone. The heads of the streams flowing easterly or westerly cut into the upper portion of the Parachute Creek Member. This moderate dissection contrasts with the extreme dissection of streams cutting lithologies in the Roan Creek and Parachute Creek areas (Figure 5).

The analysis of variance of the nested design for the major streams in the Piceance Basin is summarized in Table 3. From the table two variance components stand out: the variance from 0 - 10 m for the individual streams, and the variance between streams for all stream data. The significance from 0 - 10 m for Mo cannot be tested because the 0 - 10 m scale of variance and the analytical variance are combined in the lowest level, but the high percentage of the variance at this lowest level is a good indication that 0 - 10 m would be significant if a test could be made. In general, the consistency of the significance at the 0 - 10 m scale may be a reflection of the power (degrees of freedom) of the sample design being concentrated at the lower levels. Except for Zn, there are significant differences between streams for all the constituents. A similar study done in the same area and in Utah also brought out the significant difference between streams for many other elements. Semi-quantitative optical spectrography data for B in sediments from Roan and Black Sulfur Creeks indicate an elevated concentration

Figure 8. Regional distribution of Zn (ppm) in surface soils in the Piceance Creek Basin, Colorado. Values are supertownship means.

TABLE 2. SUMMARY OF GEOCHEMICAL DATA ON SURFACE SOILS IN
PICEANCE CREEK BASIN, COLORADO (ppm).

Element	Observed Range	Geometric Mean	Geometric Deviation
Al, %	3.4 - 7.8	5.5	1.17
Ca, %	.46 - 9.8	1.9*	2.48
Fe, %	1.1 - 2.9	1.8*	1.22
Mg, %	.51 - 2.7	1.0*	1.49
K, %	.77 - 3.2	2.3	1.22
Si, %	15 - 34	26*	1.15
Na, %	.18 - 3.5	1.4	1.65
Ti, %	.15 - 38	.28*	1.21
C(total), %	.87 - 12	3.0	1.69
As	<2.0 - 21	6.4	2.01
B	25 - 102	61*	1.35
Ba	600 - 13,000	1,400	1.50
Be	.88 - 4.4	2.4	1.46
Co	1.2 - 16	7.9	1.77
Cr	12 - 110	60*	1.63
Cu	<8.7 - 122	29*	1.94
F	<400 - 1,600	490	1.52
Ga	<2.2 - 39	18*	1.82
Ge	<.14 - 2.5	.87	2.37
Hg	.01 - 22	.041	2.56
Li	16 - 140	34*	1.55
Mn	82 - 1,200	490	1.65
Mo	<1.04 - 14	5.3	2.05
Nb	<2.2 - 21	6.9	2.11
Ni	<3.4 - 42	21	1.83
Pb	<3.3 - 56	26	2.09
Rb	40 - 190	105	1.29
Sb	<.14 - 4.5	.90	2.70
Sc	<2.1 - 13	6.7	1.66
Se	<.11 - 1.2	.28	2.02
Sn	<.11 - 11	.80	3.90
Sr	61 - 660	280	1.55
V	7.5 - 120	56	1.58
Y	4.9 - 36	15*	1.52
Yb	<.28 - 6.2	2.1*	2.06
Zn	45 - 140	80*	1.23
Zr	54 - 700	270	1.55

(geometric mean of 44 ppm) with most of the variance concentrated at intermediate distances. Summary data published by McNeal and others (9) gives geometric means of 6.5 and 7.8 ppm, respectively for As and F in stream sediments. The As is elevated in concentration with respect to the earth's crust but not with respect to an average shale. The F is substantially depleted, possibly due to solubility under the alkaline conditions of the basin.

The approach toward defining baselines for the above constituents can be done in two ways. First, if interest was being directed toward streams draining possible plant sites, one would want to define a baseline for that particular stream since it has been determined that there can be significant differences between streams. For the constituents being discussed in this paper it would be recommended from the analysis of variance results that an expected range be used as a baseline for all the streams under consideration. In these instances, to develop stable geochemical maps which will describe a reasonable percentage of the variance of the streams, sample localities will have to be chosen a few meters apart.

Secondly, if one were interested in characterizing the Piceance Creek Basin as a whole, it might be feasible, for Mo, Hg and organic matter, to choose streams as localities. From the analysis of variance results for these constituents, one could conclude that a few samples a short distance apart within these localities would provide enough information to make a stable geochemical map that would express a large percent of the total variation. The analysis of variance predicts Hg and organic matter could be treated in a similar manner.

Table 4 is a comparison between the expected range of the constituents (one sample taken from each locality and analyzed once) and their average abundance in the earth's crust and in shale.

Note the expected range in Table 4 and Table 5 as compared with the expected ranges from the nested model design (Table 3). The ranges from the nested model are smaller. The analytical error is removed from the nested ranges, but analytical errors are too small to account for the difference. The most probable explanation is that stream junction samples are being affected by geographic variance at a larger scale than the upper limit (10 km) expressed by the nested model. As will be recalled, the nested model does predict a large percentage of variance at the between-stream level. The level could also be interpreted as expressing a variance of larger scale than 10 km as well as the between stream level.

Since the Piceance Creek drainage is much larger than the 10 km scale and since it was more extensively sampled than the other creeks, it appears to show the higher scale variance for Zn and Mo. Both distributions of Zn and Mo for the stream junction samples (data transformed to $\log_{10}$) are bimodal or trimodal. The upstream end of Piceance Creek has high Zn and low Mo concentrations where the creek cuts through the Green River Formation. The bi- or trimodal character for these elements is probably a reflection of the geology.

From stream junction data, it is found that for all the measured constituents - Zn, Mo, Hg, and organic carbon - there is a significantly greater

TABLE 3. GEOCHEMICAL SUMMARIES FOR STREAM SEDIMENTS OF MAJOR CREEKS IN THE PICPANCE BASIN.
(Data given in parts per million)

Element	Stream	Analysis of Logarithmic Variance							Summary Statistics			
		Total Log ₁₀ Variance	Percent of Total Variance						Geometric Mean	Geometric Deviation	Geometric Error	Expected 95% Range
			Between Streams	1-10 Km	100 m -1 Km	100 m -10 m	0 - 10 m	Anal. Error**				
Mo	All	.0052	73*	0.2	0	3	17	6	4.2	1.64	1.09	1.6-11.1
	Roan	.0159	-	0	13	0	87	-	3.5	1.28	-	2.1-5.7
	Black Sul.	.0365	-	15	1	0	76	8	2.9	1.41	1.09	1.5-5.6
	Piceance	.0143	-	0	0	21	79	-	4.2	1.33	-	24-7.4
	Parachute	.0044	-	5	4	0	91	-	9.5	1.14	-	7.3-12.3
	Yellow	.0215	-	38	0	4	58	-	3.3	1.34	-	1.8-5.9
Zn	All	.0066	36	18	2	3*	33*	7	61.0	1.20	1.03	28.6-129
	Roan	.0134	-	27	10	0	47	17	63.8	1.28	1.08	39.9-102
	Black Sul.	.0030	-	46	3	10	37*	4	53.3	112.	101	42.5-66
	Piceance	.0011	-	0	0	9	91*	0	67.8	1.08	100	58.1-79
	Parachute	.0012	-	14	0	37	40	9	68.9	1.06	1.02	61.3-77
	Yellow	.0036	-	30	0	9	48	14	52.5	1.13	1.04	41.7-66
Hg	All	.0614	66*	6*	0	0	20*	8	.29	1.67	1.12	.11-78
	Roan	.0162	-	8	6	0	80*	9	.58	1.27	1.07	.37-.92
	Black Sul.	.0375	-	38	0	13	43*	6	.36	144	1.08	.18-.73
	Piceance	.0214	-	11	0	25	54*	12	.23	1.35	1.09	.13-41
	Parachute	.0333	-	0	6	0	61*	33	.28	1.39	1.19	.16-.49
	Yellow	.0085	-	1	0	26	0	73	.15	1.19	1.14	.12-.19
Organic	All	.1831	69*	12*	3	0	16*	0	.19	2.47	1	.15-5.55
	Roan	.0835	-	20	6	4	71*	0	1.26	1.87	1	.36-4.41
	Black Sul.	.1416	-	50	8	0	39*	0	.79	2.01	1	.20-3.19
	Piceance	.0198	-	60	10	0	30	-	1.02	1.30	-	.60-1.72
	Parachute	.0011	-	17	43	12.4	22	5	254	1.07	1	2.22-2.9
	Yellow	.0326	-	1	22	0	76	1	.24	1.46	1	.11-.51

* Indicates variance component is significantly different from zero at the .05 probability level.

**The analytical component is included in the 0 - 10 m component.

TABLE 4. STREAM JUNCTION DATA OF PICEANCE CREEK BASIN COMPARED
WITH AVERAGE CRUSTAL AND SHALE ABUNDANCES.

Element	GM (ppm)	GD	Expected Range @ 95% Level (ppm)	5 Highest Ranked Values (ppm)	Ave. Crustal Abundance (ppm)	Ave. Shale Abundance (ppm)
Cd*	2.4	1.56	1.0 - 5.9	4,7,4.8, 4.8, 5.0, 5.9	.2	3
As	9.2	2.38	1.6 - 52	21,28,30, 36,50	1.8	6.6
Zn	60	1.34	33 - 108	70,82,83, 84,116	70	80
Hg	.33	1.50	.14 - 74	.62,.64, .65,.73, .91	.04	.40
Mo	4.7	2.14	1.0 - 21.6	11.1,11.2, 12,8,13.0, 17,7	1.5	2
Organic Carbon %	.54	2.50	.09 - 3.38			

* Treated as censored data, parameters calculated accordingly

TABLE 5. STREAM JUNCTION DATA GROUPED BY INDIVIDUAL STREAMS

	Gm (ppm)	GD	95% Expected Range
Mo			
Piceance	2.8	2.72	.3 - 20.6
Roan	5.6	1.56	2.3 - 13.2
Parachute	5.5	1.55	2.3 - 13.2
Yellow	6.7	1.42	3.3 - 13.5
Zn			
Piceance	53.8	1.22	36.1 - 80.1
Roan	66.4	1.34	37.0 - 119
Parachute	64.8	1.16	48.2 - 87.2
Yellow	53.7	1.20	37.3 - 77.3
Hg			
Piceance	.33	1.50	.15 - .73
Roan	.34	1.16	.25 - .45
Parachute	.38	1.22	.25 - .57
Yellow	.24	1.35	.12 - .46
Organic Carbon %			
Piceance	.32	2.20	.06 - 1.77
Roan	1.23	2.35	.22 - 6.80
Parachute	1.09	1.75	.36 - 3.32
Yellow	.41	1.82	.12 - 1.38

concentration in the population of individuals making up the perimeter of the basin (all samples in the Green River Formation and Wasatch Formation) as compared to the population of the interior (all samples in the Uinta Formation). There is also a significantly greater concentration of Mo, Zn, Hg and organic carbon in samples taken south of the Roan Plateau as compared to samples taken north of the plateau. This is similar to the data for Zn, Cu, Li, and Be in surface soils (6).

From this comparison, it appears that the stream junction expected (Tables 4 and 5) is a more realistic estimate than the nested expected range because it reflects a larger scale variance component and/or the between stream variance component more completely. If the result of the two sampling plans had shown the majority of the variance at the low scale level, the nested and stream junction samples could have been combined in estimating the expected range.

TRACT C-a AND VICINITY

Surface soil and plant samples of the three species discussed in the section on materials were collected in a grid pattern over an area eight miles by six miles, incorporating oil shale Tract C-a (Figure 9). This work was the subject of a thesis by Candito (10). The grid sampling interval was $\frac{1}{2}$ mile (0.8 km) which was determined as an appropriate interval from the earlier study of Ringrose and others (6). The analysis of variance sampling was done as previously described.

The trace element data exhibit a distribution that approaches lognormal, consequently geometric means and deviations are calculated for the summary statistics (Tables 6, 7). Assuming a lognormal distribution, the 95% range shown in Tables 6 and 7 can be calculated from the geometric mean and deviation.

The variance ratio (V) is used to determine the significance of the regional component of variance. The variance ratio is the ratio of the variance at the highest level (>1.6 km or 1 mi.) to the sum of the variance to all other lower levels. Due to the nature of the hierarchical model, the degrees of freedom at the highest level of the model are low, requiring a high F-value for significance. Only organic carbon and As are significant at the 0.10 probability level. With the variance ratio, the effective number of random samples, N_r per sq. mi., required for a reasonable representation of the area can be determined graphically (5).

The maximum permissible error variance for a balanced design (E_r) is the ratio of the sum of all the variances except the highest level to N_r :

$$E_r = \frac{S_{\beta}^2 + S_{\gamma}^2 + S_{\delta}^2 + S_{\epsilon}^2}{N_r} \quad (4)$$

The observed error variance, E_s is found by

$$E_s = \frac{S_{\beta}^2}{N_b} + \frac{S_{\gamma}^2}{N_b \cdot N_c} + \frac{S_{\delta}^2}{N_b \cdot N_c \cdot N_d} + \frac{S_{\epsilon}^2}{N_b \cdot N_c \cdot N_d \cdot N_e} \quad (5)$$

Figure 9. Tract C-a and vicinity.

TABLE 6. GEOMETRIC MEANS AND DEVIATIONS AND VARIANCE
RESULTS FOR TRACT C-a AND VICINITY SOILS.

Element	95% Expected Range	Geometric Mean*	Geometric Deviation*	Variance Ratio**	Variance Mean Ratio	N _r	E _r	E _s	Number Samples
Hg (ppb)	30-58	42	1.18	--	--	--	--	--	253
Zn (ppm)	39-123	70	1.33	0.02	4.17	45	0.019	0.0002	253
Li (ppm)	9-40	20	1.43	0.41	4.32	3	0.011	0.003	253
B (ppm)	78-195	123	1.26	--	--	--	--	--	253
Mo (ppm)	0.46-4.7	1.6	1.70	0.23	4.28	4	0.011	0.003	253
As (ppm)	4-18	8.7	1.43	1.36	4.40	2	0.0071	0.0048	32
Organic Carbon(%)	0.46-2.9	1.2	1.58	1.03	3.96	3	0.013	0.010	253
pH	7.1-8.5	7.8*	0.353*	--	--	--	--	--	253

* Arithmetic mean and standard deviation for pH (pH is a log measurement).

** If the estimated variance between sections is zero; V_m, N_r, E_r, E_s are not calculated.

TABLE 7. GEOMETRIC MEANS AND DEVIATIONS AND VARIANCE RATIO
RESULTS FOR TRACT C-a AND VICINITY PLANT MATERIALS.

	Element and Media	95% Expected Range	Geometric Mean	Geometric Deviation	Variance Ratio**	Variance Mean Ratio	N _r	E _r	E _s	Number of Samples
BIG SAGE	Zn (ppm)	0.43-11.	2.2	2.26	0.02	2.96	45	0.004	0.001	32
	B (ppm)	21.5-42.6	30.3	1.19	0.46	3.74	2	0.0024	0.0006	249
	Mo (ppm)	0.25-1.7	0.65	1.63	0.22	3.90	5	0.0089	0.0026	243
INDIAN RICEGRASS	Hg (ppb)	11-52	24	1.47	0.05	2.97	60	0.00059	0.00061	32
	Zn (ppm)	0.49-18	2.6	2.46	--	--	--	--	--	32
	B (ppm)	3-32	10	1.81	0.02	2.96	45	0.0004	0.0001	32
	Mo (ppm)	0.48-2.3	1.1	1.48	0.24	3.95	4	0.0068	0.0017	32
WESTERN WHEATGRASS	Hg (ppb)	7.5-70	23	1.75	--	--	--	--	--	25
	Zn (ppm)	5.1-18	9.6	1.38	--	--	--	--	--	25
	B (ppm)	7.7-28	15	1.38	--	--	--	--	--	25
	Mo (ppm)	0.54-2.4	1.2	1.45	--	--	--	--	--	25

** If the estimated variance between sections is zero; V_m, N_r, E_r, E_s are not calculated.

where N_b to N_e are the number of nested levels at each of the sub-levels of the model (4).^e If E_r is greater than E_s , the map produces the variance of the study area, at greater than 80% confidence. Most constituents analyzed in the surface soils and sage exhibit a regional variance component. Mercury, B, and soil pH have a greater proportion of the variance at more local levels and in the case of Hg, at the analytical level.

The variance mean ratio (V_m) is used to determine the stability of maps derived from the data. If V_m is equal to 1.0, gross differences can be shown and if V_m is 3.0 or greater the geochemical maps are quite stable and representative of the actual distribution (4). This also supports the stabilities of the estimated geometric means of Tables 6 and 7 and indicates the sampling design was adequate to display the variations over the study area.

Figures 10 to 12 are the results of trend surface analysis of the grid samples for Mo in all soils, Mo in Uinta derived soils, and Mo in Big sage. The trends are similar, indicating that differences in lithology and climate are additive, affecting the distribution in the same direction. By comparison of the results for Mo in Uinta derived soils and in all soils, the impact of the Parachute Creek member can be determined. Organic carbon (Figures 13, 14), and B in Big sage (Figure 15) exhibit very similar distributions with higher concentrations in the western part of the area. The combination of lithologic variation, grain size, and climatic influence contribute the major portion of the regional trends found in the analysis of variance design and displayed in the trend surface maps.

About 80% of the soil and plant samples were collected above the Uinta formation. The soil samples derived from the Parachute Creek member are located only in the western part of the study area. There is also a climatic influence, with the western area being higher in elevation, receiving more moisture, and having a thicker vegetation cover. These factors also influence the regional component of the trace element distribution.

In order to differentiate between the geologic and climatic factors, hypothesis testing was employed. The Uinta derived soil samples are distributed throughout the area and were tested for difference in means against the Parachute Creek derived samples. Essentially all the measured trace elements in soil and Big sage display significantly higher means (95% confidence) in the Parachute Creek derived soil samples. The Uinta derived samples were randomly separated into groups moving east to west across the study area. The t-tests exhibit significantly higher means within the Uinta formation in the western part of the area, suggesting a climatic influence or a trace element trend within the Uinta formation.

TRACT C-b AND VICINITY

The Tract C-b studies were carried out in a manner analogous to the Tract C-a studies and as outlined in the section on sample design. This study was the subject of a thesis by Zuccaro (11). An area five miles by nine miles was sampled on a $\frac{1}{2}$ mile grid (Figure 16). Surface soils and the three selected species of plants were collected. Four sections of the 45 sq. miles involved in the soil-plant collections were randomly selected for an analysis of variance sampling experiment. The four sections were quartered and re-quartered as in Figure 6. The surface soil and three species of plants were collected from the eight locations in each section.

Figure 10. Mo (ppm) in all surface soils.

Figure 11. Mo (ppm) in surface soils on Unita formation.

Figure 12. Mo (ppm) in Big Sage.

Figure 13. Organic carbon (%) in all surface soils.

0 1/2 1
Miles

Figure 14. Li (ppm) in all surface soils.

Miles

Figure 15. B (ppm) in Big Sage.

TO
HIGHWAY 64

PICEANCE CREEK ROAD

N

5 MILES

C - b

TO
RIO BLANCO

9 MILES

Figure 16. Soil and plant sampling area on Tract C-b and vicinity.

Stream sediments were collected at $\frac{1}{2}$ mi. (0.8 km) channel intervals from the streams and gulches in and around Tract C-b (Figure 17). The samples were composites of at least 10 m of channel. The $\frac{1}{2}$ mi. interval and compositing were determined appropriate for this area by Ringrose (7). There has not been any analytical work completed on the 232 stream sediments collected but they remain available for future reference.

The analysis of variance sampling experiment is planned prior to going into the field. The precise locations at the smallest geographic scale were selected during the field program. The final locations that were sampled were selected to have an abundance of all of the plants to be collected and was relatively flat so that soils were not colluvial, but developed in place. All samples were preferably dry when collected and if not, were air dried before storage. All soil samples were a composite of the surface soil down to one inch in depth and over a 10 m radius. They were sieved to -4 mesh in a stainless steel sieve and stored in stream sediment bags.

At least six different plants were sampled for Big sage or six bunches for the grasses were collected at each site. If there were fewer than six plants per species available at any particular site, all of the plants within a 10 m radius were sampled. When there was an abundance of plant material the sampled plants were from across the entire 10 m radius circle.

The technique used to collect soils and plants at each sample site resulted in a heterogeneous mix of materials at that site. Localized variance (0 - 10 m) that was shown to exist by Candito (10) will be reduced and is normally not of interest.

Big sage is extremely abundant in the upland sagebrush country and pinyon-juniper woodlands. Big sage is an important native plant in the C-b region. Subspecies Artemisia tridentata wyomingensis was collected at all but three sample sites. Subspecies Artemisia tridentata tridentata was collected at two of the sample sites. Both of these sites were at low elevations. The differences between the two subspecies of Big sage is difficult to determine and can only be done with certainty utilizing chromatographic techniques. However, the subspecies can be determined on the basis of morphology with about 90% certainty. A previous study by Candito (10) demonstrated no significant difference of means in the two subspecies for the trace elements studied.

Western wheat grass is an abundant grass type in the C-b area. The most common occurrence of Western wheat is in chained pinyon-juniper rangeland and mountain grasslands. Indian rice grass is sufficiently abundant for collection and is also an important food source for herbivores. Only one sample site was moved slightly due to inadequate vegetation. The collections were made in the period May - July, 1977 when the region was in an extensive drought.

As previously discussed in the section on materials and methods, the grasses were washed but the sage was not due to disintegration of the sage in the ultrasonic bath. To verify the validity of unwashed Big sage, one sample was split and washed while the other split was ground without being washed. The sample was from the ridge near Occidental's 60 m meteorological tower which is a windier location on C-b. This single sample, which was

Figure 17. Streams sampled as part of Tract C-b stream sediment collection.

analyzed in quadruplicate, indicated that soil contamination is not obvious (Table 8). Additional samples would have to be analyzed in make this conclusion certain.

Table 8. TRACE ELEMENTS IN WASHED AND UNWASHED BIG SAGE (ppm).

	Washed	Unwashed
B	22.9, 25.3	22.1, 25.5
F	4.1, 5.1	2.7, 2.9
Mo	0.5, 0.1	0.3, 0.4

Several singular and multivariate statistical tests were used in the analysis of the data, the most useful of which is the hierarchical analysis of variance. Most statistical tests require normally distributed data for rigorous application. However, most geochemical data tends to be positively skewed as is the case in this study. The data was log-transformed which changes the distribution to near normal.

A geometric deviation calculated from log-transformed data can be adjusted for analytical error. This is particularly useful in estimating a concentration range expected for a material in a large area. The adjusted geometric deviation is calculated:

$$(GD)_n = [(GD)^2 - (GE)^2]^{\frac{1}{2}} \quad (6)$$

where $(GD)_n$ is the normalized geometric deviation, GD is the geometric deviation and GE is the geometric deviation of the analytical replicates. A 95% expected range for the materials of the region can be estimated according to Miesch (4):

$$95\% \text{ Expected Range} = \frac{GM}{(GD)_n^{1.96}} - GM \cdot (GD)_n^{1.96} \quad (7)$$

The calculated mean can be adjusted for values less than the analytical detection limit, which frequently occurs in trace element data. This data is said to be left censored. The adjusted mean is calculated by:

$$\bar{X} = \bar{X}' - \lambda(\bar{X}' - X_0) \quad (8)$$

where $\bar{X}'$ is the mean of uncensored data, X_0 is the detection limit, and λ is from Cohen (12). An alternative method is to assume that all left censored data will average 70% of the lower detection limit (4). It was only necessary to apply this correction to Hg in soils where approximately 10 samples were below the detection limit. Tables 9 and 10 tabulate the geometric mean, deviation, and expected range for the Tract C-b and vicinity data.

TABLE 9. GEOMETRIC MEANS AND DEVIATIONS AND VARIANCE
RATIO RESULTS FOR TRACT C-b AND VICINITY SOILS.

Element	95% Expected Range	Geometric Mean*	Geometric Deviation*	Variance Ratio**	Variance Mean Ratio	N _r	E _r	E _s	Number of Samples
B (ppm)	73-208	136	1.28	0.0	--	--	--	--	40
F (ppm)	334-645	483	1.17	0.43	4.36	4	0.001	0.0004	58
Li (ppm)	21.4-26.2	23.8	1.20	0.54	4.23	3	0.001	0.0006	242
Hg (ppb)	16.8-26.3	21.5	2.39	0.0	--	--	--	--	243
Mo (ppm)	0-4.02	0.91	1.56	0.24	4.40	5	0.047	0.002	241
Zn (ppm)	63.1-67.7	65.4	1.16	0.42	4.39	3	0.001	0.0004	242
Organic Carbon (%)	0-6.73	1.52	2.60	0.40	4.36	4	0.020	0.008	243
pH	7.00-8.73	7.87	0.43	0.16	3.15	6	0.040	0.012	243

* Arithmetic mean and standard deviation for pH (pH is a log measurement).

** If the estimated variance between sections is zero; V_m, N_r, E_r, E_s are not calculated.

TABLE 10. GEOMETRIC MEANS AND DEVIATIONS AND VARIANCE RATIO
RESULTS FOR TRACT C-b AND VICINITY PLANT MATERIALS.

	Element and Media	95% Expected Range	Geometric Mean	Geometric Deviation	Variance Ratio	Variance Mean Ratio	N _r	E _r	E _s	Number of Samples
BIG SAGE	B (ppm)	24.7-29.6	27.1	1.22	0.13	4.32	7	0.001	0.0002	242
	Mo (ppm)	0-3.63	0.35	1.64	0.94	4.34	3	0.012	0.008	242
	F (ppm)	1.66-12.5	8.36	1.40	0.026	3.66	29	0.002	0.0003	36
INDIAN RICEGRASS	B (ppm)	2.13-17.7	9.18	1.49	1.53	4.37	2	0.007	0.005	57
	Mo (ppm)	0.03-2.16	0.97	1.64	2.21	4.39	2	1.106	0.010	55
	F (ppm)	0.0-3.08	0.75	2.81	0.78	4.40	3	0.045	0.024	56
WESTERN WHEATGRASS	B (ppm)	3.11-14.6	8.36	1.42	0.08	2.72	10	0.003	0.0008	42
	Mo (ppm)	0.28-1.16	0.52	1.39	0.38	4.39	4	0.004	0.001	40
	F (ppm)	0.0-4.81	0.82	3.83	0.61	4.37	3	0.088	0.037	43

The analysis of variance design used in this study is shown in Figure 7, which will partition the variance at five different levels. The highest level is regional variance, three are for more localized variance, and the bottom level for analytical variance. The F-test is used to determine whether the sampling intervals and grid intervals are sufficient to describe the natural variance, that is, the variance component is significantly different from zero. The variance ratio (V) is used to determine the significance of the regional component of variance as was done in the section on Tract C-a studies:

$$V = \frac{N_v}{D_v} = \frac{S_\alpha^2}{S_\beta^2 + S_\gamma^2 + S_\delta^2 + S_\epsilon^2} \quad (9)$$

where N_v is the estimated variance among mapped units and D_v is the total estimated variance between mapped units. If V is large, little sampling is required to describe the compositional differences among mapped units. When the ratio is small, more samples are required per unit area. The greatest amount of variance should be on the regional level for map stability. The number of samples per section (N_r) necessary for a stable geochemical map can be estimated graphically (4).

The maximum permissible error variance (E_s) and the observed error variance (E_s) can be estimated using equations (4) and (5). The variance mean ratio (V_m) will estimate the stability of the map:

$$V_m = S^2/E_s \quad (10)$$

The larger V_m , the more reproducible is the geochemical map. Generally, the number of samples required for a stable map is 2-4 samples per square mile. The grid sample program was 209 samples/45 sq. mi. or approximately 4.6/sq. mi. The $\frac{1}{2}$ mile grid interval was again confirmed as a reasonable balance between need and analytical capability. Tables 9 and 10 contain the variance ratio (V), variance mean ratio (V_m), the required number of samples per square mile for a stable map (N_r), the maximum permissible error variance (E_r), the observed error variance (E_s), and the number of samples analyzed at this point in time.

Figures 18-24 illustrate geochemical maps for selected constituents in various media. Tract C-b and vicinity has only rocks of the Uinta formation exposed at the surface in contrast with Tract C-a. Consequently, the observed trends are much weaker and if present are higher in the east which is down-section.

ANVIL POINTS AND VICINITY

The Anvil Points study is analogous to the Tracts C-a and C-b studies with surface soils, stream sediments, and the same three plant materials being collected over 36 square miles in the Anvil Points vicinity (Figures 25 and 26). The area is one of extreme relief, climatic variation, and a large portion of the Wasatch formation, the entire Green River formation, and the lower portion of the Uinta formation (Figure 1). The sampling of the area was done in the summer of 1978 and analytical and interpretive work is underway by Rutherford (13).

Figure 18. pH in surface soils.

Figure 19. Organic carbon (%) in surface soils.

Figure 20. Mo (ppm) in surface soils.

Figure 21. Li (ppm) in surface soils.

Figure 22. Zn (ppm) in surface soils.

Figure 23. B (ppm) in Big Sage.

Figure 24. Mo (ppm) in Big Sage.

Figure 25. Soil and plant sampling area at Anvil Points and vicinity.

Figure 26. Streams sampled as part of Anvil Points stream sediment collection.

Only the analysis of the analysis of variance samples have been completed and the interpretation is incomplete. Some preliminary general conclusions indicate the soils on the plateau are higher in organic carbon and of lower pH than the soils developed on the Wasatch formation. This is to be expected considering the climate. Trace elements in soils do not show this contrast because of the likely existence of trends within the Wasatch formation itself. Plant materials are exhibiting regional trends which have not been interpreted. Plant material is also elevated in F and Mo, relative to the C-a and C-b areas but lower concentrations of B.

The mean concentrations of the various media for selected trace elements in the 32 analysis of variance samples are compiled in Table 11. For purposes of summarizing and comparison, the Anvil Points data is compared with C-a, C-b, regional soils and rock data in Table 11.

ATMOSPHERIC DISPERSAL OF CONTAMINANTS

The estimation of the impact of atmospheric emissions of an oil shale industry on baseline soil composition has been attempted and will be improved upon in future work. The greatest uncertainty will be in the distribution of the impact on surrounding terrain. The nature of the emissions and their magnitude has more certainty, but are subject to change as processes are modified. The baseline concentrations of the selected trace elements in soils and plants is known with the most certainty. The continued availability of the baseline samples for future studies or additional determinations will allow expansion of the baseline data if necessary.

A number of studies have been made on the atmospheric dispersal of contaminants on Tracts C-a and C-b (16,17,18,19). 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. 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 on the Piceance Creek basin is the strong terrain influence on local meteorological conditions. A common situation will be the development of a strong shear and turbulence at some point up to several hundred meters above ground level. Koch and others (20) discuss plume dispersal in complex terrain. 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 establishes 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

TABLE 11. TRACE ELEMENT CONCENTRATION OF VARIOUS MATERIALS (ppm).

	Earth's ¹⁴ Crust	Average ¹⁴ Shale	Parachute ¹⁵ Creek Member	Piceance ⁶ Basin	C-a ¹⁰	C-b ¹¹	Anvil ¹³ Points
<u>Soil</u>							
F	625	500	1700	490	--	489	422
B	10	100	104	61	123	140	152
Mo	1.5	2	17	5.3	1.6	1.0	2.3
Hg	0.08	0.4	0.48	0.041	0.042	.031	0.026
Se	0.05	0.6	2	0.28	--	--	--
As	1.8	6.6	33	6.4	8.7	--	--
Zn	70	80	47	80	70	66	--
<u>Big Sage</u>							
B					30.3	27.7	22.4
F					--	6.4	14.2
Mo					0.65	0.52	0.91
Zn					2.2	--	--
<u>Western Wheat Grass</u>							
B					15	8.4	5.0
F					--	0.82	--
Mo					1.2	0.68	1.5
Zn					9.6	--	--
<u>Indian Rice Grass</u>							
B					10	9.2	5.1
F					--	0.75	--
Mo					1.1	0.97	1.9
Zn					2.6	--	--

rapid ground heating. In the winter, during snow cover, synoptic flow near ground level may not be established at all on many days.

The detailed development plans (DDP) for the tracts have exhibits of the expected particulate and gas dispersion from the sites during development and commercial phases. These were derived using the EPA Valley model and Gaussian plume dispersion. The development (C-a) or ancillary (C-b) phase has begun on both tracts. The commercial phase is expected after 1986 for C-a and after 1982 for C-b. Koch and others (20) and the tracer studies on the tract (18,19) indicate the inadequacies of the Valley Model in this case and the impact of contaminants on surrounding terrain will have to be modified to incorporate the tracer studies results.

The DDP for C-b (13) estimates particulate emission at 133 lbs/hr. for full scale operation. Utilizing data from Zuccaro (11) 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. samples, 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 (16) estimates the particulate emission at 576 lb/hr. An analogous calculation with the soil baseline data of Candito (10), results in detectable contamination in 87 years.

These calculations are quite simple but indicate there is potential for significant contamination in much shorter time when dispersal is non-uniform as is the case. The non-uniform dispersal modeling will be much more difficult and subject to considerable uncertainty. Of particular concern are the alluvial valleys downslope from the tracts. The Piceance Creek area down valley from C-b is currently under cultivation and cattle and sheep are raised in other valleys as well. Estimates for the time for significant impact will be determined for these alluvial valleys adjacent to oil shale tract operations in the next phase of the studies.

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Progress Report: 1976 - 1979

Chemical Analysis of Inputs and Outputs of Oil Shale Retorts Thomas R. Wildeman

INTRODUCTION

This is a three year summary of the accomplishments that have been made in the research program on the Chemical Analysis of Inputs and Outputs in Oil Shale Retorts headed by Thomas Wildeman from the Department of Chemistry/Geochemistry, Colorado School of Mines. Three general tasks have been pursued in this project:

1. The sampling, preparation and analysis of oil shale materials for use by all the ETSRP projects.
2. An elemental mass balance study of the Fischer assay as a bench scale retort.
3. Sampling and analysis of Paraho retort materials.

The sampling and analysis program has been going on continuously while the Fischer assay study was made early in the project and the Paraho study is the current task. During the course of the project there was a definite shift in the objectives of the research. When the study of elemental abundances in the Fischer assay was started, the primary objective was to obtain a mass for each element between the original oil shale and final products of spent shale, oil, water, and gas. It was soon discovered that almost all elements are retained in the spent shale during retorting and that this solid product comprises about 80% of the product mass (1,2). Consequently, establishing a mass balance for an element depends primarily on how precisely the concentration differences in raw and retorted shale can be determined. This conclusion is amplified in the Fischer Assay section of this report. This result brought about two changes in objectives. The first was that since accuracy and precision are so important, interlaboratory comparison of results is necessary to insure that the conclusions that are made are reliable. The second shift in objectives was to the analysis of oil shale materials to uncover the chemical relations in the feedstock and products and away from a mass balance as the primary objective. This latter objective is seen in the design of the Paraho sampling program and the conclusions that have been drawn on the studies of the Paraho solids.

PROFESSIONAL ACTIVITIES

Most of the conclusions which are contained in this progress report already have been presented in talks and papers. By the conclusion date of May 31, 1979, this project will generate 6 papers in journals and symposium proceedings (1, 2, 3, 4, 5, 6) and 5 talks at regional and national meetings (7, 8, 9, 10, 11).

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PREPARATION AND ANALYSIS OF OIL SHALE MATERIALS

This section summarizes work that started one year prior to this project when 25 kg of raw shale (OS-1) and two 10 kg fractions of spent shale (SS-1 and SS-2) were obtained from the TOSCO Co. (1, 12). The work on this project continues with the preparation of those samples for use in the various projects, the handling of the Fischer assay material (2,3), the interlaboratory study of standards (6), and the handling of the Paraho retort materials (5). Much of this portion of the project parallels the accomplishments of Dr. Meglen of the Central Analytical Lab of ETSRP. The interlaboratory studies of oil shale material especially serve as an independent quality control check on the results of the central lab.

The conclusions in this section have been developed through handling materials on this project. However, they have been corroborated in the experiences which other people have had in handling oil shale materials. Of special note in this regard are the studies of Fox at Lawrence Berkeley Labs (12) and Fruchter at Battelle Northwest Labs (13). Many of the conclusions in this section will be presented at the EPA Oil Shale Symposium in Denver in March, 1979 (5, 6, 10, 11).

This section of the progress report, as well as the sections on Fischer Assay and the Paraho Retort will have a form in which the general results and conclusions are itemized and then a discussion follows with greater substantiation of those conclusions.

CONCLUSIONS ON THE PREPARATION AND ANALYSIS OF OIL SHALE MATERIALS

Preparation of Solids

1. Concerning the crushing and grinding of oil shale, it is difficult to pulverize the rock to less than 100 mesh, and this step can add contamination to the sample.

2. The crushing of surface retorted shales poses no problems because the solids have lost much of their mechanical strength. Preparation of retorted shale samples does raise considerable dust so handling procedures should be designed so that fractions of the retorted shale are not lost.
3. Blending of raw and retorted shales is easily achieved during preparation. No unusual precautions have to be taken to insure a homogeneous sample. In fact, these samples are among the most homogeneous of geologic specimens.
4. Surface retorted shale is more homogeneous than raw shale. The retorting evidently homogenizes the rock.
5. Many of the conclusions stated for surface retorted shale will not hold for in situ retorted shale because the retorting conditions are not uniform in the latter case. Also, temperature in an in situ retort may reach the fusion temperature of the rock. The retorted shale in this case will become like basaltic cinders and grinding may become quite difficult.

Preparation of Liquids

1. Concerning the liquid products, there is a distillation of the oils and waters from solids in surface retorts so that minimal particulate matter occurs in the liquids. This makes filtration of the samples unnecessary.
2. Handling of the oils and waters cannot be done in a uniform fashion for all studies. Some studies require the liquids to be bubbled with N_2 , while others do not. Some require storage in glass, others in plastic.
3. The waters cannot be acidified since they contain appreciable thiosulfate and this decomposes at low pH's, resulting in the formation of free sulfur.
4. Water samples can be held under refrigeration and freezing for over a year without decomposition. However, once opened the water does start changing within a month.

Analysis of Solids

The results of interlaboratory analyses of raw and retorted shales have led to the following conclusions:

1. Multielement techniques that do not require sample digestion, such as x-ray fluorescence (XRF) analysis or instrumental or neutron activation analysis (INAA), provide analytical results which can undergo the rigors of interlaboratory comparisons. Such instrumental methods are almost essential to the establishment of an analytical program on oil shale.

2. Using instrumental methods, concentrations of trace elements which compare to within $\pm 10\%$ on an interlaboratory basis are capable of being achieved.
3. Consistent analyses of major elements such as Na, Al, K, and Ca are more difficult to achieve. For example, interlaboratory analyses cannot be made to agree within $\pm 10\%$ on the concentration of Ca in raw shales.
4. Of the five elements which concern this program, good interlaboratory agreement has been achieved on the concentrations of As, Se, and Mo in oil shales. For B and F, these elements are not capable of being easily analyzed by INAA or XRF and interlaboratory comparisons of analyses have not yet been achieved.
5. With regard to methods of analysis which can be considered to be less expensive, the methods which ETSRP has developed for the analysis of As, Se, and Mo are consistent with the results of the interlaboratory comparison.
6. With regard to other trace elements, interlaboratory comparisons of the concentrations of Cd and Hg have yet to be completed. On the other hand, comparisons of the concentrations of Rb and Sr are amazingly close by all methods of analysis.
7. The interlaboratory comparison program constitutes the first time that energy dispersive x-ray fluorescence (EDXRF) has been subjected to this type of analytical test. The results compare well among the different methods for EDXRF and also with INAA.

Analysis of Liquids

1. Interlaboratory comparisons of analyses on oil and water have been attempted. These analyses appear to be less consistent. Oil results are more consistent than those for water.
2. A method for analysis of oils by EDXRF has been developed. It gives results on the concentrations of trace elements in NBS fuel oil which are consistent with the certified values. It is capable of the analysis of Fe, As, and Se in shale oils. The same technique is now being used for the analysis of retort waters.

DISCUSSION

Preparation of Solids

Conclusion 1 on crushing requires the attention of research groups. When being pulverized, if too much time is spent in the grinder, oil shale can become heated. Disk pulverizers are unacceptable for sample grinding because they can become fouled with shale materials. Currently, this project uses a SPEX shatter box for pulverizing. If the grinding chamber is to be used for over 5 minutes, it is first cooled in a freezer. Concerning

contamination, the abundances of trace elements in oil shale are low enough that this is possible for grinding and sieving equipment. Table 1 compares the concentrations of elements in our standard oil shale (OS-1) with estimates of the concentrations that can occur in the worst cases of contamination from grinding in a shatter box (14, 15). No sieves should be used; instead, grinding tests should be made on spare amounts of raw shale. Alumina is not dense enough to crush small shale particles; tungsten carbide is expensive. Thus, hardened steel seems a reasonable grinding surface. In the worst case, it could add 10% to the concentration of Ni and Mn, and 5% to Fe, Cu, and Mo (16).

TABLE 1. CONCENTRATIONS OF ELEMENTS IN OIL SHALE OS-1 COMPARED WITH ESTIMATES OF CONTAMINATION FROM GRINDING AND SIEVING MATERIALS. ALL CONCENTRATIONS ARE IN PPM.

Element	ROCK		CONTAMINANTS		
	Oil Shale OS-1	Sieve Stainless Steel	Grinding Materials		
			Tungsten Carbide	Alumina	Hardened Steel
Al	34000		60	5000	
Ti	1400			30	
V	130		6		2
Cr	40			20	
Mn	270	3			50
Fe	19000	20	300	60	500
Co	12		150	60	
Ni	30	3			20
Cu	50		5		10
Ga	10			80	
Mo	30				5

Conclusion 2 on the dust raised from retorted shale becomes important when the element concentration levels in the Paraho retorted shale bag house dust are considered. In the Paraho Retort section the conclusion is made that Ni, Cu, Zn, As, Mo, and Pb are definitely higher in Paraho retorted shale dust than in the bulk retorted shale. If this is because certain phases are more prone to dusting, then segregation can occur by raising considerable dust while handling retorted shale.

Concerning the homogeneity of oil shale, it is remarkable how uniform it is. Table 2 contains the results of analyses for Rb and Sr in raw shale (OS-1) and retorted shale (SS-2) by x-ray fluorescence. The remarkable feature in the numbers is that the method which uses only 300 ug of sample gives results which have uncertainties similar to those of the method which used 0.500 g (3). Most analytical chemists would refuse to accept a 300 ug split as a representative portion of the sample. In the case of oil shale, it appears that it is representative. Note that in the relative standard deviations there is a hint that retorted shale gives more certain concentration values than raw shale. This indication of retorted shale being more homogeneous than raw shale was confirmed when the concentrations of elements in Paraho materials were examined. The element concentration for Paraho raw and retorted shale in Tables 12 and 15 show that the concentration ranges and relative standard deviations for most elements in retorted shale are lower than in raw shale. Surface retorts homogenize the solid materials.

TABLE 2. RESULTS OF HOMOGENEITY TESTS FOR Rb AND Sr ON THE STANDARD SHALE AND A SPENT SHALE.

	<u>Raw Shale</u>		<u>Spent Shale</u>	
	0.500 g	300 ug	0.500 g	300 ug
Target Size				
Number of Samples	8	6	8	6
Average for Sr (ppm)	584	584	771	735
Std dev for Sr (ppm)	24	90	17	23
Rel Std Dev for Sr (%)	4.1	15	2.2	3.1
Average for Rb (ppm)	60.1	63.3	80.7	93.4
Std Dev for Rb (ppm)	2.7	1.9	1.5	4.4
Rel Std Dev for Rb (%)	4.5	3.0	1.9	4.8

Preparation of Liquids

This area of sample handling is still not firmly established. During the sampling of the Paraho retort the uncertainty in how to handle liquids was great enough that for both the oils and waters, four procedures were used. A number of splits were made of the sample and some were bubbled with N₂, some were not; some were refrigerated, some were not. The differences in these oil and water samples will hopefully yield the best manner of preservation of the liquids.

Some results have been accumulated on the waters and they are summarized in Table 24 in the Paraho Section of this report. The conclusions made on the liquids are valid and require some comment.

Conclusion 1 on the distillation is an important advantage in sampling surface retort liquids. Filtering the water using methods such as pressure filtration through Millipore filters can cause precipitation of some constituents (17). Filtering oil typically requires vacuum or pressure methods and this may cause the loss of volatile constituents. When the Fischer assay oil was filtered, there was no residue in 600 mL of oil. The same was true of the water. These observations held true for the Paraho liquids. Concerning the separation of the two liquids, the oil predominates over the water by a ratio of 10 to 1 and the separation is clean. A good oil sample is easily procured. The water usually has oil in it. This can be stripped from the water by cooling the mixture to just above freezing and filtering through cotton. The solid particles of oil are easily trapped.

Conclusion 2 on handling and storage has to be addressed in any analysis program. In the Paraho program it appeared that our four handling procedures of refrigerated, frozen, N_2 bubbled and refrigerated, and N_2 bubbled and frozen would be sufficient. However, some analysts felt that some splits should have been stored in glass for the analysis of organics in water and for Hg in liquids. Dr. Sievers' group has shown that even in virgin polyethylene that has been rinsed in HNO_3 some plasticizers can be leached from the bottle (18). Fruchter of Battelle routinely stores liquids for mercury analysis in specially prepared glass bottles. The obvious conclusion is that preparation and storage of a liquid sample dictates the analyses that can be performed on the sample.

Conclusion 3 was observed when Fischer assay water was acidified. Leenheer and Stuber (19) first confirmed that $S_2O_3^{2-}$ was a major constituent in the water and that it would disproportionate with elemental sulfur precipitating when the water was acidified. From Table 24 it can be seen that $S_2O_3^{2-}$ ranges from 0.1 to 26 mg/mL as elemental S. A concentration of 26 mg/mL is a 0.41 molar solution of $S_2O_3^{2-}$. At first the restriction of not acidifying is disconcerting because this is a standard method of assuring that trace metals are stabilized in solution (20). However, the dissolved solids level in these waters is high, the pH is stabilized by NH_4HCO_3 in solution, and the oxidizing capacity is stabilized by the $S_2O_3^{2-}/SO_4^{2-}$ oxidation-reduction couple. Consequently, little aging occurs as long as the sample is refrigerated.

The bases for conclusion 4 are the results on the Paraho waters in Table 24. It appears that freezing preserves the pH and Eh values better than refrigeration. The deterioration of the waters after opening can be observed in the consistent rise in the conductivity after one month of being opened. In this case, the first set of analyses were performed and the waters were returned to the refrigerator, then the analyses were repeated about 30 days later.

Analysis of Solids

An interlaboratory program of analysis of oil shale materials has been conducted by this project in conjunction with Phyllis Fox of Lawrence Berkeley Labs and Jon Fruchter of Battelle Northwest Labs. The

program began as a comparison of instrumental neutron activation analysis (INAA) and energy dispersive x-ray fluorescence (EDXRF) methods. Now it has included colorimetric and flame methods. The first report on the results of the analysis program will be given at the EPA Oil Shale Symposium in Denver in March, 1979 (6, 10). The following is a summary of the methods of analysis used by the Colorado group.

The Central Analytical Laboratory of the Environmental Trace Substances Program concentrates on the development and use of methods which do not require large investments in capital equipment and would, therefore, be accessible to most reasonably equipped chemical laboratories (21). For example, in the column under other methods, the analysis of Se was by a fluorometric method which used diaminonaphthalene (22), the analysis for Mo was by a colorimetric method which used potassium thiocyanate (23), the analysis for B was by a colorimetric method which used Azomethine-H (24), and the analysis of F is by molecular absorption of AlF in a flame (25). In all these methods, the fusion or digestion of the sample has been published (3), but some of these have been revised so that the loss of volatiles is reduced.

The x-ray fluorescence method used for the trace element analyses is an energy dispersive type. An outline of the procedure has been published for solids (26) and for liquids (2). It differs from the Berkeley and Battelle methods in two areas. First, it is set up for the analysis of thin films so that only 300 ug of solid material is used for an analysis. Second, since thin films are used, concentrations of the elements in a sample are determined directly from calibrations made on thin films of that element and not on secondary standards such as U.S.G.S. standard rocks. So, the comparison of x-ray fluorescence results in the tables really is a test of usefulness of this technique by a number of different procedures.

The instrumental neutron activation analyses (INAA) were performed on a service basis by the reactor facility of the U.S. Geological Survey at the Denver Federal Center. The procedures used are quite similar to those used by Berkeley and Battelle. The one difference that can be seen in this procedure was that it was estimated that the abundance of Na in oil shale would be high enough to mask the As gamma rays. Consequently, an attempt at determining the concentration of As by measuring the intensity of gamma rays from the As^{76} was not done at 2 days after irradiation. Rather, the first count was taken at 7 days after irradiation. The Battelle and Berkeley results show that the As concentration in oil shale is high enough that analysis by INAA is possible. A description of the INAA method used by the U.S.G.S. has been published (27). In addition to the typical INAA analyses, the concentration of uranium in the oil shales was determined by a delayed neutron activation analysis method (28). The results of the interlaboratory comparison program for the TOSCO shale materials OS-1, SS-1, SS-2, and the Fischer assay spent shale (FASS) are presented in Tables 3, 4, 5, and 6. These tables were prepared by Phyllis Fox, who acts as the secretary of the program. A discussion of the conclusions of the interlaboratory comparison follows.

TABLE 3. ELEMENTAL COMPOSITION OF DOW MINE RAW SHALE (OS-1).

	Neutron Activation Analysis			X-ray Fluorescence Spectrometry				Other		
	(A)	(B) (2)	(C) (3)	High Energy (A)	High Energy (B) (1)	High Energy (D) (6)	Low Energy (B) (1)	(A)	(B)	(D)
Al (Z)	-	3.41±0.12	-	-	-	-	3.4±0.2	3.4±0.3 ^a	-	3.5±0
As	77±1	77±6	-	65±5	65±3	64±6	-	-	-	75±6
B	-	-	-	-	-	-	-	77±88	-	110±25 ^c
Ba	-	1225±47	1410±60	-	-	-	-	-	-	-
Br	-	-	-	-	<1.5	-	-	-	-	-
Ca (Z)	-	10.1±0.5	-	10.3±0.7	-	7.9±1.3	9.0±0.4	9.9±0.5 ^a	-	7.3±0
Cd	-	-	-	-	-	-	-	-	1.05±0.11 ^b	-
Ce	-	36±2	34±2	-	-	-	-	-	-	-
Cl	-	<700	-	-	-	-	-	-	-	-
Co	9.2±0.2	10.8±0.3	18±5	-	<30	-	-	-	-	-
Cr	28±1	35±2	46±7	-	-	-	-	-	-	-
Cs	-	4.49±0.34	4.4±0.2	-	-	-	-	-	-	-
Cu	-	-	-	49±5	52±4	44±2	-	-	-	-
Dy	-	1.87±0.11	2.4±0.2	-	-	-	-	-	-	-
Eu	0.49±0.04	0.54±0.02	0.54±0.01	-	-	-	-	-	-	-
F	-	-	-	-	-	-	-	-	-	-
Fe (Z)	1.87±0.02	1.89±0.06	1.87±0.03	1.95±0.31	1.88±0.07	1.5±0.2	1.8±0.1	1.94±0.31 ^a	-	1020±100 ^g
Ga	-	-	-	8.7±1.1	8.1±0.2	3.7±0.4	-	-	-	-
Ce	-	-	-	-	2.8±1.6	-	-	-	-	-
Hf	-	1.44±0.12	1.45±0.03	-	-	-	-	-	-	-
Hg	-	-	-	-	-	-	-	0.14±0.007 ^a	0.16±0.02 ^b	-
In	-	<0.20	-	-	-	-	-	-	-	-
Ir	-	<0.01	-	-	-	-	-	-	-	-
K (Z)	-	1.36±0.13	1.33±0.06	1.25±0.01	-	-	1.2±0.1	1.17±0.11 ^a	1.20±0.01 ^f	-
La	18.4±0.4	18.8±0.8	19±1	-	-	-	-	-	-	-
Lu	-	0.16±0.02	0.20±0.02	-	-	-	-	-	-	-
Mg (Z)	-	2.3±1.1	-	-	-	-	2.6±0.1	2.60±0.1 ^a	-	2.7±0.
Mn	-	275±9	272±14	262±22	258±26	196±16	-	290±70 ^a	-	-
Mo	-	32±4	-	27±2	-	29±2	-	-	-	26±2 ^c
Na (Z)	1.31±0.01	1.40±0.04	1.47±0.06	-	-	-	1.4±0.1	1.46±0.2 ^a	-	1.54±0.
Nb	-	-	-	-	-	4.5±0.2	-	-	-	-
Nd	-	16±4	15±1	-	-	-	-	-	-	-
Ni	32±3	30±4	-	33±4	26±5	25±1	-	-	-	-
Pb	-	-	-	32±3	30±3	28±1	-	-	29±2 ^b	-
Pb	72±4	80±8	68±2	72±5	65±3	68±3	-	-	-	-
Sb	2.6±0.1	3.2±0.2	3.2±0.1	-	-	-	-	-	-	-
Sc	4.5±0.1	5.16±0.16	5.0±0.1	-	-	-	-	-	-	-
Se	4.2±0.3	-	-	4.6±0.6	4.1±1.0	-	-	-	-	3.5±0.
Si (Z)	-	-	-	13.5±1.0	-	-	13.0±0.6	13.5±1.0 ^a	-	13.0±0.
Sm	3.0±0.4	2.49±0.11	2.7±0.1	-	-	-	-	-	-	-
Sr	653±	-	650±40	-	595±23	620±10	-	660±60 ^a	-	-
Ta	-	0.39±0.02	2.0±0.6	-	-	-	-	-	-	-
Tb	-	0.28±0.05	0.33±0.03	-	-	-	-	-	-	-
Th	4.6±1	5.17±0.20	4.8±0.1	-	6.0±2.0	-	-	-	-	-
Ti (Z)	-	0.13±0.05	-	0.18±0.01	0.14±0.02	-	0.11±0.01	0.14±0.03 ^a	5.35±0.21 ^f	-
U	-	4.54±0.18	6.1±0.5	-	-	-	-	-	4.24±0.07 ^f	5.4±0.
V	-	127±30	-	-	-	-	-	-	-	-
W	-	2.8±0.4	-	-	-	-	-	-	-	-
Y	-	-	-	8.2±1.0	7.8±1.6	8.3±0.4	-	-	-	-
Yb	-	1.04±0.04	1.0±0.1	-	-	-	-	-	-	-
Zn	91±5	-	-	72±6	74±4	70±5	-	-	91±9 ^b	-
Zr	-	-	63±2	54±7	-	49±1	-	-	-	-

A - Battelle Pacific Northwest Laboratory
 B - Lawrence Berkeley Laboratory
 C - U.S. Geological Survey
 D - University of Colorado

a - atomic absorption spectroscopy
 b - Zeeman atomic absorption spectroscopy
 c - colorimetric
 d - fluorometric
 e - delayed neutron
 f - gamma-ray spectrometry
 g - plasma emission spectroscopy

TABLE 4. ELEMENTAL COMPOSITION OF FISCHER ASSAY SPENT SHALE (FASS).

	Neutron Activation Analysis			X-ray Fluorescence Spectrometry				Other		
	(A)	(B) (2)	(C) (2)	High Energy (A)	High Energy (B) (1)	High Energy (D) (6)	Low Energy (B) (1)	(A)	(B)	(D)
Al (Z)	-	4.05±0.13	-	-	-	-	4.0±0.2	4.04±0.25 ^a	-	4.2±0
As	91±1	89±8	-	86±6	79±3	79±3	-	-	-	87±4
B	-	-	-	-	-	-	-	91±9 ^g	-	145±1
Ba	-	1761±55	1940±50	-	-	-	-	-	-	-
Br	-	-	-	-	<1.8	-	-	-	-	-
Ca (Z)	-	12.2±0.6	-	13.3±1.0	-	9.7±1.2	10.8±0.5	12.7±0.5 ^a	-	9.3±0
Cd	-	-	-	-	-	-	-	-	1.28±0.13	-
Ce	-	44±2	41±1	-	-	-	-	-	-	-
Cl	-	<1355	-	-	-	-	-	-	-	-
Co	11.0±0.2	13.1±0.4	15.8±0.2	-	<34	-	-	-	-	-
Cr	34±1	43±2	52±8	-	-	-	-	-	-	-
Cs	-	5.65±0.42	5.6±0.1	-	-	-	-	-	-	-
Cu	-	-	-	68±7	66±5	47±1	-	-	-	-
Dy	-	2.28±0.12	2.7±0.1	-	-	-	-	-	-	-
Eu	0.58±0.02	0.65±0.03	0.68±0.01	-	-	-	-	-	-	-
F	-	-	-	-	-	-	-	-	-	1420±200 ^f
Fe (Z)	2.23±0.04	2.34±0.07	2.36±0.02	2.5±0.3	2.42±0.09	1.8±0.2	2.2±0.1	2.68±0.31 ^a	-	-
Ga	-	-	-	10.7±1.3	8.4±2.0	4.6±0.1	-	-	-	-
Ge	-	-	-	-	-	-	-	-	-	-
Hf	-	1.78±0.14	1.82±0.04	-	-	-	-	-	-	-
Hg	-	-	-	-	<3.9	-	-	0.041±0.001 ^a	0.035±0.003 ^b	-
In	-	<0.21	-	-	-	-	-	-	-	-
Ir	-	<0.01	-	-	-	-	-	-	-	-
K (Z)	-	1.51±0.14	1.54±0.02	1.6±0.1	-	-	1.5±0.1	1.41±0.11 ^a	-	1.52±0
La	21.0±0.4	22.0±0.9	23±1	-	-	-	-	-	-	-
Lu	-	0.15±0.02	0.16±0.01	-	-	-	-	-	-	-
Mg (Z)	-	3.0±1.3	-	-	-	-	3.1±0.2	3.2±0.1 ^a	-	2.94±0
Mn	-	339±11	340±10	370±30	351±32	224±25	-	375±70 ^a	-	-
Mo	-	38±5	-	39±3	-	36±2	-	-	-	28±2
Na (Z)	1.62±0.01	1.74±0.05	1.76±0.02	-	-	-	1.8±0.1	1.67±0.10 ^a	-	1.90±0
Nb	-	-	-	-	-	5.6±0.2	-	-	-	-
Nd	-	19±4	18±1	-	-	-	-	-	-	-
Ni	38±0	33±5	-	41±5	33±6	29±3	-	-	-	-
Pb	-	-	-	43±4	38±3	37±3	-	-	32±8 ^b	-
Rb	91±0	97±10	87±2	81±6	82±3	86±1	-	-	-	-
Sb	3.6±0.1	3.8±0.2	4.1±0.2	-	-	-	-	-	-	-
Se	5.3±0.1	6.35±0.20	6.2±0.1	-	-	-	-	-	-	-
Si	5.2±0.3	-	-	-	4.9±1.0	-	-	-	-	4.3±0
Sm (Z)	-	-	-	16.1±1.0	-	-	15.6±0.8	16.3±1.2 ^a	-	15.7±0
Sr	3.6±0.2	3.01±0.13	3.3±0.1	-	-	-	-	-	-	-
Ta	790±0	-	860±50	810±60	770±30	771±40	-	-	-	-
Tb	-	0.47±0.02	1.18±0.06	-	-	-	-	-	-	-
Ti	-	0.35±0.06	0.46±0.02	-	-	-	-	-	-	-
Th	5.4±1.0	6.35±0.25	5.9±0.1	-	7.2±2.2	-	-	-	-	-
Tl (Z)	0.23±0.04	0.15±0.06	-	-	0.16±0.02	-	0.13±0.02	-	-	-
U	-	5.38±0.22	7±1	-	-	-	-	-	-	6.4±0
V	-	161±36	-	-	-	-	-	-	-	-
W	-	3.1±0.4	-	-	-	-	-	-	-	-
Y	-	-	-	12.6±1.9	12±2	10.2±0.7	-	-	-	-
Yb	-	1.25±0.05	1.3±0.1	-	-	-	-	-	-	-
Zn	109±0	-	-	96±9	92±4	72±3	-	-	103±10 ^b	-
Zr	-	-	110±20	72±10	-	61±2	-	-	-	-

A = Battelle Pacific Northwest Laboratory

B = Lawrence Berkeley Laboratory

C = U.S. Geological Survey

D = University of Colorado

a = atomic absorption spectroscopy

b = Zeeman atomic absorption spectroscopy

c = colorimetric

d = fluorometric

e = delayed neutron

f = gamma-ray spectrometry

g = plasma emission spectroscopy

TABLE 5. ELEMENTAL COMPOSITION OF TOSCO II SPENT SHALE FROM RUN 1 (SS-1).

	Neutron Activation Analysis			X-ray Fluorescence Spectrometry				Other		
	(A)	(B) (2)	(C) (2)	High Energy (A)	High Energy (B) (1)	High Energy (D) (6)	Low Energy (B) (1)	(A)	(B)	(D)
Al (Z)	-	3.52±0.28	-	-	-	-	3.8±0.2	3.60±0.34 ^a	-	3.6±0
As	11±6	72±6	-	60±5	63±2	72±5	-	-	-	74±5
B	-	-	-	-	-	-	-	97±10 ^g	-	140±25
Ba	-	5909±201	7200±380	-	-	-	-	-	-	-
Br	-	-	-	<1.1	<1.8	-	-	-	-	-
Ca (Z)	-	13.6±0.7	-	16.3±1.0	-	14.2±0.9	12.5±0.6	14.9±0.5 ^a	-	-
Cd	-	-	-	-	-	-	-	-	0.41±0.04 ^b	-
Ce	-	41±2	35±1	-	-	-	-	-	-	-
Cl	-	<1280	-	-	-	-	-	-	-	-
Co	9.0±0.3	11.0±0.4	13±1	-	37±23	-	-	-	-	-
Cr	28±2	36±2	42±4	-	-	-	-	-	-	-
Cs	-	4.24±0.32	4.2±0.1	-	-	-	-	-	-	-
Cu	-	-	-	55±5	48±5	42±3	-	-	-	-
Dy	-	1.94±0.11	2.4±0.2	-	-	-	-	-	-	-
Eu	0.50±0.03	0.63±0.03	0.61±0.01	-	-	-	-	-	-	-
F	-	-	-	-	-	-	-	-	-	1580±200
Fe (Z)	2.00±0.08	2.19±0.06	2.07±0.02	2.34±0.16	2.20±0.08	1.9±0.1	2.0±0.4	2.3±0.3 ^a	-	-
Ga	-	-	-	8.5±1.2	10±2	4.2±0.6	-	-	-	-
Ge	-	-	-	-	4.1±1.8	-	-	-	-	-
Hf	-	1.46±0.12	1.55±0.04	-	-	-	-	-	-	-
Hg	-	-	-	-	<4.2	-	-	0.058±0.004 ^a	0.053±0.005 ^b	-
In	-	<0.14	-	-	-	-	-	-	-	-
Ir	-	<0.01	-	-	-	-	-	-	-	-
K (Z)	-	1.24±0.13	1.35±0.02	1.47±0.12	-	-	1.3±0.1	1.24±0.11 ^a	1.32±0.01 ^f	1.3±0
La	18.3±0.6	20.3±0.8	20±1	-	-	-	-	-	-	-
Lu	-	0.14±0.02	0.15±0.01	-	-	-	-	-	-	-
Mg (Z)	-	4.0±1.8	-	-	-	-	3.4±0.2	3.6±0.1 ^a	-	-
Mn	-	316±11	330±10	333±26	307±33	260±25	-	330±70 ^a	-	-
Mo	-	32±4	-	-	-	30±2	-	-	-	26±2
Nb (Z)	1.59±0.04	1.70±0.05	1.80±0.03	-	-	-	1.9±0.1	1.58±0.10 ^a	-	1.86±0
Nb	-	-	-	56±8	-	4.6±0.4	-	-	-	-
Nd	-	14±3	16±1	-	-	-	-	-	-	-
Ni	32±2	30±4	-	30±4	27±6	29±2	-	-	-	-
Pb	-	-	-	28±3	28±3	30±3	-	-	-	-
Rb	74±7	84±9	76±2	73±5	72±3	77±5	-	-	-	70.2±2
Sb	2.3±0.1	2.6±0.2	2.65±0.04	-	-	-	-	-	-	-
Sc	4.7±0.1	5.62±0.18	5.5±0.1	-	-	-	-	-	-	-
Se	4.7±0.3	-	-	3.9±0.6	4.7±1.2	-	-	-	-	3.4±0
Si (Z)	-	-	-	14.5±1.0	-	-	14.6±0.7	14.5±1.0 ^a	-	14.3±0
Sm	3.1±0.1	2.74±0.12	2.9±0.1	-	-	-	-	-	-	-
Sr	1011±45	-	1120±20	980±70	960±38	980±69	-	990±60 ^a	-	1006±2
Ta	-	0.42±0.02	1.1±0.1	-	-	-	-	-	-	-
Tb	-	0.26±0.06	0.40±0.01	-	-	-	-	-	-	-
Th	4.7±0.1	5.83±0.23	5.2±0.1	-	5.8±2.2	-	-	-	5.19±0.20 ^f	-
Ti (Z)	-	0.12±0.07	-	0.20±0.02	0.12±0.02	-	0.18±0.02	-	-	-
U	-	4.84±0.20	6.9±1	-	-	-	-	-	4.58±0.06 ^f	5.5±0
V	-	108±30	-	-	-	-	-	-	-	-
W	-	2.5±0.3	-	-	-	-	-	-	-	-
Y	-	-	-	11±2	12±2	10.3±0.7	-	-	-	-
Yb	-	1.10±0.04	1.05±0.13	-	-	-	-	-	-	-
Zn	96±4	-	-	82±5	75±4	73±5	-	-	-	-
Zr	-	-	61±6	-	-	62±7	-	-	-	-

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a - atomic absorption spectroscopy
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TABLE 6. ELEMENTAL COMPOSITION OF TOSCO II SPENT SHALE FROM RUN 2 (SS-2).

	Neutron Activation Analysis			X-ray Fluorescence Spectrometry				Other		
	(A)	(B) (2)	(C) (2)	High Energy (A)	High Energy (B)	High Energy (D) (6)	Low Energy (B)	(A)	(B)	(D)
Al (Z)	-	4.22±0.14	-	-	-	-	-	4.12±0.31 ^a	-	4.3±0.
As	88±6	90±7	-	77±6	74±3	80±3	-	-	-	86±4
B	-	-	-	-	-	-	-	101±10 ^g	-	146±1
Ba	-	1454±47	1700±40	-	-	-	-	-	-	-
Br	-	-	-	<1.4	2.8±1.2	-	-	-	-	-
Ca (Z)	-	11.5±0.5	-	11.5±0.8	-	9.9±0.3	-	12.3±0.4 ^a	-	-
Cd	-	-	-	-	-	-	-	-	0.98±0.09 ^b	-
Ce	-	46±3	41±1	-	-	-	-	-	-	-
Cl	-	<1125	-	-	-	-	-	-	-	-
Co	12±0.3	14.0±0.4	16.4±0.4	-	<34	-	-	-	-	-
Cr	34±2	41±2	52±3	-	-	-	-	-	-	-
Cs	-	6.10±0.45	5.9±0.2	-	-	-	-	-	-	-
Cu	-	-	-	72±6	62±5	52±3	-	-	-	-
Dy	-	2.35±0.13	2.7±0.1	-	-	-	-	-	-	-
Eu	0.57±0.03	0.68±0.03	0.68±0.01	-	-	-	-	-	-	-
F	-	-	-	-	-	-	-	-	-	1490±200
Fe (Z)	2.36±0.08	2.50±0.07	2.44±0.04	2.46±0.17	2.5±0.1	2.0±0.04	-	2.46±0.28 ^a	-	-
Ga	-	-	-	9.2±1.2	8.6±2.0	-	-	-	-	-
Ce	-	-	-	-	3.3±1.8	-	-	-	-	-
Hf	-	1.84±0.15	1.86±0.04	-	-	-	-	-	-	-
Hg	-	-	-	-	<3.9	-	-	-	0.045±0.005 ^b	-
In	-	<0.22	-	-	-	-	-	-	-	-
Ir	-	<0.01	-	-	-	-	-	-	-	-
K (Z)	-	1.46±0.14	1.46±0.06	1.50±0.11	-	-	-	1.5±0.1 ^a	1.58±0.01 ^f	1.66±0.
La	21±0.6	22.5±0.9	23±1	-	-	-	-	-	-	-
Lu	-	0.16±0.02	0.18±0.01	-	-	-	-	-	-	-
Mg (Z)	-	4.5±2.0	-	-	-	-	-	3.4±0.1 ^a	-	-
Mn	-	335±11	330±20	310±26	335±31	243±7	-	360±50 ^a	-	-
Mo	-	41±5	-	-	-	38±1	-	-	-	30±3
Na (Z)	1.63±0.04	1.73±0.05	1.80±0.08	-	-	-	-	1.69±0.10 ^a	-	1.86±0.
Nb	-	-	-	-	-	6.0±0.6	-	-	-	-
Nd	-	18±4	18±1	-	-	-	-	-	-	-
Ni	38±7	36±5	-	33±4	33±6	31±2	-	-	-	-
Pb	-	-	-	42±4	42±3	39±1	-	-	-	-
Rb	105±4	100±10	90±2	92±4	85±3	91±3	-	-	-	-
Sb	3.4±0.1	3.8±0.2	3.9±0.1	-	-	-	-	-	-	-
Sc	5.4±0.1	6.48±0.20	6.2±0.1	-	-	-	-	-	-	-
Se	5.5±0.3	-	-	4.2±0.6	5.5±1.2	-	-	-	-	4.4±0.
Si (Z)	-	-	-	14.5±1.2	-	-	-	15.9±1.0 ^a	-	16.0±0.
Sm	3.6±0.1	3.05±0.14	3.4±0.1	-	-	-	-	-	-	-
Sr	798±45	-	830±40	780±60	739±29	750±22	-	780±60 ^a	-	-
Ta	-	0.48±0.02	1.3±0.1	-	-	-	-	-	-	-
Tb	-	0.34±0.06	0.42±0.03	-	-	-	-	-	-	-
Th	5.4±0.1	6.29±0.25	5.6±0.5	-	7.3±2.2	-	-	-	6.27±0.20 ^f	-
Ti (Z)	-	0.15±0.06	-	0.20±0.02	0.19±0.02	-	-	0.23±0.04 ^a	-	-
U	-	5.76±0.23	8±1	-	-	-	-	-	5.90±0.06 ^f	6.6±0.
V	-	148±33	-	-	-	-	-	-	-	-
W	-	3.4±0.4	-	-	-	-	-	-	-	-
Y	-	-	-	12±2	12±2	10.6±0.1	-	-	-	-
Yb	-	1.32±0.05	1.2±0.1	-	-	-	-	-	-	-
Zn	126±4	-	-	110±5	103±4	82±11	-	-	-	-
Zr	-	-	75±2	60±6	-	68±5	-	-	-	-

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Concerning conclusions 1 and 2, as a rule of thumb interlaboratory comparisons of $\pm 10\%$ are about the best that can be expected for the concentrations of most trace elements when INAA is used as the instrumental method (29). In most cases, the group that develops the method is actively involved in the comparison program. In the case of the ETSRP and LBL groups, the instrumental analyses were done by other research groups on a client basis. The degree of comparison of these instrumental methods is remarkable. For INAA the results from all three groups are generally within $\pm 5\%$ for Cs, Eu, Fe, Hf, K, La, Mn, Na, Ni, Sb, and Yb. For EDXRF the results are generally within 5% for As, Fe, Ni, Pb, Rb, Sr, and Y. The comparison between INAA and EDXRF is also close for Fe, Mn, Ni, Rb, and Sr. Such close agreement has really put the elemental analysis of oil shale on a strong footing. Without this agreement the other conclusions which result from the interlaboratory comparison would be difficult to make.

Conclusion 3 is curious. It may be the result of the emphasis on trace element analysis over the last decade. This point was first mentioned in the element balance paper where the poor results for the concentrations of K and Fe as determined by different methods were noted (3). The point is that analyses for major elements are often less precise than those for trace elements. A scan of calcium concentrations in OS-1 provides a vivid example. In addition to the results in Table 3, Ca assayed at 7.3% in OS-1 by a wavelength dispersive XRF method.

Calcium is the structural cation in calcite and dolomite which are 2 major minerals in oil shale. Its concentration is of importance to energy balance determinations within retorts because calcite is one of the first minerals to decompose when the temperature of the retort is raised above 500 °C. In spite of this, the concentration of Ca in oil shale cannot be determined to an accuracy of better than $\pm 10\%$ at this time.

An interesting turn of events has occurred with regard to the assay of the major elements by INAA and EDXRF. Originally, these methods were developed for the analysis of trace elements and major elements such as Na, K, and Fe were by-products of the method. In the case of oil shale, INAA and EDXRF have been used to establish reliable concentrations of Na, K, and Fe so that spurious results determined by more traditional methods can be eliminated.

The five elements on which the ETSRP oil shale program concentrates are B, F, As, Se, and Mo. Conclusions 4 and 5 concern these elements. First, with regard to the comparison results, good interlaboratory comparisons are possible for As, Se, and Mo. Values for these three elements were generated by both INAA and EDXRF. The results typically compare to within 5% for Se and Mo and $\pm 10\%$ for As. Conclusion 5 contains one of the important objectives of our analytical program. INAA and EDXRF methods are not generally available. More reasonable methods have to be developed for these trace elements. The methods which Dr. Meglen has developed for As, Se, and Mo give concentrations which compare well with the instrumental methods (22, 23, 25). The results of our analyses can be considered to be reliable in every respect. Concerning B and F, an interesting situation develops. These two elements are incapable of being analyzed by INAA and XRF.

Battelle has developed a plasma emission spectroscopy method for the analysis of boron. Our assays and theirs still need development to make the comparison within 10%. Concerning fluorine, the ETSRP lab is the only one routinely reporting fluorine concentrations in oil shale materials.

An analysis of the results from the interlaboratory program also shows two other elements that require methods development; these are cadmium and mercury. These elements also are not capable of analysis by INAA and EDXRF. Berkeley is the only lab that has established methods for both elements. In the Fischer Assay and Paraho sections the importance of the behavior of these two elements will be discussed. In this year's research proposal development of methods of analysis for Cd and Hg at ETSRP is an important objective.

On the other hand, a scan of the results on Rb and Sr shows remarkable agreement between the INAA and XRF methods. These elements are also easily analyzed by atomic absorption spectrometry. A survey of Table 1 on the homogeneity results and Tables 12 and 15 on the Paraho results confirms the precision by which the two elements can be analyzed. Also, the mass balance results generally show that Rb and Sr remain immobilized in the spent shale during retorting. Consequently, these elements are good benchmark elements. If comparisons are to be made to determine if other elements are mobilized or lost during retorting, Rb and Sr should serve as good basis elements for making that comparison. This idea will be used in the Fischer Assay and Paraho section to establish secondary criteria for suspecting that an element has been mobilized during retorting.

Conclusion 7 is a useful by-product of the interlaboratory comparison program. Trace element analysis by EDXRF as opposed to wavelength dispersive XRF is a relatively new method of analysis. The ETSRP group and the Berkeley group are the only two labs which have broadly published their procedures (2, 26, 30). Also, the two groups have quite different procedures for performing the analysis (2, 26, 30). This program constitutes the first time EDXRF has undergone a formal interlaboratory comparison. Considered from this viewpoint, the degree of comparison among the laboratories is remarkable. The effort spent by the three groups in developing good EDXRF methods for trace elements has been extensive, but if the results from this program are typical, the future is promising for this instrumental method.

Analysis of Liquids

The same three laboratories that have participated in the interlaboratory program on solids have started a similar program for liquids. Tables 7 and 8 present the preliminary results from ETSRP and Berkeley on trace elements in Lawrence Livermore products. The descriptions of the samples and retort conditions as well as the Berkeley results come from reference (12). Where comparisons are possible, it is obvious that the results are not nearly as good for the liquids as they are for the solids. Generally speaking, the comparison is to within a factor of two instead

of $\pm 10\%$. The results for the oil are a bit better than for the water. This can be ascribed to the fact that storage procedures for the oil are better established than they are for the water. At this time analyses for the liquids that are precise to within 10% can be expected, but accuracy established by interlaboratory comparisons is not available.

TABLE 7. COMPARISON OF ANALYSES OF LIQUID PRODUCTS FROM THE LAWRENCE LIVERMORE RETORT. RUN NUMBER S-9.

	Colorado (XRF)				Berkeley (12)			
	Water		Oil		Water		Oil	
Fe	1.38	± 0.06	43	± 3				
Ni	0.24	0.03	3.5	0.8				
Cu	3.3	0.3	4.3	0.4	5.3	± 0.5	4.7	± 0.4
Zn	0.10	0.02	1.8	0.2	0.48	± 0.05	0.53	± 0.11
As	0.47	0.08	19	2	0.23	± 0.02	6.2	± 0.6
Se	0.30	0.09	0.8	0.2				
Br	0.53	0.05	0.24	0.02				
Rb								
Sr								
Mo			0.29	0.04				
Pb	0.06	0.01	2.3	0.6	0.02	± 0.01	1.4	± 0.2

TABLE 8. COMPARISON OF ANALYSES OF LIQUID PRODUCTS FROM THE LAWRENCE LIVERMORE RETORT. RUN NUMBER S-11.

	Colorado (XRF)				Berkeley (12)			
	Water		Oil		Water		Oil	
Fe	8.3	± 0.1	38	± 1				
Ni	0.46	0.06	1.8	0.1				
Cu	94	14	2.0	0.1	106	± 20	7.9	± 0.8
Zn	10	1.5	4.2	0.3	15	± 2	3.6	± 0.8
As	1.9	0.3	16.7	0.8	0.52	± 0.05	7.0	± 0.7
Se	0.8	0.2	2.2	0.1				
Br	0.34	0.1	0.34	0.03				
Rb	0.05	0.01						
Sr	0.019	0.006						
Mo	0.016	0.005	0.92	0.03				
Pb	0.59	0.02	0.33	0.04	0.83	± 0.18	1.1	± 0.3

In light of the previous paragraph, conclusion 2 on the development of an EDXRF procedure for the analysis of trace elements in oil and water is quite important. The method involves spiking the liquid with an element that is not of interest so that little sample preparation is required (2). This is quite important since many methods of analysis of oil for trace elements involve digestions that are quite difficult. The method was checked using NBS fuel oil (SRM 1634); V, Fe, Ni, and Mo were detected and the results of the analyses correspond well with the certified values. In shale oil, the elements shown in Tables 7 and 8 were detected. Recently, the method was adapted to water samples. In this case, the high content of dissolved solids makes it difficult to prepare uniform XRF targets by evaporation. With spiking, one only has to compare the analyte peaks with the spike peak to determine concentrations.

FISCHER ASSAY OF OIL SHALE: MASS BALANCES AND ELEMENT RELATIONS

The study of the element abundance in raw shale and the Fischer assay products of that shale was the primary work done in 1975, the first year of the project. At that time the Paraho retort was operating in a developmental phase and the TOSCO pilot plant had just ceased operation. Earlier, Atwood and Goodfellow (31) had shown that the TOSCO Modified Fischer Assay was a good simulation of the TOSCO II process. So the objective of this study was to use the Fischer assay as a bench scale simulation of a surface retort. The assays could then provide representative and reproducible fractions of oil, water, and spent shale for use in mass balance studies. It should be noted that the research staff at TOSCO had performed a similar experiment shortly before our study (32). The comparison between the two experiments is quite good.

THE FISCHER ASSAY EXPERIMENT

Heistand (33) has described the Fischer assay as a bench scale performance test which gives a measure of the quantity of liquid hydrocarbons that can be retorted from a solid sample. As stated above, the procedure used in this study is the TOSCO Modified Fischer Assay, which is one of the acknowledged testing methods (31, 35). In this procedure, 100 g of -65 mesh material is weighed in an aluminum cup and placed in a stainless steel retort. A controlled pyrolysis temperature program lasting for 72.5 minutes is used. This includes a 20 minute soak period at the maximum temperature of 500 °C. Liquid products of the retorting are collected in a condenser and receiver both cooled by ice water. In this study gases not condensed at 0 °C were allowed to escape; however, provisions can be made for their collection (31). By determining the mass of oil, water, and spent shale produced, the oil yield can be calculated (31, 1). Two aspects of Fischer assays render the test inadequate as a standard analytical procedure. It appears that the oil yields vary, depending on the procedure used, and the assay is subject to uncontrollable variables in technique which adversely affect the precision (33). Some of the variables leading to poor reproducibility are the size to which the sample is ground, the uniformity of

the grain size, the degree to which the fine particles are retained, the diligence used in controlling the retort temperature program, and the temperature at which the receiver is maintained (31, 33).

The oil yield results of the Fischer assay obtained by the modified TOSCO procedure have been discussed previously (1) and are summarized in Table 9. The relative standard deviation in this set of assays was 2.5% of 9 oil-yield assays. TOSCO has obtained precision limits of 0.6%. Further examination of the weight fractions in 46 retort runs showed that the major source of this scatter was in the weight of liquid product obtained. This can probably be attributed to the inadequate control of the retort temperature program. The above summary indicates that the Fischer assay has limitations. However, in the absence of any adequate alternative, it will probably continue to be used as a standard bench retort test.

TABLE 9. RESULTS OF FISCHER ASSAY ANALYSES ON THE STANDARD SHALE (1, 31).

	Value	Rel Std Dev %	No. of Analyses
Oil Yield (gal/ton)	39.8	2.5	9
Oil Specific Gravity	0.909	0.4	9
Raw Oil Shale Weight (gm)	100.0	0.1	120
Spent Oil Shale Weight (gm)	80.4	0.4	46
Liquid Weight (gm)	16.3	2.6	46
Oil Weight (gm)	14.9	2.6	46
Water Weight (gm)	1.4	8.0	46

While the Fischer assay is plagued by variations, the sources of variability encountered in sampling a pilot plant or full scale production retort are obviously greater. The feedstock is much less uniform and the temperature profile of the retorting chamber may be subject to large variations. The Fischer assay was chosen for the mass balance study because it is likely to become a standard bench test and it offers the best prospects for control of retorting parameters. The Fischer assay is similar to above ground retorts where the shale is heated indirectly such as the TOSCO II or Paraho Indirect Process (34). In the Fischer assay, the liquid product is distilled from the shale; whereas in situ retorting permits liquid oil and water to remain in contact with unretorted shale and this will raise the elemental abundances in these liquids (35, 36). Also, the Fischer assay does not introduce combustion gases as do the direct combustion and in situ retort processes. This may change the oxidation state of some elements such

as As or Hg and aid in the transfer of some of the volatile elements from the retort (34, 36).

CONCLUSIONS ON THE FISCHER ASSAY EXPERIMENT

Specific Conclusions

1. The Fischer assay serves as a reasonable bench scale approximation of a surface oil shale retort.
2. All elements analyzed in the Fischer assay products are primarily retained in the spent shale, except for Hg which was not completely recovered in the solid or liquid products.
3. A parameter has been defined called the enrichment ratio (ER). This is the ratio of the concentration of the element in the product to that in the raw shale. If the element is retained in the spent shale, then the value of the ER should be 1.24, which is the weight loss during retorting. If the value of the ER falls below 1.0, that is a strong indication that that element has moved from the solid shale during retorting.
4. Based on ER values, Hg is the only element that appears to have moved during Fischer assay.
5. Mass balances in the Fischer assay show that, except for Hg, no elements are lost at an uncertainty of $\pm 10\%$. The imbalance on mercury is about 80%.
6. The five elements of primary concern, B, F, As, Se, and Mo all have ER values greater than 1.0 and provide a mass balance to within $\pm 15\%$.
7. When the water produced by the Fischer assay is compared with drinking water standards for trace elements, As, Se, and Ba are in concentrations above the maximum permissible concentration.

General Conclusions

1. The first general conclusion on elemental balances from Fischer assays is that since most elements are retained in the retorted shale, the degree of balance is dominated by how well the analyses can be performed on the two solids. Using analytical results that are precise to within $\pm 10\%$ gives mass balance results that show no elements are lost except for Hg.
2. The second general conclusion from the Fischer assay study is that the above conclusion requires a new approach to the question of environmental impact on surface retorts. Specifically, there are product streams such as the gas and water which amount to a few percent or less of the total mass. Consequently, they do not affect the mass balance. Nevertheless, the concentrations of

contaminants in these by-products may be at levels which cause technological or environmental concern. Consequently, research should shift from an emphasis on mass balance to determining concentration levels in product streams.

3. An example of conclusion 3 is provided by arsenic. In the Fischer assay the concentration of As in the oil is about 20 ppm. This amount is of technological concern because it will poison the catalysts used in oil refining. It may also cause an industrial health problem. Yet the ER values for As are 1.20 and the mass balance values are within 10% when the As in the oil is neglected.

TOSCO II Process

1. The elemental concentrations in the retorted shale that was produced in the TOSCO II pilot plant is very similar to the Fischer assay retorted shale. Both were produced from the same raw shale. This cannot be considered as a complete sampling of the TOSCO II retort, but initial considerations indicate that the conclusions reached for the Fischer assay experiments should hold true for the TOSCO II process.

DISCUSSION

The first conclusions on the Fischer assay experiment were published in the elemental balance paper which appears in the Advances in Chemistry Series on oil shale and tarsands (3). At that time the analytical results of the interlaboratory program were not available. Now that those results can be used, updated tables on elemental concentrations in OS-1, SS-2, and FASS can be prepared. So from Tables 3, 4, and 6 a list of best values for the elemental concentrations in these materials was produced in Table 10, that implies the results in the earlier tables are suspect. Also, the Fischer assay oil and water have been analyzed by INAA and EDXRF. The full suite of elements found in oil shale by these methods should be found in the oil and water to better than the sensitivity shown for the solids. This is because the matrix causes less interference for the liquids. For example, the concentration levels to which Sc and Sb can be reported are an indication of the sensitivities of INAA for the liquids. So, where there is a blank for the oil or water it implies that the abundance is below that found in oil shale.

From an environmental viewpoint, the mass balance analysis is aided by the calculation of two parameters (12, 37):

1. Enrichment Ratio (ER). This parameter is determined by dividing the elemental concentration in each output by that in the raw shale. This ratio expresses the relative enrichment in each output stream independent of the mass of the input and output stream.

TABLE 10. BEST VALUES FOR THE ELEMENT CONCENTRATIONS IN
TOSCO RAW SHALE (OS-1), TOSCO SPENT SHALE
(SS-2), AND THE FISCHER ASSAY PRODUCTS.

Conc.	TOSCO		FISCHER ASSAY		
	Raw Shale OS-1	Spent Shale SS-2	Spent Shale FASS	OIL	WATER
B ppm	110	146	145	NA	2.8
F ppm	1020	1490	1420	<3	1.7
Na %	1.43	1.74	1.75	1.5×10^{-3}	3.9×10^{-3}
Mg %	2.6	3.9	3.1		
Al %	3.4	4.2	4.07		
Si %	13.0	16.0	15.9		
K %	1.25	1.50	1.51		2.0×10^{-3}
Ca %	9.8	11.3	11.3		1.4×10^{-4}
Sc ppm	4.9	6.0	6.0	0.0026	0.0023
Ti %	0.14	0.19	0.17		
Cr ppm	36	42	43	0.41	0.3
Mn ppm	271	334	355	0.08	
Fe %	1.89	2.45	2.39	1.6×10^{-3}	1.2×10^{-4}
Ni ppm	29	34	35	0.6	2.3
Cu ppm	48	62	60		
Zn ppm	72	105	92	0.5	0.2
As ppm	70	82	85	22	5.4
Se ppm	4.1	4.9	4.9	0.70	2.7
Rb ppm	71	94	87		0.04
Sr ppm	640	780	800		0.02
Y ppm	8.1	12	11.6		
Zr ppm	55	68	81		
Nb ppm	4.5	6.0	5.6		
Mo ppm	28	36	35		0.13
Cd ppm	1.05	0.98	1.28		
Sb ppm	3.0	3.7	3.8	0.035	0.16
Cs ppm	4.4	6.0	5.6		
Ba ppm	1310	1580	1850		4
La ppm	18.7	22	22		
Ce ppm	35	44	42		
Nd ppm	16	18	18		0.6
Sm ppm	2.7	3.3	3.3		
Eu ppm	0.52	0.64	0.64		
Tb ppm	0.31	0.38	0.41		
Dy ppm	2.1	2.5	2.5		
Yb ppm	1.0	1.26	1.27	0.008	
Hf ppm	1.44	1.85	1.80		
Hg ppm	0.15	0.045	0.038	NA*	NA
Pb ppm	30	41	38	0.33	
U ppm	5.4	6.6	6.4		
Th ppm	5.2	6.2	6.2		

* NA means not analyzed

2. Relative Imbalance (RI). This parameter is determined as a percent by the following equation:

$$RI = \frac{\text{Mass In} - \text{Mass Out}}{\text{Mass In}} \times 100$$

This percent measures the degree of closure obtained, taking into account the mass of the respective element involved in the input and output streams.

In some instances, the RI value obtained is a large negative number. This is usually an indication that the retort process has added that respective element or that contamination occurred during sample handling. In this study, care was taken to minimize this problem. All the retorts and aluminum inserts used in this Fischer assay were scrubbed and rinsed with HNO_3 (31). All new glassware was used and was also rinsed with HNO_3 prior to use. All equipment was used in a Fischer assay of OS-1 before samples were collected for the mass balance studies.

The RI values were obtained using the masses of the raw shale feedstock and the oil, water, and spent shale products shown in Table 11. The gas plus loss amounts to 3.3% in these Fischer assays. The gas was not analyzed for trace elements and was neglected in the calculation of RI.

Specific Conclusions

Conclusion 1 was developed from the discussion in the Fischer Assay Experiment section. The point is brought up again as a reminder that this can be considered as a good model of a surface retort. Indeed, in this case the products can be more directly related to the feedstock and a representative sample is easier to obtain.

Concerning conclusion 2, a scan of the elemental concentrations in Table 10 shows that there is no element which is more concentrated in the oil and water than in the spent shale. Only arsenic and selenium come close. The concentration of arsenic in oil is 20% of that in spent shale and the selenium in water is 50% of that in spent shale. Mercury is not retained in the spent shale. The analyses of Hg in oil and water were not made, but Fox (12) reports that concentration is about comparable to that found in the spent shale.

Concerning conclusion 3 on enrichment ratios (ER), this ratio quantifies the idea that the elements are retained in the spent shale. From Table 9, the weight ratio of OS-1 to FASS is 1.24. This is the value that the ER for an element should have in spent shale to raw shale due to the release of liquids during retorting. A scan of Table 11 shows close adherence to this value for all elements except Hg. Here the value is 0.25. The next lowest value of the ER for Fischer assay is Nd at 1.13. So, the only strong indication of movement is that for mercury and that is conclusion 4.

TABLE 11. ENRICHMENT RATIOS (ER) FOR THE TOSCO PROCESS AND FISCHER ASSAY, AND RELATIVE IMBALANCES (RI) IN THE FISCHER ASSAY OF OIL SHALE.

Element	TOSCO	FISCHER ASSAY	
	ER ^a	ER ^{b,c}	RI in %
B	1.33	1.32	-6
F	1.46	1.39	-12
Na	1.22	1.22	+2
Mg	1.50	1.19	+4
Al	1.24	1.20	+4
Si	1.23	1.22	+2
K	1.20	1.21	+3
Ca	1.15	1.15	+7
Sc	1.22	1.22	+2
Ti	1.36	1.21	+2
Cr	1.17	1.19	+4
Mn	1.23	1.31	-5
Fe	1.30	1.26	-2
Ni	1.17	1.21	+3
Cu	1.29	1.25	0
Zn	1.46	1.28	-3
As	1.17	1.21	-2
Se	1.20	1.20	0
Rb	1.32	1.23	+1
Sr	1.22	1.25	0
Y	1.48	1.43	-15
Zr	1.24	1.47	-18
Nb	1.33	1.24	0
Mo	1.29	1.25	0
Cd	0.93	1.22	+2
Sb	1.23	1.27	-2
Cs	1.36	1.27	-2
Ba	1.21	1.41	-13
La	1.18	1.18	+5
Ce	1.26	1.20	+3
Nd	1.13	1.13	+10
Sm	1.22	1.22	+2
Eu	1.23	1.23	+1
Tb	1.23	1.32	-6
Dy	1.19	1.19	+4
Yb	1.26	1.27	-2
Hf	1.28	1.25	0
Hg	0.30	0.25	+80
Pb	1.37	1.27	-2
U	1.22	1.19	+5
Th	1.19	1.19	+4

a - ER calculated from the concentrations in SS-2 and OS-1 given in Table 8.

b - ER calculated from the concentrations in FASS and OS-1 in Table 8.

c - From Table 9, the mass ratio of OS-1/FS is 1.24.

Conclusion 5 on the mass balance of the elements is based on the values of the relative imbalance (RI) listed in Table 11. Even though many of the elemental concentrations are not listed for the oil and water, the discussion on Conclusion 1 states that the concentrations of all elements are lower in the liquid products than in the spent shale. The weight fraction of the oil is 14.9% and of the water 1.4%. These products only have a secondary effect on the value of RI. The balance is to within 10% for all elements except Hg. Note that some elements like Y, Zr, and Ba have high negative values. This could be due to contamination or an aberrant value for the concentration of that element in the raw shale or spent shale. Geochemical arguments presented later dictate that these elements should exhibit a balance. The only low value is for Hg at +80% imbalance.

Some comments are necessary on how conclusions 1-5 relate to previous work. The conclusion on the loss of mercury from oil shale retorts was first reported by Fox (12) and Fruchter (13) on the Lawrence Livermore in situ pilot plant retort. Also Fox and others (38) have performed extensive experiments on the simulated in situ retort at Laramie to better discover how the mercury was distributed. The conclusion was that 75% of the mercury was in the off-gases. The imbalance for mercury shown in Table 11 is comparable. Donnell and Shaw (39) reported that the mercury distribution during a Fischer assay was 57.5% to gas, 24.9% to oil, 5.5% to water, and 1.9% to the spent shale. Obviously, the conclusions on mercury stated here are confirmations of previous studies.

In the conclusions in the mass balance paper it was suggested that F and Zn may have been mobilized during Fischer assay (3). The results shown in Table 11 indicate that this is not the case. The ER for F and Zn are 1.39 and 1.28 respectively. However, the results of analyses for both these elements are not as precise as for some of the other elements. There is only one value for F in Table 11. The TOSCO study on Fischer assay does show results that are similar to those in Tables 10 and 11. Consequently, the previous suggestions on F and Zn have not been substantiated by further studies on the Fischer assay product. However, in the Paraho study the strange behavior of Zn appears again. This will be discussed in the Paraho Section.

Conclusion 6 concerns the elements of interest to the ETSRP program, which are B, F, As, Se, and Mo. All these elements appear to not have been lost or mobilized during Fischer assay. The RI for B came out to be -12%, implying a net gain. This value is based on ETSRP results. If Battelle results from Table 3 and 4 are used, the RI is +5%. All the RI values would then be within $\pm 6\%$ for these five elements.

Conclusion 7 concerns the comparison of water by the Fischer assay with the criteria for what is clean water. If the water is considered for domestic or irrigation use, it would have to be treated to remove a number of contaminants. Of the major constituents in retort water, the NH_4^+ , HCO_3^- , $\text{S}_2\text{O}_3^{2-}$, and organic compounds in the water clearly make it unsuitable for other uses (35). A survey of the Paraho waters in Table 24 shows this.

Of the trace constituents, the old drinking water standards present a reasonable guide to purity (40). These list the maximum permissible concentrations of arsenic, selenium, and barium to be 0.05, 0.01, and 1.0 ppm respectively. All of these levels are exceeded in the retort water as can be seen in Table 10. In addition, the boron concentration may make the water unsuitable for irrigation (41). Other studies have found Ag, Pb, and Hg concentrations have exceeded the maximum permissible concentrations for drinking water (12, 13, 40). Numerous studies for the treatment of the retort water have been initiated (42). The objectives of these studies are usually to find a method to recover the ammonia and organic material from the water so that treatment costs will be lowered through by-product recovery.

General Conclusions

Conclusion 1 concerns how precisely a value of ER or a value of RI can be calculated. Some statistical analysis is needed to answer this question. If it is assumed that the relative standard deviation in the analyses is $\pm 10\%$, then the relative probable error in ER would be $\pm 14\%$ if the analytical errors were indeterminate and $\pm 20\%$ if the errors were determinate (43). The values of RI contained in Table 11 show a similar dependence on analytical precision. The probable errors in these values are also between 14 and 20% if the relative standard deviation in the analytical results is assumed to be $\pm 10\%$. These results indicate that, within experimental error, only mercury has been lost during Fischer assay. More definitive conclusions on whether elements are mobilized or lost can be reached with more precise analytical data. This dependence on the precision of the analyses originates from the fact that spent shale makes up 80% of the product and contains almost all the elemental concentrations. So all values of RI rely on the difference between two large numbers. Mercury is the only exception.

Conclusion 2 concerns what can be done about this dilemma. Considerable effort and expense will be required to improve the precision of the analytical methods. The analytical dilemma shows up in a number of ways. The results for arsenic discussed in Conclusion 3 are a good example. As stated in Specific Conclusions, Discussion, As is one element which is appreciably concentrated in the oil and water. The amount of As in water exceeds the maximum permissible concentration of As in drinking water. The amount of As in oil is a technological problem because it will poison the catalysts used in oil refining (32). Also, the concentration of As in oil may cause an industrial health problem if vapors of arsine emanate from the oil. Even though the concentration of As in the liquid products is of concern, the ER for As is 1.21. The value of RI for As is -2% if the liquid concentrations are considered and $+3\%$ if the liquids are neglected. The percentage of As in the raw and spent shale are so large that the concentrations in the liquids are negligible in comparison. The changes in the conclusions concerning F and Zn are due to the strong dependence that the values of ER and RI have on the analytical results. Also, the dependence that the values of ER and RI have on the analytical method is shown in the original results in the mass balance paper (3).

The first approaches to circumventing the strong dependence on analytical precision were suggested in the mass balance paper (3). Specifically, it is useful to try to establish some further criteria by which to evaluate the mass balance results so that efforts can be focused on the elements that appear to be mobilized or lost. Based on the analytical results and the values of ER and RI, the following two criteria are useful:

1. Typically spent shale amounts to 80% or more of the mass retort products. Assuming a value of 80% and equal concentrations of a trace element in the raw shale and spent shale and zero abundances in the oil and water, one would obtain an ER of 1.00 and an RI of +20%. These values are just at the limits of the probable error in ER and RI found here. Thus, a reasonable criteria for suspicion that an element has been mobilized from the solids during retorting is that the concentration of that element in the spent shale is at or below that found in the feedstock.
2. Lithophile elements such as Mg, K, Ca, Rb, Sr, the rare-earth elements, and U (44) are not expected to be mobilized during oil shale retorting. Many of these elements can be determined quite precisely at trace element levels. Thus, investigation of the values of ER and RI for these elements should help establish the reliability of the ER and RI values.

The first criterion provides a reasonable method of establishing which elements may be of concern even when the liquid and gas products are not available for analysis. The second criterion provides a means of establishing the fraction of liquid and gas products that were released when those mass values are not available.

Criterion 2 also brings in the question of whether geochemical relations can be used to establish better approaches to how elements will partition in an oil shale retort. If this can be done, then the high values of ER for Y, Zr, and Ba can be dismissed as aberrant since these elements should behave as the lithophile elements listed above (44). Geochemical and metallurgical reasoning also dictates what other elements should be mobilized during retorting. Specifically, it is established that Hg is released. Cadmium and zinc are chemically similar to Hg. Cd is known to have a low melting point; in fact that is the basis for its separation from most metals in metallurgical extraction processes (45). All three elements may be bound in the same phase in oil shale. Consequently, it is logical to concentrate on Cd and Zn as possible elements that would escape during oil shale retorting.

These new concepts and criteria were applied to the design of the sampling of the Paraho retort and the analytical studies which were carried out on the samples. As will be seen in the next section, the emphasis is not so much on mass balance as it is on characterizing the feedstock and products as fully as possible. The mass balance results from the Fischer assay experiment and

from the experiments of other groups provide a number of avenues of approach to the study of other retorts.

The TOSCO II Process

Spent shale SS-2 was produced from the TOSCO II pilot plant using the raw shale OS-1 as the feedstock (16). It is difficult to say how representative the 25 kg of OS-1 is of the 100 tons of $\frac{1}{2}$ inch mesh feedstock. It is also difficult to say how representative the 12 kg of SS-2 is of the spent shale. TOSCO determined that the 100 tons assayed at 37-38 gal/ton of oil. The Fischer assays performed in this study yield a value of 39.8 gal/ton (1). The difference in oil yields is outside of analytical uncertainties. However, it has been determined in the Paraho study that oil yield and the concentrations of inorganic elements are unrelated (4). If these two samples can be considered to be representative, then the abundances of elements in SS-2 compared with those in OS-1 give ER values greater than 1.0 for all elements except Cd and Hg. The conclusion that Hg escapes from the raw shale during the TOSCO II process seems reasonable in the light of all the evidence that Hg is released from the solids during all other oil shale retorting processes. The result for Cd seems to confirm that it is an element which requires further investigation. In the Fischer Assay Experiment section it was suggested that the TOSCO Modified Fischer Assay and the TOSCO II Retort Process were quite similar. The results in Table 10 show that the concentrations of elements in SS-2 and FASS are identical. Cadmium is the only possible exception. If this similarity is the case, then all of the results on the Fischer assay study should hold true for the TOSCO II Process.

THE PARAHO RETORT: ELEMENT RELATIONSHIPS AND PATHWAYS

In the 1960's, Camaron and Jones (46) designed a vertical kiln which could continuously process lump-sized material under uniform and controllable conditions. Among the important features on the kiln were: 1) a cylindrical design which achieves greater uniformity, 2) a special discharge grate which achieves uniform withdrawal, 3) a feeder system which keeps the solids uniform across the cross-section of the kiln, and 4) a counter current gas glow system which allows good energy exchange between solids and vapors without gas streaming. In late 1973, the Paraho Oil Shale Project was launched to test this kiln on the pilot plant and semi-works scale as an above-ground, oil shale retort (47, 48). The program is being conducted at the Anvil Points oil shale facilities near Rifle, Colorado. This section of the report describes experiments which were jointly conducted by the research project and Development Engineering Inc. (DEI) on the semi-works retort during the summer of 1977. The whole second year of the project was spent in sampling and preparing the materials. This year analyses were started on the solids and some of the retort waters. This report will be divided into the following sections:

- Description of the Retort
- The Sampling Program
- Element Relations in the Raw Shale Feedstock
- Element Relations in Retorted Shale
- Special Results Concerning Relations Between Raw and Retorted Shale

- Element Relations in the Crushing Fines and Bag House Dust
- Characteristics in the Retort Waters

DESCRIPTION OF THE RETORT

A schematic diagram of the 10½ foot O.D. semi-works retort is shown in Figure 1. 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.

Uniform flow of solids and gases within the retort is essential in order to maintain a continuous operation and a high efficiency. In the Paraho semi-works retort, the bottom grate, the air-gas distributors, and the rotating shale distributor are designed to assure uniform flows. In addition, the raw shale feed is carefully screened and handled to a uniform feed. Feedstock for the retort consists of +½ inch to -3 inch nominal size. Fines and non-uniform shale size can result in gas chaneling, high pressure drops, and uneven bed temperatures. These problems cause low oil yields and could, eventually, result in a retort shutdown. In addition to providing good operations and high efficiencies within the retort, the resulting lump-size retorted shale reduces considerably the environmental impact caused by dusting.

Although lump-size feed improves retort operation, minimizes environmental impacts, and reduces crushing costs, this feed creates problems in securing a representative sample for laboratory analysis. A raw shale sampling system was designed to meet the accepted criteria for sampling this lump-size, non-homogeneous material (49). A diagram of the Paraho sampling system is shown in Figure 2. A motorized gate diverts flow from the retort at preset intervals (usually 30-50 minutes). Approximately 200 pounds of material is taken in a single cut. The sample is crushed to -¾ inch and passes through a four-stage splitter. The retained sample is crushed to -¼ inch and passed

Figure 1. Schematic of Paraho retort for the direct heated mode.

Figure 2. Feedstock sampling system for the Paraho retort.

through a second four-stage splitter. This system provides a 24-hour composite laboratory sample (20-30 lbs, $\frac{1}{4}$ inch) from the $2\frac{1}{2}$ - 4 tons of the lump material sampled from the raw shale feed. An examination of the Paraho raw shale sampling system showed it to be unbiased (50). Careful analyses of the grade (gallons oil/ton shale) indicated no significant differences between reject streams A and B and the laboratory sample. This laboratory sample was used in the studies presented in this paper.

THE SAMPLING PROGRAM

The sampling program has a number of objectives that are related to the final goals of the Paraho research program. For the feedstock the goal is to determine the concentrations of trace elements and uncover any relations among the elements. Sampling to attain this goal for the oil shale feedstock presented problems and dictated the sampling for all the other materials, so it will be described in detail. Specifically, the problem is that lumps of rock $\frac{1}{2}$ - 3 inches to $\frac{1}{4}$ inch in size are not an ideal size of sample. One or two lumps are all that would be needed for most analyses, but that can hardly be considered representative. However, if the Paraho sampler were used to secure a sample, the amount would be about 6 kg. The sample is obviously physically heterogeneous. Does this also mean that it will be chemically heterogeneous? In addition, mining, hauling, crushing, and retorting are a continuous operation at Anvil Points; little stockpiling is done. Does this mean that feedstock sampled on one day will differ significantly from that used in the retort on another day? Fundamental sampling questions such as this require a sampling program that is based on a strong foundation of statistical theory.

The statistical model followed in the sampling was a hierarchical or nested analysis of variance (52, 53). In this case, one month of 30 days in which the retort was operating was subdivided or nested into 24 hour, 8 hour, and 1 hour periods. Of these 30 days, 6 were chosen as test days. Samples were taken on each of the three 8 hour periods. Then, on one randomly chosen 8 hour shift, eight 1 hour samples of oil shale feedstock were taken. This nested sampling design is shown in Figure 3. Now, for some constituent, such as iron, if all the samples were the same then

$$\text{concentration of Fe}_i = u_{Fe} \quad (1)$$

where u_{Fe} is the mean of Fe concentrations and i designates the i^{th} sample. This is not the case. There can be a deviation or error due to the time in which the sample was taken and the imprecision of the analysis. So the equation 1 becomes

$$\%Fe_{ijk} = u_{Fe} + \alpha_i + \beta_{ij} + \gamma_{ijk} + \delta_{ijk} \quad (2)$$

Mean + 24 hr + 8 hr + 1 hr + analysis

where i designates the retort day and α_i is the deviation from the mean due to the sample being taken on that day. Similarly, β_{ij} represents the deviation due to the sample being taken in the j^{th} 8 hr shift of the i^{th} day, γ_{ijk} means the same for the 1 hr period, and δ_{ijk} is the error for the analysis. By carefully setting up a nested sampling design and randomly selecting the sampling periods, an estimate of magnitude of the error or deviation for each time

Figure 3. Time nested Paraho sampling design.

period can be obtained. Certainly, if more periods were sampled, the estimates of error would be better, but the design choice is such that a minimum of samples yields meaningful estimates of all the error parameters.

One cannot actually determine the errors and deviations, but if the sampling design is properly constructed, estimates of the errors can be made (54, 53). Such an estimate is called a variance. The variance equation corresponding to equation 2 is

$$S_{Fe}^2 = S_{\alpha}^2 + S_{\beta}^2 + S_{\gamma}^2 + S_{\delta}^2 \quad (3)$$

These variances are similar to estimates of the standard deviation but in this case the variance is partitioned among several components. The partitioning of the variance allows the following questions to be answered:

1. Is the mean of all the samples representative of the whole retort month or is there a trend over the month?
2. Is there significant scatter in any one of the 24 hr, 8 hr, or 1 hr time periods?
3. Are the analytical procedures precise enough or do they contribute to most of the scatter in the concentration values?

The sampling plan for the feedstock required extensive time at the Anvil Points facility. Thus, it was best to fit the sampling for the other materials to the sampling of the raw shale. For the retorted shale, the same design as for the feedstock was used. The liquid products were sampled every shift and the fines and dusts every day. Retort Day 2 was 8/23/77 and Day 30 on 9/20/77. All samples included in the design were taken except for shift 3 on Day 6 when the retort shut down at 1330 hr. Over 250 samples of solids and liquids were collected. A report on the sampling and a log of the samples were included in last year's progress report (51).

One other goal of the Paraho program is to try to uncover elemental relations between the feedstock and the products. Thus, the timing of the collection of the various materials has to be considered. It takes about 4 hours for feedstock to pass through the retort and exit as retorted shale. Paraho measures the amount of oil collected in a day at midnight. Thus the retort day starts at 2200 of the previous day for the raw shale, at 0000 for the product oil and water and at 0200 for the retorted shale. On this time scheme, the raw shale, retorted shale, oil and water are related to one another. Figure 4 is a diagram of when samples were collected on a typical retort day.

Conclusions on the Sampling Program

1. Concerning the raw and retorted shale, sampling every hour using the systems on the Paraho retort pushes the retort personnel and the mechanical systems to their limits. Fortunately, as stated

RETORT DAY 3 SAMPLING TIMES

Figure 4. Retort day 3 sampling times.

below, samples do not have to be taken that often.

2. Concerning the liquid products, sampling these streams can only be done every 8 hours. The reasons is that the water has to be separated from the oil by settling and the amount that settles out is about 1% or less of the oil. Thus, accumulating 1 gallon of water requires the settling of 500 gallons, which is about 8 hours of retorting.
3. Also, sampling oil and water at this interval requires the manipulation of numerous valves. Due to the complexity of this system there is a high probability for human error.
4. Concerning the miscellaneous solids and liquids produced during retort operation, collection of these materials on more than a daily basis is difficult. This is because sampling stations for these materials were designed to be used only on an 8 hour schedule or only during the daylight hours.

Discussion on the Conclusions

The conclusions on the sampling program do not have great scientific significance but they are of practical importance for the design of future retorts and for sampling in environmental or toxicological programs. The situation developed that ours was probably the most extensive sampling program that was ever carried out on a semi-works size of retort. DEI took considerable care in designing the sampling system and in general it performed well. However, in the design of the new module which will be about ten times larger than the semi-works retort, the above conclusions on the sampling system will dictate some changes.

Conclusions 2 and 3 on the liquid handling system are quite frustrating. Continuous monitoring of the oil is now impossible. Securing a sample of the liquid product water from one shift is so difficult that in some instances it was not obvious that the proper tank was being sampled. Another situation also dictates against sampling the liquids more often than every shift. As was discussed in the Sampling section, the water and oil require much handling immediately after sampling. The water has to be separated from the oil, splits have to be prepared, and some splits bubbled with N_2 . All this typically took about two or three hours. So collection of the liquids at more frequent intervals is almost impossible.

SPECIAL CONCLUSION ON THE PARAHO SAMPLING PROGRAM

As of now, the analysis program has only yielded a broad range of results on the solids. However, the conclusions that already have been made are numerous and of great importance to oil shale research. It is my opinion that over the years this will be one of the most important experiments on oil shale development. The basis for this opinion lies in the design and execution of the sampling program. The result of the program was that these samples represent the only batch of oil shale materials that can be con-

sidered as a mathematical set. That is, the collection was based on statistical theory and the population of samples is large enough that conclusions based on statistical tests have a high degree of validity. Consequently, when certain elemental relations show up in the set of feedstock samples, the interpretation of that relation can be made in confidence. The discussion on the Paraho solids which follows will provide numerous examples of the significance of the idea of a statistical set.

ELEMENT RELATIONS IN THE RAW SHALE FEEDSTOCK

DEI performed the Fischer assay analyses on the raw shale samples by a procedure that has been described previously (4). The precision of the analyses has been determined to be 2% relative standard deviation for the oil yield and 15% and 20% relative standard deviation for the water yield and gas plus loss yield. All 70 oil shale feedstock samples that were collected were analyzed for oil yield.

The elemental analyses were done by the EDXRF and by the methods typically used by the ETSRP central analytical laboratory. They were described in the Preparation and Analysis section. For the analyses, four samples were chosen for analysis in each of the six hourly sample sections and three of the eight hour shift samples were analyzed for each day for a total of 37 samples. Also, duplicates of eight samples were analyzed to determine the variance of the analysis procedure. The relative standard deviation for the analysis for each element is listed in Table 1. They range from above 10% for light elements to below 5% for heavier elements. These results are typical of the precision of the EDXRF method. Comparison of analyses of NBS standard coal (SRM 1632) and round robin analyses done on oil shales show the accuracy of the analyses to be within $\pm 10\%$ (3,6). K and Se concentrations do not compare well with other analytical methods; the results are aberrant by about 30%.

In Table 12, the results for the Fischer assays and EDXRF analyses are listed. The average, mean, range, standard deviation of the mean, and relative standard deviation of the mean are based on all samples. The average analysis relative standard deviation is based on the variations found in the eight samples for which multiple analyses were performed. The percent of variance for 24 hr, 8 hr, 1 hr and analysis level is determined from the analysis of variance program. The meaning of the variances requires an explanation.

For each level (i) analytical, 1 hour, 8 hour, 24 hour, and analysis, a variance S_i^2 is determined for each element. Then, the percent of total variance for the level for the concentration of Fe is:

$$\%(S_{Fe})_i^2 = \left(\frac{(S_{Fe})_i^2}{n \sum_{i,j,k,m} (S_{Fe})_n^2} \right) \times 100$$

Table 12. Concentration parameters of Paraho oil shale. The sampling period is from August 23, 1977 through September 20, 1977.

Substance	Conc. Unit	Grand Mean	Grand Standard Deviation	Grand Rel.	Range	Avg. Analysis	% OF VARIANCE			
				Std. Dev. %		Rel. Dev. %	24 hr Level	8 hr Level	1 hr Level	Analysis Level
Oil	gpt	27.0	3.2	11.9	22-39	2	63	0	37	-
Water	gpt	4.4	1.7	39	1.6-11.4	15	0	93	7	-
Gas & Loss	gpt	2.2	0.6	28	1.0-3.7	20	0	26	74	-
Ca	%	12.3	1.5	12	7.2-15	13	3	0	0	97
Mn	ppm	313	34	11	191-380	10	12	0	0	88
Fe	%	2.13	0.21	10	12.2-25	9.2	6	0	0	94
Ni	ppm	32	3	9.5	18-36	6.6	0	0	55	45
Cu	ppm	35	4	10.1	20-40	6.6	8	22	2	68
Zn	ppm	83	24	29	40-180	9.8	14	0	68	18
Ga	ppm	7.0	0.8	12	4-8	7.6	18	0	32	50
As	ppm	44	5.6	13	26-58	8.7	25	0	23	52
Se	ppm	1.5	0.26	17	1.0-2.3	15	7	0	0	93
Rb	ppm	80	6	7.4	45-85	1.7	24	0	73	3
Sr	ppm	770	66	8.6	410-830	2.2	32	0	62	6
Y	ppm	12	1.2	10.6	6.2-14	4.9	8	0	49	43
Zr	ppm	56	14	25	26-120	8.3	10	0	80	10
Nb	ppm	5.7	0.5	9.7	3.3-6.6	2.4	19	0	72	9
Mo	ppm	23	2.5	10.8	13-28	2.3	0	0	89	11
Ba	ppm	480	67	14	240-670	1.7	14	0	84	2
Pb	ppm	24	3.1	13	15-35	3.2	0	26	65	9

This parameter measures where the majority of the variation lies for each concentration in the 4 level sampling scheme design. For example, for oil yield, the % variance is greatest on the 24 hr level, the value being 63%. This implies that the samples taken on the 1 hr and 8 hr periods each day did not change significantly with respect to the day-to-day changes. Thus, the samples taken on one day are appreciably different from the samples taken on other days. The 24 hr averages for oil yield for the 6 days were 23.8, 25.8, 30.4, 24.5, 31.2, and 26.9 gallons per ton respectively. The daily variation is readily apparent. For day 3 where the 24 hr average is 25.8, the 8 hr oil yields are 25.2, 26.7, and 25.4 gpt and the 1 hr oil yields are 25.5, 22.4, 27.8, 21.2, 26.7, 27.4, 25.3, and 25.0 gpt. These results are about typical. The tight range of the 8 hr samples is obvious; the 1 hr samples range a bit more but not as much as the daily averages. The percent of variance for the 1 hr level is 37%. Thus, the percent of variance is a measure of how much scatter there is in the concentration of a substance at each level.

In addition to the analysis of variance study, the concentrations of all the substances in all the samples were compared in a linear correlation program. The results for the correlation coefficients are listed in Table 13. Also, the results of the analyses for B, F, and Mo on the Paraho solids were recently completed. These results are presented in Table 14.

Conclusions on Element Relations in the Raw Shale Feedstock

1. The elemental abundances in the Paraho feedstock are quite homogeneous from sample to sample and from day to day. The typical range in the samples analyzed is a factor of two. On the other hand, in the formation the range in abundances is usually a factor of four. The mining, crushing, and stockpiling of the raw shale obviously blends the feedstock.
2. The oil in the feedstock is not associated with any of the elements analyzed. This implies that, on the first order level, the inorganic and organic fractions in oil shale are unrelated.
3. Analysis of variance conclusions:
 - a) For the oil amount, 63% of the variance is on the 24 hour level, which implies that a daily trend did exist for the oil amount over the retort month and an average for the month cannot be made.
 - b) For all the elements, the majority of the variance is on the analytical and hourly level. This implies that elemental averages for the retort month can be made.
 - c) The relative standard deviations are typically on the order of 10%, yet this amount of imprecision often contributed the majority of the uncertainty. This implies

TABLE 14. RECENT ANALYTICAL RESULTS ON PARAHO RAW AND RETORTED SHALE.

Substance	Conc. Unit	Grand Mean	Grand Standard Deviation	Grand Rel. Std. Dev. %	Range	Analysis Rel. Dev. %	24 hr Level	% of Variance		Analysis Level
								8 hr Level	1 hr Level	
RAW SHALE										
B	ppm	140	19	14	110-200	9.1	11	13	9	67
F	ppm	1340	170	12	1000-1600	7.9	21	0	34	45
Mo	ppm	29	3.7	13	22-39	6.2	37	0	0	63
Oil *	gal/ton	28.4	3.1	10.9	25.2-39.2	2	69	0	31	0
Water *	gal/ton	4.2	1.6	39	2.6-9.4	15	32	0	68	0
RETORTED SHALE										
B	ppm	190	25	13	140-250	6.6	0	50	0	50
F	ppm	1900	24	12	1500-2600	7.9	0	12	32	56
Mo	ppm	43	6	13	37-61	8.9	26	0	12	62

* Special analyses of oil and water by pulsed nuclear magnetic resonance.

that a reasonable analytical design is the study of one sample with emphasis on the precision of the results rather than study many samples with less precise techniques.

4. The conclusions generated from the analysis of variance study imply the following conclusions of practical interest:
 - a) For studying the elemental concentrations in raw shale feedstock in surface retorts it is best to sample once a week and analyze the sample thoroughly rather than sample once a shift and do only a few analyses.
 - b) Results of analyses from the typical oil testing laboratory will yield little information on the concentration of the inorganic elements.
 - c) Concerning the other studies that were performed on the Paraho Retort during the same period, the analysis of variance study shows that the raw shale taken was not just an isolated sample. Instead, all the studies done Paraho raw shale can be generally related to one another.

Discussion on the Conclusions

Conclusion 1 dispells the original concern that the feedstock would be chemically heterogeneous because it was physically heterogeneous. Instead, this conclusion reinforces the conclusions made in the Preparation and Analysis of how homogeneous oil shale is. Fox and others (17) have recently completed an analysis program of a core taken from the U.S. Naval Oil Shale Reserve No. 1. They sampled the Mahogany Zone which is the portion of the Green River Formation which is mined at Anvil Points. In the formation the range of concentrations of the same trace elements analyzed in this program was greater, typically a factor of four. This is about normal for a set of geologic samples. The results in Table 12 show ranges of only a factor of two. The mining, hauling, and crushing obviously blends the feedstock.

Conclusion 2 states that the inorganic and organic portions of oil shale are unrelated. The bases for this conclusion lie in Tables 12, 13, and 14. First, Table 12 shows that the oil yield measurably changed from day to day, whereas the elements did not. Then, in the table of correlation coefficients, the oil does not correlate with any of the elements, major or trace. The conclusion has to be that the organic portion as measured by oil yield and the inorganic portion as measured by all the other elements are unrelated on the first order level. From a geochemical point of view, the deposition of the organic material that formed the kerogens cannot be strongly related to any of the other features in the environment that caused the deposition of oil shale.

The sections of Conclusion 3 are contained in Tables 12 and 14. The conclusion on the oil was stated before. It simply means that the oil yield varies from day to day. The average values of the oil yield for the six days

were given in the introduction to this section. The trend is readily apparent. On the other hand, for the six days the averages for Rb are 83, 82, 78, 82, 75, and 81 ppm respectively. There is no trend. This means that there is no representative sample over the 30 days for the organic fraction of the feedstock. The conclusion on being able to generate a representative sample for the month for the elemental concentrations is based on the result that the majority of the variance lies on the hourly and analysis level. A scan of the values in the relative standard deviation for the grand mean and the relative standard deviation for the analysis is illuminating. For most of the values down to Pb, the two values are comparable. This is true even though the analysis deviation is about 10%, which is about as good as can be expected from a multielement instrumental method. In this case, elemental averages for the month can be made. Thus, the grand mean column for the elements in Table 12 is a reasonable average for the retort month. So, by paying careful attention to the sampling program a reliable average for the element concentration for the Paraho retort has been obtained.

The final conclusion in the analysis of variance section contains the meaning of these results for future research projects. Oil shale feedstock is so homogeneous that the analyses dictate the uncertainty in the concentrations. Consequently, it would be just as reasonable to extensively study one sample as it would be to study many samples using less precise techniques. In retrospect, this conclusion legitimizes the study done on the Fischer Assay of the TOSCO shale OS-1.

Conclusion 4 continues with the practical implications of the analysis of variance results. Firstly, for inorganic information on oil shale feedstock, a surface retort would do better to collect a sample once a week and study it extensively. Secondly, most of the organic tests that are typically performed by an oil analysis lab will yield few clues on the inorganic portion. This means that a reasonable environmental plan for controlling unintentional releases of trace elements is to make certain that the feedstock is blended to the degree that the oil yield changes little from day to day. If this is done the variation in the inorganic elements will be about the same as for the oil yield. The sample chosen once a week for inorganic analysis can be extensively studied to make certain that nothing unusual is occurring. Such an analysis program based on indicative analyses of the oil content rather than specific analyses for the elements could save public and private organizations involved in oil shale many times the money spent on this project.

The final conclusion in this section concerns the comparison of this study with the other studies performed on the Paraho retort during the summer of 1977. It is a good example of how verification of a representative sample can be useful to other studies. Specifically, those other studies are not studying isolated materials but the results can be compared with one another. Furthermore, if another type of surface retort was studied, the results would probably be similar since the materials do not vary that much. The studies performed on Paraho will be significant to the development of all surface retorts.

ELEMENTAL RELATIONS IN RETORTED SHALE

On the Paraho retort, the sampling system for retorted shale is similar to that for the feedstock. Also, the sampling program for the retorted shale

is the same as that for the feedstock. Also, the analysis program for the retorted shale has been the same as that for the raw shale. Consequently, the previous description and discussion of the raw shale sampling and analysis program applies also to the retorted shale. Tables 15 and 16 contain the analysis of variance results and the correlation coefficients for the retorted shale samples. The following conclusions can be made concerning the set of retorted shales.

Conclusions on Elemental Relations in Retorted Shales

1. The elemental abundances in retorted shale form an even more homogeneous group than the raw shales. This means that retorting homogenizes the solid material even further.
2. For most elements, the analytical results are precise to 5% for the relative standard deviation rather than 10% for the raw shale. This confirms the conclusion stated earlier that the retorted shale is more homogeneous than raw shale.
3. With better analyses, the percent of variance falls in the analysis level and rises in the 8 hour level. The 24 hour level contributes little to the variance. This result means that all the conclusions developed for raw shale hold just as well for retorted shale.

Discussion on the Conclusions

Most of the conclusions which were discussed in the Raw Shale Feedstock section apply to the retorted shale. There is only a small amount of organic carbon remaining in the retorted shale and this cannot be measured by Fischer Assay. There are no measurements of organic carbon in retorted shale. Consequently, the conclusions on the organic portion of the raw shale feedstock are not applicable to the retorted shale.

Conclusions 1 and 2 concern the two columns on relative standard deviation. The one grand relative standard deviation measures the scatter in all the results. The analysis standard deviation measures the scatter in the analytical method. In both cases, the relative standard deviations are usually smaller for each element in the retorted shale than in the feedstock. Less scatter in the results means that retorting homogenizes the solid material. There is some mixing of the feedstock as it travels through the retort. Less scatter in the analyses means that retorted shale yields more precise results than raw shale. The results on Rb and Sr are remarkable in this regard. The relative standard deviations in the grand mean are 2.8% for Rb and 2.7% for Sr. These are reasonable values for the deviation for the analysis alone. But here, for a whole month, the concentrations of Rb and Sr stayed within $\pm 10\%$ of the concentrations of 97 and 935 ppm. Such consistency is remarkable.

Conclusion 3 concerns what happens when the analytical uncertainty is decreased. In this case, the percent of variance in the analysis level drops as would be expected. The question then becomes where in the time levels

TABLE 15. CONCENTRATION PARAMETERS FOR PARAHO RETORTED SHALE

Substance	Conc. Unit	Grand Mean	Grand Standard Deviation	Grand Rel. Std. Dev. %	Range	Analysis Rel. Dev. %	% of Variance			
							24 hr Level	8 hr Level	1 hr Level	Analysis Level
Oil, Water Gas & Loss										
Ca	%	12.0	1.5	12.5	9.6-15.3	7.8	0	38	0	62
Mn	ppm	332	33	10.0	278-408	6.2	0	43	0	57
Fe	%	2.31	0.22	9.4	1.95-2.87	5.6	5	44	0	51
Ni	ppm	35	3.8	10.6	30.2-47.1	5.4	0	24	25	51
Cu	ppm	42	4.8	11.5	33-60	3.8	0	18	54	28
Zn	ppm	79	21	26	66-92	3.0	0	96	2	2
Ga	ppm	7.8	0.7	8.5	6.6-9.1	6.3	0	19	0	81
As	ppm	60	10	16.5	46-96	1.9	30	0	68	2
Se	ppm	1.6	0.2	14.2	1.1-2.1	10.4	0	21	32	47
Rb	ppm	97	2.7	2.8	92-107	1.4	5	0	58	37
Sr	ppm	935	25	2.7	860-970	1.5	52	0	15	33
Y	ppm	13.7	0.8	5.6	11.3-15.6	2.5	0	0	78	22
Zr	ppm	68	8.9	13.1	58-96	15.0	0	32	0	68
Nb	ppm	7.0	0.4	6.0	6.1-8.0	3.7	22	0	27	51
Mo	ppm	33	4.2	13.1	29.0-48.3	2.8	9	0	79	12
Ba	ppm	586	33	5.7	521-655	4.6	15	32	0	53
Pb	ppm	32	3.3	10.5	27.2-44.2	3.5	18	0	65	17

TABLE 16. CORRELATION COEFFICIENTS FOR PARAHO RETORTED SHALE

Ca	1.00																
Mn	0.95	1.00															
Fe	0.86	0.90	1.00														
Ni	0.66	0.66	0.77	1.00													
Cu	0.53	0.50	0.66	0.89	1.00												
Zn	-.01	0.06	0.14	0.10	-.07	1.00											
Ga	0.65	0.72	0.62	0.45	0.28	0.22	1.00										
As	0.19	0.14	0.36	0.69	0.85	-.03	0.02	1.00									
Se	0.42	0.38	0.39	0.49	0.44	-.18	0.40	0.39	1.00								
Rb	0.43	0.47	0.56	0.75	0.78	0.08	0.41	0.72	0.50	1.00							
Sr	0.24	0.23	-.08	-.14	-.29	-.17	0.27	-.56	0.06	-.21	1.00						
Y	0.07	0.07	-.12	-.31	-.50	0.16	0.31	-.52	-.15	-.33	0.38	1.00					
Zr	0.16	0.07	0.04	0.22	0.22	-.07	0.08	0.12	0.08	0.05	0.16	0.17	1.00				
Nb	0.11	0.13	0.18	0.39	0.43	-.11	0.16	0.29	0.30	0.50	0.10	-.21	0.15	1.00			
Mo	0.02	-.02	0.20	0.58	0.74	-.16	-.12	0.81	0.33	0.59	-.40	-.59	0.22	0.61	1.00		
Ba	0.04	0.06	-.08	-.07	-.24	0.10	0.32	-.36	0.06	0.04	0.50	0.41	0.23	0.40	-.08	1.00	
Pb	0.21	0.22	0.45	0.75	0.82	0.12	0.05	0.84	0.33	0.76	-.51	-.57	0.05	0.45	0.78	-.26	1.00
Ca	Mn	Fe	Ni	Cu	Zn	Ga	As	Se	Rb	Sr	Y	Zr	Nb	Mo	Ba	Pb	

will the variance increase. It appears that most of the increase is in the one hour and eight hour levels. In general, the majority of variance is not on the 24 hour level. This means that the ideas on representative samples and averages that were developed in the Raw Shale Feedstock section are also true for the retorted shale.

SPECIAL RESULTS CONCERNING RELATIONS BETWEEN RAW AND RETORTED SHALE

It has been substantiated that the grand means for the raw and retorted shale are representative averages. So now the criteria that were developed in the Fischer Assay section to test for elements that may be mobilized can be applied to the Paraho retort. The value for the enrichment ratio (ER) for each element has been calculated from the grand means for the raw and retorted shale from Tables 12, 14 and 15. The ER values are presented in Table 17.

Also, the 46 raw shale samples and the 45 retorted shale samples form two statistical sets. Thus, various statistical studies can be made to see if the two sets are really different or if certain elements within a set behave in similar or different fashions (54). The generation of linear correlation coefficients has already been performed. Also, pattern recognition studies have been made by Dr. Robert Meglen and Dr. Donald Denney at the University of Colorado. These studies result in dendrograms which show which elements form clusters and which elements are not related to other elements (54). The dendrograms are a two dimensional way of looking at correlation coefficients. Figure 5 is a dendrogram of how the elements in raw shale cluster. Figure 6 is a dendrogram for the retorted shale. Figure 7 is a dendrogram of the raw shale feedstock compared with the time correlated retorted shale. To generate Figure 7, 12 of the feedstock samples from the eight hour level were chosen and the retorted shale samples from the same shifts were compared to them.

Conclusions on the Special Results of Raw and Retorted Shale

1. The values of the enrichment ratios of retorted to raw shale are above 1.0 for all elements except Zn, which has a value of 0.95.
2. When linear correlation coefficients between the elements are calculated for raw and retorted shale, many of the results are predictable. The conclusion concerning oil and water not correlating with any other elements is confirmed. The startling result is that Zn does not correlate with any other constituents, organic or inorganic.
3. When pattern recognition is tried among the elements in raw and retorted shale the following results are obtained:
 - a) In raw shale, there is a large cluster of lithophile elements (Ca, Fe, Mn, Rb, Sr, Ga, Nb, and Y), an unusual cluster of Ba and As (see note added in proof, discussion section, page), and a cluster of siderophile elements (Ni, Cu, Mo, and Pb). Oil, water, and Zn cluster with nothing.

TABLE 17. VALUES OF THE ENRICHMENT RATIO (ER) BETWEEN A RETORTED AND RAW SHALE FOR THE PARAHO RETORT.^a

Element	ER	Element	ER
B	1.36	Se	1.07
F	1.42	Rb	1.21
Ca	0.98	Sr	1.21
Mn	1.06	Y	1.14
Fe	1.08	Zr	1.21
Ni	1.09	Nb	1.23
Cu	1.20	Mo	1.43
Zn	0.95	Mo ^b	1.51
Ga	1.11	Ba	1.22
As	1.36	Pb	1.33

a - The mass ratio of raw/retorted shale is usually 1.22 for the Paraho retort.

b - Molybdenum by colorimetric method.

Figure 5. Cluster dendrograms for the Paraho raw shale.

CLUSTERING DENDROGRAM FOR RETORTED SHALE

Figure 6. Cluster dendrograms for the Paraho retorted shale.

Figure 7. Clustering dendrogram comparing raw and retorted shales.

- b) In retorted shale, the clusters seen in raw shale are not as strong. There is a large group of siderophile elements (Ni, Cu, Pb, As, Mo, and Rb) and lithophile elements (Fe, Mn, Ca, and Ga). Zinc shows some clustering tendencies with the siderophile group.
 - c) Pattern recognition was tried between raw and retorted shales which were matched time-wise, that is, 12 pairs of raw and retorted shale were taken from 8 hour shifts. The results were that all the samples clustered together with a fantastic degree of similarity. Other than that the group was random. There was no consistent matching of raw to retorted, raw to raw, or retorted to retorted.
 - d) The above conclusion implies that so far no element in oil shale can be used as a tracer to mark the passage of the feedstock through the retort.
4. On sampling day 6, the Paraho retort shut down because high grade oil shale was used as feedstock and this caused bridging in the top of the kiln. When the samples of raw and retorted shale for that day are studied in detail, there is no apparent aberration in the elemental concentration in the samples. In particular, no unusual concentrations of elements occur in the retorted shale because of shutdown.

Discussion of the Conclusions

Conclusion 1 applies the mobilization criteria from the Fischer Assay section and statistical tests to see if any elements have been mobilized during retorting. The values of ER in Table 17 are all above 1.0 for most elements. Robert Heistand reports that the typical weight ratio of raw to retorted shale is 1.22 for the Paraho retort. Most of the values of ER cluster around this number. The only value which lies below 1.0 is Zn at 0.95. Here again there is suspicion that Zn is mobilized. Zinc appeared to be suspicious in the Fischer Assay but later analyses did not confirm the low values of ER for this element. Now the same question arises again. Every test that we have developed shows Zn to exhibit unusual behavior. It would be useful to analyze Zn by another method to see if this suspicion holds up under other methods of analysis.

Conclusion 2 concerns the correlation coefficient matrices in Tables 13 and 16. The results are interesting and show what elements do not correlate with other elements. It is difficult to pick out correlations because there are many. The pattern recognition dendrograms show the correlations more clearly. When the oil values in the raw shale are scanned there is no high positive correlation. There are many anti-correlations but these also are not high. This confirms the previous conclusion on no relation between the organic and inorganic portion of the feedstock. The other result of the correlation matrix is the poor correlation of Zn with all other elements. One would expect correlation with Ni, Cu, As, and Pb;

but in all cases the correlation coefficient is less than 0.50. This is another piece of evidence on the strange behavior of Zn in oil shale.

Conclusion 3 concerns the pattern recognition studies. For the most part the dendrograms in Figures 5, 6, and 7 can be considered to be another way of presenting correlation coefficient data. On the abscissa is plotted the correlation coefficient. The substances are positioned in the vertical part of the array. Consider that a correlation coefficient of 0.7 is meaningful, 0.6 is tolerable, and 0.5 is stretching the similarity. The pattern recognition program will place all the elements which are strongly correlated in the same vertical area. Thus, they will form a group or "cluster". The isolation of highly related factors into a group is a key feature of a pattern recognition study. When scanning a correlation coefficient matrix, two factors which are related are easily found but the question of how a third factor is related to the other two is difficult to answer.

In Figure 5, the clustering dendrogram is presented for the 20 substances tabulated in Tables 13 and 14 for the raw shale. The same 46 samples make up the set. Now one begins to see how the elements are related in raw shale. Three groups are seen:

Group I: Lithophile elements with possible subgroups of carbonate forming cations (Ca, Fe, Mn, Rb, Sr) and other cations (Ga, Nb, and Y).

Group II: A cluster containing Ba and As.

Group III: Siderophile elements of Ni, Cu, Mo, and possibly Pb.

Non-clustering Substances: Se, Zr, Oil, Zn, Gas and Loss, and H₂O.

Groups I and III are reasonable from a geochemical point of view (44). Group II is a curiosity. Ba should be in Group I and As in Group III. A scan of Table 13 shows the highest correlation of As is with Cu and Mo; the highest for Ba is with Mn, Ga, Rb, and Sr.

(Note added to Proof:

Since preparing this manuscript the data have been augmented; the Ba and As have joined the appropriate clusters. The dendrogram based upon this corrected data is shown in Meglen's section of this report, in which he outlines the application of pattern recognition.)

The non-grouping of Zr and Zn is remarkable. Usual reasoning would put Zr in Group I and Zn in Group III. If one were convinced of the non-correlation, the conclusion would be that these two elements form their own separate phases.

All the statistical studies on oil shale help to bring together an elemental relation picture for this sedimentary rock. The following relations are suggested:

1. There is an organic portion to oil shale. It may contain metallo-organic compounds, but this portion does not contain any of these metals in major amounts. Release of the oil will not cause the majority of any trace metal to release except Hg.
2. There is a sulfide portion in oil shale. It contains some of the usual metals associated with sulfides (Cu, Ni, Rb). This phase appears to carry Mo. Although there is some association of Fe with these elements, Fe is more correlated with the cations forming carbonates. Arsenic does appear to be primarily associated with this group. Zn is not associated with this group. During surface retorting it appears that the sulfides do not break down.
3. There is a carbonate portion in oil shale. It contains Ca, Fe, Mn, Rb, and Sr. Other lithophile elements such as Y, Ba, Ga, and Nb are also associated with this portion. This portion does not break down during surface retorting.

Figure 6 is the dendrogram for the retorted shale. A scan of the correlation coefficients in Table 16 shows that the correlation coefficients are generally not as large as for the retorted shale. My opinion for this situation is that the ranges on the retorted shale are smaller because the material has been homogenized in the retort. This makes the statistical window through which one is viewing the set smaller. Consequently, the statistical measures which one used are exceeding their ability, and the correlation coefficients and cluster diagrams are poorly resolved.

There are some clusters which correspond with the raw shale group. There is a lithophile group and siderophile group, but now there is mixing of the elements in the groups. Iron and Mn group more with the sulfides. There are pairs of lithophile groups such as Ga and Rb, Ba and Sr, Nb and Mo. One problem is that this dendrogram was run using only twelve samples. When the full set of samples is used, the clusters should be somewhat better resolved.

Figure 7 shows a powerful feature of pattern recognition. In the first two studies the samples were independent variables and interrelations among the elements were investigated. Now, the elements are treated as the independent variables and interrelations among the samples are being investigated. Specifically, there are 12 raw shales from 8 hour shifts and the corresponding retorted shales from the specific 8 hour shift. Three possibilities for clustering occur:

1. Matching of raw and retorted shales into 6 clusters of pairs.
2. Matching of retorted shales among themselves and raw shales among themselves. The result is 2 clusters of 6 each.

3. Random scatter.

As can be seen in Figure 7, random scatter is the result. The most important feature is that all the samples really cluster into one group. The lowest correlation coefficient is 0.93. Then, using the elements that have been analyzed so far, there is no way to separate the samples in the group. The result is random scatter.

As stated in general in Conclusion 3-d and specifically in Conclusion 4, this random scatter has severe implications. What it means is that there is no way at this time to trace a specific raw shale feedstock through the retort and pick out that raw shale by analyzing the retorted shale. This conclusion possibly implies the following:

1. Making a mass balance on a retort by the analysis of one specific raw shale and one specific retorted shale is difficult. One cannot say the two are related. Mass balances using average values of many samples is more reasonable.
2. A situation where the raw shale is not available is an expired in situ retort. An analysis of the retorted shale will not yield any specific information on the raw shale. Specific information means oil yield, position in retort prior to firing, and perhaps conditions to which the sample was subjected, such as oxidizing capacity of the retort or wetting by fluids.
3. If a batch of feedstock that had unusually large concentrations of trace metals came through the retort, it would be difficult to detect this batch of feedstock by analysis of the retorted shale.

The third implication has already been confirmed to some extent. On Day 6, shale of an unusually high oil content was fed into the retort. This caused bridging in the top of the retort and subsequent shut down at 1330 hours of day 6. Nothing in the elemental concentrations in the raw and retorted shales has given any clue that the feedstock was high in oil content or that the retort shut down. Perhaps that is good since then a shut down due to high oil content does not automatically imply releases of unusual amounts of trace elements into the solids.

Clearly, the amount of information that has been uncovered using the statistical studies is impressive. There are a number of other tests which we want to make to see if some of these conclusions can be sharpened. This is one of the studies which is proposed in this year's research.

ELEMENTAL RELATIONS IN THE CRUSHER FINES AND BAG HOUSE DUSTS

Introduction

There are five primary places where solid materials are rejected from the Paraho retort. Four of these areas can be seen in Figure 8. This is a diagram of the raw shale feed preparation facilities taken from the Paraho Final Report (55). All these materials were sampled the same way as shown

in Figure 4. Grab samples were taken four times a day and these were combined in equal amounts to make a daily sample.

The rejected fines from the crushing and blending operations are transported on conveyors to disposal piles. Conveyors #1 and #2 transport fines from the crushing facilities. These are labeled conveyor #1 and #2. This material represents rejects from the unblended shale arriving from the mine. Conveyor #3 transports fines rejected by the polishing screen just after the feedstock has left the blending facility and just before the raw shale goes to the retort. In the blending facility the air is sucked into a bag house for cleaning the dust from it. This is located at the same place as the polishing fines conveyor, and is where the raw shale bag house dust was collected. The retorted shale bag house dust was collected at the bag house which sucks air from the retorted shale handling system. This sampling point is not shown in Figure 8.

In Tables 18 and 19 are listed the elemental concentrations for the daily samples from the crusher reject conveyors; Table 20 is the same from the polishing screen reject conveyor. Tables 21 and 22 are the same for the bag house dust. Note that samples were also taken on a day that was a week prior to the usual sampling period, that is, on 8/17/77. So there are seven samples instead of six. Table 23 is a compilation of the enrichment ratio (ER) values for each reject site. These were made using the averages for the raw shale in Table 13 and the averages in Tables 18-22.

Conclusions on the Crusher Fines and Bag House Dust

1. All the rejected materials appear to be as homogeneous as the raw shale feedstock.
2. For the crusher and polishing screen fines, there is a close correlation of the elemental concentrations with the raw shale feedstock. Thus, no unusual concentrations occur because of rejection of the fines.
3. The raw shale bag house dust is also similar to the raw shale feedstock. Thus, the raw shale dust to which workers may be exposed is the same as the bulk raw shale.
4. The retorted shale bag house dust is different from the raw shale and the retorted shale. Enrichment ratios show that Ni, Cu, As, Mo, and Pb are concentrating in the retorted shale dust even over the bulk retorted shale. These are all metals which are in the sulfide portion of oil shale. Thus, the retorted shale dust to which workers may be exposed is perhaps more hazardous than the bulk raw or retorted shale.

Discussion on the Conclusions

Conclusion 1 concerns homogeneity. A scan of the relative deviations in Tables 18-22 compared with those for the raw shale in Table 13 shows that the values are similar. Thus, the samples coming from the mine are already

TABLE 18. ELEMENT CONCENTRATIONS FOR CRUSHER FINES, #1 CONVEYOR

		8/17 CF100	8/23 CF103	8/24 CF106	8/27 CF109	9/7 CF112	9/15 CF113a	9/20 CF116	Avg	Std Dev	Rel Dev %
K	%	2.88	2.98	3.50	2.59	3.03	2.88	3.04	2.99	±0.27	9.2
Ca	%	13.15	12.52	14.54	11.58	12.37	12.71	12.08	12.70	±0.94	7.4
Mn	ppm	360	333	382	277	349	336	334	339	±32	9.6
Fe	%	2.23	2.27	2.50	2.08	2.35	2.19	2.22	2.26	±0.13	5.9
Co	ppm	<960	<1200	<1350	<826	<1100	<925	<1000			
Ni	ppm	35.9	37.9	36.1	35.0	37.4	33.0	32.1	35	±2	6.1
Cu	ppm	32.1	36.3	35.4	41.0	35.6	32.1	36.4	35	±3	8.6
Zn	ppm	64.6	70.6	71.9	63.8	67.4	63.1	69.0	67	±3	5.2
Ga	ppm	6.8	7.8	8.2	5.7	7.9	7.0	7.7	7.3	±0.9	11.8
As	ppm	48.6	39.5	50.9	51.9	44.6	45.8	42.6	46	±4	9.7
Se	ppm	1.5	1.6	1.0	1.9	1.7	1.7	1.2	1.5	±0.3	21
Br	ppm	<1.3	<1.4	<1.4	<1.1	<1.2	<1.1	<1.1			
Rb	ppm	81.2	85.1	90.7	77.8	84.9	79.3	84.1	83	±4	5.2
Sr	ppm	727	733	757	651	723	706	733	718	±33	4.6
Y	ppm	10.1	10.3	12.1	9.6	12.0	10.6	10.7	10.8	±0.9	8.8
Zr	ppm	53.8	62.6	56.8	98.0	117	56.1	59.0	72	±25	35
Nb	ppm	5.6	6.0	6.8	5.0	5.5	5.8	5.8	5.8	±0.5	9.5
Mo	ppm	17.6	22.9	21.8	22.2	17.2	23.6	17.9	20.	±3	13.5
Cd	ppm	<1.3	<1.1	<1.1	<1.1	<1.2	1.0	<1.1			
Sn	ppm	<2.0	1.6	<1.9	<1.8	<2.0	1.7	1.6			
Ba	ppm	498	476	512	518	486	464	452	486	±24	5.0
Pb	ppm	25	26	24	28	25	23	23	25	±2	7.1

TABLE 19. ELEMENT CONCENTRATIONS FOR CRUSHER FINES, #2 CONVEYOR.

		8/17 CF101	8/23 CF104	8/24 CF107	8/27 CF110	9/7 CF113	9/15 CF114a	9/20 CF117	Avg	Std Dev	Rel Dev %
K	%	2.61	2.57	3.08	2.33	3.24	2.98	2.38	2.74	±0.30	13
Ca	%	13.26	11.63	12.62	10.78	14.06	11.54	10.60	12.07	±1.3	11
Mn	ppm	301	322	342	269	366	332	295	318	±32	10
Fe	%	2.08	2.17	2.31	1.92	2.39	2.52	1.96	2.19	±0.22	10
Co	ppm	<842	<740	<979	<750	<1170	<1044	<610			
Ni	ppm	37	33	35	32	34	41	34	35	±3	8.6
Cu	ppm	34	34	33	33	35	38	32	34	±2	6.3
Zn	ppm	63	62	66	54	82	69	62	65	±9	13
Ga	ppm	6.4	7.4	6.8	5.1	7.6	7.1	7.3	6.8	±0.8	12
As	ppm	44	45	43	45	47	53	41	45	±4	8.4
Se	ppm	1.2	1.5	1.4	2.0	1.6	1.6	1.6	1.6	±0.2	16
Br	ppm	<1.1	1.2	<1.2	<1.1	<1.4	0.7	<1.0			
Rb	ppm	78	81	86	78	84	84	81	82	±3	3.8
Sr	ppm	815	765	775	648	781	673	751	740	±61	8.2
Y	ppm	10.7	11.3	12.0	10.8	12.1	11.0	11.3	11.3	±0.5	4.9
Zr	ppm	45	55	55	42	67	48	71	55	±11	20
Nb	ppm	5.2	6.4	6.0	4.5	5.8	6.0	5.8	5.7	±0.6	11
Mo	ppm	18.6	17.7	19.1	27	17.7	23	18.9	20	±3	17
Cd	ppm	<1.1	<1.2	<1.2	<1.2	<1.1	<1.2	<1.4			
Sn	ppm	<1.8	<2.0	<1.9	<2.0	<1.8	<1.9	<1.9			
Ba	ppm	605	489	473	349	514	522	475	490	±77	16
Pb	ppm	23	24	23	25	23	28	23	24	±2	7.7

TABLE 20. ELEMENT CONCENTRATIONS FOR POLISHING SCREEN FINES,
#3 CONVEYOR.

		8/17	8/23	8/24	8/27	9/7	9/15	9/20		Std	Rel
		CF102	CF105	CF108	CF111	CF114	CF115	CF118	Avg	Dev	Dev %
K	%	2.84	2.70	2.91	3.11	2.79	2.90	2.91	2.88	±0.13	4.4
Ca	%	13.23	13.12	12.96	13.69	11.72	12.89	12.64	12.89	±0.61	4.7
Mn	ppm	341	329	331	369	340	329	311	336	±18	5.3
Fe	%	2.15	2.28	2.26	2.40	2.35	2.23	2.41	2.30	±0.09	4.1
Co	ppm	<920	<960	<1000	<1110	<1000	<960	<1000			
Ni	ppm	37	35	32	39	43	31	34	36	±4	11
Cu	ppm	36	33	34	37	35	32	35	35	±2	5.0
Zn	ppm	66	64	66	81	66	67	66	68	±6	8.5
Ga	ppm	7.3	7.6	7.4	7.1	7.9	7.4	7.0	7.4	±0.3	4.1
As	ppm	50	40	41	48	45	40	50	45	±4	10
Se	ppm	1.5	1.2	1.1	1.8	1.8	1.7	1.5	1.5	±0.3	18
Br	ppm	<1.2	<1.2	<1.2	<1.4	1.3	<1.1	<1.2			
Rb	ppm	84	82	87	84	84	80	83	83	±2	2.6
Sr	ppm	775	806	809	751	769	763	780	779	±21	2.8
Y	ppm	28	11.3	10.6	10.3	11.7	10.8	11.6	11.0	±0.6	5.1
Zr	ppm	54	57	59	49	66	50	55	56	±6	10
Nb	ppm	4.6	6.1	6.4	5.5	6.1	5.7	6.0	5.8	±0.6	10
Mo	ppm	21	21	20	21	19	19	22	20	±1	5.6
Cd	ppm	<1.3	<1.1	<1.1	1.2	<1.1	<1.1	<1.1			
Sn	ppm	<1.9	<1.9	<1.9	<1.9	<1.9	1.8	1.5			
Ba	ppm	620	585	517	489	532	509	478	530	±52	9.7
Pb	ppm	26	22	24	26	25	22	26	24	±2	7.4

TABLE 21. ELEMENT CONCENTRATIONS FOR RAW SHALE BAG HOUSE DUST

		8/17 BH100	8/23 BH102	8/24 BH104	8/27 BH107	9/7 BH109	9/15 BH111	9/20 BH113	Avg	Std Dev	Rel Dev %
K	%	2.41	2.24	2.18	2.65	2.59	2.51	2.26	2.41	±0.18	7.5
Ca	%	12.52	11.61	10.64	12.65	10.79	10.50	10.07	11.19	±1.0	9.0
Mn	ppm	322	304	285	319	303	274	292	300	±17	5.8
Fe	%	2.05	2.01	1.97	2.19	2.15	2.04	2.06	2.07	±0.08	3.7
Co	ppm	<600	<500	<600	<800	<700	<1000	<500			
Ni	ppm	41	38	35	39	36	34	37	37	±2	6.5
Cu	ppm	29	30	28	30	31	27	30	29	±1	4.7
Zn	ppm	78	77	74	81	76	68	77	76	±4	5.4
Ga	ppm	5.8	6.5	6.6	7.5	7.5	6.8	6.6	6.8	±0.6	8.8
As	ppm	48	53	52	49	46	49	50	50	±2.5	4.8
Se	ppm	2.1	1.3	1.3	1.4	1.4	1.2	2.0	1.5	±0.4	24
Br	ppm	0.7	<1.1	1.5	0.9	0.8	<1.3	1.0	1.0	±0.3	32
Rb	ppm	79	80	81	82	84	77	83	81	±2.4	3.0
Sr	ppm	806	797	769	759	721	693	754	757	±40	5.3
Y	ppm	10.8	10.9	11.0	13.4	11.6	11.1	10.9	11.4	±0.9	8.1
Zr	ppm	62	64	68	149	55	59	64	62	±4	7.3
Nb	ppm	5.3	5.5	5.6	5.5	6.4	5.8	7.7	6.0	±0.8	14
Mo	ppm	22	25	28	29	26	28	29	27	±2.6	9.6
Cd	ppm	<1.2	<1.2	1.3	<1.1	<1.2	<1.1	<1.2			
Sn	ppm	1.8	<2.0	1.5	<1.9	<1.9	2.2	<2.0			
Ba	ppm	580	525	538	527	555	554	546	546	±19	3.0
Pb	ppm	26	26	28	28	25	25	27	26	±1.2	4.8

TABLE 22. ELEMENT CONCENTRATIONS FOR RETORTED SHALE BAG HOUSE DUST

		8/17 BH101	8/23 BH103	8/24 BH105	8/27 BH108	9/7 BH110	9/15 BH112	9/20 BH114	Avg	Std Dev	Rel Dev %
K	%	2.95	2.83	3.37	2.81	3.08	2.68	2.82	2.93	±0.22	7.8
Ca	%	16.55	14.29	18.15	15.26	16.47	14.56	15.72	15.86	±1.3	8.4
Mn	ppm	418	405	478	398	432	376	410	417	±32	7.7
Fe	%	2.69	2.55	3.03	2.56	2.69	2.65	2.47	2.66	±0.18	6.8
Co	ppm	<1300	<1200	<1600	<1200	<1400	<1100	<1150			
Ni	ppm	51	46	55	50	48	48	48	49	±3	5.9
Cu	ppm	65	62	64	62	64	63	61	63	±1	2.2
Zn	ppm	108	106	98	104	104	96	100	102	±4	4.3
Ga	ppm	7.6	8.1	7.0	6.8	8.0	7.0	8.6	7.6	±7	8.9
As	ppm	141	103	108	125	102	112	112	115	±14	12
Se	ppm	1.8	1.4	1.3	1.9	2.1	1.4	1.5	1.6	±0.3	19
Br	ppm	<2.8	4.8	<2.8	<2.4	<2.4	<2.1	<2.3			
Rb	ppm	107	107	100	105	110	104	106	106	±3	2.9
Sr	ppm	957	937	915	927	997	942	1006	954	±35	3.6
Y	ppm	10.7	11.9	10.4	11.9	11.6	12.3	12.5	11.6	±0.8	6.8
Zr	ppm	52	73	59	58	64	91	66	66	±13	19
Nb	ppm	6.2	8.5	6.9	7.0	8.2	7.9	7.7	7.5	±0.8	11
Mo	ppm	45	56	46	44	50	46	48	48	±4	8.6
Cd	ppm	1.8	2.0	1.6	2.0	2.3	2.7	<1.3	2.1	±0.4	1.9
Sn	ppm	<2.0	<2.0	<1.9	1.9	<1.9	<1.8	<1.9			
Ba	ppm	435	567	498	482	564	492	516	508	±47	9.2
Pb	ppm	45	39	41	41	40	41	39	41	±2	5.0

TABLE 23. ENRICHMENT RATIOS OF PARAHO FINES MATERIALS
COMPARED WITH PARAHO FEEDSTOCK.

Element	Crusher		Blender	Bag Houses	
	#1 Conveyor	#2 Conveyor	#3 Conveyor	Raw Shale	Retorted Shale
Ca	1.03	0.98	1.05	0.82	1.29
Mn	1.08	1.02	1.07	0.96	1.33
Fe	1.06	1.03	1.08	0.97	1.25
Ni	1.09	1.09	1.12	1.16	1.53
Cu	1.00	0.97	1.00	0.83	1.80
Zn	0.81	0.78	0.82	0.92	1.23
Ga	1.04	0.97	1.06	0.97	1.08
As	1.04	1.02	1.02	1.14	2.61
Se	1.00	1.07	1.00	1.00	1.07
Rb	1.04	1.02	1.04	1.01	1.32
Sr	0.93	0.96	1.01	0.98	1.24
Y	0.90	0.94	0.92	0.95	0.97
Zr	1.29	0.98	1.00	1.11	1.18
Nb	1.02	1.00	1.02	1.05	1.32
Mo	0.87	0.87	0.87	1.17	2.09
Ba	1.01	1.02	1.10	1.14	1.06
Pb	1.04	1.00	1.00	1.08	1.71

blended to some degree. A comparison of the relative deviations for the polishing screen fines in Table 20 compared with the crusher fines in Tables 18 and 19 shows a slight decrease in relative standard deviation of the elements after the feedstock has been blended. If one were to choose an alternate place to sample the feedstock, the rejects from the polishing screen would be a reasonable choice.

Conclusions 2, 3, and 4 concern how similar the rejects are to the feedstock. In the case of the crusher fines, polishing screen fines, and bag house dust, the ER values show close similarity. For the crusher and polishing screen fines, this implies that nothing of unusual interest is being thrown away by rejection. For the bag house dust this implies that the raw shale dust to which workers may be exposed is the same as the bulk raw shale. Thus, for those groups studying the toxicological effects of raw shale dust, grinding up a raw shale and using it for the study should not impair the conclusions of the experiment.

Conclusion 4 on retorted shale dust is another matter. It is different from bulk raw and retorted shale. As can be seen in Table 23, it is noticeably enriched in Ni, Cu, As, Mo, and Pb. The ER values for these elements are definitely higher than what is found in retorted shale as shown in Table 17. Note that for some of the lithophile elements the ER values are fairly close to 1.22 which is the typical mass ratio value of raw to retorted shale for the Paraho retort. Note also that these elements form the sulfide cluster in the raw shale which is shown in Figure 5. Thus, the concentration probably has something to do with sulfides. Note in the diagram of the retort (Figure 1) that the liquids and gases exit from the top and the retorted shale from the bottom. Also note that the recycle gases are returned to the retort at the middle and bottom after retorting occurs.

Three possible mechanisms come to mind for the enrichment of the sulfide phases.

1. Simple phase segregation of the retorted shale such that sulfide phases are more likely to form solid aerosols than other phases.
2. Vaporization of the metallic sulfides in the retorted shale zone of the retort and crystallization of the vapors onto aerosol particles of retorted shale.
3. Stripping of these metals from the recycle gases as they re-enter the retort and deposition onto retorted shale dust particles.

The first possibility is mostly a physical phenomenon while the other two involve some chemical reactions. For assessing the last two possibilities recall the work of Natusch and others on coal fly ash (56, 57). They have shown that elements such as As, Sb, Cd, Pb and Se are volatilized during combustion in a coal-fired power plant and then are preferentially adsorbed or condensed onto the small particles. This is why the second possibility is included. However, the temperatures during coal combustion reach 1500 °C, whereas the temperature of a retort seldom exceeds 650 °C (57, 34). Possibility

3 has no basis for acceptance right now. However, when the Paraho liquids are studied for trace elements, these elements should be assayed in the recycle condensates. Obviously, there is reason to further study this retorted shale bag house dust.

There are several implications that result from the possibilities presented above:

1. If it is physical segregation, then preparation and handling of retorted shale samples may cause concentration segregation of the elements if too much dusting occurs. This possibility was referred to in the Preparation and Analyses section.
2. If vaporization does occur, then the mobilization is occurring and toxic trace elements may be released from the retort or else these elements may condense on the surfaces of retorted shale which will be most prone to attack by leaching solutions.
3. On the other hand, if stripping of these elements from the recycle gas occurs, then gaseous retort emissions can be cleansed by simple passing the gas through a retorted shale bed. In the Paraho direct mode, the process would be self-cleansing with all toxic trace elements ending up in the retorted shale.

Whatever the situation is for the enrichment of toxic trace elements in the retorted bag house dust, it is clear that retorted bag house dust may be more hazardous than bulk retorted shale. Also, toxicological studies which use pulverized retorted shale in place of the actual dust may have their conclusions impaired because there is a difference between the dust and the retorted shale.

SUBSTANCES IN THE PARAHO WATERS

During the Paraho sampling program, water samples were secured from eight different sites. Three of the sites were associated with the retort, two of the sites were associated with the oil storage facility, and three of the sites were at the evaporation pond. For all eight samples, the techniques of handling and storing the water by refrigeration freezing, bubbling with N_2 and re-freezing were used on at least one of the sample sets. The detailed sampling and handling procedures are contained in last year's progress report (51). The next section contains a short description of each sample.

The experiments that have been made on the waters up until now are preliminary in nature. They are designed to determine which samples would best be used for analysis, what results will change among the four handling and storage procedures, and what are the best ways to proceed with the full scale analyses. As such, indicative analyses such as Eh, pH, and conductivity have been made and specific analyses for the major substances of NH_3 , S_2O_3 , total sulfur, and alkalinity have been attempted. Some of the analyses have been difficult. The determination of total sulfur and conductivity have been especially difficult. An assessment of the analysis of retort waters will be the

subject of a paper that will be given at the ASTM Symposium on Analysis of Waters Associated with Alternate Fuel Production in Pittsburgh in June, 1979 (58). The results of the analyses are presented in Table 24.

Description of Water Samples

Retort Waters--

Water can be collected from three sites associated with the retort. The three sites are shown on the retort diagram (Figure 9). Site A is at the 8 hour shale-oil storage tank. Although it is at the storage tank, this water would be the first stripped from the product stream at the oil and gas separator facility. This is sample LPW-116. Site B is at the blowers on the recycle gas line. The blower compresses the recycle gas which causes condensation of liquids. Most of the liquid is water. This blower condensate is sample RC-139. Site C is a recycle gas sampling line whose diversion point is on the discharge side of the blowers. It is possible to collect this condensate from the recycle line by sending the vapor through gas washing bottles that are cooled in an ice bath. This recycle condensate sample is RC-141.

Oil Storage Waters--

During normal operation, 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--

There are two inputs into the evaporation pond which lies in an arroyo about 200 feet below the retort. Waste water from general operations as well as the process and product water tanks discharge into an acid treatment facility which then discharges into the evaporation pond. Sample M-107 is the effluent from the acid treatment facility. Surface waters which may leach from the retorted shale pile are diverted by various channels into the evaporation pond. Sample M-109 is this retorted shale leachate. The pond water itself was taken as a grab sample from the middle of the pond. The pond water is sample M-108.

Conclusion on Paraho Waters

1. On the retort, the majority of the sulfur species that end up in the water go off at the oil separator stage. The majority of the

TABLE 24. CHARACTERISTICS AND CONCENTRATIONS OF SOME MAJOR CONSTITUENTS IN PARAHO WATERS.

Water	Handling	Bulk pH	Eh mV	Cond.	Alkalinity		N as NH ₃ in mg/ML	S ₂ O ₃ = mgS/mL	Total S as mgS/mL
					meq/mL high pH	meq/mL low pH			
LPW-116	Initial	8.88	-310						
6/78	R	9.16	-155	1.64 x 10 ⁵	0.080	0.720	23.1	9.25	27.1
7/78		8.86	-225	2.34 x 10 ⁵	0.105	0.703	22.3	6.80	31.4
6/78	N ₂ ,R	9.15	-165	1.64 x 10 ⁵	0.090	0.720	23.5	9.25	30.9
7/78		8.63	-112	2.24 x 10 ⁵	0.112	0.705	22.7	7.17	29.2
6/78	F	8.78	-200	1.23 x 10 ⁵	0.092	0.726	19.5	7.28	31.1
7/78		8.64	-210	2.30 x 10 ⁵	0.038	0.730	21.6	7.17	27.8
6/78	N ₂ ,F	8.75	-225	1.23 x 10 ⁵	0.092	0.762	23.7	7.28	30.3
7/78		8.54	-210	2.26 x 10 ⁵	0.082	0.705	22.7	7.02	27.1
RC-139	Initial	8.95	-420	3.25 x 10 ⁴					
6/78	N ₂ ,R	9.20	-42	3.96 x 10 ⁴	1.10	4.08	1.83	2.19	
7/78		9.12	-30	5.00 x 10 ⁴	0.123	0.413	7.35	1.96	≈ 0.12
RC-141	Initial	8.70	-410						
6/78	N ₂ ,R	8.56	+2	1.26 x 10 ⁵	0.430	1.71	25.1	0.130	≈ 0
7/78		8.76	+20	1.94 x 10 ⁵	0.395	1.73	23.5	0.151	≈ 0.21
M-102	Initial	8.80	-250						
6/78	R	8.97	-150	1.90 x 10 ⁵	0.333	0.618	30.0	23.3	42.5
7/78		8.60	-182	3.14 x 10 ⁵	0.119	0.594	28.8	21.2	41.7
6/78	N ₂ ,R	9.07	-140	2.98 x 10 ⁵	0.280	0.568	28.2	22.9	41.2
7/78		8.80	-180	2.53 x 10 ⁵	0.118	0.615	29.4	21.4	42.8
6/78	F	8.63	-215	1.49 x 10 ⁵	0.296	0.528	23.6	9.7	45.4
7/78		8.60	-140	1.73 x 10 ⁵			29.8	26.0	
6/78	N ₂ ,F	8.68	-230	1.72 x 10 ⁵	0.368	1.56	29.3	22.7	45.0
7/78		8.68	-138	3.16 x 10 ⁵			29.5	19.8	34.0
M-103	Initial	9.40	-100						
6/78	N ₂ ,R	8.93	-25	4.58 x 10 ⁴	0.071	0.217	19.0	4.87	1.1
7/78		8.95	-30	6.82 x 10 ⁴	0.075	0.223	6.72	3.50	6.5
M-107	Initial	7.70	+35	1860					
6/78	R	7.50	+110	2560	0.0022	0.0039	≈ 0	≈ 0	≈ 0
7/78		7.65	+140	3520		0.0035	0.03	0.01	0
M-108	Initial	8.13	-10	2500					
6/78	F	8.56	+50	3600		0.0053	≈ 0	0.045	≈ 0
7/78		8.68	+90	4800		0.0062	0.10	0.039	≈ 0.12
M-109	Initial	8.00	+40	1610					
6/78	R	7.36	+150	5480		0.0029	0.09	0.092	≈ 0
7/78		7.26	+180	3200		0.0026	0.08	0.083	≈ 0.32

Figure 9. Diagram of the Paraho retort showing the sampling sites on the retort for water.

ammonia is recycled back into the retort.

2. Product water that is stored for a few days in the oil holding tank is not much different in major species than the product water taken from the 8 hour holding tanks.
3. The leachate from the retorted shale pile does contain thiosulfate and this thiosulfate persists in the evaporation pond.

Discussion of Results

The analysis of retort waters is quite frustrating. Only recently has it become true that most of the major constituents are known (19, 35). A study of the results for LPW-116 compared with other retort waters suggests that the results are reasonable (19, 35). As was mentioned in the Preparation and Analysis section, the waters do change in storage and it appears freezing maintains the original values better than refrigeration. The question of how the conductivity increases during aging is not readily answered.

Conclusion 1 on the sulfur species is based on the comparison of the amounts of total sulfur in LPW-116, RC-139, and RC-141. The amount drops sharply after the oil-gas separator. This implies that the separator is a reasonably good scrubber of sulfur species. Thus, the sulfur should end up in the oil and water and not in the gaseous emissions. Comparison of the three retort waters for ammonia shows that most of this substance is recycled back into the retort.

Conclusion 2 is based on the comparison of holding tank water M-102 with the liquid product water LPW-116. Note that the values increase slightly. The largest change is the increase in sulfur species in the holding tank water. This may imply that the sulfur continues to be extracted from the oil and into the water upon storage.

Conclusion 3 concerns the sulfur species in the evaporation pond and retorted shale leachates. Runnells' group has reported thiosulfate species from laboratory leaching studies. The appearance of thiosulfate in the leachate from the Paraho retorted shale pile confirms this in an actual retort operation. When the pond water is analyzed, the thiosulfate is still present. On the other hand, there is no measureable thiosulfate from the acid treatment facility so somehow the sulfur species are almost eliminated during the treatment of the retort operations water.

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Progress Report 1976-1979

Release, Transport, and Fate of Some Potential Pollutants in Waters Associated with Oil Shale

Donald D. Runnells

Michael Glaze

Ola Saether

Kenneth Stollenwerk

INTRODUCTION

OVERVIEW

As time passes it seems more certain that an oil shale industry will soon be established in western Colorado. Although many studies are being conducted by various groups of researchers, it is still unclear as to what the total impact upon the environment will be when the industry goes into full operation (1). Perhaps least clear of all are the potential effects on the waters of western Colorado, including the drainage of the Colorado River. Even the most recent reports (see for example reference 2) must call upon rather old and sketchy data in an attempt to assess how an oil shale industry will affect waters of the region. We feel that our work fills an important gap in understanding the potential mobilization and movement of contaminants from disturbed oil shale into the environment, especially into surface and ground waters of the region.

Our original plan was to study, in reconnaissance fashion, the solubility and movement of a wide variety of potential contaminants from oil shale into water, with particular emphasis on fluorine, molybdenum, boron, arsenic, and selenium. Our reasons for paying particular attention to the latter five elements were: 1) they are relatively toxic, 2) they are relatively abundant in oil shale, and 3) they can form soluble, anionic complexes in aqueous solutions at the elevated pH values associated with aqueous leachates from oil shales. In contrast, many other trace species, such as lead, copper, zinc, and mercury, tend to form insoluble hydroxide precipitates at high values of pH. Our original research plan seems to have been largely justified by the results so far obtained. We have demonstrated that most trace contaminants are present in insignificant concentrations in aqueous leachates from oil shales; the only trace and minor elements of real concern seem to be fluorine, boron, and molybdenum. In addition to the original suite of elements, we have verified that high concentrations of sulfur are present in leachates in several valence states, and that sulfur should be investigated further for its potential contaminating effects.

Our work initially focused on aqueous leachates produced through contact with fresh and retorted shale from the TOSCO II process (The Oil Shale Company), as this seemed to be the most promising process for commercial retorting at the time (1975-1976). With the continued development of the Paraho process at Anvil Points, we shifted our emphasis to also include fresh and

retorted shales from this facility. It now appears that some type of in situ retorting may be an early entry into the field. In response, we have conducted some preliminary experiments on a sample of retorted shale from the in situ facility of Geokinetics Corporation in Utah. As discussed in our Proposal for 1979-1980, we will study the leaching of samples of in situ retorted shale from the Occidental process if such samples can be obtained. As pointed out in a recent review article (1), regardless of the methods of mining and retorting ultimately adopted, the potential will exist for contamination of both surface and ground waters by leachates from oil shale.

REVIEW OF IMPORTANT PAST RESULTS

We began our study in 1975 with a small grant from the Colorado Energy Research Institute. It was clear at that time that many agencies and research groups were concerned about potential pollution of water as a result of extraction of oil from the shale (3), and in an important study, workers at the Laramie Energy Research Center (4) had shown that our choice of elements for study was probably well founded. In examining the chemistry of groundwaters associated with in situ production of oil from shale in Wyoming, they found B, Mo, F, and As in much higher concentrations in waters from production wells than in adjacent waters from observation wells; selenium, in contrast, did not occur in higher concentrations near the burned area.

Our initial work consisted of mixing known quantities of finely crushed shale with deionized water in flasks, then allowing the slurries to react for various periods of time while being agitated on a shaker table. The samples of fresh and retorted shale (TOSCO) were prepared and supplied to us by Dr. Thomas Wildeman of this project. The slurries were allowed to react for 7 days, then analyzed for Mo, F, and B; we did not have the analytical capability at that time to measure low concentrations of dissolved As and Se. The results for two different sets of slurries, representing different ratios of shale to water, showed that retorted TOSCO oil shale released significantly more Mo and B to solution than the equivalent fresh shale. In contrast, the fresh oil shale released somewhat more F to solution than the retorted material. This was also the first time that we discovered the release of very high concentrations of F; in the range of approximately 6 to 20 mg/L, to aqueous leachates by oil shale. The experimental data are available in the unpublished Final Report to the Colorado Energy Research Institute, entitled Trace Elements in Oil Shale (1976).

Beginning in 1976, funding from the U.S. Department of Energy allowed us to expand both the scope and intensity of our work. An early part of this work involved determining the reliability of the analytical methods for the various elements in oil shale. Discussion of the methods and analytical precision can be found in our Progress Report to D.O.E. for 1977. Continuing our shaker studies on TOSCO shales, we were able to monitor the rate of release of Mo, B, and F from the shales into aqueous solutions for periods of time up to 127 days. The results showed that Mo apparently attained equilibrium with the leachate after about 7 days of agitation, F after approximately 30 days, and B required more than 127 days to reach equilibrium. The retorted TOSCO shale released about 300%

more Mo to solution than the fresh material, reaching a concentration of 3.2 mg/L in the leachate; this is more than three times the maximum concentration (1.0 mg/L) considered by one state agency, the New Mexico Environmental Improvement Agency, to be safe for irrigation water (5). Similarly, the retorted TOSCO shale released about twice as much B to solution as the fresh shale, about 5 mg/L at the end of 127 days; this concentration would be harmful to such fruit crops as apples, cherries, and peaches (6). The experiments verified our earlier observation that fresh TOSCO oil shale releases more F to aqueous solution than does the retorted equivalent, but not by a large amount; the final concentration in solution was about 25 to 35 mg/L for both materials. Such concentrations are more than an order of magnitude greater than the limit of about 2 mg/L placed on drinking water by the U.S. Environmental Protection Agency. Treatment or dilution of the leachate would be required to bring this high concentration of F down to an acceptable level for drinking water.

During 1976-1977 our analytical laboratory was able to develop acceptable techniques for As and Se. The results from our shaker experiments were quite interesting for these two elements; after 33 days of agitation and contact, the aqueous leachate contained less than 0.1 mg/L of either As or Se, with As being the less soluble of the two. These results led us to conclude that release of As and Se to natural waters from either fresh or retorted oil shale would probably not be a significant problem. Studies of uptake of As by plants, conducted by Dr. Willard Lindsay and his students of this project, confirm the low mobility and availability of As (Progress Report, 1978).

In 1976-1977 we also began work on the chemistry of leachates generated by passing water through columns of crushed oil shale, recognizing that this was a more realistic approach to a field situation in which rainfall or snow-melt could be expected to percolate downward through disposal piles of oil shale. Small glass columns (3.0 by 30 cm) were packed with TOSCO materials, both fresh and retorted, and saturated with water. A constant head of about 3 cm was maintained, with a resulting rate of flow of about 25 mL/day. The calculated darcy permeabilities were between 1 and 6×10^{-5} cm/sec; these permeability values were probably higher than would be found in the field because we were not able to compact our samples as thoroughly as will be done with the disposal piles. One great advantage in using columns instead of shaker studies is that the chemistry of the leachates can be followed as a function of the number of pore volumes which have passed through the shale. The results of this early work with columns showed that the pH of the leachate remained at about 8.5 for TOSCO shale, regardless of the number of pore volumes passed through; this was expected because of the large buffering capacity of the shale. In contrast, the specific conductance dropped rapidly with continued rinsing, corresponding to a drop in the total dissolved solids. In one experiment the specific conductance dropped from an initial value of 17,710 micromhos/cm in the first pore volume to 260 micromhos/cm in the sixteenth pore volume (corresponding approximately to 12,000 mg/L and 180 mg/L total dissolved solids, respectively). We found also that the concentration of Mo and B in the leachates was a function of the number of pore volumes passed, with the high concentrations (12 mg/L Mo and 10 mg/L B) found in the first pore volume dropping rapidly to low values with continued

rinsing. The concentrations of Se and As were again, as in the shaker studies, very low. The big surprise was in the results for fluorine. The concentrations of F in leachate from retorted TOSCO shale were as high as 18 mg/L, with very little change as a function of the number of pore volumes, up to about 20 pore volumes passed through the columns. In other words, the concentration of F remained high, despite the rinsing action of the percolating water. This clearly means that there is a solid reservoir of F in the shale, capable of supplying fresh material to the solution as fast as the water passes through. The most obvious such reservoir would be a mineral phase, and some of our current research is directed toward identifying this presumed solid phase. The importance of our observations regarding the solubility of F is that this particular contaminant cannot simply be rinsed out of the shale by passage of a few pore volumes of water; instead, the F will remain in high concentrations for extended periods of rinsing.

During 1977-1978, as reported in the Progress Report of 1978, we expanded our study to include more work on column leachates, determination of the source and mechanisms of release of fluorine, and interaction between leachates and native soils of the Piceance Basin. Much work was done on fresh and retorted shales from the Paraho process, with less emphasis on TOSCO materials. The Paraho materials came from the large lysimeters of retorted shale, constructed by Dr. William Berg and Dr. Trey Harbert at Anvil Points, Colorado, and from discarded fresh feedstock material from the Paraho plant; the latter was provided by Dr. Wildeman of this project. The shaker table experiments were continued, comparing the leachates generated by retorted Paraho shale to those from additional TOSCO materials. We found a much higher slurry pH from Paraho shale (about 10.5) than from TOSCO shales (pH of approximately 8), but the specific conductance of the leachates from Paraho retorted shale was slightly less than from retorted TOSCO shale. The concentrations of Mo, B, and F were all significantly lower in leachates from retorted Paraho shale than from TOSCO retorted shale. The concentrations of As and Se were, again, so low from all materials as to be insignificant. This additional work on TOSCO materials also confirmed our earlier results on the concentration and behavior of the elements.

At the invitation of Dr. William Berg of Colorado State University, we sampled leachate generated by irrigation of the lysimeters that he and Dr. Trey Harbert had constructed near the Paraho site. These lysimeters seem to offer a reasonable approximation to the situation that will prevail if Paraho waste shale is placed on the surface of the ground in this region. Although the values obtained from the lysimeters differ in detail from our laboratory results, the concentrations of each element of interest, and the pH and specific conductance, are so similar as to give us confidence in the usefulness and applicability of our laboratory work to the actual field situation that will prevail, at least in some retorting locations.

Perhaps the most interesting new information to come from our analyses of the leachate from the Paraho lysimeters was the very high concentrations of total and reduced forms of sulfur (ranging from about 9000 to 25000 mg/L as sulfate). Analysis of some of these leachates showed that as they aged in containers in the laboratory, the pH dropped significantly, probably as a result of oxidation of reduced species of dissolved sulfur to sulfuric acid. We recognized that such a chemical change could have significant

environmental consequences if the leachates were to be discharged into the environment.

During the 1977-1978 period we also began an intensive study of the source and chemical behavior of fluorine in oil shale. Of particular interest is the fact that high concentrations of F are maintained in aqueous leachates that may contact the shale, through many pore volumes of rinsing. It is important to identify the source of F in the shale, because if the source in the shale can be identified, it may be possible to devise strategies to reduce or eliminate the release of dissolved F to waters that may pass through discarded shales. The fact that fresh oil shale releases more F to water than retorted shale is also of concern. Regardless of the ultimate technology to be used in retorting shale, it is probable that large quantities of fresh oil shale will be broken and stored or discarded in areas where it can be leached by percolating natural waters. We began the investigation by collecting 136 samples of fresh shale from the U.S. Bureau of Mines Corehole 01-A, courtesy of the U.S. Geological Survey in Denver. The same core samples had previously been used by the Laramie Energy Research Center for Fisher Assay and x-ray diffraction analysis. We had 25 of the samples analyzed for bulk content of F, using the molecular absorption method developed by Dr. Robert Meglen of our Central Analytical Laboratory. The samples were selected to determine how F varies with depth and to look for correlations between the content of F, the stratigraphic position, content of organic matter, and mineralogy. The results of this initial work suggested that F is distributed in an erratic fashion through the Mahogany Zone, with no obvious correlation with either organic matter or mineralogy. Values as high as 1500 ppm F were found in some samples in the Mahogany Zone. Our work on this topic is continuing, with interesting new results reported later in this report. We also conducted an extensive search of the literature, trying to establish the concentrations of dissolved F and total dissolved solids presently found in the various important bodies of surface and ground water of the Piceance region. This information should be of value in checking baseline values and in devising methods for disposing of contaminated waters that may be produced in either the mining or processing of the shale. Concentrations of F as high as 80 mg/L have been reported from ground waters of the Upper Aquifer on the C-a tract in Colorado, and in Wyoming values of F as high as 300 mg/L have been recorded (Progress Report, 1978).

The last research topic in 1977-1978 was preparation for a study of the interaction of soils from the oil shale region with F and B dissolved in aqueous leachates from Paraho oil shale. Our purpose in this continuing study is to determine whether or not the native soils have an ability to remove F and B from aqueous leachates that may be generated. Such knowledge should be useful in establishing locations and procedures for disposal of waste shale, with protection of ground water being an important consideration. This work is largely funded by an NSF Energy Traineeship to the student involved, Michael Glaze. The leachate used in the investigation was generated by allowing retorted Paraho shale to react with water on a shaker table for periods of time up to about two weeks. In generating the leachates we found that the grain size of the shale is not important, but that the ratio of solid to liquid and the time of shaking are important. The fact that the ratio of solid to liquid exerts a control

on the final concentrations of F and B in the leachates strongly suggests that surface chemistry is playing a role in the dissolution of the elements from the solids. The concentrations of B and F ultimately achieved, using a 1:1 ratio of shale to water, were similar and quite consistent with earlier results on leachates from Paraho shale in columns, shaker studies, and the lysimeters at Anvil Points. Soils were collected, with the aid of Dr. Ronald Klusman of this project, from three locations in the Piceance Basin; the locations were some of those that had been designated as disposal sites in the Environmental Impact Statements.

OVERVIEW OF PRESENT RESEARCH

Our current research efforts are proceeding along three lines: 1) determination of the chemistry of leachates generated by passing waters through columns of shale, with particular emphasis on the role of aging, cycles of wetting and drying, and on the chemistry of dissolved sulfur, 2) the interaction of aqueous leachates with soils of the oil shale region, with emphasis on boron and fluorine, 3) the source and chemical behavior of fluorine in the oil shale.

We feel that our efforts are relevant and important. As mentioned earlier, relatively little is known about the probable impact on water resources of western Colorado due to mining and retorting of oil shale. It is imperative that we determine the types and behavior of possible contaminants that may move out of oil shale into waters of the area. A recent report from the Office of Technology Assessment of the U.S. Congress concludes that the single topic of highest national priority is "Impact of Technology on National Water Supply and Demand" (7); the oil shale industry may play a significant role in this problem. Regardless of the technology that is finally adopted for recovering oil from the shale, it is inevitable that either freshly broken shale or retorted waste products will be subject to leaching action by natural waters, and our efforts are directed toward understanding how the chemistry of these waters will be altered, together with the resulting environmental impacts. A recent review article (1) states that: "It is important, for predictive purposes, to understand the mechanisms of transformation, solubilization, and redistribution of inorganic and organic residuals after disposal as they are influenced by environmental factors over the long term," and: "The effects of shale composition, retorting, and disposal methods and environmental factors on leachate composition have not been extensively investigated."

CHEMISTRY OF LEACHATES

This work is a continuation and extension of the column experiments that were initiated in 1976. The questions and procedures have become quite specific, as will be clear from the following discussion.

Materials and Methods

Five different types of oil shale are being used in our laboratory experiments, three of which were prepared by Dr. Thomas Wildeman of this project. The three samples from Wildeman represent retorted (spent) and unretort-

ed (fresh) shale supplied by TOSCO from the Mahogany Zone at the Colony Development site near Grand Valley, Colorado. We have used Wildeman's fresh shale (OS-1) and two spent shales (SS-1 and SS-2); SS-2 represents the spent residue from retorting of fresh shale OS-1. Retorted shale SS-1 came from feedstock mined from a lower stratigraphic interval in the Mahogany Zone at the Colony site. Wildeman reports that the spent shales, SS-1 and SS-2, were very fine grained, with 90% passing a 200 mesh sieve (0.074 mm). The other 10% of the spent material was very coarse, greater than 10 mesh (2.0 mm). Wildeman ground the coarser fragments by hand until 95% would pass a 100 mesh screen (0.23 mm). The crushed samples were then blended by Wildeman, and 14 splits were supplied to us. Chemical analyses of these materials were given in our Progress Report in 1977.

Oil shale retorted by the Paraho process was collected from the lysimeters constructed by Drs. William Berg and Trey Harbert at Anvil Points, Colorado for use in our laboratory leaching experiments. The shale was collected from three plots that had been compacted to approximately 105 lbs/3 ff³, which is the packing density Paraho plans to use in the construction of its disposal piles. This retorted shale is representative of the waste that will be subjected to leaching by natural precipitation in the field. In this report the retorted Paraho shale is labeled PSS-1; only the (-) 2 mm size fraction was used in the experiments reported here.

We are also using a sample of fresh shale collected at the Paraho site. This material was too fine-grained to be retorted and represents material that must be discarded at the site. This shale is labeled POS-1 in this report and was also supplied by Dr. Wildeman. Table 1 gives the size breakdown of the five materials used. Both fresh shales are predominantly sand size, whereas the majority of TOSCO II retorted shale is in the silt range.

TABLE 1.

<u>Oil Shale</u>	<u>% Clay</u>	<u>% Silt</u>	<u>% Sand</u>	<u>% 2-10 MM</u>
POS-1	2	10	75	13
OS-1	4	17	79	0
SS-1	3	87	10	0
SS-2	4	86	10	0
PSS-1	2	15	66	18

Analytical Methods--

Leachates were analyzed by the following procedures: 1) F was determined by a molecular absorption technique developed by Dr. Robert Meglen of our central analytical laboratory; 2) B was determined by the azomethine-H colorimetric method; 3) Mo by a colorimetric procedure using the thiocyanate complex (8); 4) As and Se 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. Total sulfate was determined after oxidizing the leachate with 30% of H₂O₂, by the nitrochromeazo titration

method (9). Determination of thiosulfate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$), and the other polythionates ($S_4O_6^{2-}$, $S_5O_6^{2-}$, and $S_6O_6^{2-}$), was based on the conversion to SCN^- under different reaction conditions, followed by the measurement of the ferric thiocyanate color complex (10,11). Thiocyanate in leachate was determined by the ferric thiocyanate complex without any other chemical preparation.

Column Studies--

Leachate was produced by percolating water through laboratory columns of the five types of shale. The columns are made of Pyrex glass, approximately 30 cm high and 3.0 cm I.D. Based on our experiences with the shaker experiments (Progress Report, 1977), we do not feel that loss of F or gain of B due to contact with the Pyrex would be significant because of the limited surface contact between solution and the walls of the columns. Approximately 200 grams of shale were packed into each column, one or two centimeters at a time, with a rubber plunger. Nylon plugs were used to contain the shale within the columns. In early column experiments (Progress Report, 1978) the shale was moistened with water first to aid in compaction. We found that due to the limited packing pressures attainable in the laboratory, there is no significant difference in density or porosity whether the shale is packed dry or wet, and all subsequent columns have been dry packed. Table 2 shows the porosity and density of the various shale samples within the columns. Paraho spent shale in the columns was compacted to about 65-75% of the density expected in the field (100-105 lbs/ft³ (12) and TOSCO II spent shale to about 75-85% (90-100 lbs/ft³ (13,14)). Porosity was measured by allowing water to flow upward (to eliminate air bubbles) from a burette into the shale until the shale was saturated, and the volume lost from the burette was then recorded. Leaching of the shale was carried out by applying deionized water to the top of the column in increments of 1/3 the pore volume of the shale in the column. Each 1/3 pore volume was collected for analysis before applying the next fraction of water in order to get a better idea of the leaching mechanism operating within the shale. A total of six samples (two pore volumes) were collected from each column.

Equilibrium and Wet-Dry Column Experiments

Two different leaching conditions were modeled. In the first the shale in the column was allowed to equilibrate with the interstitial water for 10, 209, and 400 days before leaching in order to evaluate the effect of time and approach to equilibrium on leachate composition. The second experiment attempted to model the wet-dry condition which is likely to exist in the near-surface environment of any disposal pile; repeated infiltration of rainfall, snowmelt, and irrigation water into a disposal pile followed by evaporation will create a wet-dry situation which could change the leachate composition. This is of direct concern to the establishment of stable ecosystems on waste oil shale piles as well as to questions of pollution. In our experiments, the shale was placed in plastic beakers, saturated, and then placed under a heat lamp (40-50 °C) to dry. This process was repeated 20, 50, 100, and 150 times. After drying for the last time, the shale was packed into columns, saturated, allowed to equilibrate for 10 days, and then leached in increments. Ten days were chosen on the basis of earlier shaker experiments as an adequate amount of time to approach equilibrium for most of the measured parameters (Progress Reports, 1977 and 1978).

TABLE 2.

<u>DRY PACKED</u>						
		SS-1*	SS-2*	PSS-1**	OS-1*	POS-1*
<u>Porosity (%)</u>	Ave.	44	44	48	37	28
	Range	43-47	42-46	44-49	35-39	28-30
<u>Density (gms/cm³)</u>	Ave.	1.2	1.2	1.1	1.1	1.4
	Range	1.1-1.2	1.1-1.3	1.0-1.1	1.0-1.1	1.3-1.4
<u>(Lbs/ft³)</u>	Ave.	74	73	66	67	86
	Range	71-77	71-78	64-71	66-69	83-88
<hr/>						
<u>WET PACKED</u>						
		SS-1***	SS-2***			
<u>Porosity (%)</u>	Ave.	47	46			
	Range	46-51	46-48			
<u>Density (gms/cm³)</u>	Ave.	1.2	1.1			
	Range	1.2-1.3	1.1-1.2			
<u>(Lbs/ft³)</u>	Ave.	76	71			
	Range	74-79	69-74			

*Based on 5 columns

**Based on 6 columns

***Based on 3 columns

Table 3 shows the hydraulic conductivities of the five shale types from both column experiments determined by a falling head method. Because the bulk densities of the shales within the columns are lower than would be achieved under actual field compacting conditions, the hydraulic conductivity values in Table 3 may be somewhat higher than would be found in an actual disposal pile. Nevertheless, unless a thorough self-cementing takes place within the waste pile, the hydraulic conductivities show that water will be able to migrate through the shale. The limiting factor will be the amount of water entering the shale.

Results and Conclusions

Column Equilibrium--

Figures 1 through 11 show the effect of time on the release of dissolved species to water in contact with various shales in columns. In each figure, 1 through 11, the solid vertical bar represents the value found in the first pore volume of leachate, and the hollow vertical bars represent subsequent pore volumes. The numbers along the abscissa represent the number of days that the column of shale was allowed to equilibrate with water. The PSS-1 column labeled "field" is the average value for leachate generated from the Berg-Harbert lysimeters during the initial irrigation of the plots containing the shale control and the 8" soil cover (see our Progress Report, 1978, for a diagram of the lysimeters). As was previously mentioned, the Paraho retorted shale used in our laboratory experiments was collected from these lysimeters as they were being filled and compacted. Thus, we can get some idea of the extent to which our laboratory models approximate field conditions.

As can be seen from figures 1 and 2 there is little difference in pH between leachate from fresh oil shale and from shale retorted by the TOSCO II process. Retorting by the Paraho process, however, results in an initial increase in pH to 11 or greater. The lower pH values (9.5) measured in our laboratory column leachates appear to be a result of aging and possibly of uptake of carbon dioxide gas; over 1½ years elapsed between collection of the Paraho spent shale and our column experiments. Shaker experiments with this shale immediately after collection resulted in a pH of about 11 (Progress Report, 1978). The high pH values are a result of partial decomposition of carbonate minerals into their respective oxides. Length of time that water and shale are in contact in the laboratory does not appear to have a major effect on pH, and there is no apparent pH change when more than one pore volume of water is passed through the shale. In contrast, the field study of the retorted Paraho shale (PSS-1) in the Berg-Harbert lysimeters showed a drop in pH from about 10.5 to about 7.3 after a few hundred liters of water had percolated through; this is discussed later with reference to Table 7 and Figure 14.

Figures 3 and 4 show the change in specific conductance of the leachates with time. To convert approximately to mg/L total dissolved solids, multiply by a factor of .7. Higher concentrations of dissolved solids are released from retorted oil shale than from unretorted oil shale. This is especially noticeable when comparing the TOSCO II retorted shale, SS-2 (Fig. 3), with its unretorted equivalent, OS-1 (Fig. 4). After 400 days of water-shale contact, leachate from SS-2 had a specific conductance of 26,500 umhos/cm (19,000 mg/L) compared to 8,000 umhos/cm (5,600 mg/L) for OS-1. Some of

TABLE 3.

<u>COLUMN EQUILIBRIUM</u>					
Hydraulic Conductivity (cm/sec)	SS-1	SS-2	PSS-1	OS-1	POS-1
Average	1.5×10^{-4}	1.4×10^{-4}	8.5×10^{-4}	1.3×10^{-4}	9.8×10^{-5}
Range	$1.1-1.8 \times 10^{-4}$	$1.2-1.6 \times 10^{-4}$	$5.4 \times 10^{-4}-1.0 \times 10^{-3}$	$7.3 \times 10^{-5}-1.6 \times 10^{-4}$	$7.1 \times 10^{-5}-1.2 \times 10^{-4}$
<u>COLUMN WET-DRY</u>					
Hydraulic Conductivity (cm/sec)					
Average	1.7×10^{-5}	6.5×10^{-5}	2.7×10^{-4}	2.8×10^{-4}	5.7×10^{-4}
Range	$1.1-3.4 \times 10^{-5}$	$4.5-8.0 \times 10^{-5}$	$1.6-3.2 \times 10^{-4}$	$2.6-3.0 \times 10^{-6}$	$4.2-6.9 \times 10^{-4}$

Figure 1. pH of retorted oil shale leachates from column equilibrium study. Values are for the 1st pore volume (10 and 209 days), and for the 1st three pore volumes (400 days). Analytical precision = $\pm 3\%$

Figure 2. pH of unretorted oil shale leachates from column equilibrium experiment.

Figure 3. Specific conductance of retorted oil shale leachates from column equilibrium experiment. Analytical precision = $\pm 5\%$.

Figure 4. Specific conductance of retorted oil shale leachates from column equilibrium experiment.

this increase is probably due to the greater surface area of the predominantly silt-size SS-2 compared to the predominantly sand-size OS-1 (Table 1). Reactions in the retort and cooling water added to the hot spent shale result in some increased mobility of elements.

The reason for the lower concentration of dissolved salts in SS-1 than in SS-2 (Fig. 3) is not known at this time. If one assumes that both shales were retorted, treated, and collected in the same manner, then the difference must be due to variation in the initial composition of the feedstock. However, this is not obviously the case, as both shales seem to be rather similar in composition (Progress Report, 1977). Possibly, different amounts of water were used to cool the shale; this could be an important factor if high temperature reactions occur between the hot shale and the water. We will attempt to define the effect of the interaction of the water with the hot shale in future experiments. Another difference between the TDS from TOSCO SS-1 and SS-2 is the effect of time. As shown in Figure 3, the TDS from SS-1 remains essentially constant with time of aging, whereas the leachate from SS-2 has about 50% more total dissolved solids after 400 days than after 10 days of equilibrium.

The coarser Paraho retorted shale, PSS-1, releases about the same amount of TDS to the water as does the finer-grained TOSCO SS-1. The average concentration obtained for Paraho shale in the field is about 40% higher than the lab value (Fig. 3). This is apparently due to the easily soluble salts being rinsed out with the wetting front, yielding relatively high concentrations in the initial portions of leachate collected in the field. When averaged over entire pore volumes, field concentrations will probably be closer to laboratory values.

The most noticeable effect of time on equilibration (Fig. 4) is for the fresh shale collected from the Paraho plant, POS-1, where TDS increased more than 3 times from 10 to 400 days. Sample OS-1, like SS-1, shows little change with time. Samples SS-2, PSS-1, and POS-1 exhibit the greatest increase in total solubility between 10 and 209 days of water-shale contact. As shown by the incremental sampling, TDS is greatly reduced in the second and subsequent pore volumes for all shales.

Figures 5 and 6 show that Mo does not increase with time as does TDS. In fact, there is a decrease with time in the concentration of Mo in leachates from fresh oil shale, especially POS-1 (Fig. 6). The reason for this behavior is not clear at this time; however, we do have one more column filled with POS-1 which we will leach at 550 days in order to see if this trend continues. Fresh shale OS-1 releases only about 1/3 of the amount of Mo that POS-1 does, in spite of their apparently similar grain size (Table 1). The difference may be due to higher concentrations of Mo in POS-1, but we do not yet have these analyses for comparison.

As shown in Figures 5 and 6, more Mo is released from retorted SS-2 than from its fresh equivalent, OS-1. Again, this may in part be due to the size difference. In contrast to TDS, similar Mo concentrations were found in both retorted SS-1 and retorted SS-2 leachates. The coarser Paraho spent shale (PSS-1) released far less Mo than did the TOSCO II spent shale. Mo concentrations in leachate from all shale samples are greatly

Figure 5. Concentration of Mo in retorted oil shale leachates from column equilibrium experiment. Analytical precision = $\pm 10\%$.

Figure 6. Concentration of Mo in unretorted oil shale leachates from column equilibrium experiment.

reduced by passage of the 2nd and 3rd pore volumes.

Figures 7 and 8 show the concentration of B in leachate from the five columns of shales. One can see that B is still increasing in the retorted shales (Fig. 7) after 400 days of water-shale contact, in a manner similar to TDS (Fig. 2). This slow response of B was also exhibited during our earlier slurry experiments (Progress Report, 1978). In contrast, equilibrium concentrations in fresh oil shale are attained within 10 days (Fig. 8). Boron dissolved from the spent shales remains elevated in the second pore volume of leachate and then begins to decrease rapidly, whereas B in the fresh oil shale leachate greatly decreases by the 2nd pore volume. Similar concentrations are released from both of the TOSCO retorted samples and from the fresh equivalent.

As shown in Figure 8, about twice as much B is released from fresh Paraho POS-1 than from fresh TOSCO OS-1, in spite of the apparently similar grain size. This difference serves to point out the variability that can occur in leaching characteristics of shale collected from different parts of the Piceance Creek Basin.

Fluoride (Figs. 9 and 10) is one of the most interesting elements in oil shale leachate. After allowing shale and water to equilibrate for only 10 days, concentrations greater than 50 mg/L were measured in the first pore volume of leachate from the fresh Paraho fines (POS-1, Fig. 10). Fluorine in the first pore volume of leachate from the 400 day study (POS-1) is reduced by a factor of 3 compared to 10 days. And, interestingly, the concentration of F increases in the 2nd and 3rd pore volumes instead of decreasing as is the case with other elements. This striking behavior will be discussed in the next section. The other leachate from fresh oil shale, OS-1, also shows a decrease in F in the first pore volume with time; however, the decrease is not as much as for POS-1, and concentrations are lower in the 2nd and 3rd pore volumes instead of higher.

In contrast to fresh oil shale, spent oil shale releases more F to water with increasing time of contact (Fig. 9). The most dramatic increase comes between 209 and 400 days. Paraho retorted shale (PSS-1, Fig. 9) releases only about half as much F as does TOSCO retorted shale (SS-1 and SS-2, Fig. 9); this might be expected on the basis of the larger grain size of the Paraho materials. However, if a solid mineral really is controlling the solubility of F in the leachates, the final concentrations should be nearly independent of grain size, at least for sizes above about 1 micron.

Figure 11 shows the concentration of As and Se in initial core volumes of oil shale leachate up to 209 days of aging. We do not yet have the data from the 400 day experiment. There are two points worth noting in Figure 11; first, As and Se concentrations are low, and second, the concentrations of Se generally increases with time for spent shale and decreases in the case of fresh shale. This further serves to point out the significant differences in chemical behavior between retorted and fresh oil shale.

Behavior of F in Leachate--

The concentration of TDS, Mo, and B in leachate drops rapidly after passage of 1 or 2 pore volumes of water, but F remains at an elevated level

Figure 7. Concentration of B in retorted oil shale leachates from column equilibrium experiment. Analytical precision = $\pm 10\%$.

Figure 8. Concentration of B in unretorted oil shale leachates from column equilibrium experiment.

Figure 9. Concentration of F in retorted oil shale leachates from column equilibrium experiment. Analytical precision = $\pm 10\%$.

Figure 10. Concentration of F in unretorted oil shale leachates from column equilibrium experiment.

Figure 11. Concentrations of As and Se in leachate from columns after 10 and 209 days of contact. Results for 400 day experiments not yet available. All results for first pore volume. Analytical error about $\pm 10\%$ of values shown.

and in some cases, dramatically increases, as already shown in Figure 10. Figure 12 is a graph of the F concentrations from an earlier column experiment using SS-1 and SS-2 (Progress Report, 1978). The concentration of this element remained at a relatively constant, high level throughout the experiment. This clearly means that there is a solid reservoir of F in the shale that is capable of replenishing and restoring the F to the percolating water. The sudden increase in F for SS-1 between pore volume number 10 and 14 coincides with a decrease in the concentration of calcium from 320 mg/L to 60 mg/L (not shown).

Figure 13 is a composite of 58 analyses for F and Ca from leachates generated in the first column experiment (Progress Report, 1978). Although there is some clustering of SS-1 and SS-2 values, there is enough overlap of the two for a meaningful correlation to emerge between the concentration of F and Ca. The general trend indicates that as the concentration of Ca decreases, the concentration of F increases, with a molar ratio of about 10 to 1, Ca to F. Table 4 presents additional evidence for a systematic relationship. In Table 4, after 10 days of contact between water and shale, 53 mg/L of F and 56 mg/L of Ca were present in the leachate from fresh Paraho shale. But after 209 days of contact we observed an increase in Ca to 120 mg/L and a decrease in F to 29 mg/L. In the second pore volume collected from the 209 day experiment, Ca dropped greatly to 7.2 mg/L, and F rose to 57 mg/L. It is thus clear that the concentrations of F and Ca are related in a reciprocal fashion. A somewhat similar relationship is found between TDS and dissolved F, probably also related in some way to Ca. The relationship is a complicated one and will be investigated later with the help of a computer model for solid-water interactions.

TABLE 4.

POS-1			
No. of Days - No. of Pore Volume	F(mg/L)	CA(mg/L)	TDS(mg/L)
10-1	53	56	2,520
209-1	29	120	6,930
209-2	57	7.2	1,260

Wet-Dry Column Experiments--

Figures 14 through 19 show the results to date of repeated wetting and drying of shale prior to leaching in columns. The 100 and 150 cycle experiments have not been completed yet. When comparing the wet-dry experiments with the equilibrium experiments, it should be recalled that after completion of cycling, the shale from the wet-dry columns was allowed to equilibrate in columns for 10 days, and the results are therefore compared with the data for the 10 day equilibrium study, represented in Figure 14 by the 0 (zero) wet-dry value.

Repeated wetting and drying of TOSCO II retorted shale has little effect on pH of the leachate (Fig. 14). The only noticeable difference in behavior

Figure 12. Concentrations of F in leachate from columns of retorted TOSCO oil shale, shown as a function of the number of pore volumes passed through columns. Analytical error is about $\pm 10\%$ of values shown, within two standard deviations.

Figure 14. Effect of multiple cycles of wet-dry on pH for three retorted and two fresh oil shales. 10 days equilibrium time. The first bar in each column represents 10 days of equilibration, with zero wet-dry cycles.

between this cyclic experiment and the static 10-day study is in the behavior of PSS-1 and POS-1. In both cases, pH decreases significantly as the number of wet-dry cycles increases; this decrease is in agreement with the drop in pH seen in the field study of leachate from the Berg-Harbert lysimeter, suggesting that the calcined oxides in the Paraho shales are undergoing re-carbonation.

Figure 15 shows the behavior of specific conductance in the leachates. The only obvious trend is in PSS-1 and POS-1 where wetting and drying the shale 50 times results in an increase of 75% and 220% respectively. This result is again in agreement with the higher values of TDS seen in leachate from the Berg-Harbert field lysimeters than from laboratory columns (mentioned earlier with reference to Figure 3). In the case of the TOSCO shale samples, no appreciable increase in TDS is observed with repeated wet-dry cycling.

Figure 16 is a graph of Mo behavior in response to wet-dry conditions. Two trends are obvious. Alternating wet-dry cycles cause Mo to increase in the retorted shale leachates and to decrease in leachates from the unretorted shale. The reason for these two opposing trends is not known at this time, but the decrease is in accord with the decreasing trend with time that was noted in the static, equilibrium study with fresh shale (Figure 6).

Figure 17 indicates that repeated wetting and drying of the surface of fresh shale waste piles will significantly reduce the amount of B available for leaching. The concentration in POS-1 decreased from 30 mg/L to 6 mg/L and for OS-1, from 13 mg/L to 3 mg/L. The reason for this is not known at this time. No effect was observed with any of the retorted shales, with B concentrations remaining near the control.

Figure 18 shows the results for F. Fluorine exhibits the same trends as B; no change occurs in retorted shale, but the concentration in unretorted oil shale is greatly reduced by the wetting and drying action. The effect on F of passing more than one pore volume of water through the shale will be evaluated in the remaining 100 and 150 cycle part of the experiment.

Figure 19 shows that the alternating wet-dry treatment of both spent and fresh oil shale results in a dramatic increase in the concentration of Se in leachate. SS-2 exhibits the largest increase in Se concentrations, from 20 ug/L to over 250 ug/L. This latter value is five times the U.S. E.P.A. drinking water standard. We will have to wait for our results on the 100 and 150 wet-dry cycle experiments to see if this trend continues. Arsenic remains low in all leachates.

It should be re-emphasized that the wet-dry experiments model only a relatively small (but important) percentage of the total mass of the waste pile. The surface area of the pile will be exposed to alternate wetting and percolation of water from various sources. When a wetting episode has ceased, the near-surface water, with its dissolved species, will rise back to the surface by capillary action as the moisture evaporates. This process, operating over many years, could change the chemical environment in which the roots of plants must survive. It appears on the basis of our experiments that wetting and drying cycles will cause an increase in TDS in piles of both fresh oil shale and retorted Paraho shale, and an increase in Se in pore waters in most materials. However, the general loss of B and F upon wetting and drying

Figure 15. Effect of wet-dry cycles on TDS in leachates from five shales.

Figure 16. Effect of wet-dry cycles on solubility of Mo from five shale columns.

Figure 17. Effect of wet-dry cycles on solubility of B from five shales.

Figure 18. Effect of wet-dry cycles on solubility of F from five shales.

Figure 19. Effect of wet-dry cycles on solubility of Se and As from five samples. Note that values are micrograms per liter, compared to milligrams per liter for all other components discussed.

of fresh shale is an important positive factor in improving the quality of the interstitial waters.

Periodically there will probably be sufficient percolation to move some salts downward from the surface, out of the reach of capillary action, but the amount thus moved will probably be insignificant compared to the mass of salts in the rest of the pile. The opposite effect could also occur, in which capillary action moves the salts to the surface of the pile, where winds could blow the salts to adjacent areas.

Sulfur Studies--

An interesting aspect of the chemistry of oil shale is the behavior of sulfur. The concentration of sulfur in Colorado oil shale ranges from 0.56 to 1.99% by weight (15). Of the total, 19-37% occurs as organic sulfur, 63-79% as inorganic sulfides, principally pyrite, and up to 4% as sulfate (15). 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 (16) have measured 2300 mg/L total dissolved sulfur in Omega-9 retort water from the Laramie Energy Research Center, with 30% as sulfate, 55% as thiosulfate ($S_2O_3^{2-}$), 4% as tetrathionate ($S_4O_6^{2-}$), and 3% as thiocyanate (SCN^-). We have found reduced species of dissolved sulfur in leachate collected from the retorted Paraho shale in the Berg-Harbert lysimeters during the initial irrigation of the shale in June, 1977 (Progress Report, 1978). 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 for periods of time up to the present (about 1½ years). We found that the pH of the leachates had dropped significantly after only three weeks of storage, and the drop has continued to the present in many of the samples (see Table 5). As shown in Table 5, the pH in many of the samples has dropped from about 10.5 to as low as about 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 seems clear that oxidation of the reduced species of dissolved sulfur has taken place, with the production of sulfuric acid. A similar phenomenon has been noted by other researchers (14) using leachate derived from lysimeters of TOSCO retorted shale. Because thiosulfate ($S_2O_3^{2-}$) is the major reduced form of sulfur in retort waters, it seems likely to also be predominant in leachate from retorted shale, although tetrathionate ($S_4O_6^{2-}$) and thiocyanate (SCN^-) may also be significant (17). Any thiosulfate that might have still been preserved in our leachates was measured on November 22, 1978, and the results are shown in Table 5; the results show that significant concentrations of thiosulfate still existed after about 1½ years of storage. We determined thiocyanate in only a few samples, and tetrathionate was measured only in one sample (RW5311, Table 5), where 720 mg/L were found. A qualitative check for tetrathionate and thiocyanate in early January, 1979, showed that both are still present in many samples. The concentration of sulfur species in leachate at any given time depends on both the original concentration and the amount of reaction which has occurred. Table 5 serves to show that some reduced sulfur species can persist for a relatively long time in the same environ-

TABLE 5.

Sample #	Date collected	Initial pH	pH			Remaining reduced species on 11/22/78	
			7/5/77	6/22/78	11/22/78	$S_2O_3^{2-}$ (mg/L)	SCN^- (mg/L)
RW5279	6/8/77	10.2	5.4	3.6	3.6	3800	-
RW5280	6/8/77	10.5	6.2	6.5	6.4	2200	51
RW5284	6/8/77	8.2	6.4	3.3	3.2	870	30
RW5285	6/9/77	10.8	6.3	6.5	6.4	1350	-
RW5286	6/9/77	10.4	6.9	6.8	7.4	1070	-
RW5287	6/9/77	11.2	8.6	-	6.4	1180	24
RW5288	6/9/77	10.9	5.9	6.4	7.0	1350	-
RW5289	6/9/77	10.7	6.2	7.0	7.0	1250	-
RW5291	6/13/77	10.9	9.7	7.2	7.9	2680	86
RW5292	6/13/77	11.0	10.1	7.2	7.3	2200	57
RW5293	6/13/77	-	6.6	3.5	3.5	2020	-
RW5294	6/13/77	10.9	10.8	7.4	8.0	2940	-
RW5295	6/13/77	10.7	9.1	7.5	7.3	895	-
RW5296	6/13/77	10.4	8.8	6.8	7.5	760	-
RW5297	6/13/77	10.4	10.8	7.2	7.7	980	-
RW5298	6/13/77	11.7	11.5	7.9	7.7	1290	-
RW5299	6/13/77	11.3	10.6	6.9	6.9	1620	-
RW5302	6/14/77	11.3	11.2	7.9	6.7	-	-
RW5303	6/14/77	11.3	11.2	8.4	9.0	1400	-
RW5304	6/14/77	11.6	11.5	9.1	9.2	1820	-
RW5305	6/14/77	10.5	7.8	7.1	8.0	1590	-
RW5307	6/14/77	11.1	11.0	7.6	7.7	2580	-
RW5309	6/10/77	-	8.5	3.9	3.9	1480	-
RW5310	6/10/77	-	6.5	6.5	6.4	770	-
*RW5311	6/14/77	10.7	8.8	7.8	-	1250	-
RW5312	6/14/77	11.0	9.2	7.5	7.0	1180	-

*Analyzed 2/19/78 during checkout of thiosulfate procedure. $S_2O_3^{2-}$ = 2,150 mg/L, $S_4O_6^{2-}$ = 720 mg/L.
 - Not determined.

ments, even though the species may be thermodynamically unstable.

Decomposition of $S_2O_3^{2-}$ into S^0 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 (18). In order to test whether bacteria were responsible for the observed behavior, aliquots of RW5279 and RW5292 (Table 5) were sent to Ms. Corale Brierley, a chemical microbiologist with the New Mexico State Bureau of Mines and Mineral Resources. 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, both *Thiobacillus thiooxidans* and *Thiobacillus thio-parus* were found. *T. thio-parus* is a thiosulfate oxidizing bacteria which can grow between pH 4.5-10.0, although its optimum range is from 6.6-7.2. Starkey (18) and Skarzunski and Szczepkowski (19) have shown that the products of thiosulfate oxidation are SO_4^{2-} and S^0 . The presence of *T. thio-parus* in the lysimeter leachates thus offers the most plausible explanation for the behavior of the sulfur. *T. thiooxidans* is a sulfur oxidizing bacteria having growth range from pH 0.5 to 6, the optimum being between 2.0-3.5. Thus, *T. thio-parus* 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. This could lead to serious acid pollution problems in environments having a low buffering capacity. However, the abundant carbonates in the Green River Formation should be able to neutralize any acid generated by oxidation of sulfur compounds. Problems due to drainage and acidification might arise only where the leachate enters surface waters directly, with little contact with carbonate rocks; in such a case the buffering capacity of the surface waters might not be sufficient to neutralize the acid. Another potential effect is that many trace elements in the piles of waste shales might be solubilized and mobilized if the sulfur in the interstitial waters were to be oxidized, with a decrease in pH. These are questions that should be studied further.

Another problem involving the sulfur deals with the stability of the reduced species within the discarded shale. Stuber and others (16) report that water pumped from production wells from the in situ Omega 9 retort, one year after oil production, contained no thiosulfate. This loss could have been due to sorption, precipitation, and either inorganic or bacterial oxidation. We have also observed a similar loss of thiosulfate from retorted shales. Table 6 gives the concentration of thiosulfate in leachates from some of our column experiments. Note that thiosulfate is present in oil shales retorted by both the TOSCO II and Paraho processes, but the concentration present in Paraho PSS-1 (Table 6) is very low; because this shale is equivalent to that in the Berg-Harbert lysimeters, we had expected to find high concentrations. Something has apparently destroyed the thiosulfate after the sample was collected. This particular sample of shale was collected while damp and stored in the laboratory for about one month prior to drying. Either bacterial growth or an inorganic mechanism must have removed the thiosulfate during storage. This suggests that if bacteria can grow within the disposal piles, thiosulfate could be oxidized in situ. Such oxidation within the mass of shale might mitigate the problems associated with the production of sulfuric acid although, as mentioned above, other trace elements might be mobilized. In Table 6, TOSCO retorted shale

SS-2 also shows a complete loss of thiosulfate in the leachate collected after allowing the shale and water to equilibrate for 400 days. In contrast to this (Table 6) leachate from TOSCO retorted SS-1 showed no loss of thiosulfate with time, perhaps because the lower initial concentrations would not support bacterial growth.

TABLE 6.

<u>1st Pore Volume</u>	<u>S₂O₃²⁻ (mg/L)</u>		
	<u>PSS-1</u>	<u>SS-1</u>	<u>SS-2</u>
209 days	115	220	1,940
400 days	120	300	0

Paraho Field Study--

A sampling trip was made to the Berg-Harbert lysimeters in May, 1978 to collect leachate resulting from percolation of snow melt. Results are presented in Table 7, along with data obtained the previous spring. Note that only the 25% slope, high elevation plots had any leachate flowing out of them on May 10, 1978. Values for lysimeter cells H-1/H-3 and H-5/H-7 represent the average composition of the first 115 liters and the first 26 liters respectively, to flow out of the plots during the pre-seeding irrigation. As was noted earlier, most of the constituents of leachate are rapidly rinsed out of spent shale. This behavior is also evident in the lysimeters, as can be seen by the lower values obtained one year later for H-1/H-3 and H-5/H-7. Fluorine levels decreased slightly, but not as much as specific conductance, B, Mo, and SO₄²⁻. This is also in agreement with our laboratory experiments. Thiosulfate was not detected in any of leachates on May 10, 1978, indicating that it had already been leached out of the shale or was immobilized in the shale.

Preliminary Shaker Study of In Situ Retorted Shale--

Dr. Willard Chappell of this project was able to obtain a small (about 1 kg) sample of shale that had been retorted by the Geokinetics in situ method. It was light in color, very porous, and friable. We crushed the material and passed it through a sieve to obtain (-) 2 mm size fragments; we also retained several fragments between 1 and 3 cm in diameter. Fifty grams of each of these samples were placed in 250 mL polyethylene bottles with 125 mL of deionized water and agitated on a shaker table for 37 days; these were the same conditions as used for most of our earlier shaker experiments. After 37 days the supernatant liquids were filtered off, the pH and specific conductance were measured, and the samples were submitted for wet chemical and x-ray fluorescence analysis. Some of the results are summarized in Table 8. The remarkable thing about the values shown in Table 8 is how closely similar they are to concentrations of the same elements produced in shaker experiments

TABLE 7.

Date sampled	Plot #	pH	Specific conductance (umhos/cm)	B	F	Mo	As	Se	SO ₄ ²⁻	Volumetric* meter reading (L)
6/77	H-1/H-3	10.3	22,300	1.5	7.8	3.9	.09	.12	15,900	3570
5/10/78	H-1/H-3	7.5	10,220	.7	4.8	1.4	.023	.069	5,870	4560
6/77	H-5/H-7	11.1	18,900	1.4	7.5	3.0	.07	.10	14,000	700
5/10/78	H-5/H-7	7.2	12,450	.7	5.1	1.2	.044	.071	8,070	1100
5/10/78	H-9/H-11	8.5	23,250	.6	6.6	2.1	.022	.149	14,830	670
5/10/78	H-13/H-15	8.5	18,360	.5	5.4	1.5	.027	.092	10,150	1240
5/10/78	H-17/H-19	8.5	19,530	.5	5.4	2.3	.047	.112	12,660	115
5/10/78	H-21/H-23 (soil control)	7.2	10,670	.4	.4	.1	.009	.018	1,400	26

*Approximate volume of leachate which had already passed through pipe when sample was collected.

with Paraho above-ground retorted shale (Progress Report, 1978). The only significant difference is the slightly lower values of TDS shown in Table 8. We find this similarity to be encouraging, as it allows us to have some confidence in extrapolating our work with Paraho materials into the chemistry of leachates that will be produced when groundwater flows through the residue of in situ retorting. Note also in Table 8 that the size of the grains used in the experiments had relatively little influence on any parameter except for fluorine; as usual, F seems to behave in a fashion different than the other parameters.

Future Studies--

We feel that most of the sampling and laboratory work is finished. Some additional minor studies may be necessary to confirm observations on the chemistry of sulfur and to better define the relationship between F and Ca. We may also collect leachate from a few very large columns in the laboratory for purposes of complete chemical analysis of the dissolved species. However, we intend to use most of the coming year to interpret the laboratory and field data so far collected. We hope to be able to incorporate our data on the chemistry of leachates into a hydrologic transport model which can be used to predict the movement of the various potential contaminants through a pile of discarded shale. We will also be using our existing computer model of aqueous chemistry to better understand the complex relationships that exist among dissolved species in the leachates.

INTERACTION OF OIL SHALE LEACHATE WITH SOILS

We are concerned about the possibility that leachate from oil shale, either stored in surface piles or remaining in underground retorts, could contaminate groundwater in western Colorado. Although the probability of continuous downward percolation through surface piles seems remote in this semi-arid region (2), it is quite possible that extraordinary precipitation events could periodically force some leachates into the subsurface, perhaps through the bottoms of reservoirs or impoundments. Further, it is probable that groundwater could dissolve and transport contaminants away from residues left in underground in situ retorts.

If leachates are produced, the soil cover offers a potential barrier for retardation and removal of contaminants. The soil would be an especially important line of defense in preventing leachates from surface piles from reaching groundwater. As part of our research efforts, we have been investigating the potential purifying capability of native soils from the Piceance Creek Basin, with special emphasis on B and F.

Materials and Methods

We prepare our leachate for this study by shaking retorted Paraho shale with an equal weight of deionized water. The shale is fine-grained (less than 2 mm diameter) and was kindly supplied to us by Development Engineering, Incorporated. The shale-water slurry is agitated on a shaker table for 120 hours, at which time equilibrium with respect to B and F is closely approached (Progress Report, 1978). The leachate is stored in a plastic bottle, open to the atmosphere via an Ascarite[®] tube to absorb

TABLE 8.

Sample no.	Grain size, in mm	pH	specific conductance, micromhos/cm	mg/L					
				B	F	Mo	As	Se	V
RW 5396	<2	10.3	3687	1.3	12.7	2.2	0.04	0.009	1.2
RW 5370	<2	10.4	3715	1.2	12.0	1.6	0.04	0.005	1.2
RW 5371	<30	11.0	2800	2.0	3.0	2.1	0.03	0.008	1.2

*Mn, Fe, Cu, Ni, Zn, Sn, Pb, and W all measured at less than about 0.05 mg/L.

carbon dioxide gas. In an initial study the leachate was withdrawn periodically over a 40 day period and analyzed for B and F to test for the integrity of storage. The results are summarized in Table 9.

TABLE 9.

Oil shale from the disposal pile-					
Sample no.	Days after filtering	pH	F ug/mL	B ug/mL	Specific conductance umhos/cm
8074	0	10.4	12.0	0.9	10,524
8075	2	9.7	12.8	0.9	10,477
8076	3	9.8	11.3	0.9	9,745
8077	4	7.1	12.6	0.9	10,488
8078	6	7.0	-	-	10,342
8079	8	7.0	12.4	0.9	10,610
8080	10	7.0	11.4	0.9	10,194
8081	40	7.5	11.0	0.9	10,185
Oil shale directly from the Paraho retort-					
8089	0	11.9	~10	2.3	10,797

As described in the 1978 Progress Report, the study soils were collected from sites that had been designated as probable disposal locations for processed shale. After air-drying in the laboratory, the soils were sieved to (-) 2 mm and passed through a mechanical splitter. Various splits were used for determination of grain size (21), percent calcium carbonate (22), slurry pH (22), content of moisture at 105 °C, and loss of organic matter at 450 °C for 18 hours. The porosity and hydraulic conductivity of the soils were measured by saturating columns of soil and measuring the rate of flow at constant head. The results are summarized in Table 10.

As pointed out in a recent review article (1), it is important to determine the background concentrations of the elements of interest in leachates from soils of the region, before considering the interaction of the soils with leachates from oil shale. We have done this for the soils in this study by shaking equal weights of soil and water for 120 hours and analyzing the resulting leachate specific conductance, B, F, and Ca. The resulting values are given in Table 11.

Results and Conclusions

As shown in Table 9, the integrity of our leachate is preserved very nicely over a 40 day period. The content of boron and fluorine remain essentially constant, as does specific conductance. The pH drops rather dramatically, but this is probably not important; when the leachate is passed through a column of soil the pH will be buffered by the soil. We feel that we can generate and store a meaningful "standard leachate" for use in

TABLE 10.

Analysis	<u>Tract C-a</u>		<u>Tract C-b</u>	<u>Anvil Points</u>
	Rinky Dink Gulch, upper	Rinky Dink Gulch, lower	Cottonwood Gulch	Balzac Gulch
Particle size analysis 2 mm				
% sand	41.5		41.2	36.1
% silt	45.8		45.4	42.8
% clay	12.3		15.3	21.8
Percentage CaCO ₃	6.2	23.6	3.4	6.3
Moisture Content in %	2.4	2.2	1.7	1.7
Organic Matter in %	5.2	4.8	6.3	5.8
Porosity in %	44.8	52.5	49.8	58.0
Hydraulic Conductivity				
cm/sec	5.9 10 ⁻⁴	1.1 10 ⁻⁴	4.0 10 ⁻⁴	5.0 10 ⁻⁴
(ft/year)	(619)	(115)	(420)	(525)
Soil pH	7.7	7.9	7.6	-

TABLE 11.

Analysis	<u>Tract C-a</u>		<u>Tract C-b</u>	<u>Anvil Points</u>
	Rinky Dink Gulch, upper	Rinky Dink Gulch, lower	Cottonwood Gulch	Balzac Gulch
Water extractable B in mg/L	0.2	0.4	0.2	0.3
Water extractable F in mg/L	0.3	0.3	0.3	0.3
Water extractable Ca in mg/L	174	129	115	178
Specific conductance of extract in micromhos/cm	9590	9809	6859	-

the experiments with the soils. Note also, in Table 9, the close similarity between our synthetic leachate and water directly from the Paraho retort.

Table 10 shows that our soils are very coarse grained, with significant contents of calcium carbonate. Those would be considered to be immature soils, with the texture of loam. The rather high slurry pH values reflect the presence of calcium carbonate in the soils. The hydraulic conductivities are perhaps surprisingly low, being of the same order of magnitude as the hydraulic conductivities given earlier in this report for the oil shale that we compacted into columns and to values given by other researchers for TOSCO II and Bureau of Mines retorted oil shales (2).

GEOCHEMISTRY OF FLUORINE IN OIL SHALE

Fluorine is a dissolved species of major concern in leachates from oil shale. The concentrations that we have observed exceed the standards for drinking water by about an order of magnitude, and fresh shale releases more fluorine to water than does retorted shale. Piles of crushed, fresh oil shale that may be stored on the surface of the ground pose a hazard to surface waters and ground waters because of the release of fluorine. We are studying the geochemical residence and behavior of F in fresh and retorted shale.

Materials and Methods

As reported in the Progress Report for 1977-1978, we collected 136 samples of crushed shale from U.S. Bureau of Mines corehole 01-A (sec. 29, T1S, R97W, Rio Blanco County, Colorado). The samples represent stratigraphic intervals of 1 to 3 feet, ranging from the A-Groove unit above the Mahogany Zone, through the Mahogany Zone, and into the underlying B-Groove unit. Each sample was previously analyzed for F by the U.S. Geological Survey, using their standard electrode method. We have re-analyzed 25 of the samples, using the molecular absorption technique developed by Dr. Robert Meglen of this project. One of our objectives is to clearly define the mineralogical residence of fluorine in the oil shale. We have finished ashing 12 samples using a commercial radio-frequency, activated-oxygen, low-temperature asher (23). This instrument oxidizes the organic matter in the shale at a temperature below 200 °C, thus avoiding any significant alteration of the minerals. The ashed residue from each sample of shale was then suspended in columns of heavy liquids for separation by density. The columns consisted of 10 discrete mixtures of 1,1,2,2-tetrabromoethane and ethanol, with densities ranging from 2.9 g/cc at the bottom of each column to 2.1 g/cc at the top. A sample of 100 mg of ashed shale was dispersed in ethanol and laid on the top of each column. Each column of heavy liquids, contained in polymer tube, was centrifuged at 8000 rpm at 25 °C for 24 hours. The g-values ranged from 9500 at the top of each tube to 15000 at the bottom. After 200,000 gravity hours it was assumed that each particle of shale had reached its isopycnic point in its column, and each visible mineral fraction (5 to 7 isopycnic fractions per column) was carefully removed with a pipette. Each mineral separate was then subjected to x-ray diffraction and x-ray fluorescence analysis. Because F is too light to be seen by x-ray fluorescence, and because the amount of sample was too small for wet chemical analysis, we obtained the help of Dr. Rodman Smythe and

Dr. Robert Ristinen of the Department of Physics of the University of Colorado in analyzing the separates by a new method of inelastic nuclear scattering (24).

In order to obtain information on the aqueous geochemistry of fluorine, we conducted shaker-table experiments, using retorted Paraho shale in ratios of 1:1, 1:5, and 1:20 with water. We also generated a single fairly large quantity of leachate, using a 1:1 ratio of shale to water, for purposes of complete chemical analysis. A test run using this analysis as input to our computer program for aqueous geochemistry (25) yielded information on the speciation of fluorine in the leachate and on the state of saturation of the leachate with respect to fluorine-bearing minerals.

Results and Conclusions

Content of F in Density Fractions--

The results of the analyses of the 136 samples of shale from the Bureau of Mines core-hole are presented in Figure 20, together with information obtained from the Laramie Energy Research Center on the yield of oil per ton of shale (26). Two features stand out clearly in Figure 20. First, the concentration of F shows a fairly good correlation with gallons of oil yielded per ton retorted shale. This is remarkably well demonstrated near the boundary between the lean A-Groove and the minable Mahogany Zone, and it also holds for significant intervals throughout the corehole (Figure 20). Unfortunately this correlation means that the highest yielding oil shale will leave the highest concentration of fluorine in the retorted residual shale. Second, large variations in content of F occur within short intervals in the Mahogany Zone. This indicates that the F in oil shales in the Piceance Creek Basin is stratigraphically controlled, probably reflecting the large variations known to have occurred in the chemistry of the lake during deposition of this sediment. The only interval where high-fluorine oil shales might be avoided by selective mining is between 950 and 990 feet below the surface (Figure 20). It should be pointed out that this correlation between F and yield of oil may lead to a tentative conclusion that the fluorine is bound to the organic fraction of the rock. However, we have conducted experiments in which the organic fraction was extracted with toluene and then analyzed for F, with the result that less than 2% of the total F was found in the extractable portion of the organics. This indicates that most of the F is the mineral fraction of the rock. The correlation between F and yield of oil must therefore be an indirect correlation, with both factors being stratigraphically controlled.

Table 12 lists by depth below the surface, six of the samples selected for low-temperature ashing, density separation, and analysis by inelastic nuclear scattering. The bulk content of F is shown also by wet chemical analysis of the ashed sample. The results of analysis of the 6 to 8 isopycnic samples derived from each of the six bulk samples in Table 12 are shown in Figures 21 and 22. Due to different matrices in the calibration targets and the sample targets, the results obtained by nuclear inelastic scattering can only be treated semiquantitatively. Figures 21 and 22 reveal, however, that it was possible to concentrate fluorine in just one of the six samples analyzed, sample No. 1. This is the sample that was found to have the highest bulk concentration of fluorine after ashing, i.e. 2600 ppm (Table 12). The other five bulk samples were found to have from 560 to 1100 ppm fluorine.

Figure 20. Concentration of fluorine and yield of oil in gallons per ton for U.S. Bureau of Mines core-hole 01-A (sec. 29, T1S, R97W, Rio Blanco County, Colorado). Fluorine determined by two methods in 25 samples.

Figure 21. Results of analysis for fluorine by nuclear inelastic scattering in different density fractions from samples 1, 6, and 7 (listed in Table 12). The two sets of bars for each sample represent the results of the analyses using 10 keV and 97 keV peaks for fluorine.

Figure 22. Results of analysis for fluorine by nuclear inelastic scattering in different density fractions from samples 8, 10, and 12 (listed in Table 12). The two sets of bars for each sample represent the results of the analyses using 10 keV and 97 keV peaks for fluorine.

The implication here is that the fluorine in most samples of oil shale is more or less evenly distributed in the various mineral fractions, and a clear-cut mechanical separation of fluorine minerals is apparently not feasible. However, where the fluorine is present in large amounts (such as sample No.1), isolation of the fluorine fraction can be made successfully. Note in Figure 21 also that the fluorine content of subsample 1-6 is three times the fluorine content of the slightly heavier subsample 1-5. This may be an important lead in the search for the mineralogical residence of fluorine. Further studies will use the scanning electron microscope and x-ray diffraction to further identify the residence of F.

TABLE 12.

<u>Sample number</u>	<u>Sample, by depth in feet</u>	<u>Wet analysis for F(ppm) after ashing</u>
1	901.8	2600±200
6	907.0	1000
7	941.0	900
8	943.0	990
10	955.7	1100
12	1065.8	560

Aqueous Geochemistry of F in Leachates--

Using analyses of the leachates obtained from shaker table experiments, we are able to calculate the approximate state of saturation of the leachates with respect to fluorite (CaF_2). The results of these calculations are expressed as the logarithm of the ratio of the ion concentration product (i.c.p.) over the equilibrium solubility product ($K_{sp} = 10^{-10.96}$), and are shown in Figure 23. A value of the logarithm of the ratio of i.c.p. to K_{sp} greater than unity is an indication that the water is supersaturated with respect to fluorite, and as shown in Figure 23, all of the leachates generated in these experiments were apparently supersaturated. Use of our computer model to correct the concentrations to activities does not change this conclusion. Changes in the concentration of Ca in the leachates (Figure 24) only partially mirrors the changes in the ratio of i.c.p. to K_{sp} (Figure 23), indicating that the control by Ca on the apparent state of saturation of the leachate with respect to fluorite is secondary and indirect. Figure 25 shows that the concentration of Mg in the leachates drops with increasing time, probably due to the precipitation of a Mg-bearing mineral, and results from our computer model indicate that the aqueous species of Mg-F complexes are not important. Finally, in Figure 26, it is seen that the concentration of F in the aqueous leachates is nearly independent of the ratios of shale to water, apparently contradicting some of our earlier results (Progress Report, 1978); this apparent conflict will be further studied. We hope to gain considerable insight into the sources mechanisms of release, and controls on the concentration of fluorine in leachates from the shales. Without such fundamental knowledge, it will not be possible to efficiently work out techniques for controlling such pollutants.

Figure 23. Apparent state of saturation of leachate with respect to fluorite.
 Three curves represent three different ratios of solid to water
 in the shaker experiments. Paraho retorted shale, (-) 2mm fraction.

Figure 24. Concentration of Ca in leachates from different ratios of retorted Paraho shale and deionized water. Shaker table experiments.

Figure 25. Concentration of Mg in leachates from different ratios of retorted Paraho shale and deionized water. Shaker table experiments.

Figure 26. Concentration of F in leachates from different ratios of retorted Paraho shale and deionized water. Shaker table experiments.

In order to obtain some fundamental information on the overall chemistry of the leachate, we had a nearly complete analysis performed by an outside laboratory on one large batch of leachate. The leachate was generated by shaking (-) 2 mm Paraho retorted shale with deionized water for one month. We used a 1:1 ratio of shale to water because it yields the highest total dissolved solids in the leachate and it represents the highest shale:water ratio that can reasonably be handled in the laboratory. The results of the analysis are shown in Table 13. This analysis was used as input to our computer model (25) of aqueous geochemistry. We were thus able to obtain information on the distribution of ions in solution and on the state of saturation of the leachate with respect to a great many solid minerals. Among the results gathered from this test-run of the computer model, it is worth mentioning that the leachate is apparently supersaturated with respect to the minerals calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), fluorite (CaF_2), hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The control on the activity of dissolved Ca and dissolved F is thus complex. The free fluoride ion makes up to 98% of all the dissolved fluorine in this particular leachate, with the remainder of the fluorine present predominantly as CaF^+ . Neither the aluminum fluorides nor the magnesium fluoride complexes are important at this pH (=10.6).

TABLE 13.

Analysis of 1:1 Paraho (spent) shale: deionized water shaken for 1 month in closed Nalgene® container.

<u>Cation</u>	<u>mg/L</u>	<u>Anion</u>	<u>mg/L</u>
Ca	402	HCO_3	161
Mg	0.6	CO_3	60
Na	2512.5	SO_4	5276
K	472	Cl	301.5
Mo	3.6	F	7.6
Sr	12	B	1
Li	13	PO_4	0.3
Al	<1	NO_3	<1
Ba	1	V	0.16
Fe	<1		
SiO_2	12		
U	<2 ppb		

Further studies will be carried out to determine if the release of fluorine to the leachate follows a recognizable pattern of desorption, dissolution, or a combination of the two mechanisms.

Future Work

We intend to continue and intensify our investigation of the residence of

fluorine and other trace contaminants in the oil shale. We believe that the combination of low-temperature ashing, high-speed centrifugation, and analysis by nuclear inelastic scattering offers a unique opportunity to identify and isolate the source of fluorine and many other trace elements, such as As, Cu, Pb, etc. If we can achieve this isolation and identification, it may be possible to devise control technologies to reduce or eliminate the production of fluorine-rich leachates from waste piles of shale or from underground retorts. We will also intensify our computer modeling of the chemistry of the leachates to increase our understanding of the mechanisms of release and control of the trace contaminants.

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Progress Report: 1976 - 1979

Trace Elements in Plants on Processed Oil Shale

M.K. Kilkelly and W.L. Lindsay

INTRODUCTION

In recent years the need for developing new energy resources within the United States has become increasingly important. Besides the newly expanded growth of the coal industry many other alternative energy resources are being explored, among these are solar energy, nuclear energy, and energy derived from oil shales. In 1973 the U.S. Department of Interior (1) estimated that the western oil shale reserves, which consist of over 25,000 square miles located in Colorado, Wyoming, and Utah, contained over 600 billion barrels of economically recoverable crude oil. This evidence points to the inevitable development of these land areas. The largest deposition of oil shales in this area is the Green River Formation. Besides being the largest oil shale deposit it is also the richest in recoverable crude oil, and therefore, the most likely to attract industry. The Green River Formation is located predominantly in northwestern Colorado, northeastern Utah, and southwestern Wyoming. These previously undeveloped areas will be subject to vast land disturbances with the development of an oil shale industry. Various waste products will be generated by shale processing methods, making it necessary to establish procedures for preventing pollution of natural resources. Potential problems should be investigated and solutions evaluated before industrial development occurs. One of the major environmental problems occurring with retorting is the massive amounts of waste material produced by the processing of oil shales. The most promising solution seems to be revegetation of the processed shale. Revegetation would aid in stabilizing the processed shale by decreasing erosion into streams, blowing by wind, and surface runoff.

At this time the future of these revegetated shales is undetermined. In order to ascertain future possibilities, as far as a return to natural conditions, it is necessary to investigate both the chemical and physical properties of the waste material to be revegetated. The quality of the vegetation grown on the process shales must be evaluated from an environmental standpoint to determine whether certain trace elements are present in amounts toxic to animals. The increased availability of some elements may even be toxic to the plants thereby limiting the success of establishing good ground cover needed for waste stabilization. These are important questions to be answered and a great deal of research is currently being conducted in order to make reasonable and responsible predictions about the environmental impact of an oil shale industry in these areas.

This study is concerned with the concentrations of five trace elements in plants grown on revegetated processed shales: molybdenum, boron, selenium, arsenic, and fluorine. These were selected on the basis of their individual importance as well as their particular chemistry in soils. Because of the reducing conditions often associated with shale retorting and the accompanying elevation of pH, it was thought that these elements, which form anionic species in solution, might become more soluble and, therefore, available to plants.

In order to investigate the uptake of these trace elements by plants from the processed shales a field study where the influence of natural conditions predominates was designed.

The objectives of the field study were:

1. To determine whether plants growing on processed oil shales contain increased concentrations of certain trace elements, and
2. To determine if the concentration of the trace elements in the plants can be related to the different treatments imposed on the revegetated plots.

Because the five trace elements selected for study are important from both an animal health and plant growth standpoint, a brief review of these elements is included here.

BORON

Sommer and Lipman (2) established the essentiality of boron to higher green plants in 1926. Since then, a great deal of research on both the toxicity and deficiency symptoms of plants has been accomplished. Only a very small concentration is required for normal plant growth, but plant tolerances vary widely between species (Richards, 3). Grasses and other monocots are generally low in boron content with an intermediate range for oats given as 15 to 50 ppm by Bradford (4). He also noted that toxicities occurred in oats if the boron concentration exceeded 54 ppm. Boron contents of western wheatgrass sampled by Klusman (5) from the oil shale tract C-a averaged 16 ppm.

Schmehl (6) in early studies considered boron to be a potential problem for plant growth on processed shales and Woods (7) observed tip burn in western wheatgrass on TOSCO II processed shale in greenhouse studies. Pulverized fuel ash, a material with many characteristics similar to processed shales, has produced plant toxicities because of high boron levels (Hodgson and Townsend, 8).

Boron toxicity symptoms, described by Wilcox (9) include burning or necrosis of leaf tips and margins, poor seed germination, stunting, and drought symptoms of plants.

MOLYBDENUM

Molybdenum is an essential trace element for plant nutrition (Arnon and Stout, 10). Because it is involved with N_2 -fixation, legumes often accumulate higher levels of Mo than other plants. Molybdenum content of western wheatgrass sampled by Klusman (5) from oil shale tract C-a averaged 1.2 ppm.

Although large amounts of Mo do not seem to affect plants, they then become hazardous forages for livestock. Johnson (11) reviewed various levels of Mo in plant tissues. Mo levels greater than 5 ppm are considered potentially hazardous to livestock by Underwood (12). The occurrence of molybdenosis, or "hypocuprosis," actually involves the ratio of Cu:Mo in the plants. Kubota (13) indicates that nutritional problems of ruminants in the western states are most often associated with plant accumulations of 10 to 20 ppm Mo in the presence of low to moderate (4 to 10 ppm) copper. Miltimore and Mason (14) proposed that a Cu:Mo ratio of less than two could be expected to lead to molybdenosis in grazing animals.

SELENIUM

Although selenium is non-essential for plant nutrition, it is an essential trace element for animals (Hartley and Grant, 15). While a certain level of Se is necessary in animal diets, it should not exceed 4 ppm in forages (Beyers, 16 and Kubota, 13). Diseases long associated with alkaline soils, such as "blind staggers" and "alkali disease" have been attributed to Se toxicities (Robinson, 17).

Many plants have the ability to accumulate Se in high concentrations, while other plants growing on the same substrate do not. These indicator plants accumulate Se and make it more available to other plants by returning Se to the soil through foliage decomposition (Beath and Eppson, 18). These organic forms of Se are considered readily available to most plants.

ARSENIC

This element is non-essential for both plant and animal growth. Williams and Whetstone (19) determined that native plants usually contain less than 10 ppm As. Most toxicities to livestock are generally associated with soil ingestion or pesticide accidents. Leibig (20) gives a range for oats as 0.64 to 3.4 ppm As in the literature. Schroeder and Balassa (21) found a range of 0.1 to 1.6 ppm As in grasses.

FLUORINE

As a trace element, fluorine has been determined as necessary for animal nutrition but not for plant growth. Brewer (22) indicates that native plants often range from 2 to 20 ppm F with toxicities to the plant occurring at levels greater than 30 ppm. Toxicity symptoms include leaf margin necrosis and interveinal chlorosis. Most plant species have a limited capacity to absorb fluorine from soils as CaF_2 or $Al_2(SiF_6)_3$ are good sinks for fluoride. Most toxicities to either plants or animals involve an airborne fluoride source

such as aluminum and superphosphate industries, steel mills, and enamel factories (McClenahan, 23).

MATERIALS AND METHODS

In the summer of 1976, 1977, and 1978 western wheatgrass, Agropyron smithii var. "Arriba," was collected from oil shale revegetation plots established by W.A. Berg of Colorado State University. These plots, constructed in 1973, are located in the rich oil shale regions of north-western Colorado and were designed to test various treatments for revegetation and stabilization of spent shales. Although the plots were originally intended for revegetation studies only, the opportunity to investigate the trace element aspect was too great to ignore, especially since the vegetation has been left under natural conditions once it was successfully established.

Two sites, shown in Figure 1, were chosen for the construction of the plots, a low-elevation site at Anvil Points (5700 ft.) and a high-elevation site on Piceance Creek Basin (7300 ft.). These two locations were chosen to simulate conditions that might exist at proposed disposal sites. The low-elevation site has a semi-arid climate and sparse natural vegetation of low-elevation pinyon-juniper woodlands, receiving approximately 300 mm (12 in.) of annual precipitation.

The vegetation types at the Piceance Basin site are high-elevation big sagebrush shrubland and high-elevation pinyon-juniper woodland with an average annual precipitation of 430 mm (17 in.). This site is very similar in climate, elevation, and vegetation to the Colorado Federal oil shale lease sites in the Piceance Creek Basin.

Each site contains an identical set of seven treatments consisting of: 1) leached TOSCO processed shale; 2) leached TOSCO processed shale with 15 cm (6") of soil cover; 3) unleached TOSCO processed shale with 30 cm (12") soil cover; 4) leached USBM processed shale; 5) leached USBM processed shale with 15 cm (6") soil cover; 6) unleached USBM processed shale with either 30 cm (12") soil cover at the high-elevation site or 60 cm (24") soil cover at the low-elevation site; and 7) a soil control. Each of the seven treatments has a north and south exposure on a 4:1 (25") slope. A diagram of the arrangements of treatments at each site is shown in Figure 2.

Following construction of the plots, they were fertilized; seeded with a mixture of native grasses, forbs, and shrubs; mulched; and irrigated with sprinklers until vegetation was established

A more detailed description of the construction of the plots and revegetation methods applied is found in Vegetation Stabilization of Spent Oil Shales, Harbert, H.P. and W.A. Berg, Department of Agronomy, Colorado State University Environmental Resources Center Technical Report No 5 (1974).

Figure 1. Location of revegetation field study site.

Figure 2. Plot treatments and design of revegetation field study sites.

Vegetation samples were collected from both the high-elevation and the low-elevation site in July of 1976, 1977, and 1978. Western wheatgrass was selected for sampling since it comprised a dense cover over the plots at both sites and was successfully established as the predominant vegetation. This grass is also native to the oil shale regions and would most likely be included in any seeding mixture for revegetation of spent shales. Samples were composited from lines transecting each treatment plot at three points: two feet from the crest of the slope, across the center of the slope, and two feet from the bottom of the slope. Plant samples were clipped about 38 mm (1½ in.) above ground and placed in clean cloth bags and appropriately labeled.

In addition, a shrub, fourwing saltbush (*Striplex canescens*), was also collected where available on the plots. Samples were composited by collecting smaller subsamples from shrubs over the entire area of each plot.

After the first full season of growth, in 1977, alfalfa samples were collected from the newly established Paraho Lysimeter study. These plots were constructed by W.A. Berg of Colorado State University as a hydrological model and for revegetation studies. The processed shale involved in the study was produced by the Paraho direct-heated retorting method. This processed shale and various soil covers comprised the treatments illustrated in Figure 3. Samples were not collected by the transectline method but were composited from plants distributed over the entire area of each plot. All other procedures and methods are as described for western wheatgrass samples.

In the laboratory each sample was washed thoroughly with distilled deionized water to remove soil and dust adhering to the plant and to separate debris. The washed samples were placed into clean cloth bags and dried at 70 °C for 48 hours. Dried samples were ground in a small Wiley mill equipped with a stainless steel head and screen. The ground samples were stored in wax-lined paper bags.

A portion of the ground sample was sent to the x-ray facilities at C.U. in Boulder for x-ray fluorescence analysis. The results were somewhat disappointing because of low sensitivity for the particular trace elements selected (Mo, B, As, Se, F) and homogeneity problems with the plant materials.

In conjunction with the ETSRP analytical chemistry facility in Boulder, procedures were established for preparation of the plant tissues. Samples analyzed for boron, molybdenum, and fluorine were dry-ashed in three-gram aliquots at 450 °C for 24 hours. Twenty milliliters of 1 N HCl was added to dissolve the ash. This solution was sent to Boulder for analysis. One-gram plant samples for arsenic and selenium analysis were wet-ashed with a nitric, sulfuric, and perchloric acid digestion (4:1:1) and diluted with deionized water to 50 mL. These prepared samples were also sent to Boulder for analysis. Analytical results for all plant samples are found in the appendix of this report.

Figure 3. Plot plan of Paraho lysimeter study site.

RESULTS AND DISCUSSION

BORON

1976

The boron contents of western wheatgrass at the low-elevation site are represented in Figure 4. Boron content ranged from an average of 8 ppm in plants from the soil control to an average of 129 ppm in plants grown on TOSCO processed shale. Within each series of shale treatments, boron content of plants increased with decreasing soil cover. The increases were much more pronounced on the TOSCO shale treatments, with the highest boron values from plants grown on a south-aspect slope of TOSCO processed shale having no soil cover (Figure 4).

At the high-elevation site in the Piceance Basin the same trends were observed (Figure 5). Lowest boron content was measured from plants growing on the soil control (8 ppm), while the plants grown on the TOSCO processed shale averaged the highest (113 ppm).

The difference between boron values of plants on the north versus the south aspect was not nearly so great at the higher elevation due to higher precipitation and lower summer temperatures.

Analysis of variance for 1976 data indicates that the most significant difference in boron content was due to soil cover; the next most significant factor was site (Table 1). A factorial analysis involving the site, treatment, aspect, sampling position on the slope, and all interactions between these factors were performed. At the low-elevation site a significant interaction was found between the site and the aspect (Figure 6). Plants from the south-aspect slopes, on the average, were 10 ppm higher in boron content than the plants from the north aspect. This may be attributed to the effect of boron concentration caused by greater moisture loss from south slopes at this elevation.

1977

The boron content of plants from both sites increased slightly in 1977, most likely due to the severe drought conditions experienced by this area throughout the growing season. Both sites exhibited trends very similar to the 1976 data (Figures 7 and 8).

Plants on the soil control continued to average the lowest boron contents (11 ppm). A slight increase over this value was observed in plants growing on the USBM materials. Again, the TOSCO processed shale treatment supported plants with the highest average boron content (163 ppm). Due to more favorable growing conditions, including more precipitation, the plants at the high-elevation site generally contained less boron than plants at the low-elevation site.

FIGURE 4, 1976 Western Wheatgrass - Anvil Points

FIGURE 5. 1976 Western Wheatgrass - Piceance Basin

TABLE 1. 1976 WESTERN WHEATGRASS ANALYSIS OF VARIANCE FOR A FACTORIAL DESIGN.

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Squares	F _{0.05}
<u>MOLYBDENUM</u>				
1*	1	160.49	160.49	79.49
2	6	110.62	18.44	9.13
3	1	4.47	4.47	2.21
4	2	37.07	18.53	9.18
1x2	6	29.03	4.84	2.40
1x3	1	0.42	0.42	0.28
1x4	2	39.41	19.70	9.76
2x3	6	16.02	2.67	1.32
2x4	12	43.36	3.61	1.79
3x4	2	3.12	1.56	0.77
1x2x3	6	16.09	2.68	1.33
1x2x4	12	33.00	2.75	1.36
1x3x4	2	1.10	0.55	0.27
2x3x4	12	5.75	0.48	0.24
1x2x3x4	12	10.43	0.87	0.43
Within Reps	84	169.59	2.02	
TOTAL	167	679.95		
<u>BORON</u>				
1*	1	3 630.72	3 630.72	31.27
2	6	245 265.54	40 877.59	352.05
3	1	1 554.29	1 554.29	13.39
4	2	3 853.73	1 926.86	16.60
1x2	6	15 320.82	2 553.47	21.99
1x3	1	1 015.29	1 015.29	8.94
1x4	2	307.73	153.86	1.33
2x3	6	1 668.92	278.15	2.40
2x4	12	5 365.36	447.11	3.85
3x4	2	539.16	269.58	2.32
1x2x3	6	1 918.58	319.76	2.75
1x2x4	12	3 866.86	322.24	2.78
1x3x4	2	286.16	143.08	1.23
2x3x4	12	3 940.26	328.36	2.83
1x2x3x4	12	2 206.10	183.84	1.58
Within Reps	84	9 753.50	116.11	
TOTAL	167	300 492.99		
<u>SELENIUM</u>				
1†	6	0.859	0.143	11.89
2	1	0.003	0.003	0.22
3	2	0.012	0.006	0.50
1x2	6	0.073	0.012	1.01
1x3	12	0.117	0.010	0.81
2x3	2	0.020	0.010	0.85
1x2x3	12	0.119	0.010	0.83
Within Reps	42	0.505	0.012	
TOTAL	83	1.708		

* 1 is site location; 2 is treatment; 3 is aspect; 4 is position on slope
† 1 is treatment; 2 is aspect; 3 is position on slope

Figure 6. Multiple comparison plot: site x aspect for boron content of western wheatgrass. 1976.

FIGURE 7. 1977 Western Wheatgrass - Anvil Points

FIGURE 8. 1977 Western Wheatgrass - Piceance Basin

The 1977 analysis of variance indicates that boron values were significantly affected by both site and the seven treatments involved. An interaction between site and treatment was statistically significant (Table 2).

1978

Boron values for both high and low elevation remained much the same as in the previous years (Figures 9 and 10). The highest boron content was from plants at the low-elevation site on the TOSCO processed shale treatment (164 ppm). Plants from the soil control averaged 7 to 8 ppm, the lowest boron value for both sites. The boron content of plants grown on USBM shales was between these two values. Overall, the boron content of plants at the low-elevation site was elevated above plants from the high-elevation site. This was particularly noticeable on the TOSCO treatments.

Summary

The boron content in western wheatgrass grown on spent oil shale and soil treatments, shown for three years in Figures 11 and 12, increased in the following order at both site locations:

Statistically significant differences in boron content due to site location, aspect, type of processed shale, and treatment applied were observed for all years investigated (Tables 1 and 2). An interaction between the site location and treatment was also observed. TOSCO shale treatments at the Anvil Points site averaged consistently higher boron in plants than the same treatments at the higher elevation (Figure 13). This may be due to a combination of two factors. First, the lower temperatures and increased precipitation usually present at the higher elevation would decrease the concentration of boron salts, as a result of less moisture evaporation from the fine TOSCO processed shale material. This would be especially noticeable on south-aspect slopes. Second, during the establishment of vegetation on these plots the leaching of certain treatments was ineffective in removing salts, therefore, a second leaching was made. As a result, the leaching treatment at the high-elevation site was more thorough than at the low-elevation site in reducing various salts in the TOSCO shale treatments.

It would appear from these data that boron values measured on some treatments, specifically the TOSCO processed shale treatment on south slopes at low-elevation, can limit the success of revegetation efforts unless the processed shales are either covered with soil, leached, or a combination of both. Characteristic boron toxicity symptoms, such as tip burn, were not

TABLE 2. 1977 WESTERN WHEATGRASS ANALYSIS OF
VARIANCE FOR A FACTORIAL DESIGN.

Source of Variation*	Degree of Freedom	Sums of Squares	Mean Squares	F _{0.05}
<u>MOLYBDENUM</u>				
1	1	22.63	22.63	135.40
2	6	60.66	10.11	60.49
3	1	0.88	0.88	5.24
1x2	6	4.20	0.70	4.19
1x3	1	0.35	0.35	2.07
2x3	6	2.54	0.42	2.53
1x2x3	6	1.70	0.28	1.70
Within Reps	28	4.68	0.17	
TOTAL	55	97.63		
<u>BORON</u>				
1	1	10 505.16	10 505.16	126.92
2	6	129 445.75	21 574.29	260.66
3	1	21.88	21.88	0.26
1x2	6	10 360.96	1 726.83	20.86
1x3	1	0.16	0.16	0.02
2x3	6	1 986.25	331.04	4.00
1x2x3	6	1 525.46	254.24	3.07
Within Reps	28	2 317.50	82.77	
TOTAL	55	156 163.13		
<u>SELENIUM</u>				
1	1	0.4253	0.4253	23.37
2	6	0.5676	0.0946	5.20
3	1	0.0014	0.0014	0.08
1x2	6	0.1785	0.0297	1.58
1x3	1	0.0001	0.0001	0.01
2x3	6	0.1439	0.0240	1.32
1x2x3	6	0.1641	0.0273	1.50
Within Reps	28	0.5097	0.0182	
TOTAL	55	1.9905		
<u>FLUORINE</u>				
1	1	18.75	18.75	15.04
2	6	38.40	6.40	5.13
3	1	1.72	1.72	1.38
1x2	6	15.70	2.62	2.10
1x3	1	6.72	6.72	5.39
2x3	6	5.37	0.89	0.72
1x2x3	6	11.33	1.89	1.52
Within Reps	28	34.91	1.25	
TOTAL	55	132.89		

* 1 is site location; 2 is treatment; 3 is aspect

FIGURE 9. 1978 Western Wheatgrass - Anvil Points

FIGURE 10. 1978 Western Wheatgrass - Piceance Basin

Figure 11 1976 - 1978 Western Wheatgrass - Anvil Points

Figure 12 1976-1978 Western Wheatgrass Piceance Basin

Figure 13. Multiple comparison plot: site x treatment for boron content of western wheatgrass. 1977.

apparent on plants in the field but stunted plants, decreased covers, and decreased yields on treatments having high plant boron contents were noted.

MOLYBDENUM

1976

Because of the diverse and complex geomorphology of the oil shale regions a wide variety of soils (morphologically, chemically, and physically) are found here. At the low-elevation site the soil was derived from a geologic formation naturally high in Mo. The plants grown on this soil exhibited an average of 4.5 ppm Mo, while normal plant levels on uncontaminated soils are around 1 ppm (Kubota, 23). Because of this high background level of Mo, the plants grown on the soil control were not greatly different from the plants grown on the USBM and TOSCO treatments at this site. However, statistical analysis did reveal a slight but significant difference in Mo content between plants from the soil control and the USBM shale treatments, indicating that plants from the USBM treatments were higher in Mo content (Figure 14).

The soil at the high-elevation site was derived from a different geologic formation and plants grown on the soil control here exhibited Mo contents averaging 1.0 ppm, a level more nearly that found in normal agricultural soils. At this site the difference between the control and various treatments, with regard to Mo levels in plants, was easily seen (Figure 15). A significant increase in the Mo level of plants grown on USBM shale materials was evident, with plant values averaging 4.4 ppm Mo. A very slight increase of Mo content in plants grown on TOSCO shale materials was observed over the plant values from the soil control. Analysis of variance indicated that the greatest factor, with regard to Mo content in plants, was the site location, followed by treatment (Table 1). As expected, the aspect had no significant influence on Mo content of plants at either site.

Although the original intent was to sample only western wheatgrass, due to its excellent distribution on the revegetation plots, it was later decided to make additional collections of the shrub, fourwing saltbush (*Atriplex canescens*). This shrub has become increasingly dominant over the grasses in the past few years, and also possesses a marked tolerance to saline soils. Molybdenum levels for this plant, collected at the high-elevation site are depicted in Figure 16.

Some surprising results were obtained. Fourwing saltbush from the USBM shale treatments collected in 1976 contained extremely high Mo levels, ranging from 18.1 to 54.1 ppm (Table 3). This plant species is an important forage for both livestock and wildlife in this area, so further investigation of this plant species is merited.

The influence of copper levels in plants containing high Mo values has been recognized as important in producing molybdenosis in ruminants (Kubota, 24). Allaway (25) indicates that 5 ppm Mo can induce molybdenosis if Cu in the

FIGURE 14. 1976 Western Wheatgrass - Anvil Points

FIGURE 15, 1976 Western Wheatgrass - Piceance Basin

FIGURE 16. 1976 Four-wing Saltbush-Piceance Basin

TABLE 3. 1976 TRACE ELEMENT CONTENT OF FOURWING SALTBUSH
ON OIL SHALE REVEGETATION PLOTS.

Treatment	Aspect	Position	Piceance Basin		
			Mo	S	F
- - - - ppm - - - -					
12" Soil Cover, TOSCO [†]	North	Top			4.3
		Middle			4.2
		Bottom			
	South	Top			5.7
		Middle	4.9	51	2.9
		Bottom			
6" Soil Cover, TOSCO [*]	North	Top			3.7
		Middle	4.0	52	
		Bottom			
	South	Top			1.5
		Middle			1.7
		Bottom			2.8
TOSCO [*]	North	Top			5.5
		Middle	5.9	54	3.6
		Bottom			
	South	Top			5.2
		Middle	6.7	56	2.4
		Bottom			
Soil Control	North	Top	1.2	74	3.2
		Middle	5.8	60	
		Bottom	0.7	62.1	1.4
	South	Top	4.2	71.5	3.0
		Middle	6.5	56	
		Bottom	0.7	67.1	2.4
USBM [*]	North	Top	28	50.5	5.4
		Middle	31.1	54.3	
		Bottom	21.6		
	South	Top	29.55	49.9	3.2
		Middle	24.9	46.8	
		Bottom	21.5	49.6	3.5
6" Soil Cover, USBM [*]	North	Top	18.1	49.4	3.5
		Middle	22.5	53.4	2.8
		Bottom			
	South	Top	19.4	50.9	4.7
		Middle	31.6	50.7	
		Bottom	19.0	51.4	2.1
12" Soil Cover, USBM [†]	North	Top	24.5	40.5	4.0
		Middle	46.6	39.2	
		Bottom			
	South	Top	20.9	43.7	3.3
		Middle	25.5	43.4	3.7
		Bottom	54.9	45.6	3.7

* Leached

† Unleached

plants is 4.0 ppm. Miltimore and Mason (14) proposed that a ratio of Cu:Mo of less than 2 may be expected to lead to molybdenosis in grazing animals. In this instance, fourwing saltbush samples high in Mo values were analyzed for Cu and found to range from 4.8 to 6.8 ppm (Table 4). This is in the lower range of normal Cu levels for plants (5 to 20 ppm) (Ruether, 26), and would indicate that a combination of low Cu values and high Mo levels might well lead to health problems of ruminants using such plants for forage.

1977

The same general trend of Mo uptake for western wheatgrass was found in 1977 (Figures 17 and 18). Again, soil at the low-elevation site produced vegetation with a higher than normal Mo content, averaging 3.6 ppm. A slightly elevated Mo content of plants from the USBM shale materials, averaging 5.6 ppm, was also recognized.

At the high-elevation site, Mo differences between plants from the soil control (averaging 1.6 ppm) and the plants from the USBM treatments (averaging 4.6 ppm) were readily observable (Figure 18).

The most significant factor influencing Mo content of plants remained the site location, followed by treatment (Table 2).

Fourwing saltbush was also sampled in 1977 at the high-elevation site (Figure 19). Data from the previous years indicate very high Mo content in plants grown on the USBM shale treatments. The 1977 analysis confirm these high Mo levels with an average of 23 ppm in fourwing saltbush samples Table 5 and 5a). Copper content of these plants remained in the low range (5.3 to 6.8 ppm) resulting in a Cu:Mo ratio of approximately 0.3. Forages with a ratio such as this are not considered suitable for livestock.

With the construction of the Paraho Lysimeter study completed it was decided to sample the first year's plant growth. Because of contamination from the mulch applied to the treatments a large amount of alfalfa was present. Alfalfa, as a legume, has been reported to accumulate higher levels of Mo than other plants, such as grasses, growing on the same substrate. Western wheatgrass growing on the other study plots nearby ranged from 3 to 6 ppm Mo, while alfalfa samples from the Paraho Lysimeter study averaged approximately 20 ppm Mo (Table 5a). This elevated level is seen in all treatments for this study (Figure 20). In order to ascertain the hazard to livestock these plants might present it is necessary to know the level of Cu in the forage. Copper analysis are expected from the Colorado State University Soil Testing Laboratory. In order to be considered safe for livestock a Cu:Mo ratio of 2 or greater is desired. To achieve this ratio a Cu level of around 40 ppm is necessary, hardly to be expected.

1978

Molybdenum content in plants followed similar patterns and values as in previous years (Figures 21 and 22). Western wheatgrass from the soil control

TABLE 4. COPPER AND MOLYBDENUM VALUES FOR FOURWING SALT-BUSH FROM PICEANCE BASIN REVEGETATION PLOTS.

1976					
USBM [*]		USBM 6" Soil Cover [*]		USBM 12" Soil Cover [†]	
Cu	Mo	Cu	Mo	Cu	Mo
----- ppm -----					
6.6	32.2	6.6	19.4	5.8	30.6
6.2	30.6	5.6	30.0	4.8	59.4
6.4	35.6	6.0	24.4	5.2	27.2
5.8	31.2	6.6	35.0	5.0	27.8
6.4	26.2	5.6	23.2	5.6	67.2

1977					
USBM [*]		USBM 6" Soil Cover [*]		USBM 12" Soil Cover [†]	
Cu	Mo	Cu	Mo	Cu	Mo
----- ppm -----					
6.0	27.8	6.6	17.6	5.6	30.0
6.2	36.8	6.8	29.4	5.4	27.2
6.8	41.8	5.3	43.4	5.4	32.2
6.8	31.2	6.4	19.8	5.4	36.8

* Leached

† Unleached

FIGURE 17. 1977 Western Wheatgrass - Anvil Points

FIGURE 18. 1977 Western Wheatgrass - Piceance Basin

FIGURE 19, 1977 Four-wing Saltbush-Piceance Basin

TABLE 5. 1977 TRACE ELEMENT CONTENT IN FOURWING SALT BUSH
ON OIL SHALE REVEGETATION PLOTS.

Treatment	Aspect	Rep	Piceance Basin		
			Mo	B	F
			- - - - ppm - - - -		
12" Soil Cover, TOSCO [†]	North	I	5.2	66	2.0
		II	4.2	66	2.8
	South	I	3.8	58	3.8
		II	4.3	65	2.8
6" Soil Cover, TOSCO [*]	North	I	4.3	68	2.4
		II	5.0	75	2.9
	South	I	5.2	63	1.8
		II	5.3	73	2.5
TOSCO [*]	North	I	5.6	70	6.3
		II	6.0	76	7.0
	South	I	5.7	77	6.1
		II	6.5	67	4.6
Soil Control	North	I	12.4	57.9	1.1
		II	8.5	61.3	0.8
	South	I	26.3	50.4	2.7
		II	5.9	60.3	2.5
USBM [*]	North	I	23.5	43.6	2.3
		II	21.4	49.9	3.0
	South	I	21.2	40.0	2.3
		II	23.3	45.3	1.5
6" Soil Cover, USBM [*]	North	I	24.4	46.1	2.9
		II	19.2	50.0	2.3
	South	I	24.0	46.3	2.3
		II	25.5	48.1	1.9
12" Soil Cover, USBM [†]	North	I	26.5	46.4	2.8
		II	24.0	45.6	3.2
	South	I	20.2	44.5	0.7
		II	22.1	48.4	2.1

* Leached

† Unleached

TABLE 5a. 1977 FOURWING SALT BUSH ANALYSIS OF VARIANCE FOR A FACTORIAL DESIGN.

Source of Variation*	Degree of Freedom	Sums of Squares	Mean Squares	F _{0.05}
<u>MOLYBDENUM</u>				
1	1	1 510.08	1 510.08	155.68
2	6	1 137.51	189.58	19.55
3	1	0.00	0.00	0.00
1x2	6	804.03	135.01	13.82
1x3	1	5.92	5.92	0.61
2x3	6	35.57	5.92	0.62
1x2x3	6	29.86	4.98	0.51
Within Reps	28	271.60	9.7	
TOTAL	55	3 794.56		
<u>BORON</u>				
1	1	2 885.79	2 885.79	33.77
2	6	2 709.96	451.66	5.29
3	1	412.57	412.57	4.83
1x2	6	898.46	149.74	1.75
1x3	1	108.64	108.64	1.27
2x3	6	325.68	54.28	0.64
1x2x3	6	409.61	68.27	0.80
Within Reps	28	2 393.00	85.46	
TOTAL	55	10 143.71		
<u>FLUORINE</u>				
1	1	1.03	1.03	1.85
2	6	33.29	5.55	9.93
3	1	1.14	1.14	2.05
1x2	6	26.72	4.45	7.97
1x3	1	0.00	0.00	0.00
2x3	6	9.22	1.54	2.75
1x2x3	6	6.72	1.12	2.14
Within Reps	28	15.64	0.56	
TOTAL	55	93.76		

* 1 is site location; 2 is treatment; 3 is aspect.

TABLE 6. 1977 MOLYBDEMU CONTENT OF ALFALFA FROM THE PARAHO LYSIMETER STUDY.

Treatment	Slope	High-Elevation			Low-Elevation		
		Plot No.	Mo ppm	$\bar{X}$	Plot No.	Mo ppm	$\bar{X}$
Paraho Spent Shale	2%	H2, H4	11.5	16.8	L2, L4	-	13
	25%	H1, H3	22.0		L1, L3	13.0	
20-cm Soil Cover	2%	H6, H8	17.8	18.3	L6, L8	17.5	18.2
	25%	H5, H7	18.8		L5, L7	18.8	
40-cm Soil Cover	2%	H10, H12	17.5	18.8	L10, L12	14.5	21.8
	25%	H9, H11	20.0		L9, L11	29.0	
60-cm Soil Cover	2%	H14, H16	17.8	16.8	L14, L16	14.3	17.0
	25%	H13, H15	15.8		L13, L15	19.7	
80-cm Soil Cover	2%	H18, H20	25.0	22.2	L18, L20	15.8	15.6
	25%	H17, H19	19.3		L17, L19	15.3	
Soil Control	2%	H22, H24	24.0	23.4	L22, L24	12.4	12.9
	25%	H21, H23	22.7		L21, L23	13.4

FIGURE 20. 1977 Alfalfa - Paraho Lysimeter Study (High Elevation)

FIGURE 21. 1978 Western Wheatgrass - Anvil Points

FIGURE 22. 1978 Western Wheatgrass - Piceance Basin

at the low-elevation site showed higher than normal Mo levels (4.3 ppm) but despite this high background level there was an observable difference between the soil control and the USBM shale treatments, which averaged 8.4 ppm Mo in plants (Table 6 a and 6b).

The plants from the soil control at the high-elevation site continued to show fairly normal Mo values with an average of 1.7 ppm compared to the USBM shale treatments (4.8 ppm). Once again the primary influence on plant Mo content appears to be the site location, followed by treatment.

Fourwing saltbush was also collected from the high-elevation site in 1978. Since cattle had gained access to the plots here in the fall of 1977 and thoroughly grazed these species, it can be reasonably assumed that the samples collected were the result of one year's growth and any Mo values measured should have been accumulated during the past growing season. The Mo content of plants grown on the soil control here averaged 6.2 ppm while plants from the USBM shale materials averaged 34 ppm Mo (Table 7, Figure 23).

Alfalfa samples were collected for the second season from the Paraho Lysimeter study (Table 8, Figure 24). Although not as high as in 1977, Mo levels averaged 15 ppm over all treatments. Copper levels are not yet reported for these samples but these plants are not recommended for livestock forages.

Summary

Molybdenum content of western wheatgrass for three years at both sites is shown in Figures 25 and 26. The soil control at the low-elevation site produced plants having a higher than normal Mo content, averaging approximately 4 ppm over three years. The soil control at the high-elevation site averaged 1.4 ppm Mo content in plants, a value more expected for an uncontaminated soil. Because of this background difference, a statistical analysis revealed the site location to be the variable most influential in determining plant Mo content. Differences between the various treatments and the soil control were not as evident at the low-elevation site, due to the high background Mo levels found here, compared to the high-elevation site. An analysis of variance indicates that, even though masked by high Mo values, there were significant differences between the USBM shale treatments and the soil control, with higher plant Mo values on the USBM materials (Figure 27). This difference was more readily observed at the high-elevation site.

Fourwing saltbush was also collected because of its increased dominance over the grasses on the revegetation plots in the last few years. This shrub tolerates highly saline soils and is being increasingly used for stabilization of such waste materials. Upon analysis it was revealed that the plants grown on USBM shale treatments at the high-elevation site contained extremely high amounts of Mo, averaging 28 ppm for three years. These plants were also analyzed for Cu and found to be in the low range (approximately 5 ppm). Such a low Cu value would produce a Cu:Mo ratio less than 2, which could be hazardous to livestock or wildlife.

TABLE 6a. 1978 TRACE ELEMENT CONTENT OF WESTERN WHEATGRASS ON
OIL SHALE REVEGETATION PLOTS AT ANVIL POINTS.

Treatment	Aspect	Rep	Mo	B
- - ppm - -				
12" (30 cm) Soil Cover, TOSCO†	North	I	4.6	176
		II	5.5	130
	South	I	5.1	92
		II	4.5	90
	North	I	3.5	161
		II	3.0	132
6" (15 cm) Soil Cover, TOSCO*	South	I	4.4	144
		II	5.2	190
	North	I	6.3	202
		II	5.9	155
	South	I	8.5	171
		II	6.9	127
TOSCO*	North	I	3.9	7.0
		II	6.2	6.5
	South	I	3.0	6.4
		II	4.1	6.4
	North	I	7.8	32
		II	8.0	24
6" (15 cm) Soil Cover, USBM*	South	I	10.0	48
		II	8.9	26
	North	I	8.4	23
		II	7.0	18
	South	I	9.0	20
		II	11.5	22
24" (60 cm) Soil Cover, USBM†	North	I	5.7	23
		II	9.5	21
	South	I	6.2	16
		II	8.1	30

* Leached

† Unleached

TABLE 6b. 1978 TRACE ELEMENT CONTENT OF WESTERN WHEATGRASS ON OIL SHALE REVEGETATION PLOTS AT PICEANCE BASIN.

Treatment	Aspect	Rep	Mo	B
- - ppm - -				
12" (30 cm) Soil Cover, TOSCO+	North	I	3.0	82
		II	3.0	92
	South	I	2.0	73
		II	2.8	68
6" (15 cm) Soil Cover, TOSCO*	North	I	2.9	52
		II	2.3	53
	South	I	3.8	74
		II	3.5	54
TOSCO*	North	I	4.3	125
		II	4.8	142
	South	I	4.4	102
		II	3.6	111
Soil Control	North	I	1.6	8
		II	2.0	8
	South	I	1.8	9
		II	1.5	8
USBM*	North	I	3.4	22
		II	5.2	25
	South	I	5.1	19
		II	5.1	24
6" (15 cm) Soil Cover, USBM*	North	I	7.4	30
		II	3.8	20
	South	I	5.2	19
		II	5.7	18
12" (30 cm) Soil Cover, USBM+	North	I	4.4	22
		II	5.9	26
	South	I	3.4	17
		II	3.6	19

* Leached

+ Unleached

TABLE 7. 1978 TRACE ELEMENT CONTENT OF FOURWING
SALTBUSH ON OIL SHALE REVEGETATION PLOTS
AT PICEANCE BASIN.

Treatment	Aspect	Mo	B
- - ppm - -			
Soil Control	North	5.5	20
	South	6.6	21
USBM*	North	31.0	14
	South	32.0	12
6" (15 cm) Soil Cover, USBM*	North	37.0	15
	South	52.0	14
12" (30 cm) Soil Cover, USBM+	North	32.0	16
	South	22.0	14

* Leached

+ Unleached

FIGURE 23. 1978 Fourwing Saltbush - Piceance Basin

TABLE 8. 1978 MOLYBDENUM CONTENT OF ALFALFA FROM THE
PARAHO LYSIMETER STUDY.

Treatment	Slope	Plot No.	Mo ppm	$\bar{X}$
Paraho Spent Shale	2%	H2, H4	17.7	20.6
	25%	H1, H3	23.4	
20-cm Soil Cover	2%	H6, H8	14.7	16.4
	25%	H5, H7	18.1	
40-cm Soil Cover	2%	H10, H12	14.9	15.6
	25%	H9, H11	16.2	
60-cm Soil Cover	2%	H14, H16	12.4	12.4
	25%	H13, H15	12.4	
80-cm Soil Cover	2%	H18, H20	14.3	12.9
	25%	H17, H19	11.4	
Soil Control	2%	H22, H24	11.4	10.8
	25%	H21, H23	10.2

FIGURE 24. 1978 Alfalfa - Paraho Lysimeter Study (High Elevation)

Figure 25 1976 - 1978 Western Wheatgrass - Piceance Basin

Figure 26 1976 - 1978 Western Wheatgrass - Anvil Points

Figure 27. Multiple comparison plot for Anvil Points and Piceance Basin Mo content of western wheatgrass. 1977.

Another reason for concern, with regard to this shrub, is the possible recycling of elements through foliage decomposition. Large amounts of any element returned to the soil in organic form would be made more available to other plant species for uptake. This has already been observed to occur with salts for this plant species (Sharma and Tangway, 27).

With the construction of the Paraho Lysimeter study a third type of processed shale was available for study of trace element uptake by plants. Because of problems incurred by the use of an alfalfa hay mulch a good stand of seeded species was not obtained. The only plant with a fair distribution on the plots was alfalfa from the mulch. Since it is a legume, accumulations of molybdenum may occur. Although significant differences between the soil control and treatments are not shown, the overall molybdenum levels are elevated. 1977 samples averaged 20 ppm Mo and 1978 samples averaged 15 ppm. These plots are in a very unstable condition with regard to vegetation composition, and it will be some time before a more stable ecological system is reached. Continued observations and sampling during this process could be meaningful.

SELENIUM

Selenium levels in western wheatgrass collected from the various treatment plots at both sites did not exhibit noticeable differences. Samples from both 1976 and 1977 are below 1 ppm Se with the majority being less than 0.5 ppm Se. Results of all plant analyses for Se are given in Tables 9 through 12.

Statistical analysis indicated that a slightly significant increase of Se from plants grown on USBM treatments exists over plants from the soil control (Tables 1 and 2, Figure 28) at the low-elevation site. While there may be a significant difference between these treatments statistically, their environmental significance seems doubtful.

ARSENIC

Plant samples from the field plots showed concentrations of As ranging from 0.03 to 0.43 ppm (Figures 29 through 32). Apparently only minimal amounts of arsenic are accumulating in plant tissue collected from the revegetation field study. These plant levels were below those of environmental concern.

FLUORINE

There was no observable trend among the various treatments with regard to fluoride content in plants grown on the processed shale materials. Results of all plant analyses for F are shown in Tables 11 and 12, and 3, 5, 13 and 14. Ranges of F in plants grown on the soil control are fairly great for western wheatgrass (0.3 to 3.8 ppm). The overall range for all treatments was 0.3 to 7.6 ppm F, which is well below the 30 ppm generally considered to be toxic to vegetation.

TABLE 9. 1976 TRACE ELEMENT CONTENT OF WESTERN WHEATGRASS ON OIL SHALE
REVEGETATION PLOTS AN ANVIL POINTS.

Aspect	Position	Rep	12" (30 cm) Soil Cover, TOSCO†				6" (15 cm) Soil Cover, TOSCO†				TOSCO*				Soil Control			
			Mo	B	Se	As‡	Mo	B	Se	As	Mo	B	Se	As	Mo	B	Se	As
			----- ppm -----				----- ppm -----				----- ppm -----				----- ppm -----			
North	Top	I	6.1	78	0.17		3.7	94	0.09		6.4	155	0.11		5.6	11	0.23	
		II	4.4	72	0.11		4.3	92	0.16		4.9	120	0.35		6.9	11	0.34	
	Middle	I	4.5	54	0.11	0.12	4.5	80	0.13	0.18	3.5	94	0.23	0.19	3.2	8	0.30	0.05
		II	1.6	64	0.11	0.09	2.7	88	0.13	0.10	2.5	92	0.31	<0.05	6.0	4	0.22	0.05
	Bottom	I	3.4	61	0.04		3.8	84	0.07		7.1	114	0.19		3.8	8	0.31	
		II	2.8	43	0.15		2.8	81	0.06		3.9	93	0.17		3.7	5	0.10	
South	Top	I	7.8	120	0.13		6.5	116	0.08		6.3	148	0.09		8.0	10	0.08	
		II	7.0	66	0.13		7.7	81	0.05		7.8	157	0.42		3.9	10	0.06	
	Middle	I	3.4	77	0.21	0.10	4.1	100	0.18	0.12	4.0	138	0.11	0.14	3.3	9	0.29	0.07
		II	8.3	37	0.23	0.16	3.9	81	0.31	0.14	5.7	186	0.11	0.18	2.5	7	0.07	0.10
	Bottom	I	3.8	62	0.23		5.5	143	0.25		7.0	127	0.19		3.8	11	0.08	
		II	3.7	68	0.08		3.7	130	0.08		4.3	120	0.34		2.8	6	0.26	

Aspect	Position	Rep	USBM*				6" (15 cm) Soil Cover, USBM*				24" (60 cm) Soil Cover, USBM†			
			Mo	B	Se	As	Mo	B	Se	As	Mo	B	Se	As
			----- ppm -----				----- ppm -----				----- ppm -----			
North	Top	I	6.5	27	0.39		6.1	19	0.17		1.1	10	0.22	
		II	7.9	37	0.64		7.7	21	0.38		7.2	14	0.21	
	Middle	I	3.0	22	0.36	0.12	4.4	18	0.27	0.10	1.4	11	0.34	0.12
		II	4.4	25	0.39	0.10	3.2	16	0.48	0.09	5.6	9	0.30	0.12
	Bottom	I	7.6	22	0.47		11.0	23	0.10		6.1	14	0.18	
		II	5.6	18	0.53		7.1	13	0.12		4.8	10	0.34	
South	Top	I	6.9	30	0.58		6.4	21	0.40		5.4	16	0.31	
		II	6.0	29	0.49		6.7	17	0.11		5.5	15	0.33	
	Middle	I	4.0	35	0.31	0.36	4.8	15	0.19	0.26	3.1	10	0.30	0.19
		II	1.8	41	0.41	0.36	3.3	13	0.56	0.22	3.3	16	0.35	0.17
	Bottom	I	7.6	39	0.53		6.9	17	0.24		6.1	16	0.31	
		II	6.4	25	0.18		6.5	16	0.43		5.2	15	0.31	

* Leached

† Unleached

‡ Arsenic analysis were limited to samples from the middle transect-line in order to estimate the range of As concentration before extensive analysis was performed.

TABLE 10. 1976 TRACE ELEMENT CONTENT OF WESTERN WHEATGRASS ON OIL SHALE
REVEGETATION PLOTS AT PICEANCE BASIN.

Aspect	Position	Rep	12" (30 cm) Soil Cover, TUSCO†				6" (15 cm) Soil Cover, TUSCO*				TUSCO*				Soil Control			
			Mo	B	Se	As†	Mo	B	Se	As	Mo	B	Se	As	Mo	B	Se	As
			----- ppm -----				----- ppm -----				----- ppm -----				----- ppm -----			
North	Top	I	2.5	90	0.20		1.3	69	0.20		3.3	147	0.38		0.7	12	0.02	
		II	2.4	60	0.15		1.3	44	0.17		3.3	151	0.40		0.4	10	0.00	
	Middle	I	3.1	104	0.23	0.13	5.1	31	0.18	<0.05	3.0	104	0.26	0.14	0.9	4	0.21	<0.05
		II	2.7	98	0.24	0.05	1.2	37	0.24	<0.05	3.4	97	0.36	0.16	0.7	7	0.15	<0.05
	Bottom	I	2.6	49	0.09		1.6	35	0.26		2.9	104	0.35		3.3	9	0.02	
		II	2.2	34	0.20		0.8	25	0.20		2.4	85	0.31		0.9	7	0.11	
South	Top	I	3.0	88	0.17		2.6	58	0.22		3.1	120	0.12		0.7	9	0.03	
		II	2.3	73	0.19		2.4	63	0.24		4.3	112	0.10		1.1	11	0.01	
	Middle	I	2.2	66	0.23	0.09	6.8	57	0.28	<0.05	3.2	94	0.17	0.13	0.7	7	0.12	<0.05
		II	2.0	75	0.27	0.10	1.3	33	0.23	0.05	3.8	99	0.10	0.21	0.9	8	0.20	<0.05
	Bottom	I	2.4	49	0.23		3.3	51	0.20		3.1	122	0.09		0.8	9	0.02	
		II	1.5	42	0.12		1.5	41	0.43		3.1	120	0.07		0.8	6	0.04	

Aspect	Position	Rep	USBH*				6" (15 cm) Soil Cover, USBH*				12" (30 cm) Soil Cover, USBH†			
			Mo	B	Se	As	Mo	B	Se	As	Mo	B	Se	As
			----- ppm -----				----- ppm -----				----- ppm -----			
North	Top	I	4.5	31	0.18		5.9	16	0.15		3.8	13	0.11	
		II	3.3	29	0.69		3.5	13	0.12		3.5	18	0.14	
	Middle	I	3.0	24	0.25	0.39	3.7	14	0.30	0.09	4.1	18	0.25	0.15
		II	4.5	20	0.40	0.38	3.6	14	0.31	0.09	4.9	18	0.13	0.15
	Bottom	I	7.2	9	0.29		3.8	20	0.44		4.0	19	0.07	
		II	3.3	26	0.31		4.8	23	0.32		5.1	23	0.19	
South	Top	I	5.7	24	0.28		4.2	12	0.14		3.0	11	0.03	
		II	1.9	26	0.66		7.3	21	0.14		5.2	77	0.09	
	Middle	I	2.4	24	0.63	0.31	4.3	14	0.32	0.18	3.2	13	0.24	0.07
		II	5.5	24	0.33	0.36	3.9	15	0.39	0.09	3.0	13	0.11	0.12
	Bottom	I	5.5	28	0.21		4.4	23	0.13		4.1	21	0.20	
		II	4.9	20	0.78		4.8	13	0.42		4.3	18	0.05	

* Leached

Unleached

Arsenic analysis were limited to samples from the middle transect-line in order to estimate the range of As concentration before extensive analysis was performed.

TABLE 11. 1977 TRACE ELEMENT CONTENT OF WESTERN WHEATGRASS ON OIL SHALE REVEGETATION PLOTS AT ANVIL POINTS.

Treatment	Aspect	Rep	Mo	B	Se	F	As
----- ppm -----							
12" (30 cm) Soil Cover, TOSCO†	North	I	3.3	92	0.26	3.1	0.16
		II	3.2	115	0.08	3.7	0.08
	South	I	4.1	122	0.28	4.7	0.21
		II	3.6	116	0.27	3.6	0.19
	North	I	3.7	137	0.50	4.2	0.16
		II	3.7	169	0.26	2.6	0.13
6" (15 cm) Soil Cover, TOSCO*	South	I	5.0	165	0.24	3.1	0.19
		II	4.9	136	0.19	5.1	0.21
	North	I	5.5	192	0.31	10.0	0.32
		II	4.5	185	0.25	5.4	0.22
	South	I	5.0	146	0.26	4.6	0.32
		II	4.9	130	0.34	3.7	0.19
TOSCO*	North	I	5.5	192	0.31	10.0	0.32
		II	4.5	185	0.25	5.4	0.22
	South	I	5.0	146	0.26	4.6	0.32
		II	4.9	130	0.34	3.7	0.19
	North	I	3.3	12	0.58	1.7	0.11
		II	3.7	11	0.34	3.7	0.10
Soil Control	South	I	4.0	15	0.40	3.9	0.13
		II	3.3	13	0.94	1.8	0.13
	North	I	6.0	33	0.35	2.6	0.33
		II	5.7	34	0.52	4.5	0.20
	South	I	5.8	68	0.94	4.9	0.41
		II	6.3	47	0.37	2.5	0.44
USBM*	North	I	5.4	29	0.77	3.3	0.16
		II	6.6	26	0.56	0.5	0.19
	South	I	6.8	37	0.28	3.1	0.22
		II	6.2	30	0.30	1.8	0.24
	North	I	4.2	19	0.32	3.3	0.22
		II	4.8	19	0.36	1.7	0.15
6" (15 cm) Soil Cover, USBM†	South	I	5.4	18	0.24	0.5	0.19
		II	4.0	14	0.23	2.1	0.19
	North	I	4.2	19	0.32	3.3	0.22
		II	4.8	19	0.36	1.7	0.15
	South	I	5.4	18	0.24	0.5	0.19
		II	4.0	14	0.23	2.1	0.19
24" (60 cm) Soil Cover, USBM†	North	I	4.2	19	0.32	3.3	0.22
		II	4.8	19	0.36	1.7	0.15
	South	I	5.4	18	0.24	0.5	0.19
		II	4.0	14	0.23	2.1	0.19
	North	I	4.2	19	0.32	3.3	0.22
		II	4.8	19	0.36	1.7	0.15

* Leached

† Unleached

TABLE 12. 1977 TRACE ELEMENT CONTENT OF WESTERN WHEATGRASS ON OIL SHALE REVEGETATION PLOTS AT PICEANCE BASIN.

Treatment	Aspect	Rep	Mo	B	Se	F	As
----- ppm -----							
12" (30 cm) Soil Cover, TOSCO†	North	I	3.1	73	0.07	2.0	0.13
		II	3.1	50	0.20	1.2	0.13
	South	I	2.9	51	0.17	2.3	0.10
		II	2.8	62	0.17	1.5	0.16
	North	I	2.2	86	0.21	2.6	0.06
		II	2.0	63	0.14	1.7	0.10
6" (15 cm) Soil Cover, TOSCO*	South	I	2.9	75	0.12	2.1	0.13
		II	2.3	76	0.14	2.3	0.11
	North	I	3.4	124	0.14	2.2	0.14
		II	2.9	129	0.17	3.4	0.13
	South	I	3.4	121	0.17	4.6	0.17
		II	4.2	125	0.16	3.8	0.20
TOSCO*	North	I	1.6	13	0.10	0.99	0.10
		II	2.3	10	0.25	0.5	0.06
	South	I	1.2	9	0.17	2.3	0.10
		II	1.4	12	0.08	2.5	0.09
	North	I	4.3	22	0.43	2.3	0.28
		II	4.6	29	0.42	0.8	0.23
6" (15 cm) Soil Cover, USBM*	South	I	4.6	29	0.57	3.0	0.27
		II	5.4	36	0.35	2.2	0.07
	North	I	4.5	24	0.17	0.9	0.18
		II	4.8	27	0.19	1.7	0.17
	South	I	5.3	22	0.20	2.3	0.18
		II	5.7	22	0.32	2.7	0.18
12" (30 cm) Soil Cover, USBM†	North	I	4.6	22	0.35	2.1	0.16
		II	4.6	19	0.14	2.0	0.17
	South	I	3.4	15	0.09	3.8	0.18
		II	3.8	18	0.17	3.5	0.18

* Leached

† Unleached

FIGURE 28. 1976 Western Wheatgrass - Anvil Points

FIGURE 29. 1976 Western Wheatgrass - Anvil Points

FIGURE 30. 1976 Western Wheatgrass - Piceance Basin

FIGURE 31. 1977 Western Wheatgrass - Anvil Points

FIGURE 32. 1977 Western Wheatgrass - Piceance Basin

TABLE 13. 1976 TRACE ELEMENT CONTENT OF FOURWING SALTBUSH
ON OIL SHALE REVEGETATION PLOTS.

Treatments	Aspect	Anvil Points		
		Mo	B	F
- - - - ppm - - - -				
12" Soil Cover, TOSCO	North	4.3	86.7	3.5
	South	4.0	66.7	5.1
6" Soil Cover, TOSCO*	North	2.3	79.3	2.5
	South	2.7	82.7	
TOSCO*	North	3.4	77.3	
	South	4.6	68.7	3.1
Soil Control	North	1.8	54.7	1.0
	South	1.6	95.3	2.8
USBM*	North	5.9	64	2.5
	South	4.7	86.7	3.1
6" Soil Cover, USBM*	North	5.9	52.7	3.1
	South	6.1	53.7	3.7
24" Soil Cover, USBM	North			
	South	5.2	65	2.3

* Leached
Unleached

TABLE 14. 1977 TRACE ELEMENT CONTENT IN FOURWING SALTBUSH ON OIL SHALE REVEGETATION PLOTS.

Treatment	Aspect	Rep	Anvil Points		
			Mo	B	F
- - - - ppm - - - - -					
12" Soil Cover, TOSCO [†]	North	I	2.9	69.3	4.0
		II	3.1	73	3.3
	South	I	2.6	85.3	4.0
		II	2.8	72	2.5
6" Soil Cover, TOSCO [*]	North	I	3.7	85	3.5
		II	1.9	67	2.9
	South	I	2.8	76	2.4
		II	1.8	79	4.3
TOSCO [*]	North	I	3.8	71	3.3
		II	4.3	94	4.4
	South	I	2.0	77	1.7
		II	2.0	48	0.5
Soil Control	North	I	2.2	75	0.9
		II	2.8	80	2.1
	South	I	2.1	56	1.1
		II	5.7	90	1.7
USBM [*]	North	I	3.6	71	1.9
		II	6.0	89	3.1
	South	I	1.8	53	1.9
		II	6.4	62	4.0
6" Soil Cover, USBM [*]	North	I	5.4	81	2.5
		II	7.3	64	1.7
	South	I	3.2	55	1.9
		II	4.6	67	
24" Soil Cover, USBM [†]	North	I	1.8	66	1.4
		II	5.1	77	2.8
	South	I	3.6	71	1.9
		II	3.4	56	3.1

* Leached

† Unleached

CONCLUSION

This study indicates that of the five trace elements measured in plants growing on processed oil shales, only two are of environmental importance. Boron shows the greatest possibility of being toxic to plants, thereby limiting successful cover establishment. Molybdenum appears to be present in alfalfa and fourwing saltbush at elevated levels, even in plants from the soil control at one site location. Cu:Mo ratios indicate that these forages would be considered hazardous to livestock. Fourwing saltbush is of particular interest because this shrub is beginning to dominate the grasses in this semi-arid region. The recycling of some elements by this shrub should also be further investigated. Selenium and arsenic show little environmental concern from the results gathered in the field study. Fluorine concentrations in plants also appear to be below levels of concern.

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Progress Report: 1976 - 1979

Effect of Added Arsenic on the Uptake of Arsenic by Plants Growing on Processed Oil Shale in the Greenhouse R.E. McFadden and W.L. Lindsay

INTRODUCTION

Processed shale has unique characteristics that may affect the availability of various trace elements to plants. For example, the high pH of freshly processed shale is expected to increase the solubility of trace elements present as anions. Since arsenic is present in well-oxidized environments as an anion, it merits further investigation.

In the previous section of this report (Kilkelly et al., 1979) arsenic was found to be greater in plants growing on processed oil shale than from soil obtained from areas adjacent to the plots. However, the arsenic levels were below those expected to produce toxicities to either plants or animals.

There is, however, another concern that needs to be examined. In the processing of oil shale, a significant fraction of the arsenic present in the raw shale ends up in the oil fraction. It has been proposed that this arsenic be extracted from the oil and discarded with the processed shale. The question arises, can such added arsenic wastes possibly pollute the spent shale and lead to toxicities in either plants or animals?

A greenhouse study was set up to determine the availability of arsenic to plants growing on processed oil shale to which added levels of arsenic were made. The rates and forms of arsenic used were chosen to simulate conditions that may occur at shale processing sites.

MATERIALS AND METHODS

Three arsenic compounds were chosen for the greenhouse study. Iron arsenide (FeAs_2) and arsenic sulfide (As_2S_3) were selected as likely forms of arsenic removed from the oil and returned to the waste shale. The third compound was calcium arsenate ($\text{Ca}_3(\text{AsO}_4)_2$) which represents a likely reaction product that forms during the weathering of waste shale in an oxidizing environment as would occur near the soil surface where plants are growing.

Both iron arsenite and arsenic sulfide are unstable in soil or shale systems as shown in Figure 1. In this plot the equilibrium level of HAsO_4^{2-} is given as a function of redox expressed in terms of $\text{pe} + \text{pH}$. For this comparison pH was fixed at 8.0, SO_4^{2-} at 10^{-4} M, and Fe^{3+} by $\text{Fe}(\text{OH})_3$ (soil) (Lindsay, 1979). It is obvious that both arsenic minerals are highly unstable

Figure 1. Solubility of FeAs_2 and As_2S_3 is a function of redox ($\text{pe} + \text{pH}$) when $\text{pH} = 8$, $\text{SO}_4^{2-} = 10^{-4} \text{ M}$. and Fe^{3+} fixed by Soil-Fe.

except in extremely reduced environments. In soils where $p_e + p_H$ is near 15, these minerals should oxidize to arsenate. The details of these calculations are reported in the thesis of the senior author (McFadden, 1979).

TOSCO estimated they would add approximately 10 ppm of arsenic back to the shale pile. From this estimate, the three arsenic compounds were added to processed shale to supply: 0, 5, 10, 20, and 40 ppm of arsenic. In the case of calcium arsenate an additional rate of 80 ppm was included. The TOSCO processed oil shale was used for this study.

The shale was first leached to remove excess salts so that plant growth would be possible. Leaching was accomplished by using four large plastic containers (14-inch diameter and 36 inches high) with 1/8-inch holes drilled in the bottom. The containers were filled with 18 inches of shale and leached with the equivalent of 48 inches of water. Saturated extracts of the leached materials gave conductivities of 2.0 mmhos/cm. The leached shale was then dried, mixed, and separated into kilogram portions. The arsenic compounds were added to the shale materials and mixed in a V-blender. The lower treatment rates were mixed first. The V-blender was washed after each type of arsenic compound was mixed to minimize contamination. All pots received 75 ppm of phosphorus as dicalcium phosphate (monetite). When phosphorus deficiencies later appeared, $(NH_4)_2HPO_4$ was added to supply an additional 50 ppm of phosphorus. This fertilizer was injected into the root zone by means of a syringe and a 20-gauge needle. Additional nitrogen as $Ca(NO_3)_2 \cdot 4H_2O$ was added as needed to prevent nitrogen from being deficient.

The pots were first seeded in the spring of 1977 using 40 seeds of western wheatgrass (*Agropyron smithii*, var. Arriba). After 20 days the plants were thinned to 20 plants per pot. Water was added daily to bring all pots to field capacity. Three cuttings were taken from the first seeding at approximately 75-day intervals. The plants were cut 3 cm above the shale surface. The above ground plant materials were dried at 70 °C for 24 hours and weighed. Samples of the plant materials were ground in a Wiley mill equipped with stainless steel cutting parts and digested in a mixture of nitric, perchloric, and sulfuric acids.

After the third harvest the root systems were broken up and the shale was remixed and reseeded as before. One additional harvest was then taken after 75 days.

RESULTS

Results of the greenhouse study are plotted in Figures 2 through 5.

In the first cutting (Figure 2) the greatest uptake of arsenic resulted from As_2S_3 and the least from $FeAs_2$ whereas $Ca_3(AsO_4)_2$ was intermediate. The highest uptake was only 0.80 ppm of arsenic, which is not expected to be toxic to either plants or animals.

In the second cutting (Figure 3), the uptake had leveled off fairly well in the range of 0.15 to 0.3 ppm of arsenic with little difference among

Figure 2. Uptake of arsenic by western wheatgrass from arsenic amended processed shale (first cutting, first seeding).

Figure 3. Uptake of arsenic by western wheatgrass from arsenic amended processed shale (second cutting, first seeding).

Figure 4. Uptake of arsenic by western wheatgrass from arsenic amended processed shale (third cutting, first seeding).

Figure 5. Uptake of arsenic by western wheatgrass from arsenic amended processed shale (first cutting, second seeding).

treatments except possibly for the decreased uptake from the FeAs_2 treatment at the high rate. There is no logical explanation as to why this should have been low.

The third cutting also showed arsenic uptake in the range of 0.15 to 0.40 ppm of arsenic with only slightly lower uptake from the FeAs_2 source.

After the third cutting the shale was remixed, and a new seeding was made. The subsequent harvest of western wheatgrass showed considerably higher uptake of arsenic as seen from Figure 5. The highest uptake of arsenic reached 1.3 ppm of arsenic at the 80 ppm treatment of $\text{Ca}_3(\text{AsO}_4)_2$. The FeAs_2 source showed the lowest uptake of arsenic.

DISCUSSION AND CONCLUSIONS

The results of this study show that the uptake of arsenic by western wheatgrass growing on processed TOSCO oil shale was generally less than 0.5 ppm. Addition of arsenic minerals such as As_2S_3 , FeAs_2 , or $\text{Ca}_3(\text{AsO}_4)_2$ at rates up to 40 ppm of arsenic increased the content of arsenic in the plants but it was still below the 1.6 ppm level reported by Schroeder and Belassa (1966) as normal for plants.

After removal of 3 cuttings of western wheatgrass and reseedling, the subsequent crop showed higher uptake of arsenic approaching 0.9 ppm of arsenic for the 40 ppm treatment and 1.3 ppm for the 80 ppm treatment. The increased uptake of arsenic in the fourth cutting may reflect the fact that phosphorus fertilizer added during the first growth period had become less available. Woolson (1973) demonstrated that increased available phosphate can depress the uptake of arsenic since the two elements are chemically somewhat similar. Since the roots were broken up and distributed through the soil prior to seeding for the last harvest, the release of arsenic from the old roots may have contributed to greater availability of arsenic in the final cutting.

The greenhouse study demonstrates that all three arsenic compounds have similar availabilities after the first cutting suggesting they had reached similar reaction products in the shale media.

The uptake of arsenic from plants growing on processed shale does not appear to be a serious problem. Even though arsenic was added to shales in this study at levels several times those expected in processing operations, the arsenic levels of the plants were below the 1.6 ppm level reported by Schroeder and Belassa (1966) as only slightly elevated for normal plants.

TABLE 1. ARSENIC UPTAKE FOR WESTERN WHEATGRASS GROWN ON ARSENIC AMENDED PROCESSED SHALE (FIRST AND SECOND CUTTING, FIRST SEEDING).

Compound Treatment Rep	As ppm added	Calcium Arsenate					Iron Arsenide				Arsenic Sulphide				Control
		5	10	20	40	80	5	10	20	40	5	10	20	40	Shale
FIRST CUTTING, FIRST SEEDING															
I	As ppm in plant	0.35	0.32	0.36	0.59	0.84	0.23	0.24	0.31	0.34	0.40	0.38	0.47	0.62	0.28
II	As ppm in plant	0.30	0.23	0.38	0.41	0.73	0.20	0.22	0.21	0.31	0.21	0.33	0.57	0.99	0.37
III	As ppm in plant	0.37	0.48	0.58	0.76	0.98	0.34	0.32	0.45	0.44	0.35	0.57	0.57	0.77	0.34
IV	As ppm in plant	0.43	0.41	0.51	0.65	--	0.44	0.39	0.43	0.48	0.38	0.41	0.51	0.77	0.29
Mean	As ppm in plant	0.36	0.36	0.46	0.60	0.85	0.30	0.29	0.35	0.39	0.34	0.42	0.53	0.79	0.32
SECOND CUTTING, FIRST SEEDING															
I	As ppm in plant	0.13	0.20	0.29	0.24	0.30	0.12	0.12	0.24	0.09	0.28	0.14	0.28	0.26	0.12
II	As ppm in plant	0.17	0.17	0.16	0.34	0.32	0.13	0.08	0.23	0.16	0.13	0.07	0.18	0.37	0.16
III	As ppm in plant	0.19	0.23	0.18	0.35	0.35	0.12	0.16	0.25	0.21	0.21	0.26	0.22	0.32	0.17
IV	As ppm in plant	0.15	0.25	0.24	0.31	0.19	0.18	0.16	0.25	0.17	0.09	0.14	0.15	0.11	0.08
Mean	As ppm in plant	0.16	0.21	0.22	0.31	0.29	0.14	0.13	0.24	0.16	0.18	0.15	0.21	0.27	0.13

TABLE 2. ARSENIC UPTAKE FOR WESTERN WHEATGRASS GROWN ON ARSENIC AMENDED PROCESSED SHALE (THIRD CUTTING, FIRST SEEDING AND FIRST CUTTING, SECOND SEEDING).

Compound Treatment Rep	As ppm added	Calcium Arsenate					Iron Arsenide				Arsenic Sulfide				Control
		5	10	20	40	80	5	10	20	40	5	10	20	40	Shale
THIRD CUTTING, FIRST SEEDING															
I	As ppm in plant	0.31	0.28	0.39	0.33	0.41	0.07	0.22	0.19	0.24	0.25	0.25	0.25	0.42	0.24
II	As ppm in plant	0.31	0.17	0.20	0.35	0.40	0.18	0.14	0.24	0.22	0.21	0.14	0.28	0.29	0.13
III	As ppm in plant	0.15	0.12	0.29	0.23	0.36	0.11	0.17	0.18	0.17	0.13	0.34	0.33	0.20	0.01
IV	As ppm in plant	0.24	0.24	0.20	0.28	0.49	0.19	0.19	0.23	0.37	0.23	0.33	0.31	0.36	0.13
Mean	As ppm in plant	0.25	0.20	0.27	0.30	0.42	0.14	0.18	0.21	0.25	0.21	0.27	0.29	0.32	0.13
FIRST CUTTING, SECOND SEEDING															
I	As ppm in plant	0.45	0.50	0.69	0.94	1.45	0.51	0.64	0.59	0.93	0.60	0.58	1.06	0.63	0.44
II	As ppm in plant	0.73	--	0.64	1.00	1.27	0.40	0.57	0.52	0.57	0.45	0.51	0.66	1.00	0.27
III	As ppm in plant	0.90	0.41	0.69	0.81	1.32	0.40	0.43	0.49	0.70	0.35	0.46	0.79	0.85	0.43
IV	As ppm in plant	0.47	0.48	0.50	0.76	1.14	0.48	0.45	--	0.45	0.33	0.53	0.81	1.04	0.52
Mean	As ppm in plant	0.64	0.46	0.63	0.88	1.30	0.45	0.52	0.53	0.66	0.43	0.52	0.83	0.88	0.46

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Investigation of Trace Organic Compounds
in Oil Shale Wastes

MaryAnn Caolo, Robert E. Sievers, and John Stanley

INTRODUCTION

The great amount of retort wastewater produced by the various operations of shale oil recovery has raised many questions concerning the impact upon the quality of the water supply in surrounding areas. The sources of water emissions from various operations of shale oil recovery are summarized in Table 1 (1).

In addition, solid wastes produced in enormous quantities from ex situ and modified in situ retorting processes will be deposited on the surface of the ground where they will be exposed to leaching by rain and melting snow. The in situ retorting process will also yield large quantities of 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 fluorine, cadmium, molybdenum, arsenic and selenium.

This study was conducted to determine the speciation of selected metal ions and the identification of associated organic ligands in water samples (leachates, retort process water, and water from in situ processes) arising from oil shale recovery operations. These complexes are important since they may be more toxic than the simple inorganic species and frequently exhibit a "solubilization effect" (2). A comparison of the levels of these elements in raw and retorted shale is shown in Figure 1. The major portion of these trace metals was retained in the retorted shale.

Samples of shale oil, retorted shale, ex situ and in situ retort waters, and lysimeter water were investigated using the techniques of column chromatography, liquid-liquid extraction, gas chromatography (GC), gas chromatography/mass spectrometry/data system (GC/MS/DS), and atomic absorption analysis.

EXPERIMENTAL

The detection of individual components of the complex mixtures was accomplished by gas chromatography employing a flame ionization detector (FID) and a nitrogen-phosphorous detector (NPD). The gas chromatographic columns used in this study were high resolution glass capillary columns. The columns were ~20 m long and coated dynamically with 10% OV-101 in methylene chloride. FID analyses were conducted on a Hewlett-Packard HP5830A, while an HP5730A was used for the NPD analyses. Both instruments are equipped with Hewlett-

Table 1. Water Emissions from Oil Shale Operations

Process Step	Activity	Water Emission
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

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August 28-31, 1977, Denver, Colorado. Vol. I., p. 456.

Figure 1. Trace metal concentrations in raw and retorted shale.

Ref. A.D. Shendrikar and G.B. Favdel. Environ. Sci. Technol. 12, 332 (1978).

Packard capillary inlet systems. The operating conditions for the HP5830A equipped with a FID were: column temperature held at 70 °C for 4 minutes, then increased 4 °C/min to 230° for 16 minutes; nitrogen carrier gas 1 mL/min at 7 psig inlet pressure; hydrogen, 30 psig; air 30 psig; injection port temperature, 250 °C; detector temperature, 300 °C. Analyses with a nitrogen-selective detector were performed on a Hewlett-Packard HP5730A GC apparatus. Temperature programs and carrier gas flow rate were identical to those in experiments with the HP5830A. The hydrogen flow rate was 3 mL/min and air flow rate was 50 mL/min. The alkali bead heater voltage was held at approximately 17V. The nitrogen-phosphorous detector (NPD) displays a marked sensitivity to compounds containing nitrogen or phosphorous atoms, and is relatively insensitive to hydrocarbons (Figure 2). Metal analyses were carried out with a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer equipped with a high temperature graphite furnace, Perkin-Elmer HGA 2100, and a Perkin-Elmer Auto-Sampling System AS-1. Conditions under which the metal analyses were conducted are shown in Table 2.

Gas chromatography/mass spectrometry analyses were conducted using the Hewlett-Packard HP5980A/5933A GC/MS/DS. The gas chromatographic separations were effected using a 1.6 x 1/4" OD x 2 mm ID glass column packed with 100/120 mesh AP. As the components 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 is stored in the 5933 A computer data system. The mass spectral data can then be recalled to produce a reconstructed gas chromatogram, which is a plot of total ion intensity versus retention time; thus the term Total Ion Chromatogram (TI or TIC) is often used to describe this type of plot. In addition, the computer can search the mass spectral data collected from an analytical sample for particular mass-to-charge (m/e) intensity values and plot the intensity of any m/e value versus retention time. This type of a plot, a "mass chromatogram", allows one to locate the peak in the TIC of compounds which display a characteristic m/e ion.

The data system can also utilize a computer program to further resolve the chromatographic data on the basis of the slopes of m/e intensity values as they change with time. The program checks all m/e values as a function of time and if the majority of m/e values at a particular retention time have a positive slope, then m/e values which have a negative slope are rejected. The Total Ion Chromatograms resulting from the application of this computer program are referred to in this report as a Biller-Biemann Stripped Total Ion Chromatograms (3).

Mass spectral data were interpreted by comparison with reference compilations where available or by manual (non-computer) literature search and interpretation procedures. Reference compilations exist as computer files and our laboratory subscribes to one such system, the Interactive Sciences Corporation. Access to this system is accomplished via an acoustic coupler and standard telephone lines. Information is relayed and received via the Tektronix video terminal of the HP5980/5933A system. To aid in interpreting mass spectra obtained from this study, several spectral searches were conducted using the MSSS files.

Figure 2. FID and NPD chromatograms of a standard hydrocarbon solution.

Table 2. Operating Conditions for 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	HCl**	228.8	0.7	10	110	400	1500
Cr	EDL	357.9	0.7	20	110	1350	2700
Pb	EDL	283.3	0.7	10	110	550	2000
Se	EDL	196.0	0.7	20	110	850	2500
Zn	EDL	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).

The types of samples obtained and/or investigated during these studies are given in Table 3, along with the quantities.

SPENT SHALE STUDIES

(a) Methylene Chloride Extractable Compounds

The spent shale was a very fine powder and attempts to extract samples using an all glass Soxhlet extraction apparatus failed due to clogging of the coarse porosity glass frit of the Soxhlet thimble. The extraction of particulate matter collected on high volume air filters by ultrasonic action has been reported (4) and this method was used to extract spent shale samples. Approximately 10 g of each spent shale sample were placed in a 250 mL round-bottom flask to which 200 mL of reagent grade methylene chloride (CH_2Cl_2) was added. The samples were ultrasonicated for $1\frac{1}{2}$ hours and the spent shale was removed by gravity filtration. The CH_2Cl_2 extracts were concentrated to 1 mL on a rotary vacuum evaporator and used for direct analysis by GC and GC/MS. The GC-FID chromatograms of the CH_2Cl_2 extractable compounds are shown in Figures 3 and 4. Since most components in the TOSCO sample are present in the Paraho sample and this particular Paraho sample had more extractables, the Paraho sample was analyzed by GC/MS/DS. Examination of mass spectral data in conjunction with chromatographic retention time data resulted in the tentative identification of compounds listed in Table 4 for the numbered peaks in Figures 3 and 4.

(b) Compounds Extractable with Distilled Water

Approximately 10 g of each spent shale were ultrasonicated for 2 hours with 200 mL of distilled water. The spent shale was removed by gravity filtration and the water extract was batch extracted with reagent grade methylene chloride. The CH_2Cl_2 extracts were concentrated to 1 mL by rotary vacuum evaporation and analyzed by gas chromatography. The resulting chromatograms are shown in Figures 5 and 6. The identities of the major components have not been confirmed, but mass spectral data tend to indicate the presence of phthalate esters, possible contaminants from plastic containers. The samples were obtained from others, so it was not possible for us to designate the container material. In future sample collection we hope to be able to better guard against sample contamination. Plastic containers are probably best if only inorganic constituents are to be measured, but they are unsuitable if organic compounds are to be identified and quantitated.

RETORT WATER

A 25 mL sample of water obtained from a surface retort was batch extracted with methylene chloride and the extract was concentrated to 1.0 mL on a rotary vacuum evaporator for analysis. Preliminary mass spectral data suggested the presence of numerous compounds which contained odd numbers of nitrogen atoms. To confirm the presence of nitrogenous compounds, the sample was chromatographed on a Hewlett-Packard HP5710A equipped with interchangeable flame ionization and nitrogen-phosphorous detectors. A 1.8 m glass column was used to obtain a GC-FID chromatogram and the detector was changed to obtain a GC-NPD chromatogram under the same analytical conditions. The resulting chromatograms are shown

TABLE 3. SAMPLES INVESTIGATED*

A.	<u>PARAHO</u>	
	Shale Oil	1 L
	Retort Water	4 L
	Retorted Shale	5.6 kg
	Lysimeter Water, RW5283	1 L
B.	OMEGA-9 Retort Water	.8 L
C.	TOSCO Spent Shale,	150 g
	MS 0075	
	M & E Run, Barrels 2 & 3	

* Our thanks are due to R.A. Atwood and R.N. Heistand of Paraho and D.S. Farrier of LETC for recently supplying our laboratory with water samples.

Figure 3. Methylene chloride extract of TOSCO spent shale.

Figure 4. Methylene chloride extract of Paraho spent shale.

Table 4. Identifications of Numbered Peaks in Figures III and IV

Peak number	Identity	Molecular Weight
1	n-C ₁₁ H ₂₄	156
2	n-C ₁₂ H ₂₆	170
3	n-C ₁₃ H ₂₈	184
4	Naphthalene	128
5	n-C ₁₄ H ₃₀	198
6	Methylnaphthalene	142
7	n-C ₁₅ H ₃₂	212
8	Dimethylnaphthalene	156
9	n-C ₁₆ H ₃₄	226
10	C ₁₈ H ₃₈	254
11	n-C ₁₇ H ₃₆	240
12	n-C ₁₉ H ₄₀ Pristane	268
13	n-C ₁₈ H ₃₈	254
14	C ₂₀ H ₄₂ Phytane	282
15	n-C ₁₉ H ₄₀	268
16	n-C ₂₀ H ₄₂	282
17	n-C ₂₁ H ₄₄	296
18	n-C ₂₂ H ₄₆	310
19	n-C ₂₃ H ₄₈	324
20	n-C ₂₄ H ₅₀	338
21	n-C ₂₅ H ₅₂	352
22	n-C ₂₆ H ₅₄	366
23	n-C ₂₇ H ₅₆	380
24	n-C ₂₈ H ₅₈	394
25	n-C ₂₉ H ₆₀	400
26	n-C ₃₀ H ₆₂	422
27	n-C ₃₁ H ₆₄	436
28	n-C ₃₂ H ₆₆	450

Figure 5. FID chromatogram of water extract of TOSCO Spent shale.

Figure 6. FID chromatogram of water extract of Paraho spent shale.

in Figure 7. The sample was analyzed by GC/MS/DS. Many of the nitrogen-containing compounds could not be assigned structures since adequate reference spectra were not available. Several spectra gave reasonable assumptions as to a molecular formula and the proposed identities or molecular formulae are given in Table 5.

The presence of nitrogenous bases in shale and shale-related products has been reported often (5-8), although few spectra have been described and where they are, isomeric structures are not specified (7). A few of the structures of the nitrogenous bases are shown in Figure 8. Nitrogen-containing compounds have a considerably greater probability of exhibiting biological activity than those without nitrogen, and consequently may cause greater ecological damage. A great deal more attention needs to be focused on these compounds.

LYSIMETER WATER

A sample of lysimeter water from an 8' pit of Paraho spent shale was obtained and analyzed for volatile components. A 200-mL aliquot was sparged with nitrogen at a flow rate of 100 mL/min while the water was heated to 70 °C. The volatiles sparged from the solution were trapped on Tenax^R absorbent and subsequently thermally desorbed into the inlet of a GC column at -20 °C. After thermal desorption at 225 °C, the temperature of the oven was quickly raised to 0 °C and was programmed at 1°/min. The column was a 50 m x 0.25 mm ID glass capillary column coated with OV-101. The resulting chromatogram is shown in Figure 9.

SHALE OIL STUDIES

Since all available water samples from shale oil recovery operation had been used during preliminary studies (9), initial investigations were conducted on samples of Paraho shale oil, which had been obtained earlier. These samples had been stored longer than desirable. Therefore, data obtained from these samples should be interpreted bearing in mind the age of the sample.

We have been particularly interested in the development of a method for separating the nitrogen- and sulfur-containing compounds from the bulk of the organics present in the oil sample. Attention was focused principally on these compounds, since they represent the greatest potential for involvement in the mobilization of toxic inorganics by the formation of stable metal complexes.

(a) Adsorption of Shale Oil onto Neutral Alumina

A chromatographic separation procedure developed for the fractionation of coal-derived solids and liquids (10) has been applied to the fractionation of the shale oil. An aliquot (3.2 g) of Paraho shale oil was dissolved in 5 mL of methylene chloride. Neutral alumina (activity I, ICN), 12 g, was then added to the solution while stirring with a glass rod to give a material the consistency of wet sand. The flask containing the mixture was subsequently put on the rotary vacuum evaporator until all the solvent had been removed and the alumina flowed smoothly. The alumina with adsorbed sample was then added to a 1.8 cm OD x 340 cm chromatography column containing 92 g of neutral alumina,

Figure 7. FID and NPD chromatograms of a shale oil retort water sample.

Table 5. Proposed Identities of Chromatographic Peaks

Identity of Formula	Molecular Weight
Trimethylpyridine, $C_8H_{11}N$	121
Dimethylethylpyridine, $C_9H_{13}N$	135
Dimethylethylpyridine, $C_9H_{13}N$	135
Dimethylpiperdine, $C_7H_{15}N$	113
N-Butylcyclohexylamine, $C_{10}H_{21}N$	155
Quinoline, C_9H_7N	129
$C_8H_{15}N$	125
Phenol, C_6H_6O	94
Dimethylpyrrolidine, $C_6H_{13}N$	99
Cresol, C_7H_8O ;	108
Methylquinoline, $C_{10}H_9N$	143
Ethylpiperidine, $C_7H_{15}N$	113
$C_9H_{17}N$	139
Cresol, C_7H_8O	108
Dimethylquinoline, $C_{11}H_{11}N$	157
Ethylphenol, $C_9H_{10}O$	122
Ethylmethylpiperidine, $C_8H_{17}N$	127
Alkylpiperidine, $C_9H_{19}N$	141
$C_8H_{15}N$	125
$C_9H_{17}N$	139
$C_8H_{15}N$	125
$C_9H_{17}N$	139
$C_8H_{13}N$	123
N-phenylmethylene-2-propylamine, $C_{10}H_{13}N$	147

QUINOLINE

PYRIMIDINE

PYRIDINE

INDOLE

ANILINE

PIPERIDINE

PIPERAZINE

PYRAZOLE

PYRROLIDONE

PYRROLE

PYRROLINE

PYRROLIDINE

Figure 8. Structures of some nitrogen bases.

Figure 9. FID chromatogram of sparged volatiles from lysimeter water.

activity I. The column was eluted to give the fractions shown in Table 6. Solvents were removed from the fractions by rotary evaporation until the volume was reduced to a few milliliters. A sample from each fraction was saved for GC analysis. The remaining solvent in each of the fractions was allowed to evaporate. Table 6 gives the weights of the collected fractions. Each of the fractions was spotted on silica gel TLC plates and developed in acetone/ CHCl_3 (1:1). The plates were allowed to dry and then sprayed with chloroplatinic acid. This reagent is specific for most nitrogen-containing compounds and indicates their presence by a bluish-purple color. Fractions 4 and 5 were found to contain the majority of the nitrogen bases. These results indicated that the separation achieved with the sample of shale oil is similar to that obtained with coal-derived solids and liquids (shown in Table 7).

Trace Metal Analysis of Shale Oil Fractions

Trace metal analyses of the various fractions obtained from the alumina column separation of the shale oil were conducted to determine whether selected metal ions would tend to be associated with specific classes of compounds. Analyses for chromium, lead, zinc, arsenic, cadmium and selenium were performed by Dr. Robert Meglen, Director of the ETSRP Analytical Lab, using the atomic absorption-graphite furnace method. Three of these elements, (arsenic, cadmium and selenium) were chosen because of their toxicity, while the remaining three (chromium, lead, and zinc) were chosen because their chemistries are representative of other elements present in the retorted shale.

Initially, each of the fractions was taken to "dryness" by removing the volatile solvents and weighed (Table 6). The residue was dissolved in one, two, or three milliliter aliquots of p-xylene. Direct injection of the solution sample into the graphite furnace, however, did not produce reproducible elemental analytical results. It was necessary to take the samples to dryness again and perform a nitric acid-peroxide digestion on the residue before analysis of the aqueous digest by the atomic absorption graphite furnace method. A minimum volume of fuming nitric acid was added to each of the fraction residues and allowed to react until a white precipitate formed. To ensure the complete oxidation of the material, 30% hydrogen peroxide was added. Each sample was then diluted to 25 mL with distilled water, and the resulting solution analyzed by the atomic absorption-graphite furnace method.

The results from these experiments (shown in Table 8) indicate that there is a tendency toward association of the metal ion with specific fractions obtained from the separation. Most of the cadmium, selenium, and chromium present in the oil sample are concentrated in the chloroform-eluted fraction, which also contains the majority of nitrogen-containing compounds. Zinc is concentrated in the toluene-eluted fraction, while most of the lead is in the THF/ETOH fraction. Of the six elements, only arsenic appears to be distributed between the chloroform and methanol fractions. These data tend to suggest specific metal associations with classes of organic compounds, notably, the nitrogenous bases. These bases are assumed to possess the greatest ability to form metal complexes.

Table 6. Alumina Column Fractionation of Shale Oil*

Fraction number	Eluant	Weight (g)	
1	100 ml hexanes	0.6916	
2	275 ml toluene	0.3075	
3	275 ml chloroform (to the point before a large dark band began to be eluted from the column)	0.0399	]—1.5352
4	350 ml chloroform (elution of dark band)	1.3765	
5	275 ml chloroform (volume sufficient to remove any remaining dark color)	0.1188	
6	200 ml tetrahydrofuran/ethanol (9:1)	0.3295	
7	250 ml methanol	0.1132	
Total		2.9770 g	

*3.2 g of shale oil was introduced into the alumina column.

Table 7. Fractionation Observed for Coal-derived Solids and Liquids

Fraction Number	Solvent	Principal Compound Type Eluted
1	hexane	saturates
2	toluene	aromatics
3	chloroform	ethers
4	chloroform	nitrogen compounds
5	tetrahydrofuran/ ethanol (9:1)	hydroxyl compounds

Ref: J. E. Schiller and D. R. Mathiason. Anal. Chem., 49:1225, 1977.

Table 8. Elemental Concentrations of a Shale Oil Sample Being Eluted from an Alumina Column by Solvents with Increasing Polarity

Fraction	ug/g					
	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. MeOH	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.

Scientists at Oak Ridge National Laboratory have studied the mutagenicity of shale oil (11). The general approach involved fractionation of the complex mixture, followed by testing in the Salmonella histidine reversion assay described by Ames (12). The fractionation scheme (shown in Figure 10) involved an extensive acid-base extraction procedure. The results of the mutagenicity testing of the various fractions are summarized in Table 9. The basic fractions are seen to exhibit the highest mutagenic activities. A closer study was made of the ether soluble basic fractions (BE) and it was found to contain a wide variety of alkyl-substituted and partially-hydrogenated derivatives of nitrogen heterocycles.

In view of the toxicity of the three metals (cadmium, arsenic and selenium) found to be concentrated in the nitrogen-containing fractions and the mutagenic activity also associated with these fractions, the study of the speciation of metallo-organic complexes is of great importance, and much more work is required to fully assess the potential danger of ground water contamination. Analysis of these fractions by GC/MS/DS is currently being undertaken.

Gas Chromatographic Analysis of Shale Oil Fractions

The fractions obtained from the alumina column fractionation of the sample of shale oil have been analyzed by gas chromatography and the chromatograms are shown in Figures 11 to 17. Figure 2 indicates the relative FID and NPD responses for a series of normal hydrocarbons. While the FID shows good sensitivity to hydrocarbons, the NPD exhibits essentially no response.

Figures 11 and 12 correspond to fractions eluted by hexane and toluene during the shale oil fractionation. These studies with a flame ionization detector show that a large proportion of the hydrocarbons are being eluted from the column by these solvents. There appears to be little or no evidence for the presence of nitrogen compounds in these two fractions as shown by the negligible NPD response in these chromatograms.

An indication of the presence of significant amounts of nitrogen-containing compounds is given by the nitrogen-selective detector for the three chloroform fractions. The NPD responses for these extracts are shown in Figures 13, 14, 15, and 16. The flame ionization results for these fractions (also shown in the same Figures 13, 14, 15 and 16) give no evidence of appreciable amounts of hydrocarbons present, although Figure 16 shows strong detector response to a few constituents. The methanol fraction should contain components of high polarity; it produced relatively little response in FID and NPD (Figure 17). The large number of compounds present in each of these fractions is demonstrated by these chromatograms, and further analysis of individual components is being undertaken using retention indices and mass spectral data.

RETORT WATER STUDIES

Paraho Retort Water

The sample of retort water obtained from the Anvil Points area was not homogenous in composition and contained suspended matter and oil. Continuous

Figure 10. Oak Ridge method for acid-base extractive separation of shale oil.

Table 9. Distribution of Mutagenic Activity by Fractionation Procedures

Extractive Fractionation			Sephadex Gel Chromatographic Fractionation		
Fraction ¹	Activity ² rev/mg	Weighted activity ³ rev/mg	Fraction ¹	Activity ² rev/mg	Weighted activity ³ rev/mg
NaOH Insol.	256	3	Hydrophilic	1300	78
Weak Acid (WA _I)	185	<1	Polymeric 1	54	3
Weak Acid 1 (SA _I)	52	<1	H-Bonding	1040	52
Strong Acid 1 (SA _I)	0	0	Polymeric 2	0	0
Strong Acid 2 (SA _E)	159	<1	Aliphatic	180	108
Strong Acid 3 (SA _W)	160	<1	Mono/Diaromatic	24	3
Basic 1 (B _{Ia})	1377	3	Tri/Tetraaromatic	132	7
Basic 2 (B _{Ib})	800	2	>Tetraaromatic	1220	49
Basic 3 (B _E)	952	68			
Basic 4 (B _W)	223	1			
Neutral	112	97			
TOTAL		178			300
Unfractionated		-			204,268,196

¹Shale derived crude oil "B", separate aliquots 6 months apart.

²Revertants per milligram of fraction using TA98, S-9, and Arocolor.

³Revertants per milligram of starting material computed by multiplying activity of fraction by weight percentage of total recovered weight constituted by the fraction.

Ref: M. R. Guerin, J. L. Epler, C. W. Gehrs. Oak Ridge National Laboratory.

Figure 11. FID and NPD chromatograms of hexane fraction from alumina column separation of shale oil.

Figure 12. FID and NPD chromatograms of toluene fraction from alumina column fractionation of shale oil.

Figure 13. FID and NPD chromatograms of 1st chloroform fraction from alumina column fractionation of shale oil.

Figure 14. FID and NPD chromatograms of 2nd chloroform fraction from alumina column separation of shale oil.

Figure 15. FID and NPD chromatograms of 3rd chloroform fraction from alumina column separation of shale oil.

Figure 16. FID and NPD chromatograms of THF/ETOH fraction from alumina column separation of shale oil.

Figure 17. FID and NPD chromatograms of methanol fraction from alumina column separation of shale oil.

liquid-liquid extraction of this retort water was performed before and after the separation of this material from the water, and is described below.

- One hundred milliliters of unfiltered retort water was placed in a continuous liquid-liquid extractor with ~500 mL of hexane and extracted overnight. The hexane was separated and the same water sample was subsequently extracted overnight with ~500 mL of toluene. The toluene was then replaced with ~500 mL of chloroform and the water again extracted overnight. Each of the three organic extracts was then concentrated to a few milliliters with a rotary vacuum evaporator for analysis. A small sample was removed for GC analysis, the remainder was placed in an acid-washed vial, and the remainder of the solvent removed in VACUO. The weight of each fraction is listed in Table 10.
- One hundred milliliters of Paraho retort water was centrifuged and the dark yellow water was drained from the oil and particulate matter floating above the solution. The water sample was then placed in a continuous liquid-liquid extractor and successively extracted with hexane, toluene, chloroform, and ethyl acetate in the manner described above. Each of the extracts was then concentrated to a few milliliters and a small sample removed for GC analysis. The remainder was taken to dryness; the weight of each fraction is listed in Table 10.

OMEGA-9 RETORT WATER

One hundred milliliters of retort water from the Rock Springs project was placed in a continuous liquid-liquid extractor and successively extracted with hexane, toluene, chloroform and ethyl acetate as described above. Each of the extracts was concentrated to a few milliliters and a sample removed for GC analysis. The remainder was taken to dryness; the weight of each is listed in Table 10.

SUMMARY

Preliminary studies to determine the presence of trace organics were conducted on three types of samples (retorted shale, retort water, and lysimeter water) from shale oil recovery operations.

Retorted shales from both the TOSCO and Paraho processes were extracted with methylene chloride while being subjected to sonification in an ultrasonic bath. The extracts were concentrated and analyzed by GC and GC/MS. Results indicated that the major organic constituents were saturated normal hydrocarbons, including the isoprene hydrocarbons, phytane, and pristane. Naphthalene, methyl naphthalenes, and dimethyl naphthalenes were present in minor quantities.

A retort water sample from a surface retort was batch-extracted with methylene chloride and the extract concentrated for analysis by GC/FID, GC/NPD, and GC/MS/DS. The results from this investigation indicated the presence of

TABLE 10. CONTINUOUS LIQUID-LIQUID EXTRACTION OF SHALE OIL RETORT WATER

Sample	Weight (g) of residue from Organic Extract			
	Organic Extract			
	<u>Hexane</u>	<u>Toluene</u>	<u>Chloroform</u>	<u>Ethyl acetate</u>
PARAHO retort water (100 mL unfiltered)	0.1411	0.1091	0.9194	-----
PARAHO retort water (100 mL filtered)	0.1753	0.0725	0.619	1.6203
OMEGA-9 retort water	0.0071	0.0151	0.0047	0.0364

numerous nitrogenous bases. However, for many of the compounds, structures could not be assigned due to the lack of reference mass spectra and retention time data for authentic samples. Until better reference spectra and chromatographic data on compounds with known structures are obtained, efforts to fully characterize the constituents will be less effective than desired.

A sample of lysimeter water was analyzed for volatile components by sparging and desorption into a GC column, but to date we have not yet identified the individual components.

Since all the water samples available had been used during the preliminary studies described above, initial investigations in the development of an easy and improved method for the separation of the bulk organics from the nitrogen- and sulfur-containing compounds were conducted on a sample of shale oil. A reasonably good column chromatographic fractionation of the crude oil was achieved with alumina packing by successive elutions with solvents of increasing polarity. These fractions were analyzed by GC/FID and GC/NPD and showed the majority of the nitrogen-containing compounds to be present in the chloroform fractions.

Trace metal analyses of the seven fractions were conducted to determine whether selected metal ions would tend to be associated with specific classes of compounds. Atomic absorption spectrometry measurements of chromium, lead, zinc, arsenic, cadmium, and selenium were performed using the graphite furnace method. The results from these experiments indicated that there is a tendency toward association of the metal ion with specific fractions in the separation. Most of the chromium, cadmium and selenium present in the oil sample was concentrated in the chloroform-eluted fraction, which also contained the majority of nitrogen-containing compounds. Zinc was concentrated in the toluene fraction, while most of the lead was in the THF/ETOH fraction. Of the six elements, only arsenic appears to be uniformly distributed between the chloroform and methanol fractions. These data tend to suggest specific metal association with classes of organic compounds, notably the nitrogenous bases. Since nitrogen bases are assumed to possess the greatest ability to form metal complexes, these fractions are being analyzed by GC/MS/DS to identify and quantitate the organic ligands and any metallo-organic complexes that may be present.

The results from these experiments will provide the background for the study of the speciation of selected metal ions and the identification of metallo-organic complexes in water samples (leachates, retort process water and water from in situ processes). Liquid-liquid extraction (using solvents of increasing polarity) of Paraho and Omega-9 retort waters have been performed. The extracts are currently being analyzed by GC/FID, GC/NPD, and atomic absorption spectrometry. Future work will concentrate on GC/MS/DS studies of these extracts. These data will provide the information necessary to obtain a clearer picture of possible environmental damage to surface and ground waters from shale oil recovery operations.

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Progress Report: 1976 - 1979

Analytical Chemistry
Robert Meglen

SUMMARY OF PROGRESS

The Analytical Chemistry Laboratory of the Environmental Trace Substances Research Program (ETSRP) provides analytical service to the project investigators. This service includes development of accurate analytical procedures, routine analysis of samples, and data interpretation techniques such as pattern recognition. Significant progress achieved between February 1978 and February 1979 is summarized below. Details of these developments and a short review of progress made since 1976 are provided following the summary.

1. A single geological sample fusion procedure has been developed for boron and fluoride analysis. This method replaces the two fusion method previously required.
2. High pressure acid bomb digestions of geological materials for Mo and other refractory metals have been under study. If successful this method will replace the time-consuming digestion currently in use.
3. A new fluoride analytical procedure has been developed to replace the method developed in 1977 and described in last year's progress report. The new method is more rapid, reliable and capable of being automated.
4. Work has begun on the detection and analysis of lithium isotopes in oil shale related matrices. If successful, the technique could provide a method for source identification of shale related ground water contamination.
5. In January 1979 we accepted delivery of a new atomic absorption spectrophotometer. This instrument has significantly improved our efficiency and our ability to perform the increasing number of requested analyses.

6. In December 1978 we received a used Technicon Autoanalyzer. This instrument is currently being used to automate the colorimetric analytical methods.
7. The boron chemical analysis method developed in 1977 has been automated, i.e. a flow system to perform the chemistry has been designed, built, and implemented for use with the Technicon Autoanalyzer.
8. An extensive automated analytical system including atomic absorption, colorimetric, and fluorometric methods has been designed. Funds obtained through other grants have been used to purchase a data handling and acquisition system. When complete (April, 1979) the system will significantly increase our analytical capacity.
9. We have recently written several computer programs to perform pattern recognition calculations. These methods will be used to facilitate interpretation of complex multielement data.

METHODS DEVELOPMENT

BORON, FLUORIDE - SAMPLE PREPARATION

The samples encountered in this study present two problems which make accurate analysis difficult. Many of the samples represent baseline or naturally low concentrations. In order to detect basin wide or regional trends in the data, highly reproducible analyses are required. Secondly, analysis of silicates for low concentration of fluoride and boron requires complete destruction of the silicate matrix which binds the analyte. The rigor of the sample treatment can volatilize some of the analyte and the flux or digestion mixture can interfere with the detection method used. Table 1 shows the variability of apparent boron concentration for various sample treatment techniques. Reproducible boron analyses can be obtained using either sodium carbonate or sodium carbonate-potassium carbonate as a fusion flux. The results obtained in this laboratory using colorimetric analysis compare well with results obtained at Battelle North West Labs using neutron activation analysis.

The preparation of geological materials for fluoride analysis exhibits similar difficulties. In the past it has been necessary to use separate fusions for boron and fluoride analyses since the sodium carbonate fusion does not provide quantitative release of fluoride. We have developed a single fusion procedure which is suitable for both fluoride and boron analysis. This method is described in the addendum.

MOLYBDENUM - SAMPLE PREPARATION

The geological samples from baseline studies are sufficiently low in molybdenum that a special treatment is required to obtain useful analyses. Conventional fusions such as the one described above are not useful for Mo

TABLE 1. COMPARISON OF SAMPLE PREPARATIONS FOR BORON ANALYSIS
(RESULTS IN ugB/g SAMPLE)

Sample	HF Digest	NaOH fusion	Na ₂ O ₂ fusion	Na ₂ CO ₃ Ash/fusion	Na ₂ CO ₃ fusion	Na ₂ CO ₃ /K ₂ CO ₃ fusion	Battelle NW Neutron Act
Raw Shale (OS-1)	54±13	51±5	157±19	66±11	126±11	119±26	126±8
Retorted Shale (SS-1)	66±5	61±7	159±34	79±4	144±14	138±10	145±8
Fischer Assay Spent Shale (FASS)	---	60±4	-----	47±9	145±13	145±13	145±12

analysis when the analyte is present at less than 5 ug/g. A special procedure for analyzing Mo in soils and sediments has been developed. This method requires a time consuming, labor intensive hydrofluoric acid digestion procedure. The hydrofluoric acid digestion is required since it is the only acid digestion method which effects quantitative release of Mo from the silicate matrix. (This method is described in the addendum.) Several days are required to complete digestion of 30 samples. Therefore, the thousands of samples which are submitted require large amounts of technician time. In order to reduce the labor we have initiated a study to evaluate the feasibility of using high pressure acid digestion in teflon lined steel reaction bombs. This method has been successfully used for other trace element analyses, but owing to the susceptibility of Mo analyses to interferences, it has not yet proved adequate for low Mo concentration in geological materials. These studies will continue.

FLUORIDE - SOLVENT EXTRACTION

We reported a new fluoride analysis procedure in the 1977-78 progress report. The two step method requires quantitative separation of fluoride from potential interferants and conversion of fluoride to aluminum monofluoride which is detected by molecular absorption in a graphite furnace. In this procedure fluoride is separated from an aqueous solution of the sample by complexation-solvent extraction. The complexing agent used is diphenylsilanediol (DPSD) in the solvent xylene (xyl).

The fluoride is quantitatively extracted (free of interferants) into the xylene phase which is then introduced to an electrothermally heated graphite analyzer. In the furnace the solvent is evaporated and an aqueous solution containing aluminum is added to the dried residue. (This two-step addition precludes automated analysis, see subsequent paragraphs.) When the graphite furnace is heated to 2250 °C the stable gaseous AlF is detected via its absorption of 227.5 nm light.

Detect 227.5 nm

This improved method is based upon the method described by Tsunoda et al. (1). Figure 1 shows the absorption spectrum of AlF(g) obtained by successive measurement of the absorbance of a 5 ug/L fluoride sample at various wavelengths. (A hydrogen continuum lamp is used as the light source.) A blank spectrum containing no fluoride, treated in the same way is also shown in Figure 1.

Figure 1. The absorption spectrum of gaseous aluminum monofluoride.

Figure 2 shows a typical calibration curve obtained for fluoride standards. The extent of quantitative extraction of fluoride from the aqueous phase can be seen in the analysis of the fluoride remaining in the aqueous phase. Figure 3 shows the percent recovery of fluoride from aqueous solutions when various interfering ions are present at 1000 ppm. Open bars show the apparent fluoride in solution without extraction. The shaded portion shows the improved recovery obtained by performing the solvent extraction and analyzing the organic phase. In all cases the recovery is better than 90%. The presence of aluminum suppresses the extraction recovery unless 6 M acid is added prior to extraction. The arrow shows the improved recovery obtained by proper pH adjustment prior to extraction.

Table 2 shows the results obtained on six geological samples analyzed using this method. The results are compared to analyses reported by a different technique (fluoride selective electrode). The fusion method described in the addendum was used to prepare the samples for analysis. Table 3 shows the results obtained on four plant Standard Reference Materials analyzed by this method.

FLUORIDE - GASEOUS DIFFUSION SEPARATION

We have developed an alternate fluoride separation technique to replace the solvent extraction method described above. This technique requires less time, is more reproducible, and is capable of being automated. The use of an organic solvent for graphite furnace analysis is prone to pipetting errors when a sample is introduced into the furnace. Sample volatilization characteristics change from sample to sample and as the graphite tube ages, a sample can be "lost" when the solvent penetrates the failing graphite matrix. In addition to this difficulty, the method requires two injections, one of the organic solvent containing the complexed fluoride and a second injection of an aqueous reactant solution. This reactant contains aluminum for producing the AlF species which is detected. It also contains other ions which enhance the sensitivity of the method. With this required two injections and our existing equipment it is not possible to use automated sample introduction techniques.

We have adapted the gaseous fluoride diffusion separation of Taves (2). In this method hexamethyldisiloxane (HMDS) is used to form a volatile trimethylfluorosilane (TMFS).

The gaseous TMFS is trapped in an alkaline solution and undergoes hydrolysis to form an aqueous solution of fluoride. This solution contains the quantitatively extracted fluoride and is free of potential interferants. This procedure also permits preconcentration of large volumes of low fluoride content samples. (Concentration factors of more than 100 have been achieved.)

Figure 2. Typical calibration curve for fluoride analysis by molecular absorption in a graphite furnace.

Figure 3. Recovery efficiency for solvent extraction of fluoride in the presence of various interferants.

TABLE 2. RESULTS OBTAINED ON U.S.G.S SOILS

Sample	This Work	Lit. Val.*
UG/G		
GxR-1	1280	1180±190
GxR-2	435	450±180
GxR-3	87000	79400±14600
GxR-4	2930	2800±490
GxR-5	290	286±116
GxR-6	290	304±131

* D.M. Hopkins, J. Res. U.S. Geol. Survey, 5 589(1977).

TABLE 3. RESULTS OBTAINED ON N.B.S. SRMs

SRM	This Work	NBS
UG/GM		
1570 Spinach	4.5±1.7	---
1571 Orchard Leaves	3.9, 3.6	(4.0)*
1573 Tomato Leaves	6.3	---
1575 Pine Needles	1.9	---

* Not Certified, information only.

The aluminum reactant solution required for graphite furnace analysis is added to the trapping solution. Thus, with only one injection both reactant and sample are introduced to the furnace. Therefore, an automatic sampling device can be used for analyzing samples. The gaseous diffusion and trapping can be done in a single container overnight. It does not require the messy operations that the previously described solvent extraction entails. This technique requires less than five minutes labor per sample and when an automated sampler is used 25 samples can be analyzed per hour. Details of this method are given in the addendum.

BORON - DETECTION AND SEPARATION

The detection of boron in complex matrices has been accomplished by adapting a colorimetric method which uses azomethine H reagent. This method is more precise than the widely used curcumin method. The details of this procedure are given in the addendum. We have also adapted the technique to be used on a Technicon Autoanalyzer. Work has also been completed on a simple solvent extraction technique which could be used to separate boron from potential spectral interferants. Several laboratories are beginning to use plasma emission spectroscopy for boron analysis. The presence of high concentrations of major elements adversely affect this technique. While we do not presently have the instrumentation for plasma spectroscopy we have performed initial tests to examine the utility of this extraction technique. The method should be useful when we obtain the multielement plasma capability.

Lithium Isotope Analysis

Lithium is elevated in oil shale above the concentrations found in soils from the same region. The solubility of this element in waters suggests that leachates from retorted shales may also be elevated. We have begun a study to examine the feasibility of using isotope analysis for source identification. The average relative abundances of Li-6 and Li-7 isotopes are 7.5 and 92.5% respectively. However this abundance may vary in different geological formations. It is possible to determine the isotopes using atomic absorption spectrophotometry. If shale derived Li shows a different isotope ratio than non-shale derived Li it may be possible to determine the source of Li detected in surface and ground waters. This could provide a simple method for monitoring ground water for contamination from shale related activities. While this proposal is still highly speculative we will continue to expend some effort in its development. Our preliminary results indicate that if the shale derived lithium-6 is more than 2% (abs) from the non-shale derived lithium, we will be able to detect it with 95% confidence.

LABORATORY AUTOMATION

In previous years this laboratory had only 50% time access to an atomic absorption spectrophotometer. The large number of samples submitted for analysis and limited instrumentation precluded rapid turn-around time for

principal investigators. In January, 1979 we accepted delivery of a Perkin-Elmer Model 5000 A.A. Spectrophotometer. Funds were provided through DOE. This instrument has enabled us to begin automation of several A.A. procedures. In the flame analysis mode the instrument can sequentially analyze up to six elements on 50 samples without analyst intervention. Changes of flame conditions, lamps, and all instrumental parameters are performed by a built-in micro processor.

We also obtained an auto sampler device for graphite furnace analysis. This device has been coupled with our graphite furnace (purchased 5 years ago with NSF funds). The system has been in operation for one month and we have effectively doubled our analytical output and reduced the technician time required for analysis. However, the furnace has received extensive use prior to this project and its continued operation is uncertain. In addition it is not possible to automate the system to change conditions for different elements. We anticipate a major change in analytical emphasis such that the majority of elemental analyses will be performed using graphite furnace analysis. We will be seeking funds to update this system and to replace the old furnace.

In January we obtained a used Technician Autoanalyzer with DOE funds. We have automated the colorimetric boron analysis and are currently designing a system to automate colorimetric boron, fluorometric selenium, and cold vapor mercury analyses. At present the system is operating in a stand-alone mode. By April this system and the A.A. will be interfaced with a Data General Microcomputer (funds obtained from other grants). When the full system is in operation all data acquisition, calculations, and reporting will be automated. The improved efficiency will increase our analytical capacity by a factor of at least two without adding staff. We anticipate that this system will enable us to complete the doubled rate of analyses requested by principal investigators for next year. Figure 4 shows a schematic of the automated system to be completed in April.

X-RAY FLUORESCENCE

In addition to the chemistry laboratory we have continued to use the multielement capabilities provided through the Nuclear Physics Laboratory on campus. This laboratory provided 530 multielement analyses between February 1978 and February 1979. They continue to supply the complementary techniques which are essential to quality control checks and the ability to perform elemental analyses on samples which are too small for wet chemical analysis.

PATTERN RECOGNITION

Modern analytical techniques have provided a rapid and relatively inexpensive method for obtaining multielement data on many samples. Multielement techniques provide information on some elements which would not be determined if they had to be analyzed separately. These "bonus" data represents a resource which has not been effectively used in the past. The reason for the existence of under-used data can be traced to our reliance upon two dimensional representations of relationships between variables.

Schematic of Laboratory Automation

Figure 4. Schematic diagram of automated laboratory analysis system.

Simple calculation of correlation coefficients is often used as a means of quantifying similarities among pairs of variables. Such linear regressions provide a statistically rigorous basis for relating functional relationships. While these techniques do not yield any information of causality, they make it possible to depict data in a simple two dimensional graphical representation. However multi-component analysis produces so many possible combinations that it becomes difficult to prepare all possible plots. (Measurement of 25 variables on a number of samples would require the preparation of 300-two dimensional graphs.) A computer can be used to prepare a correlation matrix. From this, "interesting" pairs of variables can be selected for plotting. This technique can be useful but it remains a two element view of a more complex multidimensional element space. Patterns, groupings, or simultaneous correlations among more than two elements are neglected.

Pattern recognition techniques provide a method for examining complex relationship in multidimensional variable space. Their use permits the reduction of the dimensionality of the problem for easier interpretation while preserving the valuable information included in the multidimensional data space.

Since the beginning of this project, massive amounts of data have been obtained. We have begun to examine this data using several pattern recognition techniques. An example of the kinds of information which can be derived from this data handling technique is presented below. This very simple treatment is preliminary but when refined we believe that its application will improve our understanding of the accumulated data.

Pair-wise cluster analysis has been applied by Meglen and Denney to Dr. Wildeman's data on 20 elements in 48 samples of raw shale. Table 4 shows the correlation matrix between pairs of elements in the 48 samples. Figure 5 shows the pair-wise clustering dendrogram obtained from the correlation matrix. This graph represents all of the data shown in Table 4.

The correlation coefficients are used as a measure of similarity between the element concentration in the 48 samples. Iron and calcium are highly correlated ($r \approx .9$). Taken as a group, the concentration trends for these two elements are next most like the manganese concentration trend in the 48 samples ($r \approx .85$). This cluster of three elements is next most like the cluster formed between strontium and rubidium ($r \approx .82$). General features apparent from this dendrogram are:

1. Two distinct groups or clusters of elements are apparent. The elements Ba, Y, Nb, Sr, Rb, Ga, Mn, Fe, Ca form clusters with $r \geq .5$. These elements are associated with carbonate minerals.
2. A second cluster is formed among Se, Pb, As, Mo, Cu, and Ni. These elements are usually associated with sulfide minerals.

Figure 5. Pairwise clustering dendrogram for 20 components in 48 raw shale samples.

3. Gas + loss, oil, and water content do not correlate well with either group of elements. It is also significant that Zn and Zr do not correlate well with either group of elements. Of all the elements, Zn shows the poorest correlation. This finding is in agreement with Wildeman's finding that Zn acts differently in the trace metals balance for the retort. (see Wildeman's section of this progress report.)

The dendrogram shown here was prepared from refined data available only after Wildeman's manuscript was completed. It shows a much closer agreement between the computed similarities and the expected results, i.e., Ba joins the elements in the carbonate cluster and As joins the sulfide cluster. This refinement does not alter Wildeman's conclusions.

These results are presented merely to acquaint the reader with the data reduction technique. Further interpretation will be found in Wildeman's progress report. We hope that the power of this technique to assist in data interpretation will be demonstrated as we continue to study its application to oil shale related problems.

The total laboratory output by year is shown in Table 5. The anticipated sample analysis load will increase to about 10,000 in the coming year.

TABLE 5. LABORATORY ANALYSIS PERFORMED

Year	Chemistry Lab	XRF Lab
1976 - 1977	613	130
1977 - 1978	4,385	600
1978 - 1979	4,430	530
Subtotal	14,825	1,260
TOTAL	16,085	

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ADDENDUM: ANALYTICAL CHEMISTRY

- A. Fusion Method for Geological Samples: Preparation for Fluoride and Boron Analysis
- B. Analysis for Boron: Reagents for the Azomethine Method
- C. Acid Digestions of Geological Samples for Low Mo Concentrations
- D. Analysis of Fluoride (Solvent Extraction)
- E. Analysis of Fluoride (Gas Diffusion)

FUSION METHOD FOR GEOLOGICAL SAMPLES:
PREPARATION FOR FLUORIDE AND BORON ANALYSIS

A 0.1 g sample of 1.0 g $\text{Na}_2\text{CO}_3:\text{K}_2\text{CO}_3$ flux (1:1 by weight) are mixed and fused in a 25 mL platinum crucible at 1000 °C for 0.5 hours. After cooling the crucibles, 10 mL of 1.0 M HCl is added to the fusion mixture to initiate dissolution of the fusion mixture. The contents are then transferred to a 100 mL plastic specimen cup. A second 10 mL portion of 1.0 M HCl is added to the crucible, stirred, and transferred to the plastic cup. The third rinse consists of 1.0 mL concentrated HCl and 4.5 mL deionized water. The sides of the crucible are scraped with a rubber spatula and the contents transferred to the specimen cup. The final rinse is 4.5 mL of deionized water. (If fused material remains in the crucible an additional rinse of 10 mL 1.0 M HCl may be necessary.) The final volume of 50.0 mL is obtained by addition of 1.0 M HCl.

ANALYSIS FOR BORON: REAGENTS FOR THE
AZOMETHINE METHOD

Buffer:

500 gm ammonium acetate
30 gm disodium EDTA
800 mL deionized H₂O
250 mL glacial acetic acid

The pH of the buffer is roughly 5.0 - 5.5.

The ammonium acetate does not dissolve completely, however, this does not seem to affect the analysis.

Asomethine - H solution:

1.0 gm ascorbic acid is dissolved in 100 mL deionized H₂O. 0.45 gm azomethine-H (available from Pierce Chemical Co.) is added to the solution. The azomethine-H should dissolve completely. Due to the instability of the azomethine-H, the solution must not be allowed to sit at room temperature overnight. It can be stored in the refrigerator for one week or in the freezer for approximately one month. Upon thawing the solution for reuse make certain that the azomethine has completely dissolved since it can precipitate out while freezing.

NOTE: Prepare and store all reagents in plastic containers.

Analysis for Boron:

Experimental for the azomethine method 1.0 mL of sample or standard is pipetted into a plastic test tube followed by 2.0 mL of buffer. The contents are stirred on a Vari-Whirl. 2.0 mL azomethine-H solution is then added and stirred. The tubes are allowed to sit for 0.5 hours before reading the absorbance values at 420 nm. The range of standards used is from 0-5 ppm B although the standard curve is linear up to 10 ppm B. (see attached Beer's law plot) Often the samples are too concentrated, as is the case with plants where 0.5 mL of sample is pipetted into the test-tube and then brought up to 1.0 mL with 0.5 mL deionized H₂O.

In some cases the samples may exhibit color before or after the addition of buffer. This is a potential interference in the absorbance measurements and therefore sample blanks are also prepared. The preparation involves the addition of 2.0 mL of a 1.0% ascorbic acid solution instead of the 2.0 mL of the azomethine-H solution. The absorbances are read at 420 nm and subtracted from the absorbances of samples with the azomethine-H solution.

When a yellow coloration is present in the samples (in the absence of the azomethine reagent) it is possible to prepare a "correction" calibration curve.

This correction curve may be obtained by randomly selecting a number of samples to be analyzed as sample blanks; i.e. without the addition of azomethine reagent. The absorbance values of all azomethine containing samples are read. The concentrations are calculated from the Beer's law plot. These are designated as uncorrected since they include absorbance of the interfering species. The absorbance values of the selected sample blanks are then read and subtracted from the corresponding absorbance values of the azomethine-containing samples. These corrected absorbance values are then used to calculate "corrected" concentrations from the Beer's law plot. A plot of uncorrected values (y-axis) against "corrected" (x-axis) may then be used to correct samples which have a similar matrix but for which no blanks have been prepared. This procedure has been used with excellent reproducibility for a given sample type. Occasional blank checks have shown that this procedure is accurate to within 3%.

Analysis of Boron: Sample Preparation Plants

Ashing:

3.00 gm of plant are weighed into a porcelain crucible and placed in a muffle furnace. The temperature is brought up to 450 °C and maintained at that temperature for 12 hours or overnight. An ambient air flow is introduced to the furnace after the plants have stopped smoking - roughly 3-4 hours after placing the plants in the furnace.

Sample Work-up:

The plant ash is transferred to a 7 dram or 20 mL plastic vial. 20 mL 1.0 M HCl is added slowly since it can cause splashing of the sample.

Boron Analysis:

Usually 0.5 mL of sample is required for the analysis. In some cases 0.2 mL is used due to a high concentration of B in the plant.

ACID DIGESTIONS OF GEOLOGICAL SAMPLES FOR LOW Mo CONCENTRATIONS

Geological samples submitted to this laboratory which are suspected to have less than 2 ug/g sample of Mo are prepared for analysis by acid digestion. This process allows for a greater amount of the sample to be used and is rigorous enough to break up the silicate matrix of the samples.

One gram of the sample is weighed into a 100 mL Teflon beaker. This is followed by the addition of 2.5 mL HNO_3 , 2.5 mL H_2SO_4 and 5.0 mL HF. The beakers are placed on a hot plate at 240 °C and the acids are allowed to evaporate to dryness. This acid treatment is generally carried out three times on the sample but the number of times may vary with the grain size of the sample. The sample is considered "digested" when the dry residue is a white or yellow crust.

After allowing the sample to cool, 1.0 mL of concentrated HCl and 4.0 mL of deionized water are added. The beakers are covered with a watch glass and placed on low heat for five minutes to help dissolve the sample. It is then filtered and washed with deionized water. The volume is brought up to 15.0 mL in a test tube.

To analyze the samples, 10 mL aliquots are withdrawn and pipetted into test tubes. The following steps are modified for Mo-thiocyanate colorimetric analysis scheme:

- 1) Add 0.5 g sodium tartrate and stir.
- 2) Add 0.1 mL 1% ferrous ammonium sulfate solution.
- 3) Add 0.5 mL 10% potassium thiocyanate solution; stir; wait 15 minutes.
- 4) Add 2.0 mL 10% stannous chloride solution; stir; wait 15 minutes.
- 5) Add 2.0 mL of *i*-amyl alcohol to the samples and 4.0 mL to the standards; shake; allow 15 minutes for layers to separate; centrifuge for about 5 minutes.
- 6) Analyze the organic extract for Mo using flame atomic absorption.

AA parameters - Perkin-Elmer Model 5000

Lamp wavelength - 313.3 nm
 Lamp current - 25 ma
 Flame N_2O Acetylene - fuel rich
 Burner height - 2 cm below the light beam
 Aspiration rate - the nebulizer system is slightly adjusted for the alcohol to aspirate moderately slow.

The standards are 100, 200, 300, and 500 ug/L mo. An isoamyl alcohol blank is used. The common practice in this lab is to include two or three of each standard, depending on the size of the run, to insure that there is surplus to monitor the calibration of the instrument.

The samples are analyzed using 5-second integration times. After analysis the peak heights are measured and the concentrations are calculated.

NOTE: Atomic Absorption is used to detect the Mo instead of colorimetry. Soil samples after digestion leave a yellow coloration (as yet of unknown origin) which interferes with the amber 460 nm complex band used in the colorimetric method.

ANALYSIS OF FLUORIDE (SOLVENT EXTRACTION)

Reagents:

- 1) 5 mM diphenylsilanediol in xylene
- 2) Aluminum reactant
 - 0.01 M $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$
 - 0.005 M $\text{Ni}(\text{NO}_3)_2$
 - 0.005 M $\text{Sr}(\text{NO}_3)_2$

Extraction of F into the organic phase:

Five mL of sample or standard is pipetted into a 20 mL plastic vial. Generally the range of standards used is from 0 to 3.0 ppm F. The samples and standards are acidified with 0.5 mL concentrated HCl followed by the addition of 5.0 mL diphenylsilanediol (DPSD) solution. The vials are capped tightly and then shaken for 1 hour on a wrist action shaker. The extracts may be stored for at most a week in the refrigerator. The efficiency of the extraction is 90-100%.

Detection of Fluoride

The fluoride is detected via AlF formation in the heated graphite analyzer using a hydrogen continuum lamp at 32 mamp as the light source. The maximum absorbance of the AlF molecule occurs at 227.5 nm. Ten uL of the organic layer is injected into the HGA followed by 10 uL aluminum reactant. The optimum conditions of the HGA are shown below.

Optimum Conditions for HGA

	Drying Stage	Char Stage	Atomize Stage
Temp °C	105	500	2250
Time sec	30	30 ramp	7

Argon flow continuous 25

Ramp Program - Temperature is increased from 105 - 500 °C over the indicated time.

A.A. Conditions

Hydrogen continuum lamp
 Slit 0.2 nm
 Wavelength 227.5 nm
 Scale x 1.0

A.A. Conditions

Hydrogen or Deuterium continuum lamp

Slit: 0.2 nm

Wavelength: 227.5 nm

Scale x 1.0

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