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Assessment and Control of Water Contamination Associated with Shale-Oil Extraction and Processing

October 1, 1979—September 30, 1980

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ASSESSMENT AND CONTROL OF WATER CONTAMINATION ASSOCIATED WITH SHALE OIL EXTRACTION AND PROCESSING

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by

E. J. Peterson, A. V. Henicksman, J. P. Fox,
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ABSTRACT

The Los Alamos National Laboratory's research on assessment and control of water contamination associated with oil shale operations is directed toward the identification of potential water contamination problems and the evaluation of alternative control strategies for controlling contaminants released into the surface and underground water systems from oil-shale-related sources. Laboratory assessment activities have focused on the mineralogy, trace element concentrations in solids, and leaching characteristics of raw and spent shales from field operations and laboratory-generated spent shales. Process parameters in modified *in situ* (MIS) retorting are extreme. Mineralogic characterization of field-generated spent shales indicate that carbonate decomposition and silication reactions occurred in Occidental Oil Shale, Inc., retort 3E at Logan Wash, Colorado. However, evaluation of leachate compositions and comparison with water quality criteria and Multi-Media Environmental Goals/Minimum Acute Toxicity Effluents indicate that several environmentally sensitive trace elements, including potassium, lithium, fluoride, vanadium, lead, boron, molybdenum, nickel, selenium, and arsenic are *not* rendered immobile by *in situ* processing and could be of environmental concern. These conclusions are verified by investigations of laboratory-generated spent shales. This report details the chemical, mineralogic, and solution behavior of major, minor, and trace elements in a variety of shale materials (spent shales from Occidental retort 3E at Logan Wash, raw shale from the Colony mine, and laboratory heat-treated shales generated from Colony mine raw shale). Control technology research activities have focused on the definition of control technology requirements based on assessment activities and the laboratory evaluation of alternative control strategies for mitigation of identified problems. Based on results obtained with Logan Wash materials, it appears that the overall impact of *in situ* processing on groundwater quality (leaching and aquifer bridging) may be less significant than previously believed. Most elements leached from MIS spent shales are already elevated in most groundwaters. Analysis indicates that solubility controls by major cations and anions will aid in mitigating water quality impacts. The exceptions include the trace elements vanadium, lead, and selenium. With respect to *in situ* retort leaching, process control and multistaged counterflow leaching are evaluated as alternative control strategies for mitigation of quality impacts. The results of these analyses are presented in this report.

I. SUMMARY

A. Task Descriptions

The objectives of this program are to elucidate the nature and assess the magnitude of water contamination that might result from surface or *in situ* shale oil extraction. As the major problem areas become defined, technologies for water pollution control will be evaluated experimentally. Two tasks are being implemented to accomplish these goals.

The first activity, assessment, is to develop a data base that can delineate potential environmental problems, and to identify and define control technology requirements by conducting baseline, field, and laboratory studies. This year, the focus was the Occidental Oil Shale, Inc., vertical modified *in situ* (MIS) process. Collection and analysis of baseline groundwater samples from several potential MIS field sites was accomplished. A comprehensive characterization study of three spent shale cores from Occidental retort 3E was completed, and a similar study of a preburn raw shale core was initiated. Major, minor, and trace elements in the core samples were determined by instrumental neutron activation analysis, and the major mineralogy was studied using x-ray diffraction and infrared spectroscopy. Batch leaching studies were conducted on the core material to determine the nature and magnitude of *in situ* leaching of abandoned MIS retorts. To aid in interpreting the field data, laboratory heat-treatment experiments in which Colony Mine raw shale was processed over a range of potentially important retorting conditions were conducted in conjunction with field studies. This year, leaching studies of these laboratory spent shales were completed; trace element and mineralogical analyses are in progress.

The second activity, control technology research, is to determine environmental control requirements and to identify and assess alternate strategies and technologies. This is accomplished by analyzing the data from the assessment studies to identify potential environmental problems; then, knowledge of the chemistry is used to formulate management strategies or engineering procedures to abate or solve the problems. These controls are assessed to evaluate their technical and economic feasibility. If they appear promising, laboratory experiments are designed to evaluate them and to obtain data to refine preliminary calculations. This year, the focus has been on the control of major, minor, and trace elements in leachates from abandoned MIS retorts. Field and laboratory leaching data from the Assessment Task were analyzed to determine potential problems and control requirements. This analysis revealed that less expensive technologies, such as process control and forced leaching (compared with grouting, for example) might be suitable to control *in situ* leaching. Preliminary assessments of these methods were conducted.

B. Conclusions

The principal conclusions from this year's work are summarized here. The data and analyses that support these conclusions are presented in Sec. II.

1. Investigations of Occidental Retort 3E. This year, three cores from retort 3E were characterized and batch leaching studies were conducted on each core segment. Mineralogical and trace element data for preburn raw shale cores are required before a comprehensive interpretation of these data is possible. Following are the major conclusions from this work.

- The mineralogical investigations of retort 3E revealed four groups of minerals: (1) raw shale minerals that survive the retorting process (quartz, albite, orthoclase); (2) decomposition products (periclase, calcite); (3) high-temperature reaction products (augite, akermanite, etc.); and (4) regeneration products (aragonite, gypsum, calcite).
- The mineralogical data indicate five separate zones in retort 3E. Zonation is probably related to retort operating conditions. However, because of the complexity of the solid phase reactions that occur and because preburn data are unavailable, correlation of these zones exactly with retorting conditions was not attempted.
- Based on their chemical behavior throughout both cores, the elements measured in retort 3E leachates can be placed into three groups. The first includes lithium, strontium, lead, barium, calcium, and tungsten. The concentrations of elements in the second group, which includes titanium, fluoride, vanadium, boron, silicon, arsenic, selenium, and iron, are inversely related to those of the first group. The third group includes electrical conductivity, sodium, molybdenum, nickel, aluminum, and potassium.
- Trace elements of potential environmental concern are mobilized from spent shales containing

akermanite-gehlenite solid solution as the major high-temperature silicate phase. Trace elements appear to be less mobile from spent shales containing diopside as the major silicate phase.

- The solubility of alkali and alkaline earth elements was reduced in core sections that contained high-temperature silicate phases. However, many trace elements, including fluoride, vanadium, boron, arsenic, and selenium, show *increased* solubilities from these same sections. This tends to refute claims by other investigators that MIS retorting will immobilize trace elements by incorporating them in the high-temperature mineral phases.
- The leachate concentrations of many trace elements appear to be controlled by the solubility of secondary minerals. Examples include CaF_2, $BaAsO_4$, and $CaMoO_4$. However, some elements, such as vanadium and boron, appear not to be controlled by secondary solubility of mineral phases.
- The most soluble elements in MIS leachates are sodium, potassium, vanadium, and calcium. About 1% to 20% of the available mass of these elements is readily leached. Typically, less than 0.1% of the available mass of all other elements is leached. Boron and molybdenum are probably in the most soluble category, but elemental abundances in the solids are not yet available.
- The sequential leaching studies demonstrated that three successive fresh water changes did not affect the 2-day leachate concentrations of arsenic, barium, calcium, fluoride, lithium, magnesium, nickel, silicon, strontium, or sodium. This suggests that leachates are in quasi-equilibrium with mineral phases and that the available reservoir of material is not exhausted. Concentrations of other elements, such as boron, molybdenum, potassium, and vanadium, decreased with each fresh water change, suggesting that soluble material was being exhausted.
- The extended leaching experiments indicate that equilibrium concentrations of total dissolved solids and most of the elements studied reach equilibrium concentrations relatively rapidly, in less than 2 days. The exceptions are boron, cobalt, and nickel, whose concentrations increase with time, suggesting that significant time periods may be necessary to establish equilibrium.
- Leaching experiments using Tract C-a groundwater indicate that the concentrations of calcium, titanium, iron, lead, cobalt, aluminum, barium, and nickel are significantly lower in groundwater leachates than in distilled water leachates. This is probably due to precipitation reactions with the anions hydroxide, carbonate, or sulfate. The concentrations of boron, molybdenum, vanadium, potassium, and lithium are about equal in distilled water and groundwater leachates, whereas the concentration of sodium is much higher in groundwater leachates.

2. **Investigations of Laboratory-Retorted Spent Shale.** A small quartz reactor was used to study the effect of temperature and gas atmosphere on the leaching characteristics of spent shales. Trace element and mineralogical analyses of the solids are in progress.

- The elements studied can be placed into five groups based on the effect of retort operating conditions on the leachability of resulting spent shales.

  Group I: electrical conductivity, lithium, strontium, iron, lead, and titanium;
  Group II: calcium and tungsten;
  Group III: aluminum, molybdenum, and boron;
  Group IV: sodium, potassium, and nickel;
  Group V: magnesium and vanadium.
- Most trace elements studied are less soluble in raw shale leachates than in spent shale leachates. Retorting the shale at temperatures from 673 to 1273 K in air, N_2, and CO_2 atmospheres increases the solubility of most trace elements. Notable exceptions are aluminum and boron. Retorting decreases their solubility for all conditions studied except in a CO_2 atmosphere at 1073 K.
- The leachate concentrations of most trace elements studied decrease at temperatures in the range of 873 to 1273 K compared with lower temperatures. Notable exceptions are magnesium and vanadium, which increase rapidly with temperature in this range; potassium and nickel, which increase in N_2 atmospheres; and barium and silicon, which increase in CO_2 atmospheres. This further demonstrates that not all trace elements are insoluble in high-temperature spent shale leachates.
- A comparison of leachate concentrations from shales heat-treated at 1273 K with water quality criteria indicates that the concentrations of vanadium, molybdenum, lead, and lithium exceed recommended limits under these conditions.
- These studies suggest that vanadium may be used to estimate the temperature of MIS spent shales of

unknown retorting history (such as retort 3E materials). The concentrations of vanadium in leachates increase approximately linearly from 873 to 1273 K, relatively independent of gas atmosphere. Additional data on the effect of vanadium minor mineralogy and absolute vanadium abundances in spent and raw shales are required to validate this hypothesis.

3. **Control Technology Requirements.** The potential impact of *in situ* leaching on local groundwater quality was estimated by comparing predevelopment and postdevelopment quality in the vicinity of MIS retorts with water quality criteria for domestic supply, agricultural supply, and livestock watering. Postdevelopment groundwater quality was estimated from our distilled water batch leaching studies.

- The quality of native groundwater is generally poor. These waters are unsuitable for agriculture, livestock, or domestic supply because the concentration of one or more trace elements exceeds recommended limits.
- MIS retorting may affect local groundwater by leaching and by intermingling of lower and upper aquifer waters. Analyses indicate that intermingling has negligible impact on groundwater quality. Leaching, however, may increase the concentrations of vanadium, lead, and selenium above criteria limits.
- The overall impact of MIS leaching on groundwater quality may be less significant than previously believed. Most elements of concern are already elevated above criteria limits in native groundwaters. Secondary solubility may actually improve groundwater quality by providing anions such as sulfate or carbonate, which precipitate toxic metals. The only elements that may be significantly elevated in groundwater are vanadium, selenium, and lead. Thus, the major impact of *in situ* leaching may be to increase the existing hazard of using these waters.
- Low-cost control technologies may be suitable for controlling MIS leaching since intermingling of upper and lower aquifer waters is not an important source of degradation.

4. **Process Control.** Field and laboratory leaching data were analyzed to determine whether process control could minimize the concentrations of trace elements in MIS leachates.

- Process control may not be feasible for control of MIS-produced leachates because of the effects of minor mineralogy on spent shale leachability and the difficulty of achieving uniform operating conditions in field retorts. Also, conditions that minimize the concentrations of some toxic elements simultaneously maximize the concentrations of other equally toxic elements. In particular, vanadium and lead, which are of great potential environmental concern, are inversely related in leachates. However, more research is required to establish relationships among retorting conditions, mineralogy, and leaching behavior and to decide whether process control is an effective environmental control.

5. **Multistaged Leaching.** Preliminary studies were conducted to assess the feasibility of using multistaged forced leaching to control the concentrations of trace elements in MIS leachates.

- Analysis of multistaged leaching indicates that it is more economic and consumes less water than multiple pore-volume leaches in a single-staged system. However, secondary solubility may limit the ability of this approach to reduce trace element concentrations to low enough levels.

II. TECHNICAL ACTIVITIES

Experiments are under way to assess and characterize field and laboratory samples of raw and spent shales and their leachates and to identify and define control strategies to mitigate any identified environmental problems. During 1980, we characterized several cores of spent shale from Occidental retort 3E at Logan Wash, Colorado. The resulting data were analyzed and interpreted to identify retort operating conditions responsible for spent shale mineralogy. These samples were leached with distilled water in static tests, and the leachates were analyzed for selected cations and anions. Leachate composition was related to the mineralogy and chemical composition of the spent shales. To aid in interpreting the field data, raw shale was heated in a small-scale laboratory reactor under controlled conditions and leached using procedures similar to those used for field samples. The knowledge gained from the characterization and interpretation of the spent shale mineralogy and leaching behavior was used to assess process control and multistaged leaching.

For clarity, the technical activities are classified as assessment of potential problem areas or research of alternative control strategies. Division of these main areas into experimental activities is discussed in this section.

A. Assessment

1. Task Description. The assessments are performed to develop a data base that can identify and assess control technology requirements. This is being accomplished by conducting baseline studies, field process studies, and laboratory studies.

Baseline studies require the acquisition of raw shale materials (preferably core material from the vicinity of development sites or run of mine shale for surface retorting) and surface and groundwater samples from the area to be experimentally or commercially developed. The water samples are analyzed to confirm the water quality before shale oil extraction operations begin. Studies of the raw shale involve physical characterization of the material as a function of source or depth and leaching of the raw shale to establish the magnitude of trace element release from these materials. The baseline data are essential to the ultimate definition of the physical (for example, surface area effects, permeability, and mineral environment effects) and chemical (for example, oxidation-reduction, decomposition, and mineral reactions) processes that enhance elemental mobilities from retorted shales. Standard static shaker leaching experiments are used because initial interest is focused on the identification and relative magnitude of elemental releases for mechanistic rather than kinetic studies. Materials deemed representative on the basis of elemental release (if possible) are singled out for further study by optical microscopy, scanning electron microscopy, and electron microprobe analysis. In addition, bulk mineralogical and elemental data are gathered so that vertical variability of spent shales can be related to the parent material.

The field process investigations involve the study and analysis of spent shale, postabandonment surface and groundwaters, and process waters from experimental or developmental oil shale operations. Data from these studies help to evaluate postretorting changes, and with this information, environmental concerns related to oil shale operations can be defined. Emphasis is placed on the trace element analysis and physical characterization of spent shales, along with the nature and magnitude of soluble constituents in the spent shale. These studies provide information necessary to define the physical and chemical processes responsible for enhancement or attenuation of trace elements and retort operating conditions responsible for observed trends. Element analyses of solid materials and leachates indicate the extent of availability of trace elements, are invaluable to mechanistic studies (either experimental or modeling), and provide a basis for current and future kinetic studies.

Nonuniform conditions (sampling problems, inadequate preretorting data, and extensive inhomogeneities in field materials) during experimental retorting have made field data difficult to interpret. Thus, controlled laboratory studies conducted to develop an analytical basis for interpretation of field data will also help to develop a general understanding of mineralogical changes that occur during retorting and the relationship of these changes to the leaching process. The effects of such variables as temperature, time at temperature, and reaction atmosphere on the chemical decomposition and mineral reactions are studied. These experiments, coupled with laboratory leaching experiments of the resulting spent materials, are used to understand and correlate reaction variables of potential importance in oil shale surface and underground processing, mineralogy, and trace element mobility. These studies address not only the concern of increased salinity from mobilization of major cations, but also the increase in availability of toxic trace elements to the biosphere.

This year, the focus was on the MIS process being developed by Occidental. In this process, large chambers of rubbled shale are processed underground, leaving behind the spent shale. The deposits suitable for this type of processing are located in wet areas of the Piceance Creek Basin. Groundwaters may invade these chambers on abandonment of operations, and soluble materials leached from the shale may be transported in local groundwater aquifers and eventually discharged in local wells and streams.

A number of management and engineering strategies have been proposed to mitigate this problem.[1] However, there is not enough information to properly assess the magnitude, and hence required degree of control, of the potential leaching problem. Thus, characterization studies are being made to place the *in situ* leaching problem in perspective by working with samples from field retorts and from laboratory reactors run under carefully controlled conditions. Batch leaching tests on well-characterized spent shale cores from the Occidental Logan Wash site have been conducted to identify constituents of potential environmental concern. The suite of elements present in the leachates and their concentrations have been related to the basic mineralogy and elemental composition of the original spent shales to identify mechanisms for observed trends.

Because of the difficulty of interpreting field data, laboratory experiments have been conducted in which samples of raw shale from the Colony Mine were retorted under a range of conditions chosen according to our analysis of the field data. The resulting samples were characterized and leached. The data were analyzed and related to data obtained from the field studies. In this manner, a coherent framework for interpreting the field samples was developed. The resulting information was used to assess control strategies required for an *in situ* industry. (These strategies are discussed later in this report.)

2. Investigations of Occidental Retort 3E. This year, the mineralogy, elemental concentrations, and leaching characteristics of spent shales from Occidental retort 3E were studied. The results of these studies are summarized here in four sections: (1) process description, (2) spent shale characterization, (3) leaching studies, and (4) environmental implications. Experimental procedures are presented either in the appendixes or in last year's annual report.[2]

This is the first reported comprehensive study of *in situ* generated materials. Although some unique aspects of retort 3E operations were not representative of a commercial operation, the study of *in situ* generated materials has provided insights into the chemical, mineralogical, and solution reactions that occur during and after underground retorting. Characterization of the solid materials has verified that *in situ* processing occurs in a thermodynamic and kinetic regime not previously encountered in surface retorting. Carbonate decomposition and silication reactions that form high-temperature products, such as akermanite-gehlenite and diopside-augite solid solutions, have been identified by x-ray diffraction. Observations from characterization of solids were substantiated by analysis of the leachates. Although the chemistry of the *in situ* materials is similar to that of surface-retorted materials, compositions and concentrations are different. Major and trace elements needing further investigation are potassium, lithium, fluoride, vanadium, boron, molybdenum, nickel, and arsenic. Several trace elements, including fluoride, vanadium, boron, and arsenic, show increased mobilities from spent shales containing akermanite-gehlenite solid solutions as the major mineral phase. The chemical, mineralogical, and solution behaviors of major, minor, and trace elements in these materials are discussed.

a. Process Description. Occidental has been experimenting with a MIS technique at Logan Wash, Colorado since 1972. The method involves mining to remove 20-25% of the rock from a chamber (or room), explosive fracturing of the rock to uniformly redistribute the void created by mining, and igniting the organic-bearing rock to pyrolyze and then distill the organic material from the solid. A heavy oil-type liquid condenses at the bottom of the retort and is pumped to the surface. Heat for the retorting process is provided by combustion of the residual organic carbon left on the rock after the major organic material has distilled away. Six retorts have been fired by Occidental at Logan Wash and two more are in final stages of preparation.

One of these small experimental retorts, retort 3E, is the subject of this investigation. This retort, the third tested by Occidental, was designed to evaluate blasting to a horizontal free face rather than to a center rise, as was done in previous retorts. The location of retort 3E and local stratigraphy are shown in Fig. 1, and pertinent retort characteristics and operating conditions are summarized in Table I. The combustion front terminated after about 44% of the bed was retorted.

Cores R3E1, R3E2, and R3E3 from this retort were studied, as shown in Fig. 1. Previously completed studies[3] of materials from initial core R3E1 provided

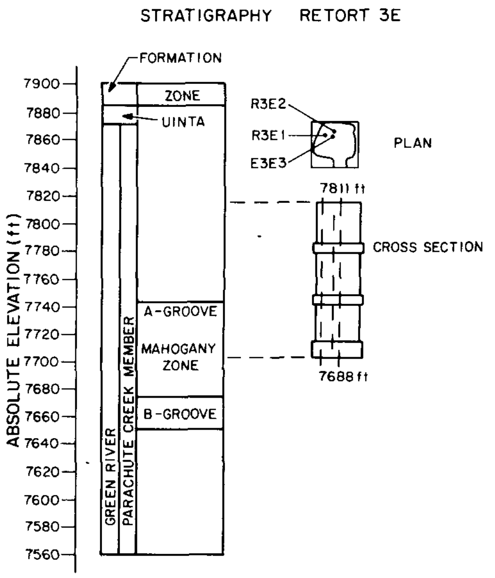


Fig. 1. Location and stratigraphy in vicinity of retort 3E.

TABLE I. Characteristics and Operating Conditions of Retort 3E.

Retort dimensions	32 by 32 by 113 ft
Void volume	?
Fischer assay of raw shale	19.1 gpt
Input gas	70% air + 30% recycle gas
Water injection	43 416 gal. were intermittently injected between May 21 and July 18, 1975
Average offgas composition	H_2, 1.8%; N_2, 71.7%; O_2, 14.1%; Ar, 1.1%; CO, 1.5%; CH_4, 0.3%; CO_2, 9.4%
Postretorting treatment	On shutdown, recycle gas with composition of 17.7% H_2, 29.3% N_2, 4.2% CO, 20.0% CH_4 and 24.8% CO_2 was cycled through the retort for 2 weeks
Operating period	February 10—July 18, 1975

Source: Summarized from Ref. 3.

useful data but revealed that core drill lubrication methods used to retrieve these samples led to uncertainties. These doubts prompted retrieval of two more cores, R3E2 and R3E3, supervised by personnel from Battelle Pacific Northwest Laboratory. Information on core recovery is presented in Appendix A.

At this point, some important differences between retort 3E and a potential commercial MIS operation are noted. These differences are primarily related to retort size and geometry; void fraction, permeability, and rubble size; input gas; and postretorting treatments.

Retort 3E was a small experimental retort measuring 32 ft square by 113 ft high. Occidental projects that its commercial-sized retorts will measure 155 by 390 ft in cross section and 310 ft high. This size difference should not have a significant effect on postretorting mineralogy and leaching behavior, but retort bed characteristics such as shale particle size and void volume distribution will affect spent shale and leaching characteristics. High yields in MIS retorts require uniform void volume and particle size distribution. These variables are determined by the rubbling procedure, which is the single most significant technical constraint to the development of the MIS process.

Rubbling procedures used to date have caused channeling of the reaction zone and concomitant poor oil recovery. The rubbling procedure Occidental used for retort 3E was one step in a long series of experiments to improve rubbling. The three cores studied here reveal significant inhomogeneities, suggesting channeling in retort 3E. If the MIS process becomes commercial, a satisfactory rubbling procedure that produces uniform void volumes and particle size distributions will have to be developed. Thus, in a commercial process, we anticipate more uniform bed conditions and so more homogeneous spent shale characteristics and leaching behavior than are observed here.

The input gases used in retort 3E were 70% air and 30% recycle gas. Subsequent work by Occidental indicates that because retorting is more efficient in an air/steam atmosphere, recycle gas will probably not be used. Therefore, regeneration products formed by the reaction of CO_2 and other gaseous species in the input gas with spent shale, perhaps moistened after processing, may not occur in spent shales from commercial processes.

Finally, postretorting treatments in a commercial operation will probably differ from those used here. In retort 3E, offgas was cycled through the retort for 2 weeks after retorting. The high concentrations of CO_2, SO_2, and other species in the offgas probably caused precipitation of such mineral phases as aragonite, calcite, and gypsum. We do not know what postretorting treatments will be used in commercial operations, but they may include a water quench to cool the spent shale. In that case, the mineral assemblages could differ in quantity from those found here.

These differences do not invalidate or detract from the present study. Because of the inhomogeneities in retort 3E, retorting conditions spanned a wide range of variables that adequately encompass those anticipated for commercial operation. Also, the fundamental approach used in this study has helped us to understand the chemical reactions that occur during retorting. The resulting model of retort chemistry can be satisfactorily extrapolated to other cases.

b. Spent Shale Characterization. The mineral phases and elemental composition of the spent shale samples from the three Occidental cores were determined, and the resulting data were analyzed to develop an understanding of the solid-phase chemistry that occurs during MIS retorting and to relate the observed trends to retort operating conditions. The solid-phase reaction chemistry that possibly occurs during MIS retorting is discussed as a basis for evaluating and understanding the experimental data.

- *Solid-Phase Reaction Chemistry in MIS Retorts.* Various authors have reported investigations of mineral species in raw oil shale.[4-7] The mineral composition varies stratigraphically, but carbonates and silicates predominate in most zones. Carbonate minerals found in raw shale include dolomite/ankerite, calcite, and, in the depositional center of the basin, lesser amounts of nahcolite and dawsonite. Silicate minerals found in raw shale include the α-quartz, albite and orthoclase, as well as illite, other clay minerals, and analcime. In addition, small amounts of pyrite are widespread throughout the Green River formation. The compositions of these minerals are summarized in Table II.

These raw shale mineral phases undergo a variety of decomposition and solid-phase reactions during retorting, depending on the original raw shale composition, maximum retorting temperature, time at maximum temperature, heating rate, gas atmosphere, postburn conditions, etc. The extent of carbonate decomposition and silicate formation, as well as the disappearance of α-quartz, albite, and potassium feldspars, indicate the extremes of temperature and retorting atmosphere experienced by the spent shales. This work indicates that the predominant high-temperature silicate products in field samples are akermanite-gehlenite and diopside-augite solid solutions. Other product silicate minerals identified include kalsilite, monticellite, and the magnesium olivine, forsterite.

TABLE II. Compositions of Mineral Species in Raw Oil Shale and Their Decomposition, High-Temperature, and Regeneration Products

Thermally Unstable Raw Shale Minerals	
Analcime	$NaAlSi_2O_6 \cdot xH_2O$
Dolomite/Ankerite	$(Mg,Fe)Ca(CO_3)_2$
Calcite	$CaCO_3$
Illite	Clay mineral—$KAl_2(Si_3Al)O_{10}(OH)_2$
Pyrite	FeS_2
Biotite	$K(Mg,Fe)_3(Si_3Al)O_{10}(OH)_2$
Thermally Stable Raw Shale Phases	
Quartz	SiO_2
Albite (Na feldspar)	$NaAlSi_3O_8$
Orthoclase (K-feldspar)	$KAlSi_3O_8$
Decomposition Products	
Periclase	MgO
Calcite	$CaCO_3$
Dehydrated Analcime/Wairakite	$CaAl_2(SiO_3) \cdot H_2O$
High-Temperature Products	
Augite	$(Ca,Mg,Fe,Ti,Al)_2(Si,Al)_2O_6$
Akermanite-Gehlenite	$Ca_2Mg(Si_2O_7)$—$Ca_2Al(AlSiO_7)$
Kalsilite	$K(AlSiO_4)$
Monticellite	$CaMg(SiO_4)$
Forsterite	$Mg_2(SiO_4)$
Regeneration Products	
Aragonite	$CaCO_3$
Calcite	$CaCO_3$
Gypsum	$CaSO_4 \cdot 2H_2O$

Some of the mineralogical reactions that possibly occur during oil shale retorting are summarized in Table III; the principal mineral phases that arise from these reactions are classified in Table II. Mineralogical changes that occur during oil shale retorting are dominated by silicate and carbonate reactions and depend on the gas environment.[8,9] At less than ~770 K, the minor saline sodium carbonate minerals dawsonite, nahcolite, shortite, and trona decompose to yield sodium carbonates, CO_2, and water. At slightly higher temperatures, the major carbonate minerals calcite and dolomite begin to decompose significantly. Dolomite decomposition proceeds at 925-1025 K with evolution of CO_2 and formation of periclase and calcite. The periclase persists at the lower temperatures but disappears at the higher temperature because of silicate formation. The calcite formed is chemically indistinguishable from the original calcite.[8] Calcite decomposes with evolution of CO_2 above 1075 K. Steam greatly enhances the decomposition of dolomite and calcite and promotes silicate formation, whereas CO_2 inhibits calcite decomposition and depresses silicate formation relative to N_2.[8] At greater than 1075 K, calcite may also react with quartz to form calcium silicates, or perhaps with feldspars to form calcium aluminum silicates. This competing reaction does not occur until a temperature is reached at which k_{eq} for the reaction is greater than the partial pressure of CO_2; then it proceeds very rapidly.[8]

At ~1075 K, silicate minerals, such as analcime and various clays, decompose, forming titanium, aluminum, and iron oxides. These oxides also may react with each other to form nonreactive silicates of the augite or akermanite-gehlenite series.

Postburn mineralogical reactions are dominated by aqueous and gas-phase precipitation reactions. Abandoned retorts may require water or gas cooling to promote structural stability. Retort 3E was cooled by recycle gas with high CO_2 concentration. Water was also injected into this retort five times during retorting to dilute the inlet air with steam.[3] Commercial retorts may be cooled by a water quench, which may cause chemical reactions between the mineral phases in the hot spent shale and the coolant. Aragonite, which was identified in cores from retort 3E is the preferred crystalline form of calcium carbonate precipitating from warm solutions. This type of reaction may occur during water injection in the gas-recycle mode. Some calcite may also have precipitated after cooling because of high alkalinity of groundwaters seeping into the retort. Gypsum also may be formed during postburn treatment or during recycle retorting. Sulfur dioxide in the offgas is known to react with CaO in the spent shales to form gypsum.[10]

TABLE III. Proposed Reactions That Occur During MIS Retorting

Carbonate Decompositions	Dolomite	$Ca(Mg_x, Fe_{1-x})(CO_3)_2 \rightarrow xMgO + (1-x)FeO + CaCO_3 + CO_2$
	Calcite	$CaCO_3 \rightleftarrows CaO + CO_2$
	Dawsonite	$2NaAl(OH)CO_3 \rightarrow NaCO_3 + Al_2O_3 + H_2O + CO_2$
	Nahcolite	$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
Silicate Decompositions	Analcime	$NaAlSi_2O_6 \cdot 2H_2O \rightarrow NaAlSiO_4 + SiO_2 + 2H_2O$
	Albite	$NaAlSi_3O_8 \rightarrow NaAlSiO_4 + 2SiO_2$
	Illite	$KAl_2(Si_3Al)O_{10}(OH)_2 \rightarrow KAlSiO_4 + Al_2O_3 + 2SiO_2 + H_2O$
	Orthoclase	$KAlSi_3O_8 \rightarrow KAlSiO_4 + 2SiO_2$
Sulfide Decomposition	Pyrite	$2FeS_2 + 11/2O_2 \rightarrow Fe_2O_3 + 4SO_2$
High-Temperature Silication Reactions	Akermanite	$CaCO_3 + MgO \cdot CaCO_3 + 2SiO_2 \rightarrow Ca_2MgSi_2O_7 + 2CO_2$
	Gehlenite	$2CaCO_3 + Al_2O_3 + SiO_2 \rightarrow Ca_2Al(AlSiO_7) + 2CO_2$
	Diopside	$MgO \cdot CaCO_3 + 2SiO_2 \rightarrow CaMgSi_2O_6 + CO_2$ $Ca_2MgSiO_7 + CO_2 \rightleftarrows CaMgSi_2O_6 + CaCO_3$
	Augite	$2(CaO, MgO, FeO, TiO_2, 1/2Al_2O_3) + 2(SiO_2, 1/2Al_2O_3) \rightarrow (Ca,Mg,Fe,Ti,Al)_2(Si,Al)_2O_6$
	Forsterite	$2CaMg(CO_3)_2 + SiO_2 \rightarrow Mg_2SiO_4 + 2CaCO_3 + 2CO_2$
	Monticellite	$CaMgSi_2O_6 + Mg_2SiO_4 + 2CaCO_3 \rightarrow 3CaMgSiO_4 + 2CO_2$
Regeneration Reactions	Calcite	$CaO + CO_2(g) \rightleftarrows CaCO_3$ $Ca(OH)_2 + CO_3^{2-}(aq) \xrightarrow{25^\circ C} CaCO_3 + 2OH^-$
	Aragonite	$Ca(OH)_2 + CO_3^{2-}(aq) \xrightarrow{100^\circ C} CaCO_3 + 2OH^-$
	Gypsum	$CaO + SO_2 + 1/2O_2 + 2H_2O(g) \rightleftarrows CaSO_4 \cdot 2H_2O$

These considerations show that the disappearance of raw shale minerals and the formation of a new suite of minerals in the processed shale can be accomplished through a variety of reaction pathways determined by process variables such as maximum temperature, time at maximum temperature, heating rate, and atmosphere.

These mineral reactions are accompanied by chemical reactions of the minor and trace elements. Both the mineral and chemical reactions that occur during retorting affect the mobility of the major, minor, and trace elements from the shale when contacted with water. The mobility of elements can be affected by several factors, including decomposition or reaction of the original mineral hosts, the ability of newly formed spent shale minerals to accommodate major, minor, and trace elements in their crystalline structures, and the oxidizing or reducing nature of the atmosphere. These factors, as well as solution chemical considerations, must be considered in investigations of leachate compositions generated from *in situ* spent shales. Thus, mineralogy of *in situ* generated spent shales is important in process assessment and in evaluation of the environmental acceptability of groundwater leachability of spent shales.

- *Spent Shale Mineralogy.* The mineralogy of the spent shale samples from cores E1, E2, and E3 was determined by infrared analysis (carbonate minerals) and x-ray diffraction.[11] (Our analytical methods are discussed in Ref. 2.) Analysis of the data indicates that five major zones occur in retort 3E, delineated as Zones 1 through 5 from the top to the bottom of the retort. These zones, their stratigraphic positions, characteristic mineral phases, and probable retorting conditions are summarized in Table IV.

Zone 1, sampled in R3E1 and R3E3, consists of almost no carbonate minerals, very little quartz, and a great many high-temperature silicate products (akermanite-gehlenite, diopside, monticellite, and kalsilite). These observations suggest that ignition of the retort was accomplished here. Zone 2, extending through 15 ft, is characterized by similar amounts of calcite and aragonite, moderate amounts of quartz, and very few high-temperature silicate products. The mineral composition indicates that calcite has probably survived the

TABLE IV. Zonation in Occidental Retort 3E

Zone	Absolute Elevation (ft)	Retorting Conditions	Characteristic Mineral Phases
1	7823-7803	Retort ignition. High-temperature zone, probably 1400-1600 K.	Almost no carbonates, very little quartz, large quantity of high-temperature silicate products.
2	7813-7798	Relatively complete pyrolysis; temperatures probably from 800-1000 K for short heating periods. Affected by postburn operations.	Moderate amounts of calcite, aragonite, and quartz, very few high-temperature silicates.
3	7798-7768	Reaction front terminated at bottom of zone. Probably experienced higher temperatures than zone 2; affected by postburn operations.	Some calcite and aragonite, almost no quartz, and large amounts of high-temperature silicate products, predominantly akermanite-gehlenite solid solution, with lesser amounts of diopside.
4	7768-7733	Probable temperatures similar to zone 3. Core log description in Appendix C indicates zone experienced combustion. No evidence of postburn operations effects.	Few carbonates, very little quartz, large amounts of high-temperature silicate products, predominantly diopside, with lesser amounts of akermanite-gehlenite. Forsterite detected in core E3.
5	7733-7693	Bottom plug of retort; low temperatures, probably less than 1025 K. The reaction zone did not reach this area, and combustion occurred only locally.	Large amounts of carbonates, quartz, and feldspars, few high-temperature silicate products.

retorting process, whereas aragonite is a regeneration product due to postburn operation. The appearance of quartz and the lack of high-temperature silicates suggests that these sections have undergone low to intermediate temperatures (800-1000 K) for short heating durations.

The next two zones are the most difficult to interpret, but these regions differ markedly. Zone 3 has some calcite and aragonite, almost no quartz, and a great many high-temperature silicate products. The high-temperature silicates are predominantly akermanite-gehlenite solid solution and lesser amounts of diopside. Zone 4 consists of few carbonates, very little quartz (but more than in zone 3), and a great many high-temperature silicate products. The product phases in this region are predominantly diopside with lesser amounts of akermanite-gehlenite. It is also significant that forsterite was detected in this zone in core E2. The implications of these observations are not certain because of the lack of baseline information about the raw material in this zone. The most probable reasons for the indicated mineralogical changes from zone 3 to zone 4 are higher temperatures and/or different heating rates for one section, or a change in the bulk composition of the raw shale, which would alter the mineralogic reactivity patterns. It is not known what combination of retorting conditions will favor particular high-temperature silicate products, although a recent investigation suggests tradeoffs between maximum temperature and the time at temperature.[12] However, these two zones experienced the most extreme process conditions.

Zone 5, the "bottom plug" of the retort, is characterized by large amounts of carbonate minerals (which apparently were unaffected by postburn operations), large quantities of quartz and feldspars, and few high-temperature silicate phases. These core segments experienced only moderate temperatures, and the small quantities of product silicates may be friable materials that previously existed in zones 3 and 4.

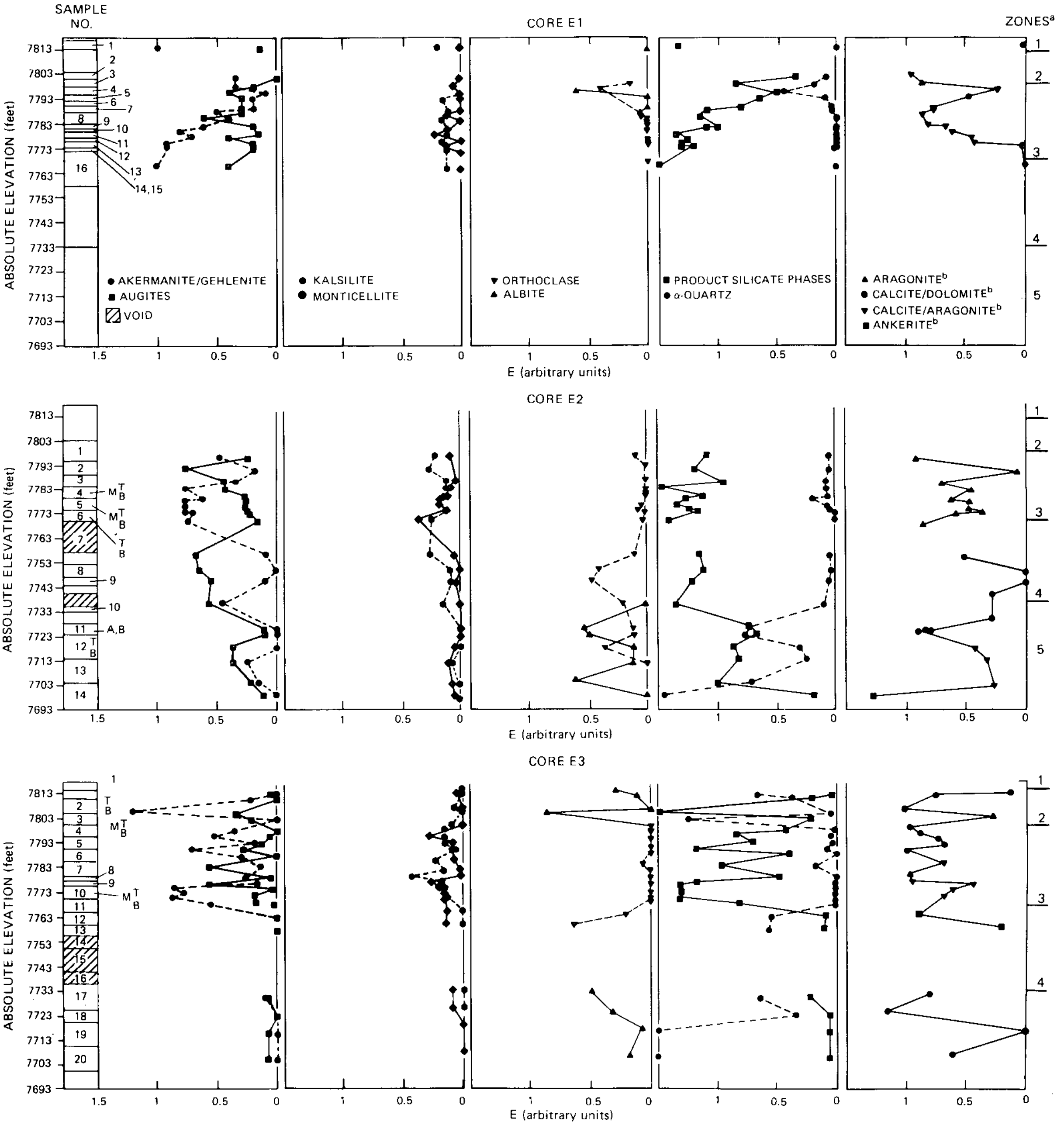
The detailed mineralogical data on which Table IV is based are presented in Fig. 2 and Table V. The relative quantity of each mineral phase was derived from the peak height of the most intense characteristic reflection (or reflections) for each mineral species. Since our samples were not calibrated against internal reference materials, peak heights are not related to concentrations, however, changes in peak height as a function of core depth are a rough quantitative estimate of the relative amount of each mineral from section to section. This type of comparison is valuable in identifying trends, but comparisons between mineral phases do not indicate relative quantities of each present.

Relative amounts of mineral phases shown in Table V and Fig. 2 should be evaluated cognizant of such variables as raw shale composition and retorting conditions. These variables are not well characterized for retort 3E but the quantity and identity of carbonate minerals shown in Table V and Fig. 2 suggest several observations about these cores and more generally about retort 3E. The carbonate minerals in the various core sections can be present as survivors of decomposition reactions yielding CO_2 (dependent upon temperature and pressure) or as regeneration products caused by postburn chemical reactions in the retort. Because retort 3E was run with recycle product gases that continued after shutdown, CO_2 exposure is certain. Also, because water was injected, the possibility of solution reactions exists.

The aragonite form of $CaCO_3$ in zones 2 and 3 indicates that most, if not all, of the carbonate minerals in these regions are regeneration products formed as a result of postburn conditions. Either recarbonation of CaO with warm water or the carbonation of $CaSO_4$ (gypsum identified by x-ray diffraction) are possible synthetic pathways to this mineral species. The calcite in zones 4 and 5 probably survived retorting because lower temperatures occurred here. The absence of aragonite in this region suggests that the postburn treatment responsible for aragonite formation in zones 2 and 3 did not occur. This is consistent with Occidental's statement that water injection only affected the top half of the retort. (Water was injected to form steam during retorting. Most of it was absorbed by the hot spent shale behind the reaction front that was extinguished at the midpoint of the retort.)

The quantity and identity of silicate phases also suggest several observations about these cores and retort 3E. Silicates can be present as survivors of decomposition reactions such as those for analcime and clay shown in Table III, or they can be formed by solid-phase chemical reactions between silica, aluminum, magnesium, calcium, titanium, and other oxides. The relative quantities of the various silicates depend on the original raw shale mineralogy and retort operating conditions.

Relationships between mineral phases, as indicated in Fig. 2, can be analyzed to indicate probable retorting conditions. The relationship between product silicate phases and quartz in Fig. 2 indicates an inverse relationship: silicate products increase as silica decreases.



[a]Note: See Table IV for delineation of zones.

[b]Determined by infrared analysis.

Fig. 2. Variation of mineral products as a function of depth in the retort.

TABLE V. Mineral Compositions of Retort 3E Core Samples

Core R3E1[a]

Sample Number	Absolute Elevation	Calcite	Dolomite	Quartz	$NaAlSi_3O_8$	$KAlSi_3O_8$	Akermanite	Diopside	Aragonite	Kalsilite	Monticellite	Depth (ft)
1	7807						10	1.5		2		443
2	7796	9		2			3.5		2			455
3	7792	2		4	0.5	1.5	3.5	2	4	0.5	0.5	458
4	7789	4		9	6	4	1	4	1			461
5	7786	8		2			2	3	0.5	1.5		464
6	7782	9		1		1	2	3		1		468
7	7781	6		1	0.5	0.5	5	3		1	1	469
8	7778	6					4	6		1.5		472
9	7774	5					6	2	0.5	1	1	476
10	7773	5					6	2	1	1	1	476
11	7771	4					8	1.5	1	2	2	478
12	7770	2					7	4		1.5		481
13	7767	1					9	2		1	1	483
14	7767						9	2		1	1	484
15	7766						9	2		1		484
16	7758						10	4		1		493

Core R3E2[b]

Sample Number	Absolute Elevation	Calcite	Dolomite -Ankerite[c]	Aragonite	α-Quartz	Akermanite -Gehlenite[c]	Diopside -Augite[d]	Orthoclase	Albite	Monticellite	Kalsilite	Others
1	7788	T	0	M-S	VW	M-S	M	VW	0	W-M	M	Gypsum(T)
2	7783	0	0	VW	VW	W-M	S	0	0	0	M	Zircon(W),Gypsum(W)
3	7778	W	0	W	VW	M	M-S	0	0	T	W-M	Gypsum(T)
4T	7773	W	0	W	VW	S	M-S	0	0	W-M	W-M	
4B		W	0	W	VW	M-S	M	0	0	W-M	W-M	Gypsum(T)
5T	7768	T	0	W	W-M	S	M	0	0	W-M	W-M	
5M		W	0	W	VW	S	M	T	0	W-M	W-M	
5B		W	0	W	T	S	M	T	0	W-M	M	
6T	7764	W-M	0	M	0	M-S	M	T	0	W-M	M	
6B		M	0	W	0	M-S	M	T	0	M-S	M	
7	7753	M	0	T	T	W	S	W	0	VW	M	Forsterite(T)
8	7743	0	0	0	T	0	S	S	0	0	W	Forsterite(T)
9	7738	0	0	0	T	VW	S	S	0	VW	W	Forsterite(T)
10	7728	W-M	0	T	W	M	S	W-M	0	0	W-M	Forsterite(VW)
11	7718	M-S	M-S	0	M-S	0	W	W	M-S	0	0	Biotite(T),Wairakite(W)
11A		M-S	M-S	0	S	0	W	W	M-S	0	0	Wairakite(W-M)
12	7711	W-M	0	W	M	0	M-S	M-S	W	T	0	Wairakite(T)
13T	7701	M	0	W	W-M	M	M-S	0	W	W	VW	
13B		M	0	W-M	M-S	W	M	0	M-S	W	0	Biotite(M),Wairakite(W)
14	7691	M-S	S	0	S	0	T	VW	0	T	0	Wairakite(W)

Core R3E3[b]

Sample Number	Absolute Elevation	Calcite	Dolomite -Ankerite[c]	Aragonite	α-Quartz	Akermanite -Gehlenite[d]	Diopside -Augite	Orthoclase	Albite	Monticellite	Kalsilite	Wairakite	Others
1	7807	W	0	0	S	0	W	0	M-S	0	0	M	Illite(T), Montmorillonite(S)
2T	7802	S	T	T	M	W-M	0	0	W	T	0	W	Unidentified(W)
2B		W	0	T	T	S	M-S	0	0	0	T	0	Lucite(W-M)
3	7797	W	0	W	S	0	M	0	S	0	0	0	
4	7792	M-S	0	M	T	M	0	0	0	0	W	0	Gypsum(T)
5T	7787	M-S	0	0	W	M-S	W	0	0	W-M	W-M	0	
5M		M-S	0	0	T	M-S	W-M	0	0	M	W-M	0	
5B		M	0	W-M	W	M-S	M-S	0	0	W	W-M	T	
6	7782	S	0	T	0	M	0	0	0	W	W	0	Hydrobiotite(W) Vaterite(W) Apatite(W-M)
7	7777	T	0	M-S	M	W-M	S	W	0	W	M	0	Gypsum(T)
8	7773	M	0	S	0	M	W	0	0	T	W-M	0	
9	7770	S	0	W-M	0	W-M	S	0	0	T	M-S	0	
10T	7767	W-M	0	T	0	S	W	0	0	M	W-M	0	
10M		M	0	M	0	S	M	0	0	W-M	M	0	
10B		M	0	W-M	0	S	M	0	0	W-M	W-M	T	Unidentified(W)
11	7762	M-S	0	M-S	0	M-S	T	0	0	W-M	W	0	Gypsum(W)
12	7757	M	0	0	M-S	0	0	M	0	W-M	0	0	Periclase(W-M) Illite(T)
13	7752	W-M	0	0	M-S	0	0	S	0	W-M	0	0	Illite(W) Periclase(W) Gypsum(T)
17	7724	M	M	0	M-S	W	W	0	M-S	W	0	W-M	Illite(W) Periclase(T)
18	7716	S	T	0	M	0	0	0	M	W	0	W	Illite(T) Periclase(W)
19	7709	0	0	0	S	0	T	0	T	0	0	S	
20	7699	M	M-S	0	S	0	T	0	W	0	0	S	Gypsum(T)

[a] Numerical values indicate peak heights of major reflections of mineral species as determined by Occidental Research Corporation.[10]

[b] Legend (relative phase content): S = major, M = moderate, W = minor, VW = very minor, T = trace, 0 = none detected.

[c] Orthorhombic phase with parameters and relative peak intensities between dolomite and ankerite. Sample 14 was pure ankerite.

[d] Tetragonal phase with parameters and relative peak intensities intermediate between akermanite and gehlenite.

[e] Monoclinic phase with slightly varying parameters and peak intensities between diopside and augite.

Also, akermanite (mellilite solid solution) and diopside (augite solid solution) are inversely related in the three cores. Monticellite is correlated with kalsilite and akermanite. Table V indicates that orthoclase and albite, members of the original suite of raw shale minerals, also occur in these cores.

An examination of the minor minerals listed in the last column of Table V indicates that hydrated $CaSO_4$ is present in some samples in the upper half of the retort, which is consistent with water injections being absorbed in the upper regions of the room. The presence of the hydrated minerals, biotite and analcime/wairakite, and the clay minerals in zones 4 and 5 indicate that very little heating occurred in the lower half of the retort, consistent with the major mineralogy discussed above.

• *Spent Shale Trace Element Composition.* The elemental composition of spent shale samples from cores E2 and E3 was determined by instrumental neutron activation analysis (INAA) using methods described in Ref. 2. The concentration ranges for these elements are typical of shale materials from the region as reported by other investigators.[7,13] The resulting data, summarized in Tables VI and VII, are shown in Fig. 3 for those elements subsequently studied in the leaching investigations.

Many of the elements listed in Tables VI and VII are not of environmental concern and are not included in our leaching studies. This occurs because different analytical techniques, which determine different suites of elements, were used for the solids and liquids. Only those elements subsequently investigated in our leaching studies are discussed here. The others reported in Tables VI and VII are for information only.

The elements listed in Tables VI and VII that were subsequently studied in leaching work and that were detected by INAA are aluminum, arsenic, barium, calcium, cobalt, iron, magnesium, manganese, potassium, strontium, sodium, titanium, vanadium, and zinc. Examination of the vertical variation of these elements in both cores (Fig. 3) reveals that these elements can be placed into at least three groups based on their chemical behavior/associations. The first group includes the conventional carbonate-associated elements calcium, magnesium, strontium, barium, and manganese. The vertical variations of these elements through both cores are directly related to each other. The second group includes the major elements sodium, aluminum, and potassium. Their variations are similar in both cores and are inversely related to the carbonate group of elements. The third group includes only iron and titanium. The remaining elements, cobalt and zinc, do not fit into these groups.

Some of these associations in the Logan Wash spent shale cores had been noted by Fox[13] and Giauque et al.[7] in raw shales. Similar variations in nonvolatile elements in raw and spent shales are expected because retorting does not change the relative elemental concentrations; it only alters mineral associations of each element. Fox, in studies of a raw shale core from the Naval Oil Shale Reserve, noted that calcium, strontium, and barium were directly related to each other and inversely related to iron and aluminum. Manganese did not fall into the carbonate group in Fox's study.[13] Giauque, in his study of two cores from the Naval Oil Shale Reserve, found that calcium, strontium, and barium were strongly related, as were iron, potassium, titanium, and aluminum.[7]

The effect of these vertical variations and associations in spent shales on leachate composition is discussed in Sec. II.A.2.c.

*c. **Leaching Studies**.* Leaching experiments were used to determine the solubility of major, minor, and trace elements as a function of the mineralogical and chemical properties of spent shales from retort 3E. The experimental and analytical methods used are described in Ref. 2. This year, the reproducibility of the standard leaching procedure was determined and the use of direct current argon plasma emission spectrometry (DCAPES) as an efficient and reliable method for elemental analysis of oil shale leachates was verified. The results of these investigations are presented in Appendixes B and C.

Several considerations determine the usefulness of the information derived from leaching studies of cores R3E1, E2, and E3. One of the most important is the method of core retrieval. Drilling agents such as pipe dope, foam, and surfactants used to facilitate recovery of core E1 caused complications in the results of the analysis of the core (analyses of these agents appear in Ref. 3). Therefore, this discussion will center on cores E2 and E3, where water was the only drilling aid used. Complications associated with interpretation of leaching data include (1) the lack of preburn mineralogical information, (2) the variable recovery of materials with depth as a result of the coring operation, and (3) the difficulty of deducing the effects of pre- and postburn processes on the leaching characteristics of the solid spent shales.

Four types of leaching experiments were conducted: (1) the standard 48-h static leaching test described in Ref. 2; (2) sequential 2-day leachings of the same sample; (3) extended leachings for 2, 7, and 28 days; and

(4) leaching experiments with groundwater. Each set of experiments is described below.

- *Leaching Experiments.* The absolute concentrations of major, minor, and trace elements in leachates from cores E1, E2, and E3 are presented in Table VIII. Percentages of available elements leached from each sample are shown for the more mobile elements in Table IX. Figure 4 shows the variations in leachate concentration as a function of depth.

Analysis indicates that the leaching behavior of spent shales from retort 3E correlates well with the mineral suites identified in each core section. Leachate compositions depend on the extent of occurrence of minerals in the solid material, the amount of each element available in the solid material, the dynamic effects that control the mobilization of a particular element from the bulk solid to solution at the solid-liquid interface, and the chemical processes that occur as the bulk solution constituents move to establish equilibrium. The present study has addressed these questions in varying degrees except for study of the dynamic processes that control mobility rates. To understand the equilibrium processes that affect the solution chemistry, dynamic experiments were postponed for future studies, and we decided to negate, or at least standardize, dynamic effects by carefully performing the identical experimental technique on different materials so that the above factors could be considered and chemical trends identified.

The leaching behavior observed for retort 3E is summarized in Table X and compared with elemental associations in spent shales. The elements measured in retort 3E leachates can be divided into three groups based on their chemical behavior throughout both cores. These groupings are consistent with similar groups of elements identified from an analysis of spent shale elemental abundances (Fig. 3).

Group A includes the carbonate-forming elements lithium, strontium, lead, barium, and calcium, as well as tungsten. The concentrations of these elements are directly related to each other in most of the spent shale samples in both cores. That their concentrations decrease and increase in harmony suggests that leachate concentrations are controlled by similar mechanisms that might include relative solubility of the spent shale mineral phase and/or secondary solubility controls. Calcium concentration in the leachates appears to be controlled by the calcite and/or calcium silicate concentrations in the spent shale. Similar carbonate mineral phases may control leachate concentrations of other Group A elements. Although these elements (calcium, magnesium, strontium, barium) are related in the spent shale solids, there is no apparent relationship between the concentration of Group A elements in the spent shale and concentrations in the leachates. This is because mineral phases, rather than elemental abundances, control solubility.

The Group B elements, which include titanium, fluoride, vanadium, boron, silicon, arsenic, selenium, and iron, are inversely related to the Group A elements in leachates. Two of these elements, iron and titanium, are also chemically related in the spent shales. Arsenic in the spent shales did not fall into Group B. Arsenic concentrations in spent shale and leachates are inversely related. The inverse relationship between leachates of Groups A and B is not understood at present, but is believed to be due to both secondary (calcium and fluoride) and primary solubility controls. This suggests that conditions that minimize element concentrations of one group in the leachates may increase element concentrations of the other group.

Group C includes electrical conductivity, sodium, molybdenum, nickel, aluminum, and potassium in the leachates, and sodium, aluminum, and potassium in the spent shales. The occurrence of electrical conductivity in this group is probably related to the chemical behavior of cations and anions such as SO_4 or HCO_3, which have not yet been measured. This work is in progress and will be reported next year. A comparison of the variation of Group C elements in spent shales and leachates indicates that aluminum concentrations in the spent shales is inversely related to electrical conductivity in leachates from both cores and that potassium concentrations in the spent shales are directly related to nickel and boron concentrations in the leachates of core E3. No other relationships between leachate and spent shale abundances were noted.

Leachate compositions for cores E2 and E3 reflect retort processing conditions. In core sections that contained high-temperature silicate products, the major element cations (alkali and alkaline earth elements) were generally less soluble, with concomitant decrease in conductivities. The presence of the high-temperature minerals and the decreased solubility of major cations suggest that the most extreme retorting conditions occurred in zones 3 and 4. Within this section of the retort, some of the environmentally important trace elements behave in a manner not directly correlated with major element solubility trends. Trace elements such as arsenic,

TABLE VI

Multielement Analysis of Solid Core Sections R3E2

(μg/g)

Element/Section	1	2	3	4T	4B	5T	5M	5B	6T	6B	7	8	9	10	11	11A	12	13T	13B	14	RSD	D.L.
Al (%)	3.54	5.23	4.81	4.67	4.68	4.80	4.54	4.80	4.25	4.12	4.51	6.64	7.00	5.33	3.94	4.34	6.43	5.73	5.96	3.04	4.1	
Sb	1.3	2.2	1.7	1.8	2.0	2.2	2.2	2.7	1.2	1.3	1.6	3.2	2.5	1.9	4.1	3.5	2.9	2.8	2.2	0.7	8	0.8
As	19.0	31.9	31.8	30.5	33.1	33.3	33.3	33.9	23.3	20.3	24.5	34.6	23.3	30.9	114	96	42	58.9	44.0	11.4	3.5	
Ba	655	740	650	580	635	734	795	780	737	736	517	<155	364	<163	<172	626	490	742	449	598	9.3	175
Be																						
Bi																						
B																						
Br	<3.7	<5.0	<4.8	<4.8	<4.2	<4.6	<3.9	<5.4	<5.6	<4.9	<4.2	<4.0	5.5	<4.3	<6.3	<6.7	<4.3	<5.1	<6.6	<3.0		6
Ca(%)	16.70	14.54	15.85	18.19	17.80	18.55	19.08	18.97	17.97	18.22	13.50	7.31	7.10	11.05	9.73	11.20	8.77	14.80	9.61	14.23	5.5	0.14
Cd																						
Ce	54	61	53	62	60	85	76	63	45	70	73	80	93	67	50	60	80	75	126	60	8	
Cl	<125	<142	<145	<175	<145	<149	<140	<194	<155	<155	<156	<123	<97	<146	<191	<171	<145	<136	<190	<111	12.3	175
Co	7.9	9.7	9.6	10.7	9.2	11.6	10.7	10.6	7.4	9.2	11.2	11.6	11.9	10.8	13.1	6.1	11.6	11.8	20.5	6.1	10	
Cr	49	65	63	38	61	70	63	51	52	56	61	60	87	59	48	47	81	70	111	47	11	10
Cs	<1.9	3.4	5.4	<3.9	5.3	6.0	5.3	4.9	2.9	3.8	<3.0	4.0	5.3	4.8	4.1	2.8	5.4	5.1	6.3	2.8	10	2
Cu	<340	<310	<362	<422	<320	<352	<336	<420	<346	<381	<381	<316	<258	<340	<447	<398	<336	<315	<478	<265		450
Dy	2.8	3.0	3.5	2.4	3.6	3.6	2.8	<1.7	2.9	<1.4	4.1	3.9	3.5	4.5	<1.4	3.0	3.8	3.5	2.8	2.5	9.0	1.6
Eu	1.1	0.87	1.1	0.88	0.88	1.3	0.90	1.0	1.2	1.1	1.0	0.59	1.1	0.95	0.65	0.87	1.3	0.54	1.7	0.9	10	
Ga	<35	<48	<48	<47	<41	<47	<39	<54	<57	<52	<42	<40	<36	<44	<67	<73	<46	<55	<74	<33		70
Hf	3.3	<1.7	<2.3	<2.8	3.4	<2.0	3.0	<2.1	2.6	3.9	3.6	3.8	3.6	3.0	<1.4	2.5	3.6	3.5	5.6	2.5	10	2
I	<28	<25	<31	<35	<24	<29	<28	<31	<25	<30	<36	<25	<23	<26	<27	<24	<25	<21	<30	<22		25
Fe (%)	2.32	2.79	2.74	2.55	2.72	3.07	3.21	2.53	2.10	2.47	2.57	3.41	4.17	2.63	2.48	1.79	3.34	3.02	5.97	1.79	4.5	
Pb																						
La	19.1	30.2	23.8	22.7	26.8	24.5	26.4	24.8	23.1	22	25	36	20	27	23.3	24.7	34.2	31.4	24	18	1.7	
Li																						
Lu	<0.15	<0.14	<0.18	<0.35	<0.18	<0.11	0.37	<0.16	<0.16	0.40	0.39	<0.13	0.30	0.30	<0.14	0.23	0.28	0.25	0.51	0.23	20	0.15
Mg (%)	10.39	10.94	9.73	10.27	10.36	11.26	10.86	10.33	12.62	14.71	13.98	7.75	8.38	10.61	7.29	8.24	7.26	10.03	7.51	9.67	5.6	0.31
Mn	395	416	454	432	423	448	432	428	405	474	433	465	452	418	279	314	438	437	352	279	1.5	<24
Hg	<0.04	<0.03	<0.04	<0.07	<0.03	<0.04	<0.04	<0.04	<0.03	<0.037	<0.056	<0.030	<0.032	<0.031	<0.024	<0.029	<0.028	<0.025	<0.045	<0.029		0.03
Mo																						
Ni																						
K (%)	2.52	4.06	2.78	2.66	2.90	2.58	2.54	3.29	2.27	2.58	3.46	6.03	6.33	4.94	1.86	1.78	5.12	2.95	2.33	2.04	11	0.45
Rb	146	121	<55	<100	<44	98	128	<59	94	<48	<75	172	205	<52	<49	88.4	113	154	245	88	20	40
Sc	6.7	7.5	7.7	7.6	7.5	8.2	8.8	7.2	6.6	8.0	11.0	8.8	11.2	10.2	6.1	6.0	7.9	8.9	19	6.0	2.5	
Se	<8.4	<7.8	<9.8	<16.1	<6.3	<8.8	<8.1	<8.9	<7.0	<8.7	<12.1	<7.1	<7.4	<7.5	<7.7	<6.7	<6.6	<5.8	<10.6	<6.7		7
Si																						
Sm	2.4	3.5	3.0	2.4	4.1	3.4	3.5	3.8	3.2	3.2	2.9	4.1	2.6	3.6	3.2	3.4	3.9	4.1	3.3	2.5	4.5	
Sn																						
Sr	1 329	<377	1 311	<548	1 467	1 311	1 656	1 510	1.185	1 694	1 250	931	890	883	597	649	775	1 055	1 221	1 147	12	400
Na(%)	0.84	0.78	0.88	1.01	1.04	1.07	1.03	1.05	1.28	1.27	0.47	0.54	0.51	0.81	2.01	2.16	0.99	1.52	2.95	0.65	1.8	
Ta	<1.3	1.8	<2.0	4.1	<0.9	<1.2	<1.2	2.1	1.6	<1.8	1.9	<1.5	<1	<1.7	<0.9	<1.5	<1.3	<0.8	<1.3	<1.5	50	1.0
Tb	<2.2	<1.9	<2.5	<1.3	<1.7	2.3	<2.3	<2.2	<1.8	<2.2	<3.2	<1.9	<1.9	<1.9	<2.0	<1.7	<1.7	<1.5	<3.7	<1.7	30	1.5
Tl																						
Th	8.4	6.8	10.1	6.6	9.1	10.1	10.4	9.9	9.0	10.2	11.6	9.2	9.3	10.6	6.5	9.0	7.8	10.2	16.5	9.0	7	
Ti	<1 031	2 157	2 265	2 231	<832	2 576	2 070	<1 094	1 705	<1 131	2 658	3 454	2 713	<903	<931	2 154	2 457	3 190	2 930	1 710	15	1 000
W	<0.10	<2.6	5.2	5.4	6.0	4.1	<0.09	<3.0	7.2	<2.7	<0.14	<2.2	<0.07	<2.4	<3.4	<3.6	<2.4	<2.8	<3.5	<0.07	18	2
U	5.0	4.0	3.9	4.7	5.1	5.4	5.3	5.3	4.8	5.3	4.8	4.1	4.2	5.0	6.8	6.5	4.3	4.7	4.2	3.8	1.8	
V	71	90	75	89	83	79	91	93	79	91	112	123	121	108	167	142	110	108	75	67	7	<10
Yb	<3.0	<2.9	<3.6	<8.6	3.2	<3.3	<3.3	<3.5	<2.7	<2.9	<4.5	<2.8	<3.4	<2.6	<2.9	<2.6	<2.7	<2.3	<3.8	<2.6	25	2.5
Zn	<81	<45	2 087	691	340	1 602	1 524	1 465	851	988	<94	<59	231	127	1 555	91	73	268	214	91	10	30

TABLE VII

Multielement Analysis of Solid Core Sections R3E3
(μg/g)

Element/Section	1	2T	2B	3	4	5T	5M	5B	6	7	8	9	10T	10M	10B	11	12	13	17	18	19	20	RSD	D.L.
Al(%)	7.34	2.77	4.57	7.41	3.24	3.78	3.68	4.40	3.30	4.85	3.23	4.73	4.45	4.45	4.37	3.24	4.63	6.68	4.51	3.78	6.91	5.35	4.1	
Sb	<0.7	1.2	<0.5	<0.9	1.3	1.4	1.7	2.4	1.8	2.1	2.6	2.4	1.8	2.3	2.4	1.1	1.7	2.7	3.0	4.4	3.2	2.9	8	0.8
As	12.6	2.97	4.6	9.0	19.0	16.1	27.0	44.7	32.1	28.0	23.3	31.9	43.4	44.5	38.3	36.7	21.3	30.8	80.4	103	122	95	3.5	
Ba	1 012	532	740	453	580	905	728	764	568	568	551	658	845	635	614	627	475	<157	435	690	<190	395	9.3	175
Be																								
Bi																								
B																								
Br	<6	<3.4	<4.4	<8.6	<4.5	<4.0	<4.8	<4.5	<4.7	<4.2	5.5	<4.8	<5.1	<4.2	<4.1	<4.5	<3.3	<4.0	<6	<5.5	<7.0	<6.1		6
Ca(%)	2.11	18.36	18.68	4.05	18.19	18.91	19.72	18.95	20.60	13.55	18.54	16.18	23.54	19.02	20.99	11.20	11.75	5.35	9.99	19.48	<0.14	5.50	5.5	0.14
Cd																								
Ce	97	53	61	74	66	53	50	68	52	58	54	59	64	75	76	58	72	77	74	52	54	94	8	
Cl	549	<128	<161	<200	<175	<155	<182	<128	<164	<115	1 437	<130	<145	<127	<144	<171	<114	226	<171	316	<203	<160	12.3	175
Co	14	7.1	8.5	4.4	12	8.1	6.5	9.7	7.5	11.9	8.6	10.0	9.9	12.2	11.0	8.1	9.9	12.5	17	9.2	4.7	6.6	10	
Cr	112	48	59	14	70	70	48	54	47	48	59	55	51	66	53	47	42	72	57	51	<11	27	11	10
Cs	7.0	4.0	3.2	5.7	6.3	3.7	4.5	4.1	5.5	4.1	3.2	3.7	<1.5	5.5	6.0	3.1	<2.8	<4.3	6.6	2.7	9.0	6.6	10	2
Cu	<460	<310	<351	<496	<422	<365	<392	<286	<364	<272	<306	<310	<325	<307	<351	<398	<295	<308	<428	<324	<578	<427		450
Dy	3.52	1.53	3.02	3.04	2.43	2.48	<1.6	2.22	7.0	3.04	2.29	3.51	2.65	3.15	3.35	3.04	3.51	3.61	2.94	2.22	8.09	5.87	9.0	1.6
Eu	1.6	0.65	0.78	0.71	1.3	1.0	0.58	0.67	1.3	0.69	0.78	0.92	0.86	0.88	0.95	1.2	0.84	0.75	0.96	0.69	0.88	1.0	10	
Ga	<64	<34	<43	<87	<46	<41	<47	<45	<47	<42	<34	<49	<54	<45	<43	<50	<35	<42	<70	<59	<80	<71		70
Hf	8.4	<1.3	2.6	4.7	<2.1	2.8	<1.8	2.6	<1.7	<1.3	2.5	<1.6	2.5	2.6	3.3	<1.4	<2.0	3.2	3.1	2.2	5.3	4.8	10	2
I	<32	<25	<25	<24	<35	<30	<31	<21	<25	<21	<25	<24	<24	<23	<26	<24	<27	<24	<27	<21	<27	<24		25
Fe(%)	3.86	1.88	2.29	1.33	3.05	2.07	2.26	2.64	1.82	2.43	2.24	2.47	2.66	2.72	2.84	2.06	3.10	3.50	3.10	1.97	1.84	2.59	4.5	
Pb																								
La	38.6	16.9	26.0	34.3	16.4	20.3	22.7	27.7	20.9	25.9	20.4	27.4	26.1	25.8	25.2	22.3	29.0	34.0	24.2	22.6	24.8	29.8	1.7	
Li																								
Lu	0.26	0.25	<0.1	0.18	<0.15	0.24	<0.14	0.24	0.48	<0.11	<0.13	<0.13	0.29	<0.11	0.23	<0.11	<0.24	<0.13	<0.15	<0.10	0.44	0.36	20	0.15
Mg(%)	1.88	9.38	9.62	1.53	9.54	10.32	11.98	10.69	8.07	9.98	9.22	10.14	11.95	9.98	9.28	9.82	11.94	6.42	7.12	7.84	<0.31	3.01	5.6	0.31
Mn	599	503	472	198	437	377	491	532	330	431	374	383	444	359	381	434	437	411	316	342	24	182	1.5	<24
Hg	<0.04	<0.03	<0.03	<0.02	<0.04	<0.04	<0.03	<0.02	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.02	<0.05	<0.03	<0.03	<0.02	<0.03	<0.02		0.03
Mo																								
Ni																								
K(%)	2.68	0.97	2.03	<0.44	1.41	2.27	1.62	2.16	1.76	3.91	1.92	4.00	1.72	2.25	1.96	1.49	3.59	6.23	1.59	1.42	<0.45	1.54	11	0.45
Rb	104	94	<41	<29	115	113	51	115	<48	118	<43	120	<42	113	138	<36	<64	157	<46	85	<43	<37	20	40
Sc	11.6	5.8	6.1	1.7	9.8	7.1	6.7	7.5	6.9	6.5	6.9	7.5	8.1	7.6	7.5	5.6	11.3	7.7	7.4	5.6	0.59	3.5	2.5	
Se	<9	<5.9	<9.4	<4.9	<9.2	<9.3	<7.8	<5.2	<8.5	<6.1	<7.1	<7.3	<6.6	<6.8	<7.3	<6.2	<11	<7.0	<8.3	<5.6	<6.3	<6.2		7
Si																								
Sm	4.8	2.3	3.3	3.5	2.3	2.6	2.8	3.7	5.4	3.4	2.6	3.7	3.7	4.3	3.5	3.1	3.7	4.0	3.5	3.0	4.0	5.2	4.5	
Sn																								
Sr	<507	1 017	1 326	<373	1 250	1 197	1 552	1 273	2 067	833	1 454	1 010	1 533	1 621	1 563	1 352	852	<377	<437	1 323	<435	<376	12	400
Na(%)	2.0	1.16	1.29	5.23	1.06	0.93	0.90	1.21	1.10	0.69	0.86	0.72	1.17	1.16	1.40	1.76	0.56	0.53	2.44	1.76	4.60	3.27	1.8	
Ta	<1.3	<0.9	<0.9	<0.7	<1.9	2.0	1.9	<1.2	<1.7	1.4	<1.0	1.6	<1.5	<0.9	<1.6	<0.8	<2.5	<1.6	<1.1	1.3	<1.2	<1.3	50	1.0
Tb	<3	<1.6	<1.6	<1.1	<2.3	<2.4	<1.9	<1.4	<2.6	<1.6	<2.2	<1.8	<1.7	<1.7	<2.0	<1.7	<0.8	<1.9	<2.0	<1.8	2.8	<1.5	30	1.5
Tl																								
Th	19.4	9.3	9.2	9.4	10.1	9.0	4.8	8.1	36.1	6.9	9.6	8.4	10.5	11.8	10.5	6.5	6.6	7.4	8.4	9.2	5.4	6.2	7	
Ti	4 124	<915	2 098	<865	2 332	1 982	<1 068	1 908	<864	2 162	1 689	1 948	<838	2 230	<976	<942	2 243	3 729	<1 019	1 993	<1 037	<885	15	1 000
W	3.2	<0.06	9.7	8.8	<2.4	<0.10	<2.6	<2.4	<2.5	<2.2	<0.07	<2.6	<2.8	<2.3	<0.07	<2.5	<0.09	<2.2	<3.3	<3.0	<0.08	<3.4	18	2
U	3.66	2.23	4.02	3.47	3.57	4.81	2.51	2.74	18.14	3.00	4.70	4.77	6.30	7.95	6.62	4.32	3.90	3.79	7.22	4.22	2.13	3.21	1.8	
V	84	57	79	21	71	69	75	79	57	89	73	113	90	94	101	62	125	104	153	94	<10	44	7	<10
Yb	5.1	3.1	<2.1	<1.7	<3.4	<3.5	<2.9	<2.0	8.7	<2.4	<2.7	<2.7	<2.6	<2.6	<3.0	<2.3	<5.6	<2.8	<3	2.3	7.2	6.8	25	2.5
Zn	145	71	<19	<32	297	199	<52	156	<7	<69	132	175	119	269	327	148	213	114	357	88	132	176	10	30

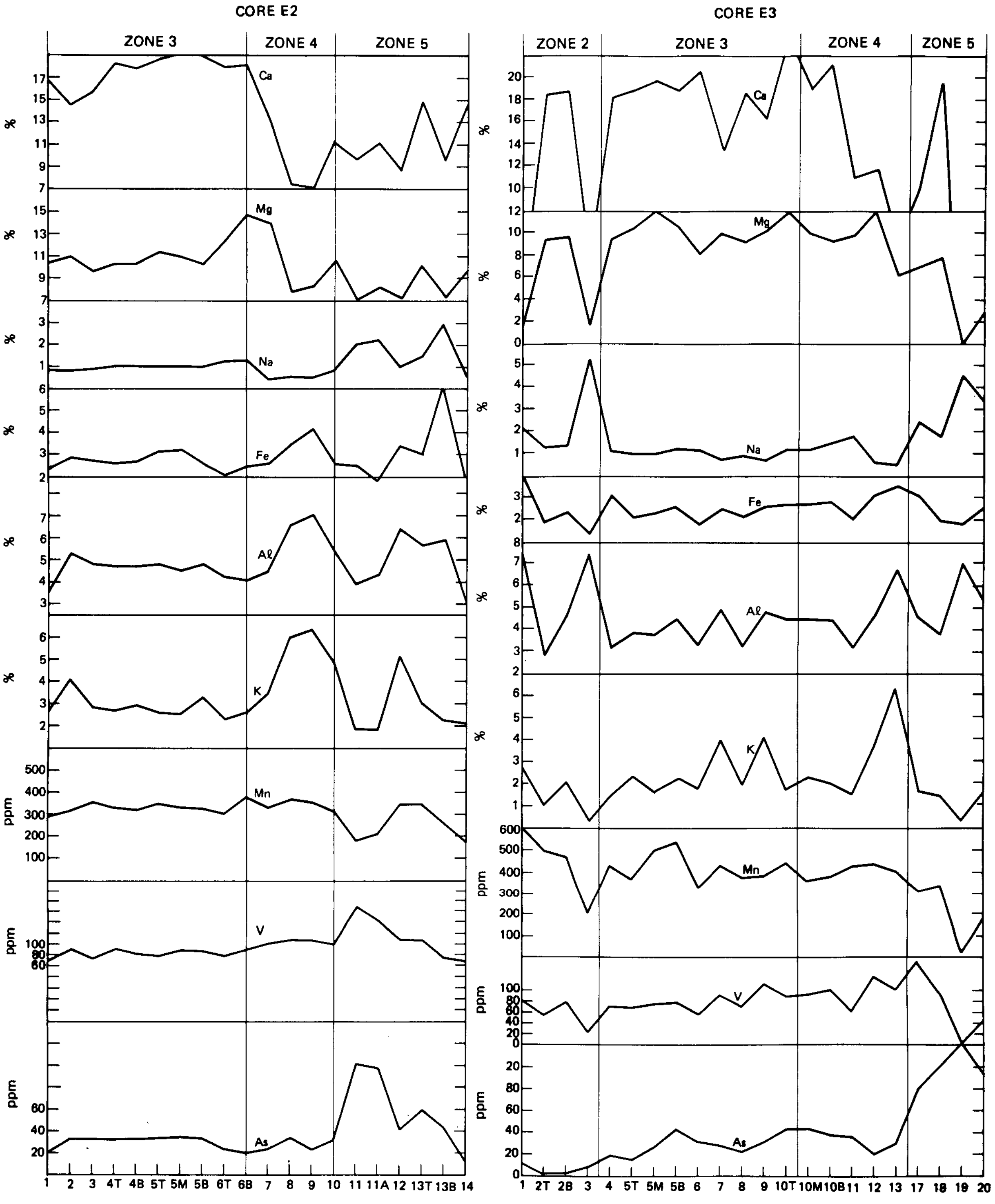


Fig. 3. Variation of some trace elements in spent shales from retort 3E.

boron, fluoride, and vanadium show increased solubilities from materials that experience extreme retorting conditions. These retorting conditions also inhibit alkaline earth concentrations in the leachates.

These data suggest that trace elements of potential concern are not immobilized in spent shales containing akermanite-gehlenite solid solution as the major high-temperature silicate phase. Trace elements appear to be less mobile from spent shales containing diopside as the major silicate phase. It is possible that the retorting conditions that favor the formation of akermanite-gehlenite also favor the mobilization of these trace elements (primary and secondary solubility control), or that akermanite leaches in a manner that releases larger quantities of these trace elements compared with other product silicate phases. Another reason for the difference in mobility from zone 3 to zone 4 could be the ability of the diopside crystal structure to accommodate a variety of trace elements as substitutes for calcium, magnesium, or silicon, whereas the akermanite-gehlenite structure is not so flexible.[14] An explanation that cannot be ruled out, because baseline information on raw shale is not complete, is that compositional variations in the raw shale could have changed near 7763 ft with concomitant effect on the final composition and leaching behavior of the product phases. Akermanite-gehlenite and monticellite are relatively calcium rich compared with diopside and forsterite, which lends credence to this possibility. Furthermore, compositional variations in the raw shale may have been accompanied by variations in trace element concentrations, but this was not reflected in the solid spent shales analyzed by neutron activation analysis.

Other trends are also probable, but some may not be immediately obvious because elemental analyses of solids for molybdenum and nickel are not yet available. Figure 5 shows these trends for calcium, fluoride, and vanadium. These elements were chosen because they represent two different mechanisms of trace element mobility. The mechanism for fluoride mobility from high-temperature silicate phases requires fluoride solubility to be uncontrolled because of a lack of calcium ions. When moderate calcium ion concentrations are available (50-100 ppm), the insolubility of fluorite (CaF_2) controls fluoride mobility (secondary mineral solubility control). Using the solubility product of CaF_2, $K = 3.4 \times 10^{-11}$ at 290 K, and neglecting complicating phenomena such as the common ion effect, calculation indicates that calcium concentrations in excess of 8 $\mu g/m\ell$ will depress and control the fluoride ion concentration. The lack of soluble alkaline earth ions caused by formation of high-temperature silicates probably also encourages the molybdenum mobility by limiting solubility control by $CaMoO_4$, and the arsenic mobility by limiting solubility control by $CaAsO_4$. Vanadium as vanadate ion (VO_4^{3-}) apparently has no secondary minerals influencing mobility. Thus, increased solubility could be due to a number of factors.

The percentage of available vanadium mobilized as a function of depth in the retort is shown in Fig. 5, which shows that vanadium solubility increases above zone 4. This also seems to be the case for boron, another trace element with no apparent secondary mineral controls. There are at least three possible explanations for these observations. Along with the solubility trends associated with the 7763-ft depth, a change occurred in the mineralogy, whereby akermanite-gehlenite solid solution was the predominant high-temperature silicate above 7763 ft and diopside-augite was predominant below. This trend could be due to a change in the extremity of the retorting conditions in zone 3 compared with zones 4 and 5. Also, the relative amounts of raw shale minerals may have changed in this vicinity, thus favoring a change in the mineral suites present after retorting. Increased vanadium and boron solubilities in zone 3 could be explained by retorting conditions that favored the decomposition of these elements' original mineral residences and discouraged subsequent incorporation into the new mineral hosts. It is also possible that the crystalline structure of akermanite is not as efficient for incorporation of trace elements as the more versatile crystalline structure of diopside-augite. This could be important for vanadium and boron because these elements could substitute for silicon in the lattice. The third possible explanation is a change in the chemical and mineral makeup of the raw shale in this vicinity, which is reflected in the leaching behavior of the resultant spent shale. Raw shale from the Logan Wash area is being characterized and this analysis will help us interpret these solubility trends.

The behavior of the alkali elements is also worth examination. The range of solubility of sodium ions was approximately 3 to 20% of the available sodium (Table IX). Sodium behavior is probably correlated with the thermal behavior of analcime and sodium and potassium feldspars. Qualitatively, conditions that favor akermanite formation appear to discourage sodium mobility; conditions that favor diopside formation seem to encourage sodium mobility. In addition, potassium and lithium solubilities could warrant environmental consideration

TABLE VIII. Elemental Analyses for Leachates from Occidental Retort 3E

CORE E1[a]

Sample No.	Absolute Elevation	pH	Al	As	B	Ca	Co	Cu	F	Fe	Mg	Mn	Mo	Se	Na	V	Zn
1	7807	10.7	0.3	0.005	0.6	93	<0.04	<0.02	0.9	<0.02	<0.4	<0.02	0.10	<0.001	33	<0.50	<0.003
2	7796	8.4	<0.2	0.029	1.2	1340	<0.12	<0.02	2.2	0.02	24	<0.02	<0.13	<0.050	600	<0.47	<0.035
3	7792	9.2	0.2	0.072	1.2	17	<0.04	<0.02	1.6	<0.04	2.3	<0.02	0.07	<0.007	80	1.57	0.003
4	7789	8.3	<0.2	0.031	0.9	141	<0.04	<0.02	1.7	0.02	7.5	<0.02	0.07	<0.005	58	0.33	0.015
5	7786	9.1	2.4	0.036	<0.6	14	<0.04	<0.02	1.7	0.87	8.3	<0.02	<0.04	<0.001	73	0.80	0.143
6	7782	9.6	3.3	0.081	6.7	6	<0.04	<0.02	11.5	1.90	13.8	0.05	0.10	0.014	135	2.63	0.105
7	7781	9.8	2.1	0.062	1.5	18	<0.04	<0.02	22.5	1.76	6.8	0.02	0.10	<0.023	103	0.47	0.023
8	7778	9.6	4.4	0.056	1.7	20	<0.04	<0.02	15.2	2.72	13.0	0.04	0.13	0.007	100	0.57	0.041
9	7774	9.7	6.8	0.051	3.5	36	<0.04	0.04	15.8	2.52	37	0.13	0.23	0.038	128	0.70	0.063
10	7773	10.3	2.7	0.150	2.5	28	0.04	<0.02	7.3	4.68	16	0.07	0.13	0.050	123	1.13	0.054
11	7771	10.7	2.2	0.200	2.5	27	<0.04	0.03	5.4	4.08	10.8	0.06	0.27	0.040	155	1.63	0.093
12	7770	10.5	1.7	0.090	2.3	30	<0.04	<0.02	5.1	2.40	7.3	0.04	0.20	0.040	155	1.30	0.022
13	7767	9.6	0.2	0.010	1.7	52	<0.04	<0.02	5.9	0.12	1.1	<0.02	0.50	<0.010	98	0.27	<0.003
14	7767	10.2	0.3	0.005	<0.3	170	<0.04	<0.02	4.4	0.02	1.1	<0.02	0.40	<0.010	33	<0.10	<0.003
15	7766	9.9	0.2	0.099	0.5	610	0.07	<0.02	2.5	0.02	11.0	<0.02	0.40	<0.010	155	0.53	<0.003
16	7758	10.4	0.2	0.036	0.6	173	<0.04	<0.02	0.8	0.02	8.8	<0.02	0.47	<0.010	103	0.57	<0.003
			10	0.025	25									0.025		0.15	

CORE E2[b]

Section No	Absolute Elevation	pH	Cond µmho/cm	Al	As	Ba	B	Cd	Ca	Co	Cu	F	Fe	Pb	Li	Mg	Mn	Mo	Ni	K	Se	Si	Sn	Sr	Na	Ti	W	V
1	7788	9.09	2260	0.158	0.010	0.096	1.93	<0.081	133	<0.006	0.003	3.9	<0.032	<0.096	0.506	3.83	<0.006	0.84	0.039	185	<0.004	19.5	<0.078	0.718	273	<0.008	0.47	0.163
2	7783	9.07		1.22	<0.01	1.99	2.69	<0.030	566	0.046	0.010	0.3	0.98	0.300	1.90	9.84	0.019	1.18	0.080	215			0.30		219	0.034	0.90	0.618
3	7778	8.78	2780	0.27	<0.01	0.316	2.40	<0.081	352	0.075	0.002	5.2	<0.032	0.29	0.772	18.2	<0.006	0.293	0.041	179	<0.02	17.4	<0.078	3.69	295	0.026	0.46	0.129
4T	7773	10.28	2250	0.395	<0.002	0.92	1.96	<0.030	223	<0.006	<0.002	4.3	<0.034	0.22	0.650	0.235	<0.006	0.474	0.035	200.3	0.006		<0.060		207	<0.014	0.36	0.401
4B		10.20	2210	0.317	0.008	0.127	2.41	<0.030	237	<0.006	<0.002	5.2	0.06	0.14	0.816	0.88	<0.006	0.429	0.038	182	<0.004	35.7	<0.078	2.81	191	<0.014	0.99	0.437
5T	7768	10.41	1490	0.078	0.010	0.065	2.11	<0.081	39.6	0.014	<0.002	5.2	<0.032	<0.096	0.442	0.303	<0.006	0.541	0.044	176	<0.004	46.2	<0.078	0.76	131	<0.008	0.44	0.87
5M		10.19	1350	0.100	<0.002	0.067	1.63	<0.030	48.7	<0.006	<0.002	4.4	<0.034	<0.042	0.497	0.311	<0.006	0.528	0.024	178.7	<0.002		<0.060	0.766	112	<0.014	0.050	1.08
5B		10.24	1500	0.081	0.006	0.086	1.91	<0.081	64.0	<0.012	<0.002	5.3	0.035	<0.096	0.420	0.323	<0.006	0.520	0.038	179	<0.004	43.1	<0.078	0.988	127	<0.008	0.37	0.77
6T	7764	10.34	1120	0.148	0.026	0.028	6.55	<0.014	4.51	<0.012	<0.006	12	0.09	<0.082	0.125	0.554	<0.004	0.814	0.011	129	0.004	30.7	<0.064	0.088	166	<0.008	0.164	1.90
6B		10.00	880	0.401	0.034	0.057	5.33	<0.081	3.54	<0.012	<0.002	21	0.407	<0.096	0.053	0.609	0.011	0.659	0.039	122	0.004	36.6	<0.078	0.080	118	0.028	0.13	1.75
7	7753	10.02	1400	0.222	<0.01	0.076	4.13	<0.030	14.8	<0.006	0.008	17.0	0.064	<0.042	1.02	1.22	<0.006	0.726	<0.002	132		20.3	<0.060	0.360	192	<0.014	<0.048	0.569
8	7743	9.43	1450	0.243	0.011	0.149	1.88	<0.030	106	<0.006	<0.002	2.1	0.036	0.13	1.46	13.9	<0.006	0.788	0.028	163	0.006	13.2	<0.060	1.74	102	<0.014	0.173	0.212
9	7738	9.78	995	0.11	0.016	0.067	1.91	<0.030	46.1	<0.012	0.017	5.4	0.061	0.06	0.575	9.24	0.017	0.64	0.019	134	<0.02	15.7	<0.078	0.475	158	<0.014	0.157	0.23
10	7728	9.47	2390	0.073		0.103	1.93	<0.081	42.3	<0.012	0.012		0.034	<0.096	0.497	10.8	<0.006	1.65	0.053	215		16.4	<0.078	0.791	308	<0.008	0.24	0.229
11	7718	11.60	1240	0.138	<0.01	0.31	0.330	<0.081	106	0.020	<0.002	9	<0.032	<0.096	0.423	0.650	0.013	1.28	0.045	52.9	<0.008	5.4	<0.078	1.82	137	<0.008	0.43	0.100
11A		11.54	2150	0.553	<0.002	0.37	0.292	<0.030	285	<0.006	<0.002	12.0	<0.034	0.26	1.86	0.499	<0.006	1.48	0.038	77.0	0.010	6.73	<0.064	3.35	266	<0.014	0.41	0.222
12	7711	9.82	1460	0.456	<0.002	0.216	1.10	<0.030	200	<0.006	0.006	2.9	0.044	0.14	1.18	7.37	<0.006	0.522	0.009	139	<0.006	16.9	0.06	1.83	92	<0.014	0.27	0.144
13T	7701	10.24	2660	1.02	<0.002	2.80	1.11	<0.030	493	0.024	0.002	2.4	0.055	0.410	1.97	3.01	<0.006	0.382	0.060	220	0.004		0.24		155	<0.014	0.91	0.305
13B		10.55	2380	0.278	<0.01	0.40	0.917	<0.081	372	0.045	<0.002	3.0	<0.032	0.1	1.15	2.42	<0.006	0.458	0.035	176	<0.008	19.1	<0.078	4.72	161	0.020	0.54	0.095
14	7691	9.62	330	0.022	0.020	0.33	0.262	<0.030	3.89	<0.006	<0.002	4.2	<0.034	<0.042	0.236	1.13	<0.006	0.838	0.018	33	0.006		0.10	0.090	40	<0.014	<0.048	0.251

CORE E3[b]

Section No	Absolute Elevation	pH	Cond µmho/cm	Al	As	Ba	B	Cd	Ca	Co	Cu	F	Fe	Pb	Li	Mg	Mn	Mo	Ni	K	Se	Si	Sn	Sr	Na	Ti	W	V
1	7807	8.89	590	0.079	0.007	0.205	0.171	0.02	63	<0.01	0.002	1	0.064	0.104	0.127	2.82	0.016	0.081	0.023	5.68	<0.004	11.0	0.13	0.400	24	0.017	0.24	0.063
2T	7802	10.03	630	0.140	0.023	0.057	1.19	<0.02	6.5	<0.01	<0.002	26	<0.050	<0.03	0.204	0.10	0.017	0.170	0.035	71.6	<0.008	39.0	<0.11	0.10	63	0.011	0.45	0.265
2B		10.81	660	0.058	0.008	0.077	0.74	<0.02	25	<0.01	0.012	5.2	<0.050	<0.04	0.791	0.109	<0.008	0.404	0.030	61.7	<0.008	63.8	<0.11	0.203	55	0.009	<0.07	0.440
3	7797	9.62	560	0.010	0.048	0.020	0.37	0.03	5.0	0.014	0.005	1.9	0.07	0.05	0.086	0.98	0.023	0.246	0.039	8.81	0.004	32.7	<0.11	0.021	82	0.012	<0.07	0.300
4	7792	9.92	2350	0.033	0.016	0.068	3.76	<0.02	51	0.016	<0.002	5.5	<0.050	0.07	0.186	0.172	0.018	0.64	0.060	122	<0.004	51.1	<0.11	0.472	335	0.004	0.15	1.22
5T	7787	9.75	900	0.125	0.014	0.037	2.78	<0.02	4.5	0.01	0.004	31	0.066	0.05	0.089	0.138	0.008	0.284	0.049	56.1	<0.02	34.2	<0.11	0.102	132	0.008	<0.007	1.06
5M		9.80	970	0.105		0.061	3.58	<0.02	8.3	<0.01	0.003		0.05	0.04	0.09	0.132	0.012	0.420	0.045	97.6		43.1	<0.11	0.243	135	0.004	<0.07	1.11
5B		9.88	890	0.022	0.016	0.058	1.79	<0.02	8.4	0.02	<0.002	15.2	0.064	0.06	0.203	0.198	0.028	0.365	0.046	68.6	<0.004	29.8	<0.11	0.144	108	0.022	<0.07	0.682
6	7782	11.05	2040	1.27	0.036	0.041	3.70	<0.02	3.5	0.02	0.002	28	0.67	0.08	0.058	2.71	0.020	0.684	0.066	156	0.075		<0.11	0.023	321	0.058	<0.07	0.636
7	7777	9.13	3400	0.172	0.015	0.60	13.0	<0.02	223	0.016	0.003	4.8	0.03	0.30	1.08	12.2	<0.004	0.458	0.034	289	0.008	10.6	<0.04	1.98	230	0.002	0.60	0.301
8	7773	11.47	3100	0.49	0.004	0.118	4.11	<0.02	43	<0.01	<0.002	3.5	0.057	0.09	0.112	0.19	0.021	0.192	0.053	191	0.030	51.9	<0.11	0.343	283	0.015	0.15	0.794
9	7770	9.91	1450	0.56	0.104	0.047	12.2	<0.02	3.8	0.022	<0.022	10	0.48	0.03	0.244	1.43	0.009	0.487	0.056	131	0.075	38.6	<0.11	0.099	212	0.022	<0.07	1.70
10T	7767	10.29	1520	0.068	0.020	0.183	3.38	<0.02	69	0.03	<0.002	6.0	0.06	0.09	0.412	0.29	0.011	0.53	0.047	165	0.004	55.3	<0.11	0.858	182	<0.002	0.27	0.751
10M		9.54	2630	0.122	0.006	0.63	4.31	<0.02	198	0.012	0.001	2.9	0.02	0.23	0.50	2.26	<0.004	0.608	0.032	216	<0.004	24.4	<0.04	1.53	279	0.002	0.53	0.269
10B		10.45	1670	0.070	0.013	0.123	4.10	<0.02	79	0.021	<0.002	2.4	<0.050	0.06	0.176	0.158	<0.008	0.444	0.046	164	0.004	52.9	<0.11	0.861	161	<0.002	0.29	0.620
11	7762	9.00	6990	0.183	0.035	0.59	5.78	<0.02	293	0.016	<0.001	5.7	0.03	0.41	0.61	8.7	<0.004	2.34	0.046	358	0.060	15.5	<0.04	1.61	1137	<0.002	0.82	0.560
12	7757	11.61	2330	0.161	<0.004	0.042	2.65	<0.02	1.6	0.012	<0.002	17.5	<0.050	<0.03	1.05	0.004	0.009	0.12	0.034	150	<0.008	8.5	<0.11	0.24	123	0.008	<0.07	0.062
13	7752	10.18	1660	0.173	<0.004	0.96	1.35	0.03	293	0.01	0.001	9.4	0.022	0.30	1.20	5.42	<0.004	0.828	0.014	88.6	<0.02	8.6	<0.04	3.00	35	0.004	0.61	0.042
14-16																												

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[a] The following elements were below detection limits (μg/mℓ) for all samples: Cr(0.025); Ni(0.04); Be(0.007).

[b] The reported values are the result of three 5-s replicate analyses from the DCAPES. Significant figures were determined from the standard deviation of the replicater and the working detection limit for the analytical emission line.

TABLE IX

Percentages of Available Elements Soluble from Cores R3E2 and R3E3

Core R3E2

Section	Na ±3%	K ±10%	As	V ±9%	Ca ±5%	Mg ±4%	Ba ±10%	Sr ±10%
1	16.25	3.67	0.26	1.15	0.40	0.02	0.07	0.27
2	13.06	2.65	<0.16	3.45	1.95	0.04	1.34	
3	16.76	2.57	<0.16	0.86	1.24	0.08	0.24	1.41
4T	10.25	3.76	<0.03	2.26	0.61	<0.01	0.79	
4B	9.18	3.14	0.12	2.63	0.67	<0.01	0.10	0.96
5T	6.12	3.22	0.15	5.51	0.14	<0.01	0.04	0.27
5M	5.44	3.52	<0.03	5.95	0.13	<0.01	0.04	0.23
5B	6.05	2.34	0.09	4.14	0.15	<0.01	0.06	0.28
6T	6.48	2.84	0.56	12.03	0.01	<0.01	0.02	0.04
6B	4.65	1.89	0.84	9.62	0.01	<0.01	0.04	0.02
7	20.43	1.91	<0.04	2.55	0.05	<0.01	0.07	0.14
8	9.44	1.35	0.16	0.86	0.73	0.09	>0.48	0.93
9	16.93	1.17	0.34	0.95	0.36	0.07	0.10	0.28
10	19.01	1.62	<0.01	1.06	0.22	0.05	>0.32	0.43
11	3.41	1.04	<0.01	0.30	0.57	<0.01	>0.90	1.52
11A	6.16	2.17	<0.02	0.78	1.27	<0.01	0.30	2.58
12	4.65	1.36	<0.002	0.66	1.14	0.05	0.22	1.18
13T	5.10	3.73	<0.002	1.41	1.67	0.02	1.89	
13B	2.73	2.71	<0.11	0.63	1.76	0.01	0.45	1.93
14	3.08	0.81	0.88	1.89	0.01	<0.01	0.28	0.04

Core R3E3

Section	Na ±3%	K ±10%	As	V ±9%	Ca ±5%	Mg ±4%	Ba ±10%	Sr ±10%
1	0.46	0.11	0.28	0.38	1.49	0.08	0.10	>0.39
2T	2.72	3.69	0.39	2.32	0.02	<0.01	0.05	0.05
2B	2.13	1.52	0.87	2.78	0.07	<0.01	0.05	0.08
3	0.78	>1.0	2.67	7.14	0.06	0.03	0.02	>0.03
4	15.80	4.33	0.42	8.59	0.14	<0.01	0.06	0.19
5T	7.10	1.24	0.43	7.68	0.01	<0.01	0.02	0.04
5M	7.50	3.01		7.40	0.02	<0.01	0.04	0.08
5B	4.46	1.59	0.18	4.32	0.02	<0.01	0.04	0.06
6	14.59	4.43	0.56	5.58	0.01	0.02	0.04	<0.01
7	16.67	3.70	0.27	1.69	0.82	0.06	0.53	1.19
8	16.45	4.97	0.09	5.44	0.12	<0.01	0.11	0.12
9	14.72	1.64	1.63	7.52	0.01	<0.01	0.04	0.05
10T	7.78	4.80	0.23	4.17	0.15	<0.01	0.11	0.28
10M	12.03	4.80	0.07	1.43	0.52	0.01	0.50	0.47
10B	5.75	4.18	0.17	3.07	0.19	<0.01	0.10	0.28
11	32.30	12.01	0.48	4.52	1.31	0.04	0.47	0.60
12	10.98	2.09	<0.09	0.25	0.01	<0.01	0.04	0.14
13	3.30	0.71	<0.06	0.20	2.74	0.04	>3.1	>3.98
17	6.00	3.59	<0.01	0.23	1.23	<0.01	1.29	>4.5
18	4.32	1.95	<0.01	0.09	0.68	<0.01	0.94	2.15
19	1.38	>3.3	<0.01	<1.0	>55	>15	>1.9	>2.5
20	3.03	2.24	0.04	0.25	1.76	2.16	0.92	>2.9

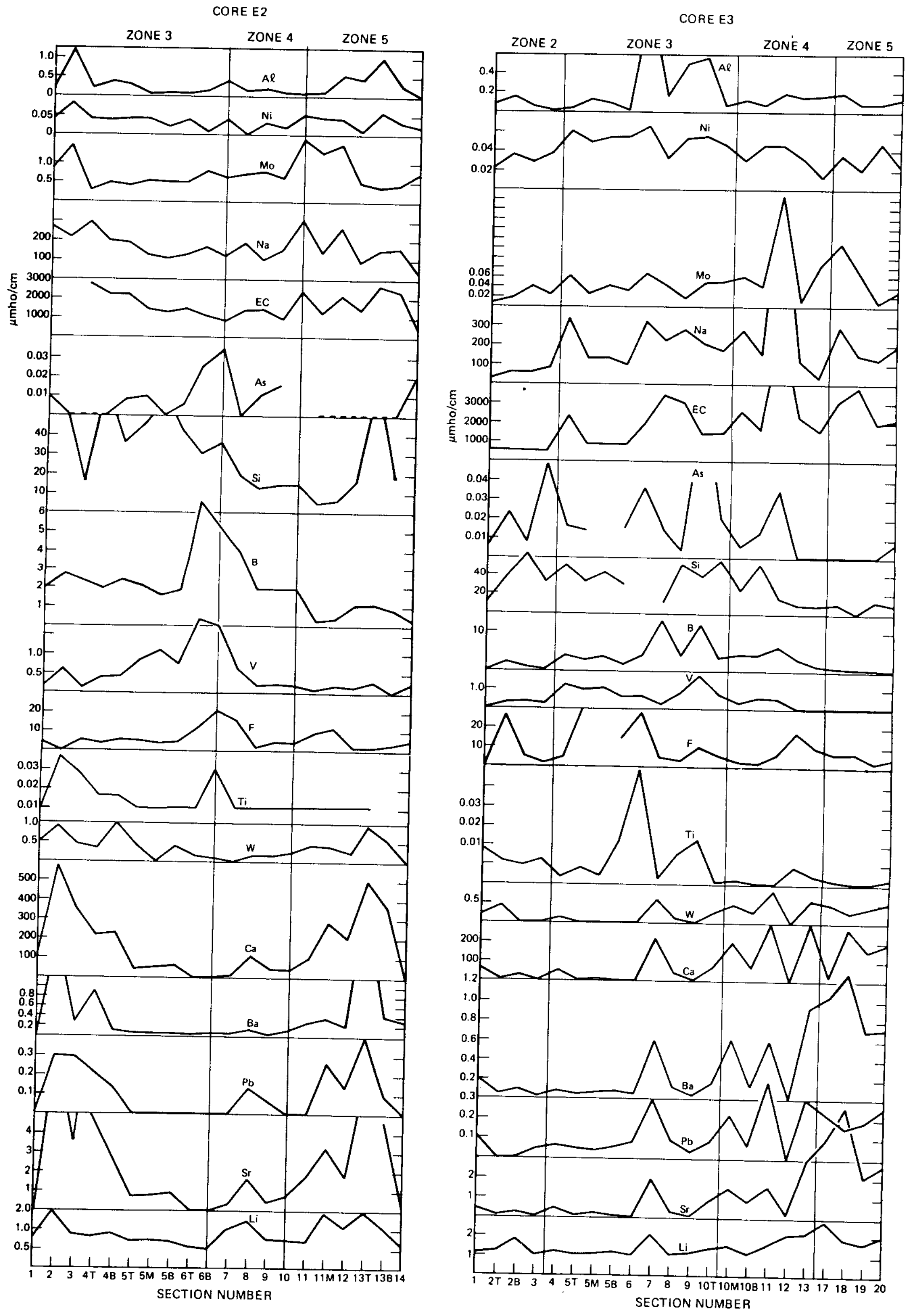


Fig. 4. Variation in leachate concentrations in cores E2 and E3. All measurements in mg/ℓ except where noted.

TABLE X. Elements Showing Similar Leaching Behavior and Spent-Shale Variability in Retort 3E

Group	Elements Showing Similar Leaching Behavior[a]	Elements Showing Similar Associations in Spent Shales
A	Li, Sr, Pb, Ba, Ca, W	Ca, Mg, Sr, Ba, Mn
B	Ti, F, V, B, Si, As, Se, Fe	Fe, Ti
C	Electrical conductivity, Na, Mo, Ni, Al, K	Na, Al, K

[a] The same suite of elements was not measured in both cases.

because of the amounts of material to be processed. Data in Table IX indicate that conditions that favor akermanite formation encourage potassium mobility, and conditions that favor diopside formation discourage potassium mobility. In contrast, absolute lithium concentrations appear to follow trends in sodium mobility. Ionic radii could be a contributing factor in the mobility trends for these ions (Li > Na > K, with actual radius dependent upon coordination number).

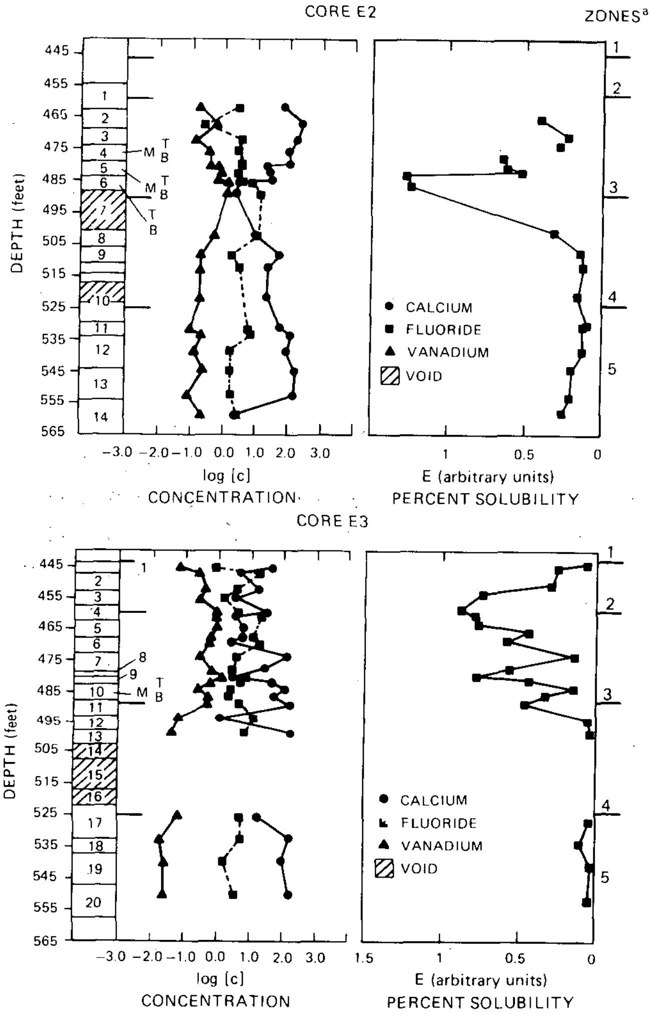
- *Sequential Leaching Experiments.* The effect of drying and subsequent wetting on the solubility of elemental species from section 6T of core E2 was evaluated by three successive standard 2-day leaches. The spent shale was dried after each leach.

The experimental results are compiled in Table XI. These data show that the specific conductance of the leachates decreases with subsequent exposures of solids to water, as is expected, because continued contact removes solubles from the shale solids. The pH also decreases with increasing contact; indicative of the mineralogical and chemical changes that occur with continued leaching. Cation concentrations of major and trace elements behave differently during the several exchanges of fresh water. For example, calcium, magnesium, and silicon concentrations are uniform for the three leachates, suggesting that the solutions are in quasi-equilibrium with a calcium magnesium silicate or silicates. The data further indicate that the solubilities of arsenic and fluoride are relatively constant for the three successive leaches, which would be expected if the proposed secondary solubility controls (CaF_2 and $CaAsO_4$) are exerted. Even though secondary solubility control by $CaMoO_4$ was suggested to explain molybdenum mobility, the obvious decrease of molybdenum solubility as a function of increased leaching could be explained by almost complete depletion of available molybdenum in the solid (concentrations of 5-20 mg/g have been reported for retort 3E materials[3]). Boron and vanadium, for which no solubility controls were proposed, also decrease with successive leaching, undoubtedly a result of exhausting available soluble material. Most of the other trace elements, except for nickel and titanium, which show no discernible trends, are below the detection limits of the analytical methods. These conclusions are based on only one set of results and must be supported by more comprehensive experimental data.

- *Extended Leaching Experiments.* Another set of experiments was performed to elucidate the effect of leaching time on leachate composition and to find which chemical processes occur relatively rapidly and which might not be obvious from a single 2-day leach. Three samples from zone 3, a high-temperature section, and one sample from zone 5 (13T), a low-temperature section (Table IV), were used. Each sample was leached for 2, 7, and 28 days using the standard leaching test. The results are presented in Table XII. Observations concerning trends in these data as a function of leach time are summarized below.

The pH values dropped for core sections 4T and 4B and apparently fluctuated for sections 5M and 13T. The specific conductances of these leachates were reasonably constant over the 28 days. This suggests that concentrations of the total dissolved solids, as represented by the major cationic and anionic species, are established rapidly (within the 2-day period) and subsequent changes in leachate composition can be considered minor adjustments in the establishment of equilibrium. These changes with time do not appear to have a large effect on major ions, as indicated by small fluctuations in the conductivity, but can have a profound effect on the trace element concentrations.

The behavior of ions as a function of leaching time can be summarized as follows. (1) Concentrations of boron, cobalt, and nickel increase with time. (2) Concentrations of molybdenum and potassium are constant with time. (3) Concentrations of aluminum, calcium, lithium, silicon, strontium, sodium, and vanadium decrease but level out after 7 days. (4) Concentrations of barium, iron, lead, magnesium, tin, titanium, tungsten, and zinc show no discernible trends. (5) Concentrations of beryllium, cadmium, copper, manganese, and mercury were below detection limits. (6) Concentration data were not available for arsenic, fluoride, and selenium.



[a]Note: See Table IV for delineation of zones.

Fig. 5. Calcium, fluoride, and vanadium concentration variations and percentage vanadium soluble as a function of depth for cores R3E2 and E3.

TABLE XI. Successive 2-Day Leaching Experiments of Core Section R3E2-6T

	OSL-6-1[a]	OSL-6-23[b]	OSL-6-30[b]
pH	10.35	9.56	9.30
Cond (μmho/cm)	1070	500	430
Al	0.148	0.607	0.260
As	(0.026)[c]	(0.024)	(0.038)
Ba	(0.028)	0.029	0.032
Be	<0.001	<0.001	<0.001
B	6.55	2.74	1.88
Cd	<0.014	<0.081	<0.020
Ca	4.51	2.6	3.5
Co	<0.012	<0.006	<0.012
Cu	<0.006	<0.006	0.005
F	(12)	10	13
Fe	0.09	0.69	0.05
Pb	<0.082	<0.096	0.06
Li	0.12	0.070	0.12
Mg	0.554	1.30	0.63
Mn	<0.004	0.014	<0.004
Hg	<0.082	<0.023	<0.2
Mo	0.814	0.150	0.124
Ni	0.011	0.030	0.029
K	129	94.3	63.8
Se	(0.004)	(<0.004)	(<0.008)
Si	(30.7)	31.9	29.5
Sn	<0.06	<0.078	<0.1
Sr	0.088	0.027	0.040
Na	190	199	90.5
Ti	<0.008	0.045	0.011
W	0.16	0.09	<0.07
V	1.90	0.62	0.376
Zn	<0.5	(0.08)	(0.01)

[a]Original extraction of R3E2-6T solid.
[b]Successive re-extraction of solid residues.
[c]Values in ( ) were obtained by AAS.

The solubility behavior of calcium, silicon, and vanadium correlates with concentrations that decrease but level off somewhere between the 7- and 28-day leach times. This suggests that after an initial pulse of soluble vanadium, the concentration is adjusted in solution by incorporation of the vanadium in a precipitated calcium silicate. Thus, the conditions that favor vanadium solubility at the solid particle-liquid interface do not extend to the bulk solution, and the vanadium solubility after leaving the particle is attenuated by other equilibrium processes (the precipitation of calcium silicate). This is a probable example of ion mobility being altered by the chemistry of the bulk solution.

The solubility behavior of molybdenum appears to be relatively insensitive to longer leaching times, which is consistent with the earlier suggestion of secondary solubility control by alkaline earth molybdates ($CaMoO_4$). Also, the increasing solubility of boron and nickel with increasing leaching time indicates that significant time periods may be necessary for attainment of equilibrium, which suggests that dynamic factors are probably quite important to the understanding of the mobility of these elements. More data will be required to test these speculations.

- *Groundwater Leaching Experiments.* Standard leaching experiments using groundwater from Tract C-a and four spent shale samples from retort 3E were conducted. The results of these analyses are shown in Tables XIII and XIV.

TABLE XII. Extended Leaching Experiments Using Four Samples of Spent Shale from Core E2

Element	Sample 4T			Sample 4B			Sample 5M			Sample 13T		
	Time (days)			Time (days)			Time (days)			Time (days)		
	2	7	28	2	7	28	2	7	28	2	7	28
pH	10.28	9.58	9.40	10.20	9.97	9.82	10.19	10.35	10.25	10.24	10.79	10.68
Spec. Cond. (μmho/cm)	2250	2250	2000	2210	2125	1850	1350	1420	1350	2660	2920	2750
Al	0.345	0.124	0.105	0.317	0.123	0.095	0.100	0.115	0.108	1.02	0.343	0.272
As	<0.002			0.008			<0.002			<0.002		
Ba	0.092	0.106	0.090	0.127	0.102	0.099	0.067	0.088	0.097	0.280	0.187	0.168
Be	<0.006	0.002	0.001	<0.006	0.001	0.002	<0.006	0.001	0.001	<0.006	0.001	0.001
B	1.96	2.30	2.48	2.41	2.15	2.36	1.63	2.06	2.38	1.11	1.31	1.47
Cd	<0.030	<0.012	<0.012	<0.030	<0.012	<0.012	<0.030	<0.012	<0.012	<0.030	<0.012	<0.012
Ca	223	186	167	237	165	161	48.7	58.8	54.3	493	464	462
Co	<0.006	0.025	0.016	<0.006	0.019	0.024	<0.006	0.009	0.009	0.024	0.032	0.033
Cu	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.002	<0.002	<0.002
F	4.3			5.2			4.4			2.4		
Fe	<0.034	0.017	<0.012	0.06	<0.012	0.023	<0.034	0.065	0.063	0.055	0.028	0.031
Pb	0.22	0.135	0.13	0.14	0.13	0.14	<0.042	0.03	0.02	0.410	0.27	0.28
Li	0.650	0.475	0.540	0.816	0.734	0.695	0.497	0.418	0.456	1.97	1.42	1.45
Mg	0.235	1.13	1.21	0.88	0.99	0.454	0.311	0.205	0.102	3.01	1.03	0.350
Mn	<0.006	<0.004	<0.004	<0.006	0.004	<0.004	<0.006	0.026	0.027	<0.006	0.006	<0.004
Hg	<0.174	<0.050	<0.050	<0.230	<0.050	<0.050	<0.174	<0.050	<0.050	<0.174	<0.050	< 0.050
Mo	0.474	0.371	0.390	0.429	0.341	0.390	0.528	0.372	0.400	0.382	0.325	0.360
Ni	0.035	0.056	0.055	0.038	0.054	0.075	0.024	0.047	0.050	0.060	0.078	0.084
K	200.3	213	219	182	203	219	178.7	191	188	220	219	227
Se	0.006			<0.004			<0.002			0.004		
Si		16.4	13.2	35.7	21.9	19.9		31.3	27.2		12.6	13.6
Sn	<0.060	0.014	<0.008	<0.078	<0.008	<0.008	<0.060	0.04	0.031	0.24	0.013	0.012
Sr		1.99	1.82	2.81	1.97	1.80	0.766	0.734	0.642		4.85	4.99
Na	207	137	145	191	133	128	112	91.7	95.8	155	108	116
Ti	<0.014	<0.002	<0.002	<0.014	<0.002	<0.002	<0.014	<0.002	<0.002	<0.014	0.004	0.002
W	0.36	0.41	0.45	0.99	0.41	0.45	0.050	0.23	0.19	0.91	0.68	0.68
V	0.401	0.189	0.202	0.437	0.297	0.270	1.08	0.681	0.588	0.305	0.110	0.123
Zn	<0.8	0.19	0.11	<0.8	0.13	0.19	<0.8	0.20	0.18	<0.8	0.32	0.26

TABLE XIII. Leachate Compositions Using Tract C-a Upper Aquifer Water (GW) and Distilled Water (DW) (ppm)

Element	Upper Aquifer Tract C-a	R3E3-5B		R3E3-9		R3E3-10B		R3E3-18	
		DW	GW	DW	GW	DW	GW	DW	GW
Mg	>10	0.198	4.50	1.43	5.05	0.158	0.833	0.018	0.085
Si	8.08	29.8	33.1	38.6	26.1	52.9	> 60	1.2	3.14
B	0.15	1.79	1.47	12.2	8.94	4.10	3.57	0.63	1.05
Cu	0.005	<0.002	<0.003	<0.022	0.004	<0.002	0.006	<0.001	0.007
Cd	<0.01	<0.02	<0.015	<0.02	<0.015	<0.02	<0.015	<0.02	<0.02
Ca	20.7	8.4	7.0	3.8	5.3	79	66.3	266	29.6
Ti	<0.003	0.022	<0.01	0.022	0.004	<0.002	<0.01	<0.002	<0.003
Fe	<0.01	0.064	<0.01	0.48	0.028	<0.05	0.02	<0.02	<0.01
Mo	0.014	0.365	0.293	0.487	0.406	0.444	0.314	0.732	1.20
Mn	<0.01	0.028	<0.01	0.009	<0.01	<0.008	<0.015	<0.004	<0.01
Pb	0.14	0.06	<0.04	0.03	<0.04	0.06	0.05	0.16	0.052
V	0.009	0.682	0.511	1.70	1.10	0.620	0.637	0.017	0.012
Co	0.025	0.02	<0.01	0.022	<0.01	0.021	<0.01	0.019	<0.01
Al	0.052	0.022	0.011	0.56	0.009	0.070	0.030	0.097	0.055
Ba	0.23	0.058	0.027	0.047	0.028	0.123	0.046	1.30	0.227
Sr	>4	0.144	0.278	0.099	0.294	0.861	1.37	5.68	5.46
K	1.4	68.6	71.9	131	128	164	147	55.5	70.2
Ni	<0.01	0.046	<0.02	0.056	<0.02	0.046	0.04	0.021	0.04
Li	0.09	0.203	0.24	0.244	0.37	0.176	0.23	0.86	1.00
Na	133	108	208	212	302	161	264	152	246
pH	8.50	9.88	10.20	9.91	9.82	10.45	10.44	11.70	12.08
Cond (μmho/cm)	1200	890	1320	1450	1700	1670	1750	3860	3200
IC[a]	83	5	10	14	31	1	3	0	1
OC[a]	59	6	10	26	29	10	14	11	11

[a] IC = inorganic carbon; OC = organic carbon.

An analysis of these data reveals some significant differences between distilled water and groundwater leaching experiments. The most notable result is the significant decrease in concentrations of calcium, titanium, iron, lead, cobalt, aluminum, barium, and nickel in groundwater leachates compared with distilled water leachates. These elements are probably removed from solution by precipitation with the ligands carbonate/bicarbonate, hydroxide, or sulfate or by precipitate scavenging (adsorption onto precipitates). The carbonates, hydroxides, and oxides of these elements are relatively insoluble at reported leachate pHs. Experimental evidence for this removal mechanism is provided by the inorganic carbon concentrations (sum of bicarbonate and carbonate carbon). The inorganic carbon concentrations are considerably lower in groundwater leachates than in aquifer waters, suggesting that carbonate species have been removed from solution by precipitation. Additional experimental data are required to further evaluate this removal mechanism.

On the other hand, the concentrations of boron, molybdenum, vanadium, potassium, and lithium are about equal in distilled water and groundwater leachates. Differences in concentrations between these leachates generally fall within limits of experimental error and are not statistically significant. This suggests that equilibrium concentrations for these elements are controlled by secondary solubility and/or the amount of soluble material in the spent shale, rather than by an external ion supply.

The concentration of sodium, unique among all the elements studied, is approximately equal to the sum of the concentration of sodium in aquifer water and in distilled water leachates. This suggests that secondary

TABLE XIV. Leachate Compositions Using Tract C-a Lower Aquifer Water (GW) and Distilled Water (DW) (ppm).

Element	Lower Aquifer Tract C-a	R3E3-5B		R3E3-9		R3E3-10B		R3E3-18	
		DW	GW	DW	GW	DW	GW	DW	GW
Mg	3.85	0.198	0.561	1.43	1.97	0.158	0.111	0.018	0.085
Si	3.58	29.8	55.6	38.6	31.8	52.9	> 60	1.2	7.2
B	0.63	1.79	2.59	12.2	9.86	4.10	5.65	0.63	1.70
Cu	<0.003	<0.002	<0.003	<0.02	<0.003	<0.002	0.005	<0.001	0.006
Cd	<0.015	<0.02	<0.015	<0.02	<0.015	<0.02	<0.01	<0.02	<0.01
Ca	7.4	8.4	1.2	3.8	1.6	79	7.1	266	26.4
Ti	<0.003	0.022	<0.01	0.022	<0.01	<0.002	<0.01	<0.002	<0.003
Fe	<0.01	0.064	0.02	0.48	0.02	<0.05	<0.01	<0.02	0.02
Mo	<0.02	0.365	0.311	0.487	0.355	0.444	0.299	0.732	1.54
Mn	<0.02	0.028	<0.02	<0.01	<0.01	<0.008	<0.01	<0.004	<0.01
Pb	<0.1	0.06	<0.1	0.03	<0.04	0.06	<0.04	0.16	0.04
V	<0.003	0.682	0.693	1.70	1.25	0.620	0.981	0.017	0.052
Co	<0.01	0.02	<0.01	0.022	<0.01	0.021	<0.01	0.019	<0.01
Al	<0.01	0.022	0.020	0.56	0.007	0.070	0.012	0.097	0.119
Ba	0.544	0.058	0.017	0.047	0.012	0.123	0.023	1.30	0.227
Sr	0.681	0.144	0.037	0.099	0.070	0.861	1.57	5.68	2.28
K	2.5	68.6	60.9	131	120	164	131	55.5	66.7
Ni	<0.01	0.046	<0.01	0.056	0.02	0.046	0.02	<0.021	<0.01
Li	0.06	0.203	0.19	0.244	0.314	0.176	0.09	0.86	0.84
Na	293	108	271	212	362	161	341	152	426
pH	8.50	9.88	9.81	9.91	9.92	10.45	10.99	11.70	12.1
Cond (μmho/cm)	1500	890	1190	1450	1700	1670	1850	3860	3700
IC[a]	238	5	64	14	119	1	8	0	3
OC[a]	66	6	18	26	11	10	13	11	13

[a] IC = inorganic carbon; OC = organic carbon.

mineral solubilities are not important for sodium mobilization and that sodium leachate concentrations are probably controlled by the solubility of sodium-containing minerals in the spent shale.

d. Environmental Implications. It is impossible to predict the magnitude of trace element releases to be expected from a commercial *in situ* facility once a bank of retorts or the entire facility is abandoned and dewatering of the area is concluded. However, laboratory-scale studies can indeed identify the relative environmental acceptability of spent shale materials generated by *in situ* processing. In this research, we attempted to relate mineralogy and leaching behavior of field-generated materials with leachate composition and solution chemical processes. The ultimate effect of *in situ* processing on surface and groundwater quality will depend on the interaction of these factors.

It is obvious from the previous discussion that zones characterized by different mineral suites are produced, depending upon the processing conditions. Different mineral reactions will occur in materials in the retorting zone when compared with those produced as a result of the combustion process. Thus, the mineral suites encountered in this study are expected to occur in most commercial retorts. Even for ideal burns, a wide range of variability will occur from raw shale, through spent shale with partially decomposed carbonates, and finally to spent material containing partially silicated species or essentially all high-temperature silicate phases. The question of environmental acceptability of these partially retorted and partially reacted materials has been addressed in these laboratory studies of field-generated materials.

To put the leaching information in perspective, the concerns associated with increased salinity of groundwater and with increased concentrations of toxic trace elements have been divided because they are not necessarily directly related. The present study and previous results indicate that the solubility of most major cations is reduced to low levels and conductivity values are reduced with formation of high-temperature silicate products during processing. However, the calcium ion concentrations (as well as other alkaline earth elements) for sections containing only partially silicated materials or lacking silicated materials could be misleading. In these core materials, the amount of carbonate mineral aragonite is a reasonable indicator of the amount of soluble calcium available without gas recycle and water injection. Thus, it is probable that higher concentrations of alkaline earth elements would have been evident if not for this processing. However, the data show that the salinity associated with high conductivity levels and high pH values is not severe with *in situ* generated spent shales. They are in general lower compared with surface retorted material.[15,16]

As indicated previously, the trace element concern associated with leaching of *in situ* spent shales is not necessarily mitigated by formation of high-temperature silicate phases. This study indicates a positive correlation between increased mobilities of arsenic, boron, fluoride, molybdenum, nickel, and vanadium and the formation of akermanite-gehlenite solid solution. Although it is not apparent whether this is an artifact of the raw shale composition or a consequence of the extremity of conditions necessary for the formation of akermanite favoring decomposition of the original mineral residences of these elements (or indicative of the ability of the diopside-augite solid solutions to incorporate trace elements), it does suggest that not all high-temperature silicate phases render all major and trace elements insoluble. These preliminary results indicate possible benefit from using conditions that encourage diopside formation relative to akermanite formation. Further research will be necessary to corroborate these observations.

In addition to the trace elements worthy of future consideration, two major elements exhibit mobility patterns that suggest potential toxicity problems. Potassium and lithium have maximum percentage solubilities in different regions of the retort, suggesting that mobility trends may be inversely related or at least maximized under different conditions. Again, further investigation of the mechanisms responsible for these observations is appropriate.

3. Investigations of Laboratory-Retorted Spent Shales. This year, the effect of retorting temperature and input gas on spent shale mineralogy and leaching characteristics was investigated. The mineralogical analyses in progress will be presented next year. The results of the leaching experiments are discussed here.

Twenty-four laboratory retorting experiments using the conditions shown in Table XV were conducted using raw shale from the Colony Mine. The experimental reactor used in these experiments is shown in Ref. 2.

In a typical experimental run, 50 g of –3/8-in. + 20-mesh crushed oil shale was heat-treated in the vertical quartz reactor tube installed in a resistance-heated tube furnace. The required gas was metered by a Dwyer rotometer and flowed through the reactor from top to bottom. The shale was brought to temperature with the gas flowing. The system was closed except for a 5-mm-i.d. exit opening, about 24 in. from the shale, downstream from the two hydrocarbon traps. Temperatures were monitored by Type K thermocouples. The furnace controller was programmed to cycle the furnace to the desired temperature, the material was left at temperature for 6 h, and allowed to cool for about 3 h. Gas flow was maintained throughout the experiment.

The results of these experiments are shown in Table XV and Fig. 6. Complete analyses of these data await the mineralogical analyses, which are in progress. The following comments are based on observed trends in the trace element concentrations in raw and spent shale leachates.

An analysis of the available data reveals six significant conclusions. (1) Retorting increases the leachability of most elements studied. (2) Organic complexing does not appear to be a significant mechanism in mobilization of trace elements from raw shale. (3) Raw shale particle size from –100 mesh to –3/8 in. does not affect leachability. (4) Concentrations of most of the elements studied decrease at temperatures above 1073 K with a few notable exceptions. (5) Trace elements can be divided into at least five groups based on their leaching behavior (Table XVI). (6) There are some differences between leaching trends observed in retort 3E and laboratory-generated samples.

The first three columns in Table XV summarize the leaching behavior of three raw shale samples from the Colony Mine using the standard leaching test. The first column reports data for a –100-mesh sample, the second column, for a –3/8-in. sample, and the third column, for a –100-mesh sample extracted with tetrahydrofuran

TABLE XV. Leachate Composition for Various Laboratory Retorting Conditions

Temp (K)				673	873	873	1073	1273	873	873	1073	1273	873	873	873	1073	1273	873	873	1073	1073	873	1073	873	1073
Atm				N_2	N_2	N_2	N_2	N_2	CO_2	CO_2	CO_2	CO_2	Air	Air	Air	Air	Air	CO_2	CO_2	CO_2	CO_2	N_2	N_2	Air	Air
H_2O (g)				0	0	0	0	0	0	0	0	0	0	0	0	0	0	12.2	12.3	2.2	24.2	10.0	16.4	7.0	18.8
pH	10.55	8.91	8.95	11.58	12.35	12.29	11.61	10.51	11.77	11.58	11.32	11.20	12.47	12.54	12.23	11.40	10.31	11.50	11.97	11.40	11.35	12.23	11.67	12.28	11.52
Cond (μmho/cm)	520	405	420	4300	12300	11500	3170	3000	3430	3200	1400	580	11000	11100	11000	3200	1930	1850	3650	1580	1060	7040	1900	9500	3150
Al	1.6	1.9		0.544	0.503	0.542	0.738	0.374	0.211	0.261	<2	0.392	0.521	0.440	0.498	0.593	0.192	0.540	0.134	>2	>2	0.404	1.71	0.464	0.367
Ba	0.249	0.238	0.197	0.86	>10	>10	0.551	0.788	0.826	0.675	2.38	4.03	>10	>10	>10	1.19	0.579	1.90	9.53	2.01	1.63	>10	>10	>10	2.40
Be	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
B	0.625	0.651	0.672	2.01	0.36	0.13	0.05	0.11	<0.032	<0.032	0.71	0.18	0.137	0.09	0.05	0.071	0.100	0.032	0.589	0.018	0.223	0.478	0.078	0.124	0.034
Cd	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Ca	4.4	17.2	16.8	667	542	631	37.9	125	94.0	96	43.3	46.2	732	579	691	178	86.6	104	153	56.5	53.4	744	136	903	191
Co	0.020	0.017	0.021	0.048	0.056	0.038	0.051	0.056	0.012	<0.006	0.021	0.012	0.091	0.083	0.023	0.049	0.029	0.047	0.025	0.021	0.023	0.042	0.025	0.094	0.039
Cu	0.009	0.021	0.018	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Fe	0.047	0.051	0.068	0.065	0.102	0.104	<0.034	<0.034	0.038	<0.034	0.048	0.029	0.076	0.175	0.082	0.062	0.033	0.049	<0.02	0.020	0.026	0.059	0.02	0.093	0.044
Pb	<0.042	0.13	0.18	0.4	0.58	0.70	<0.042	0.07	<0.042	0.3	0.10	0.06	0.43	0.4	0.07	0.22	0.09	0.17	0.15	0.11	0.10	0.43	0.14	0.52	0.18
Li	0.109	0.064	0.065	1.21	6.61	6.00	0.972	0.944	1.11	0.87	0.258	0.158	>4	2.86	3.11	1.68	0.861	0.432	0.744	0.421	0.245	1.24	0.382	1.78	1.44
Mg	1.34	6.85	6.31	0.209	0.022	0.022	0.023	1.88	0.015	0.063	0.052	0.154	0.011	0.293	0.010	0.160	2.85	0.070	0.015	0.045	0.061	0.024	0.020	0.040	0.140
Mn	<0.006	0.014	0.026	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	0.014	0.013	<0.006	<0.006	<0.006	0.018	0.007	0.019	<0.002	<0.002	<0.002	0.009	<0.002	0.018	0.010
Hg	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mo	0.77	0.760	0.945	0.113	0.52	0.53	2.36	1.80	2.57	2.48	2.66	2.06	0.43	0.37	0.486	2.21	1.02	1.25	0.213	2.34	2.45	0.559	1.77	0.426	2.24
Ni	0.043	0.040	0.035	0.051	0.038	0.047	0.046	0.050	0.033	0.032	0.048	0.015	0.053	0.057	0.042	0.069	0.054	0.055	0.032	0.044	0.034	0.044	0.024	0.065	0.065
K	4.90	4.39	5.30	96	113	117	137	138	139	143	65.4	10.3	115	120	119	165	82.8	79.1	72.2	84.9	30.4	44.6	21.2	99.8	165
Si	1.5	1.1	1.2	1.2	0.6	0.5	19.1	6.0	8.63	14.8	1.80	20.5	0.15	0.40	0.19	20.3	7.2	14.4	1.01	4.78	5.58	0.91	1.49	0.53	16.3
Sn	<0.8	<0.8	<0.8	<0.8	0.21	0.21	<0.8	<0.8	<0.8	<0.8	<0.04	<0.04	0.15	0.12	0.14	0.09	0.04	0.04	<0.04	0.04	0.02	0.02	<0.04	0.07	0.13
Sr	0.57	0.24	0.234	7.3	>10	>10	2.23	4.06	4.21	3.62	1.61	0.326	>10	>10	>10	4.40	2.81	2.54	3.33	1.58	0.675	5.10	2.84	>10	4.16
Na	154	152	150	234	191	199	181	187	214	211	126	13.9	152	161	161	321	212	84.2	87.7	116	50.9	51.0	31.0	117	232
Tl	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ti	0.01	<0.008	<0.008	0.131	0.548	0.55	0.049	0.096	0.062	0.035	<0.004	<0.004	0.376	0.332	0.356	0.008	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
W	<0.048	<0.048	<0.048	<0.83	<0.84	<0.90	<0.048	<0.048	0.06	0.3	0.11	0.11	0.85	0.76	1.06	0.305	0.19	0.22	0.25	0.10	0.110	0.75	0.24	0.88	0.282
V	0.041	0.045	0.030	0.082	0.755	0.248	0.280	0.856	0.110	0.183	0.424	1.14	0.171	0.158	0.179	0.579	1.11	0.136	0.016	0.446	0.893	0.042	0.044	0.081	0.436
Zn	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	0.8	0.9	<0.8	<0.8	<0.8	<0.8	0.84	1.05	<0.8	<0.8	<0.8	0.92	<0.8	<0.8	<0.8	1.3	<0.8	1.7	0.7

(THF), a nonpolar solvent, for oil removal before leaching. Comparison of these three columns indicates that neither the two particle sizes investigated nor the THF extraction affects the leachability of the elements studied. This result suggests that the elements mobilized from raw shale are not soluble in THF, and therefore are available for subsequent aqueous leaching.

The rest of Table XV summarizes the results of experiments in which spent shales, produced by retorting at temperatures from 673 to 1273 K in N_2, air, and CO_2, were leached using the standard test. Most of these data are plotted in Fig. 6 as a function of maximum retorting temperature. A comparison of raw and spent shale leachate concentrations shown in Fig. 6 indicates that retorting significantly increases the leachability of most of the trace elements studied. Groups I and II elements and potassium and vanadium (Table XVI) are relatively insoluble in raw shale, and their solubility is significantly increased in spent shales for all the retorting conditions studied. Aluminum and boron, on the other hand, are relatively soluble in raw shale, but retorting decreases their solubility for all conditions except retorting in a CO_2 atmosphere at 1073 K. The solubility of nickel, sodium, magnesium, and silicon are intermediate between these two extremes. Generalizations are not possible because the leachability of these four elements in raw shale relative to spent shale depends on the specific temperature-gas atmosphere used in retorting.

Spent shale leaching trends indicate that the concentration of most trace elements decreases between 873 and 1273 K, reaching relatively low levels at 1273 K. However, this does not mean that the concentrations are not of environmental concern as some authors have suggested.[17,18] Figure 6 also shows water quality criteria for key elements (dashed horizontal line). If a concentration exceeds its limit, the resulting water is not suitable for the indicated use. A comparison of these limits with concentrations at 1273 K indicates that vanadium, molybdenum, lead, and lithium exceed recommended limits.

Although most constituents decrease at higher temperatures (such as those expected in MIS retorts), certain other elements increase at these temperatures. Both magnesium and vanadium increase rapidly with temperature from 873 to 1273 K in air, N_2, and CO_2 atmospheres. Also, potassium and nickel increase slightly with temperature in N_2 atmospheres, and barium and silicon increase rapidly in CO_2 atmosphere. Thus, although the mobility of many elements decreases at high temperatures, the mobility of certain other elements is enhanced. This result casts doubt on Smith's hypothesis that trace elements are incorporated in the high-temperature silicates formed during MIS retorting where they are "unavailable to water extraction."[17]

The concentration of a given element in spent shale leachate is uniquely determined by its mineral residence in the raw shale, by retort operating conditions, and by bulk solution chemistry of the aqueous phase. Because of the complexity of these interactions, it is not possible at present to predict trace element mobility. However, the data can be divided into five groups based on leaching characteristics as a function of temperature (Table XVI).

The Group I constituents include electrical conductivity, lithium, strontium, iron, lead, and titanium. This group is characterized by a concentration peak at 873 K for N_2 atmosphere, and leachate concentrations are approximately equal for both air and N_2 atmospheres. Retorting in a CO_2 atmosphere tends to decrease the concentration of Group I elements.

Group II consists of calcium and tungsten. The leachate concentrations of both are relatively constant and high for temperatures from 673 to 873 K, they rapidly decrease between 873 and 1073, and they level out at low values from 1073 to 1273 K. Leachate concentrations for shales processed in air atmospheres tend to be slightly higher than for shales processed in N_2 atmospheres for these two elements.

Group III elements consist of aluminum, boron, and molybdenum. The concentrations of aluminum and molybdenum peak at 1073 K in both air and N_2 atmospheres, and CO_2 significantly increases leachate concentrations of all three elements.

Group IV elements include sodium, potassium, and nickel. The similarity in sodium and potassium behavior is probably related to the occurrence of these elements in feldspars in raw shale. Their concentrations in air peak at 1073 K. Temperature has little effect on their concentrations in N_2, and CO_2 depresses their concentrations.

Group V elements include magnesium and vanadium, which occur at relatively low and constant concentrations in air, N_2, and CO_2 between 673 and 1073 K. Between 1073 and 1273 K, leachate concentrations increase rapidly.

Several other interesting trends are apparent in Fig. 6 and Table XV. First, the leaching behavior of silicon and boron are inversely related. The silicon concentration peaks at 1073 K in air and N_2 and reaches a minimum at this temperature in CO_2, whereas boron concentrations peak at 1073 in CO_2 and reach minimum in air and N_2. The barium and silicon behavior are similar, except that

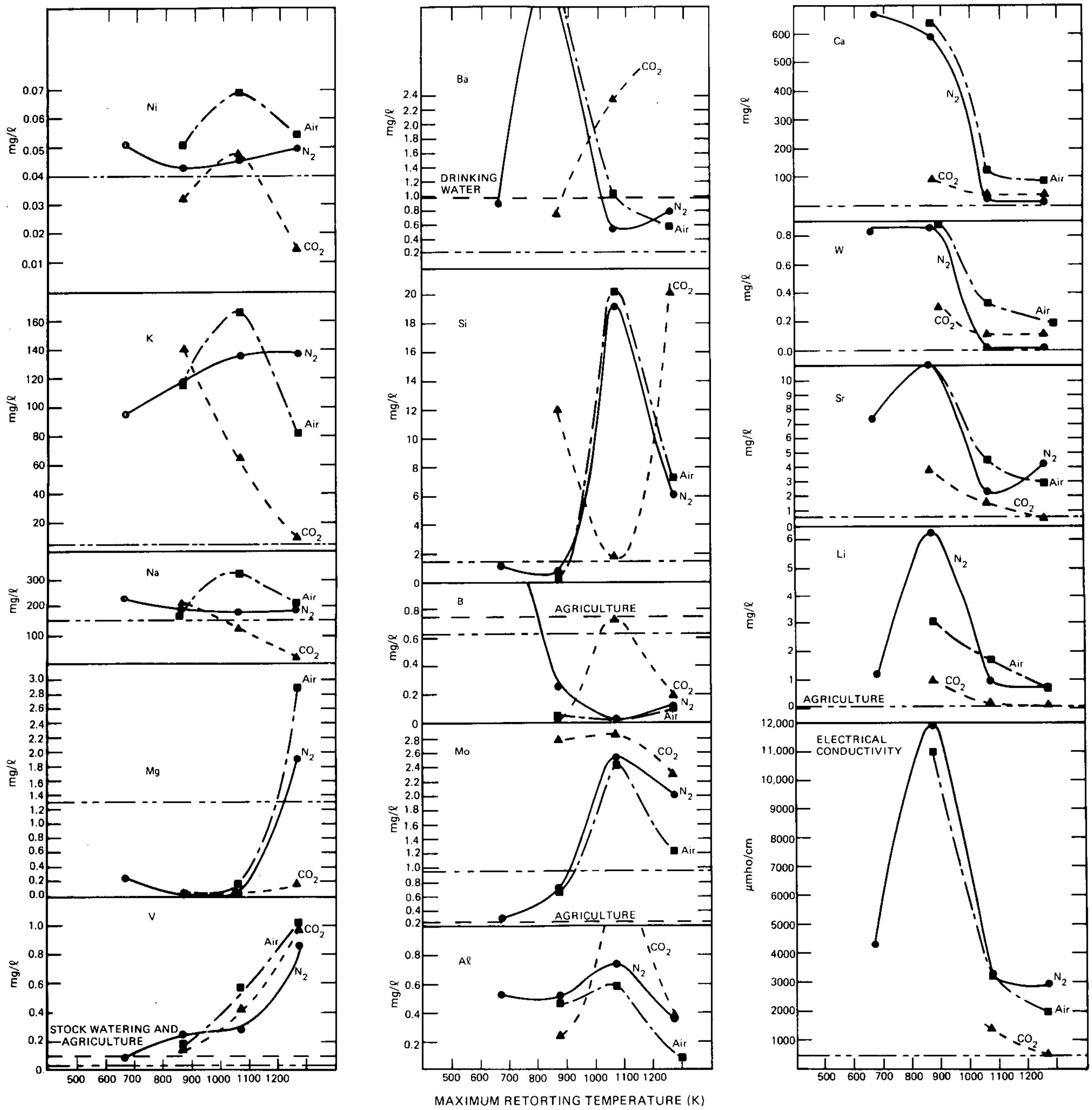


Fig. 6. Effect of retorting temperature and atmosphere on the concentrations of some trace elements in laboratory-produced spent shale leachates. Legend: ——— raw shale leachate concentration; ---- water quality criteria. The lithium water quality criterion for agricultural use coincides with the raw shale leachate concentration.

the peak concentration for barium occurs at lower temperatures. Concentrations of cobalt are relatively constant for all conditions examined. The leaching behavior of Group II (calcium, tungsten) and Group V (magnesium, vanadium) elements are inversely related. The effect of steam on the mobility of specific elements is uncertain at present because of the limited data base. However, data presented here indicate that steam decreases the electrical conductivity and some of the major elements.

Data from our laboratory heating experiments suggest a method for estimating the maximum temperature

TABLE XVI. Summary of Leaching Behavior Observed in Laboratory Heating Experiments

Group	Elements	Raw Shale Leaching Characteristics	Spent Shale Leaching Characteristics
I	Electrical Conductivity Li, Sr, Fe, Pb, Ti	Very insoluble; retorting significantly increases concentration for all conditions studied.	Concentration in N_2 peaks at 873 K; CO_2 decreases concentration.
II	Ca, W	Very insoluble; retorting significantly increases concentration for all conditions studied.	Concentration decreases with temperature above 873 K in air, CO_2, and N_2; highest concentrations occur in air atmosphere.
III	Al, Mo, B	Very soluble; retorting decreases solubility for most conditions.	Concentration in CO_2, air, and N_2 peaks at 1073 K; CO_2 increases concentration.
IV	Na, K, Ni	Moderately soluble; retorting increases solubility for most conditions.	Concentration in air peaks at 1073 K; in N_2, it is independent of temperature; CO_2 decreases concentration.
V	Mg, V	Variable.	Concentration increases with temperature for air, N_2, and CO_2.

reached in field MIS retorts such as retort 3E. The data in Table XV and Fig. 6 clearly demonstrate that the concentration of an element in leachates is a complex function of the maximum temperature and gas atmosphere. Although not investigated here, time at temperature is also important. Because the behavior of vanadium is unique among the elements studied, it may be used as an estimator of temperature. The leachate concentration of vanadium increases approximately linearly over the temperature range of interest, and it is relatively independent of gas atmosphere. The functional relationship between vanadium concentration and temperature shown in Fig. 6 was used to estimate retort 3E temperatures. The results were checked using calcium, which is inversely related to vanadium, and which also is approximately linear and independent of gas atmosphere. These elements yield temperature estimates that agree within 100 to 300 K. The accuracy of this approach depends on the effect of the concentration and form of vanadium in the original raw shale on its leaching behavior. This is presently unknown.

A comparison of the groups of trace elements identified in the laboratory heating studies (Table XV) with similar groups identified in retort 3E leachates (Table X) indicates some differences in their behavior. Groups I and II (laboratory studies) approximately correspond to Group A (retort 3E studies). The exceptions are electrical conductivity, iron, and titanium. Similarly, Groups III and IV (laboratory studies) approximately correspond to Group C (retort 3E studies) except for boron. The cause of differences in behavior of boron, iron, titanium, and electrical conductivity is uncertain and may be due to variables not considered in our laboratory studies (such as time at temperature or raw shale composition).

B. Control Technology

1. Task Description. This activity is to evaluate environmental control requirements and to identify and assess alternate strategies and technologies. This year, emphasis was focused on the control of major, minor, and trace elements in leachates from MIS retorts. We analyzed the leaching data presented in the previous section to determine environmental control requirements. The use of multistaged forced leaching and process control as means to attenuate high concentrations of some elements was also evaluated. These analyses are based on our mineralogical and leaching investigations of Occidental retort 3E.

2. Control Technology Requirements. MIS retorting will be used in the Piceance Creek Basin, where the deep continuous seams of oil shale required for this technology are located. Groundwater aquifers are located above and below the target resource, the stratigraphic horizon including the Mahogany Zone. Thus, MIS retorts will create the potential for leaching of the abandoned retorts and for intermingling of aquifer waters of variable quality. These phenomena are discussed in detail in Ref. 19. This section evaluates the magnitude and significance of groundwater contamination for *in situ* retorting and discusses control technology implications.

The impact of *in situ* leaching was estimated by comparing pre- and postdevelopment groundwater quality near MIS retorts with water quality criteria. The analysis is based on a hypothetical 300-ft-high, 120-ft by 120-ft retort containing 25% burned void volume and located at tract C-a or C-b. The results of these calculations, together with groundwater quality data and pertinent water quality criteria, are summarized in Table XVII.

Each column of Table XVII is discussed and the results of the analysis are presented. The first column, leachate concentration, summarizes the average quality of leachate from cores E2 and E3 generated in the batch experiments (Table VIII). The analysis assumes that leachate generated in a field retort at tracts C-a or C-b will have a composition similar to that in column 1. This is a reasonable assumption even though the liquid-to-solids ratio in these experiments (5 mℓ/g) differs from that for field cases (0.25 mℓ/g) because sequential and time-extended leaching experiments (Tables XI and XII) indicate that equilibrium could be reached rapidly.

TABLE XVII. Effect of *In Situ* Leachates on Groundwater Quality in Vicinity of Tracts C-a and C-b

		Postdevelopment Groundwater Quality		Predevelopment Groundwater Quality				Water Quality Criteria		
	Leachate Concentration[a] (mg/ℓ)	Hypothetical Retort[b] C-a (mg/ℓ)	Hypothetical Retort[b] C-b (mg/ℓ)	Lower Aquifer C-a (mg/ℓ)	Upper Aquifer C-a (mg/ℓ)	Lower Aquifer C-b (mg/ℓ)	Upper Aquifer C-b (mg/ℓ)	Water Supply (mg/ℓ)	Agri-culture (mg/ℓ)	Live-stock (mg/ℓ)
Al	0.253	0.49	0.55	0.24	0.15	0.3	0.3	---	5,[c] 20[d]	
As	0.021	0.03	0.04	0.01	0.01	0.02	0.01	0.1	0.1,[c] 2.0[d]	0.2
Ba	0.39	0.39	1.2	0.97	0.98	0.8	0.1	1		---
B	2.72	3.5	39	0.84	0.33	36	1.4	1.0	0.75,[c] 2.0[d]	5.0
Ca	128	135	141	8.8	34.8	14	32			---
Co	0.022	---	0.03	---	---	0.006	0.003		0.05,[c] 5.0[d]	1.0
Cu	0.005	0.09	0.06	0.09	0.07	0.06	0.09	1	0.20,[c] 5.0[d]	0.5
F	8.0	23	29	14.7	0.41	21	10	1.4-2.4	1,[c] 15[d]	2.0
Fe	0.134	0.91	0.93	0.78	5.0	0.8	0.5	0.3	5,[c] 20[d]	None[e]
Pb	0.168	---	0.20	---	---	0.03	0.01	0.05	5,[c] 10[d]	0.1
Li	0.668	0.79	11	0.13	0.13	10	---		0.075[c] 2.5[d]	---
Mg	8.25	28	19	20	52	11	42			---
Mn	0.016	0.09	0.1	0.075	0.13	0.1	0.1	0.05	0.20,[c] 10[d]	None[e]
Mo	0.638	0.7	0.7	0.1	0.13	0.04	0.02		0.010[c] 0.050[d]	---
Na	193	588	2691	397	212	2500	330	None		
Ni	0.039	0.039	0.05	<0.02	0.02	0.01	0.02		0.20,[c] 2.0[d]	
K	137	138	156	2.64	2.19	21	2.2			
Se	0.02	0.02	0.02	<0.01	0.01	0.004	0.006	0.01	0.02[c,d]	0.05
Si	26.2	31	39	4.7	12	13	17			
Sr	1.34	2.0	---	0.68	2.89	---	---			
Ti	0.015	---	0.1	---	---	0.1	0.1		None	
W	0.42	---	0.4	---	---	0.02	0.05		None	
V	0.51	0.51	0.51	<0.05	0.05	0.01	0.002		0.10,[c] 1.0[d]	0.1

[a] Average concentration for cores E2 and E3, Table VIII.

[b] Computed assuming lower aquifer water, with quality indicated in columns 4 and 6, leaching a MIS 120-ft by 300-ft retort with 25% burned void volume.

[c] Continuous irrigation, all soils.

[d] Short-term (<20 yr) irrigation, neutral to alkaline fine textured soils.

[e] A few ppm can result in clogging, staining, and deposits on watering equipment.

The second and third columns of Table XVII summarize postdevelopment groundwater quality near the hypothetical MIS retorts at tracts C-a and C-b. These concentrations assume that the retort is leached with lower aquifer water and that the groundwater quality in the retort vicinity approaches that of the leachate leaving the retort. These groundwater concentrations were calculated from

$$C_i = \frac{RM_i m/1000 + (C_g)_i nV}{nV} \quad ,$$

where

C_i = average concentration of the i^{th} constituent at the retort exit in mg/ℓ.
M_i = concentration of i^{th} constituent in batch leaching experiments in mg/ℓ.
m = mass of spent shale in a single retort = 1.21×10^{11} g.
R = liquid-to-solids ratio = 0.25 mℓ/g.
$(C_g)_i$ = concentration of i^{th} constituents in groundwater in mg/ℓ.
n = number of pore volumes required to remove soluble material = 1.
V = volume of water within a single retort = 3.06×10^7 liters.

$RM_i m/1000$ is the mass of material that could be leached from a single *in situ* retort, based on batch leaching experiments with distilled water. The second term, $(C_g)_i nV$, is the mass of the i^{th} constituent present in the groundwater that fills the retort, and the denominator nV is the total volume of water required to remove most of the soluble material. The resulting leachate concentrations in columns 2 and 3 are approximately equal to the sum of the leachate concentration from the batch experiments (column 1) and the groundwater concentrations (columns 4 and 6) for n = 1. The leaching experiments that used tract C-a groundwater (Tables XIII and XIV) indicate that the concentrations of calcium, magnesium, lead, cobalt, aluminum, barium, and strontium were reduced in groundwater leachates compared to distilled water leachates because of precipitation of carbonates, hydroxides, and/or sulfates. Therefore, the concentrations in columns 2 and 3 represent conservative upper limits on concentrations.

Columns 4-7 summarize the average composition of upper and lower aquifer waters on tracts C-a and C-b for the period 1974-1976. Columns 8-10 summarize water quality criteria for the beneficial uses of water supply, agriculture, and livestock watering. These criteria are upper limits that should not be exceeded in the main water mass, and they are based on a wealth of scientific data that are summarized in Ref. 20. These three are the most likely uses for groundwater in the Piceance Creek Basin, based on present and projected development in the area. Industrial water supply (cooling water, etc.) may become important if significant energy development occurs in the basin.

The suitability of groundwaters for these anticipated uses can be estimated by comparing the criteria in columns 8-10 with groundwater quality in columns 2-7. This comparison is presented in Table XVIII, which shows those constituents that exceed recommended limitations. This comparison has been made for three cases: (1) undeveloped, natural conditions, (2) replacement of upper aquifer water with lower aquifer water and no leaching, and (3) leaching. The second case is representative of postdevelopment conditions in which leaching is arrested but aquifer bridging is allowed. Examples include process control to eliminate soluble materials or forced leaching. The third case is representative of no control technology.

Table XVIII indicates that predevelopment groundwaters are unsuitable for many uses. These waters are presently unacceptable as a drinking water supply (boron, fluoride, iron, manganese) and as an agricultural supply (boron, fluoride, lithium, molybdenum) due to elevated concentrations of some elements. This means that these waters would have to be treated to remove these constituents before use, probably by expensive precipitation and/or ion exchange treatment. Thus, local groundwaters probably would not be developed unless other supplies were exhausted.

MIS retorting may degrade groundwater quality further by leaching and by intermingling of lower and upper aquifer waters. MIS retorts will act as conduits, connecting the upper and lower aquifers. Because the water quality in these aquifers differs, this connection will alter water quality. Initially, water from the lower aquifer will move under a hydraulic head through the retorts and into the upper aquifer, replacing upper aquifer water with lower aquifer water. This may either increase or decrease upper aquifer quality. The potential impacts of this effect may be determined by comparing column 4 with column 5 and column 6 with column 7 in Table XVII. At tract C-a, the concentrations of aluminum, boron, copper, fluoride, and sodium can be

TABLE XVIII. Summary of Potential Violations of Water Quality Criteria

	Predevelopment				Postdevelopment			
	C-a		C-b		Replacement Only		Leaching	
	Lower	Upper	Lower	Upper	C-a	C-b	C-a	C-b
Al								
As								
Ba								
B	A		A,D,L	A,D	A	A,D,L	A,D	A,D,L
Ca								
Co	---	---			---		---	
Cu								
F	A,D,L		A,D,L	A,D,L	A,D,L	A,D,L	A,D,L	A,D,L
Fe	D	A,D	D	D	D	D	D	D
Pb	---	---			---		---	D,L
Li	A	A	A	---	A	---	A	A
Mg								
Mn	D	D	D	D	D	D	D	D
Mo	A	A	A	A	A	A	A	A
Na								
Ni								
K								
Se							D	D
Si								
Sr			---	---		---		
Ti					---		---	
W					---		---	
V							A,L	A,L
Zn								

Note: The above designators indicate those water quality criteria that are exceeded in groundwaters at tracts C-a and C-b for (1) undeveloped natural conditions, (2) replacement of upper aquifer water with lower aquifer water, and (3) leaching *in situ* spent shale by lower aquifer waters. Dashes indicate that no groundwater quality data are available. A blank indicates that criteria are not set or that criteria are not exceeded. A = agriculture, D = drinking, L = livestock.

expected to increase and calcium, iron, magnesium, manganese, silicon, and strontium can be expected to decrease in the upper aquifer. And at tract C-b, vanadium, potassium, sodium, molybdenum, iron, fluoride, barium, boron, and cobalt concentrations can be expected to increase and tungsten, nickel, magnesium, calcium, copper, and selenium can be expected to decrease in the upper aquifer. However these changes will not alter significantly the suitability of the resultant water for use as a domestic, agricultural, or livestock supply. This is so because the troublesome constituents in these aquifers (boron, fluoride, iron, lithium, manganese, molybdenum) exceed criteria in *both* aquifers; only the *degree* to which criteria are exceeded differs.

Water quality may also be affected by leaching of soluble material from the spent shale. However, most of the constituents that occur at elevated concentrations in the leachates are also present at elevated concentrations in the predevelopment groundwater. This occurs because the aquifers in the area are composed of raw shale. Thus, leaching may not significantly affect the suitability of these waters for beneficial uses. There are a few exceptions. Concentrations of lead and selenium exceed federal drinking water standards and water quality criteria, lead and vanadium exceed livestock watering criteria, and vanadium exceeds recommended irrigation criteria. Lead concentrations may be reduced, however, because of carbonate precipitation. Other constituents, although elevated in the leachate relative to the native groundwater, are not elevated enough to affect potential water uses. Many other constituents, such as calcium, silicon, strontium, and titanium, although elevated in the postdevelopment groundwater, do not have any known adverse effects on domestic, agricultural, and livestock uses, and thus, are not considered important.

This analysis suggests that future research should be focused on vanadium, selenium, and lead in MIS spent shale leachates. Vanadium occurs at low concentrations (0.002-0.01 mg/ℓ) in native groundwaters in the Piceance Creek Basin. Our leaching experiments indicate that the average vanadium concentration in MIS leachates will be about 0.5 mg/ℓ. Concentrations in this range are known to be toxic to flax, soybeans, and peas. Vanadium also is known to accumulate in certain organs and is known to be toxic to chicks at concentrations above 10 mg/ℓ. The National Academy of Sciences (NAS), in a review of existing data on vanadium, recommended a maximum vanadium concentration of 0.1 mg/ℓ for continued irrigation on all soils and for livestock watering.[20]

Lead also occurs at low concentrations in native groundwaters in the Piceance Creek Basin (0.01 to 0.03 mg/ℓ). The few high concentrations observed are believed to be due to analytical problems. These leaching experiments indicate that lead can be mobilized from MIS spent shale, and mean concentrations of 0.2 mg/ℓ may result in the leachates. Lead is well known for its toxicity in both acute and chronic exposures. Acute lead toxicity is characterized by burning in the mouth, severe thirst, inflammation of the gastrointestinal tract with vomiting and diarrhea. Chronic toxicity produces anorexia, nausea, vomiting, severe abdominal pain, paralysis, mental confusion, visual disturbances, anemia, and convulsions. For livestock water, cattle and sheep are considerably more resistant to lead toxicosis than are horses, but there is some tendency for lead to accumulate in tissues and to be transferred to milk at levels that could be toxic to man. These considerations led the NAS to recommend a maximum level for lead in livestock water of 0.1 mg/ℓ and for domestic water supplies, of 0.05 mg/ℓ. Since these criteria are exceeded by a factor of 5 to 10 in MIS leachates, lead may have to be removed before these waters can be used, if precipitation reactions do not limit solubility to the required level.

Elevated concentrations of selenium were also noted in MIS leachates. Selenium occurs at low concentrations (0.004 to <0.01 mg/ℓ) in native groundwater of the Piceance Creek Basin. Acute selenium toxicity is characterized by nervousness, vomiting, cough, dyspnea, convulsions, abdominal pain, diarrhea, hypertension, and respiratory failure. Chronic exposure leads to marked pallor, red staining of fingers, teeth, and hair, debility, depression, epistaxis, gastrointestinal disturbances, dermatitis, and irritation of the nose and throat. Because of these known toxic effects, the NAS recommended a maximum concentration in domestic water supply of 0.01 mg/ℓ. This level is exceeded by a factor of 2 in MIS leachates, and thus, removal of selenium may be required.

This analysis indicates that groundwaters in the Piceance Creek Basin are unsuitable for use as irrigation, domestic, or livestock watering supplies, and that extensive treatment would be required before wide-scale development of this water resource could take place. MIS retorting in this area would alter existing water quality as a consequence of leaching and intermingling of lower and upper aquifer waters. Leaching would generally increase the concentrations of elements such as fluoride and boron, which are already high in native groundwaters, and of certain additional elements that are not elevated at present. This would increase the hazard of using these waters and also the cost of treating them. Intermingling does not appear to be a significant concern because the toxic elements are elevated in both aquifers.

These conclusions have some interesting environmental control technology implications. First, they reveal that intermingling of upper and lower aquifer waters will not alter the acceptability of the resulting waters for projected beneficial uses. This means that control technologies applied to this problem need not prevent aquifer bridging. Thus, less expensive technologies, such as process control and forced leaching, may be used instead of the more expensive technologies that reduce flow through the retorts (grouting, grout curtains). Two of these less expensive technologies, forced multistaged leaching and process control, are evaluated later in this report. Second, they demonstrate that certain trace elements, such as vanadium, selenium, and lead, may be significantly elevated above background concentrations and may have to be removed before the waters can be used. The area is sparsely populated and most water users would be individuals or single farms and ranches, so it is unlikely that treatment would be affordable or even that its requirement would be known. Because some of the constituents in postdevelopment groundwaters may be toxic or carcinogenic, the use of these waters by unsuspecting parties could result in local or regional public health problems. Thus, developers will have to take steps to assure that public health and agricultural production are protected.

3. **Process Control.** Other authors (listed in Ref. 1) have suggested that MIS spent shale leachate concentrations might be controlled by selecting retorting conditions that minimize the solubility of chemical constituents. Although not previously suggested, this concept can be extended to surface retorted spent shales, which will be evaluated in the future.

A number of previous studies (listed in Ref. 1) showed that the leachability of organics and inorganics from spent shales depends upon retort operating conditions. These authors also suggested that combustion retorting in the presence of steam at slow retorting rates and high temperatures (>1200 K) would minimize the leachability of spent shales. Because these were the conditions already anticipated for MIS retorting, it was concluded that MIS spent shale leachates would not pose an environmental problem. However, this early optimism was based on a limited number of chemical parameters: electrical conductivity, organic carbon, and certain major ions.[17,18] Similarly, leachability was enhanced at temperatures of 873 to 1073 K, the conditions anticipated for most surface retorts.

The present work has extended these studies to include important minor and trace elements of potential environmental concern, as well as certain major ions in these studies of retort 3E and of laboratory heat-treated materials. The data have been analyzed to evaluate leachate modification by process control. This work indicates that process control may not be a tenable control strategy for MIS leachates because of (1) effects of minor mineralogy on spent shale leachability, (2) inverse relationship at high temperatures between many environmentally important elements, and (3) difficulty of achieving uniform operating conditions in field retorts. The previous evaluation of control technology requirements indicated that the elements of greatest concern from an environmental standpoint are lead, vanadium, and selenium. The following discussion reaffirms that conclusion and demonstrates that it may not be possible to control all three elements simultaneously using process modifications; however, it also indicates that further research is required to understand the relationships among retorting conditions, mineralogy, and leachability so that these preliminary conclusions can be verified.

Both laboratory heat-treatment studies and the retort 3E investigation demonstrated that although some element concentrations decrease at high temperatures, others increase. And, although the concentrations of many elements are indeed lower at these high temperatures, they still exceed recommended environmental limits (Table XVIII).

The laboratory heat-treatment study showed that both magnesium and vanadium concentrations increased rapidly with temperature from 873 to 1273 K in air, N_2, and CO_2, and that barium, potassium, and nickel also may increase with temperature, depending on the gas composition. A comparison of the leachate concentration at 1273 K with recommended water quality criteria (Fig. 5) indicates that vanadium, molybdenum, lead, and lithium exceed these limits. Since vanadium and lead concentrations are now low in groundwaters in the region, these two elements may pose an environmental problem.

The field leaching studies, on the other hand, demonstrated that many of the trace elements in MIS spent shale leachates are inversely related; that is, as the concentration of one element decreases, the concentration of the others increases. This inverse behavior may be due to secondary solubility controls in the aqueous phase (such as between calcium and fluoride) or due to spent shale mineralogy. This work identified three groups of elements, based on their behavior in leachates (Table X). Most of the environmentally important elements are in Groups A and B. Group A, which includes the carbonate-forming elements lithium, strontium, lead, barium, calcium, and tungsten, are inversely related to Group B, which includes titanium, fluoride, vanadium, boron, silicon, arsenic, selenium, and iron. In general, the conditions encountered in MIS retorts enhance the concentrations of Group B elements and decrease the concentrations of Group A elements in leachates. Since both groups contain trace elements of potential environmental concern (lithium and lead in Group A, and fluoride, vanadium, boron, and iron in Group B), it may not be possible to control trace element leachate concentrations by controlling retort operating conditions.

A comparison of the leachate concentrations from cores E2 and E3 (Fig. 4) with recommended water quality criteria (Table XVII) indicates that lithium, fluoride, molybdenum, vanadium, boron, manganese, lead, and iron exceed these limits in most of the samples. Most of the elements that exceed these criteria are in Group B, which are the most mobile at Logan Wash after MIS processing. It would be technically difficult and expensive to modify retorting conditions to minimize the concentration of the Group B elements. First, the precise temperature control required would be hard to obtain in MIS retorts. Second, the conditions that minimize these elements would significantly reduce oil yields, adversely affecting process economics.

And finally, it may be difficult to control retorting conditions within narrow enough limits to achieve environmental goals. The leaching studies on the retort 3E material indicate that spent shales and their leachates are inhomogeneous because of raw shale mineralogy and nonuniform retorting conditions. Most process developers believe that close control to eliminate these variations will be difficult and/or impractical.

4. **Multistaged Leaching.** A preliminary engineering and economic analysis was performed on the feasibility of using countercurrent multistage leaching for mitigation of elevated trace element concentrations in flooded, abandoned MIS retorts. A laboratory protocol was developed for experimental evaluation of the strategy.[21]

a. Engineering and Economic Analysis. Persoff and Fox[1] indicate that the concentration of many elements in MIS leachates may be satisfactorily reduced by intentionally leaching the retorts and treating the leachate. However, the large volume of water required, 580-660 gal. per barrel of oil, may exceed available water supplies and result in high pumping and water treatment costs. To reduce the expense and the amount of water required, multistaged leaching has been proposed and evaluated as an alternative to the single-stage system proposed by Persoff and Fox.

Multistage counterflow leaching means that the overflow solution (water, in this case) from one contactor is used as feed leach solution to another contactor that has had fewer leaches. This continues in progression for as many stages as necessary for the desired reduction in soluble contaminants. "Clean" wash water is first admitted to a contactor containing nearly "clean" solids and progressively moves to "dirtier" solids until it encounters a completely "unwashed" material. The very dirty (highly concentrated) overflow from this last stage is then sent (pumped to the surface) to some recovery/disposal process. This technology is well established in the extractive industries and has been the subject of quantitative engineering evaluation.[22,23] Some of these procedures were used to evaluate the process. A hypothetical system is proposed, its major components are priced, and its ability to reduce the concentration of trace elements is evaluated by solubility calculations.

- *Hypothetical System Design.* A schematic for the proposed system is shown in Fig. 7 and pertinent assumptions and parameters used in the cost comparison are summarized in Table XIX. A realistic

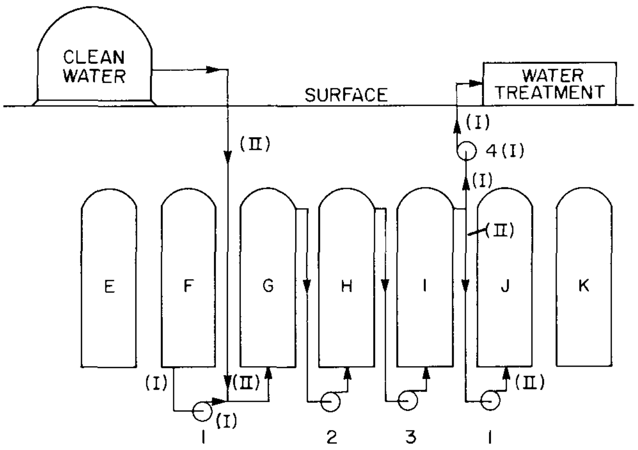


Fig. 7. Schematic of multistage counterflow leaching.

TABLE XIX. Assumptions and Parameters Used in Forced Leaching Cost Comparisons

Size of plant	50 000 bbl/day
Operating days per year	300 days
Assay and yield	25 gal./ton; 60%
Retort size	120 by 120 by 300 ft
Retort position	retort bottom is 800 ft below surface
Mined shale	20%
Void volume after burn	25%
Mass of rubbled shale	291 133 tons
Pumping efficiency	81%
Retort head loss	20 ft
Piping length and diameter	4400 ft of 8-in. welded steel pipe
Electrical energy cost	$0.05/kWh
Rehydration	Water for rehydration of the spent shale was not included in calculating total consumptive use. Calculations were made for both 25 and 50 vol% water uptake by burned shale.
Number of stages	The conditions for underground multistage leaching are such that each retort can only pass through an odd number of stages. Three and seven were chosen for evaluation. The smallest number of individual leaches (if required at all) would probably be two, but for direct comparison with multistage, three was chosen. The smallest number of multistage might be three with seven another possibility.

retort configuration and a mine site were assumed to emphasize the advantages of multistage leaching without the necessity of calculating costs that depend on site-specific leachate compositions (unknown). A block of n = 30+ retorts was assumed, with sequential ignition of burns proceeding from one edge of the block to the opposite edge over a period of time. The leaching procedure began at the burned-out edge of the block while the center and far edge were still burning if crude oil collection and mine safety arrangements permitted. Mine dewatering water from nearby blocks was assumed to be available.

Processed retorts would already have a bottom connection that could be used as a solution inlet to provide upflow in the retort, except for one final drainage step. A horizontal overflow pipe level with the top of the retort could probably take advantage of the air/steam inlet used for the burn.

- *Calculated Comparisons of Leaching Options.* Tables XX-XXII present comparative data for four postulated leaching conditions: (1) three pore-volume leaches in a single-staged system, (2) three-stage counterflow leaching, (3) seven pore-volume leaches in a single-staged system, and (4) seven-stage counterflow leaching.

Table XX shows water consumption for these conditions in three ways: (1) per retort leached, (2) per barrel of product, assuming all retorts are leached, and (3) per year, assuming all retorts are leached. This table indicates that multistaged leaching significantly reduces the water demand for forced leaching of MIS retorts. A three-stage system (16 gal./bbl) reduces the water demand by 54% relative to a single-stage system using three pore-volume (35 gal./bbl), and a seven-staged system reduces the demand by 77% from 82 gal./bbl to 19 gal./bbl. The water consumption for the two multistaged options evaluated here, 16 and 19 gal./bbl for three and seven stages, is 15 to 30% of the total projected water consumption for a MIS process, exclusive of retort abandonment.[19] Recent dewatering studies by Mehran et al.[24] for tracts C-a and C-b suggest that there will be adequate dewatering water in the center of the basin for forced multistaged leaching.[17] However, it may be difficult to reliably meet the demand of 35-82 gal./bbl for single-staged leaching using three and seven pore-volume leaches. The energy required to pump water between retorts and to the surface treatment plant was calculated from postulated design and operating parameters. Both frictional losses in the piping and the retort and potential energy losses are included. The kinetic energy loss was omitted as negligible and the turbulence losses in fittings were not considered. Because turbulence losses cannot be calculated without a detailed piping layout (unavailable at this time), the calculations could be low by 1 or 2%. Table XXI shows the comparisons, indicating a major saving of high-quality energy with multistage leaching. Savings in electrical energy are a minor consideration;

TABLE XX. Comparative Use of Water for Forced Leaching

Leach Method	Per Retort (MGD)	Per Barrel Crude (gal.)	Per Year (MGD)
3 individual p-v leaches	3.6	35	524
3-stage counterflow leaching	1.6	16	233
7 individual p-v leaches	8.5	82	1224
7-stage counterflow leaching	2.0	19	291

TABLE XXI. Annual Electricity Consumption and Cost of Pumping Energy

Leach Method	Energy Consumption (kWh)	Cost ($)[a]
3 individual p-v leaches	9 404 000	470 000
3-stage counterflow leaching	~3 900 000[b]	~195 000[b]
7 individual p-v leaches	21 844 000	1 097 000
7-stage counterflow leaching	3 922 000	196 000

[a]Electricity cost $0.05/kWh.
[b]Estimated.

TABLE XXII. Relative Capacities of Water Treatment Plant and Sludge Disposal Pond (gal./day)

Leach Method	Plant Capacity	Disposal Capacity
3 individual p-v leaches	11 653 000	1 748 000
3-stage counterflow leaching	3 885 000	777 000
7 individual p-v leaches	27 192 000	4 079 000
7-stage counterflow leaching	3 885 000	971 000

the maximum anticipated savings amount to only $0.05 per barrel of product.

The big savings, in terms of dollars, would be accrued by reducing the size of water treatment and disposal facilities. The most important elements of costs are the capital and operating costs of the water treatment plant for leachate and of the disposal area for reject water and/or sludge. Neither can be determined accurately at present, but the relative costs can be estimated from comparative projected capacities. The data are more accurate for the treatment plant than for the disposal area because we have a better idea of the variables determining throughput volume than those involved in reject volume. In both cases, capital costs are roughly proportional to daily volume. The comparative information on daily volumes is shown in Table XXII in terms of gallons per day of throughput and waste.

A very rough estimate of the possible savings using multistage as compared with individual pore-volume leaches is $0.50 per barrel ($132 per m^3) of product. This saving would be possible if the average retort required three to five volumes to meet acceptable quality standards. Obviously, the less treatment required, the smaller the plant needed, so the per-barrel savings in plant size would be reduced.

- *Evaluation of Effectiveness of Multistaged Leaching.* The amount of material that can be removed by forced leaching depends on the solubility of the spent shale mineral phases in contact with the leach water (primary solubility) and on the solubility of the leached constituents in the resulting leachate (secondary solubility). The preliminary evaluation, reported here, indicates that both primary and secondary solubilities may limit the application of the multistaged concept. However, because of system complexity and limited data, a more exhaustive experimental test will be conducted next year. The procedure is presented in the next section.

Primary and secondary solubilities can be estimated by sophisticated chemical modeling techniques, or they can be evaluated experimentally. The modeling approach is beyond the scope of this study. We conducted some simple preliminary batch experiments to evaluate the chemical issues involved in multistaged leaching, and we have developed an experimental protocol for more sophisticated experiments, which will be implemented next year.

This year, the effect of primary and secondary solubility controls on multistaged forced leaching has been estimated using the leaching experiments reported in Tables XI and XII. The data from the sequential (Table XI) and extended (Table XII) leaching experiments are summarized in Table XXIII in terms of observed trends. In this table, D signifies that the concentration increases, and C signifies that the concentration remains constant, for either successive 2-day leaches or for increasing time (2-28 days).

In the sequential leaching experiments, samples were batch leached for 2 days, dried, and releached. These experiments give an indication of the potential for exhaustion of the soluble material in spent shale. Most of the leachable material should be removed by forced leaching in a small number of pore volumes if the method

TABLE XXIII. Evaluation of Primary and Secondary Solubility Controls Using Results of Sequential (Table XI) and Extended (Table XII) Leaching Experiments

Element	Sequential Leaching Experiments	Extended Leaching Experiments
Al	?	C
As	C	?
Ba	C	C
B	D	I
Ca	C	C
Co	?	I
Cu	?	?
F	C	?
Fe	?	?
Pb	?	C
Li	C	C
Mg	C	C
Mn	?	?
Mo	D	C
Ni	C	I
K	D	C
Se	?	?
Si	C	C
Sr	C	C
Na	C	C
Ti	?	?
W	?	C
V	D	C

C = concentration remains constant
D = concentration decreases
I = concentration increases for conditions of experiment (Tables XI and XII)
? = data inconclusive

is to be economic and effective. A decrease in concentration for successive leaches indicates that soluble material is being removed. Column 1 of Table XXIII indicates that boron, molybdenum, potassium, and vanadium can be removed from spent shales by multistaged leaching. The results for all other constituents were either inconclusive (indicated by a question mark) or the concentration remained constant (arsenic, barium, calcium, fluoride, lithium, magnesium, nickel, silicon, strontium, and sodium) for three fresh-water changes, indicating that the soluble material was not exhausted. Thus, the apparently large reservoirs of readily soluble material may limit the use of forced leaching. However, drying, which would not occur in a field application of this method, may result in the deposition of readily soluble salts on the surface of the spent shale. Continuous-flow experiments are required to better define the amount of material that can be removed by multistaged leaching.

In the extended experiments, spent shales were leached for up to 28 days and these leachates were analyzed at 2-, 7-, and 28-day intervals. An increase in the aqueous phase concentration over time indicates that secondary solubility does not control the concentration and that successive leaches will continue to remove the constituent. Thus, we expect boron, cobalt, and nickel to be removed in successive stages of a multistaged leaching system. On the other hand, those elements for which the concentration remains constant over time are probably controlled by primary or secondary solubility. This means that the leachate solution is saturated, and successive leaches will not remove additional material, even if soluble material is present in the spent shale. Thus, solubility controls could limit the application of multistaged leaching and may require the use of individual pore-volume leaches with fresh leaching solution. The data in Table XIX indicate that most of the elements studied here (aluminum, barium, calcium, lead, lithium, magnesium, molybdenum, potassium, silicon, strontium, sodium, tungsten, and vanadium) may be controlled by reservoirs of soluble material. However, secondary mineral control of leachate composition may actually enhance the desirability of multistage leaching by producing mineral suites that immobilize trace elements that may otherwise be mobile without this mineral control.

b. Experimental Protocol. The major uncertainties associated with multistaged leaching involve the leaching behavior of spent shales in a multistage mode and the contaminant loading of the leachate at various stages of the procedure. These questions will be addressed in order to assess the feasibility of this approach. An experimental protocol for laboratory studies has been developed this year and will be implemented next year.

Multistaged leaching is not readily amenable to standard computational methods in such complex systems as forced spent shale leaching because of common-ion effects, solubility controls, ion exchange reactions, and kinetic controls. Thus, continuous-flow laboratory experiments will be conducted to complement the preliminary batch experiments reported this year. An experimental protocol has been developed and is described here.

In forced multistaged leaching, soluble material in spent shale is transferred to the aqueous phase, which will probably be dewatering water. This is carried out in a number of steps called equilibrium or ideal stages, which means that the solution leaving a stage has the same composition as that in the bulk of the reactor. To evaluate and design such a system, the number of ideal stages required to meet environmental goals must be determined, and experiments must be performed for each stage. Three to eight upflow reactors, 5.0-cm i.d. by 6.5 cm high, in series (Fig. 8), will be used. The reactors will

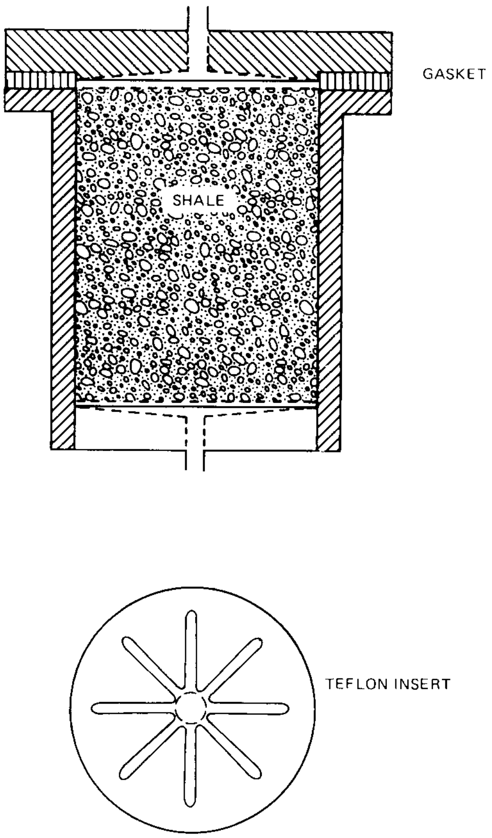


Fig. 8. Schematic of reactor used to evaluate multistage leaching.

be packed with prewet spent shale and they will be operated to simulate a filling time of 1 week. Initial experiments will use distilled water and will evaluate deviations from ideality as particle size increases and approach equilibrium as soaking time increases. Key trace elements, total dissolved solids, and total organic carbon will be measured between stages and in the leach water and system effluent.

We will also evaluate experimental treatment of the resulting leachates. The use of alum flocculation for the removal of organics and polyvalent metal ions and the use of reverse osmosis for the removal of total dissolved solids will be investigated.

REFERENCES

1. P. Persoff and J. P. Fox, "Control Strategies for Abandoned In-Situ Oil Shale Retorts," Lawrence Berkeley Laboratory report LBL-9040 (April 1979).

2. P. Wagner, E. J. Peterson, and P. L. Wanek, "Assessment and Control of Water Contamination Associated with Shale Oil Extraction and Processing, October 1, 1978—September 30, 1979," Los Alamos National Laboratory report LA-8506-PR (March 1981).

3. "Environmental Research on a Modified In-Situ Oil Shale Process: A Progress Report from the Oil Shale Task Force," US Department of Energy report DOE/EV-0078 (1980).

4. G. A. Desborough, Janet K. Pitman, and Claude Huffman, Jr., "Concentration and Mineralogical Residence of Elements in Rich Oil Shales of the Green River Formation, Piceance Creek Basin, Colorado, and the Uinta Basin, Utah—A Preliminary Report," Chem. Geol. 17, 13-26 (1976).

5. W. A. Robb and J. W. Smith, "Mineral Profile of the Green River Formation Oil Shales at Colorado Core Hole No. 1," in *Guidebook to the Energy Resources of the Piceance Creek Basin, Colorado,* D. K. Murray, Ed. (Rocky Mountain Association of Geologists, Denver, Colorado, 1974), pp. 91-100.

6. W. A. Robb and J. W. Smith, "Mineral and Organic Relationships Through Colorado's Green River Formation Across Its Saline Depositional Center," in *10th Oil Shale Symposium Proceedings,* John B. Reubens, Ed. (Colorado School of Mines, Golden, Colorado, 1977), pp. 136-147.

7. R. D. Giauque, J. P. Fox, and J. W. Smith, "Characterization of Core Holes from the Naval Oil Shale Reserve Number 1," Lawrence Berkeley Laboratory report LBL-10809 (December 1980).

8. J. H. Campbell, "The Kinetics of Decomposition of Colorado Oil Shale, II. Carbonate Minerals," Lawrence Livermore Laboratory report UCRL-52089-9 (1978).

9. A. K. Burnham, E. T. Stubblefield, and J. H. Campbell, "Effects of Gas Environment on Mineral Reactions in Colorado Oil Shale," Lawrence Livermore Laboratory report UCRL-81951 (1979).

10. M. A. Hasanain, A. L. Hines, C. L. Murphy, and J. J. Duvall, "Sorption of SO_2 on Spent Shale in Packed Beds," Proc. Second Pacific Chemical Engineering Congress, Vol. I, p. 416 (1977).

11. E. J. Peterson, A. Henicksman, and P. Wagner, "Investigations of Occidental Oil Shale, Inc., Retort 3E Spent Shales," Los Alamos National Laboratory report LA-8792-MS (June 1981).

12. W. C. Park, A. E. Lindemanis, and G. A. Raab, "Mineral Changes During Oil Shale Retorting," *In Situ* 3, 4, 353-381 (1979).

13. J. P. Fox, "The Partitioning of Major, Minor, and Trace Elements During Simulated In-Situ Oil Shale Retorting," Ph.D. Dissertation, University of California at Berkeley (1980).

14. W. A. Deer, R. A. Howie, and J. Zussman, *Rock-Forming Minerals,* Vol. 1 *(Ortho and Ring Silicates)* and Vol. 2 *(Chain Silicates)* (Longman Group, Ltd, London, 1962), pp. 237 and 42.

15. T. R. Garland, R. E. Wildung, and H. P. Harbert, "Influence of Irrigation and Weathering Reactions on the Composition of Percolates from Retorted Oil Shale in Field Lysimeters," in *12th Oil Shale Symposium Proceedings,* James H. Gary, Ed. (Colorado School of Mines, Golden, Colorado, 1979), p. 52.

16. D. D. Runnels, "Geochemistry of Oil Shale Leachates," in "Trace Elements in Oil Shale," Willard R. Chappell, Ed., University of Colorado report COO-10298-1 (1980), p. 186.

17. J. W. Smith, W. A. Robb, and N. B. Young, "High Temperature Reactions of Oil Shale Minerals and Their Benefit to Oil Shale Processing in Place," in *11th Oil Shale Symposium Proceedings* (Colorado School of Mines, Golden, Colorado, 1978).

18. M. C. Tom Kuo, W. C. Park, A. Lindemanis, R. E. Lumpkin, and L. E. Compton, "Inorganics Leaching of Spent Shale from Modified In Situ Processing," in *12th Oil Shale Symposium Proceedings*, James H. Gary, Ed. (Colorado School of Mines, Golden, Colorado, 1979).

19. J. P. Fox, "Water-Related Impacts of *In Situ* Oil Shale Processing," Lawrence Berkeley Laboratory report LBL-6300 (December 1980).

20. *Water Quality Criteria 1972*, A Report of the Committee on Water Quality Criteria, Environmental Studies Board, National Academy of Sciences (1972).

21. E. F. Thode, E. J. Peterson, and P. Wagner, "Multistage Leaching of Spent Modified *In Situ* Oil Shale Retorts," Los Alamos National Laboratory report LA-8744-MS (April 1981).

22. E. M. Baker, "Simplifying the Calculation for Countercurrent Extraction," Chem. Metall. Eng. **42**, 669-71 (1935).

23. W. L. McCabe, *Unit Operations of Chemical Engineering* (McGraw-Hill Book Co., New York, 1956), p. 760.

24. M. Mehran, T. N. Narasimhan, and J. P. Fox, "An Investigation of Dewatering for the Modified *In Situ* Retorting Process, Piceance Creek Basin, Colorado," Lawrence Berkeley Laboratory report LBL-11819 (October 1980).

APPENDIX A

SAMPLE RECOVERY, FISCHER ASSAY RESULTS, AND SAMPLE INVENTORY FOR CORES R3E2 AND E3

I. SAMPLE RECOVERY AND FISCHER ASSAY RESULTS

The percent material recovery for cores E2 and E3 is shown in Fig. A-1, which shows that inefficient coring operations yielded recovery of less than half the available material in most sections. The highest recoveries were obtained in the top half of the retort. Most of these samples were well combusted and consisted of moist and caked material. Very poor material recoveries were achieved in the lower half in the more friable, dry, or dense material.

Fischer Assay results for retort 3E, also presented in Fig. A-1, indicate that the highest oil yields occur in the bottom of the retort, below the point at which combustion terminated.

II. SAMPLE INVENTORY

An inventory of spent shale samples from cores E2 and E3, together with sample depth, section number, and sample weight and description are presented in Table A-I. The zones delineated in Table IV (main text) and noted in this summary indicate that the physical descriptions are consistent with the zonation determined by mineralogy.

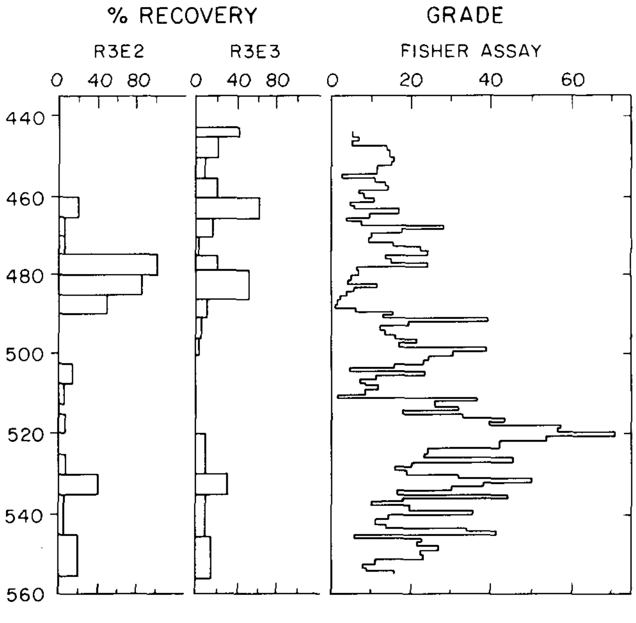


Fig. A-1. Material recovery and Fischer assay results for retort 3E.

TABLE A-I. Sample Inventory/Spent Shale Cores from Retort 3E

Section	Absolute Elevation (ft)	Sample No.	Weight (g)	Comment
				CORE R3E2
1	7788	122179-R3E2-1	36	Two solid yellow-orange chunks, layering evident.
2	7783	122179-R3E2-2	29	Two chunks, one yellow-orange and one beige. Both with layering.
3	7778	122179-R3E2-3	39	Moist yellow-orange material in small pieces. Pungent odor.
4 Top	7773	122179-R3E2-4T	166	Moist, crumbly, yellow-orange material.
4 Middle		122179-R3E2-4M	13	Yellow-orange dirtlike material.
4 Bottom		122179-R3E2-4B	96	Caked yellow-orange material previously moist.
5 Top	7768	122179-R3E2-5T	129	Caked, dirtlike, yellow-orange material.
5 Middle		122179-R3E2-5M	144	Caked, dirtlike, yellow-orange material.
5 Bottom		122179-R3E2-5B	87	Dirtlike yellow-orange material with, possibly, 2 intact chunks.
6 Top	7764	122179-R3E2-6T	207	Yellow-orange fine material with several chunks.
6 Bottom		122179-R3E2-6B	102	Yellow-orange fine material with several chunks.
7	7753	122179-R3E2-7	52	One intact chunk, beige.
8	7743	122179-R3E2-8	87	One large grayish-brown chunk, layered.
9	7738	122179-R3E2-9	28	One layered brownish chunk.
10	7728	122179-R3E2-10	77	One large chunk, some layering, brown with grayish areas.
11 A	7718	122179-R3E2-11A	81	Few whitish chunks ($\sim\frac{1}{2}$ in.), one layer charcoal-gray with holes, some fine material.
11B		122179-R3E2-11B	57	Two large blackish chunks with holes and whitish coating.
12	7711	122179-R3E2-12	33	Two chunks, blackish with brown coating.
13T	7701	122179-R3E2-13T	140	Moist blackish chunks of various sizes.
13B		122179-R3E2-13B	54	Hard, heavy, intact blackish chunk with some fine material.
14	7691	122179-R3E2-14	212	Several hard layered chunks with brownish-gray layers and some blackened areas.
				CORE R3E3
1	7807	122779-R3E3-1	311	Gummy dark-brown material, moist.
2T	7802	122779-R3E3-2T	44	Light-gray chunk with no layering evident; some tan material.
2B		122779-R3E3-2B	11	Light-gray chunks with pumicelike appearance.
3	7797	122779-R3E3-3	43	Light-gray chunk with yellowish to rusty brown lines and light-yellow coating.
4	7792	122779-R3E3-4	14	One thin light-gray piece. One light-tan, slightly layered piece.
5T	7787	122779-R3E3-5T	22	Light-tan chunk, slightly layered with one pronounced white layer.
5M		122779-R3E3-5M	18	Light-tan layered chunk with whitish patches.
5B		122779-R3E3-5B	20	Light-tan layered chunk. One dark-gray chunk with no obvious layers.
7	7777	122779-R3E3-7	21	Dark-brown layered chunk.
8	7773	122779-R3E3-8	30	Flat chunks, light-gray yellowish, w/prominent layers.
9	7770	122779-R3E3-9	37	Layered pieces varying from white to light-yellow tan.
10T	7767	122779-R3E3-10T	57	Layered chunks from pink to drab brown.
10M		122779-R3E3-10M	90	Layered chunks from pink to drab brown.
10B		122779-R3E3-10B	80	Layered pieces dark-gray to greenish-white.
11	7762	122779-R3E3-11	45	Light-tan layered chunk.
13	7752	122779-R3E3-13	18	Charcoal-gray chunks with cracked layers.
17	7724	122779-R3E3-17	46	Light- to dark-gray chunks.
18	7716	122779-R3E3-18	61	Dense charcoal-gray chunks.
19	7709	122779-R3E3-19	69	Two black chunks with pinkish, greenish patches.
20	7699	122779-R3E3-20	31	Dense black piece with small rust-colored patch.

APPENDIX B

REPRODUCIBILITY OF STANDARD LEACHING TEST

The reproducibility of the standard leaching procedure was tested by using four splits of spent shale from section 6T of core E2 and repeating the standard test described in Ref. 2 under identical conditions. The results of these experiments are shown in Table B-I.

Experiments OSL-6-1, -2, and -3 were carried out simultaneously, and experiment OSL-6-24 was conducted several months after the initial leaching experiments. Table B-I shows that the experimental leaching technique used for study of Occidental core material is reproducible. Concentrations of major, minor, and trace elements, pH values, and conductivities are in generally good agreement for the four leachates. These observations suggest that the experimental technique is not a variable in comparisons of analytical results for leachates generated from different solid spent shale materials. The physical and/or dynamic processes that affect leachate composition are either negated or at least standardized; thus, leaching results can be compared and contrasted on the basis of thermodynamic and chemical considerations with minimal influence from other effects.

TABLE B-I. Analytical Results for 48-Hour Leaching Experiments of Core Section R3E2-6T

	OSL-6-1	OSL-6-2	OSL-6-3	OSL-6-24
pH	10.35	10.34	10.35	10.15
Cond (μmho/cm)	1070	1120	1120	1180
Al	0.148	0.075	0.121	0.052
As	<0.5	<0.5	<0.5	(0.026)
Ba	---	---	---	0.028
Be	<0.001	<0.001	<0.001	<0.001
B	6.55	6.66	6.76	6.52
Cd	<0.014	<0.014	<0.014	<0.081
Ca	4.51	4.25	4.37	4.49
Co	<0.012	<0.012	<0.012	<0.006
Cu	<0.006	<0.006	<0.006	<0.002
F	---	---	---	(12)
Fe	0.09	<0.032	0.06	<0.032
Pb	<0.082	<0.082	<0.082	<0.096
Li	0.12	0.116	0.115	0.068
Mg	0.554	0.172	0.369	0.068
Mn	<0.004	<0.004	<0.004	<0.006
Hg	<0.082	<0.082	<0.082	<0.2
Mo	0.814	0.807	0.826	1.00
Ni	0.011	0.018	0.021	0.044
K	129	130	131	140
Se	---	---	---	(0.004)
Si	---	---	---	30.7
Sn	<0.06	<0.06	<0.06	<0.08
Sr	0.088	0.087	0.088	0.052
Na	190	189	189	261
Ti	<0.008	<0.008	<0.008	<0.008
W	0.16	0.12	0.11	0.15
V	1.90	1.88	1.88	2.41
Zn	<0.5	<0.5	<0.5	(0.01)

APPENDIX C

APPLICABILITY OF DIRECT CURRENT ARGON PLASMA EMISSION SPECTROMETRY FOR THE ANALYSIS OF LEACHATES

I. INTRODUCTION

To provide techniques that complement our atomic absorption spectroscopy (AAS) capabilities, we investigated direct current argon plasma emission spectrometry (DCAPES) and found it to be a reliable, efficient method for trace element analysis of oil-shale-related waters. The results demonstrate that the technique is acceptable with respect to selectivity, sensitivity, accuracy, and speed and economy of sampling for analysis of many of the elements investigated. Results from flame AAS and DCAPES are in good agreement for many elements.

II. EXPERIMENTAL

The instrument used for these comparisons is a Spectrospan III (Spectrometrics, Inc.) d.c. argon plasma spectrometer with a three-electrode plasma torch, a sample nebulization system, an echelle grating direct-reading spectrometer, and a microprocessor for control and data acquisition. The available instrument has four cassettes, each capable of simultaneous analysis of 20 elements. The element analysis capabilities of the three cassettes applicable to oil-shale-related waters are shown schematically in Table C-I. The cassette selected determines the suite of elements to be analyzed. The cassette acts as an optical mask that allows only certain atomic emission wavelengths to impinge on the instrument's photomultiplier tubes. One multielement standard is used for all calibrations. The analyses are made by standard analytical procedures. If an element of interest is not included on any cassette, the instrument can be operated in a single-element sequential mode. To examine the applicability of DCAPES for trace analysis of oil-shale-related waters, a commercially prepared wastewater standard and three previously characterized oil shale leachates were analyzed. The origins of these samples are listed below.

- Commercial Standard obtained from Environmental Research Associates, Chicago Heights, Illinois. Trademark: Waste Wat R, Lot #3500. The Environmental Protection Agency has certified trace metal values.
- OSL2-0: raw oil shale leachate from Colony shale, standard static shaker leaching procedure used. Material was sized to 1/8 in. AAS values reported at 95% confidence levels.
- OSL2-6: spent shale leachate from laboratory heat-treated Colony shale (1283 K, N_2/H_2O atmosphere). Standard static shaker leaching procedure used. Material was sized to −100 mesh. AAS values reported at 95% confidence levels.
- OSL2-7: raw shale leachate from Colony shale. Standard static shaker leaching procedure used. Material was sized to −20 mesh. AAS values reported at 95% confidence levels.

TABLE C-I. Elements Measured by Each of Three Cassettes Using DCAPES

Cassette	Elements
Cassette 1	**Li, Na, Mg, K, Rb, Sr, Ba, Ti, V, Mn, Fe, Ag, Au, Al, Ga, Si, Sn**
Cassette 2	**Li, Na, K, Rb, Mg, Ca, Sc, Ti, V, Mo, W, Cd, Hg, Al, Ga, Tl, Pb, Sb, Bi**
Cassette 3	**Li, Na, K, Be, Mg, Ca, Sr, Co, Ni, Cu, Zn, B, Al, Ga, In, Si, Ge, As, Se**

The comparison of results (in ppm) obtained from DCAPES and AAS for these samples and also typical limits of detection for each technique are listed according to each cassette in Table C-II. The numbers in parentheses are standard deviations derived from replicate analyses in the standard way. More than one series of replicates were run with the DCAPES for some samples, which explains multiple ES columns in some of the tables. Also note that several elements either recur on several cassettes (for example, vanadium, aluminum, magnesium, and calcium) or several times on the same cassette. As a general rule, multiple occurrence of an element on one cassette is due to the use of two atomic emission analysis lines of different sensitivity (one for low and one for high concentrations). If the same element occurs on two cassettes, it is probably a matter of convenience.

Trace element concentration comparisons presented in Table C-II verify that the precision and accuracy of DCAPES numbers are acceptable (compared with AAS). The agreement between element concentrations ranges from excellent (Mg, V, K, Al, Cd, Mo, B, Be, Ni, Co, and Ti) to very good (Cu, Fe, Pb, Li, Mn, Si, and W). Other elements, including Sb, As, Bi, Se, Sn, and Tl, have limits of detection at or near the levels of that trace element in oil-shale-related waters. Analysis of these elements will require rigorous sample treatment (for example, preconcentration or hydride generation technique) before analysis. Unfortunately, about 1 year elapsed between the time that the AAS numbers were generated and the time that DCAPES analyses were performed, but time constraints on the analytical capabilities precluded simultaneous analysis.

At this time, we believe that the use of DCAPES for trace element analysis of oil-shale-related waters has several advantages. DCAPES will complement existing analytical capabilities. A great many samples can now be handled in a reasonable time by generating high-quality numbers for a variety of trace elements by DCAPES, while reserving the more difficult trace element analyses for conventional AAS techniques. This allows us to continue our assessments on the wide range of samples that are becoming available. Other advantages of the DCAPES technique include (1) the instrument's throughput capability, which allows efficient generation of analytical results, (2) the minimum sample volume (usually about 2.5 mℓ) necessary (because of the 20-element simultaneous-analysis capability), (3) the time saved in preparing standards (for most elements, analytical working curves are linear over 1-3 orders of magnitude), and (4) the relative ease of operation and maintenance.

TABLE C-II. Comparison of Results of DCAPES and AAS

CASSETTE 1

	Sample OSL2-0			Sample OSL2-6		Sample OSL2-7			Limit of Detection (ppb)	
	No. 1 DCAPES	No. 2 DECAPES	AAS	No. 1 DCAPES	AAS	No. 1 DCAPES	No. 2 DCAPES	AAS	DCAPES	AAS
Mg	0.503(0.005)	0.508(0.003)	<1	0.581	<1	7.89	7.81(0.066)	7.0(0.5)	1	1
Mn	<0.001	<0.001	<0.1	<0.001	<0.01	<0.001	<0.001	<0.01	1	10
Au	<0.001	<0.001	---	<0.001	---	<0.001	<0.001	---	1	---
Sn	<0.200	<0.200	---	<0.200	---	<0.200	<0.200	---	200	10
Ga	<0.025	<0.025	---	<0.025	---	<0.025	<0.025	---	25	---
Si	2.09(0.033)	2.02(0.030)	---	15.9	---	0.756	0.808(0.043)	---	100	---
Ca	0.800(0.045)	1.19(0.056)	2.5(1.2)	5.49	6.4(2.3)	11.4	11.2(0.080)	13.3(2.6)	1	10
Fe	0.037(0.008)	0.070(0.026)	0.07(0.02)	0.013	0.03(0.02)	<0.020	<0.020	<0.02	20	20
Sr	0.005(0.000)	0.007(0.000)	---	0.095	---	0.185	0.185(0.001)	---	1	---
Ba	<0.010	<0.010	---	0.154	---	1.01	1.06(0.037)	---	1	100
V	<0.005	<0.005	<0.08	0.284	0.34(0.08)	<0.005	<0.005	0.14(0.08)	5	100
Ti	<0.010	<0.010	---	<0.010	---	<0.010	<0.010	---	10	---
Ca	0.936(0.010)	0.945(0.009)	2.5(1.2)	5.71	6.4	12.0	12.0(0.106)	13.3(2.6)	1	10
Li	<0.005	<0.005	---	1.17	---	<0.005	<0.005	---	5	10
K	1.19(0.016)	1.16(0.017)	1.5(0.1)	13.6	11(1)	18.2	18.1(0.007)	13.7(0.06)	50	10
Na	83.3(0.501)	83.8(0.089)	37(3)	106	47	145	146(0.631)	148(3)	1	10
Al	1.20(0.032)	1.24(0.013)	1.10(0.06)	1.95	1.70(0.06)	1.96	2.04(0.027)	1.83(0.06)	1	100

CASSETTE 2

	Sample OSL2-0			Sample OSL2-6		Sample OSL2-7			Limit of Detection (ppb)	
	ES No. 1	ES No. 2	AAS	ES No. 1	AAS	ES No. 1	ES No. 2	AAS	ES	AAS
Tl	0.025(0.013)	a	---	0.045(0.062)	---	0.040(0.018)	<0.029(0.011)	---	---	100
Mo	0.285(0.102)	a	0.37(0.07)	3.82(0.080)	3.95(0.07)	2.00(0.108)	1.97(0.176)	2.01(0.07)	2	10
Sb	<0.5	a	0.006(0.001)	<0.5	---	<0.5	<0.5	---	500	1
Cd	<0.01	a	---	<0.01	---	<0.01	<0.01	---	10	~1
Bi	<0.05	a	---	<0.05	---	<0.05	<0.05	---	50	---
Hg	0.140(0.093)	a	---	<0.2	---	<0.2	<0.2	---	200	---
Mg	0.599(0.010)	0.593	<1	0.704(0.007)	<1	8.54(0.056)	8.45(0.045)	7.0(0.5)	1	1
Mo	0.430(0.011)	0.437	0.37(0.07)	4.27(0.012)	3.95(0.07)	2.32(0.011)	2.30(0.019)	2.01(0.07)	2	10
Ti	0.020(0.002)	0.021	---	0.031(0.005)	---	0.021(0.002)	0.016(0.001)	---	10	---
Al	1.57(0.011)	1.59	1.10(0.06)	2.39(0.006)	0.70(0.06)	2.57(0.023)	2.56(0.022)	1.83(0.06)	1	100
Sc	0.008(0.012)	<0.001	---	0.017(0.023)	---	0.045(0.005)	<0.002(0.012)	---	---	---
Pb	0.030(0.010)	0.099	<0.001	0.094(0.024)	<0.001	0.141(0.064)	0.126(0.027)	<0.001	50	1
W	0.087(0.010)	0.119	---	0.301(0.018)	---	0.138(0.022)	0.096(0.017)	---	200	---
Ca	0.701(0.009)	0.692	2.5(1.2)	5.97(0.102)	6.4(2.3)	14.2(0.151)	14.0(0.204)	13.3(2.6)	1	10
Li	0.021(0.006)	0.018	---	1.42(0.019)	---	0.126(0.008)	0.119(0.011)	---	5	10
K	1.26(0.017)	1.19	1.5(0.1)	15.0(0.134)	11(1)	20.7(0.193)	20.1(0.234)	13.7(0.6)	50	10
Na	97.1(0.675)	96.9	37(3)	126(0.841)	47(3)	155(0.763)	153(0.122)	148(3)	1	10
Ga	<0.025	<0.025	---	<0.025	---	<0.025	<0.025	---	25	---
V	0.025(0.008)	0.018	<0.08	0.420(0.005)	0.34(0.08)	0.021(0.008)	0.022(0.010)	0.14(0.08)	5	100

CASSETTE 3

	Sample OSL2-0		Sample OSL2-6		Sample OSL2-7		Limit of Detection (ppb)	
	ES	AAS	ES	AAS	ES	AAS	ES	AAS
B	0.394(0.015)	0.5(0.2)	0.705	0.6(0.3)	1.49(0.032)	0.9(0.2)	10	500
Se	<0.5	<0.002	<0.5	0.04(0.01)	<0.5	0.030(0.008)	500	1
As	<0.2	0.018(0.004)	<0.2	0.018(0.002)	<0.2	0.012(0.001)	200	10
Cu	<0.001	<0.01	<0.001	<0.01	<0.001	---	---	---
Be	<0.001	<0.001	<0.001	<0.001	<0.001	<0.01	1	10
Zn	<0.005	0.013(0.005)	<0.05	0.010(0.005)	<0.001	<0.001	1	1
Ge	<0.05	---	<0.05	---	<0.005	0.012(0.005)	5	10
Sr	0.008(0.001)	---	0.115	---	0.221(0.007)	---	---	---
Ni	<0.01	0.017(0.013)	<0.001	<0.013	<0.001	---	---	---
Mg	0.578(0.002)	<1	0.665	<1	8.25(0.106)	<0.013	10	10
Si	2.23(0.561)	---	16.0	---	0.899(0.433)	7.0(0.5)	1	1
Na	90.9(0.606)	37(3)	121	47	156(1.22)	148(3)	1	10
Co	<0.012	<0.01	<0.012	<0.01	<0.012	<0.01	1	10
Al	1.09(0.005)	1.10(0.06)	1.78	1.70(0.05)	1.93(0.027)	1.83(0.06)	1	100
Ca	0.796(0.006)	2.5(1.2)	5.45	6.4(2.3)	11.6(0.190)	13.3(2.6)	1	10
K	1.17(0.064)	1.5(0.1)	15.6	11(1)	21.1(0.310)	13.7(0.6)	50	10
Sr	<0.12	---	<0.12	---	<0.12	---	---	---
Ga	<0.05	---	<0.05	---	<0.05	---	---	---
Li	<0.15	---	0.960	---	<0.15	---	---	---

[a] Sampled too early for values to be obtained.

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