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

October 1, 1978—September 30, 1979

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545

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by

P. Wagner, E. J. Peterson, and P. L. Wanek

ABSTRACT

An integrated assessment of environmental control technologies applicable to shale oil development is reported. Air quality, water quality, potential surface disruption, potential problem areas, and research needs have been assessed, and finally, environmental control technologies have been indicated. The experimental program attempts to identify mechanisms and kinetics of trace element release from raw and spent shales, the effects of these releases on water quality, and methods for control of potential contaminants. Our study emphasizes the nature, extent, transport, and fate of contaminants occurring as waste and as an effect of retort parameters. Our experiments confirmed that concentrations of soluble species in product waters, laboratory-generated leachates, and natural water systems are controlled by the variables mentioned.

Although preliminary experiments have pointed to some concerns as yet unresolved and have indicated the difficulty of developing an integrated environmental control technology, a *complete* information and data base must be developed to avoid premature judgments based on these incomplete findings.

SUMMARY

The main objectives of this program are to elucidate the nature and assess the magnitude of the water contamination that might result from surface or *in situ* shale oil extraction methods. As the major problem areas become defined, suitable technologies for water pollution control will be evaluated experimentally. Two primary tasks are being implemented to accomplish these goals.[1]

The first was a review of the literature concerning the types and distribution of water contaminants produced during recovery and upgrading of shale oil. Potential problems include contamination of water during surface shale retorting, contamination of surface and groundwater caused by *in situ* retorts, the effects of water on raw and spent shale disposal sites, and the effects of effluents from on-site upgrading of shale oil. We have identified water pollution controls necessary for various aspects of shale oil recovery and have already revealed areas that require additional research to support control technology development. Los Alamos National Laboratory report LA-8378, "An Integrated Environmental Control Technology approach to Oil Shale Commercialization," details the review and evaluation (Ref. 7). Some preliminary information and conclusions drawn from that study are outlined in this report.

The second activity is to begin an experimental program to define and support the necessary environmental control research. The objectives of the experiments reflect the concerns discussed in LA-8378. These experiments will provide necessary information about the nature and time-dependent behavior of contaminants in various shale-associated leachates and the evaluation of water quality control options available to the oil shale industry. These studies will focus on both chemical and physical methods of prevention and/or control to reduce the contaminants in retort waters and disposal site effluents to acceptable levels, and on measures to prevent groundwater contamination caused by flooding of abandoned *in situ* retorts. Emphasis is on collection and analyses of raw shale, spent shale, retort waters, and local surface and groundwaters. Analytical results from these samples will determine the probable magnitude of water contamination. Physical and chemical characterizations of raw and spent shale samples, including x-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), and electron microprobe analysis, are being pursued because structural and mineral associations of trace impurities in both the raw and spent shales are vital for mechanistic studies of the release of these trace elements into the environment during or after retorting. Recent investigations in these areas include (1) physical characterization of spent shale and elemental analysis of leachates from samples obtained from a core of Occidental Oil Shale, Inc., retort 3E; (2) analysis of groundwater samples from the vicinity of Occidental retort 6, Logan Wash area, and upper and lower aquifer water samples from the region of the Rio Blanco Oil Shale Company lease tract C-a; and (3) laboratory heating experiments using Colony mine shale samples.

I. TASK 1. INFORMATION REVIEW AND EVALUATION

Much of our work in FY 1979 consisted of review and evaluation of literature dealing with environmental control technology for oil shale commercialization. This has been completed.

In the past 3 years, the Environmental Protection Agency (EPA) and the Department of Energy (DOE) have published reports on environmental impacts and environmental control technology for an oil shale industry.[2,3] In addition, studies in the laboratory[4] and in the field[5,6] have revealed problems not previously considered. Some of the environmental control measures that will alleviate these problems are being studied at various laboratories. Environmental control technology for oil shale commercialization falls into three categories: (1) airborne pollutants including gases, mists, and particulates; (2) liquid discharges and leachates affecting the water environment; and (3) solid waste disposal. Some of the potential problems and control technologies overlap. For example, the manner of storage of spent shale can affect both air, by fugitive dust emissions, and water, by leaching. Los Alamos National Laboratory report LA-8378,[7] which documents results of our literature search, was organized according to these categories.

LA-8378 reflects the difficulty of developing an integrated environmental control technology and discusses unresolved concerns about oil shale commercialization, but a *complete* information and data base must be developed to avoid premature judgments based on the incomplete findings of the evaluation. Water consumption may place a limit on the ultimate scale of commercialization. Possible degradation of aquifers by bridging, leaching, etc., is a problem that must be solved. These issues can probably be solved, but cost will be an important factor. Finally, the operation is immense; that is, approximately one ton of waste is produced for each barrel of desired product. The only close precedent commercial experience is open-pit copper mining. The overall scale of full commercial operations, estimated at 10^6 barrels per day of shale oil, is without parallel in the energy extraction industry.

Appendix A is a summary of all concerns addressed in LA-8378. Below is a discussion of the potentially serious, unresolved problem areas revealed by the information review and evaluation, along with the present status of knowledge in each case.

A. Control of Airborne Pollutants

The types of airborne pollutants addressed in this evaluation included gaseous materials, vapors, mists, aerosols, and particulate suspended solids. Some unresolved environmental health hazards may exist within the plant perimeter, but three potentially serious airborne pollution problems have been identified that may not be amenable to existing control technology.

- Fugitive gaseous emissions from leaking underground MIS (modified *in situ*) or TIS (true *in situ*) retorts or burning above-ground raw shale piles. At present, the severity of this problem is unknown.
- Particulate emissions of (untreated) oil shale from the TOSCO II above-ground process. This can probably be handled by rigorous application of existing control technology.

- The unknown fate of mercury in surface and *in situ* retorting. Whether this issue is serious is unknown. The low concentration of mercury in most oil shales and the possibility that it can be removed during removal of sulfur suggests that the problem may not be serious. But because contamination from mercury compounds can be very serious, the issue must be assessed thoroughly before a decision can be made.

Although many of the problems related to control of point-source airborne contaminants have been resolved in related technological areas, transfer of the control methods to the oil shale industry may be difficult because of unique problems, especially the immense scale, of supply and materials handling. In addition, the climatic conditions in the Western oil shale region, including low annual precipitation and its uneven distribution throughout the year, also raise a series of unresolved issues. Conventional control methods may be hampered by certain characteristics of retort gases: (1) large volumes of gases requiring clean-up; (2) high concentrations of particulates and toxic vapors in the gas plumes; and (3) possible interference of some substances with the control systems themselves. Complete assessment must be made of the magnitude and implications of (1) CO_2 emissions, (2) particulates, (3) volatile trace element release, and (4) release of polynuclear aromatic hydrocarbons.

B. Control of Water Pollution

Water pollution control in surface production of shale oil is internal to the particular operation in that none of the proposed operations anticipates intentional outflow from the plant perimeter, but spent-shale-pile leachates from above-ground retorting may present water pollution problems. The control technologies for these are considered well established by some writers (Ref. 3, pp. 153-159), but their adequacy is challenged by others.[8]

Special problems are possible with underground processes for which no definitive answers are available. The two principal problems associated with the MIS process are groundwater contamination from leaching of flooded retorts and aquifer bridging. Aquifer bridging is the flow of water from a saline aquifer into a fresh water aquifer, but this probably can be prevented by careful siting, rubbling, and extraction techniques.

Because optimum control of process parameters is more difficult to achieve underground than with surface retorting, leachable organic and inorganic residues will be left in many of the *in situ* retorts at the completion of the oil extraction process. Contamination of groundwater by these residues as the water backfloods (at unknown rates) through abandoned underground retorts is another potential problem associated with *in situ* retorting of oil shale.[9-12] The Green River oil shale formation contains active aquifers that can be affected by groundwater that may become contaminated by that process. Both organic and inorganic contaminants could be mobilized as the water passes through the abandoned (spent) retort. Although these leachates would probably contain much lower concentrations of contaminants than the product water from the retorting process,[11] the possibility of large quantities of pollutants being transported into local water supplies has not been adequately assessed.

Even though the extent of the groundwater contamination caused by leaching of abandoned retorts has not yet been fully defined, various control technologies under investigation may be applicable if needed.[9] Because data are scarce on spent flooded retorts and their leaching properties, controls considered for spent retort abandonment are necessarily conservative. An example is the grouting or filling of a spent retort with an insoluble matrix to prevent transport of trace elements and organics beyond the boundaries of the retort. Another control technology being considered is backflooding the spent retort (by groundwater intrusion, flushing from the surface, or a combination of the two), removing the leachate, treating it on the surface, and either reinjecting the water into the retort or making some other use of it. Such a control can be implemented only after verification of groundwater contamination in the abandoned retort. This process, along with complete characterization of the treated water after purification and before use, holds promise that the level of treatment and the economics of retort abandonment may be within the realm of realistic analysis.

Finally, a crucial impact of shale oil production on the water of the intermountain area is in the socioeconomic realm. The comparative scarcity of any water, let alone good surface and groundwater, in this region means that some as yet undefined upper limit of shale oil production capacity will be established by water available.

C. Control of Solids and Solid Wastes

The sheer magnitude of the solid waste disposal problem is unparalleled in US energy production: the amount of waste from shale oil production will be about *fifteen* to *thirty* times (about 25 times by weight) that from coal cleaning operations.[7]

Analogies with coal mining waste and coal cleaning waste are limited because the chemical differences in the two types of waste produce different environmental effects. But to the extent that mechanical properties may be similar, lessons can be derived from the older technology. Potentially serious mechanical problems include accidental ignition, slumping, sliding, and gullying of waste shale piles, but control measures similar to those for coal piles or coal-rich waste piles will probably be applicable.

Whether dust control, transportation, piling, stabilization, and other solid waste procedures can be successfully conducted on so vast a scale even with the advantage of analogous prior experience is the major question for solid waste management.

D. Summary

Fugitive gaseous emissions and groundwater contamination may be the most difficult problems to be dealt with. Further assessment of these and other potential problems is necessary. Environmental control technology development is under way at several laboratories, but further research is necessary to understand and evaluate the applicability of various environmental control technology options.

II. TASK 2. TECHNICAL ACTIVITIES

Experiments are under way to (1) implement a program that reflects the concerns expressed in LA-8378, (2) acquire necessary additional information about the nature and time-dependent behavior of contaminants in shale-associated waters, and (3) do the necessary control technology research. This program is necessarily broad and flexible because the nature of the problems may be site-specific. Emphasis is on the acquisition of a wide variety of samples that include raw and spent shales from active development sites, process waters, and local surface and groundwaters both before and after site development. We will collect as broad a range of samples as possible. These materials will be studied to define extremes of contaminant concentrations for each type of waste or effluent, which will ultimately allow design or assessment of control strategies with broad application. A summary of acquired samples is given in Table I.

Analytical studies have been conducted to identify potential contaminants on samples collected, and laboratory leaching experiments are being used to reveal mechanisms and time-dependent release of these contaminants from raw and spent shale. The emphasis is on the identification of types, levels, transport, and fate of contaminants mobilized as a function of waste structure and retort parameters. As the assessments begin to provide more information, more current environmental control technologies will be investigated in the laboratory. These studies will focus on methods to reduce contaminants in process waters to acceptable levels and to prevent groundwater contamination, if necessary. The major purpose is to explore new control strategies, and, at the same time, provide additional information that will supplement previous research efforts.

A. Laboratory Heat-Treating Experiments. Effects of Thermodynamic and Compositional Variables on the Chemistry and Mineralogy of Oil Shale

1. **Approach.** These investigations are being made to determine the effects of such variables as temperature, time at temperature, and reaction atmosphere, on the chemical decomposition and mineral reactions of raw shale. These experiments in conjunction with laboratory leaching experiments of the heat-treated material are used to understand and correlate process variables, mineralogy, and trace element mobility. The studies will be more useful when spent shale from burned retorts becomes available. This basic chemical and mineral information will provide understanding of the retort history during shale oil extraction, and insight into the nature and magnitude of trace element release to be expected from field samples. Correlation of field and laboratory information will be essential for a detailed understanding of the nature and extent of water contamination problems generated by MIS processes.

The first experiments on raw shale (from the Colony mine in Garfield County, Colorado) were designed to study temperature effects in both inert and water-vapor-saturated inert atmospheres. Leaching experiments were also performed on the raw and heat-treated materials in order to correlate trace element mobilities with reaction conditions. These studies complement other investigations of chemical and mineral reactions

TABLE I

SAMPLE LOGS

Liquids

	Retort Water	Leachates (Spent Shale)	Other
Anvil Points	√		
Colony		√	
Occidental	√	√	surface water groundwater
C-a Tract			upper and lower aquifer water

Solids

	Raw Shale	Spent Shale
Anvil Points (LLL)	√	√
Colony	√	√
Occidental (Logan Wash)	√	√

related to oil shale,[13-15] and extend our knowledge to include the relation of chemical and mineralogic changes due to reaction variables with mechanisms responsible for trace element release.

2. Experimental Set-Up. The experimental apparatus is shown in Fig. 1. The shale materials were heat treated in a 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 downstream from two hydrocarbon traps, about 24 in. from the shale. Temperatures were monitored by type K thermocouples as shown in Fig. 1.

3. Heating Experiments. Blocks of Colony mine oil shale were crushed to -3/8 in. for these experiments. Approximately 50-60 g of the crushed material was placed in the quartz tube (Fig. 1). The following list shows the maximum temperature and corresponding reaction atmosphere for each experiment.

REACTION CONDITIONS

Experiment	T_{max}(K)	Atmosphere
1	735	N_2
2	765	$N_2 + 1.5\% H_2O$
3	1035	N_2
4	1010	$N_2 + 1.5\% H_20$
5	1310	N_2
6	1290	$N_2 + 1.5\% H_20$

A nitrogen flow of 3.34 cm^3s^{-1} was used throughout each experiment, which consisted of an initial rapid heating rate to the desired temperature, 6 h at the maximum temperature, and a rapid cooling rate.

The spent shale from the heating experiments was prepared for leaching experiments as described in Appendix B, except that the material was not ground. Instead, the -3/8-in. heat-treated materials were subjected to the static shaker leaching procedure, also described in Appendix B. The resultant leachates were vacuum-filtered through Whatman #541 paper, gravity-filtered through Whatman #42 paper, and preserved

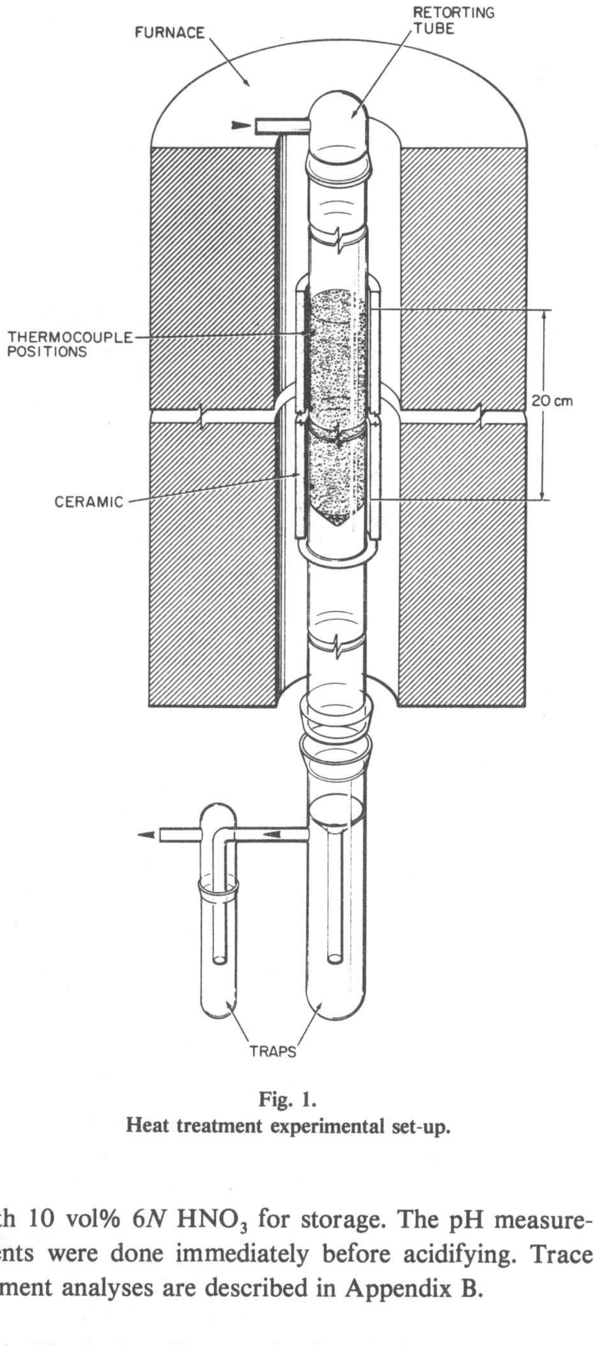

Fig. 1.
Heat treatment experimental set-up.

with 10 vol% $6N$ HNO_3 for storage. The pH measurements were done immediately before acidifying. Trace element analyses are described in Appendix B.

4. Physical Characterization of Heat-Treated Shale. Physical characterization of the initial raw shale and the spent shale generated from the heating experiments consisted of x-ray diffraction (XRD) analysis. Results are listed in Table II. The mineralogy of these solids is quite consistent (and thus understandable) with Cambell's observations.[13] The raw shale XRD analysis indicates that the material contains minerals typical of oil shale from the Green River Formation, with large amounts of dolomite, albite, and alpha-quartz, and a lesser amount of calcite. Further examination reveals that reaction temperatures of ~720 K[*] disrupt the major mineral matrix only slightly, with a small amount of periclase (MgO) and an increase in calcite indicating some dolomite decomposition.

However, at 975 K, XRD showed major mineralogic changes. Dolomite and calcite phases disappeared and the amounts of MgO and CaO (to a lesser extent) increased. Albite was still present as a major phase, but the amount of alpha-quartz decreased. The slight decrease of the alpha-quartz and the minor amount of CaO with relation to periclase may suggest that the unidentified phases in this material are minor amounts of calcium silicates that began to form from solid-state reactions in this temperature regime. That the major reaction under these conditions was carbonate decomposition to form oxides and not carbonate-silica solid-state reactions is undoubtedly due to (1) the inert-gas sweep of the reaction vessel, which insures that the dissociation equilibrium constant at 975 K is much greater than the CO_2 partial pressure, or (2) the combination of the rapid heating rate and the possibility that limited silica availability on the micron scale did not allow kinetic control of the reactions.

The XRD analysis of the material heated to 1270 K indicates complete mineral transformation, in that none of the original phases (except a minor amount of alpha-quartz) is present. The term "pseudo" used with augite and gehlenite indicates mineral forms that closely resemble the parent mineral but that have slightly different lattice parameters. Augite $(Ca,Mg,Fe,Ti,Al)_2(Si,Al)_2O_6$, is the intermediate member in a continuous solid-solution series with diopside, $CaMgSi_2O_6$, as the magnesium-rich end member and hedenbergite, $CaFeSi_2O_6$, as the iron-rich end member. The fact that dolomite and not ankerite is the major carbonate phase in the original raw shale suggests that the pseudoaugite phase in the 1270 K-heated material lies toward the magnesium-rich end of the solid solution. Gehlenite, $Ca_2Al(AlSiO_7)$, is an end member of a continuous solid-solution series of minerals whose intermediate members are called melilites. The other end member of this series is akermanite, $Ca_2Mg(Si_2O_7)$. Again, pseudogehlenite suggests a composition close but not identical to the aluminum-rich member, gehlenite. Formation of major silicate minerals resembling augite and gehlenite (or melilites) at high temperatures is consistent with but not strictly identical to data from other studies, perhaps indicating small compositional

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[*] Temperatures cited in text are approximate for convenience: temperatures cited in tables are measured.

TABLE II

MINERALS IN COLONY SHALE RETORTED UNDER VARIOUS TEMPERATURES[a]

Mineral	Raw		723 K		973 K		1273 K
Dolomite	+	>	+		−		
Alpha-quartz	+		+	>	+	>	±
Calcite	±	<	+				
CaO[b]					+		
MgO[b]			±		+		
Albite (Low)	+	=	+		+		
?				=	+		
?					+		
Pseudoaugite[c]							+
Pseudogehlenite[c]							+

[a] Transformations most noticeable in samples retorted with dry N_2 as opposed to like samples retorted with $N_2 + 1.5\% H_2O$.

[b] Oxides more prevalent in samples retorted with dry N_2.

[c] Hybrid forms that most nearly resemble indicated parent material.

variations in the raw shale compositions or slightly different interpretations of the XRD data. We are not certain to what extent the experimental methods affect the mineral transformations and final mineral identities. The techniques used favor decomposition reactions followed by silication reactions, as opposed to original mineral-phase reactions with silica to form silicates.

Other general observations can be made by examining the XRD results. The mineral transformations are most noticeable in samples heated in dry nitrogen as opposed to the same sample heated in the nitrogen/water atmosphere. This could be caused by the experimental procedure, or the newly formed minerals may crystallize poorly in the presence of steam. Also, the oxide formation was more prevalent in samples retorted in dry nitrogen. Campbell points out that steam accelerates the decomposition of dolomite,[13] and thus, the prevalence of oxides in the dry atmosphere must be traced to the enhanced reactivity of Ca^{+2} and Mg^{+2} with SiO_2. This enhanced reactivity may be due to increased mobility of Ca^{+2} ions in silica due to H_2O disruption of the SiO_2 lattice,[16] or to SiO_2 reacting with H_2O to form $Si(OH)_4$ in the gas phase, which enhances silicon mobility with respect to solid-state diffusion.[17] Finally, differences in mineral reactions that occur in the laboratory using shales from different sites suggest that mineralogy as a function of depth for raw and spent shale is essential to the interpretation of results from field experiments.

5. Results of Laboratory Leaching Experiments. Trace element analyses and pH measurements of selected elements generally found in oil-shale-related waters are shown in Table III. Trends for selected elements are shown in Fig. 2. Also, the MEG/MATE (Multi-Media Environmental Goals/Minimum Acute Toxicity Effluent) values established by the EPA are listed for those elements whose concentrations approach levels of environmental concern. Comparison of the raw shale leaching data with that from spent shales indicates that neither the major mineral matrix nor the chemistry of the trace elements was altered substantially by heating to 720 K. With very few exceptions, the elemental analyses of raw and spent shales agree fairly well, which confirms the results (very little matrix disruption) of XRD analysis of low-temperature spent shales.

Another observation involves the pH measurements of the leachates. These data are difficult to quantify and understand in such complex solutions as oil-shale-related waters. However, the mineralogy of the leachates of the shales heated to 980 K shows pH values of 12.4 to be reasonable. A major mineral phase in these materials is CaO. A saturated-lime (CaO) solution has a pH of 12.4, and the lime solubility at 283 K is 0.131 g/100 mL. An 800-ppm calcium solution translates to 0.112 g/100 mL CaO if we assume that the sole source of Ca is CaO. The pH measurement, the trace element analysis, and the

TABLE III

TRACE ELEMENT CONCENTRATIONS IN LEACHATES FROM HEAT-TREATED COLONY MINE SHALE[a]

Sample	Raw	718 K	743 K	983 K	983 K	1293 K	1283 K	Ecology
Atm	Shale	N_2	N_2/1.5% H_2O	N_2	N_2/1.5% H_2O	N_2	N_2/1.5% H_2O	Mate
pH	8.71	11.45	10.16	12.42	12.47	8.30	9.52	
Al	1.83	0.94	0.67	0.20	0.09	0.39	1.70	1.0
As	0.012	0.009	0.22	<0.002	<0.004	0.13	0.018	0.025
B	1.8	<1	<1	2.4	1.8	<1	1.8	25
Be	0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	
Ca	13.3	12.1	7.2	840	760	400	6.4	
Co	<0.01	<0.01	<0.1	<0.01	<0.01	<0.01	<0.01	
Cr	<0.006	<0.006	<0.006	<0.006	<0.006	0.21	<0.006	
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
F	49	37	51	2.7	2.8	14	4.6	
Fe	<0.02	<0.02	0.02	<0.02	<0.02	<0.02	0.03	
K	13.7	13.3	13.9	50	150	324	11	
Mg	7.0	<1	<1	<1	<1	5.0	<1	
Mn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Mo	2.0	1.40	2.41	<0.07	0.10	4.73	3.95	7
Na	148	243	263	131	147	1080	47	
Ni	<0.013	0.013	<0.013	0.022	0.022	<0.013	<0.013	0.01
Pb	<0.001	<0.001	<0.001	<0.001	<0.003	<0.003	<0.001	
Sb	0.085	0.011	0.074	<0.003	<0.003	<0.003	<0.003	0.2
Se	0.030	0.08	0.49	0.008	0.006	0.06	0.04	0.025
V	0.14	0.06	0.24	0.10	<0.06	1.79	0.34	0.15
Zn	0.012	0.013	0.013	0.018	0.008	0.008	0.010	

[a] Forty-eight-hour static leach with ratio of 5:1 Milli-Q water: solid shale on -3/8-in. material heated for 6 h at indicated temperatures and atmospheres. Values in ppm solid.

mineralogy of the original shale indicate that the leachates resulting from shale heated to 980 K are essentially saturated-lime solutions. An almost unlimited calcium-ion reservoir also explains the apparent anomalies in trace element release from shale heated to 980 K. The anomalies are caused by the insolubility of Ca salts such as CaF_2—not by a decrease in mobility due to the mineralogy of the heat-treated shale. Thus, the trace element results for the 980 K-heated shale reflect pH control of the generated leachates and not an effect of mineralogy!

Comparison of the shale heated to 1300 K in both dry and water-vapor-saturated nitrogen is also quite interesting. The mobility of the major cations is greatly enhanced in the shale heated to approximately 1300 K in dry nitrogen over that of raw shale, shales heated to other temperatures in both dry and water-vapor-saturated nitrogen, and even shale heated to 1300 K in water-vapor-saturated nitrogen. The enhanced mobility at 1300 K in dry nitrogen is undoubtedly caused by incomplete transformations of minerals to insoluble silicates. Also, enhanced sodium and potassium mobilities are likely because of incomplete decomposition of albite and other less prominent feldspathic material. These reactions appear to be essentially complete at 1300 K in the nitrogen/steam atmosphere. The effect of steam on silication reactions was discussed in Sec. II.A.4. Further examination indicates that under these experimental conditions, the mobilities of early transition elements (for example, chromium, molybdenum, and vanadium) are enhanced at 1300 K, although to a greater extent in dry nitrogen than in nitrogen/steam. This suggests that these elements are being oxidized to their refractory oxides, which are reasonably soluble in basic media. Further study of the effects of temperature and oxidizing atmosphere on the

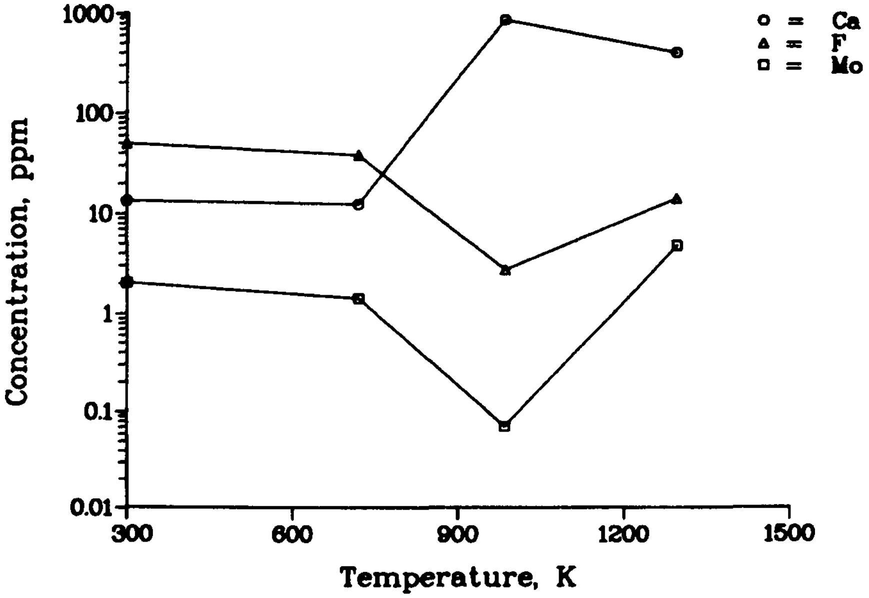

Fig. 2.
Trace element concentrations in leachates from heat-treated Colony mine shale.

early transition elements is warranted because these preliminary observations suggest that these elements may become *more* available to the natural water system (neutral to basic) as the retorting conditions become more extreme.

The following observations about trace element release from Colony mine shales are made in the context of the reaction variables (temperature and atmosphere) and the solution chemistry that occurred in leachate solutions generated from the 980 K spent material. Beryllium, cobalt, copper, iron, manganese, and lead were below the detection limits of the AAS (atomic absorption spectrometry) method, thus no conclusions about these species are possible. There is no discernible change in the mobilities of boron, sodium (except where albite decomposition is expected), nickel, zinc, or aluminum as a function of temperature or steam in an inert atmosphere. Arsenic, selenium, and magnesium show no obvious trend as a function of the reaction variables and may only be a consequence of the microscopic elemental variability of these shales. Identifiable changes in trace element release caused by reaction variables occur for calcium, chromium, fluoride, potassium, molybdenum, antimony, and vanadium. An explanation for the increases of chromium, molybdenum, and vanadium concentrations in leachates from shales exposed to higher temperatures has been postulated and will be investigated. Reasons for increases and decreases of calcium and potassium are obvious by the identity and extent of the major mineral transformations that occur with specific reaction conditions. Finally, concentrations of fluoride and antimony in the leachates seem to decrease as the heat-treatment temperature increases.

6. Conclusions. These preliminary experiments were initial attempts to understand the effects of reaction variables, such as temperature and atmosphere, on the nature and magnitude of trace element release. Experiments to determine the effects of temperature on the mineralogy and chemistry of shale in an inert atmosphere will provide information necessary for future investigations of the temperature effects on oil shale (chemistry, mineralogy, and leaching behavior) in oxidizing (air), reducing (CO/hydrocarbon), and other reactive atmospheres (CO_2). In addition, these preliminary experiments confirmed the importance of steam on the kinetics of mineral transformations, and will be the basis for understanding the collective effects of reactive atmospheres with steam on the chemistry of trace elements in oil shale. These experiments, in conjunction with other studies,[13-15] also indicated the importance of reaction variables that may occur during processing, such as heating rate, time at maximum temperature, and cooling rate, on the major mineral and trace element chemical

reactions. The final disposition of minerals and trace elements in spent shale will depend on these variables.

General conclusions drawn from these preliminary heating experiments are summarized below.

1. Controlled laboratory experiments allow complete correlation of composition of raw shale and the effects of reaction variables with the mineralogy and trace element behavior of the spent shale. Whether these results (especially the effects of specific reaction variables on trace element release) can be applied to field experiments depends on how well process variables can be controlled and/or monitored in the field.
2. The mineralogy of spent shale depends on the original composition of raw shale. The aluminum-rich shale investigated in these experiments contains mineral products that are members of the appropriate continuous solid solutions but lie toward the aluminum-rich end members of the series. This is, as expected, in contrast to investigations of silica-rich raw shales.[13-15]
3. Many mineral and chemical reactions that can occur during oil shale processing are not controlled exclusively by thermodynamics or kinetics. Reaction control, whether thermodynamic and/or kinetic, is exerted by reaction variables. This is extremely important in the study of field retorts.
4. Fundamental solution chemistry must be included in conclusions drawn regarding trace element mobilities from laboratory- or field-generated spent shales based on trace element analyses from laboratory-generated leachates. Superficial examination of trace element analytical results for heated shales subjected to 980 K indicated almost total mitigation of trace element mobility, but further examination revealed that suppression of trace element concentrations was due to an essentially unlimited calcium-ion reservoir, and therefore, lower trace element solubilities.
5. We infer from these experiments that the notion that complete transformation to silicate minerals significantly attenuates the mobility of *all* trace elements is an oversimplification of a very complex system. For example, release of early transition elements from spent shales subjected to 1300 K is enhanced compared with that from shales heated to lower temperatures in an inert atmosphere. If this can be traced to the formation of higher oxidation state metal oxides not intimately associated with the major silicate matrix, then the trace elements might be further mobilized by a larger oxygen partial pressure, which would provide mobilization from materials subjected to lower temperatures. Each group of trace elements must be considered with respect to the individual chemistry, the alkalinity of the natural water system, and the reaction variables to which they have been exposed. Sweeping generalizations will not always be valid.

B. Investigation of Spent Shale, Leachates, Process Waters, and Groundwaters from Occidental Oil Shale, Inc., Operations, Logan Wash Site, Garfield County, Colorado

1. Purpose. To identify areas of water contamination caused by MIS retorting of oil shale and to develop effective controls, assessment of potential problems must be completed early in the shale oil development process so that implementation of control technology can be accomplished after field tests of suggested controls. The results of these studies may also have a direct bearing on the classification of the solid waste from shale oil production under the Resource Conservation and Recovery Act (RCRA), an area of considerable interest to the shale oil industry. These considerations prompted the formation of a task force comprising members of government, government contractor laboratories, scientists from Colorado, and representatives of Occidental Oil Shale, Inc., and the Rio Blanco Oil Shale Company, who are working to define and minimize any environmental impacts associated with shale oil commercialization. The work began with Occidental Oil Shale, Inc., operations at Logan Wash Site, Garfield County, Colorado. Characterizations of samples from retorts 3E and 6 are complete. A summary[5] of the Oil Shale Task Force findings has been published, and the Los Alamos contribution is detailed below.

2. Approach. The pilot-scale experiments on field samples were to (1) assess the nature and magnitude of trace element release from processed materials, (2) identify areas of water contamination caused by leaching of MIS-retorted shales, and (3) classify generated solid wastes with respect to RCRA.

The Occidental Research Corporation supplied the Oil Shale Task Force with samples taken from a coring of exhausted and cooled MIS retort 3E. Sampling depth was from 442 to 515 ft; the cores were sectioned into 18 samples each with an average weight of ~50 g. Task Force members at Pacific Northwest Laboratory directed the grinding and distribution of these samples. Sample identification, weight, and depth are listed in Table IV. In addition, groundwater samples were taken from the vicinity of retort 3E and from retort 6 process waters. The studies consisted of (1) characterization of the spent shale, (2) static leaching experiments followed by trace element analyses of the leachates, (3) data analyses to reveal trace element mobility patterns, and (4) elemental analyses of water samples.

3. Results and Discussion.

a. Characterization of Spent Shale. The solid material was characterized by OES, NAA, optical microscopy, SEM, electron microprobe analysis, and XRD. These techniques are described in Appendix B. The semiquantitative elemental analyses of the solid materials by OES are shown in Table V. Concentration ranges are indicated in Fig. 3. Uranium analyses on samples 5 and 16 by NAA indicated 2.3 and 6.2 ppm uranium. XRD results for samples 5 and 16 are given in Table VI. Results of microscopic and electron microprobe analyses are discussed below.

TABLE IV

SAMPLE LOG: GROUND SPENT SHALES SUPPLIED TO LOS ALAMOS FROM RETORT 3

Depth (ft)	Sample	Weight (g)
442-445	1	10
454-457	2	20
457-460	3	10
460-463	4	10
463-466	5	10
468-469	6	20
469-470.5	7	20
470-475	8	20
475-477	9	20
475.5-477.5	10	20
477-480	11	20
480.5-481.5	12	20
481.5-485.5	13	20
483-485	14	10
483.5-485.5	15	10
485.5-500.5	16	20

The OES semiquantitative elemental analyses indicate (Table V) that there is no extreme variation in the major cations (sodium, potassium, calcium, aluminum, and magnesium) from section to section for the spent shale. This could reflect a small degree of mineralogical, and thus compositional, variation in the raw shale from the stratigraphic zone that contains the retort. Also, there appears to be little variation in trace metal concentrations in the spent shale, although the technique is not sensitive enough to indicate differences due to micron-sized detrital or authigenic minerals that vary from section to section. Other subtle compositional differences, such as trace elements suspected of being associated with kerogen, will also be obscure. NAA indicates finite amounts of uranium in samples 5 and 16. This trace element may be associated with detrital sand grains (for example, monazite) deposited in the sediment.

XRD data presented in Table VI indicate radically different mineralogy for samples 5 and 16, which reflects the difference in retorting conditions. The major mineral phase of sample 5 (465 ft from the top part of the retort) is calcite, with minor amounts of diopside ($CaMgSi_2O_6$), quartz (SiO_2), kalsilite ($KAlSiO_4$), and to a lesser extent, akermanite ($Ca_2MgSi_2O_7$). XRD data for sample 16 (493 ft from the middle of the retort) indicate that silication reactions are essentially complete in this region. The major minerals are akermanite and diopside with a trace amount of kalsilite. These data imply that temperatures in the middle of the room 3E retort were higher than those at the top of the retort; however, this conclusion is speculative without prior knowledge of the starting shale composition and mineralogy. These data agree with results published by Park et al.,[18] and the conclusion concerning retorting conditions has been reaffirmed by other Task Force members using complementary experimental results.[5]

The -100-mesh samples, 5 and 16, were also examined by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) in metallographic mounts as described in Appendix B. These powders were also attached to a stub for surface examination, but the -100-mesh powder was covered with submicron fines that obscured the surface. Examination of the material in the metallographic mounts was more productive. In general, particles from sample 5 were solid and consisted of calcite and possibly clay. SEM-EDS results of sample 5 metallographic mounts are shown in Figs. 4-10. Each

TABLE V
SPECTRAL ANALYSES OF SAMPLES 1–9, RM 3 CORE[a]

1

Li	400–4000	Ca	3–30%	Zn	60–600	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	10–100	Sn	<60
B	50–500	V	50–500	Ge	<30	Sb	<100
Na	0.3–3%	Cr	40–400	Sr	0.1–1%	Ba	400–4000
Mg	3–30%	Mn	300–3000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.5–5%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	<30	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	<60
K	1–10%	Cu	20–200	Cd	<30	Bi	<30

2

Li	300–3000	Ca	3–30%	Zn	100–1000	In	<30
Be	0.3–3	Ti	600–6000	Ga	<30	Sn	<60
B	30–300	V	40–400	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.1–1%	Ba	400–4000
Mg	2–20%	Mn	300–3000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.4–4%	Nb	<100	W	<1000
Si	4–40%	Co	10–100	Mo	<30	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	20–200
K	0.3–3%	Cu	20–200	Cd	<30	Bi	<30

3

Li	200–2000	Ca	3–30%	Zn	50–500	In	<30
Be	0.3–3	Ti	600–6000	Ga	<30	Sn	<60
B	30–300	V	40–400	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.1–1%	Ba	400–4000
Mg	2–20%	Mn	300–3000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.4–4%	Nb	<100	W	<1000
Si	4–40%	Co	10–100	Mo	<30	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	20–200
K	0.3–3%	Cu	20–200	Cd	<30	Bi	<30

4

Li	100–1000	Ca	2–20%	Zn	50–500	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	30–300	V	30–300	Ge	<30	Sb	<100
Na	0.4–4%	Cr	30–300	Sr	600–6000	Ba	400–4000
Mg	1–10%	Mn	400–4000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.6–6%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	10–100	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	20–200
K	0.3–3%	Cu	30–300	Cd	<30	Bi	<30

5

Li	400–4000	Ca	3–30%	Zn	200–2000	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	40–400	V	50–500	Ge	<30	Sb	<100
Na	0.2–2%	Cr	50–500	Sr	0.1–1%	Ba	500–5000
Mg	2–20%	Mn	400–4000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	<30	Tl	<100
P	<300	Ni	40–400	Ag	<6	Pb	30–300
K	1–10%	Cu	30–300	Cd	<30	Bi	<30

6

Li	400–4000	Ca	3–30%	Zn	50–500	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	100–1000	V	50–500	Ge	<30	Sb	<100
Na	0.2–2%	Cr	40–400	Sr	0.1–1%	Ba	400–4000
Mg	2–20%	Mn	400–4000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	<30	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	20–200
K	1–10%	Cu	50–500	Cd	<30	Bi	<30

7

Li	300–3000	Ca	4–40%	Zn	30–300	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	50–500	V	60–600	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.2–2%	Ba	500–5000
Mg	2–20%	Mn	500–5000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	<30	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	20–200
K	1–10%	Cu	40–400	Cd	<30	Bi	<30

8

Li	300–3000	Ca	3–30%	Zn	30–300	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	50–500	V	60–600	Ge	<30	Sb	<100
Na	0.2–2%	Cr	30–300	Sr	0.2–2%	Ba	500–5000
Mg	2–20%	Mn	500–5000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	<30	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	20–200
K	1–10%	Cu	40–400	Cd	<30	Bi	<30

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[a] ppm unless otherwise specified.

TABLE V
(continued)
SPECTRAL ANALYSES OF SAMPLES 10–16, RM 3 CORE

9

Li	300–3000	Ca	3–30%	Zn	30–300	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	50–500	V	60–600	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.2–2%	Ba	500–5000
Mg	2–20%	Mn	500–5000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	<30	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	20–200
K	1–10%	Cu	40–400	Cd	<30	Bi	<30

10

Li	400–4000	Ca	3–30%	Zn	30–300	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	50–500	V	60–600	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.2–2%	Ba	500–5000
Mg	2–20%	Mn	400–4000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	10–100	Tl	<100
P	300–3000	Ni	30–300	Ag	<6	Pb	<60
K	1–10%	Cu	40–400	Cd	<30	Bi	<30

11

Li	400–4000	Ca	3–30%	Zn	30–300	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	50–500	V	60–600	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.2–2%	Ba	500–5000
Mg	2–20%	Mn	400–4000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	10–100	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	<60
K	1–10%	Cu	40–400	Cd	<30	Bi	<30

12

Li	400–4000	Ca	3–30%	Zn	30–300	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	50–500	V	60–600	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.2–2%	Ba	500–5000
Mg	2–20%	Mn	400–4000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	10–100	Tl	<100
P	<300	Ni	30–300	Ag	<6	Pb	<60
K	1–10%	Cu	40–400	Cd	<30	Bi	<30

13

Li	300–3000	Ca	3–30%	Zn	30–300	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	50–500	V	100–1000	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.1–1%	Ba	500–5000
Mg	2–20%	Mn	500–5000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	30–300	Tl	<100
P	<300	Ni	40–400	Ag	<6	Pb	20–200
K	1–10%	Cu	40–400	Cd	<30	Bi	<30

14

Li	300–3000	Ca	3–30%	Zn	30–300	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	50–500	V	100–1000	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.1–1%	Ba	500–5000
Mg	2–20%	Mn	500–5000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	30–300	Tl	<100
P	<300	Ni	40–400	Ag	3–30	Pb	20–200
K	1–10%	Cu	40–400	Cd	<30	Bi	<30

15

Li	300–3000	Ca	3–30%	Zn	30–300	In	<30
Be	0.3–3	Ti	0.1–1%	Ga	20–200	Sn	<60
B	50–500	V	100–1000	Ge	<30	Sb	<100
Na	0.3–3%	Cr	30–300	Sr	0.1–1%	Ba	500–5000
Mg	2–20%	Mn	500–5000	Zr	40–400	Ta	<1000
Al	1–10%	Fe	0.8–8%	Nb	<100	W	<1000
Si	5–50%	Co	10–100	Mo	30–300	Tl	<100
P	<300	Ni	40–400	Ag	<6	Pb	30–300
K	1–10%	Cu	40–400	Cd	<30	Bi	<30

16

Li	400–4000	Ca	3–30%	Zn	30–300	In	<30
Be	<1	Ti	500–5000	Ga	<30	Sn	<60
B	50–500	V	40–400	Ge	<30	Sb	<100
Na	0.6–6%	Cr	20–200	Sr	300–3000	Ba	200–2000
Mg	1–10%	Mn	300–3000	Zr	20–200	Ta	<1000
Al	1–10%	Fe	0.6–6%	Nb	<100	W	<1000
Si	3–30%	Co	<30	Mo	10–100	Tl	<100
P	<300	Ni	20–200	Ag	2–20	Pb	20–200
K	1–10%	Cu	30–300	Cd	<30	Bi	<30

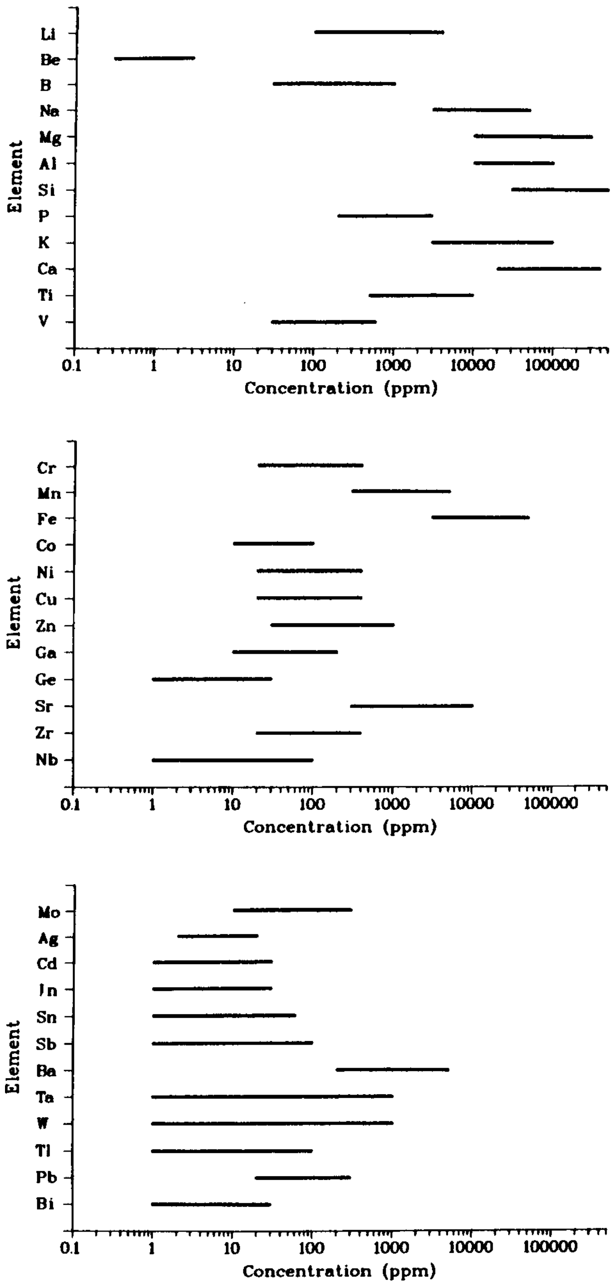


Fig. 3.
Trace element concentrations in spent shales from Occidental retort 3E.

TABLE VI

MINERALOGICAL ANALYSES OF SELECTED SAMPLES FROM ROOM 3 SPENT SHALE CORE

	Sample 5	Sample 16
Mean depth (ft)	464.5	493
Major minerals	Calcite	Akermanite
Minor minerals	Diopside α-Quartz Aragonite Kalsilite	Diopside
Trace mineral(s)	Akermanite	Kalsilite 2 unidentified phases

figure shows the characteristic x-ray spectrum and the relative counts/second intensity data for the characteristic Kα x ray of the element and the area sampled by the EDS. Most of the pertinent information is in the figure captions, and thus, only generalities will be discussed in the text. Figures 4 through 7 appear to be representative of the predominant mineral constituents suggested by XRD. Figure 4 shows an area of high calcium content, with silicon, aluminum, potassium, and some iron also present. Figure 4 shows a crystalline area with only calcium present (probably calcite). Figure 6 shows an area rich in iron and magnesium, with relatively smaller amounts of calcium, silicon, and aluminum (possibly an area that is or was iron-rich dolomites). Figure 7 shows an area rich in calcium and silicon, with lesser amounts of magnesium, aluminum, and iron, which might indicate the presence of the trace mineral silicates suggested by XRD. On the other hand, Figs. 8-10 show some irregular or relatively minor constituents of the mounted powder. Figure 8 shows a piece of possibly detrital material containing calcium and titanium (either $CaTiO_3$ or discrete oxides). Figure 9 shows an area whose appearance and elemental analysis suggests that this is an area of clay minerals. The most startling information, shown in Fig. 10, was the appearance of many nodules of zinc metal. This observation was originally reported to be an artifact, but a later report stated that Occidental had used a commercial pipe dope that contains copious amounts of zinc metal particles to lubricate a coring drill during the recovery operation (see Appendix A in Ref. 5).

SEM-EDS analysis of a metallographic mount of -100-mesh powder from sample 16 provided no surprises. Most of the particles had small voids probably caused by gas-evolving mineral and decomposition reactions. Calcium, aluminum, potassium, magnesium, and

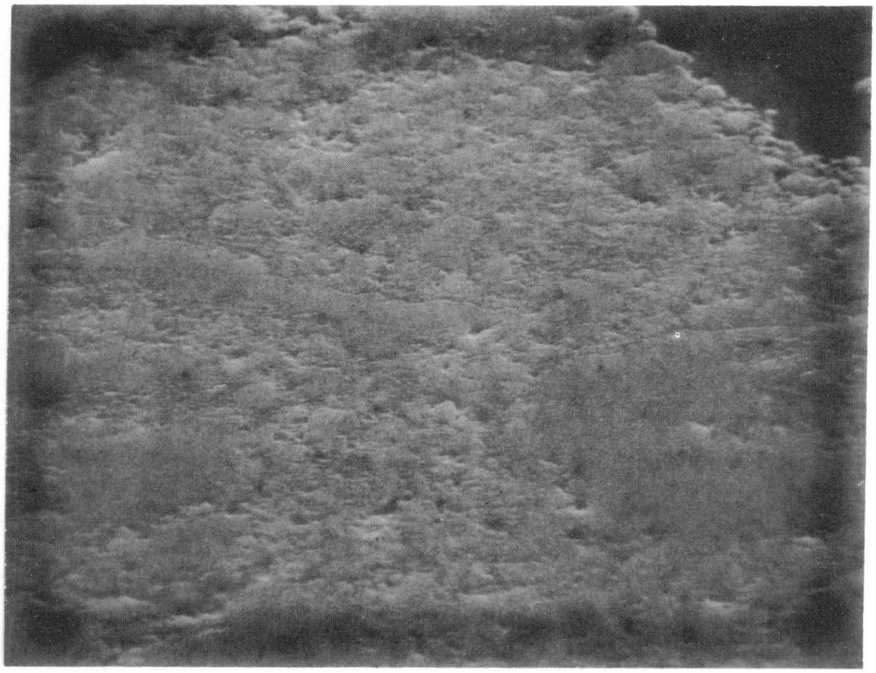


Fig. 4a.
SEM of average rock material from sample 5. 2500X

```
SAMPLE  10
ID: WS5 16

TIME:    100 SEC

ELEMENT     INTENSITY     BACKGROUND
               CPS            CPS
-------    -----------    ----------
NA            0.0000        14.0933
MG           15.7633        17.0867
AL           27.7216        18.6184
SI          128.1482        16.8418
P             0.0000        14.4302
S                           11.6436
CL                           8.9585
CD                           8.8609
K            22.0709         8.3291
CA          169.0235         7.2065
TI            1.8020         4.9680
MN                           3.8676
FE            6.9538         3.2162
CD                           2.9386
NI                           2.6384
CU            0.0000         2.7161
ZN            0.0000         2.2918
```

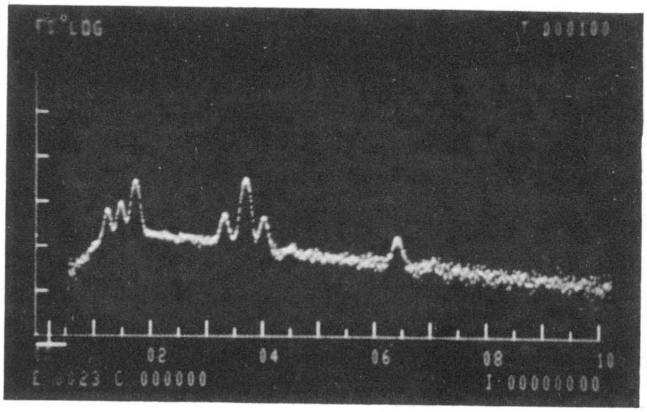


Fig. 4b.
EDS from a 10 000X sweep of area indicated in (a). Average rock material consists of Ca, Si, Al, K, and some Fe.

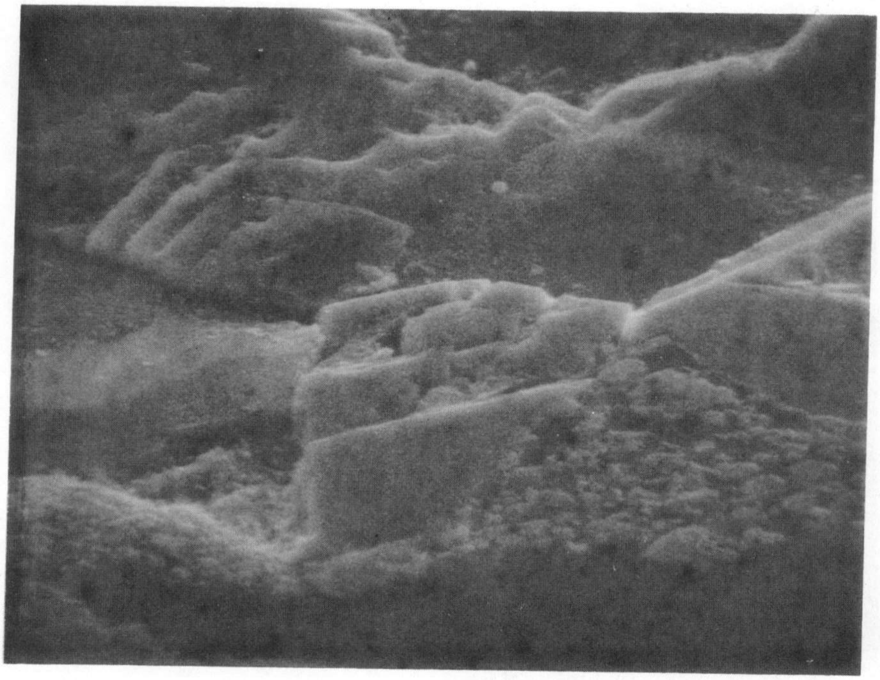


Fig. 5a.
SEM of cleavage pattern of a major mineral, probably calcite. 2000X

```
SAMPLE    7
ID: WS5 13

TIME:    100 SEC

ELEMENT    INTENSITY    BACKGROUND
              CPS           CPS
-------    ----------    ---------
NA            0.0000       10.4429
MG            0.0000       13.0151
AL            0.2745       16.5955
SI            3.0436       18.9864
P             0.0000       19.3903
S             2.1463       16.2737
CL            0.0000       13.0037
CD            0.0000       12.8025
K                          11.8718
CA          367.6929        9.9071
TI                          6.3346
MN                          4.6171
FE            0.7052        3.6948
CO                          3.2263
NI                          3.0124
CU            0.0000        2.9151
ZN            0.0000        2.4286
```

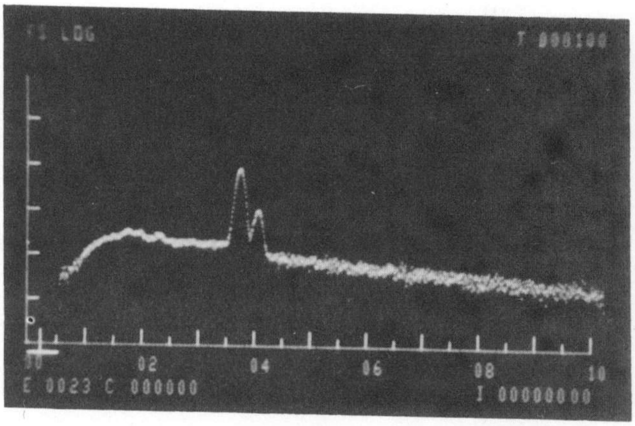


Fig. 5b.
EDS of material showing surface cleavage pattern above with calcium the only element constituent.

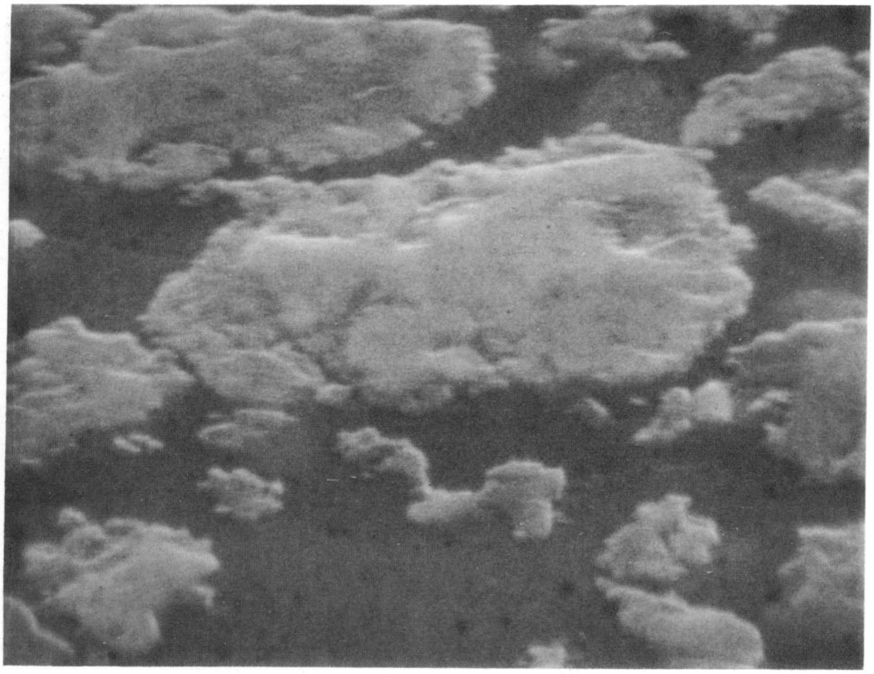


Fig. 6a.
SEM of rock material with very high iron and magnesium contents. 5000X

```
SAMPLE    5
ID: WS5 11

TIME:    100 SEC

ELEMENT      INTENSITY      BACKGROUND
                CPS             CPS
-------     ----------      ---------
NA              0.0000        74.2804
MG            113.7959        74.5641
AL             84.3396        62.1604
SI             76.0489        46.1211
P               0.0000        33.5234
S               0.0000        30.5351
CL                            24.9053
CD                            23.6381
K               2.8883        22.7217
CA             58.9029        20.7871
TI              5.6595        17.0605
MN              7.2398        12.9902
FE            269.8425        11.0275
CO                            11.2704
NI              0.0000         8.7552
CU                             6.2932
ZN                             5.4961
```

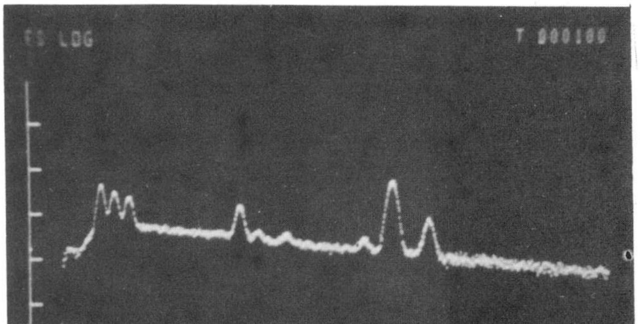


Fig. 6b.
EDS of above area with major elements Fe, Mg, Al, Si, and Ca (possibly some Mn).

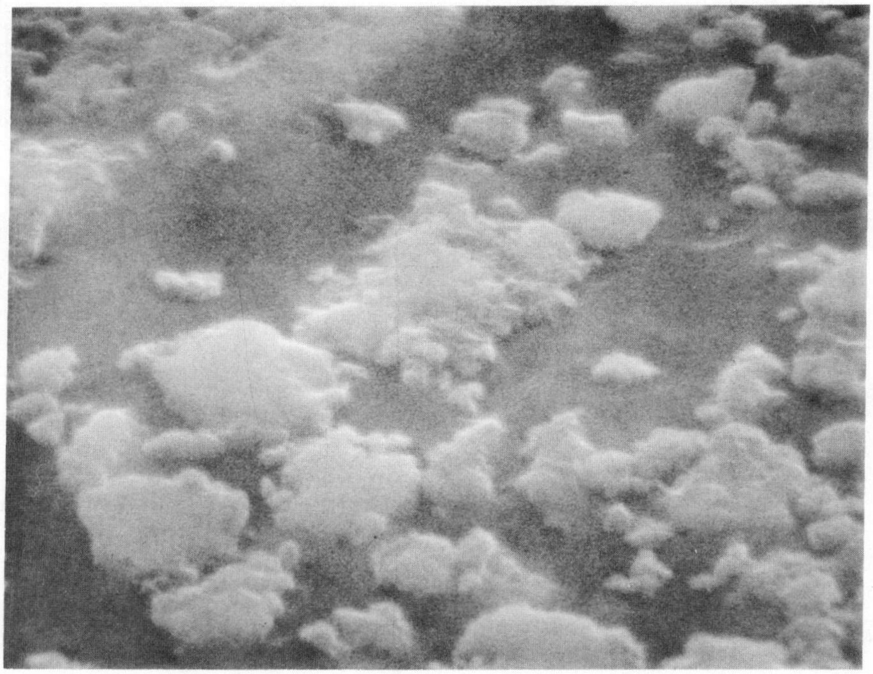
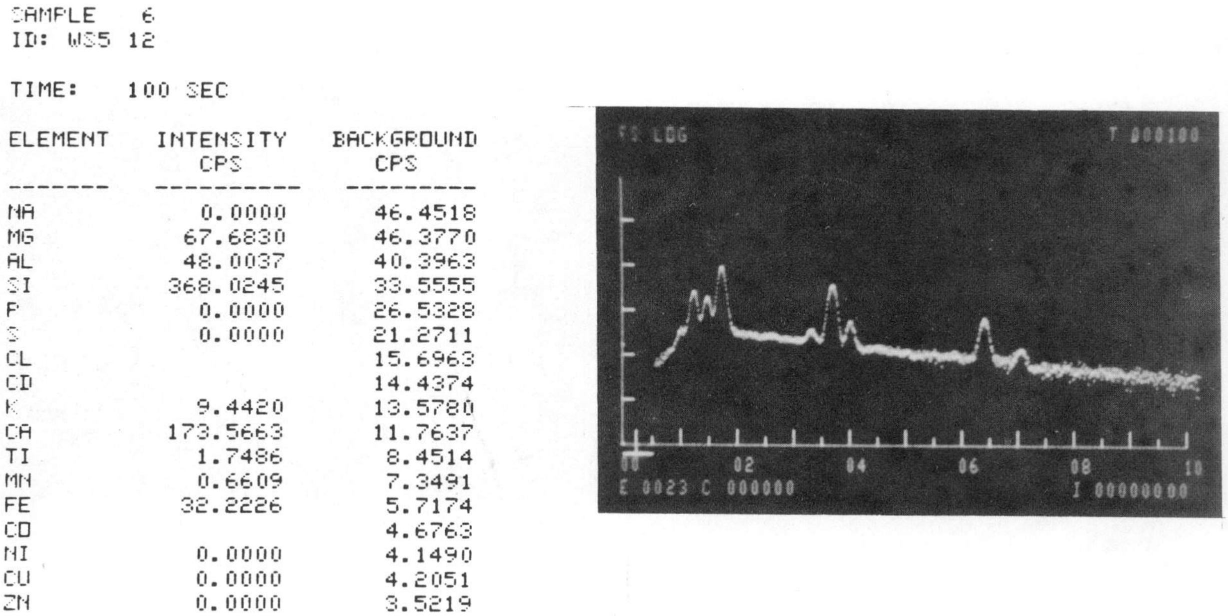


Fig. 7a.
SEM of an area of high Ca and Si content. 10 000X



```
SAMPLE   6
ID: WS5 12

TIME:    100 SEC

ELEMENT    INTENSITY    BACKGROUND
              CPS          CPS
-------    ----------   ----------
NA            0.0000      46.4518
MG           67.6830      46.3770
AL           48.0037      40.3963
SI          368.0245      33.5555
P             0.0000      26.5328
S             0.0000      21.2711
CL                        15.6963
CD                        14.4374
K             9.4420      13.5780
CA          173.5663      11.7637
TI            1.7486       8.4514
MN            0.6609       7.3491
FE           32.2226       5.7174
CO                         4.6763
NI            0.0000       4.1490
CU            0.0000       4.2051
ZN            0.0000       3.5219
```

Fig. 7b.
EDS of above area indicating presence of Si, Ca, Mg, Al, and Fe.

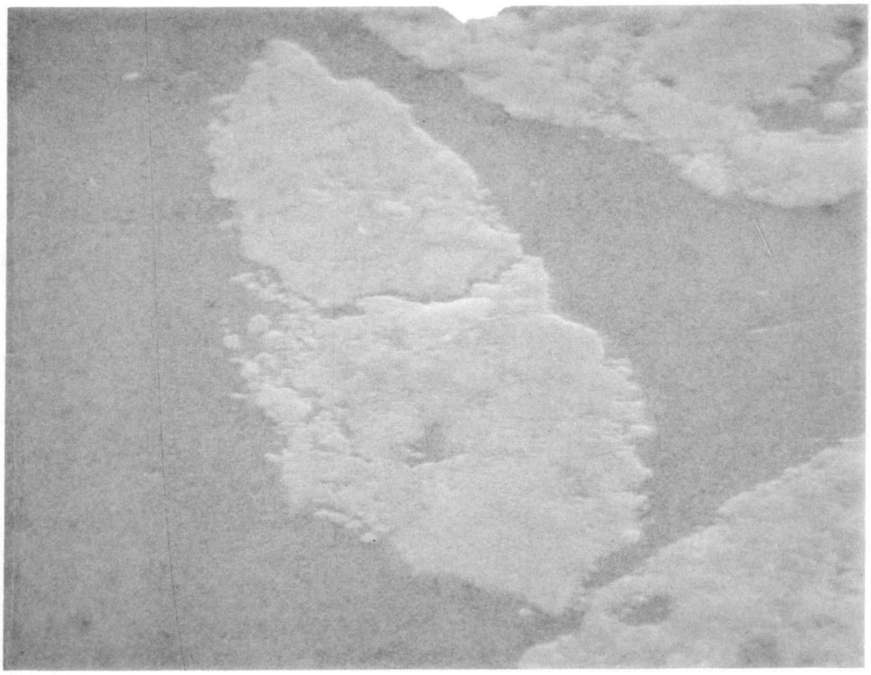


Fig. 8a.
SEM of micron-sized mineral assemblage (probably detrital) containing Ca and Ti. 2000X

```
SAMPLE   8
ID: WS5 14

TIME:    100 SEC

ELEMENT    INTENSITY    BACKGROUND
              CPS           CPS
-------   ----------   ---------
NA            2.1339     14.4261
MG            2.5214     17.5586
AL            5.5445     22.3155
SI           13.0336     25.5864
P             0.0000     26.2799
S             0.0000     22.3566
CL            0.0000     17.5967
CD            0.0000     16.9561
K             6.5943     16.1157
CA          323.9586     14.3414
TI          242.6644     23.1256
MN                        7.0447
FE            1.5620      5.7580
CD            0.0000      5.3068
NI            0.0000      4.4244
CU                        4.0935
ZN            0.0000      3.5139
```

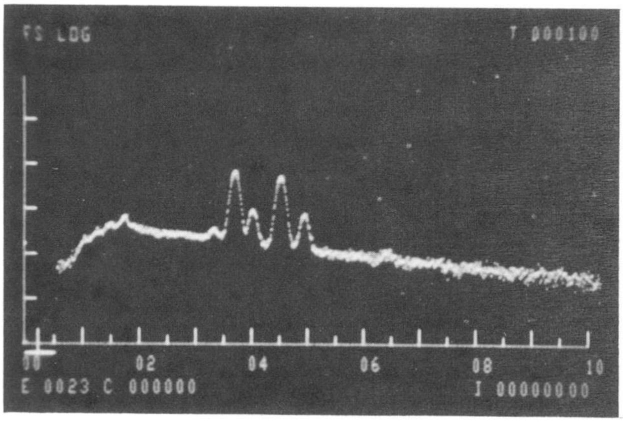


Fig. 8b.
EDS of above area.

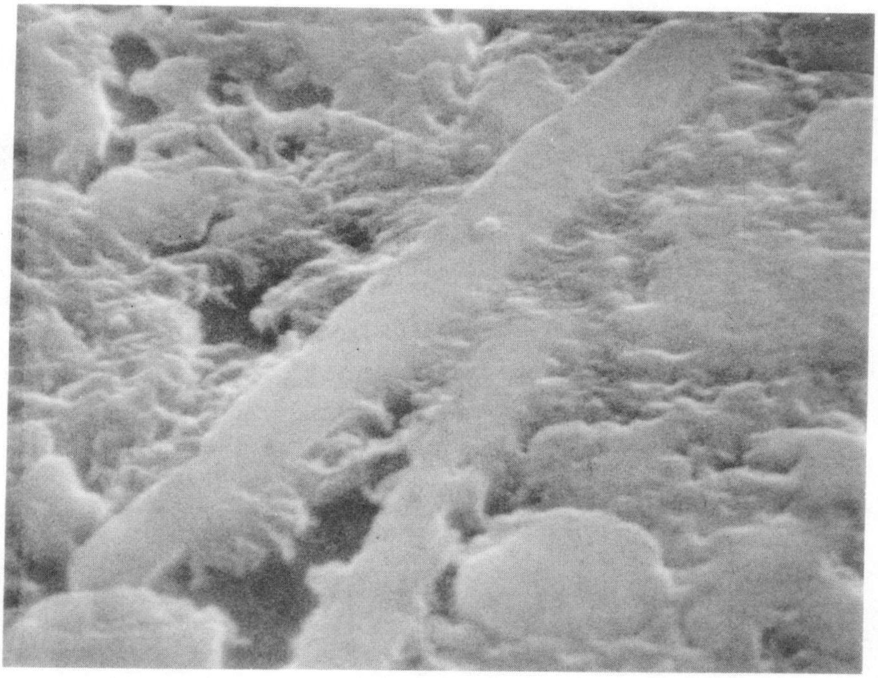


Fig. 9a.
SEM of an area with elemental composition of clay mineral. 20 000X

```
SAMPLE   3
ID: WS5 23

TIME:    100 SEC

ELEMENT    INTENSITY    BACKGROUND
              CPS           CPS
-------    ----------    ---------
NA            0.0000       31.8604
MG           82.0709       31.1491
AL           48.7986       26.2014
SI          231.5923       21.9177
P             0.0000       17.4116
S             0.0000       13.8549
CL            0.1876       10.1224
CD            1.5805        9.4795
K            46.0908        9.1092
CA           47.0027        8.3273
TI            6.1512        7.6488
MN            0.8129        4.3771
FE            7.8845        3.4355
CD            0.4424        2.8976
NI            0.3050        2.4550
CU            0.0000        2.7337
ZN            0.0000        2.3611
```

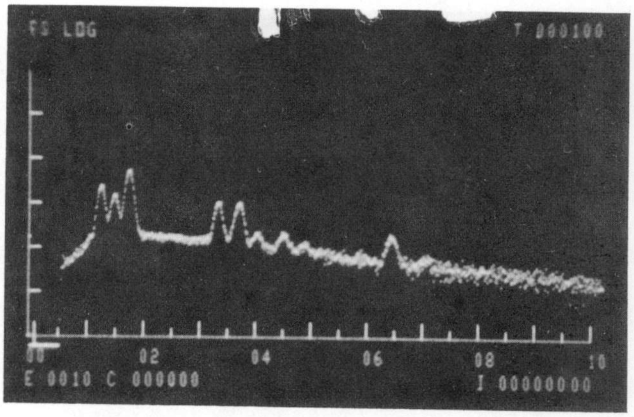


Fig. 9b.
EDS of above area. Elements include Mg, Al, Si, K, and Ca.

Fig. 10a.
SEM of discrete particle. Elemental analysis and appearance suggest probable Zn metal. 5000X

```
SAMPLE    4
ID: WS5 4

TIME:    100 SEC

ELEMENT     INTENSITY     BACKGROUND
               CPS           CPS
-------     ----------    ----------
ZN  L       357.2765       26.1235
MG            0.0000       18.0607
AL            4.1682       19.0418
SI           14.7481       22.5119
P                          24.6590
S                          23.9073
CL                         21.2154
CD            0.0386       22.1314
K             1.4151       21.4049
CA            4.7888       19.8712
TI            0.0000       17.0215
MN            0.0000       12.9349
FE            1.4399       10.8101
CO            0.0000       10.1508
NI            0.0000        8.2011
CU                          6.7086
ZN          135.8509        5.8391
```

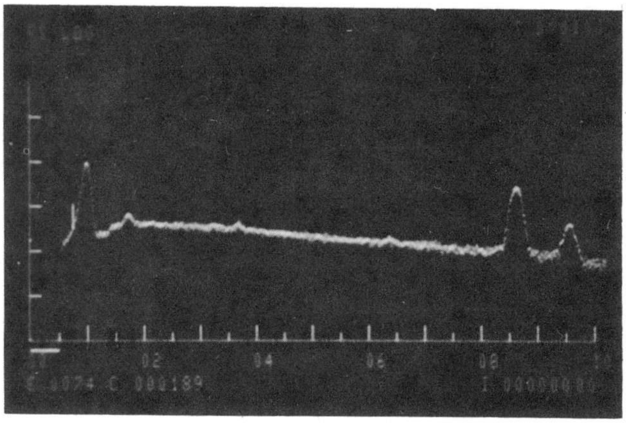


Fig. 10b.
EDS of above area indicates Zn metal.

iron were present in varying amounts, and silicon was uniformly present in large amounts. Typical scanning electron micrographs of this material are shown in Figs. 11-14. Figures 11-13 show typical areas of predominant mineral matter, whereas Fig. 14 shows an area rich in calcium and titanium and probably detrital material (as in sample 5, either $CaTiO_3$ or discrete oxides). Figure 11 shows a region rich in calcium and silicon with lesser amounts of potassium, magnesium, aluminum, and iron. This may be a mixture of akermanite and/or diopside with a smaller amount of K-Al-silicate (kalsilite?). Figure 12 reveals a silicate region rich in calcium and iron, and Fig. 13 shows a region of K-Al-silicate (kalsilite?). These observations are consistent with the XRD data.

The SEM-EDS results complement and are consistent with the XRD data discussed earlier for samples 5 and 16. In sample 5, calcium (CaO or $CaCO_3$) either occurred alone or with potassium, magnesium, iron, aluminum, and silicon. The particles were solid and textured, thus supporting the conclusion that this sample experienced low temperatures and/or short heating duration with concomitant minimal disruption of the mineral matrix. In contrast, the surfaces of particles from sample 16 were smooth with many voids. Silicon was present in all samples with varying amounts of calcium, magnesium, iron, potassium, and aluminum. These observations suggest that silication reactions occurred as well as gas evolution reactions, which supports the conclusion that this section in the middle of the retort experienced higher temperatures and/or longer heating duration with almost complete transformation of the mineral matrix.

b. Leaching Experiments. Standard shaker leaching experiments were performed on all of the sample sections for which material was received. The small sample sizes available limited quantities for leaching experiments. Typically, 6 g of spent shale were leached with 30 mL of distilled water. All other procedural aspects are detailed in Appendix B. Trace element analyses were performed on the resulting leachates by AAS. The results of these analyses are reported in Table VII. For comparison, the ecology MEG/MATE values are shown in the table for some of the trace elements of potential environmental concern.

Conclusions based on the results of these studies are tenuous because the original raw shale composition, the retorting conditions, and the retort cooling procedures are unknown. The small quantities available for leaching and the resultant *very poor* mixing also impairs the validity of the conclusions on leaching characteristics. Despite these constraints, we have made several general observations that, in conjunction with the mineralogical studies reported in Ref. 18, are confirmed independently by several Task Force participating laboratories. In summary, these studies indicate the absence of dolomite from all samples, the persistence of calcite in samples 2-13 (greater for samples 2-6 than for 7-13), and the occurrence of akermanite and diopside in all core segments, but in greatest quantity in sample 1, and in increasing quantity in samples 7-16. A summary of XRD peak heights, as reported in Appendix A of Ref. 5, is given in Table VIII.

References 5 and 18 show that core segments 1 and 14-16 experienced higher temperatures and/or longer heating durations than the other segments. Table VII shows reasonable correlation of pH and trace element analyses for these four segments. Major discrepancies occur in the analyses of the major cations calcium, magnesium, and sodium. These differences may reflect initial shale compositional variations due to changes in depth, or they may be a consequence of the crystallographic control of dissolution kinetics, which is a recent theory to explain weathering of feldspars and pyroxenes.[19-23] Uncertainties such as these highlight the necessity of further detailed studies of mechanisms of trace element release from these complicated matrices.

Further analysis of the trace element results for samples 5-16 is complicated by a change of the experimental procedures used to isolate leachates from remaining solids. We used a 0.22-μ filter for samples 1-4 and a 0.45-μ filter for samples 5-16. The high aluminum content of these leachates might reflect a clay suspension that passed through the larger filter size. However, the filtering behavior (consistency, surface area, etc.) of samples 5-12 was different from that of samples 1-4 and 13-16; thus, the procedural change may not be totally responsible! Because fluoride is postulated to reside in the clay minerals, and because of the potential for adsorption of colloidal material on the suspended particles, the behavior of fluoride and iron could also be considered suspect in these samples. The manifestation of this experimental artifact is greatest in samples 5-12 and either minimal or nonexistent in those samples exposed to the most extreme retorting conditions (samples 13-16). These speculations could have been proved if silicon analyses had been available. The only statement that can be made from available information is that the trace element concentrations of aluminum,

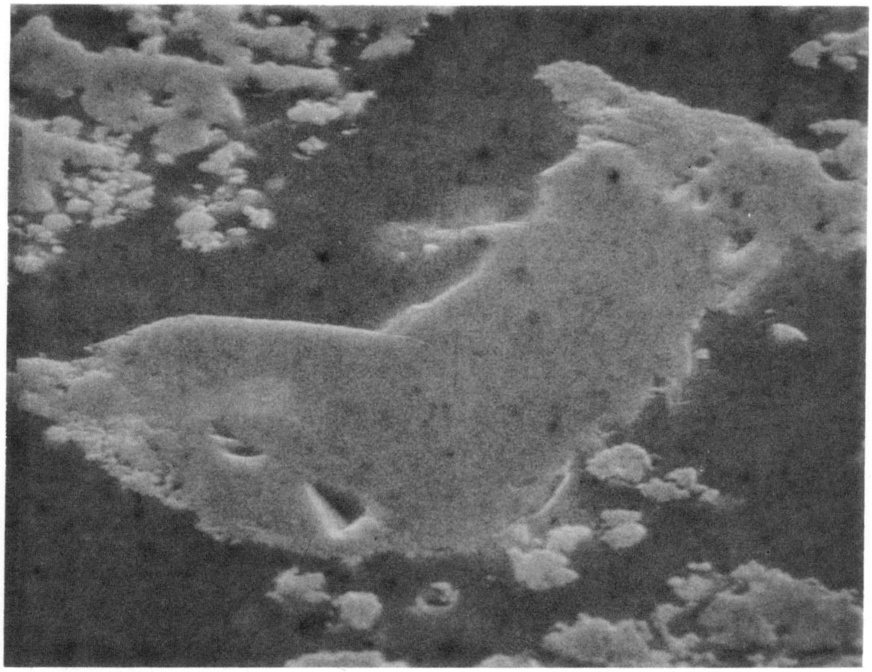


Fig. 11a.
SEM of average particle from sample 16 (probably silicate material). 2000X

```
SAMPLE  18
ID: WS16 7

TIME:    100 SEC

ELEMENT    INTENSITY     BACKGROUND
              CPS            CPS
-------   ----------     ---------
NA            0.0000       17.1039
MG            0.0000       21.8645
AL                         27.3436
SI         1270.3924       28.9376
P             0.0000       26.8425
S             0.0000       19.0509
CL                         12.8366
CD                         12.8552
K                          12.4041
CA                         11.4519
TI            0.0000        9.3977
MN            0.0000        7.0644
FE            0.0000        5.9596
CO            0.0000        5.0227
NI            0.0000        4.3193
CU            0.0000        3.5404
ZN            0.0000        3.1677
```

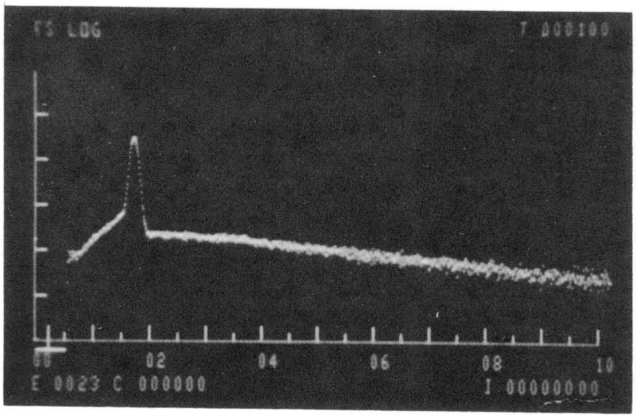


Fig. 11b.
EDS from a 50X sweep of central area to obtain the average composition.

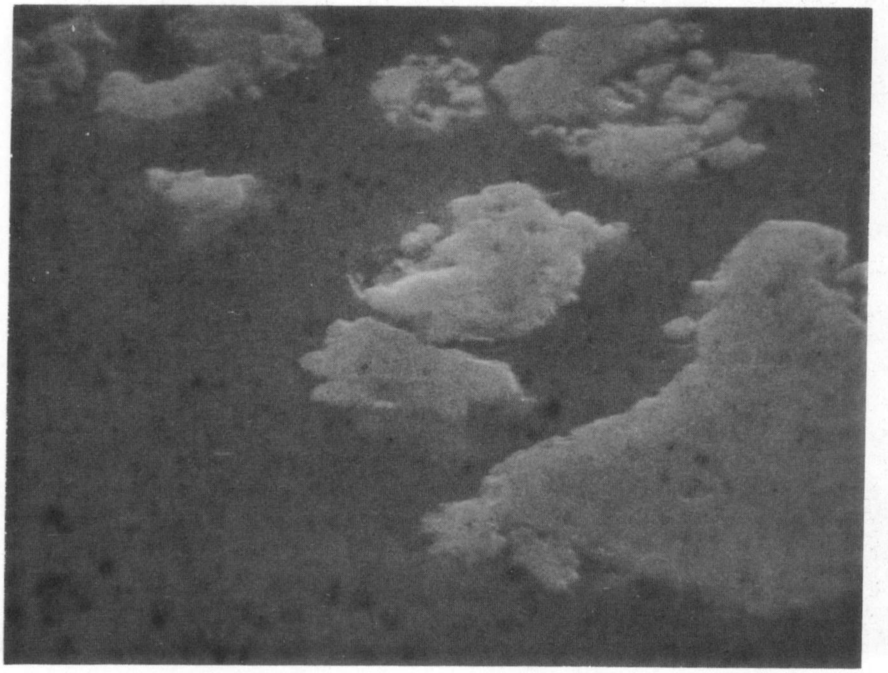


Fig. 12a.
SEM of an area rich in Ca, Fe, and Si. 5000X

```
SAMPLE  14
ID: WS16 4

TIME:    100 SEC

ELEMENT    INTENSITY    BACKGROUND
              CPS           CPS
-------   ----------    ----------
NA            0.0000       23.8233
MG           21.0826       30.8574
AL           50.2617       34.3283
SI          234.2551       29.0649
P             0.0000       23.9332
S                          20.5416
CL            0.0000       16.6780
CD                         16.7828
K             2.8851       15.8949
CA          144.6896       14.0204
TI            2.4408       10.9092
MN            0.0000        9.9680
FE          147.2440        7.9960
CO                          7.0937
NI            0.0000        5.8585
CU                          4.3665
ZN            0.0000        4.1595
```

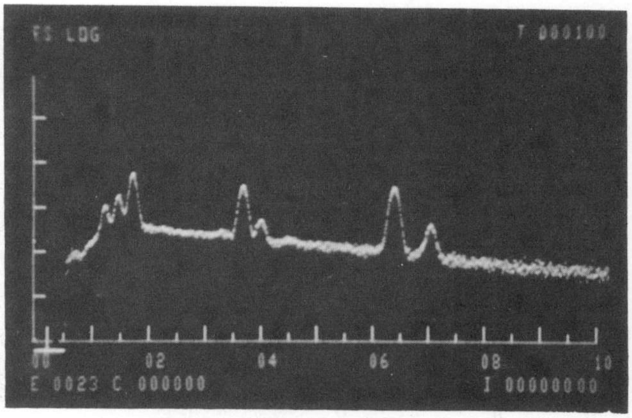


Fig. 12b.
EDS of above area.

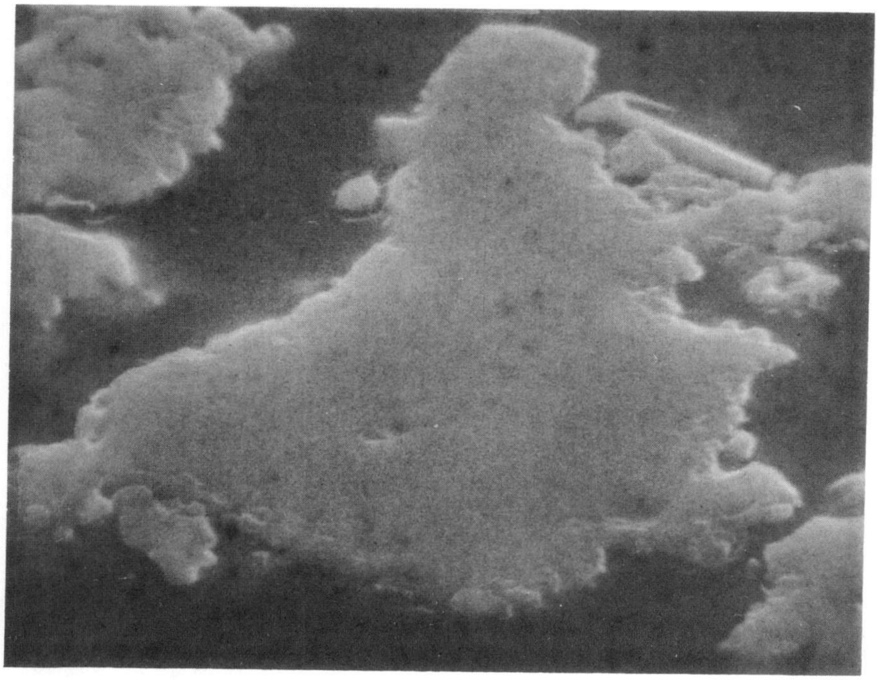
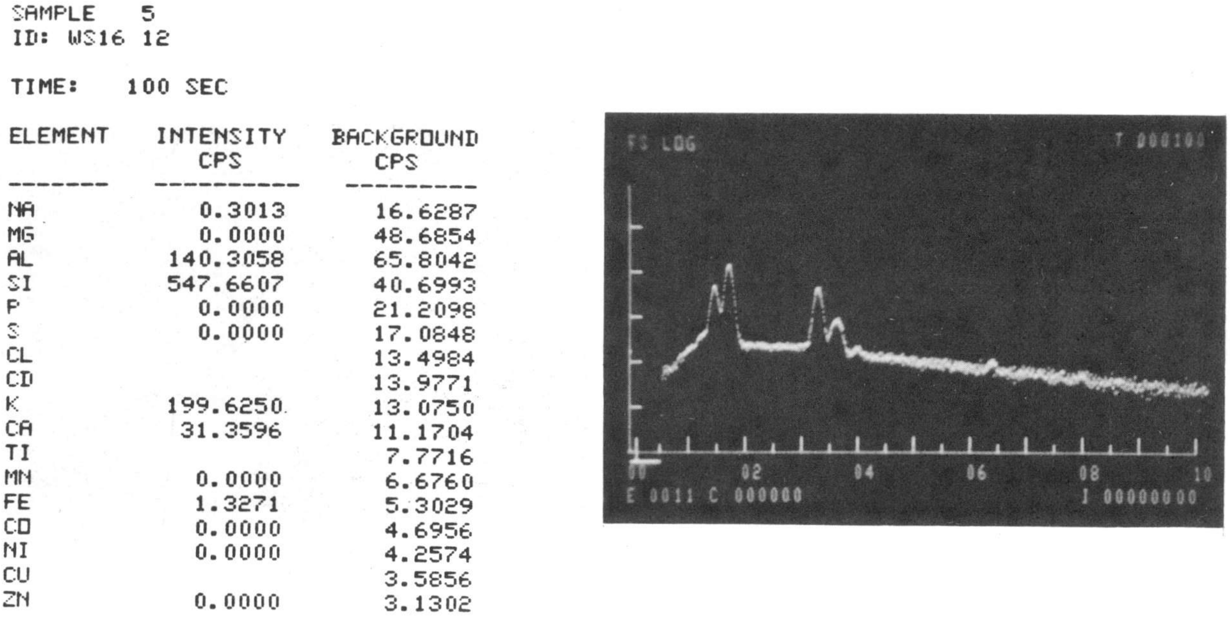


Fig. 13a.
SEM of an area whose elemental analysis indicates presence of K, Al, and Si.



```
SAMPLE    5
ID: WS16 12

TIME:    100 SEC

ELEMENT     INTENSITY      BACKGROUND
               CPS            CPS
-------     ----------     ---------
NA             0.3013        16.6287
MG             0.0000        48.6854
AL           140.3058        65.8042
SI           547.6607        40.6993
P              0.0000        21.2098
S              0.0000        17.0848
CL                           13.4984
CD                           13.9771
K            199.6250        13.0750
CA            31.3596        11.1704
TI                            7.7716
MN             0.0000         6.6760
FE             1.3271         5.3029
CO             0.0000         4.6956
NI             0.0000         4.2574
CU                            3.5856
ZN             0.0000         3.1302
```

Fig. 13b.
EDS of above area.

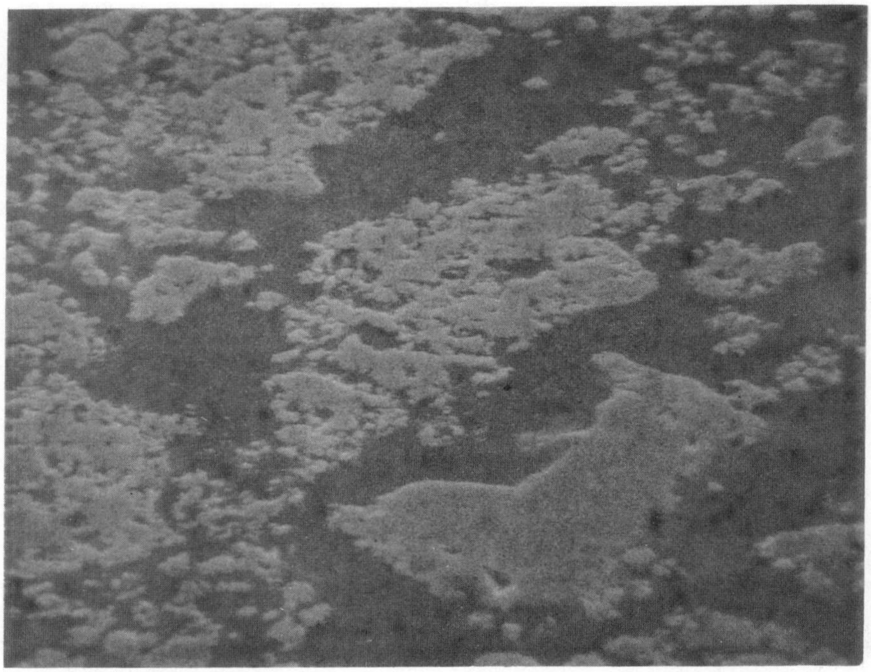


Fig. 14a.
SEM of an area not typical of the major mineral matrix. 1000X

```
SAMPLE  13
ID: WS16 3

TIME:    100 SEC

ELEMENT    INTENSITY    BACKGROUND
              CPS           CPS
-------   -----------   ----------
NA             0.6990      15.5910
MG             0.9877      18.8323
AL             3.5478      23.3622
SI            35.8101      26.5999
P             13.2829      26.8071
S                          21.7655
CL                         16.8289
CD                         17.1247
K              4.2869      16.4931
CA           327.3500      15.1600
TI           217.9597      23.2903
MN                          6.9942
FE             4.6646       5.3854
CO                          4.5352
NI                          3.9217
CU             0.2300       3.8200
ZN             0.0000       3.6233
```

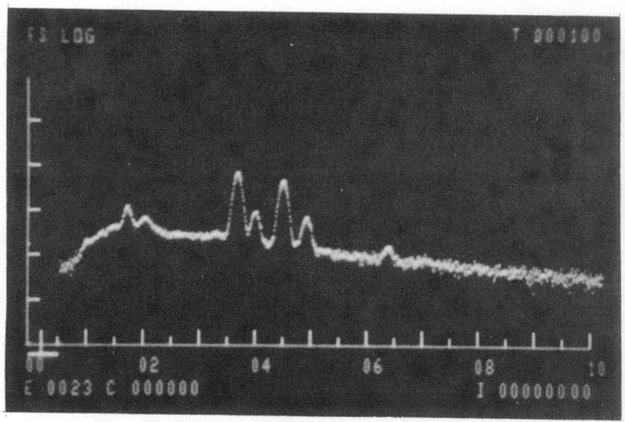


Fig. 14b.
EDS of above area, which is rich in Ca and Ti.

TABLE VII

TRACE ELEMENT ANALYSES FOR LEACHATES FROM ROOM 3 CORE SAMPLES[a]

(ppm)

Mean Depth (ft)	Sample	pH	Al	As	B	Ca	Co	Cr	Cu	F	Fe
443.5	1	10.7	0.3	0.005	0.6	93	<0.04	<0.025	<0.02	0.1	<0.02
455.5	2	8.4	<0.2	0.029	1.2	1340	0.12	<0.025	<0.02	2.2	<0.02
458.5	3	9.2	0.2	0.072	1.2	17	<0.04	<0.025	<0.02	1.6	0.04
461.5	4	8.3	<0.2	0.031	0.9	141	<0.04	<0.025	<0.02	1.7	<0.02
464.5	5	9.1	2.4	0.036	<0.6	14	<0.04	<0.025	<0.02	1.7	0.87
468.5	6	9.6	3.3	0.081	6.7	6	<0.04	<0.025	<0.02	11.5	1.90
469.75	7	9.8	2.1	0.062	1.5	18	<0.04	<0.025	<0.02	22.5	1.76
472.5	8	9.6	4.4	0.056	1.7	20	<0.04	<0.025	<0.02	15.2	2.72
476	9	9.7	6.8	0.051	3.5	36	<0.04	<0.025	<0.04	15.8	2.52
476.5	10	10.3	2.7	0.150	2.5	28	0.04	<0.025	<0.02	7.3	4.68
478.5	11	10.7	2.2	0.200	2.5	27	<0.04	<0.025	0.03	5.4	4.08
481	12	10.5	1.7	0.090	2.3	30	<0.04	<0.025	<0.02	5.1	2.40
483.5	13	9.6	0.2	0.010	1.7	52	<0.04	<0.025	<0.02	5.9	0.12
484	14	10.2	0.3	0.005	<0.3	170	<0.04	<0.025	<0.02	4.4	<0.02
484.5	15	9.9	0.2	0.099	0.5	510	0.07	<0.025	<0.02	2.5	<0.02
493	16	10.4	0.2	0.036	0.6	173	<0.04	<0.025	<0.02	0.8	<0.02
Ecology Mate			1.0	0.025	25						

---

[a] Values in milligrams/liter. Uncertainty lies in the last figure reported.

TABLE VII (cont)

Mean Depth (ft)	Sample	Mg	Mn	Mo	Na	Nl	Pb	Sb	Se	V	Zn
443.5	1	<0.4	<0.02	0.10	33	<0.04	<0.0005	<0.002	<0.001	0.50	<0.003
445.5	2	24	<0.02	0.13	600	<0.04	<0.004	0.009	<0.050	0.47	0.035
448.5	3	2.3	<0.02	0.07	80	<0.04	<0.0005	<0.002	<0.007	1.57	0.003
461.5	4	7.5	<0.02	0.07	58	<0.04	<0.0005	<0.002	<0.005	0.33	0.015
464.5	5	8.3	<0.02	<0.04	73	<0.04	0.0034	<0.002	<0.001	0.80	0.143
468.5	6	13.8	0.05	0.10	135	<0.04	0.009	<0.002	0.014	2.63	0.105
469.75	7	6.8	0.02	0.10	103	<0.04	<0.0005	<0.003	0.023	0.47	0.023
472.5	8	13.0	0.04	0.13	100	<0.04	0.004	<0.002	0.007	0.57	0.041
476	9	37	0.13	0.23	128	<0.04	<0.0005	<0.003	0.038	0.70	0.063
476.5	10	16	0.07	0.13	123	<0.04	<0.0005	<0.003	0.050	1.13	0.054
478.5	11	10.8	0.06	0.27	155	<0.04	<0.0005	<0.003	0.040	1.63	0.093
481	12	7.3	0.04	0.20	155	<0.04	<0.0005	<0.003	0.040	1.30	0.022
483.5	13	1.1	<0.02	0.50	98	<0.04	<0.0005	<0.003	0.010	0.27	<0.003
484	14	1.1	<0.02	0.40	33	<0.04	<0.0005	<0.002	<0.010	<0.10	<0.003
484.5	15	11.0	<0.02	0.40	155	<0.04	<0.0005	<0.003	<0.010	0.53	<0.003
493	16	8.8	<0.02	0.47	103	<0.04	<0.0005	<0.003	<0.010	0.57	0.003
Ecology Mate				7					0.025	0.15	

TABLE VIII

XRD PEAK HEIGHTS FOR SPENT SHALE MINERALS FROM FIRST CORE OF RETORT 3E[a]

Sample	Calcite	Dolomite	Quartz	$NaAlSi_3O_8$	$KAlSi_3O_8$	Akermanite	Diopside	Aragonite	Kalsilite	Monticellite	Depth (ft)
1						10	1.5		2		443.5
2	9		2			3.5		2			455.5
3	2		4	0.5	1.5	3.5	2	4	0.5	0.5	458.5
4	4		9	6	4	1	4	1			461.5
5	8		2			2	3	0.5	1.5		464.5
6	9		1		1	2	3		1		468.5
7	6		1	0.5	0.5	5	3		1	1	469.75
8	6					4	6		1.5		472.5
9	5					6	2	0.5	1	1	476
10	5					6	2	1	1	1	476.5
11	4					8	1.5	1	2	2	478.5
12	2					7	4		1.5		481
13	1					9	2		1	1	483.5
14						9	2		1	1	484
15						9	2		1		484.5
16						10	4		1		493

[a] As reported in Ref. 18 and as provided by Occidental Oil Shale Company, Inc., to the Oil Shale Task Force.

fluoride, and iron in samples 1-16 are consistent with the variation of filtering technique.

Excluding aluminum, fluoride, and iron, preliminary observations concerning trace element mobility from underground retorted shale can be made from examination of Table VII.

1. No conclusions are possible for cobalt, chromium, copper, nickel, lead, and antimony because the concentrations of the elements in the leachates are below the AAS limits of detection.
2. There appears to be no correlation of trace element mobility with the presumed retorting conditions for arsenic, magnesium, sodium, uranium, selenium, and manganese. This does not imply that the mobility of these elements is not dependent on process variables, but it suggests that any effects of retorting conditions on the mobility of these elements are subtle and are probably masked by compositional variations with depth for this core.
3. Mobility of the following trace elements appears to be influenced by retorting conditions. The mobility of *boron* may be a consequence of the filtering technique or may be due to compositional variations in the samples; however, the samples that experienced the most extreme retorting conditions also exhibit the least boron solubility. Conversely, the samples subjected to the most extreme retorting conditions appear to have enhanced *molybdenum* solubility, whereas those exhibiting the greatest carbonate persistence show the lowest molybdenum solubility. In general, *calcium* solubility is low in core segments exhibiting carbonate persistence, whereas segments that have undergone extensive silication exhibit solubilities between those of calcite ($CaCO_3$) and lime (CaO). Finally, *zinc* solubility appears to decrease at higher temperature. The occurrence of zinc metal nodules from the coring procedure should have minimal effect on the zinc concentration of the leachate.

We stress that because these conclusions are based on a minimum of reliable information, they are speculative, preliminary, and tentative. More substantive conclusions await analyses of samples with well-documented histories (characterization of raw shale cores, measurement of reaction variables during retorting, and completely logged coring operations). Other well-documented core samples from retort 3E are expected to be available in FY 80.

Although these experiments alone do not provide thorough assessment of potential problems associated with trace element release from flooded spent retorts, they do show that arsenic, boron, fluoride, selenium, and vanadium may be present in the leachates in undesirable concentrations.

c. Water Analyses. In addition to the above studies, the Task Force participated in a major sampling effort at the Logan Wash Site during the week of March 5, 1979. This effort was carried out during the operation of retort 6. A great many samples were obtained from effluent points at the retort, which are indicated schematically in Fig. 15. Samples of various process waters and of groundwater were received for analyses. The results of trace element analyses (AAS, except for fluoride and SO_4^{2-}) are listed in Tables IX and X.

The elemental analysis of the process waters can reveal the fate of various trace elements and the extent of treatment necessary for different effluents. The boiler-blowdown and makeup water, which are effluents after the oil-water separation, show the greatest trace element concentrations and will require the most rigorous treatment. In general, trace elements of environmental concern after contact between spent shale and groundwater are present in the process waters in unacceptable amounts. The concentrations of vanadium are smaller in these process waters than in laboratory-generated leachates.

Table X provides further understanding of the factors that affect element concentrations in groundwaters that flow across oil shale operation areas. An alluvial aquifer sample and water from two wells downstream of retort 6 were sampled. Each water sample had a precipitate by the time it was analyzed, and thus both the water samples and precipitates were analyzed. Trace element concentrations in all samples were quite low, except for the boron level in LW-108. However, the boron level had decreased below detection limits in groundwater LW-106. Major cation concentrations are the greatest in LW-108, which was a bedrock groundwater sample from between the retort and LW-106. Note that the concentrations in alluvial sample LW-101 are intermediate between the two downstream samples. These results suggest the possibility of natural attenuating mechanisms (for example, adsorption, ion exchange, etc.) that control the concentrations of trace elements as the groundwater moves away from the retort. Natural attenuation as a control of groundwater quality should be given priority attention because of its effect on retort abandonment procedures.

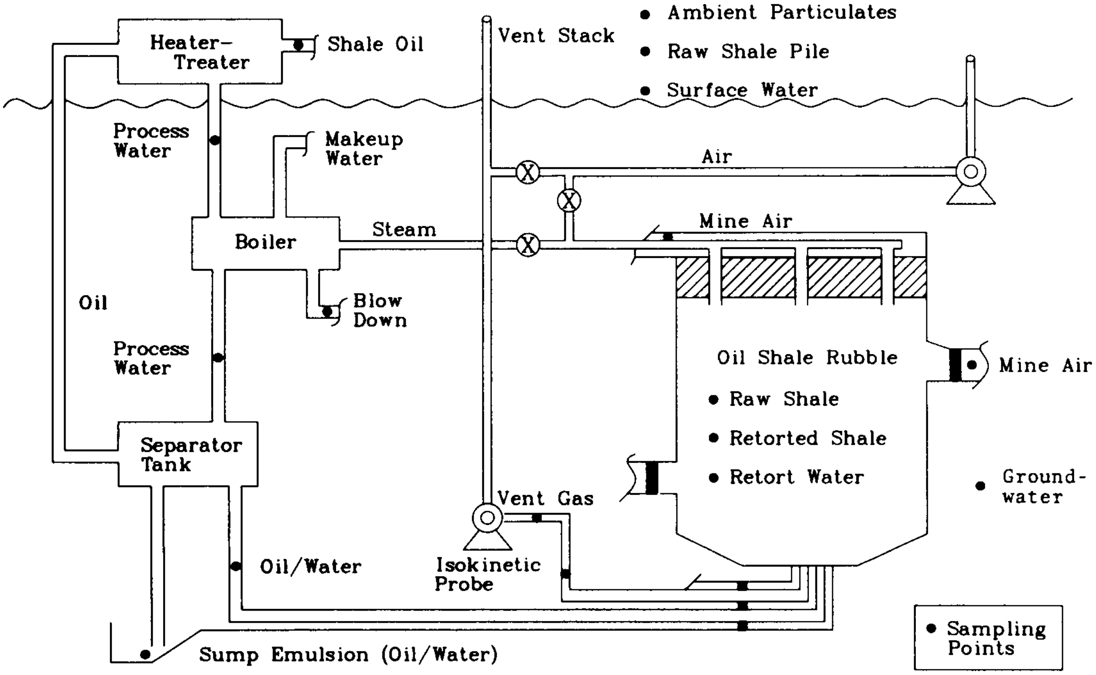


Fig. 15.
Sampling points for Occidental retort 6.

4. Conclusions. Because of the limited amount of information available from the Logan Wash site, only very general conclusions are possible. The most obvious and perhaps most important conclusion is that valid environmental assessments are not possible because basic pre- and posttest information is unavailable. Because mineral and trace element data are unavailable for raw shale at depth in the vicinity of the Logan Wash operations, interpretation of postburn mineral and trace element information is very difficult, if not impossible. A particular core of spent shale can be judged to be environmentally acceptable or unacceptable, and the mechanisms for trace element mobility can be determined, but this information cannot predict the final impact of extracting oil shale by *in situ* techniques. The assessment of impact must consider changes for the better as well as for the worse, but change cannot be determined without information on both the initial and the final states. These facts are recognized by the Task Force and by industry, and the forthcoming baseline information from raw shale cores will be an important aspect of future studies. Raw shale cores from the vicinity of planned retorts of Occidental (Logan Wash area) and Rio Blanco (lease tract C-a) oil shale companies will be made available for study in late FY 80.

The consistent and complementary data generated by applicable experimental techniques indicate the relevance of these methods to the study of oil-shale-related materials. Physical characterization of spent shale by a variety of techniques, including SEM-EDS, optical microscopy, XRD, and IR (infrared spectroscopy), provides information not only about the bulk mineral and chemical makeup of spent shale, but also about the detail of the microscopic variability of the material. Each type of information is essential to understanding the factors that affect the mobility of trace elements of potential environmental concern. Another important aspect of these initial studies was the development of reliable analytical methods, such as AAS, NAA, XRF (x-ray fluorescence), and PES (plasma emission spectroscopy), for the analysis of both trace element and major cation concentrations in oil-shale-related waters. Emphasis is currently being placed on efficient analytical methods, such as PES, so that the maximum numbers of elements and samples can be analyzed.

The investigations of spent shale from retort 3E and water samples from retort 6 operations do lead to several specific preliminary conclusions.

1. The extent of silication reactions (assuming negligible amounts of akermanite-gehlenite and

TABLE IX

TRACE ELEMENT ANALYSES OF ROOM 6 PROCESS WATERS (ppm)

Water Source	Boiler Blowdown	Makeup	Heater Treater	Product	Ecology Mate
Al	0.2	0.7	0.2	<0.05	1.0
As	0.8	0.06	0.08	0.06	0.025
B	101	37	19	11	25
Be	<0.005	<0.005	<0.005	<0.005	
Ca	17.3	13.8	2.0	3.3	
Cd	<0.006	0.008	<0.006	<0.003	
Cl	3930	1020	1500	690	
Cr	<0.015	<0.015	<0.015	<0.015	
Co	0.01	<0.01	<0.01	<0.005	
Cu	0.02	0.01	0.02	0.006	
F	73	21	35	41	
Fe	1.4	0.58	0.48	0.26	
Mg	105	58	1.5	0.8	
Mn	0.01	<0.01	0.03	0.005	
Mo	7.9	2.5	2.0	2.5	7
Na(%)	1.54	0.44	0.33	0.30	
Ni	0.02	0.01	0.04	0.02	
Pb	0.0016	0.007	0.003	0.004	
Sb	0.057	0.003	0.010	0.0003	
Se	0.013	0.015	<0.0004	0.008	0.025
SO_4^{-2}	9500	2300	150	430	
V	0.06	0.05	0.06	0.02	0.15
Zn	0.01	0.01	0.01	0.01	

diopside-augite in the original raw shale) and the persistence of carbonate minerals in the spent shale give some indication of the maximum temperature and/or heating duration experienced by any portion of the retort. However, water has a profound effect on the kinetics of carbonate decompositions and silication reactions[14] and cannot be discounted as a reaction variable. The separation of these effects in field-retorted samples appears to be difficult.

2. Even though many core segments appear to have undergone extensive silication reactions, all core segments contained water-soluble constituents. The solubility of trace elements and major cations is not inversely correlated with the extremity of retorting conditions (for example, temperature) in all cases.
3. Because of the lack of baseline data for raw shale from the vicinity of the retort, it is impossible to discern whether trace element mobilities are a consequence of physical changes associated with MIS processing or the result of chemical and/or mineralogical transformations that occurred during retorting.
4. Concentrations of arsenic, boron, fluoride, selenium, and vanadium that appear in retorted shale leachates approach levels considered to be of environmental concern.
5. Trace element analyses of groundwater samples in the vicinity of retort 6 suggest possible natural mediation of elemental concentrations in groundwater moving away from abandoned retorts. Concrete conclusions are not possible on the

TABLE X

TRACE ELEMENT ANALYSES OF WATER FROM LOGAN WASH (ppm)

	LW-101[a] Filtrate	LW-101 Precipitate	LW-106[b] Filtrate	LW-106 Precipitate	LW-108[c] Filtrate	LW-108 Precipitate
Be	<0.01	$<1 \times 10^{-4}$	<0.01	---	<0.01	---
B	---	---	---	---	11	---
F	8.3	---	7.6	---	12.3	---
K	10	---	2	---	4	---
Mg	188	---	41	---	60	---
Na	329	---	159	---	556	---
Ca	195	0.66	37	0.13	52	0.004
Al	<0.1	0.05	<0.1	0.015	<0.1	0.009
Si	19	0.08	13	---	22	---
P	<0.1	---	<0.1	---	<0.1	---
V	0.1	$<1 \times 10^{-3}$	<0.1	---	<0.1	---
Cr	<0.02	2×10^{-3}	<0.02	3×10^{-4}	<0.02	3×10^{-4}
Mn	<0.01	2×10^{-3}	<0.01	4×10^{-4}	<0.01	2×10^{-4}
Fe	<0.02	0.06	<0.02	0.02	<0.02	0.04
Co	<0.01	$<1.3 \times 10^{-4}$	<0.01	$<0.7 \times 10^{-4}$	<0.01	$<0.7 \times 10^{-4}$
Ni	<0.02	$<3 \times 10^{-4}$	<0.02	$<1 \times 10^{-4}$	<0.02	$<1 \times 10^{-4}$
Cu	<0.01	6×10^{-4}	0.02	---	0.01	---
Zn	0.01	3×10^{-3}	0.03	---	0.02	---

[a] Alluvial sample.

[b] Bedrock groundwater sample, downstream from retort.

[c] Bedrock groundwater sample, taken between retort and 106.

basis of two analyses, but the interaction between geologic media and contaminated water should be investigated. The potential for mitigation of groundwater pollution problems by natural mechanisms should be investigated in future studies.

C. Preliminary Studies of Rio Blanco Oil Shale Company Operations at Lease Tract C-a.

1. **Approach.** Rio Blanco Oil Shale Company operations at lease tract C-a in northeast Colorado present a unique opportunity to study the impact of oil shale development on a region from the inception to operation. Our initial studies are designed to obtain baseline information on groundwater quality and raw shale composition, which will be essential after planned experimental retorts have been burned. Groundwater samples from aquifers in the region have been analyzed. A raw shale core from the vicinity of the planned retorts will be obtained in late FY 80.

Efforts will be directed toward understanding the mechanisms and kinetics of release of trace elements from spent shales into surface and groundwaters in order to determine those investigations that will produce the best possible environmental control technology. The first activity, involving leaching the raw shale, will be to identify the magnitude of trace element release. These essential data will become the basis of the definition of the physical (surface area effects, permeability, and mineral environmental effects) and chemical (oxidation-reduction, decomposition, and mineral reactions) processes responsible for the enhancement of trace element mobilities from retorted shales. Standard static shaker leaching experiments will be used because initial interest will focus on the mechanical aspect of trace element release. The experiments will provide identities and relative magnitudes of release. Core sections deemed representative on the basis of trace element release (if possible) will be used for further study by optical microscopy, SEM, and electron microprobe analysis. In addition, bulk mineralogical data will be necessary so that the vertical mineral variability of this region is well understood when spent shale material becomes available.

Some of the raw shale will be investigated, in a manner similar to experiments previously discussed, to determine the effects of variables, such as temperatures, time at temperature, heating rate, and atmosphere, on mineral and chemical decomposition reactions. This basic chemical and mineral information will provide some understanding of the retort history during shale oil extraction. Subsequent leaching experiments on laboratory heat-treated materials will also provide valuable insights on what to expect from field samples. Correlation of field- and laboratory-generated information will be essential for a detailed understanding of the nature and extent of water contamination caused by MIS processes.

In conclusion, the availability of raw shale presents an unprecedented opportunity to characterize the starting material of a complicated chemical system about to be reacted. This information will be useful in future investigations to characterize spent shale, to quantify trace element releases from spent shale, to identify potential environmental concerns associated with these releases, and finally, to identify environmental controls to mitigate serious environmental problems.

2. **Results and Discussion.** Results of trace element analyses of upper and lower aquifers in C-a tract are listed in Table XI along with a USGS (US Geological Survey) analysis of upper aquifer water. Both samples had precipitates and each was dissolved and analyzed as a separate sample. These analyses indicate that trace element concentrations are high in both aquifers. Disruption caused by MIS retorting could result in degradation of the aquifers if aquifers of different qualities are mixed (aquifer bridging). Comparison of the analyses in Table XI suggests the extent of this concern.

TABLE XI

TRACE ELEMENT ANALYSES OF UPPER AND LOWER AQUIFERS IN TRACT C-a

(ppm)

	Lower		Upper		USGS Analyses of Upper Aquifer
	Filtrate	Precipitate	Filtrate	Precipitate	
Be	<0.01	3×10^{-4}	<0.01	---	
B	5	---	---	---	0.2
F	26	---	9	---	0.9-2.4
K	2	---	2	---	
Mg	7	0.7	75	---	
Na	434	---	199	---	190
Ca	41	7	32	0.09	30-50
Al	<0.1	1.1	<0.1	0.008	
Si	14	0.17	30	---	20-30
P	<0.1	---	<0.1	---	
V	<0.1	0.007	<0.1	---	
Cr	<0.02	0.007	<0.02	0.002	
Mn	0.11	0.09	0.02	0.001	0.006-0.09
Fe	<0.02	24	<0.02	0.9	5.3
Co	<0.01	0.001	<0.01	---	
Ni	0.06	0.06	<0.02	5×10^{-4}	
Cu	0.01	0.01	0.01	---	0.001
Zn	0.01	0.02	<0.01	---	0-0.02

Note: One sample each from upper and lower aquifer.

3. Conclusions. Although studies have just begun of the impact of development of lease tract C-a on water quality, indications are that these investigations will be valuable: the baseline data will be used for evaluation of retort abandonment strategies. Future studies will address the characterization of raw and spent shale and the effect of MIS retorting on trace element mobility with concomitant effect on groundwater quality. A detailed work plan summarizing planned future activities is being written.

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APPENDIX A

UNCERTAINTIES AND CRITICAL PROBLEM AREAS IN ENVIRONMENTAL CONTROL TECHNOLOGY FOR OIL SHALE COMMERCIALIZATION OPERATIONS

Concern	Pollutant	Technology	Status[a]	Current Assessment	Delay
				AIR QUALITY	
Atmosphere	Particulates, including fugitive dust emissions	Surface	ETA	Dust and particulates produced by mining, hauling, and crushing shale should be readily controlled by existing technology. Techniques include surface wetting, baghouse filters, and various wet scrubbing schemes.	Possibly slight due to scale-up.
		MIS	U	Surface problems from processing of mined shale were discussed above. Dust and particulates from *in situ* rubbling should be contained in the retort area if geology and geohydrology have been properly chosen and manipulated.	Minimal.
	SO_2, CO, NO_x, and NH_3	Surface	ETA	Existing technology for control of these emissions includes process control under reductive conditions, end-use combustion, gas recycle, scrubbers, and precipitators.	Minimal, but concern related to technology transfer.
		MIS	U	Control as fugitive emissions is unresolved. The problem has not been assessed, existing control technology has not been applied, and thus, additional work is needed.	Unknown, but should be a controllable problem.
	Mercury	Surface MIS	U	The fate of mercury in processing is unknown. Retort studies have resulted in very poor closure on Hg elemental balances. It is believed that about half the Hg escapes in the gases in a dilute form. (For surface processing, this might be alleviated by a sulfur removal unit.) Reliable data on the form and concentrations of Hg species released to the atmosphere do not exist. This could be a serious environmental problem because of the toxicity of various Hg compounds. Control technology is presumably not a problem but assessment of the nature of the Hg problem must be made.	Medium possibility of delay until problem is assessed.

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[a] ETA = Existing technology available.

U = Uncertain at present; presumed to be technologically controllable at some cost, perhaps a very high one.

P = Potential impediment to shale oil development. Proven control technology does not exist. Not possible to predict cost of proposed technologies.

Concern	Pollutant	Technology	Status[a]	Current Assessment	Delay
Atmosphere	Other volatile trace elements, e.g., arsenic, fluorine	Surface MIS	U	Comments for Hg are applicable, but this is not considered a critical problem compared with the potential major health effects of Hg—compound contamination.	Unknown, needs to be assessed.
	Hydrocarbon vapors	Surface	ETA/U	In general, controllable by existing technology unless non-deterioration requirements are rigidly applied. (However, see comment on burning raw shale piles.)	Minimal, but other control strategies should be studied.
		MIS	P	Fugitive emissions from burning raw shale piles and from underground processing could cause violation of standards. The extent of these circumstances is not known and could lead to serious difficulties. Assessment of the dangers in this area is needed.	Potential problem must be addressed.
	Polynuclear aromatics (PNAs on particles)	Surface	ETA	Suspected carcinogens can be controlled by existing technology.	None.
		MIS	U	Comments under fugitive dust emissions are pertinent. Should not be a major problem if the overburden is not extensively damaged during rubbling (this may not be true for TIS process). However, this is by no means certain and the assessment of on-site problems may be difficult.	Minimal, but careful processing will be very important. Process-dependent problem.
				WATER QUALITY	
Retort water	Organics	Surface	ETA/U	Retort water is known to contain up to 4000 ppm of organic contaminants, some of which are carcinogens. Control technology to clean up retort water is still in the research stage. Existing technology from the organic chemicals industry may apply but will likely be expensive. Less expensive routes, such as using spent shale as a contaminant absorbent, need to be investigated.	Dependent upon environmental control technology chosen.
		MIS	U	Above comments should be applicable unless re-use of the water for steam generation or cooling of retort radically alters the contaminant concentrations or distributions in various media (spent shale, groundwater, etc.). At this time, these aspects have not been assessed. Amounts of waste water to be processed will affect the costs.	Uncertain.

Concern	Pollutant	Technology	Status[a]	Current Assessment	Delay
Retort water	Inorganic major and trace elements	Surface	ETA	Retort water composition will be site-specific. Since the water will be retained within the battery limits, it should be controlled by existing technologies. However, the magnitude of the contamination needs to be assessed.	Minimal.
		MIS	U	Composition of the water will be site-specific. Research into the quantity and quality of retort water needs to be continued. The potential for groundwater contamination by retort water needs to be assessed. As with organics, compositional changes due to re-use of retort water for processing need to be understood.	Uncertain.
Process water	Organics	Surface	U	Same as retort water	Uncertain.
		MIS	U	Same as retort water	Uncertain.
	Inorganics	Surface	U	Same as retort water	Uncertain.
		MIS	U	Same as retort water	Uncertain.
Spent shale leachates	Organics	Surface	U	Leaching rates of organics and stabilization of shale piles are major questions. Environmental control technology for disposal and stabilization of rubbled mineral wastes may be applicable, but effectiveness for organics is not certain. PNAs may be a major problem if not properly isolated. See comment concerning groundwater contamination by organics. Changes in form and toxicity of organics may occur due to microbial action. This needs to be assessed. Also, further development of flash flood protection is needed with specific attention to mud-slide dangers.	Uncertain.
		MIS	P	Backflooding of spent *in situ* retorts and subsequent contamination of subsurface water may occur by mobilization of organic residues or leaching of unretorted organic materials. The nature and the magnitude of this problem must be assessed. Retorting conditions will be a major variable. The dangers of these pollutants need to be understood.	Critical problem area; uncertain until assessed.

Concern	Pollutant	Technology	Status[a]	Current Assessment	Delay
Spent shale leachates	Inorganics	Surface	U	Conventional environmental control technology may suffice, but assessment and evaluation is needed before this situation is clear. B, F, As, Se, and Mo leaching could present difficulties but probably are solvable problems. Comments above about leaching rates and shale pile stabilization (including flash flood protection) are applicable here.	Unknown, but should be controllable.
		MIS	P	This, along with the organic contaminants, is potentially the most serious problem facing *in situ* processes because of the possibility of underground water contamination. Large amounts of inorganic trace elements will be available and could be solubilized by backflooding of the spent retort. Insufficient information is available for assessment of the problem. The relationships of retorting conditions and raw shale composition with amounts of leachable inorganics are only beginning to be understood. This information is extremely important because adequate assessment of the problem depends on the high-temperature chemistry taking place during retorting. The magnitude of the problem will also depend on the hydrology and geohydrology of the region. The nature and rate of groundwater contamination by spent shale leachates is extremely site-specific, not only because of the hydrology, but because of the absorbing and attenuating characteristics of the surrounding rock medium. Even if the problem were assessed, control technologies for backflooding and subsequent groundwater contamination are only in their infancy. Much more research with regard to assessment and control technology development is necessary.	Critical problem area which needs to be assessed and controlled.
Groundwater (other than by retort or leachate waters)	Organics	Surface		None	
		MIS	P	Fugitive emissions produced during underground retorting, such as volatiles or organic liquids, could contaminate subsurface waters. This is a critical unresolved problem. The spent shale in the retort may have sufficient absorptive capacity to take care of the PNAs and PHAs, but this issue must be resolved. Research is needed.	Uncertain until assessed, but comments for leachates probably apply.

Concern	Pollutant	Technology	Status[a]	Current Assessment	Delay
Groundwater (other than by retort or leachate waters)	Inorganics	Surface		None	
		MIS	P	Comments above apply to volatile inorganics such as Hg compounds. The extent of these problems needs to be assessed. Another potential for inorganic contaminants comes from aquifer bridging where fresh water in an upper aquifer is polluted by saline water from a lower aquifer. Major control technology is probably careful selection of retort site to ensure the maintenance of a sufficient barrier between aquifers. Plugging or sealing of spent retorts may be of use. The economics of these solutions are uncertain.	Uncertain until assessed, but comments for leachates probably apply.
				SURFACE QUALITY	
Raw shale storage	Organics and inorganics	Surface MIS	U	The extent of leaching of organics and inorganics from raw shale piles is not well known, but it is not considered to be a major problem.	Minimal.
	Volatiles	Surface MIS	U	Uncontrolled burning of raw shale piles could cause serious air pollution. Technology from the coal industry may be applicable.	Minimal.
Spent shale storage	Organics and inorganics	Surface MIS	U	Pile stability is a question. Erosion protection is a question. Success of revegetation on the scale proposed is not certain. Wetting of the shale with retort water and compacting is not a demonstrated technology, and thus, requires further investigation.	Minimal.
Subsidence and surface disruption	--	Surface MIS	U	This has not been considered a major problem for either technology. However, especially for MIS, local spalling of ceiling or floor material could increase the possibility of aquifer bridging. Also, worker safety is always a concern and will be affected by considerations such as mine stability and migration of toxic gases from active retorts to adjacent mining operations. Careful choice of *in situ* or mining areas will help.	Unknown.

APPENDIX B

SAMPLE PREPARATION, ANALYTICAL METHODS, AND PHYSICAL CHARACTERIZATION OF SOLIDS

I. SAMPLE PREPARATION

A. Solids

Raw and spent shale samples are reduced to <2 in. with a corundum saw, then crushed to -3/8 in. with a jaw crusher, and if necessary, divided with a cone or riffle splitter. If desired, the divided raw or spent shales can be further reduced to about -20 mesh by pulverizing them in a rotary grinder equipped with ceramic plates. After splitting, further particle-size reduction to -100 mesh can be accomplished by grinding with an automatic agate mortar and pestle.

B. Leachates

Our leaching procedure consists of two parts. The first is a static leach, which gives inherent leachability for mechanistic studies, and is basically a water leach similar to that proposed in ASTM Method A. The second is a column leach, which gives maximum initial pollutant levels for MEG/MATE evaluation, element response to long-term leaching (kinetics), and material response to oxidation.

For static shaker leaching experiments, 50 g of the material is placed in a wide-mouth 500-mL Teflon bottle (glass if organics are sought) and 250 mL of milli-Q water is added. If smaller sample quantities necessitate smaller experiments, the materials are scaled down 1:5 solid:water with concomitant decrease in container size. The bottles are capped and placed on the shaker (90 3-in. strokes/min) for 48 h. After the appropriate time period, the mixtures are centrifuged, leachate solutions are decanted and filtered through a 0.45-μ millipore-type HTFE filter. A 50-mL aliquot is separated from the leachate for AAS analysis. All solutions are stored at their natural pH. Measurements such as pH, E_h, and conductivity are made immediately after separation and before storage.

For column-leaching experiments, the material (500 g, if available) is crushed to -3/8 in. and packed into a Pyrex column 35 cm long by 4.6 cm i.d. in a vertical position. The leaching column is equipped with a necked-down inlet at the bottom for introducing the leachates. A side arm located 5 cm below the open top serves as an effluent outlet. Both the upper and lower ends of the material bed are retained in the column with loosely packed quartz wool plugs. The column area above the leachate is protected with an inert gas. The leachate, milli-Q water, is metered at ~0.5 mL/min through the packed column from a reservoir elevated above the column outlet. An upward or countercurrent leachate flow prevents flow blockage from fine sediments that might settle to the bottom of the column. Samples are collected at five volumes:

1. 0-100 mL
2. 700-800 mL
3. 1400-1500 mL
4. 2900-3000 mL
5. 4900-5000 mL

The flow is stopped, the column is drained from the bottom, and dry air is passed upward through the column at ~1 scf/min. Air passage is continued for 3 weeks. On the tenth day of airing, 25 mL of milli-Q water is poured on the top of the column every 3 days. At the end of the third week, water flow is again started, and the first 100 mL is collected. As with the static shaker leach, critical measurements and any required sample splitting should be done quickly.

II. ANALYTICAL METHODS

A. Solids

1. **Neutron Activation Analysis.** Neutron activation analysis (NAA) is one of the most accurate and reliable methods of analyzing for trace elements in natural materials, and it is envisioned that the oil shale program will require the trace element analysis of large numbers of both raw and spent shale samples. The method relies on production of unstable nuclides by neutron irradiation and subsequent emission of gamma radiation during decay to a stable state. Gamma-ray detection and measurement are accomplished with a Ge(Li) detector. It is a nondestructive technique in most applications, and has the advantage that many elements can be observed simultaneously. However, the method is not sensitive to some elements, such as carbon, oxygen, silicon, and lead, but this is often an advantage.

TABLE B-I

LIMITS OF DETECTION IN MULTIELEMENT ANALYSES OF SEDIMENTS

Element	Limit of Detection (ppm)	Analytical Method	Element	Limit of Detection (ppm)	Analytical Method
Ag	5	XRF[a]	Li	1	ES
Al	200	NAA[b]	Lu	0.3	NAA
As	5	NAA	Mg	3000	NAA
Au	0.01	NAA	Mn	10	NAA
Ba	300	NAA	Na	150	NAA
Be	1	ES[c]	Nb	20	XRF
Bi	5	XRF	Ni	15	XRF
Br	5	NAA	Pb	5	XRF
Ca	4000	NAA	Rb	30	NAA
Cd	5	XRF	Sb	1	NAA
Ce	10	NAA	Sc	0.1	NAA
Cl	200	NAA	Se	2	NAA
Co	2	NAA	Sm	0.5	NAA
Cr	20	NAA	Sn	10	XRF
Cu	10	XRF	Sr	300	NAA
Dy	2	NAA	Ta	1	NAA
Eu	0.8	NAA	Tb	1	NAA
Fe	2000	NAA	Th	0.8	NAA
Ga	25	NAA	Ti	200	NAA
Hf	1	NAA	V	5	NAA
Hg	2	NAA	W	1	NAA
K	2000	NAA	Yb	3	NAA
La	6	NAA	Zn	20	NAA

[a] XRF = x-ray fluorescence.

[b] NAA = Neutron Activation Analysis. Because of elemental interference, the detection limits for elements determined by NAA will shift as a function of the composition of the sediment.

[c] ES = Emission spectroscopy.

The preferred methods of analysis and limits of detection for trace elements in solid natural materials are listed in Table B-I. The NAA values are representative of those obtained by the Los Alamos automated computerized system. A split of each sample is transferred to a clean 1/2-in.-diam, 4-mL polyethylene rabbit vial. After weight and sample number are computer-filed, the rabbits are pneumatically sent to an irradiation position with approximate neutron flux of 6×10^{12} n/cm^{2}s for 20 s. The sample is then blown into a large delayed-neutron detector if uranium analysis is desired, and after a 20-min delay, it is transferred pneumatically to a position in front of a Ge(Li) gamma-ray spectrometer. The spectrometer measures the gross gamma-ray spectrum emitted by the sample. The counting time is normally 8 min, after which the accumulated 4096 channel spectrum is recorded on magnetic tape for later computer analysis. In this initial Ge(Li) scan, short-lived isotopes of sodium, magnesium, aluminum, chlorine, potassium, calcium, titanium, vanadium, manganese, copper, strontium, iodine, barium, and dysprosium are identified and quantified.

To observe long-lived isotopes of various elements by Ge(Li) counting, the gamma-ray spectrum must be recorded for longer times. The timing parameters used to assay natural materials, such as coal and coal fractions, are given below.

Half-Life	Irradiation (Δt)	Delay Time	Count (Δt)
Short	**20 s**	**20 min**	**8 min**
Intermediate	**200 s**	**5 d**	**1 h**
Long	**200 s**	**24 d**	**1 h**

The elements observable at 5 d include gallium, arsenic, bromine, antimony, lanthanum, samarium, tungsten, and gold. Additional elements observable at 24 d include scandium, chromium, iron, cobalt, zinc, selenium, rubidium, cesium, calcium, europium, terbium, lutetium, hafnium, tantalum, mercury, and thorium. The limit of detection for a given element is not a fixed value, but is sample-composition-dependent.

2. Spectrochemical Analysis (Optical Emission Spectroscopy). Three spectrochemical methods developed for analysis of coal and coal ash samples have been used for oil shale samples: (1) a high-temperature ashing (HTA) method for trace elements, (2) an improved low-temperature ashing (LTA) method for trace elements, and (3) a method for major and minor elements. LTA has been the main method used. The oil shale sample is ignited at <100°C in an oxygen plasma, the ash is mixed with four parts sodium carbonate-graphite powder buffer, and weighed portions of the mixture are excited by dc arc. When the method for major and minor elements (sodium, magnesium, aluminum, silicon, calcium, titanium, iron, strontium, and barium) is applied, LTA is mixed with 40 parts copper oxide-graphite powder buffer and weighed portions are analyzed by dc arc excitation.

Results were obtained by visual comparison of standards and samples exposed on the same spectrographic plate or by photometry of those plates. A visual comparison has a precision estimated at ±50% relative standard deviation (RSD). A result obtained by photometry has an estimated precision of ±20% RSD.

B. Liquids

1. Atomic Absorption Spectrophotometry. Samples, such as leachates, groundwaters, or process waters, are prepared or acquired as discussed previously. Applicable AAS methods for each element are listed in Table B-II, along with sample and time requirements for each analysis. All elements of interest can be analyzed by AAS, except fluoride, which is analyzed with an ion-selective electrode. A brief description of each procedure is given at the conclusion of this section.

The high content of organic matter in shale process waters frequently requires a sample prepared by oxidative digestion with nitric and perchloric acids. In all cases, the as-received sample must be filtered through a 1-μ membrane filter. Digestion is done in a Bethye apparatus fitted with a quartz sample flask. The digestion with nitric and perchloric acids proceeds until the solid samples are converted to a completely colorless digest. The acid mixture, which retains all elements including selenium, is then combined with the original filtrate, or is treated as a separate sample, as required.

To prevent nonrepresentative sampling of the as-received sample, the entire volume of the submitted sample must be treated as a whole, with the exception of a small portion withdrawn for the fluoride determination, which should not exceed 1% of the total volume submitted. Better still, a separate sample for fluoride (and other anions) should be submitted.

Mean values (μ) for the individual determinations are computed from an appropriate number of independent atomic absorption measurements. Normally, a set containing several samples is analyzed at one time. For each element determined, each sample within the set will contribute several degrees of freedom to the pooled standard deviation estimated for the entire set. In this manner (with appropriate testing for nonhomogeneity of variances), we can obtain satisfactorily narrow confidence limits on μ for four or fewer measurements per determination. The values reported are the sample means at the 95% confidence level, with $\mu = \bar{x} \pm (ts/\sqrt{n})$, where the notation has the customary meaning.

Detection limits are similarly computed, but using the single-sided t-test with $\alpha = 0.05$, and incorporating the appropriate number of independent *blank* measurements. Thus, $\mathrm{D.L.} = ts\sqrt{n_x + n_3/n_x n_3}$. The "beta-error" at the detection limit is not explicitly controlled, but normally, a minimum of four sample measurements and eight blank measurements are available, so the beta error is normally 20% or less at the detection limit.

Aluminum. Aluminum is determined at 309.3 nm using the nitrous oxide-acetylene flame. Detection limit is 0.1 ppm. When high levels of chloride are present, standard addition must be used.

Arsenic. Arsenic is determined by flameless AAS using a Perkin-Elmer HGA2100 Graphite Furnace. The

TABLE B-II

CURRENT TRACE ELEMENT DETECTION LIMITS
(May 10, 1979)

Substance	Required Volume (mL)[a]	Detection Limit (95% Confidence)[b]	Approximate Time Per Sample[c] (min)	Method[d]
Al	5	0.1 ppm	10	Flame AA
Sb	1	1 ppb	30-60	Flameless
As	1	1 ppb	30-60	Flameless
Ba	5	0.1 ppm	10	Flame AA
Be	5	0.001 ppm	10	Flame AA
B	10	0.5 ppm	15	Flame AA
	5	0.002 ppm	10	Flame AA
Cd	1	<0.1 ppb	30-60	Flameless
Ca	5	0.01 ppm	10	Flame AA
Cl	5	0.5 ppm	20	Electrode
	1	1 ppb	30-60	Flameless
Cr	5	0.01 ppm	10	Flame AA
Co	5	0.01 ppm	10	Flame AA
Cu	5	0.01 ppm	10	Flame AA
F	5	0.1 ppm	20	Electrode
Fe	5	0.02 ppm	10	Flame AA
Pb	1	1 ppb	30-60	Flameless
Li	5	0.01 ppm	10	Flame AA
Mn	5	0.01 ppm	10	Flame AA
Mg	5	0.001 ppm	10	Flame AA
Mo	10	0.01 ppm	10	Flame AA
Ni	5	0.01 ppm	10	Flame AA
P	10	1 ppm	30	Flame (extraction)
K	5	0.01 ppm	10	Flame AA
Se	1	1 ppb	30-60	Flameless AA
Ag	5	0.01 ppm	10	Flame AA
Na	5	0.01 ppm	10	Flame AA
SO_4^{2-}	10	10 ppm	10	Turbidity
Si	5	1 ppm	10	Flame AA
Tl	5	0.1 ppm	10	Flame AA
Sn	1	10 ppb	60-90	Flameless
V	1	100 ppb	60-90	Flameless
Zn	5	0.01 ppm	10	Flame AA

[a] Volume is that usually required to give the stated detection limits. Smaller volumes will permit fewer measurements; thus $t/\sqrt{n}$ becomes less favorable.

[b] Procedures usually require 4-6 independent measurements. Pooled standard deviation is used to calculate $ts/\sqrt{n}$, using $t = 0.975$ for the total D.L. in the sample set. Detection limit is one-sided t-test for mean greater than blank ($T = 0.95$), using paired (sample-blank) measurements.

[c] Times are for sample run only. A complex matrix requires more time, especially for elements run by flameless AA.

[d] Relative 95% confidence limits for the flame AA work are normally less than 5% when the analyte concentration is at least 10X detection limits. $R95_{CL} = [(ts)/(\bar{x}\sqrt{n})] \times 100$. Precision for flameless is usually poorer.

detection limit is about 1 ppb. Standard addition is necessary with all flameless AAS work.

Boron. Boron is determined by nitrous oxide-flame AAS of the solvent-extracted boron. The extractant is 2-ethyl-1,3-hexanediol in xylene. The detection limit is approximately 0.5 ppm, when 5X concentration of the sample is used.

Beryllium. Beryllium is determined by nitrous oxide-flame AAS. The detection limit is approximately 1 ppb.

Calcium. Calcium is determined by nitrous oxide-flame AAS using potassium as an ionization suppressor and lanthanum as a releasing agent.

Cobalt. Cobalt is determined at 240.7 nm using the air-acetylene flame. The detection limit is 0.01 ppm.

Copper. Copper is determined at 324.7 nm using the air-acetylene flame.

Iron. Iron is determined at 248.3-nm using air-acetylene flame. Detection limit is 0.014 ppm. High-iron solutions are diluted and measured at 248.3 nm, rather than at a less sensitive wavelength, since the 372.0-nm line is sensitive to the matrix composition of the samples.

Potassium. Potassium is determined at 766.5 nm using the air-acetylene flame, with 500 ppm lithium present as ionization suppressant.

Magnesium. The nitrous oxide flame is used. No ionization suppressant or releasing agent is necessary.

Manganese. The 279.5-nm line is used with air-acetylene flame. The detection limit is 0.01 ppm.

Molybdenum. Measurements are made at 313.3 nm using the nitrous oxide flame. The samples are treated with NH_4Cl solution to give a net concentration of 2% NH_4Cl plus 2% HNO_3. Detection limit is 0.01 ppm.

Sodium. Sodium is measured at 589.0 nm using 1000 ppm potassium as ionization suppressant. High-sodium samples are diluted and run using a 5-cm burner when necessary to attenuate the sensitivity. The 330.2-nm line is not used.

Nickel. Nickel is measured at 232.0 nm using the air-acetylene flame. Standard addition is used to test response because severe signal depression occurs in high-solids samples. An alternative technique involves extraction of either the dimethylglyoxime or APDC chelate into methyl isobutyl ketone. This approach eliminates matrix problems and permits direct measurement.

Lead. Lead is measured at 283.3 nm using graphite-furnace AAS. Ascorbic acid is added. The signal is very sensitive to the calcium content of the sample, and with some low-calcium samples, the element is added to the samples to stabilize the sensitivity. As an alternative, lead is extracted with APDC/MIBK and measured by flame AAS.

Antimony. Antimony is measured at 217.6 nm using the graphite furnace. The detection limit is approximately 1 ppb. No matrix modification is required. Standard addition is required.

Selenium. No single procedure is satisfactory for all selenium determinations. Initially, samples are screened by flame AAS (detection limit ~0.14 ppm), and when necessary, the low-selenium samples are then analyzed by other techniques. Hydride evolution using borohydride reduction often is satisfactory, but samples high in iron or other borohydride-consuming substances sometimes require graphite-furnace AAS. When the graphite furnace is used, 200-400 ppm nickel is added to the solutions. Iron causes a direct spectral interference in the flame- and flameless-AAS methods when the 196.0-nm line is used, but the flame method is much preferred over the alternatives when sensitivity is not the controlling factor. The 204.0-nm line is not subject to iron interference, but gives poorer sensitivity.

Vanadium. Vanadium is determined by graphite-furnace AAS using a matrix addition of 1000 ppm lanthanum. Signals are poor, and detection limits of 0.1 ppm are about the best that have been achieved.

Zinc. Zinc is easily determined by air-acetylene flame AAS, using the 213.9-nm line. The detection limit is well below 0.01 ppm.

2. Direct Current Argon Plasma Emission Spectrometry. To provide techniques complementary to our AAS capabilities, dc argon plasma emission spectrometry (DCAPES) is being considered for trace element analysis of oil-shale-related waters. As in other studies of this type[24,25] preliminary results obtained were acceptable (that is, selectivity, sensitivity, accuracy, speed, and economy of sampling) for analysis of many of the elements of interest in oil shale waters. This approach is much more time-efficient for the quantities of samples that will ultimately be analyzed.

The instrument used for these comparisons is a Spectraspan III (Spectrametrics, Inc.) dc argon plasma spectrometer with a three-electrode torch, a sample nebulization system, an echelle grating direct-reading spectrometer, and a microprocessor for control and data acquisition. The instrument is equipped with four cassettes, each with the capability of simultaneous analysis of 20 elements. The element capabilities of the cassettes applicable to oil-shale-related waters are shown in Fig. B-1. 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.

Typically, three replicates of each analyte are obtained with the error in the measurement being the root mean square deviation. Of course, the limit of detection of each element depends on such variables as sample composition, but representative detection limits for each element are given in Table B-III.

3. Neutron Activation Analysis. Due to the very low concentrations of trace elements typically found in leachate samples and groundwaters, the solution must be concentrated in order to observe these elements by neutron activation. Freeze-drying is the method of concentration for natural waters and leachates from natural materials. Typically, 200 mL of the solution is freeze-dried and a sizeable fraction of the residue is subjected to neutron activation analysis. A 1-mL portion of the original liquid is also analyzed for sodium, which is used to normalize the assay of the freeze-dried material to that of the liquid material. Due to the small mass of the freeze-dried material, the irradiation and counting times are longer than those used for solid materials. Typical irradiation and counting parameters are given below.

Half-Life	Irradiation (Δt)	Delay Time	Count (Δt)
Short	**20 s**	**10 min**	**10 min**
Intermediate	**6 h**	**6 d**	**2 h**
Long	**6 h**	**21 d**	**2 h**

III. PHYSICAL CHARACTERIZATION OF SOLIDS

A. Optical Microscopy, Scanning Electron Microscopy, and Electron Microprobe Analysis

Shale samples are partially cut with an abrasive saw, and then broken through the saw cut to minimize saw kerf material loss. The samples are placed in 1-in.-diam molds, and vacuum-epoxy-potted. The samples are pressure-rammed to ~2000 psig to fill surface-connected voids with epoxy. The samples are then given a metallographic polish and a 15-min H^+ cathodic etch. Scribe marks are placed on the sample to help identify layers and interesting areas. The samples are examined with a metallograph and photomicrographs and macrographs are taken. The samples are then SEM-EDS examined with a Coates-Welter Field Emission Scanning Electron Microscope equipped with an Ortec Energy Dispersive Spectrometer. A 15-kV accelerating voltage is used with a beam diameter of ~50 A. The SEM resolution is 50-100 A and the EDS spatial resolution is ~1 μ, depending on the Z number of the element. The EDS energy resolution is 155 eV full width at half maximum (FWHM) on the Mn Kα line. Field emission SEM gives poor quantitative analysis because the electron beam is not stable; however, peak ratios can provide useful information. A small particle in a matrix of different composition will not be quantitatively analyzed even with a stable beam. Electron excitation of characteristic x rays also produces a large bremsstrahlung background and, thus, very long counts are required to obtain peaks from elements present at less than 1/2%.

Sediment layers of the oil shale were examined at magnifications of 5000-10 000X because many of the trace elements are present as discrete submicron particles. EDS analyses are made of a particle and its immediate environment. Low-magnification EDS analyses of typical layers are also obtained.

B. X-Ray Diffraction

Samples to be examined by XRD are thoroughly ground to -325 mesh and then (exhaustively) mixed to eliminate any inhomogeneity. Diffraction patterns were obtained on a Norelco vertical diffractometer using monochromated characteristic radiation and a scan speed of one degree per minute. All patterns were indexed by reference to the mineral subfile of the JCPDS powder diffraction file.

C. Infrared Spectroscopy

Representative -100-mesh samples are mulled with KBr and pressed into pellets. Spectra are recorded on a Perkin-Elmer Model 621 spectrometer between 4000 and 500 cm^{-1}

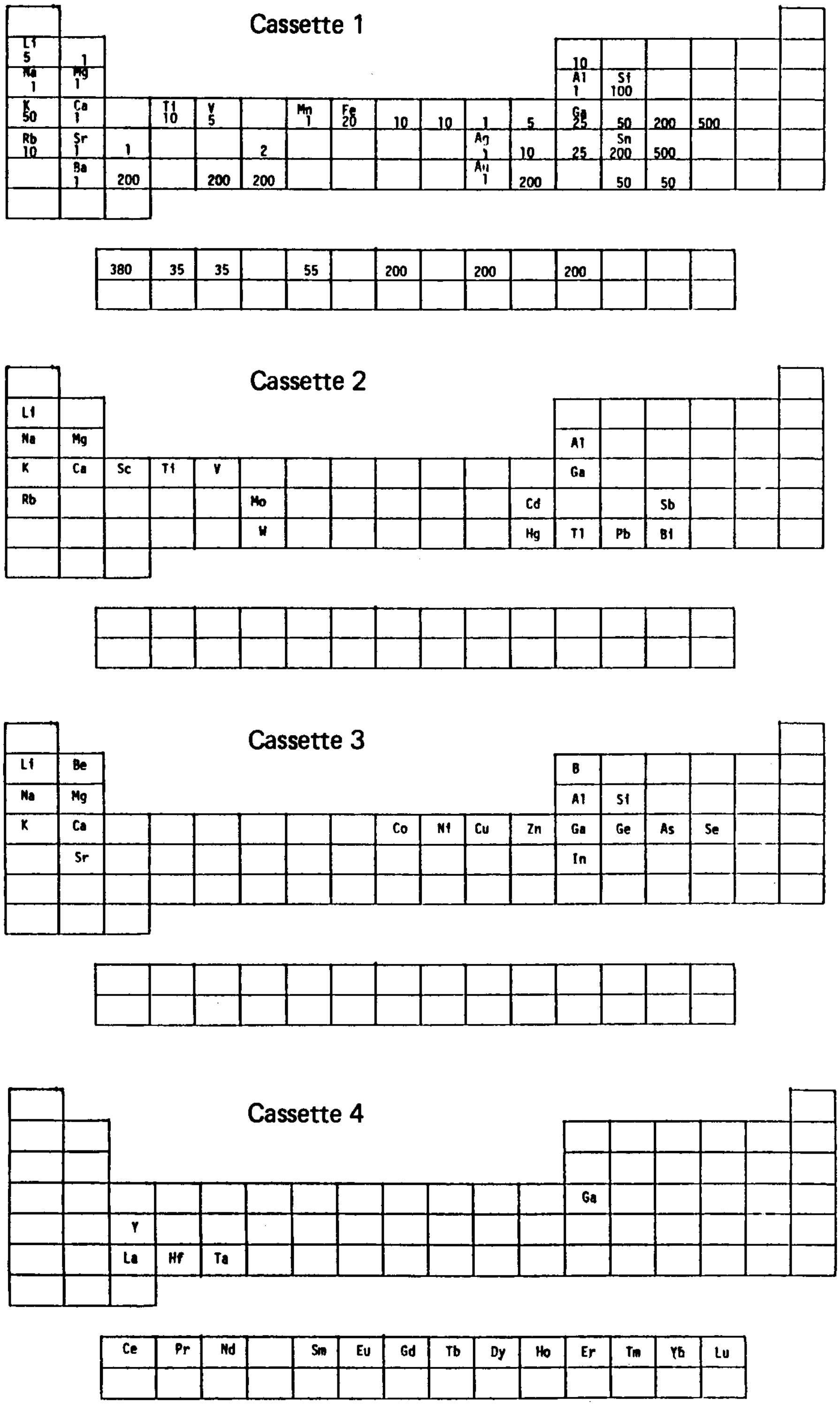

Fig. B-1.
Element measurement capabilities of four cassettes used with the dc argon plasma spectrometer.

TABLE B-III

DETECTION LIMITS

Element	Concentration (μg/L)	Element	Concentration (μg/L)
Ag	1	Mo	1
Al	1	Na	1
Au	1	Nb	100
As	200	Nd	35
B	10	Ni	10
Ba	1	Os	50
Be	1	P	100
Bi	50	Pb	50
C	[a]	Pd	50
Ca	1	Pr	35
Cd	10	Pt	20
Ce	380	Rb	10
Co	10	Re	15
Cr	2	Rh	60
Cs	1000	Ru	20
Cu	1	Sb	500
Dy	200	Se	500
Er	200	Si	100
Fe	20	Sm	55
Ga	25	Sn	200
Gd	200	Sr	1
Ge	50	Ta	200
Hg	200	Te	100
I	20000	Ti	10
In	25	U	200
Ir	40	V	5
K	50	W	200
La	200	Y	1
Li	5	Zn	5
Mg	1	Zr	25
Mn	1		

[a] We now use graphite electrodes.

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