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TITLE: CORRELATION OF MINERALOGY AND TRACE ELEMENT LEACHING BEHAVIOR IN MODIFIED IN SITU SPENT SHALES FROM LOGAN WASH, COLORADO

MASTER

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CORRELATION OF MINERALOGY AND TRACE ELEMENT
LEACHING BEHAVIOR IN MODIFIED *IN SITU* SPENT SHALES
FROM LOGAN WASH, COLORADO*

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Oil shale retorting induces mineral and chemical reactions to occur on the macroscopic and microscopic levels in the kerogen-bearing marlstone. The nature and extent of the reactions is dependent upon process variables such as maximum temperature, time at temperature, atmosphere, and raw shale composition. This report describes the investigation of the mineral, chemical, and trace element release properties of spent shales retrieved from an experimental *in situ* retort at Occidental Oil Shale, Inc.'s Logan Wash site in Garfield County, Colorado. Correlation between mineralogy of the spent materials and the mobility of major, minor, and trace elements are indicated, and relationships with important process parameters are discussed.

The progress of carbonate decomposition reactions and silication reactions is indicative of the processing conditions experienced by the shale materials and influences the mobility of major, minor, and trace elements when the solids are contacted by water. Shale minerals that are exposed to the extreme conditions reached in underground retorting form high temperature product phases including akermanite-gehlenite and diopside-augite solid solutions, kalsilite, monticellite, and forsterite. The persistence of relatively thermally stable phases, such as quartz, orthoclase, and albite provide insight into the extremes of processing conditions experienced by the spent shales. Leachate compositions suggest that several trace elements, including vanadium, boron, fluoride, and arsenic are not rendered immobile by the formation of the high-temperature silicate product phase akermanite-gehlenite.

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Introduction

Extraction of oil from kerogen-bearing marlstone, referred to as oil shale, can be accomplished by either surface or *in situ* retorting. Occidental Oil Shale, Inc. has been experimenting with a modified *in situ* technique (MIS) at Logan Wash site in Garfield County, Colorado. This method involves mining to remove 20-25% of the rock from a chamber, called a room, explosive fracturing of the rock to uniformly redistribute the void, and finally igniting the organic bearing rock to pyrolyze and then distill the organic material from the solid to the bottom of the retort where it condenses and is pumped to the surface. Heat for the retorting process is provided by combustion of the residual organic carbon left on the rock after the major organic fraction has distilled away. Six retorts have been fired by Occidental at Logan Wash and two more are in the final stages of preparation.

One of the small experimental retorts, referred to as retort 3E, has cooled sufficiently and three spent shale cores have been retrieved from this room. Several studies of materials from the first of these cores, designated R3E1 have been accomplished (1,2). These studies indicated the nature of the materials to be considered and provided insights into the effects of post-burn operations on the characteristics of the spent shale. However, the core drill lubrication methods utilized in retrieving these samples led to uncertainties concerning the utility of data generated from these samples. These doubts prompted retrieval of two more cores from retort 3E, designated R3E2 and R3E3. The spent shales from these cores have been subjected to extensive characterization, including mineral identification by x-ray diffraction. Most studies have dealt with laboratory simulated *in situ* spent shales, and thus retort 3E materials are the first field generated spent shales that have been made available for investigation.

Background Summary

Various authors have reported investigations of mineral species in raw oil shale (3-5). The mineral composition varies stratigraphically, but carbonates and silicates predominate in most zones. Carbonate minerals found in raw shale include dolomite/ankerite, calcite, and lesser amounts of nahcolite and dawsonite. Silicate minerals found in raw shale include the thermally stable phases α -quartz, albite and potassium feldspars, as well as illite, other clay minerals and analcime. In addition, small amounts of pyrite are widespread throughout the Green River formation. The compositions of these minerals are summarized in Table 1.

The identity and quantity of minerals present in spent shale are dependent upon the original raw shale composition and the retorting conditions (6). A variety of mineral and chemical reactions are possible, considering the type of reactants and the retorting variables, such as temperature and input gas composition. Temperatures reached in *in situ* retorts are sufficient to decompose the carbonate minerals or react them with other raw shale minerals to form high temperature silicate phases. The extent of carbonate decomposition and silicate formation, as well as α -quartz, albite and potassium feldspars disappearance, are indicative of the extremes of temperature and retorting atmosphere experienced by the spent shales. Product mineral phases possibly formed during *in situ* retorting are summarized in Table 1. As with most experimental studies (7-9), the predominant

Table I. Raw and Spent Oil Shale Minerals

RAW SHALE MINERALS

Analcime	$\text{NaAlSi}_3\text{O}_8 \cdot x\text{H}_2\text{O}$
Dolomite	$(\text{Mg}, \text{Fe})\text{Ca}(\text{CO}_3)_2$
Calcite	CaCO_3
Illite	Clay mineral - $\text{KAl}_2(\text{Si}_4\text{Al})\text{O}_{10}(\text{OH})_2$
Pyrite	FeS_2
Biotite	$\text{K}(\text{Mg}, \text{Fe})_2(\text{Si}_4\text{Al})\text{O}_{10}(\text{OH})_2$

THERMALLY STABLE PHASES

Quartz	SiO_2
Albite	$\text{NaAlSi}_3\text{O}_8$
Orthoclase	KAlSi_3O_8

DECOMPOSITION PRODUCTS

Periclase	MgO
Calcite	CaCO_3
Dehydrated Analcime Wairakite	$\text{CaAl}_2(\text{SiO}_3)_2 \cdot 2\text{H}_2\text{O}$

HIGH TEMPERATURE PRODUCT PHASES

Augite	$(\text{Ca}, \text{Mg}, \text{Fe}, \text{Ti}, \text{Al})_2\text{Si}_2\text{Al}_2\text{O}_6$
Akermanite-Gehlenite	$\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7) - \text{Ca}_2\text{Al}_2\text{AlSi}_2\text{O}_{11}$
Kalsilite	$\text{K}(\text{AlSi}_2\text{O}_7)$
Monticellite	$\text{CaMg}_2\text{Si}_2\text{O}_{11}$
Forsterite	Mg_2SiO_4

REGENERATION PRODUCTS

Aragonite	CaCO_3
Calcite	CaCO_3
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

High temperature silicate products expected in field samples are akermanite-gehlenite solid solution and diopside-augite solid solution. Other silicate minerals include kalsilite, monticellite, and the magnesium olivine, forsterite.

Carbonate decomposition involves evolution of CO_2 , a readily monitored product. Several studies have investigated rates of carbonate decomposition in oil shale by measuring CO_2 evolution rates (7,8). Another study has investigated the progress of laboratory retorting by x-ray diffraction (9). These studies indicate that dolomite decomposition proceeds at 925-1025 K with evolution of CO_2 and formation of periclase and calcite. The periclase persists at the lower temperatures, but disappears at the higher temperatures due to silicate formation. The calcite formed is chemically indistinguishable from the original calcite (7). Calcite decomposes with evolution of CO_2 above 1075 K, but at this temperature (or higher) a competing reaction has been recognized (7). It is also possible for the calcite to react with quartz to form calcium silicates or, perhaps, feldspars to form calcium aluminum silicates. Thus it is apparent that the disappearance of raw shale minerals and the formation of a new suite of minerals in the processed shale can be accomplished through a variety of reaction pathways which are determined by process variables such as maximum temperature, time at maximum

temperature, heating rate, and atmosphere. Thus, the minerals present in the spent shale provide insight into the conditions experienced by the solids during processing. The experimental studies (7-9) suggest relationships between retorting parameters and spent shale mineral compositions that are useful for evaluation of field generated materials.

The mineral reactions described above are accompanied by chemical reactions of the minor and trace elements. Both the mineral and chemical reactions which occur during retorting affect the mobility of the major, minor, and trace elements from the shale when contacted with water (1,9). The mobility of elements can be affected by a number of factors including decomposition or reaction of the original mineral hosts, the ability of newly formed spent shale minerals to accommodate major, minor, and trace elements in their crystalline structures, and the oxidizing or reducing nature of the atmosphere. These factors, as well as solution chemical considerations, need to be considered when leachate compositions generated from *in situ* spent shales are investigated. Thus, mineralogy of *in situ* generated spent shales is important in the process assessment and in the evaluation of the environmental acceptability of groundwater leachability of the spent shales.

Experimental Techniques

Infrared and X-Ray Diffraction Methods

Infrared spectra were recorded on a Perkin Elmer model 621 spectrometer in the range of $4000-500\text{ cm}^{-1}$, as KBr pellets. Comparison of C-O and Si-O stretching vibrations were employed to determine the relative amount of carbonates contained in the samples. C-O stretching frequencies were used to identify carbonate type (dolomite, calcite, and/or aragonite) in each sample.

X-ray diffraction methods were employed for all mineralogical phase identifications. The samples to be analyzed were ground to -325 mesh and thoroughly mixed. Portions of these samples were then pressed into aluminum holders and examined with precision aligned vertical diffractometers equipped with diffracted beam monochrometers. Copper K_{α} characteristic radiation was utilized in all instances. Scanning rates of $1/4^{\circ}$ and/or $1/8^{\circ}$ per minute, together with selected combinations of scale factors and time constants, permitted excellent sensitivity of peak detection. In reading the diffraction patterns, all peaks were recorded which exhibited consistent intensities greater than two standard deviations above background. Critical overlapping peaks were resolved with the aid of a DuPont curve resolver. All indexing was accomplished by reference to the mineral subfile of the general JCPDS powder diffraction file. All reflections within the patterns were identified, except the occasional weak or trace phases. For those mineral constituents which were obviously members of an isomorphous series, the lattice parameters were also obtained to establish the relative positions of these phases within the series (Table I for these isomorphous compositions). Estimates were made of the relative abundances of the mineral constituents by comparing the background normalized intensities of the stronger reflections from each phase.

Leaching Experiments

Leaching experiments were utilized to determine the solubility of major, minor, and trace elements as a function of mineralogic and chemical

properties of the *in situ* spent shales. These experiments consisted of 48 hour static shaker leaches of -100 mesh material with solid:liquid:container volume ratio of 1:5:10. The solutions were separated from the solid phase by centrifugation and filtration through 0.45 μ millipore filters. Analytical data were obtained by Direct Current Argon Plasma Emission Spectrometry (DCAPES), Atomic Absorption Spectrometry (AAS), and ion selective electrode for fluoride. Leachates generated by this procedure may approach maximum concentrations of most elements because of the particle size distribution of the solid material.

Mineralogic Characterization of Core Material

Infrared Studies

The results of infrared analysis of core material from R3E2 are indicated in Figure 1. This figure is a graphical representation of the persistence of carbonate minerals (dolomite, calcite and/or aragonite) as a function of depth in R3E2. The quantity and identity of carbonate minerals suggests several observations about this core and more generally about retort 3E.

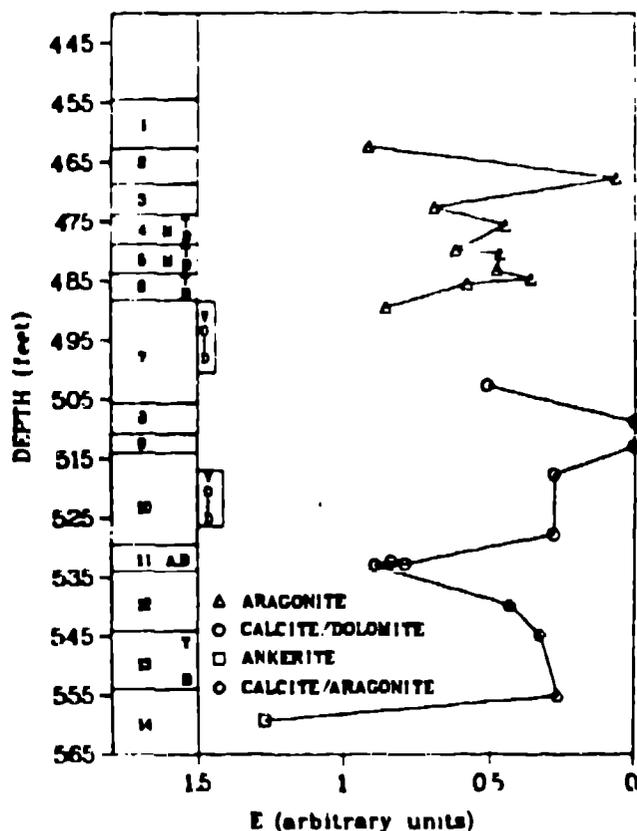


Fig. 1 - Identity and Persistence of Carbonate Minerals in Core R3E2 as a Function of Depth and Zones.

There are several reasons for the existence of carbonate minerals in various core sections. The carbonates can be present as survivors of decomposition reactions yielding CO_2 (dependent upon temperature and pressure)

or as regeneration products due to post-burn chemical or mineral reactions in the retort. Since retort 3E was run with recycle of product gases which continued after shutdown, CO₂ exposure is certain. Since water was also injected, the possibility of solution reactions exists. In determining the reasons for existence of carbonate minerals and, subsequently, the conditions experienced by various core sections, the infrared data provides information which complements x-ray diffraction data.

The identity and quantity of carbonate minerals in R3E2 samples suggest subdivision into at least three zones. Zone 1 extends from 460-495 ft and is characterized by quantities of carbonate minerals, mainly aragonite. Presence of aragonite indicates that most, if not all, of the carbonate minerals present in this zone are regeneration products formed because of post-burn conditions. At this time the recarbonation of CaO in warm water or carbonation of CaSO₄ (gypsum is identified by XRD) are possible synthetic pathways to this mineral species. X-ray diffraction data confirms this assessment. The presence of high temperature product silicates and lack of silica support the infrared results.

Zone 2 continues from 495 to 525 ft and is characterized by lesser amounts of carbonate minerals, predominantly calcite. This observation and the x-ray diffraction data indicate that calcite has survived the retorting. However, core sections 8 and 9 lack any carbonate minerals. The third zone extends from 525 to 560 ft (the bottom of the retort chamber) and the carbonate persistence suggests much lower temperatures as expected. Infrared data for section 14 indicate that this material is essentially raw shale.

X-Ray Diffraction Studies

The mineralogic composition of core R3E2 is tabulated in Table II, while information is graphically depicted in Figures 2-6. Figure 2 indicates the extent of silicate formation and the disappearance of α -quartz in core R3E2, and, as expected, they are inversely related. Silicate phases predominate and quartz is essentially absent from 475 to 530 ft. Fewer silicate minerals and varying amounts of quartz exist above 475 ft and below 530 ft. Examination of Figure 3 indicates the relative amounts of carbonate minerals, α -quartz, and high temperature silicate product phases. Above 500 ft, carbonate minerals, predominantly aragonite, exist in the presence of high temperature silicate product phases and in the absence of α -quartz. Recycle of product gases and water injection for cooling purposes provide conditions suitable for precipitation of soluble calcium as aragonite from warm solutions. Below 500 ft, trends in persistence of carbonate minerals, predominantly calcite, and relative quantities of α -quartz are quite similar. This suggests that the core materials retrieved from this region of the retort are survivors of the processing and not regeneration products.

Relative amounts of high temperature silicate product phases listed in Table II should be evaluated cognizant of unknown variables, such as raw shale composition and retorting conditions. These variables have not been well characterized for retort 3E, but several observations can be made. Figure 4 indicates the occurrence of akermanite-gehlenite solid solution and diopside-augite solid solution are inversely related. Akermanite is the predominant silicate phase from 475 ft to ca. 500 ft, while diopside is the major phase above 475 ft and from 500 to 530 ft. Below 530 ft, diopside is still the major silicate phase, but the inverse relationship of akermanite and diopside is not obvious. This could be a consequence of the retorting

Table II. Mineral Phases in Spent Shale Core R3E2

Section	Calcite	Dolomite Ankerite*	Aragonite	α -Quartz	Akermanite -Gehlenite*	Diopside -Augite*	Orthoclase	Albite	Monticellite	Kalshite	Others
1	T	0	M-S	VW	M-S	M	VW	0	W-M	M	Gypsum(T)
2	0	0	VW	VW	W-M	S	0	0	0	M	Zircon(W), Gypsum(W)
3	W	0	W	VW	M	M-S	0	0	T	W-M	Gypsum(T)
4T	W	0	W	VW	S	M-S	0	0	W-M	W-M	
4B	W	0	W	VW	M-S	M	0	0	W-M	W-M	Gypsum(T)
5T	T	0	W	W-M	S	M	0	0	W-M	W-M	
5M	W	0	W	VW	S	M	T	0	W-M	W-M	
5H	W	0	W	T	S	M	T	0	W-M	M	
6T	W-M	0	M	0	M-S	M	T	0	W-M	M	
6B	M	0	W	0	M-S	M	T	0	M-S	M	
7	M	0	T	T	W	S	W	0	VW	M	Forsterite(T)
8	0	0	0	T	0	S	S	0	0	W	Forsterite(T)
9	0	0	0	T	VW	S	S	0	VW	W	Forsterite(T)
10	W-M	0	T	W	M	S	W-M	0	0	W-M	Forsterite(VW)
11	M-S	M-S	0	M-S	0	W	W	M-S	0	0	Biotite(T), Wairakite(W)
11A	M-S	M-S	0	S	0	W	W	M-S	0	0	Wairakite(W-M)
12	W-M	0	W	M	0	M-S	M-S	W	T	0	Wairakite(T)
13T	M	0	W	W-M	M	M-S	0	W	W	VW	
13B	M	0	W-M	M-S	W	M	0	M-S	W	0	Biotite(M), Wairakite(W)
14	M-S	S	0	S	0	T	VW	0	T	0	Wairakite(W)

*Legend (relative phase content): S=Major, M=Moderate, W=Minor, VW=Very Minor, T=Trace, 0=None Detected

*Orthorhombic phase with parameters and relative peak intensities intermediate between dolomite and ankerite. Sample 14 was pure ankerite

*Trigonal phase with parameters and relative peak intensities intermediate between akermanite and gehlenite

*Monoclinic phase with slightly varying parameters and peak intensities between diopside and augite

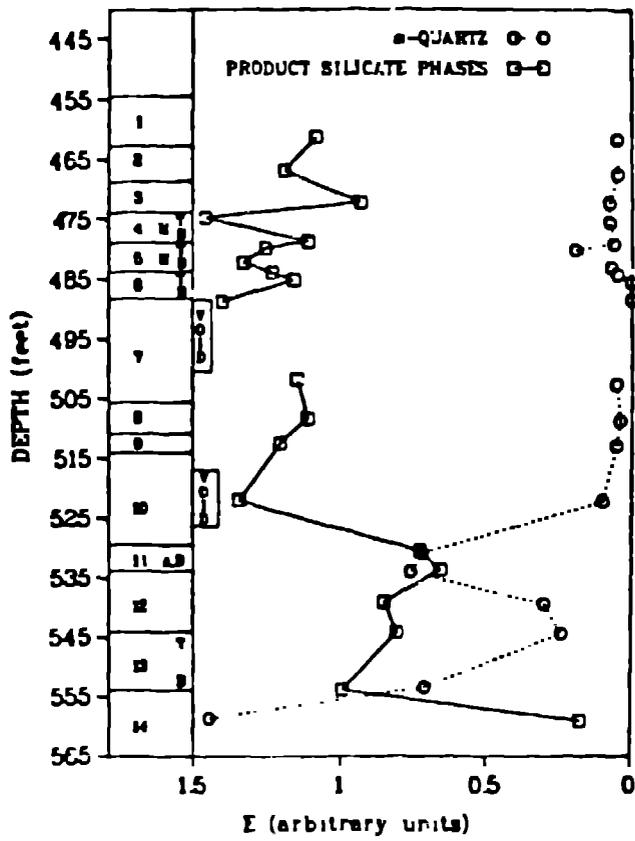
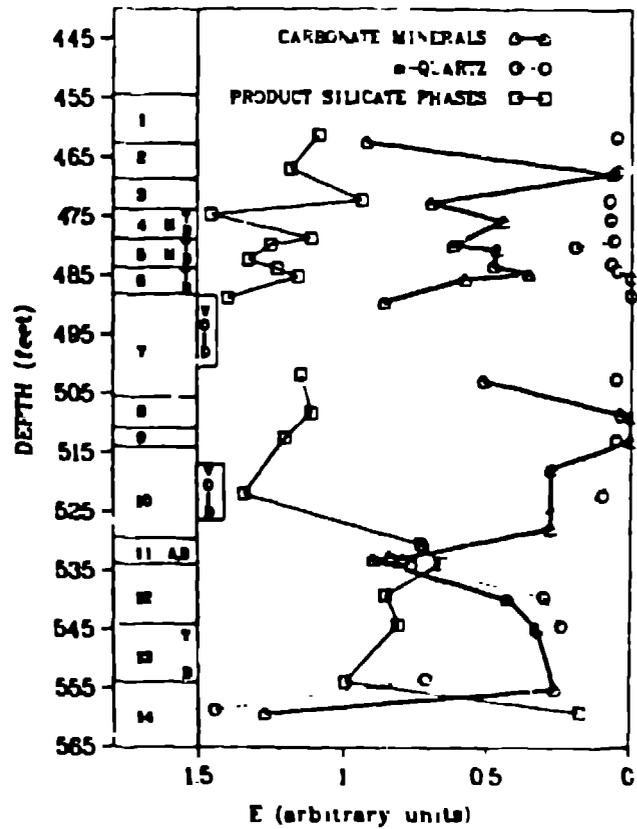


Fig. 2 - Relative Variation of Product Silicate Phases and α -Quartz as a Function of Depth and Zones.

Fig. 3 - Identity and Persistence of Carbonate, α -Quartz, and Product Silicate Minerals in Core R3E2, as a Function of Depth and Zones.



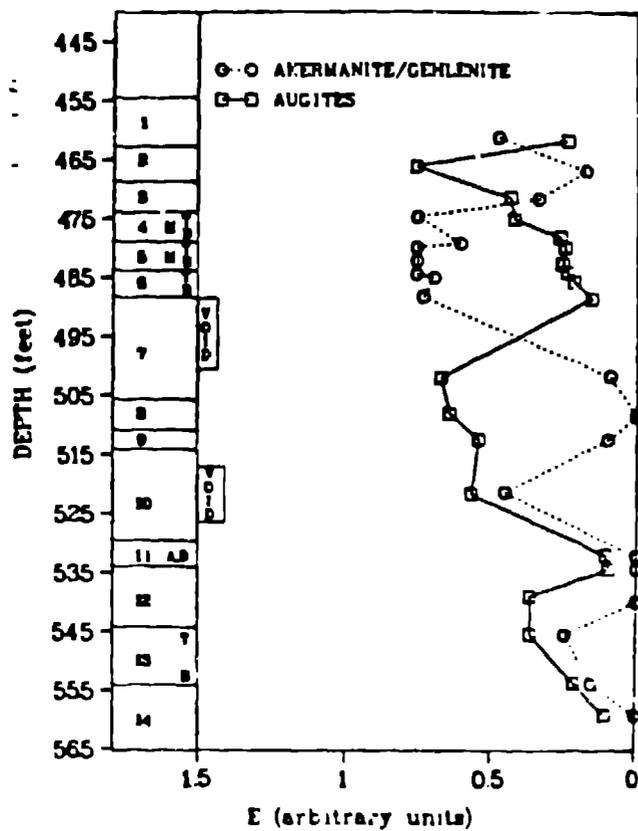
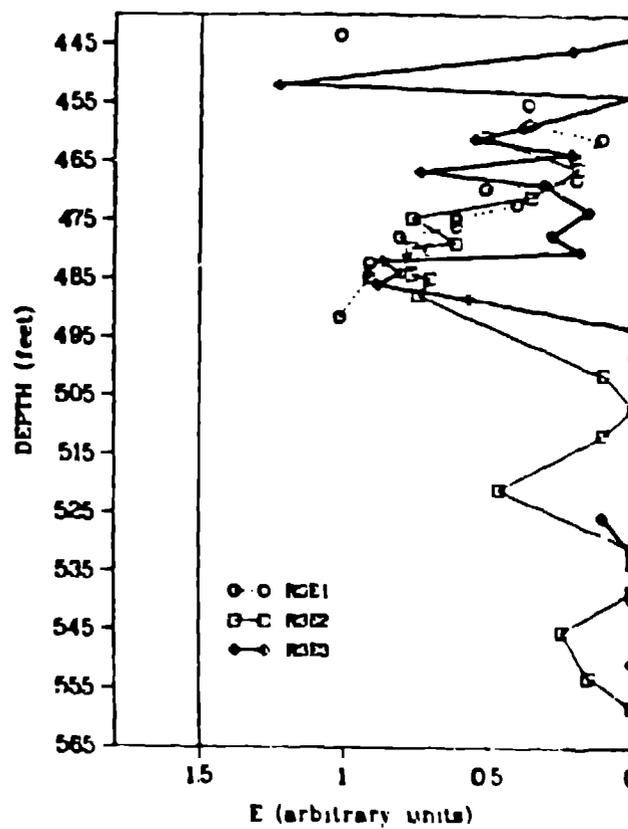


Fig. 4 - Relative Variation as a Function of Depth for Augite and Akermanite/Gehlenite Solid Solutions in Core R3E2.

Fig. 5 - Occurrence of Akermanite/Gehlenite Solid Solution as a Function of Depth for Three Cores from Retort 3E.



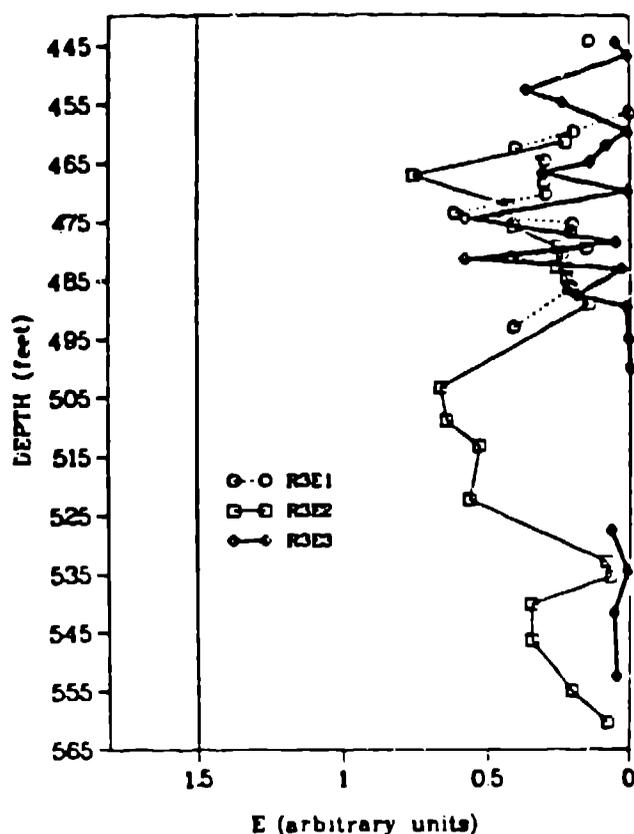


Fig. 6 - Occurrence of Augite Solid Solution as a Function of Depth for Three Cores From Retort 3E.

temperature or evidence of friable material not retrieved from the upper regions of the retort. Other trends in silicate product phase mineralogy include the direct correlation of akermanite and monticellite and the presence of forsterite in core sections where diopside-augite solid solution predominates.

Minor phase mineralogy listed in Table II also provides insight into the relationship of process conditions and presence of mineral phases. Gypsum, hydrated CaSO_4 , was identified in core sections between 455 to 480 ft. An explanation of sulfur retention in spent shales, first as sulfides, and then oxidized to sulfates, has been reported by Smith *et al.* (5). The fact that the CaSO_4 is hydrated is consistent with water injections being absorbed in the upper part of the retort. Other hydrated minerals, biotite and analcime/wairakite (partially dehydrated), exist from 530 ft to 565 ft, and are consistent with the lower temperatures and/or shorter heating times suggested by the persistence of carbonate minerals and α -quartz in the lower depths of the retort.

Discussion

An integration of infrared and XRD data from this core suggests that the information is complementary. Evaluation of core R3E2 data, combined with the mineralogic characterization reported by Park *et al.* (9), indicates

the existence of at least five major zones in retort 3E. Zone 1 is in the vicinity of 440 ft to 445 ft which was sampled in R3E1 (1,9), and consists of almost no carbonate minerals, very little quartz, and a large quantity of high temperature silicate products (akermanite-gehlenite, diopside, monticellite, and kalsilite). These observations suggest that ignition of the retort was accomplished at these depths. Zone 2 extends from approximately 445 ft to 460 ft and is characterized by comparable amounts of calcite and aragonite, moderate quartz, and very few high temperature silicate products. The mineral composition indicates that calcite has probably survived decomposition reactions, while aragonite is a regeneration product of dolomite decomposition due to post-burn operation. The appearance of quartz and the lack of high temperature silicates suggests these sections have experienced intermediate temperatures (800-1000 K) and/or short heating duration [see mineral kinetic study in (9)].

The next two zones from 460 ft to 495 ft and 490 ft to 525 ft are the most difficult to interpret. However, the infrared and XRD data indicate that these regions differ markedly. Zone 3 from 460 ft to 495 ft is characterized by the presence of some calcite and aragonite, almost no quartz (except at ca. 480 ft) and large amounts of high temperature silicate products. The high temperature silicates in this region are predominantly akermanite-gehlenite solid solution and lesser amounts of diopside. Zone 4 extends from 495 ft to 525 ft and consists of very few carbonate minerals, little quartz, and large amounts of high temperature silicate products. The product phases in this region are predominantly diopside with lesser amounts of akermanite-gehlenite. It is also significant that forsterite was detected in this region. Unfortunately, the implications of these observations are not certain because of a lack of baseline information about the raw shale in this region. The most probable reasons for the indicated mineralogic changes from zone 3 to zone 4 are higher temperatures and/or different heating durations for one section compared to the other or a change in the bulk composition of the raw shale in the vicinity of 500 ft, which would alter the mineralogic reactivity patterns. It is not certain what combination of retorting conditions will favor particular high temperature silicate products, although a recent investigation suggests that there are trade-offs between maximum temperature and time at temperature (9). However, it is apparent that these two regions have experienced the most extreme process conditions. The possibility of raw shale compositional changes at 500 ft is plausible considering that the prominent mineral phases in zone 3 (akermanite-gehlenite and monticellite) are calcium rich compared to the minerals in zone 4 (diopside and forsterite). Investigations of a raw shale core from the Logan Wash site are underway.

Zone 5 (530 ft to 565 ft) represent the "bottom plug" of the retort. This region is characterized by large amounts of carbonate minerals which appear to have been unaffected by post-burn operations, large quantities of quartz and feldspars, and few high temperature silicate phases. These core segments have experienced only moderate temperatures and it is possible that the small quantities of product silicates may be friable materials which previously existed in zones 3 and 4.

Leaching Behavior of Core Material

Selected analytical results for cations and fluoride, pH and conductivity in leachates are shown in Table III. Results for leachates generated from R3E2 appear to corroborate conclusions based on mineral data. The pH value of the leachates range from 8.8 for section 3 to 11.6 for section 11.

Table III. Selected Trace Elements, pH, and Specific Conductivity in Leachates from Core K3E2 (in ppm).

Section	Depth	pH	spec. cond. $\mu\text{mho/cm}$	As	B	Ca	F	Mo	V
1	461.5	9.09	2260	0.010	1.93	133	3.9	0.84	0.163
2	467.5	9.07		<0.01	2.69	566	0.3	1.88	0.618
3	472.5	8.78	2780	<0.01	2.4	352	5.2	0.293	0.129
4T	477.5	10.28	2250	<0.002	1.96	223	4.3	0.474	0.401
4B		10.20	2210	0.008	2.41	237	5.2	0.429	0.437
5T	482.5	10.41	1490	0.010	2.11	39.6	5.2	0.541	0.87
5M		10.19	1350	<0.002	1.63	48.7	4.4	0.528	1.08
5B		10.24	1500	0.006	1.91	64.0	5.3	0.520	0.77
6T	487	10.34	1120	0.026	6.55	4.51	12	0.814	1.90
6B		10.00	880	0.034	5.33	3.54	21	0.659	1.75
7	493	10.02	1400	<0.01	4.13	14.8	17.0	0.726	0.569
8	509	9.43	1450	0.011	1.86	106	2.1	0.788	0.212
9	513	9.76	995	0.016	1.91	46.1	5.4	0.64	0.23
10	523	9.47	2390	--	1.93	42.3	--	1.65	0.229
11	533	11.60	1240	<0.01	0.330	106	9	1.28	0.100
11A		11.54	2150	<0.002	0.292	285	12.0	1.48	0.222
12	540	9.82	1460	<0.002	1.10	200	2.9	0.522	0.144
12T	550	10.24	2660	<0.002	1.11	493	2.4	0.382	0.305
13B		10.55	2380	<0.01	0.917	372	3.0	0.456	0.025
14	560	9.62	330	0.020	0.262	3.8	4.2	0.838	0.251

Sections 4T through 14 have pH values of approximately 10.2, as would be expected for solutions in contact with silicate minerals (pH of synthetic sidermanite solution = 10.2). The relatively lower pH's of section 1-3 and the high Ca^{+2} ion concentrations suggest the presence of calcium sulfate instead of calcium oxide, and this is consistent with the mineralogy. The higher pH and larger Ca^{+2} ion concentrations in the lower sections could indicate the presence of small amounts of magnesium or calcium oxides (pH of $\text{MgO} = 10.0$, $\text{CaO} = 12.4$), not detectable by x-ray diffraction.

Conductivity data can be correlated with the identity of the solid materials, which is related to processing conditions. Conductivity values are relatively low for sections 5T through 9, but not as low as for typical raw shale leachates. Sections 4T, 4B, and 10 are relatively higher even though they have significant quantities of product silicate phases. Sections 4T and 4B have reasonably high Ca^{+2} contents, suggesting the possibility of small quantities of calcium oxide. Conductivity of section 10 is high due to

higher alkali metal ion concentrations. Conductivity and elemental analyses of section 14, as well as mineralogy data, suggest that the material is essentially raw shale.

It is obvious from Table III that calcium ion concentrations are directly related with conductivity values and go through a minimum in section 6T and 6B. This is consistent with the low solubility of alkaline earth silicates, such as akermanite and diopside. However, several elements indicate trends which are inversely related to the solubility behavior of the alkaline earth elements. These elements, including arsenic, boron, fluoride, molybdenum, and vanadium, are listed in Table III. These data suggest that trace elements of potential concern are mobilized from spent shales containing akermanite-gehlenite solid solution as the major high temperature silicate phase. Trace elements appear not to be as mobile from spent shales containing diopside as the major silicate phase. This observation is indicated graphically in Figure 7, which is a comparison of akermanite-gehlenite and diopside occurrence with percentage vanadium solubility. (Comparison of percent solubilities is routinely done for those elements known to vary significantly as a function of depth. The percentage vanadium solubility is obtained by dividing the solid concentration by the leachate concentration (both in $\mu\text{g/g}$). When comparing trends in leachate composition, it is important to negate variations of elemental concentrations in the solids.) It is possible that the retorting conditions which favor the formation of akermanite-gehlenite also favor the mobilization of these trace elements or that akermanite weathers in a manner which releases larger quantities of these trace elements compared with other product silicate phases. Another possible reason for the changes in mobility from region 3 to region 4 could be the ability of the diopside crystal structure to accommodate a variety of trace elements as substitutes for calcium, magnesium, or silicon, whereas the akermanite-gehlenite structure is not quite so flexible (10).

An alternate explanation, which cannot be ruled out because of a lack of baseline information on raw shale, is that compositional variations in the raw shale could have changed in the vicinity of 495 ft with concomitant effect on the final composition and leaching behavior of the product phases. It is noted that akermanite-gehlenite and monticellite are calcium rich compared to diopside and forsterite, which may give credibility to this scenario. Furthermore, compositional variations in the raw shale may have been accompanied by variations in trace element concentrations, but variations were not reflected in the solid spent shales analyzed by neutron activation analysis (11). Much more work in the relationships of mineralogy with trace element release behavior, both thermodynamic and kinetic information, will be necessary to unravel these problems.

The enhanced mobility of the aforementioned trace elements once they have been released from the solid particles, can be placed in an appropriate framework by consideration of fundamental solution chemistry. The mobilities of arsenic, fluoride, and molybdenum are indicated from chemical equilibrium codes to be controlled by alkaline earth ion concentrations. Adequate alkaline earth concentrations will precipitate BaAsO_4 , CaF_2 , and CaMoO_4 . Thus these secondary minerals will exert solubility control on these trace elements as long as a reservoir of alkaline earth ions is available. An example of this control is given in Figure 8, which shows the effect of decreasing calcium concentrations in core R3E2. Sections with small calcium concentrations exhibit the largest fluoride ion concentrations. Using the solubility product of CaF_2 , $K = 3.4 \times 10^{-11}$ at 18°C, and neglecting complicating phenomena such as the common ion effect, calculation indicates that

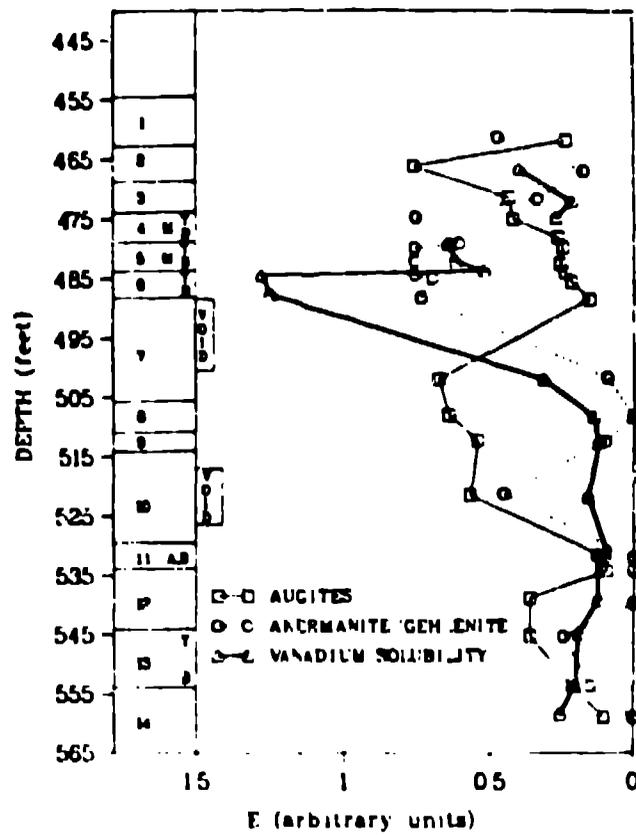


Fig. 7 - Relative Variation as a Function of Depth for Augite and Akermanite/Gehlenite Solid Solutions and Vanadium Solubility in Core R3E2.

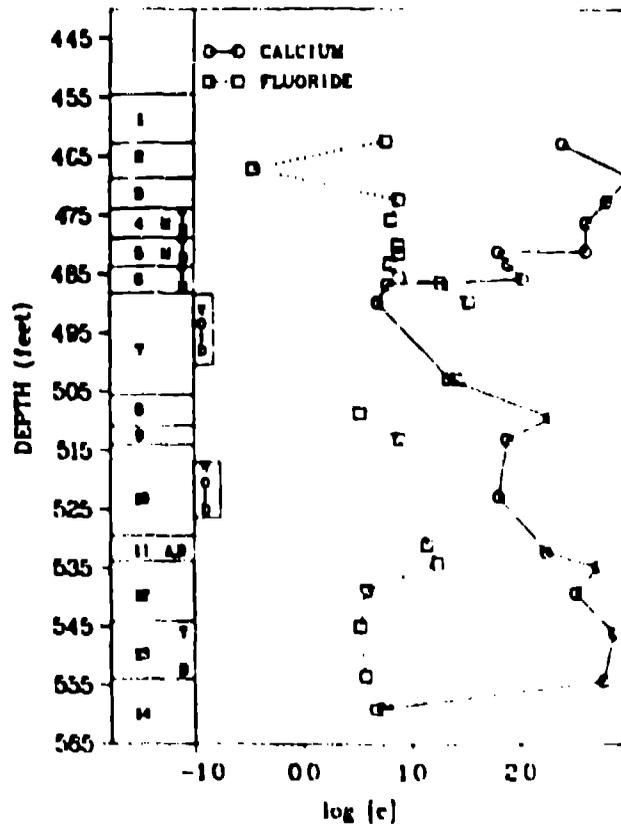


Fig. 8 - Variations in Calcium and Fluoride Concentrations in Leachates Generated from Core R3E2 Solids.

calcium ion concentrations in excess of 8 ppm will depress and control the fluoride ion concentration. Calculations such as this can also be made for molybdenum and arsenic. Thus the previous observation of the inverse relationship of conductivity and alkaline earth concentrations with arsenic, fluoride, and molybdenum concentration data are readily understood.

In contrast, the enhanced mobility of boron and vanadium does not appear to be affected by short term solubility controls. (This does not suggest that solution composition will not be altered to an extent that will favor removal of these elements from solution as the leachate moves through the geologic medium.) Thus, the increased solubility of these elements could be due to decomposition or reaction of their original mineral residences with concomitant change in their chemical form. If they are not incorporated into the newly formed mineral phases, they could be more susceptible to leaching.

Summary

Solids characterization and leaching behavior of spent shales retrieved from Occidental Oil Shale, Inc. retort 3E at Logan Wash, Colorado, have been described. Three cores have been retrieved and core R3E2 was discussed in some detail. Material recovery was less than 20% from these drillings, but mineralogical characterization revealed a wide range of mineral suites representing varied retorting conditions while leaching experiments indicated the influence of these mineral suites on the major and trace elements mobilized from these materials.

It is impossible to assess the magnitude of trace element releases to be expected from a commercial *in situ* facility once banks of retorts or the entire facility is abandoned and dewatering of the area is concluded. However, laboratory scale studies can identify the relative environmental acceptability of spent shale materials generated by *in situ* processing. In this particular study an attempt was made to relate mineralogy and leaching behavior of field generated materials with leachate composition and solution chemical processes. The interaction of these factors will ultimately affect the environmental impact of *in situ* processing on groundwater quality.

Zones identified by different mineral suites are produced depending upon processing conditions. Different mineral reactions will occur for materials in the retorting zone when compared with reactions favored by processing parameters which support combustion. Thus the mineral suites encountered in this study will be expected to occur in most commercial retorts. Even for ideal burns there should be wide variations from raw shale through shale with partially decomposed carbonates and finally to spent material containing essentially all high temperature silicate phases. The question of environmental acceptability of these partially retorted and partially reacted materials can be addressed by further examination of these laboratory studies.

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