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TITLE INFLUENCE OF CHEMICAL CHARACTERIZATION OF OIL SHALE SOLIDS ON UNDERSTANDING WATER QUALITY IMPACTS

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INFLUENCE OF CHEMICAL CHARACTERIZATION OF OIL-SHALE SOLIDS ON UNDERSTANDING WATER-QUALITY IMPACTS

by

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ABSTRACT

Synfuels technologies will yield products and effluents that are a function of the raw material being processed and the process variables. Chemical and mineralogic characterization of solids generated in synfuels production provide valuable insight into health and environmental impacts associated with synfuels processing (coal liquefaction or gasification and shale oil extraction). This report deals with considerations relating to leachate generation from solid wastes, but the suggested research approach is applicable to understanding the nature and extent of all effluents from synfuels operations. Solid characterization studies of one raw shale core and two spent shale cores from Occidental Oil Shale, Inc.'s Logan Wash site are described. These data are used to determine the effect of processing on the shale solids and also to evaluate a variety of water quality issues associated with in situ processing. The importance of solid characterization studies in developing an understanding of effluent composition and behavior and subsequently defining environmental impacts is described.

INTRODUCTION

Complex health and environmental issues will affect both the extent and rate of development of the western oil shale resource. Included among these are concerns such as, land disruption, aquifer diversion, air and water contamination, waste disposal, and health and environmental problems associated with the refining and utilization of the shale oil.[1] One of the most pressing questions that needs resolution early in the oil shale development cycle concerns the nature and seriousness of water contamination caused by the extraction and processing of oil shale, and the disposal of the solid and liquid wastes generated. There are potential water pollution problems attendant to both surface and underground processing of oil shale, and indeed the choice of recovery technology may hinge on the solvability of such health and environmental issues.

In order to develop an orderly perspective of health and environmental consequences of oil shale (or any synfuel) processing, the identity and behavior of the raw material, the fundamental chemical principles operative during processing, and the interaction of raw material and the process to yield products, effluents, and waste must be understood. The utility of this approach is illustrated with the aid of Fig. 1. This figure deals with considerations relating to leachate generation from solid wastes, but the approach is applicable to understanding the nature and extent of all products and effluents from synfuels operations. In order to understand leachate composition, it is necessary to determine the water/solid interaction, but the solid waste being considered is a dependent function of the raw shale material and the process

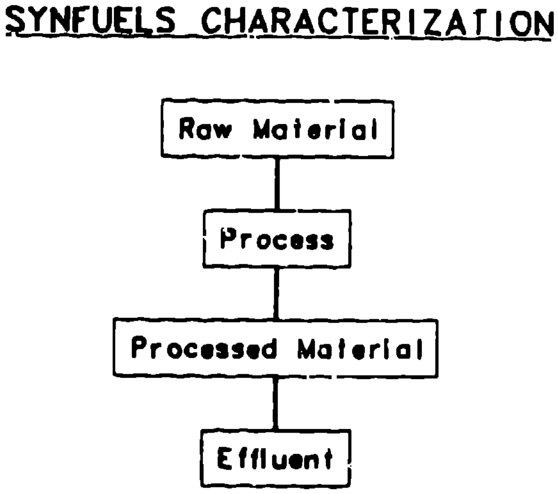

Fig. 1. Important factors determining compositions of effluents from synfuels processes.

parameters. Thus, in order to understand the chemical principles operative in the leachates (effluents), it is necessary to elucidate the interplay of the raw material and the process parameters in the formation of the waste and then the interaction of the waste form with water. The effluent and the solid waste are dependent variables, while the raw shale and the process parameters are independent variables. The role of careful characterization of solids in developing an integrated assessment of health and environmental consequences of synfuels processing is obvious.

In order to illustrate the importance of materials characterization in developing an understanding of synfuels processing impacts, research efforts concerning the question of retort abandonment after *in situ* oil shale processing will be described. The retort abandonment issue is critical with respect to maintenance of groundwater quality after commercial operations have ceased. The study of two spent shale cores and one raw shale core from Occidental Oil Shale Inc's. Logan Wash site has been completed and this information has been used to evaluate the extent of concern associated with retort abandonment. The solid core (raw and spent) samples have been characterized by infrared spectroscopy, x-ray diffraction, and, in some cases, optical microscopy and scanning electron microscopy/energy dispersive spectrometry. Trace element concentrations in the solids were determined by neutron activation analysis. These solid samples were leached by a standard procedure, leachate composition was determined by direct current argon plasma emission spectroscopy, and solution chemical principles controlling leachate composition were investigated. These data are necessary for the ultimate definition of the physical (e.g. surface area effects, permeability, and mineral environment effects) and chemical (e.g. oxidation-reduction, decomposition, and mineral reactions) processes that are responsible for enhancement of trace element mobilities from spent shale solids. The results of the characterization studies will be described, assessment of water quality implications from these data will be briefly discussed, and the role of solids characterization in determining health and environmental consequences of synfuels processing will be summarized.

PROCESS DESCRIPTION

Occidental has been experimenting with modified *in situ* (MIS) technique at Logan Wash, CO. since 1972. The method involves mining to remove 20-25% of the rock from a chamber (or room), explosive fracturing of the rock to uniformly redistribute the void created by mining, and igniting the organic bearing rock to pyrolyze and then distill the organic material from the solid. A heavy oil type liquid condenses at the bottom of the retort and is pumped to the surface. Heat for the retorting process is provided by combustion of the residual organic carbon left on the rock after the major organic material has distilled away. The third experimental retort, designated 3E, measured 32 ft. square by 113 ft high. Data indicate significant inhomogeneities in retort 3E solids suggesting channeling in retort 3E. The combustion front ceased after moving through the upper half of the chamber. The input gases in retort 3E were 70% air and 30% recycle gas. Water was injected into the retort several times for process temperature control. Offgas was recycled through the retort for several weeks after the retort was shut down. The consequences of these procedures are discussed after the characterization data is summarized.

MINERALOGY

(1). *Raw Shale*. Various authors have reported investigations of mineral species in raw oil shale.[2-4] The mineral composition varies stratigraphically, but carbonates and silicates predominate in most zones. Carbonate minerals found in raw shale include dolomite/ankerite, calcite, and in the depositional center of the basin, lesser amounts of nahcolite and dawsonite. Silicate minerals found in raw shale include α-quartz, albite and orthoclase, as well as illite, other clay minerals, and analcime. In addition, small amounts of pyrite are widespread throughout the Green River formation.

A summary of the mineralogy found in core LW-156 from the Logan Wash site is given in Table I. The zonation indicated in Table I was determined by examining differences in mineralogy and leaching behavior of the solids. The carbonate minerals do not vary detectably as a function of depth and most of the noticable differences are variations in the identity and quantity of silicate minerals. Analcime and the clay mineral illite increase steadily as a function of depth, while the plagioclase feldspars decreases steadily as a function of depth. An unidentified metamorphic mineral, similar crystalographically to the augite solid solution (listed as augite in Table I) increases steadily with increasing depth. The effects that these differences had on leachate composition will be discussed shortly.

(2). *Spent Shale.* The raw shale mineral phases discussed above undergo a variety of decomposition and solid phase reactions during retorting, depending on the original raw shale composition, maximum retorting temperature, time at maximum temperature, heating rate, gas atmosphere (and pressure), postburn conditions, etc. The extent of carbonate decomposition and silicate formation, as well as the disappearance of α-quartz, plagioclase feldspars,

TABLE I

RAW SHALE MAJOR MINERALOGY SUMMARY LOGAN WASH CORE LW-156[a]

	Zone 1 8173-7923 ft.[b]	Zone 2 7923-7698 ft.[b]	Zone 3 7698-7623 ft.[b]
α-Quartz	M	M-S	M-S
Dolomite	M-S	M-S	M-S
Calcite	M	M	W-M
Analcime	W	W-M	M
Plagioclase	M-S	VW	W
Orthoclase	W	VW	W
Augite	VW	VW	W
Pyrite	T	0	T
Illite	0-T	W	W-M

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

[b] Absolute elevation.

and potassium feldspars, indicate the extremes of temperature and retorting atmosphere experienced by the spent shales. In situ retorted spent shales experience more extreme conditions than surface retorted shales, and thus decomposition and silication reactions occur to a greater extent. The major high temperature product phases include akermanite-gehlenite and diopside-augite solid solutions. Mineralogic data for spent shale cores from Logan Wash retort 3E are summarized in Table II.

Mineralogic changes that occur during oil shale retorting are dominated by silicate and carbonate reactions and depend on the gas environment.[5,6] At less than 770 K, the minor saline sodium carbonate minerals dawsonite, nahcolite, shortite, and trona decompose to yield sodium carbonates, CO_2, and water. At slightly higher temperatures, the major carbonate minerals calcite and dolomite begin to decompose significantly. Dolomite decomposition proceeds at 925-1025 K with evolution of CO_2 and formation of periclase and calcite. The periclase persists at lower temperatures but disappears at higher temperature because of silicate formation. The calcite is chemically indistinguishable from the original calcite.[5] Calcite decomposes above 1075 K with evolution of CO_2. Steam greatly enhances the decomposition of dolomite and calcite and promotes silicate formation, whereas CO_2 inhibits calcite decomposition and depresses silicate formation. At greater than 1075 K, calcite may also react with quartz to form calcium silicates, or perhaps with feldspars to form calcium aluminum silicates. This competing reaction does not occur until a temperature is reached at which k_{eq} for the reaction is greater than the partial pressure of

TABLE II

SPENT SHALE MAJOR MINERALOGY SUMMARY
CORES R3E2 AND R3E3

	Zone A 7823-7813[b]	Zone B 7813-7798[b]	Zone C 7798-7768[b]	Zone D 7768-7733[b]	Zone E 7733-7693[b]
Dolomite	0	0	0	0	M
Calcite	0	M	M	W-M	M-S
Quartz	0	T	T	T	M-S
Orthoclase	0	0	0	W-M	0-T
Plagioclase	0	M	0	0	M
Analcime	0	W	0	0	W-M
Aragonite	0	T	W-M	W	T
Gypsum	0	0	T	T	T
Akermanite	S	W	S	M	T
Diopside	W	W	M	S	W
Monticellite	0	0	M	W-M	W
Forsterite	0	0	0	T	0
Kalsilite	W	0	W-M	M	0
Periclase	0	0	0	T	W

[a] For legend see Table I.
[b] Absolute elevation in ft.

CO$_2$; then it proceeds very rapidly.[5] In addition at ∼ 1075 K silicate minerals, such as analcime and various clays, decompose forming titanium, aluminum, and iron oxides. These oxides also may react with each other to form nonreactive silicates of the augite or akermanite-gehlenite series.

Postburn mineralogical reactions are dominated by aqueous and gas phase precipitation reactions. Abandoned retorts may require water or gas cooling to promote structural stability. Retort 3E was cooled by recycle gas with high CO$_2$ concentration. Water was also injected into this retort five times during retorting to dilute the inlet air with steam. Commercial retorts may be cooled by a water quench, which may cause chemical reactions between the mineral phases in the hot spent shale and the coolant. Aragonite, which was identified in cores from retort 3E, is the preferred crystalline form of calcium carbonate precipitating from warm solutions. This type of reaction may occur during water injection in the gas recycle mode. Some calcite may also have precipitated after cooling because of high alkalinity of groundwaters seeping into the retort. Gypsum also may be formed during postburn treatment or during recycle retorting. Sulfur dioxide in the offgas is known to react with CaO in the spent shales to form gypsum.[7]

This shows that the disappearance of raw shale minerals and the formation of a new suite of minerals in the processed shale can be accomplished through a variety of reaction pathways determined by process variables such as maximum temperature, time at maximum temperature, heating rate, and atmosphere. These mineral reactions are accompanied by chemical reactions of the minor and trace elements. Both the mineral and chemical reactions that occur during retorting affect the mobility of the major, minor, and trace elements from the shale when contacted with water. The mobility of elements can be affected by several factors, including decomposition or reaction of the the original mineral hosts, the ability of newly formed spent shale minerals to accommodate major, minor, and trace elements in their crystalline structures, and the oxidizing or reducing nature of the atmosphere. These factors, as well as solution chemical considerations, must be considered in investigations of leachate compositions generated from spent shales. Thus, mineralogy of spent shales is important in process assessment and in evaluation of the health and environmental acceptability of products and effluents from the retorting technology.

Examination of Table II indicates the range of mineral types present in the spent shale assemblages.[8,9] Each mineral type discussed above is found in varying quantities throughout retort 3E and careful evaluation of the data reveals several observations about the processing history of this retort. The extent of silicate formation and carbonate presence in retort 3E is graphically presented in Fig. 2.

There are five zones in retort 3E, each characterized by a different mineral assemblage. Each assemblage provides insight into the process conditions experienced by the material in each zone. Zone A extends from 7823 to 7813 ft (depth: 435 to 445 ft.) and contains very few carbonate minerals, very little quartz, and large quantities of high temperature silicate products. This zone has seen high temperatures probably due to ignition of the retort. Zone B extended from 7813 to 7748 ft. (depth: 445-460 ft.) and contains moderate amounts of calcite, aragonite, and quartz. There are very few high temperature silicates in this zone. The calcite probably survived the retorting process, while aragonite is due to postburn operations. This zone probably experienced temperatures in the range 800 to 1000 K for short duration. Zone C extending from 7798 to 7768 ft. (depth: 460-490 ft.) is characterized by some calcite and aragonite, almost no quartz and large amounts of high temperature silicate products, predominantly akermanite-gehlenite solid solution with lesser amounts of diopside-augite solid solution. This zone experienced high temperatures for moderately long periods of time. The combustion front terminated at the bottom of this zone and it seems to have been affected slightly by postburn operations. This zone, along with Zone D, experienced the most extreme process conditions in retort 3E. The other high temperature zone, Zone D extending from 7768 to 7733 ft. (depth: 490-525 ft.), has very few carbonates, very little quartz, and large quantities of high temperature silicates. These products were mainly diopside-augite solid solution and lesser amounts of akermanite-gehlenite solid solution. Forsterite was detected in core R3E3. The most probable reasons for the indicated mineralogic changes from Zone C to Zone D are higher temperatures for 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 7770 ft., that would alter the mineralogic reactivity pattern.

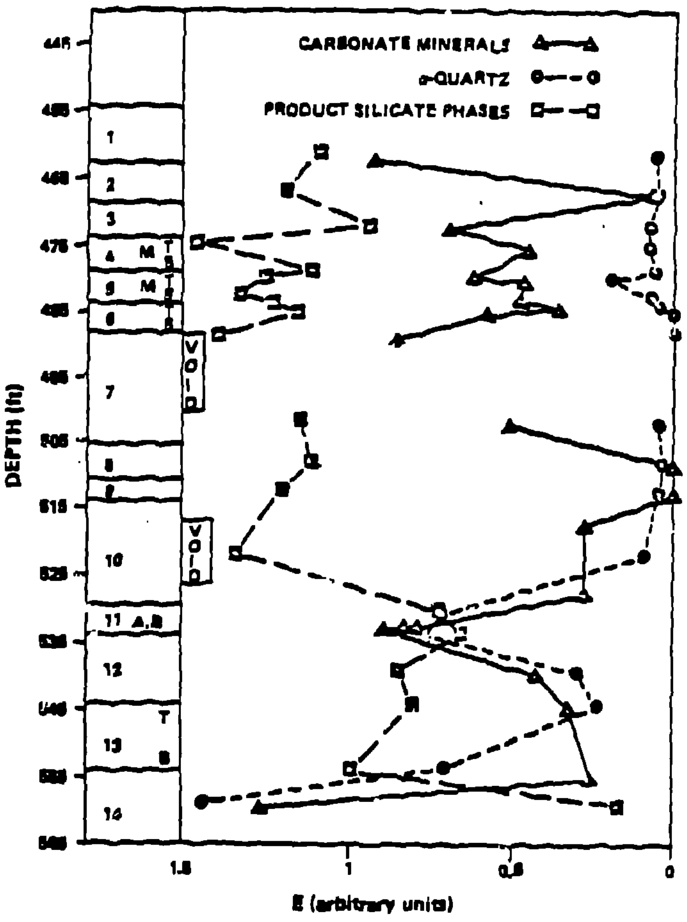

Figure 2. Carbonate, α-quartz, and product silicate minerals variation with depth OOSI core R3E2

The 7770 ft elevation corresponds to the A-Groove marker and the beginning of the Mahogany Zone, but this level falls in the middle of core LW-156 Zone 2 and there are no obvious differences in the inorganic matrix above and below that level. 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 maximum temperature.[10] However, it is obvious that Zone C and D experienced the most severe processing conditions. Zone E extends from 7733 to 7693 ft (depth: 530 to 565 ft.) and represents the "bottom plug" of the retort. This region is characterized by large amounts of carbonate minerals that appear to have been unaffected by postburn operations, large quantities of quartz and feldspars, and few high temperature silicate phases. These materials have only experienced low to moderate temperatures, probably less than 1000 K. It is also possible that the small quantities of product silicates may be friable materials previously existing in Zones C and D.

MICROMINERALOGY

(1). Raw Shale. Raw shale samples from Zone 2 of core LW-156 were examined by scanning electron microscopy/energy dispersive spectrometry and electron microprobe analysis. Low magnification EDS scans of samples from

Zone 2 had strong silicon and calcium peaks, medium magnesium and aluminum peaks, weak potassium, sodium, and iron peaks, and trace phosphorus peaks. Typical particle types included dolomite, calcite, feldspars, magnesium, calcium, and iron silicates. Apatite, zircon, and pyrite were also identified. In one of the samples examined, a particle of chalcopyrite had within it a pyrite particle and adjacent to the chalcopyrite was an area of fine material containing sulfur, lead, and selenium. The presence of selenium was confirmed by electron microprobe. The lead and sulfur suggest that the selenium was substitutionally incorporated in a lead sulfide mineral, probably galena. Other fine material in Zone 2 samples are probably illitic clays with other sub-micron mineral fragments. The kerogen present in this specimen had a weak sulfur peak

Samples examined from Zone 3 were quite similar to those from Zone 2. Dolomite, calcite, quartz, feldspars and Mg, Al, Ca, Fe silicates were commonly found minerals. There was more pyrite occurrence in Zone 3 samples compared to Zone 2 samples. The pyrites were often found with quartz and feldspars. A small amount of sphalerite, zircon and fibrous Mg, Al, K silicates were found. As in Zone 2 samples the fines may have been illite clay plus sub-micron mineral fragments (carbonates and silicates). The kerogen in these specimens also had a weak sulfur lime. These observations are consistent with the mineralogy determined by x-ray diffraction and infrared spectroscopy.

(2). <u>Spent Shale</u>. Only one sample from Zone A was examined by SEM-EDS. Low magnification EDS scans had strong silicon and calcium peaks, medium aluminum and magnesium peaks, and weak potassium and iron peaks. The intensities of the sulfur peaks varied from scan to scan. A large amount of sub-micron fine material was found in this sample. This material had strong silicon and magnesium peaks, and weak aluminum, iron, potassium, and calcium peaks. Typical particle types include: (1) A material with strong calcium and sulfur peaks most probably anhydrite or gypsum. (2) Many particles exhibited typical EDS patterns of feldspars in the center region of the particle, while the outside edges showed calcium and magnesium pickup, most likely indicating reactions of carbonate decomposition products with feldspars. (3) Particles exhibiting strong calcium, silicon, and magnesium peaks, medium aluminum, and weak iron, potassium, sulfur and sodium peaks that are probably calcium magnesium silicates from high temperature silication reactions. (4) A few quartz particles were found. These particle types suggest that Zone A samples have experienced reasonably high temperatures due to ignition of the retort in this region.

Examination of Zone B samples indicated much less severe processing than either of the zones above or below. Most of the particle types suggested little disruption of the mineral matrix in this zone. Evidence of unreacted pyrite, dolomite, calcite, and feldspars are apparent. Particles with strong calcium and sulfur peaks are probably anhydrite or gypsum. Very fine material appeared to be a mixture of mineral fragments and illite. This material had a large amount of surface area.

Zone C samples were more extensively processed than any of the material from the above zones. Low magnification scans were similar to Zone A scans and had strong silicon and calcium peaks, medium magnesium and aluminum peaks, weak iron peaks, and trace sodium, titanium, and sulfur peaks. The potassium line varied from medium to weak depending on the area, but was always present. The fine textured matrix material generally had compositions similar to the low magnification scans. The following are typical particle types. (1) Smooth particles exhibiting strong calcium and silicon peaks, medium magnesium peaks, and weak or trace sodium, aluminum, potassium, and iron peaks. These are probably calcium, magnesium silicate particles. (2) Particles with a textured surface have strong calcium and sulfur peaks with trace aluminum and silicon peaks. These are probably small areas of anhydrite or gypsum. (3) Smooth particles exhibiting strong silicon peaks, medium aluminum, potassium, calcium, and sodium lines. These were most probably potassium and sodium feldspars before processing. They ususally show a variation in composition from the center to the edge with the centermost material most closely resembling feldspathic material with increasing concentration of calcium and magnesium toward the edges. (4) Several particles were found to have a very strong iron peak, a medium magnesium peak, and weak aluminum, silicon, calcium, and manganese peaks. These are probably residues from siderite decomposition.

Examination of material from Zone D indicated that the material experienced disruption of the original mineral matrix during processing. No obvious carbonate minerals or pyrite were found. The low magnification EDS scans had strong silicon peaks, medium aluminum, potassium and calcium peaks, weak magnesium and iron, and trace titanium and sulfur peaks. There was much more potassium and aluminum present and less calcium than in shales from the upper part of the retort. Large quantities of fines showed strong silicon and magnesium peaks, potassium, calcium, and sulfur from trace to strong, iron peaks from medium to weak, and trace manganese peaks. The following are typical particle types. (1) Smooth particles with EDS scans resembling feldspars but with no calcium or magnesium pickup on the surfaces of the particles. (2) Quartz. (3) Fine grains exhibiting strong silicon and magnesium (forsterite was detected by XRD in some of these samples). (4) Porous material exhibiting strong iron peaks, probably oxidized pyrite. (5) Fines with strong calcium and sulfur peaks that are probably anhydrite or gypsum.

Samples from Zone E were not examined by SEM-EDS, but the mineralogy by XRD indicated that very little disruption probably occurred during processing.

LEACHING BEHAVIOR

Solid samples from the Logan Wash raw shale core LW-156 and from the spent shale cores retrieved from retort 3E have been subjected to a standard leaching experiment in order to determine the water: solid interaction as a function of the mineralogy of the solid material. If the experiment is done in a rigorously controlled fashion, results from the leachates should reflect differences in the solids and complement other solid characterization techniques. Baseline data for raw shale leachability and similar data for spent shales is essential to understand the physical (surface area) and chemical (mineralogy) principles controlling solubilization of contaminants from the solid by water and to determine the factors (solution chemical control, adsorption) that control the mobility of contaminants away from the solids after dissolution.

The standard leaching experiment is a static shaker experiment involving a 5:1 water to solid ratio of distilled water and -100 mesh solid material. The experiment is usually conducted for 48 hours. Details of the experimental procedures and analyses are described elswhere.[11] Leachate compositions depend on the extent of occurrance of minerals in the solid material, the amount of each element available in the solid material, the dynamic effects that control the mobilization of a particular element from the bulk solid to solution at the solid/liquid interface, and the chemical processes that occur as the bulk solution constituents move to establish equilibrium. The experiment described above is designed to address the first two and the last consideration. To understand the equilibrium process that affect the solution chemistry, dynamic effects are investigated in separate experiments. The static experiments are more useful as a solid characterization tool, because fewer variables are involved and results are more easily interpreted.

(1). Raw Shale. A summary of leachate concentrations of selected major and trace elements for leachates generated from raw shale core LW-156 materials is shown in Table III.

These data are organized according to zones delineated by mineralogy data. It is obvious that differences manifested by changes in mineralogy as a function of depth are also indicated by the leachate compositions. Zone 1 leachates have moderate pH values, low conductivities (less than 350 µmho/cm), low concentrations of major elements, and less than detectable levels of most trace elements. These results are consistent with the mineralogy of these materials. The mineral assemblages in this region consisted of relatively insoluble carbonates and silicates (quartz and feldspars) and a lack of minor minerals (clays and pyrite). Zone 2 leachates, however, are characterized by pH's of 9.5, conductivities in excess of 900 µmho/cm, and higher concentrations

TABLE III

RAW SHALE LEACHING SUMMARY
LOGAN WASH CORE LW-156[a]

	Zone 1 8173-7923 ft.[b]	Zone 2 7923-7698 ft.[b]	Zone 3 7698-7623 ft.[b]
pH	8.57	9.50	8.52
cond (umho/cm)	345.	740.	750.
As	0.01	0.6	0.01
B	0.04	10.7	0.18
Ca	27.4	2.06	75.9
Mg	15.4	9.13	20.
Mo	0.38	1.10	0.06
Na	11.0	177.	38.
Sr	1.20	0.02	1.31
V	0.01	0.5	0.01
F	1.5	6.0	2.0
CO_3^{2-}	70	200	70
SO_4^{2-}	50	30	200

[a] All values in µg/mℓ except as indicated

[b] Absolute elevation

of most elements compared to Zone 1. Leachate compositions (compared to Zone 1) have lower calcium and magnesium concentrations, increased concentrations of sodium, lithium, boron, vanadium, and molybdenum indicating increased solubility. There is also a problem associated with particulate clay mineral removal by the standard separation procedure. Millipore 0.45µ filters do not effectively remove particulates from the leachates generated from Zone 2 materials. This behavior is reflected by <u>apparent</u> increased solubilities of aluminum, iron, silicon, and titanium. However, these four elements can be removed by a Nucleopore 0.2µ filter, while the other elements listed above are not removed indicating true solution behavior. Examples of this problem are given in Table IV. These particulates have been identified by x-ray diffraction analysis of the filters to be illitic clays.

It is suggested that the different leaching behavior of Zone 2 materials with respect to Zone 1 materials are due to differences in the minor mineralogy of the two zones. Zone 2 materials have elevated levels of illite as detected by XRD and this correlates with the Zone 2 leaching behavior including the particulate removal problem and increased solubilities of arsenic, boron, molybdenum, vanadium and fluoride. It should be pointed out that Zone 2 leachates also have elevated sodium and carbonate concentrations. This suggests that a sodium carbonate mineral, such as nahcolite or dawsonite, may be occurring at concentrations not detectable by XRD. It is apparent that both

TABLE IV

APPARENT LEACHATE CONCENTRATIONS FROM ZONE 2 MATERIALS WITH SUCCESSIVE FILTRATION (IN PPM)

	Sample 16			Sample 32		
	A	B	C	A	B	C
Al	6.45	0.42	0.01	10.7	9.6	0.08
As	0.51			0.84		
B	7.34	7.07	7.10	11.4	11.3	10.5
Fe	5.78	0.28	>0.01	9.92	9.01	0.05
Mo	1.62	1.59	1.54	1.14	1.12	1.04
Si	32.3	5.8	4.5	54.1	48.0	5.4
Na	100	98	97	143	141	135
Ti	0.28	0.01	<0.01	0.84	0.49	>0.01
V	0.35	0.29	0.27	0.48	0.47	0.36

A = 0.45 µ millipore
B = 0.45 µ millipore refiltered
C = 0.2µ nucleopore

the illitic clays and the Na/CO$_3$ bearing mineral are contributing to the leaching behavior of Zone 2 solids. Subsequent analysis must be made cognizant of the effects of the minor minerals in the raw shale. Zone 3 leachates are characterized by higher calcium and magnesium solubilities, slightly higher boron, lithium, and sodium solubilities (compared to Zone 1), and slightly lower molybdenum solubilities.

From these experiments, it is observed that leaching behavior can vary as a function of depth and also, consequently from place to place in the Piceance Basin. This variation is illustrated for boron and vanadium mobility from Logan Wash core LW-156 in Fig. 3. These behavioral differences correlate with identity and amounts of the minor minerals dispersed through the major mineral matrix. In subsequent interpretations of Logan Wash data, it is important to realize that Occidental's retorting operations are positioned in the same stratigraphic horizon that contains the Zone 2 shales.

(2). Spent Shales. Selected analytical results for cations and fluoride, pH, and conductivity in spent shale leachates from core 2 of retort 3E are shown in Table V. These data encompass Zones B through E as delineated by mineralogy data. The results are similar for core 3 and appears to corroborate conclusions based on mineral data. The pH values of the leachates range from 8.8 for section 3 to 11.6 for section 11. Sections 4T through 7 have pH values

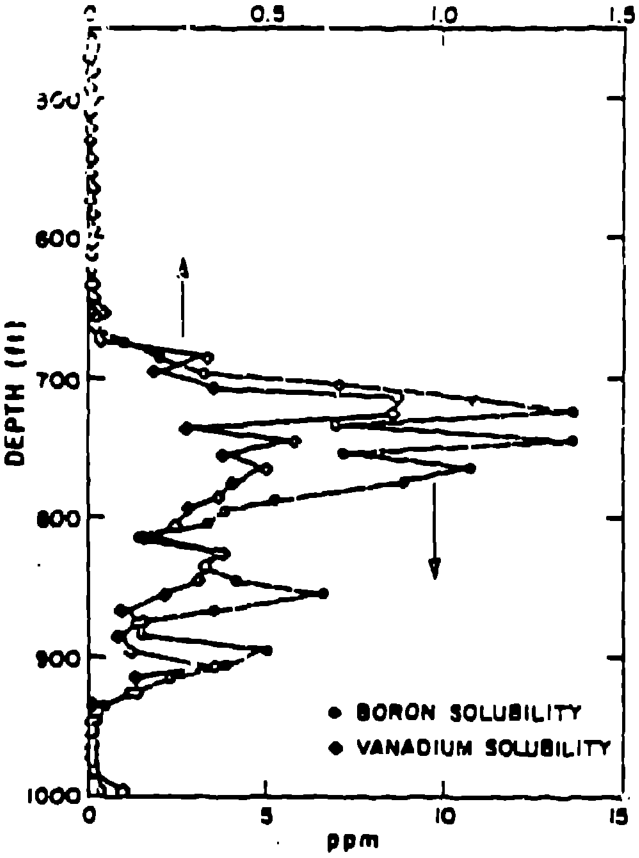

Fig. 3. Boron and vanadium solubility variations as a function of depth for core LW-156.

TABLE V

SELECTED TRACE ELEMENT CONCENTRATIONS, pH, AND SPECIFIC CONDUCTIVITIES IN LEACHATES FROM CORE R3E2 (IN PPM).

Section	Absolute Elevation	pH	Spec. cond. µmho/cm	As	B	Ca	F	Mo	V
1	7802	9.09	2260	0.010	1.93	133	3.9	0.84	0.163
2	7796	9.07		<0.01	2.69	566	0.3	1.88	0.618
3	7791	8.78	2780	<0.01	2.4	352	5.2	0.293	0.129
4T	7786	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	7781	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	7776	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	7770	10.02	1400	<0.01	4.13	14.8	17.0	0.726	0.569
8	7754	9.43	1450	0.011	1.88	106	2.1	0.788	0.212
9	7750	9.78	995	0.016	1.91	46.1	5.4	0.64	0.23
10	7740	9.47	2390	--	1.93	42.3	--	1.65	0.229
11	7730	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	7723	9.82	1460	<0.002	1.10	200	2.9	0.522	0.144
13T	7713	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	0.458	0.095
14	7703	9.62	350	0.020	0.262	3.8	4.2	0.838	0.251

of approximately 10.2, as would be expected for solutions in contact with silicate minerals (pH of synthetic akermanite solution = 10.2). The relatively lower pH's of sections 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 MgO = 10.0, 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 V that calcium ion concentrations are directly related with conductivity values and go through a minimum in sections 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 V. 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 Fig. 4, 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 µg/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 Zone C to Zone D 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.[12]

An alternate explanation that is quite plausible considering the raw shale data previously discussed is that composition variations in the raw shale could have changed at the 7770 ft. level with concomitant effect on the final composition and leaching behavior of the product phases. Although the 7770 ft. level is in the middle of Zone 2 (raw shale), the rubbling procedures undoubtedly altered the stratigraphy of the retort chamber and thus direct correlation of cores is not possible. It is, however, certain that those trace elements mobilized from Zone C (spent shale) sections are the same elements mobilized from raw shale core LW-156 in the same stratigraphic horizon. Thus, it is not certain whether compositional changes in the raw shale or differences in retorting conditions favoring one product silicate vs. another (diopside or akermanite) are responsible for trace element mobility differences from Zone C to Zone D (spent shales). It is important to note that both raw shale composition and behavior, and retorting conditions interact to define the nature and behavior of spent shales from processing activities.

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, their 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 Fig. 5, which shows the effect of decreasing calcium

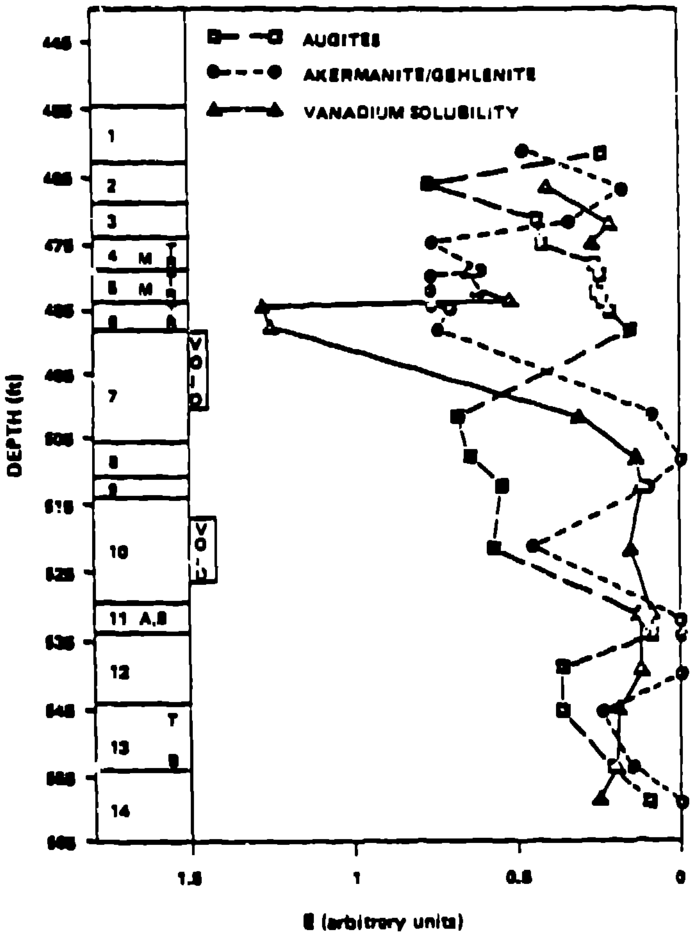

Fig. 4 Relative variation as a function of depth for augite and akermanite/gehlenite solid solutions and percentage vanadium soluble in Core R3E2.

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 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.

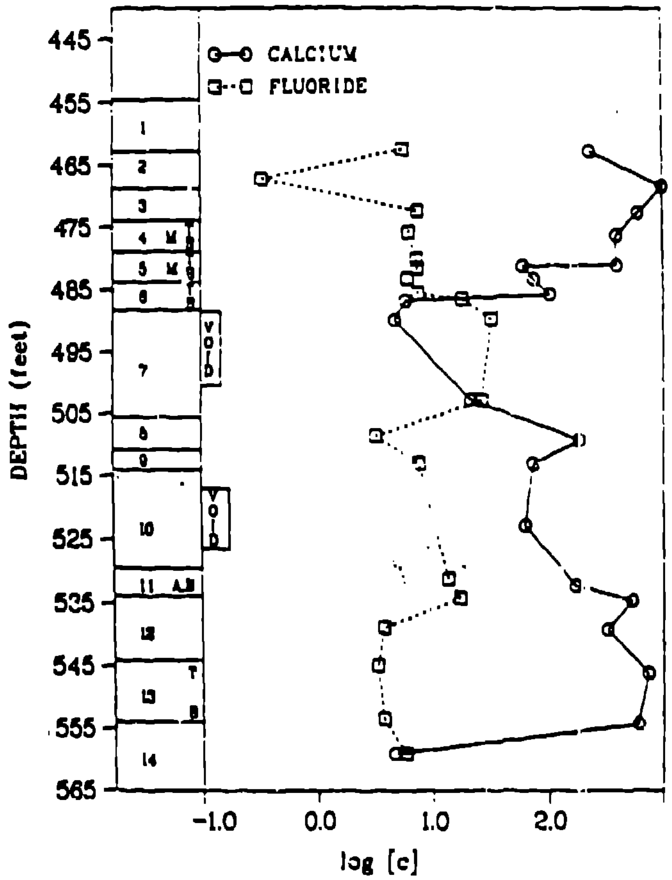

Fig. 5. Variations in calcium and fluoride concentrations in leachates generated from core R3E2 solids.

CHARACTERIZATION SUMMARY

The raw shale in the Logan Wash area varies as a function of depth. There are three zones of leachability in core LW-156 (that was drilled between Occidental's retorts 7 and 8). These differences in leachability reflect the minor mineralogy changes of the raw shale. The stratigraphic horizon that corresponds to Occidental's mining and retorting activities extends through 300 ft and leachates from these shales exhibit very low calcium and magnesium concentrations, increased concentrations of sodium, lithium, hydrogen ions, boron, vanadium and molybdenum indicating increased solubilities, and problems associated with particulate clay minerals reflected by <u>apparent</u> increased solubilities of iron, aluminum, silicon, and titanium. These solids are characterized by detectable quantities of mixed layer clays and also quantities of a soluble sodium carbonate mineral (either dawsonite or nahcolite). These observations have been confirmed by application of pattern recognition techniques to the mineralogical and leaching data.

The spent shale cores from retort 3E at Logan Wash indicate that extreme conditions were experienced by the shale materials during processing. This results in the occurrence of decomposition and/or silication reactions to form high-temperature product phases including akermanite/gehlenite and diopside/augite solid solutions, kalsilite, monticellite and forsterite. The identity and persistence of the carbonate minerals are important to the understanding of the processing conditions experienced by the shale materials. In retort 3E, carbonate minerals in the upper sixty percent of the retort have been identified as regeneration products resulting from gas recycle and water injection procedures used in post-processing of the retort. Carbonate minerals in the lower forty percent of the retort are considered to be survivors of the retorting process. In addition, the persistence of relatively stable raw shale phases, such as quartz, orthoclase, and albite, provide insight into process parameters. Even though extreme retorting conditions were experienced by the spent shales in retort 3E, leachate compositions suggest that several major and trace elements including potassium, lithium, fluoride, vanadium, boron, molybdenum, nickel, and arsenic are not rendered immobile by the formation of high temperature silicate product phases (especially akermanite/gehlenite solid solution). Comparison of raw-shale leaching behavior and spent shale leaching behavior indicates that some of the trace elements are elevated in both raw and spent shale leachates, which suggests that these elements are not incorporated in the silicate matrix or that elements which control these trace element solubilities *are* incorporated in the silicate matrix (secondary solubility control). These observations have also been verified by pattern recognition techniques.

These assessment activities have suggested that complete characterization of raw and spent shales from the same stratigraphic horizon is necessary to understand the effect of retorting parameters on the mobility of inorganic and organic contaminants and is essential to developing an understanding of the chemistry that will control water contamination as a result of contact with spent shales. These studies have also indicated several misconceptions about shale leaching. For example, it is apparent that formation of high temperature silicate phases, such as akermanite/gehlenite, does *not* necessarily guarantee the insolubility of all environmentally sensitive trace elements. These studies have also indicated a variability in raw shale leaching not previously encountered.

WATER QUALITY IMPACTS

The results presented in this report have been used in an assessment of potential water quality problems associated with modified *in situ* retort abandonment. Water quality may be affected by intermingling of differing quality aquifer waters or by leaching of spent shales in retort chambers.[13] A recent assessment of aquifer bridging has suggested that changes in water quality by intermingling will not significantly alter the suitability of the resultant water for use as a domestic, agricultural, or live stock supply.[14] This is because the constituents which are troublesome in these aquifers (boron, fluoride, iron, lithium, manganese, and molybdenum) exceed criteria in most groundwaters; only the degree to which criteria are exceeded differ.

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

Analysis indicates that groundwaters in the Piceance Creek Basin are presently unsuitable for use as irrigation, domestic, or livestock watering supplies and that extensive treatment would be required before wide-scale development of this water resource could take place.[14] MIS retorting in this area would alter existing water quality as a consequence of leaching and intermingling of lower and upper aquifer waters. Leaching would generally increase the concentrations of elements such as fluoride and boron which are already high in native groundwaters and of certain additional elements which are not elevated presently. This would increase the hazard of using these waters and also, the cost of treating them. Intermingling does not appear to be a significant concern because the problematic elements are elevated in both aquifers.

These conclusions have some rather interesting environmental control technology implications. First, they reveal that intermingling of upper and lower aquifer waters will not alter the acceptability of the resulting waters for projected beneficial uses. This means that control technologies applied to this problem need not prevent aquifer bridging. Thus, less expensive technologies, such as process control and forced leaching, may be used instead of the more expensive technologies which reduce flow through the retorts (grouting, grout curtains). Second, it demonstrates that certain trace elements, such as vanadium, selenium, and lead, may be significantly elevated above background concentrations and may have to be removed before the water can be used. Since the area is sparsely populated and because most users of the water would be individuals or single farms and ranches, it is unlikely that treatment would be affordable or that knowledge of its requirement would be available.

CONCLUSIONS

The importance of solids characterization in the assessment of health and environmental consequences of oil shale processing has been discussed. This type of information is essential for the understanding of water quality impacts from energy development. A variety of issues can be addressed aided by solids characterization information. (1) The role of process parameters in the formation of wastes and effluents can be determined. (2) The mineral: water interaction during leaching and/or weathering can be understood. (3) The influence of the microstructure of the solids on the leaching process can be investigated. (4) The avilability of major ions for solubility control is determined by spent mineral assemblages. (5) Trace element residences and their role in contaminant mobility can be understood.

The data presented in this report indicates that the spent shale wastes retrieved from Logan Wash retort 3E are a function of the material being processed and the process conditions. An understanding of the interaction of the raw material and the process in waste formation aids the interpretation of the chemistry of effluent streams and leachates. In regard to trace element contaminants in leachates, mineral residences, as well as, solution chemical control determines mobility.

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