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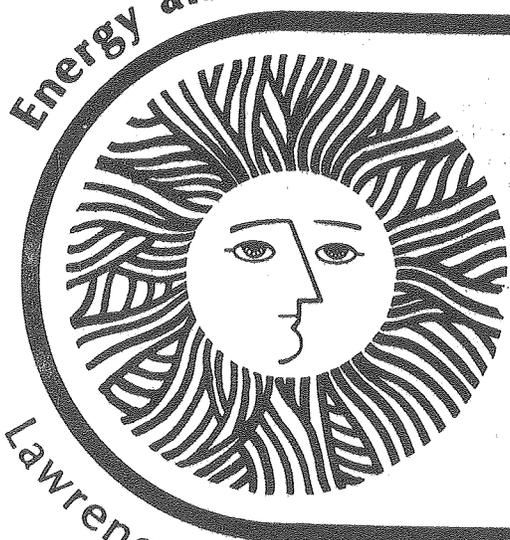
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Partitioning of Major, Minor, and Trace
Elements During Simulated In Situ Oil
Shale Retorting in a Controlled-State
Retort

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April 1979

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PARTITIONING OF MAJOR, MINOR, AND TRACE ELEMENTS DURING
SIMULATED IN SITU OIL SHALE RETORTING IN A CONTROLLED-STATE RETORT

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presented at the

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ABSTRACT

The partitioning of 49 elements during 15 runs of the Laramie Energy Technology Center's controlled-state retort was investigated. Mass balances and mobility factors were determined for each element for each run. The average mass balance closure for 47 elements (Cd and Hg excluded) for the 15 runs was $101 \pm 7\%$. Mobility was used to identify five groups of elements. Over 25% of the raw shale elemental mass of Group 1 elements (H, N, S, Cd, Hg, inorganic C, and organic C) is distributed primarily to the gas and oil. From 1% to less than 10% of the raw shale elemental mass of the Group 2 elements (Se, Ni, As, and Co) is partitioned primarily to the oil phase. The Group 3 to 5 elements, all of which have mobilities that are less than 1%, include Cr, Sb, Zn, Cu, Na, Mo, V, Ga, Fe, Mn, U, Ba, Dy, La, K, Mg, Sm, Cs, Eu, Hf, Rb, Ce, Sr, Al, Ca, Sc, Ti, Yb, and Th.

The study indicates that elemental partitioning in the controlled-state retort is affected by mineralogical residence and retort operating conditions. Significant differences in the mobility and mass distribution patterns were observed for Green River, Antrim, and Moroccan oil shales. It is proposed that for a given mineralogy, elemental partitioning is controlled primarily by high-temperature chemical reactions within the reaction zone and secondarily by interactions between the products (oil, gas, and water) and the cool shale ahead of the reaction zone. Retorting temperature and atmosphere also affect partitioning trends. Temperature controls the degree of kerogen conversion and mineral decomposition; input gas composition determines the atmosphere, that is, reducing or oxidizing (although this latter factor did not significantly affect partitioning here).

INTRODUCTION

Oil shales contain organic material in a mineral matrix which includes significant quantities of such environmentally sensitive elements as U, Zn, Cu, Pb, As, Se, Hg, Cd, and Co. These elements could be

released to the environment by the disposal of by-products, by leaching of solid wastes, or by refining and using shale oil.

Oil shale retorting produces shale oil, gas, a solid referred to as retorted shale, and an aqueous effluent known as retort water. Elements initially present in the oil shale are partitioned or distributed to those products during the retorting process. The quantity of each element distributed among the products depends on the mineralogy of the oil shale and on retort operating conditions.

This paper discusses the partitioning of 49 elements during simulated in situ oil shale retorting in the Laramie Energy Technology Center's (LETC) controlled-state retort. Samples of raw and retorted oil shale, shale oil, retort water, and retort gas were collected, analyzed (using instrumental and wet chemical methods), and the results interpreted using mass balances and mobility calculations.

EXPERIMENTAL

Retorting System

The LETC controlled-state retort was used in all experiments. This bench-scale, simulated in situ retorting facility has been previously described by Duvall and Jensen (1975) and by Bartke and Duvall (1977). A schematic of the system is shown in figure 1; retort operating conditions for the runs reported here are summarized in table 1.

The retort is a vertical stainless steel tube, 4 m (13 ft) long with an inside diameter of 8 cm (3 in); capacity of the tube is about 20 kg of oil shale. The tube is accessed at the upper end through an outside cap-type compression flange which is fitted with an inlet port for gas and a thermocouple well. Thermocouples are placed in another tube, outside diameter 2.5 cm (1 in), axially centered through the outer 8-cm (3-in) tube. The bottom of the tube is fitted with an outside cap-type compression flange provided with ports for the thermocouple well and the product collection line. The

Figure 1. Schematic of LETC's controlled-state retort.

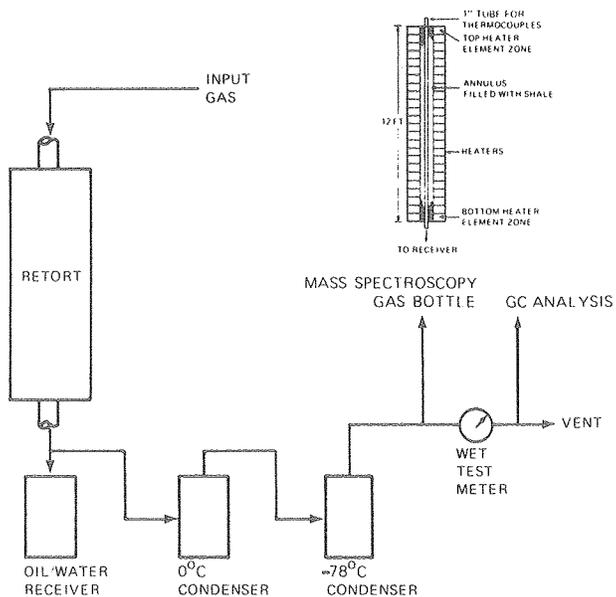


Table 1. Retort operating conditions for LETC's controlled-state retort.

Run ^a	Shale type	Run type ^b	Shale grade, liters/tonne	Shale size range, mm	Oil yield % Fischer assay, volume basis	Isothermal advance rate, m/day	Maximum temperature, °C	Sweep gas	Gas flow rate standard, m ³ /m ² min
CS-60	Colorado	I	123	3-13	46	1.83	540	N ₂	0.12
CS-61	Colorado	C	88	3-13	92	1.83	540	N ₂	0.12
CS-62	Utah	C	126	3-13	95	1.83	540	N ₂	0.12
CS-63	Antrim	C	40	3-13	77	1.83	540	N ₂	0.12
CS-64	Colorado	C	248	3-13	94	1.83	540	N ₂	0.12
CS-65	Moroccan	C	79	3-13	88	1.83	540	N ₂	0.12
CS-66	Colorado	C	128	3-13	91	1.83	540	75% N ₂ 25% steam	0.15
CS-67	Colorado	C	231	3-13	100	1.83	540	75% N ₂ 25% steam	0.15
CS-68	Colorado	C	119	3-13	97	1.83	540	N ₂	0.12
CS-69	Colorado	C	118	3-13	98	1.83	760	64.5% N ₂ , 10.5% O ₂ 25% steam	0.15
CS-70	Colorado	C	134	3-13	96	1.83	540	75% N ₂ 25% steam	0.15
CS-71	Utah	C	137	3-13	91	1.83	540	75% N ₂ 25% steam	0.15
CS-72	Colorado	C	89	3-13	97	1.83	540	75% N ₂ 25% steam	0.15
CS-73	Moroccan	C	77	3-13	97	1.83	540	75% N ₂ 25% steam	0.15
CS-74	Colorado	C	82	3-13	102	1.83	760	64.5% N ₂ , 10.5% O ₂ 25% steam	0.15

^a The designation CS stands for controlled-state.

^b C = completed run; I = interrupted run.

outer tube is surrounded between the upper and lower flanges by a contiguous series of 24 pairs of 15-cm (6-in) long electric heaters which are controlled by 24 variable transformers. Thus, the retort is div-

ided into 24 zones delineated by these heater elements. Zone 1 is the top 15 cm (6 in) of the shale bed and zone 24 is the bottom 15 cm of the shale bed.

The product collection system consists of a glass receiver maintained at ambient conditions and two knock-out traps in series; the traps are maintained at 0°C and -78°C. The glass receiver collects most of the oil and retort water and the traps collect organic and inorganic vapors. The volume of noncondensable gases is measured by a wet test meter and gas composition is determined by mass spectrometry.

Two types of experiments were conducted with this retort: they are referred to as "completed" runs and "interrupted" runs. In a completed run, the entire shale bed is retorted vertically from the top to the bottom of the shale bed. In the interrupted run reported here (CS-60), heating was stopped immediately after the shale within heater zone 14 reached 540°C. The heating elements were then opened and the retort tube was rapidly cooled with a water quench. The tube was cut into 24 sections corresponding to the heater element zones, and products from each section were recovered for analysis. Shale in the first 14 sections was completely retorted, shale in sections 15 through 17 was partially retorted and wet with oil, and shale in sections 18 through 24 was unretorted and wet with oil. The oil was removed from the shale with a cyclohexane wash before analysis.

The controlled-state retort is different in several important ways from field in situ retorts. The maximum temperature reached in this retort, 760°C, is low compared to temperatures observed in field experiments in which temperatures have reached over 1000°C. These higher temperatures may result in a greater distribution of mass from the raw shale to the products than observed here. In the controlled-state retort, the reaction zone consists of a pyrolysis zone, and heat for pyrolysis is supplied by external electric heaters; in field retorts, the reaction zone consists of a pyrolysis zone and a combustion zone, and heat for pyrolysis is derived from the trailing combustion front. Therefore, the retorting atmosphere in the controlled-state retort is reducing while in field retorts, both oxidizing

and reducing conditions may occur. The retorting rates studied here are faster than those presently used in field experiments and, therefore, oil residence times in the reaction zone are shorter. Similarly, the particle size ranges studied here are much smaller and the void fraction much higher than those anticipated for field retorts. Significant differences may also exist between the product collection system used in the controlled-state retort and in a commercial operation. A more efficient condenser system, such as may be used commercially, may remove a significant fraction of volatile elements, such as Hg and Cd, from the gas stream. These differences between the controlled-state retort and proposed commercial in situ retorts could result in significant differences in partitioning trends. Therefore, these results should not be generalized to other retorting systems or to field in situ retorts.

Sampling

Samples of raw and retorted shale, shale oil, and retort water were collected for analysis. A single sample of raw oil shale was split from an approximately 20-kg lot and ground to less than 0.15 mm (100 mesh) with most passing 0.074 mm (200 mesh) in an alumina-faced jaw crusher and an alumina-jaw pulverizer. Samples of retorted shale were split from the top, middle, and bottom sections of the shale bed and crushed using the same procedures used for raw shale. The glass receiver was removed from the retort within 24 hr after run completion, the water layer removed with a syringe (retort water) and the trap condensates mixed with the oil (wet oil). A 25 ml to 100 ml aliquot of the retort water and wet oil were collected for analysis. Pentane was then added to the receiver and the wet oil was dried by distilling off the water with the pentane. The dry oil, the water distilled over with the pentane, and the retort water were individually analyzed for C, H, N, and S. The wet oil and retort water were analyzed for all other elements.

Analytical Methods

Most of the collected samples were analyzed for 49 elements (inorganic and organic carbon are counted separately) using instrumental and wet chemical methods. Some samples were not analyzed by all techniques due to insufficient sample.

Zeeman atomic absorption spectroscopy was used to make measurements of Cd and Hg in all samples using techniques previously described by Hadeishi and McLaughlin (1975, 1978).

Energy-dispersive, high-energy x-ray fluorescence spectrometry was used to make measurements of Fe, Ti, Mn, Cu, Pb, Zn, Ni, As, Se, Ga, Y, Ge, Rb, and Sr in solids and of Zn, Fe, Ni, As, Se, Ge, Pb, Sr, Y, Rb, and Ca in selected oil and water samples. The procedures used have been previously described by Giauque, Garrett, and Goda (1977, 1978). An energy-dispersive, low-energy x-ray fluorescence spectrometry technique described by Hebert and Street (1973) was used to measure Na, Mg, K, Ca, Fe, Si, Al, and Ti in all solid samples.

The neutron activation analysis procedure described by Perlman and Asaro (1969) was used to make measurements of Al, Ca, V, Dy, Mg, Ti, Mn, Na, K, Eu, Ba, Sr, U, Sm, Lu, As, La, Mo, W, Ba, Fe, Sc, Ta, Co, Cs, Sb, Nd, Tb, Se, Ce, Hf, Th, Ni, Yb, and Cr in all solid samples. An absolute neutron activation analysis procedure described by Heft (1977) was used to measure Al, V, Cu, Ti, Ca, Na, Mg, Si, Mn, U, W, Ba, Dy, As, Ga, Sm, Mo, K, La, Lu, Yb, Sb, Zn, Fe, Cr, Co, Se, Ce, Cs, Eu, Sc, Th, Ni, Ta, Hf, and Rb in selected oils and waters.

Total C, H, and N were measured in all samples using a Carlo Erba elemental analyzer gas chromatograph, and inorganic and organic C and total S were measured using wet chemical procedures described by Fox et al. (1978).

RESULTS AND DISCUSSION

Mass Balances

Mass balances were computed for each run and used to study partitioning trends and to assess the adequacy of sampling and analysis procedures. This section discusses the computation and statistical analysis of product and elemental mass balances and mass balance closures.

Concentration data and product mass balances for each run were used to compute mass balances for each element. Some runs for select elements were omitted due to incomplete data or inadequate sampling.

The product mass balance around the retort system studied here (figure 1) is given by:

$$m_{\text{input gas}} + m_{\text{raw shale}} = m_{\text{retorted shale}} + m_{\text{oil}} + m_{\text{water}} + m_{\text{gas}} \quad (1)$$

where m is the mass of each input or output. The degree of closure of the product mass balance is expressed as the percent product closure. This quantity is the mass recovery for the system and represents the percentage of the total mass charged to the system that is recovered in products--the retorted shale, oil, water, and gas. It is computed from equation (1) as the ratio of mass outputs to mass inputs and is given by:

$$\text{Product closure} = 100 \left(\frac{m_{\text{retorted shale}} + m_{\text{oil}} + m_{\text{water}} + m_{\text{gas}}}{m_{\text{raw shale}} + m_{\text{input gas}}} \right) \quad (2)$$

The product mass balances and closures computed with equation (2) are summarized in table 2. The closures in the last column of table 2 indicate that good product recovery was obtained. All of the balances close to within $\pm 4\%$. The average closure for 15 runs of the LETC controlled-state retort is $101 \pm 1\%$. This indicates that sampling of the retort for mass balance purposes was adequate and that reliable data were obtained for mass flows into and out of the retort. One may infer from this that the average experimental error associated with sampling the various retort streams was of the order of 1%.

The elemental mass balances were computed from elemental concentrations (C) and the product masses

Table 2. Mass balance data for LETC's controlled-state retort.

Run	Raw oil shale, g	Input gas (O ₂ +H ₂ O), g	Spent shale, g	Product gas ^a , g	Oil (wet), g	Retort water, g	Closure, %
CS-60	17,140	-	15,306	385	1,159	37.1	99
CS-61	18,624	-	16,161	811	1,587	99.7	100
CS-62	16,865	-	13,989	762	2,163	74.1	101
CS-63	16,511	-	14,918	816	535	495.1	102
CS-64	14,009	-	10,074	1,031	3,377	92.9	104
CS-65	15,820	-	13,109	629	1,125	927.3	100
CS-66	16,395	618	13,114	1,527	2,151	338.2	101
CS-67	13,948	580	9,400	1,582	3,413	393.3	102
CS-68	16,252	-	13,376	727	1,959	158.5	100
CS-69	16,954	976	11,380	4,068	2,233	351.5	101
CS-70	17,377	600	13,654	1,507	2,358	401.6	100
CS-71	16,927	651	13,513	1,304	2,384	334.5	100
CS-72	18,473	639	15,350	818	1,902	294.5	101
CS-73	15,731	780	13,370	4,239	1,216	1,086.0	100
CS-74	18,858	1,568	13,212	4,239	1,995	537.2	98

^a Computed on an N₂-free basis.

(m) as:

$$\frac{M_{x, \text{input gas}} + M_{x, \text{raw shale}}}{M_{x, \text{retorted shale}} + M_{x, \text{oil}} + M_{x, \text{water}} + M_{x, \text{gas}}} \quad (3)$$

where M is the product of the elemental concentration C and the product mass m (table 2) and x is a subscript designating an individual element.

The degree of elemental mass balance closure was assessed in this study using the elemental closure which is similar to the product closure in equation (2). The elemental closure is defined as the elemental mass recovery and represents the percentage of the total elemental mass present in the raw oil shale and input gases that is accounted for in the products--the retorted shale, oil, water, and gas. It is computed from equation (3) as the ratio of elemental outputs to elemental inputs and is given by:

$$\left(\text{Elemental closure} \right)_x = 100 \left(\frac{M_{x, \text{retorted shale}} + M_{x, \text{oil}} + M_{x, \text{water}} + M_{x, \text{gas}}}{M_{x, \text{raw shale}} + M_{x, \text{input gas}}} \right) \quad (4)$$

It is assumed that values for M_{x, gas} are zero for all elements except C, H, N, and S, and that values for M_{x, input gas} are zero for all elements except N and H. Nitrogen in the input gas was directly metered in runs in which it was used, and H was computed in the steam runs as 11% of the total steam mass.

Typical concentration, elemental mass balance, and closure data for a N₂-steam run in which Colorado shale was retorted are summarized in table 3. Detailed elemental closures for each run and each element are summarized in table 4. This table indicates that the elemental closure ranges from 18% to 240% and averages $101 \pm 7\%$ (excluding Cd, Hg).

The significance of the closure data presented in table 4 depends on the uncertainty in the closure itself. If the uncertainty is known, then the elemental closure can be used to assess the adequacy of experimental procedures and to determine if an element is vaporized and lost from the retort. For example, if the elemental closure is "sufficiently" close to 100%, then one may conclude that experimental procedures were adequate and that, within the

Table 3. Elemental abundances and mass balance for run CS-67 (N₂-steam run with Colorado shale).

	Concentration, ppm				Mass Balance, mg						
	Raw oil shale	Retorted oil shale	Shale oil (wet)	Retort water	Raw oil shale	Retorted oil shale	Shale oil (wet)	Retort water	Gas	Closure, %	
Al	3.41 ± 0.06 ^a	4.85 ± 0.13 ^a	9.7 ± 0.3	(e)	476 ^c	456 ^c	0.033 ^c	(e)	(f)	96	Al
As	42.3 ± 1.7	73.4 ± 2.9	4.12 ± 0.34	3.43 ± 0.31	590	690	14.1	1.35	(f)	120	As
Ba	268 ± 14	406 ± 49	0.5 ± 0.1	0.14 ± 0.12	3740	3820	2	0.055	(f)	102	Ba
C (org)	26.2 ± 2.6 ^a	9.35 ± 0.49 ^a	85.0 ± 8.5 ^{a,8}	0.745 ± 0.006 ^a	3654 ^c	879 ^c	2517 ^{c,8}	3.40 ^{c,h}	227.6 ^c	99	C (org)
C (inorg)	3.05 ± 0.31 ^a	2.65 ± 0.25 ^a	(f)	0.697 ± 0.005 ^a	425 ^c	249 ^c	(f)	4.36 ^{c,h}	325.2 ^c	136	C (inorg)
Ca	5.77 ± 0.03 ^a	8.25 ± 0.18 ^a	(e)	6 ± 1	805 ^c	775 ^c	(e)	0.002 ^c	(f)	96	Ca
Cd	1.20 ± 0.06	1.43 ± 0.35	< 0.014	0.00069 ± 0.00045	16.7	13.4	< 0.05	0.00027	(f)	80	Cd
Ce	35.7 ± 0.8	48.2 ± 0.8	0.011 ± 0.004	< 0.011	498	453	0.038	< 0.0039	(f)	91	Ce
Co	13.3 ± 0.3	18.1 ± 0.3	1.98 ± 0.01	0.213 ± 0.002	186	170	6.76	0.0838	(f)	95	Co
Cr	33.3 ± 0.7	47.8 ± 1.5	0.22 ± 0.01	0.011 ± 0.005	464	449	0.75	0.0043	(f)	97	Cr
Cs	3.10 ± 0.14	4.55 ± 0.18	(e)	0.066 ± 0.001	43.2	42.7	(e)	0.026	(f)	99	Cs
Cu	51.2 ± 2.4	73.5 ± 3.2	< 0.72	< 0.09	714	691	< 2.5	< 0.04	(f)	97	Cu
Dy	1.71 ± 0.08	2.12 ± 0.40	0.0009 ± 0.0002	(e)	23.9	19.9	0.003	(e)	(f)	83	Dy
Eu	0.484 ± 0.011	0.685 ± 0.013	(e)	< 0.0002	6.75	6.44	(e)	< 0.00008	(f)	95	Eu
Fe	1.94 ± 0.16 ^a	2.90 ± 0.08 ^a	60.0 ± 3.0	1.21 ± 0.14	271 ^c	273 ^c	0.20 ^c	0.476 ^c	(f)	101	Fe
Ga	6.5 ± 1.0	11.0 ± 1.4	0.034 ± 0.008	< 0.06	90	104	0.12	< 0.02	(f)	116	Ga
Ge	1.6 ± 1.0	3.3 ± 1.2	< 0.48	0.06 ± 0.04	22	31	< 1.6	0.02	(f)	141	Ge
H	3.74 ± 0.37 ^a	0.34 ± 0.02 ^a	11.9 ± 1.2 ^{a,8}	0.11 ± 0.01 ^a	586 ^c	32 ^{c,8}	352 ^{c,h}	88.1 ^c	102.8 ^c	98	H
Hf	1.33 ± 0.06	1.93 ± 0.08	(e)	0.0014 ± 0.0003	18.6	18.1	(e)	0.00055	(f)	97	Hf
Hg	308 ± 81 ^b	58 ± 21 ^b	59 ± 4 ^b	95 ± 9 ^b	4296 ^d	543 ^d	201 ^d	37 ^d	(f)	18	Hg
K	1.01 ± 0.02 ^a	1.49 ± 0.02 ^a	5.0 ± 1.6	5 ± 3	141 ^c	140 ^c	0.017 ^c	0.002 ^c	(f)	99	K
La	18.0 ± 0.5	24.2 ± 0.6	0.0064 ± 0.0013	0.032 ± 0.002	251	228	0.022	0.013	(f)	91	La
Lu	0.10 ± 0.02	0.16 ± 0.05	(e)	(e)	1.45	1.49	(e)	(e)	(f)	103	Lu
Mg	2.87 ± 0.06 ^a	4.01 ± 0.07 ^a	8.2 ± 1.5	< 17	400 ^c	377 ^c	0.028 ^c	0.0067 ^c	(f)	94	Mg
Mn	242 ± 5	329 ± 7	0.156 ± 0.002	< 0.10	3050	3090	0.53	< 0.039	(f)	101	Mn
Mo	31.8 ± 2.5	45.6 ± 3.5	0.15 ± 0.04	0.53 ± 0.02	444	429	0.51	0.21	(f)	97	Mo
N	0.91 ± 0.09 ^a	0.63 ± 0.07 ^a	1.93 ± 0.19 ^{a,8}	1.14 ± 0.03 ^a	127 ^c	59 ^c	57 ^{c,8}	8.95 ^{c,h}	0 ^c	99	N
Na	2.36 ± 0.06 ^a	3.34 ± 0.02 ^a	51.5 ± 0.5	1360 ± 12	329 ^c	314 ^c	0.18 ^c	0.535 ^c	(f)	96	Na
Nd	15 ± 2	17 ± 3	(f)	(f)	210	160	(f)	(f)	(f)	76	Nd
Ni	24.2 ± 3.2	35.8 ± 4.0	4.12 ± 0.62	1.28 ± 0.08	338	336	14.1	0.503	(f)	104	Ni
Pb	35.7 ± 1.6	54.4 ± 2.2	< 1.6	< 0.24	498	511	< 5.5	< 0.094	(f)	103	Pb
Rb	56.6 ± 2.3	89.4 ± 3.6	< 0.69	0.29 ± 0.06	789	840	< 2.4	0.11	(f)	106	Rb
S	2.54 ± 0.25 ^a	1.78 ± 0.21 ^a	0.82 ± 0.08 ^{a,8}	0.24 ± 0.01 ^a	354 ^c	167 ^c	24 ^{c,8}	1.14 ^{c,h}	94.6 ^c	81	S
Sb	2.50 ± 0.19	3.79 ± 0.27	0.005 ± 0.001	0.148 ± 0.001	34.9	35.7	0.02	0.0582	(f)	103	Sb
Sc	5.30 ± 0.14	7.46 ± 0.21	0.00089 ± 0.00010	(e)	73.9	70.1	0.0030	(e)	(f)	95	Sc
Se	2.4 ± 0.6	4.3 ± 0.6	0.81 ± 0.01	1.25 ± 0.06	33	41	2.8	0.492	(f)	134	Se
Si	12.9 ± 0.1 ^a	18.2 ± 0.2 ^a	< 79	(e)	1800 ^c	1710 ^c	< 0.27 ^c	(e)	(f)	95	Si
Sm	2.29 ± 0.12	3.13 ± 0.16	0.0009 ± 0.0001	0.0007 ± 0.0005	31.9	29.4	0.003	0.0003	(f)	92	Sm
Sr	350 ± 14	541 ± 21	< 0.87	0.10 ± 0.08	4880 ^c	5080 ^c	< 3.0 ^c	0.000039 ^c	(f)	104	Sr
Ta	0.388 ± 0.005	0.557 ± 0.006	(e)	(e)	5.41	5.23	(e)	(e)	(f)	97	Ta
Tb	0.25 ± 0.07	0.33 ± 0.10	(f)	(f)	3.5	3.1	(f)	(f)	(f)	89	Tb
Th	4.66 ± 0.05	6.41 ± 0.17	< 1.4	0.0008 ± 0.0004	65.0	60.2	< 4.8	0.0003	(f)	93	Th
Ti	0.11 ± 0.05 ^a	0.19 ± 0.02 ^a	< 0.5	< 0.60	18 ^c	18 ^c	< 0.002 ^c	< 0.00024 ^c	(f)	100	Ti
U	4.79 ± 0.05	6.32 ± 0.09	< 2.3	0.046 ± 0.002	66.8	59.4	< 7.8	0.018	(f)	89	U
V	166 ± 18	225 ± 19	0.60 ± 0.04	< 0.072	2320	2110	2.0	< 0.028	(f)	91	V
W	1.4 ± 0.4	2.9 ± 0.5	(f)	(f)	20	28	(f)	(f)	(f)	140	W
Y	3.6 ± 0.8	12.3 ± 1.0	< 1.0	< 0.15	50	120	< 3.4	0.059	(f)	240	Y
Yb	0.963 ± 0.033	1.39 ± 0.07	(e)	(e)	13.4	13.0	(e)	(e)	(f)	97	Yb
Zn	69.3 ± 2.8	98.6 ± 7.4	0.69 ± 0.11	0.09 ± 0.04	967	927	2.4	0.04	(f)	96	Zn

a = percent; b = ppb; c = gm; d = ug; e = analyzed for and not detected; f = not analyzed for; g = dry oil; and h = water includes retort water and pentane-distilled water.

limits of experimental error, none of that element was vaporized. Similarly, since only C, H, N, and S were measured in the gas phase, an elemental closure "significantly" less than 100% for other elements--for example, Hg, Cd--may indicate vaporization. (Although this is a necessary condition for vaporization, it is not sufficient.) Likewise, an elemental closure "significantly" greater than 100% may indicate a sampling or an analytical problem.

The uncertainty in the elemental closure depends

on the magnitude of errors present in each measurement used to calculate it (equation (4)). This uncertainty may be estimated for any single closure using error propagation theory (Bevington 1969), if an estimate of each source of error is available, or by replicating the experiment.

The principal sources of error in the terms in equation (4) are analytical and sampling errors for the raw and retorted shales. The product collection and weighing error, which is about 1%, is negligible.

Table 4. Summary of elemental closure data for LETC's controlled-state retort, %.

	Mass balance closure															Average ($\bar{x} \pm 1\sigma$)	
	CS-60	CS-61	CS-62	CS-63	CS-64	CS-65	CS-66	CS-67	CS-68	CS-69	CS-70	CS-71	CS-72	CS-73	CS-74		
Al	100	100	104	97	93	90	111	96	93	98	96	100	100	101	109	99 ± 6	Al
As	107	111	123	112	117	108	111	120	95	108	97	95	106	103	117	109 ± 9	As
Ba	99	102	93	93	173 ^a	93	108	102	101	100	92	-	-	-	-	98 ± 5	Ba
C(org)	95	105	109	97	102	97	97	99	117	93	94	95	101	94	80	98 ± 8	C(org)
C(inorg)	105	105	107	324 ^a	107	102	112	136 ^a	103	152 ^a	108	110	114	112	123	109 ± 6	C(inorg)
Ca	100	102	102	103	108	95	92	96	94	120	90	95	107	100	92	100 ± 8	Ca
Cd	107 ^b	71	67	47	71	-	78	80	70	57	71	-	-	-	-	68 ± 10	Cd
Ce	100	96	89	102	99	96	106	91	92	98	104	-	-	-	-	98 ± 5	Ce
Co	102	101	96	99	101	92	106	95	93	91	101	-	-	-	-	98 ± 5	Co
Cr	95	100	66 ^a	98	103	95	108	97	96	92	104	-	-	-	-	99 ± 5	Cr
Cs	103	102	80	101	103	110	112	99	101	103	116	-	-	-	-	103 ± 9	Cs
Cu	105	101	116	100	107	105	101	97	99	95	107	95	100	104	103	102 ± 5	Cu
Dy	98	104	91	98	95	97	102	83	93	92	105	-	-	-	-	96 ± 6	Dy
Eu	101	99	92	101	97	95	111	95	94	100	101	-	-	-	-	99 ± 5	Eu
Fe	99	98	100	99	100	94	111	101	93	98	101	97	97	105	107	100 ± 5	Fe
Ga	105	110	105	103	110	92	123	116	104	92	93	-	108	101	107	105 ± 9	Ga
H	96	104	112	112	96	119	86	98	147	108	101	94	116	97	98	106 ± 15	H
Hf	100	110	98	100	104	96	115	97	104	104	110	-	-	-	-	103 ± 6	Hf
Hg	112 ^b	60	41	56	-	56	20	18	45	22	20	84	-	-	-	42 ± 22	Hg
K	100	96	100	97	97	94	104	99	91	99	95	94	95	102	112	98 ± 5	K
La	100	97	88	100	94	92	105	91	94	96	100	-	-	-	-	96 ± 5	La
Lu	101	107	86	85	121	87	106	103	83	106	97	-	-	-	-	98 ± 12	Lu
Mg	99	101	101	97	94	98	105	94	97	98	94	92	99	121	105	100 ± 7	Mg
Mn	101	98	97	100	111	100	103	101	95	103	98	105	101	90	-	100 ± 5	Mn
Mo	99	97	101	100	99	100	100	97	95	77 ^a	103	-	104	-	-	99 ± 2	Mo
N	91	74	108	68	82	86	90	99	97	62	86	58	147	82	104	89 ± 22	N
Na	103	109	109	99	99	98	110	96	94	90	107	99	104	-	89	100 ± 7	Na
Nd	99	97	78	109	100	117	96	76	89	104	89	-	-	-	-	96 ± 12	Nd
Ni	109	93	119	102	109	100	107	104	103	99	100	97	103	101	141 ^a	103 ± 6	Ni
Pb	112	111	119	105	109	167 ^a	112	103	110	94	105	100	111	213 ^a	120	109 ± 7	Pb
Rb	103	100	94	100	101	101	104	106	96	102	101	96	96	99	106	100 ± 4	Rb
S	104	82	119	130	183	170	150	81	141	152	121	126	129	125	101	128 ± 29	S
Sb	103	99	104	82	101	107	89	103	93	85	101	-	-	-	-	97 ± 8	Sb
Sc	101	98	84	98	103	95	107	95	94	98	95	-	-	-	-	97 ± 6	Sc
Se	118	138	134	66	143	108	129	134	127	111	141	105	122	104	128	121 ± 20	Se
Si	101	99	99	96	94	93	106	95	93	99	99	97	98	98	104	98 ± 4	Si
Sm	100	98	90	101	98	94	105	92	94	98	101	-	-	-	-	97 ± 4	Sm
Sr	103	108	105	103	117 ^a	99	97	104	101	100	93	98	99	99	93	100 ± 4	Sr
Ta	101	99	96	100	97	99	110	97	93	99	101	-	-	-	-	99 ± 4	Ta
Tb	97	96	81	107	95	102	108	89	100	92	98	-	-	-	-	97 ± 8	Tb
Th	101	152 ^a	79	98	107	92	105	93	93	99	97	-	-	-	-	96 ± 8	Th
Ti	104	107	99	100	99	89	115	100	86	100	92	100	96	94	108	99 ± 7	Ti
U	100	165 ^a	90	97	100	98	102	89	91	97	95	-	-	-	-	96 ± 5	U
V	97	81	112	102	117	93	137	91	81	94	82	-	-	-	-	99 ± 17	V
W	97	88	74	-	67	-	156	140	79	83	68	-	-	-	-	95 ± 32	W
Y	129	117	140	105	68	102	141	240 ^a	107	147	131	121	122	104	138	119 ± 21	Y
Yb	102	119	88	98	103	100	109	97	96	97	98	-	-	-	-	101 ± 8	Yb
Zn	104	103	101	106	105	107	107	96	100	104	103	100	102	103	108	103 ± 3	Zn

^a Value excluded from average based on Dixon's criterion for $\alpha = 0.02$ (Dixon 1953).

^b Value excluded from average as 100% elemental mass recovery obtained for interrupted run, i.e., run incomplete and volatilized elements condensed on shale bed.

Likewise, the sampling and analytical errors associated with the oil, water, and gases for most elements are not important in propagating random errors because they have relatively small elemental mass (Kaakinen 1974).

The analytical and sampling errors for raw and retorted shale were estimated from the interrupted run (CS-60) and used to estimate closure uncertainty for other runs using error propagation theory. Using these uncertainties, analysis of the data in table 4 indicates that there are no statistically significant differences between the closures obtained for the retort operating conditions and shale types studied. By definition, a closure should be 100% within the limits of error unless gas phase loss occurs for any element except C, H, N, or S

(recall that $M_{x, gas} = 0$ for all elements except H, N, S, C). Therefore, statistically equivalent closures imply that, within the limits of error, retort operating conditions did not effect gas phase loss of any elements except C, H, N, and S. Noted differences in closure are due to uncertainties in sampling and analytical procedures. Therefore, each retort run, relative to closure, is a replicate and the average closure (\bar{x}) and standard deviation (σ) over all 15 runs are estimates of the accuracy of the elemental mass balance.

The data presented in table 4 were analyzed using Dixon's criterion (Dixon 1953) to identify outliers, values that are gross errors. This analysis resulted in the rejection of 13 closure values. The remaining data were used to compute

the average closures and standard deviations shown in the last column of table 4. These closure data indicate that good quantitative recovery for most elements was obtained and that experimental procedures were satisfactory. The average closure (excluding Cd and Hg) was $101 \pm 7\%$ and the coefficient of variation ($100\sigma/\bar{x}$) was less than 10% for all elements except Cd, H, Hg, Lu, N, S, Se, V, W, Y, and Nd. The elevated coefficients of variation for the volatile elements Cd, H, Hg, N, and S are due to sampling errors associated primarily with the retorted shale. It is hypothesized that the sampling is complicated because these elements, which volatilize during retorting, are nonuniformly condensed in cool regions within the retort. The elevated coefficients of variation for Se, V, W, Y, Nd, and Lu are due to poor analytical precision. The measurement precisions of Se, V, W, Y, Nd, and Lu are 32%, 13%, 24%, 12%, 12%, and 10%, respectively.

The data in table 4 also indicate that, within the limits of error, 100% of all measured elements, except Hg and Cd, was recovered. About 68% of the Cd and 42% of the Hg originally present in the raw oil shale were recovered in the retorted shale, oil, and water. The balance, that is, 32% of the Cd and 58% of the Hg, was likely removed from the retort in the gas stream. This agrees with results presented previously by Fox et al. (1977, 1978) and Fruchter et al. (1979).

Partitioning Patterns

The mass balances discussed in the previous section and the single interrupted experiment are used here to study elemental distribution among the retorted shale, retort water, oil, and gas. The mass distribution patterns of the more mobile elements are presented and discussed and the effect of retort operating conditions on partitioning trends is inferred.

The mass balances computed for each run were analyzed to determine the mobility of each element where:

$$\text{Mobility}_x = 100 \left(\frac{m_{x, \text{oil}} + m_{x, \text{water}} + m_{x, \text{gas}}}{m_{x, \text{raw shale}}} \right) \quad (5)$$

Thus, the mobility is the percentage of the total elemental mass present in the raw oil shale that is distributed to the oil, gas, and water phases as a consequence of retorting. The mobility of Green

River oil shales is compared with that of Antrim and Moroccan shales in table 5. The Green River mobilities are the average (\bar{x}) and one standard deviation (σ) for all completed runs with Green River oil shales (Colorado and Utah). The Antrim (CS-63) and Moroccan (CS-65) mobilities are each for a single run. The data in table 5 indicate that there are significant differences in the mobilities of Green River, Antrim, and Moroccan shales. More specific conclusions cannot be drawn due to the limited data base for the Antrim and Moroccan shales. The important point, however, is that mobilities for Green River oil shales should not be generalized to other types of oil shales.

Table 5. Mobility of some major, minor and trace elements in Green River, Antrim and Moroccan oil shales retorted in LETC's controlled-state retort at temperatures less than 800°C.

Group	Constituent	Mobility, % ^a		
		Green River	Antrim	Moroccan
1	H	94 ± 3	79	88
	Org. C	79 ± 7	38	53
	Hg	70 ± 20	46	67
	N	49 ± 7 ^b	16	35
	Inorg. C	34 ± 13 ^b	88	14
	S	44 ± 8	46	72
	Cd	29 ± 7	53	-
2	Se	5.1 ± 1.0	2.6	7.5
	Ni	4.7 ± 1.3	0.13	0.62
	As	3.8 ± 1.3	0.22	1.5
	Co	3.8 ± 0.8	0.005	0.16
3	Cr	0.38 ± 0.78	0.0085	0.0060
	Sb	0.28 ± 0.15	0.70	1.2
	Zn	0.27 ± 0.28	0.65	0.059
	Cu	0.27 ± 0.33	0.013	0.020
	Na	0.19 ± 0.10	0.15	1.0
	Mo	0.18 ± 0.11	0.076	0.055
	V	0.11 ± 0.03	0.033	0.20
	Ga	0.10 ± 0.07	0.023	0.17
	4	Fe	0.084 ± 0.081	0.0006
Mn		0.056 ± 0.071	0.003	0.008
U		0.040 ± 0.023	0.076	0.063
Ba		0.035 ± 0.022	0.004	0.03
Dy		0.034 ± 0.017	-	0.026
La		0.024 ± 0.019	0.0007	0.002
K		0.023 ± 0.022	0.016	0.050
Mg		0.021 ± 0.019	0.009	0.008
Sm		0.020 ± 0.019	-	0.18
Cs		0.019 ± 0.019	0.034	0.016
Eu		0.018 ± 0.013	0.0004	-
Hf		0.014 ± 0.028	0.003	-
Rb		0.014 ± 0.009	0.028	0.052
Ce		0.013 ± 0.007	0.0005	-
Sr	0.012 ± 0.016	0.015	0.0028	
5	Al	0.0062 ± 0.0035	0.0002	-
	Ca	0.003 ± 0.005	0.008	0.0004
	Sc	0.0057 ± 0.0025	-	0.0002
	Ti	0.0090 ± 0.015	0.005	-
	Yb	0.0033 ± 0.0010	-	-
	Th	0.0076 ± 0.0081	0.049	-

^a Percent of elemental mass present in raw oil shale that is distributed to the oil, water and gas phases.

^b Excludes the N₂-steam-O₂ runs (CS-69, CS-74) which were significantly different from others in set. The mobility of N for these runs is 88% and of inorganic C, 94%.

The Green River mobilities were ranked according to magnitude and five separate groups delineated. These groups are:

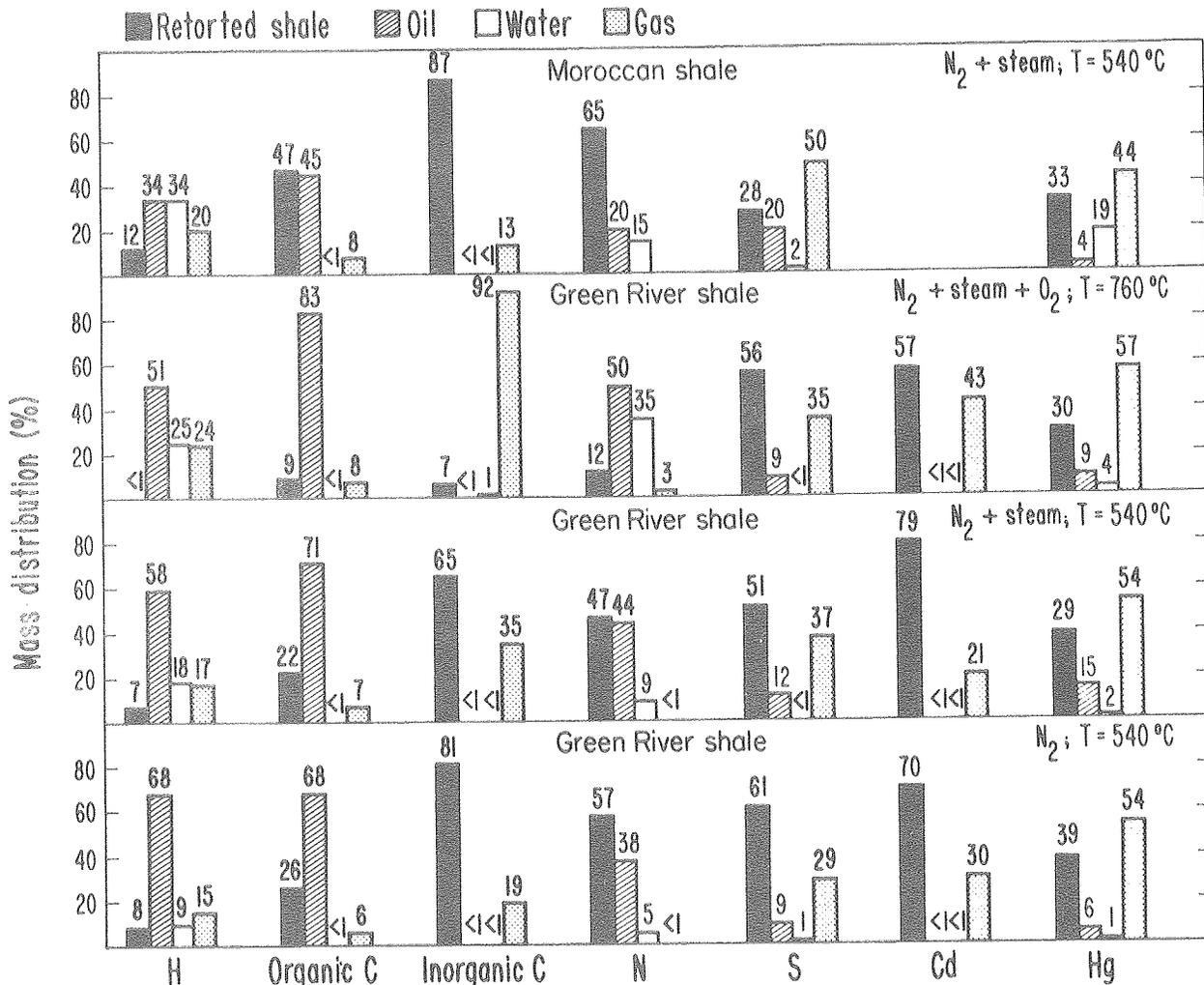
- Group 1: (25% - 100%) H, N, S, Cd, Hg, organic C, inorganic C
- Group 2: (1% - <10%) Se, Ni, As, Co
- Group 3: (0.1% - <1%) Cr, Sb, Zn, Cu, Na, Mo, V, Ga
- Group 4: (0.01% - <0.1%) Fe, Mn, U, Ba, Dy, La, K, Mg, Sm, Cs, Eu, Hf, Rb, Ce, Sr
- Group 5: (<0.01%) Al, Ca, Sc, Ti, Yb, Th

Similar rankings were not attempted for the Antrim and Moroccan shales--the data were too limited to permit assessment of variability.

Mass distribution patterns for the Group 1 elements are summarized in figure 2 in which Green River shales, retorted under N₂ and N₂-steam atmospheres at 540°C and under an N₂-steam-O₂ atmosphere

at 760°C, and Moroccan shales, retorted under an N₂-steam atmosphere at 540°C, are compared. This figure and the mobilities in table 5 indicate that Group 1 elements are significantly mobilized during retorting and are characterized by a gas-phase component. Other groups do not have a significant gas-phase component. For the Green River shales, in excess of 35% of the H, N, and organic C is distributed to the oil, and about 20% or more of the S, Cd, Hg, and inorganic C is distributed to the gas phase. In the Green River shales, the H, N, organic C, and some of the S are initially present in the kerogen (Smith 1961) and are converted to oil and gases by pyrolysis. The remainder of the S and Cd, Hg, and inorganic C, are largely present in the mineral phase of the shales and are volatilized by a series of mineral decomposition and reduction

Figure 2. Mass distribution patterns for Group 1 elements.

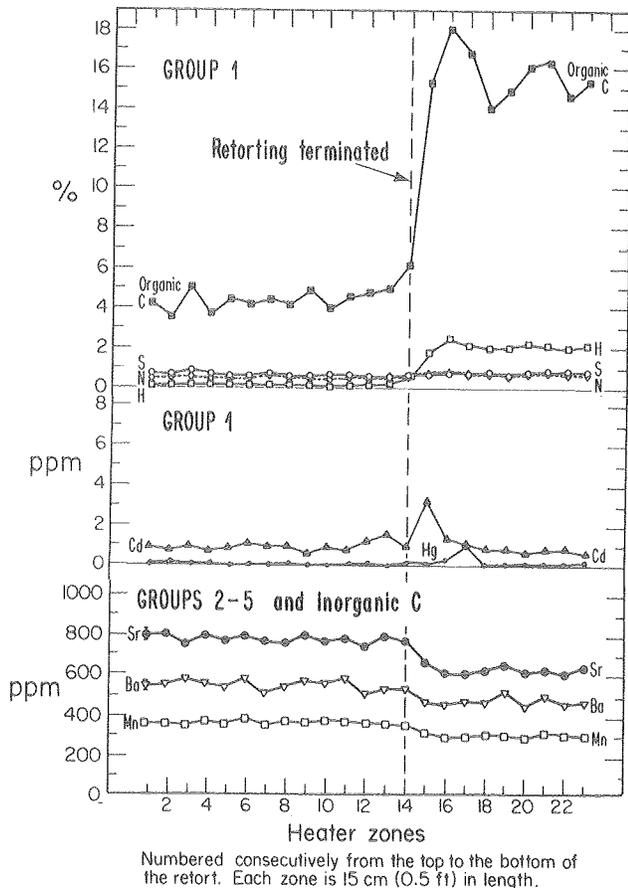


mechanisms discussed under "Partitioning Mechanisms."

As noted, all of the Group 1 elements have a statistically significant gas component. (It is not implied that these elements exist in a gaseous state but that they exit in the offgas where they may exist as condensed or gaseous matter.) The volatilization of these elements and their removal from the retort are supported by direct gas measurements of all of them, except Cd, and by the results of the interrupted experiment. Inorganic and organic C and H, N, and S were measured in the offgas by mass spectrometry, and mercury was directly measured in two runs by Zeeman atomic absorption spectroscopy or ICl impinger trains (Fox et al. 1978). The existence of Cd in the offgas, however, is inferred from mass balance calculations indicating a 32% net mass loss from the retort. This result is corroborated by the interrupted run.

The results of the interrupted experiment are summarized in figure 3. Figure 3 shows that there

Figure 3. Variation in Sr, Ba, Mn, Cd, Hg, N, S, H, and organic C along the shale bed in an interrupted run (CS-60) of LETC's controlled-state retort.



are three types of elemental profiles in the shale bed. All three occur for Group 1 elements.

The first, for Hg and Cd, supports the volatilization of these two elements from oil shale. This profile is characterized by a peak just below the point at which retorting terminated. It is consistent with on-line Hg measurements in which a pulse of Hg was found toward the end of run CS-69 and with the hypothesis that Hg is successively volatilized and condensed as the reaction front moves down the shale bed (Fox et al. 1978). The presence of a Cd pulse in figure 3 suggests that Cd is also successively volatilized and condensed. The existence of the Cd peak behind the Hg peak is consistent with the relative volatilities of these two elements and their compounds (Hg is the more volatile of the two).

The second type of profile occurs for the Group 1 elements S, N, H, and organic C. This profile is characterized by higher elemental concentrations in zones 15 - 24 than in zones 1 - 14. The profile is caused by the volatilization and removal of the element from the retort; it is consistent with the mass distribution patterns (figure 2).

The third type of profile occurs only for inorganic C among the Group 1 elements and for all Group 2-5 elements. The elemental abundances in zones 1 - 14 are higher than in zones 15 - 24 because about 20% of the oil shale matrix (organic material plus CO₂ from carbonate decomposition) has been removed, leaving behind about 100% of the elemental mass. Although some elements are removed in the oil or water, such as inorganic C and the Group 2 elements, the percentage removal is too low to affect the concentration profile.

The retort operating conditions studied here affected the mass distribution patterns only of C, H, and N of the Group 1 elements. The N₂ and N₂-steam runs have identical mass distribution patterns with the exception of H, for which a larger fraction of the total mass of H is distributed to the water in the N₂-steam runs than in N₂ runs. In the N₂-steam runs, the steam charged to the retort appears as retort water, resulting in a larger percentage mass distribution of H to the water phase. There are also statistically significant differences between the N₂-steam-O₂ runs (T = 760°C) and other runs with Green River shales and between the Moroccan and Green

River shales. In the high temperature N_2 -steam- O_2 runs, a larger fraction of the H, N, organic C, and inorganic C are distributed to the byproducts than during N_2 or N_2 -steam runs at lower temperatures. For example, 65% and 81% of the inorganic C during N_2 -steam and N_2 runs, respectively, remain in the retorted shale and only 7% remains in the retorted shale produced from the N_2 -steam- O_2 runs. The additional inorganic C that is converted during the N_2 -steam- O_2 runs is distributed primarily to the gas phase. It is hypothesized that these differences are due to more complete conversion of the kerogen and decomposition of carbonates at the elevated temperatures (the N_2 -steam- O_2 runs were at $760^\circ C$ and the other runs were at $540^\circ C$) and to reactions of O_2 in the input gas with constituents in the oil shale.

There are significant differences between the mass distribution patterns of the Moroccan and Antrim shales (not shown in figure 2) and the Green River shales. In those two shales, a relatively larger fraction of the N, H, organic C, and inorganic C remain unconverted in the retorted shale; there is less mass distribution to the oil, water, and gas phases than in Green River shales retorted under equivalent conditions. It is hypothesized that this is due to differences in mineral and organic composition of the different shales. This suggests that different retorting conditions will be required to optimally extract oil from various shales and illustrates that data developed for one shale should not be generalized to others.

Mass distribution patterns for the Group 2 elements are summarized in table 6 in which the Green River, Antrim, and Moroccan shales are compared. Table 6 and table 5 indicate that about 4% of the elemental mass of Green River shales for Group 2 elements is mobilized and about 95% of that is distributed to the oil.

The retort operating conditions studied here had no statistically significant effect on the mass distribution patterns of Green River oil shales for the Group 2 elements. This is supported by the small coefficient of variation (26%) for the percent mass distributions reported in table 5. The partitioning data summarized in table 5 indicate that from 4% to 5% of the total elemental mass of Ni, Co, As,

Table 6. Mass distribution patterns of Group 2 elements, %.

	Green River	Antrim	Moroccan
Nickel			
Retorted shale	95.4±1.0	99.9	99.3±0.1
Oil	4.4±1.0	0.1	0.5±0.0
Water	0.2±0.1	0.0	0.2±0.1
Gas	0.0	0.0	0.0
Cobalt			
Retorted shale	96.2±0.9	100.0	99.8
Oil	3.7±0.8	0.0	0.1
Water	0.1±0.1	0.0	0.1
Gas	0.0	0.0	0.0
Arsenic			
Retorted shale	96.3±1.2	99.8	97.8±0.9
Oil	3.4±1.2	0.0	1.1±0.8
Water	0.3±0.1	0.2	1.1±0.1
Gas	0.0	0.0	0.0
Selenium			
Retorted shale	94.9±1.0	64.4	92.2±0.4
Oil	4.6±0.8	1.2	5.4±0.4
Water	0.5±0.5	0.5	2.3±0.8
Gas	0.0	15.2 ^a	0.0

^a Computed by difference.

and Se originally present in the raw oil shale is distributed to the oil, and that less than 1% is distributed to the water. For the conditions studied, no evidence was found to indicate that these elements exit the retort with the offgases.

The principal differences in mass distribution patterns for Group 2 elements occur for shales of different geological origins, namely, Green River, Antrim, Moroccan. In contrast to the Green River shales, less than or about 1% of the Ni, Co, and As is distributed to the oil and water in Antrim and Moroccan shales. Although the distribution pattern of Se in Moroccan shale is similar to that of the Green River shales, the pattern for Se in Antrim shale is very different, with about 15% of the Se exiting the retort in the offgas. Because it is based on a single retort run, additional, collaborative work is required to verify and support this latter conclusion.

The elements in Groups 3 to 5 all have mobilities that are less than 1% and large coefficients of variation (27% - 205%). The large coefficients of variation are due to experimental error rather

than retort operating conditions. Because the concentrations of these elements in the oil and water phases is near the detection limit of many of the techniques used, the analytical errors are large. No significant relationships between operating conditions and mobility in any phase or combination of phases for Groups 3 to 5 were observed. The variation in the mobility of those elements is due to the propagation of experimental errors.

Partitioning Mechanisms

The specific mechanisms that determine the partitioning of a given element are not fully understood and work is proceeding to clarify them. The series of reactions thought to occur in the controlled-state retort are summarized in table 7. In general, it is proposed that elements are volatilized from the shale as a consequence of mineral decomposition (equations (1) - (3)), kerogen conversion (equation (4)), or reduction by C, CO, and other species (equations (5), (6)). These volatile species, swept ahead of the reaction front by the input gas, may be condensed on the shale bed in cool regions ahead of that front (equation (7)), entrapped in the oil-water emulsion (equation (9)), or swept out of the retort in the gas stream as gaseous or condensed species. The water that condenses out of the gas stream in the cool regions ahead of the reaction zone may leach some constituents from the unreacted shale (equations (11), (12)). Interactions may occur between the oil and water which exist as a tight emulsion (equation (10)). Finally, raw and spent shale fines may be entrained in the gas stream in the reaction zone or may be picked up as the oil-water emulsion passes over the cool shale and incorporated in the oil and water (equation (13)).

Let us now explore some specific elements within the framework proposed in table 7. The Group 1 elements S, N, H, and organic C occur largely in the organic fraction in the original oil shale and are released by pyrolysis during retorting. (Sulfur may occur in both the organic and inorganic fraction of oil shale, depending on the shale's geologic origin.) Kerogen pyrolysis, studied by a number of investigators (Fausett 1975; Duvall and Jensen 1975) is known to produce oil, gas, bitumen, and C residue in various quantities and compositions depending on the retort operating conditions. The present study,

which indicates that significant amounts of the N, H, S, and organic C are partitioned to the oil, water, and gas phases, is consistent with previous investigations of kerogen pyrolysis.

Some of the Group 1 elements also partition to

Table 7. Some proposed mechanisms that may lead to the observed elemental partitioning in LETC's controlled-state retort.

Mineral Decomposition

Sulfide



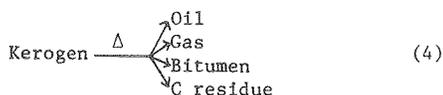
Carbonate



Oxide

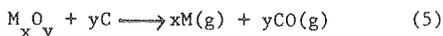


Kerogen Conversion

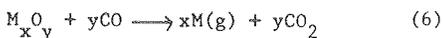


Reduction

Carbon



Carbon monoxide



Shale-Product Interactions

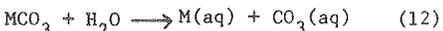
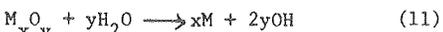
Condensation



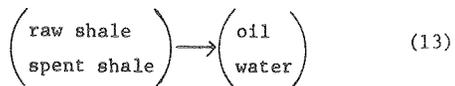
Dissolution



Solubilization



Suspension of Fines



o = oil; l = liquid; g = gas.

the water phase. In the controlled-state retort, the principal water formation mechanism is mineral dehydration. Input steam may contribute to retort water in steam retorting and some water may be produced by combustion in the N_2 -steam- O_2 runs (CS-69 and CS-74). The Group 1 elements H, N, S, inorganic C, and organic C may condense out with the water or dissolve in the water and are thus incorporated in this phase. They may also be incorporated in the water due to its contact with the oil or unretorted or partially retorted shale.

It is hypothesized that the volatilization of Cd and Hg is controlled by mineral decomposition. Those elements occur as sulfides in many crustal rocks and are thought to also exist as sulfides in oil shales (see, for example, Desborough et al. 1976). Because sulfide and other mineral compounds of Hg and Cd decompose at the temperatures reached in the controlled-state retort, reactions similar to those shown in equations (1) and (3) of Table 7 may control the distribution of these elements to the offgas. (This does not preclude the occurrence of Hg and Cd as organometallic species; such species would also be volatilized at the temperatures studied here.) The interrupted run data (figure 3) indicate that these elements volatilize and condense in cooler regions of the retort. Therefore, they may exit the retort entrained in the oil mist or as condensed particles. Although the vapor-phase existence of Hg and Cd has not been demonstrated experimentally, thermodynamic calculations support the existence of Hg.

The partitioning patterns of the Group 2 elements As, Se, Ni, and Co are particularly interesting. In the Green River oil shales, the mass distribution patterns of all four elements are identical: about 4% to 5% of each element is distributed to the oil and less than 1% is distributed to the water. In contrast, the other two shales have much lower mass distributions to the oil and water for Co and Ni, and intermediate distributions for As and Se. It is hypothesized that this behavior is related to the existence of these elements in the organic fraction of the oil shales or to their volatilization from the mineral matrix during retorting and their subsequent entrapment in the oil phase. The specific mechanism cannot be delineated from the data given

here. Some preliminary inferences can be drawn, however, based on the mass distribution patterns in table 5 and on work completed elsewhere. Inorganic Ni and Co compounds likely to exist in oil shales or to form during retorting (oxides and sulfides) are not volatile at the temperatures reached in the controlled-state retort ($<800^{\circ}C$). This suggests that the Ni and Co that are partitioned to the oil may exist in a more volatile form in the organic fraction of the oil shale. This is supported by the identification of Ni-porphyrin complexes in oil shales and conventional crudes. The presence of a Ni-porphyrin complex in an oil shale was established by Glebovskaya and Volkenshtein in 1948 and subsequently corroborated by Moore and Dunning (1955) who found 59 ppm, 82 ppm, and 137 ppm of Ni in the benzene, benzene-methanol, and pyridine extracts of a Colorado oil shale. A number of investigators have identified Ni and Co porphyrins and other organometallic compounds in conventional crude oils (Manskaya and Drozdova 1968; Filby 1975; Dunning 1963). Although there is no conclusive evidence that Co exists in the organic fraction of oil shales, the chemical similarity of Co and Ni and their similar partitioning patterns in Green River oil shales support that hypothesis. The low mass distributions of Co and Ni to the oil in Antrim and Moroccan shales ($<1\%$) suggests that the chemical association of Co and Ni in these shales is different from that in Green River shales.

Arsenic and Se, on the other hand, have not been identified in organometallic complexes in oil shales or conventional crudes and many of their compounds are considerably more volatile than Ni and Co compounds. Arsenic oxides and sulfides sublime, melt, or boil between $300^{\circ}C$ and $800^{\circ}C$ and selenium oxides melt or boil below $400^{\circ}C$ (Dean 1973). This suggests that these elements may be volatilized during retorting. Once volatilized, they may be entrapped by the organic vapors and oil mist. This is speculation at this point and does not exclude the existence of As and Se in the organic fraction of the oil shale. Considerable additional experimental work is required to elucidate the mechanism responsible for the partitioning of these elements.

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