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### Publication Date

1982-06-01



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Published in ENERGY AND ENVIRONMENTAL CHEMISTRY,  
FOSSIL FUELS, Volume One, Chapter Four,  
Ed. Lawrence H. Keith, Ann Arbor Science Publishers,  
Ann Arbor, MI, June 1982

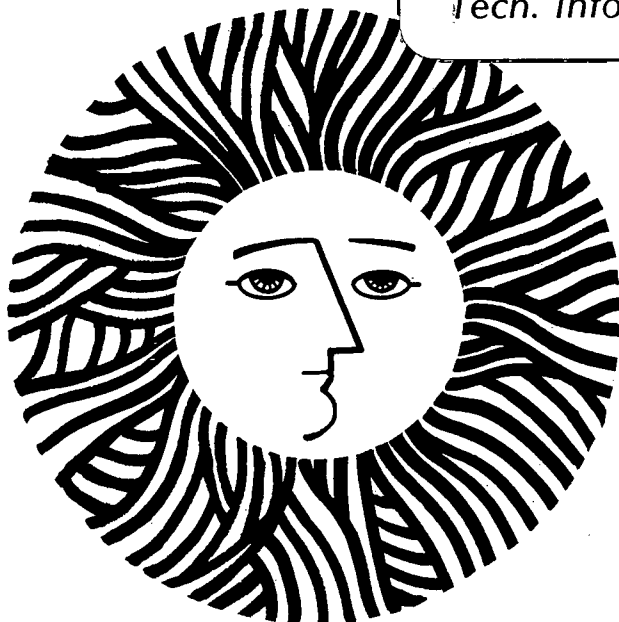
TRACE ELEMENTS IN OIL SHALE MATERIALS

J.P. Fox, A.T. Hodgson and D.C. Girvin

June 1982

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**Volume One**

**ENERGY AND  
ENVIRONMENTAL  
CHEMISTRY**

**Fossil Fuels**

**Edited by  
LAWRENCE H. KEITH**



**ANN ARBOR SCIENCE**  
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Copyright © 1982 by Ann Arbor Science Publishers  
230 Collingwood, P.O. Box 1425, Ann Arbor, Michigan 48106

Library of Congress Catalog Card Number 81-69255  
ISBN 0-250-40401-X

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Butterworths, Ltd., Borough Green, Sevenoaks  
Kent TN15 8PH, England

## CHAPTER 4

# TRACE ELEMENTS IN OIL SHALE MATERIALS

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### INTRODUCTION

Concern about toxic element mobilization and potential public health and environmental consequences has led to investigations of elemental distributions in Green River Formation oil shales and in the products of oil shale processing [1-16]. The results of those studies and other previously unreported data are presented and reviewed here as they relate to the characterization of the environmentally important elements As, B, Cd, Co, Cr, Cu, F, Hg, Mn, Mo, Ni, Pb, Sb, Se, V and Zn in spent shale, shale oil, process waters and offgases for representative surface and in situ retorting processes.

### PROCESS DESCRIPTIONS

This chapter reviews characterization data for the Fischer Assay, Paraho direct, Lawrence Livermore National Laboratory (LLNL) simulated in situ, Occidental modified in situ, and Geokinetics horizontal true in situ retorting processes. These processes were selected because they represent those which are presently under commercial development and/or because they have been the subject of elemental partitioning studies. Characteristics of these processes are discussed below and are summarized in Table 1.

Table 1. Processes and Retort Operating Conditions Considered in This Study

Process	Retort Capacity (kg)	Shale Source	Operational Mode	Shale Charge Size (mm)	Retorting Atmosphere	Maximum Retorting Temperature
Surface						
TOSCO Modified Fischer Assay	0.1	Dow Mine, CO	Batch	1.3	N <sub>2</sub>	500°C
Paraho Direct Mode	3.18×10 <sup>5</sup>	Anvil Points Mine, CO	Continuous	6-76	Air + Recycle Gas	750°C
In Situ						
LLNL Small Retort (Run S-11)	125	Anvil Points Mine, CO	Batch	13-25	Air	1000°C
LBNL Retort	4	Anvil Points Mine, CO	Batch	0.6-6.4	N <sub>2</sub>	500°C
Occidental Modified In Situ						
Retort 3	≈3.6×10 <sup>6</sup>	Logan Wash, CO	Batch	a	Air + Recycle Gas	b
Retort 6	3.28×10 <sup>8</sup>	Logan Wash, CO	Batch	a	Air + Steam	b
Geokinetics Horizontal In Situ		Book Cliff, UT	Batch	a	Air	b

<sup>a</sup>A satisfactory method has not been developed for characterizing the particle size range in a field in situ retort.

<sup>b</sup>Field retorting temperatures are not accurately known due to corrosion problems with thermocouples. However, mineral analyses of spent shales from the Geokinetics and Occidental processes suggest temperatures may reach 1000°C locally.

## Surface Retorts

Surface retorts are aboveground, vertical kilns in which crushed oil shale is thermally decomposed. There are two broad classes of surface retorting processes: direct and indirect. The indirect processes are those in which heat is transferred to the crushed shale by an externally or indirectly heated gas or solid. In these processes, the atmosphere within the retort is reducing, and carbon or char remains on the spent shale. Indirect-heated processes include Fischer Assay, TOSCO II, Lurgi, Union B, Paraho indirect, Superior, Galoter and Petrosix. The direct processes are those in which heat is supplied by the combustion of char and recycle gases within the retort. Thus, both reducing and oxidizing atmospheres exist within direct-heated retorts. Examples of direct-heated retorts include Paraho direct and Union A.

Selection of the Fischer Assay and the Paraho-direct processes as representative of surface technologies was based on the availability and quality of elemental partitioning data.

### *Fischer Assay*

A Fischer Assay is a standardized oil yield test for oil shale. Several variations of the assay have been proposed and used [17-19]. The studies by Shendrikar and Faudel [4], Wildeman and Meglen [7] and Fox et al. [20], which are reviewed here, used the TOSCO Modified Fischer Assay [18].

In the TOSCO Modified Fischer Assay, about 100 g of finely ground raw shale are heated in a steel retort with an external electric heater. A programmed temperature-time profile with a final temperature of 500°C is followed. The vapors distilled from the sample are cooled and condensed at 0°C. The products are then collected and weighed.

### *Paraho-direct*

The Paraho retort consists of a vertical kiln that may be operated in either the direct or indirect mode (Figure 1) as described by Jones [21]. The studies reviewed here used products from the 200-bbl/day Paraho direct-mode 23-m high semiworks retort [10, 11] operated by Development Engineering, Inc. at Anvil Points, Colorado. Process shale is crushed, screened and top loaded into the retort. The retort operates as a countercurrent, plug-flow reactor; recycle gas moves upward through the retort while the solids move downward. Shale entering the top of the retort is initially heated by rising hot gases. It next passes into the pyrolysis zone where the organics are thermally distilled by heat produced in the combustion zone from burning of char and recycle gas. The distilled vapors are swept upward, out of the retort, and the



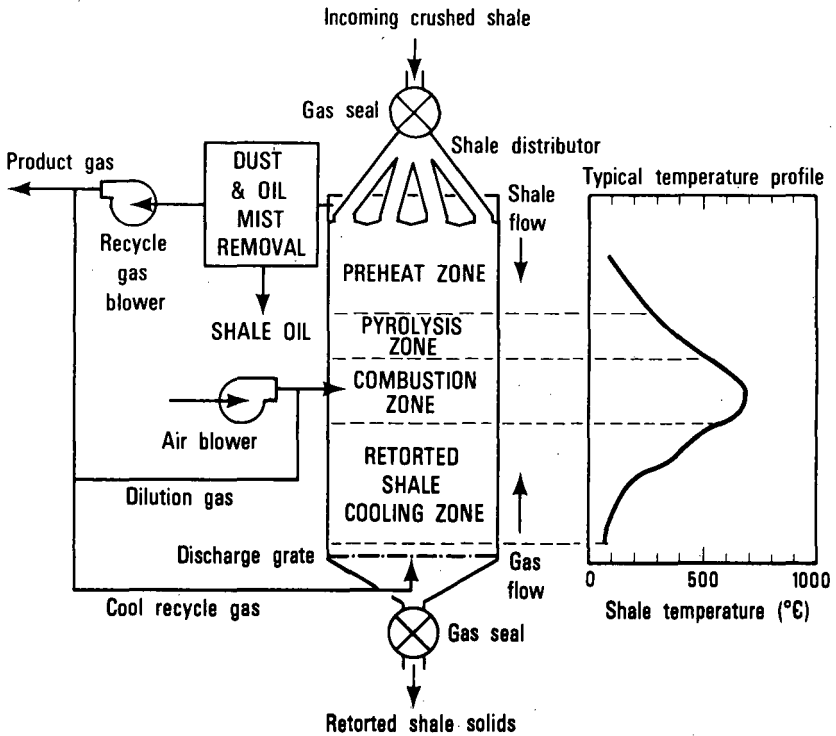


Figure 1. Schematic of the Paraho retort.

oil is separated from the gas by a coalescer and electrostatic precipitator. The oil-water emulsion is separated by settling. The hot spent shale passes through the cooling zone and is discharged at the bottom of the retort. In this retort, the maximum temperature is  $750^{\circ}\text{C}$  and both oxidizing and reducing conditions occur.

### In Situ Retorts

In situ processes are those in which oil shale is thermally decomposed in the geological formation. Permeability must first be developed to permit the flow of gases and liquids. This is accomplished either by mining out part of the formation and rubblelizing the balance (modified in situ processes) or by creating void space without shale removal by surface uplift or other means (true in situ processes). Modified in situ processes are presently under development by Occidental Oil Shale at Logan Wash and tract C-b in Colorado and

by the Rio Blanco Oil Shale Project at tract C-a. True in situ processes are under development by Geokinetics, Inc. in Utah and by Equity Oil in Colorado. In addition to these commercial projects, several organizations have built and operate simulated in situ retorts which are surface retorts designed and operated to simulate in situ conditions. These experimental reactors are used to develop an understanding of the retorting process under controlled conditions. A side benefit has been the production of valuable characterization and partitioning data that could not otherwise have been obtained.

The LLNL simulated in situ retorts, the Occidental modified in situ process, and the Geokinetics true in situ process were selected for review because of the relative abundance and quality of available data compared to other processes.

### *Simulated In Situ Retorts*

Much of the trace element characterization and partitioning data for in situ processes have been developed using simulated in situ retorts [1, 9]. This chapter focuses on the results obtained from the LLNL small retort due to the abundance of available data and to the fact that this retort simulates in situ conditions more nearly than others. Gas data from the Lawrence Berkeley National Laboratory (LBNL) retort and the LLNL large retort are also presented.

The LLNL retorts have been previously described [22]. The small retort is 0.30 m in diameter by 1.5 m high and has a capacity of 125 kg of shale; the large retort is 0.91 m in diameter by 6.1 m high and has a capacity of 6000 kg. The retorts are surrounded by a contiguous series of 15-cm vertical electrical-resistance heaters to prevent heat loss through the walls. These retorts can be operated for a wide range of conditions by varying the input gas composition and flow rate, particle size, packing density, retorting rate and other variables. To date, LLNL has completed 24 runs of the small retort for a range of conditions, and characterization and partitioning studies have been conducted on seven of these. We focus on results from run S-11 of the small retort, an air run in which temperatures reached 1000°C. We also present some gas data from run L-3 of the large retort, an air-steam run with graded lean and rich Anvil Points shale at a maximum temperature of 1000°C.

The LBNL retort is a 4-kg Fischer Assay-type retort designed to evaluate the effect of various gas environments, flow rates and heating conditions on trace element volatilization and partitioning. The retort vessel is a stainless steel tube, 8.9 cm i.d. by 90.5 cm long. The retort is heated by a single zone furnace designed for a 1200°C maximum operating temperature and a programmer capable of providing a heating ramp of 0.4-9.9°C/min.

*Occidental Modified In Situ Process*

The in situ recovery of shale oil by the Occidental modified in situ (MIS) process involves the underground pyrolysis of large chambers of rubblelized shale. These chambers are constructed by mining out ~20% of the volume of the retort and blasting the balance so that the entire chamber is filled with fractured rock. A commercial-sized retort will measure ~100 x 50 m in plan and 120 m high. Oil is recovered from such a retort (shown in Figure 2) by initiating combustion at the top of the retort with an external fuel supply and propagating the reaction zone, which consists of a pyrolysis zone and a trailing combustion zone, down the packed bed of shale with input gas. The volatile hydrocarbons condense in the cool region at the bottom of the retort and are pumped to the surface.

Occidental has tested six experimental retorts at Logan Wash, Colorado. Environmental studies have been conducted on retorts 3 and 6, which are briefly described here. Retort 3 was operated between February and July of 1975 in an air-recycle gas mode. Yield was around 60% Fischer Assay. This retort was cored in December 1978 and the spent shale characterized. An intensive, onsite sampling program was conducted during operation of Retort 6. This retort was operated in an air-steam mode. Failure of the sill pillar during operation resulted in channeling of the flame front. Yield was around 40% Fischer Assay. The run took place between August 1978 and the summer of 1979 and environmental sampling occurred from March through July of 1979.

*Geokinetics Horizontal In Situ Process*

The Geokinetics process, shown in Figure 3, is designed for areas where oil shale beds are relatively thin and close to the surface. Permeability is created by explosive fracturing, which uplifts the surface by about 3 m. A commercial-sized retort may measure ~70 m long by 70 m wide by 10 m thick. Oil is recovered from these retorts by igniting the shale bed near the air injection well and driving the reaction zone horizontally through the fractured bed with input gas. The volatile hydrocarbons condense ahead of the reaction zone and collect in the recovery wells where they are pumped to the surface.

Geokinetics has burned 24 experimental retorts to date. A field sampling program was carried out during the operation of several retorts, and raw and spent shale cores have been taken from Retort 16. Some of these data are reviewed here.

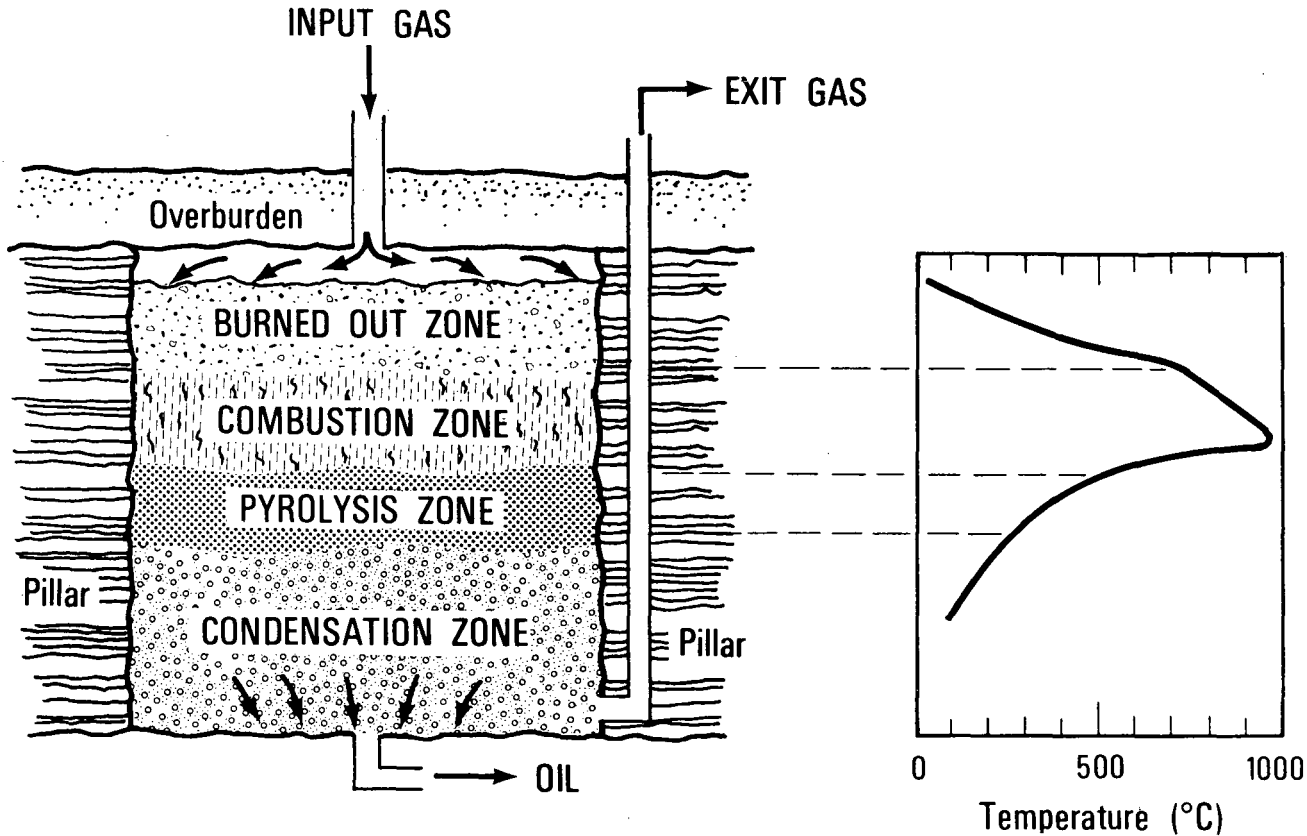


Figure 2. Schematic of the Occidental modified in situ retort.

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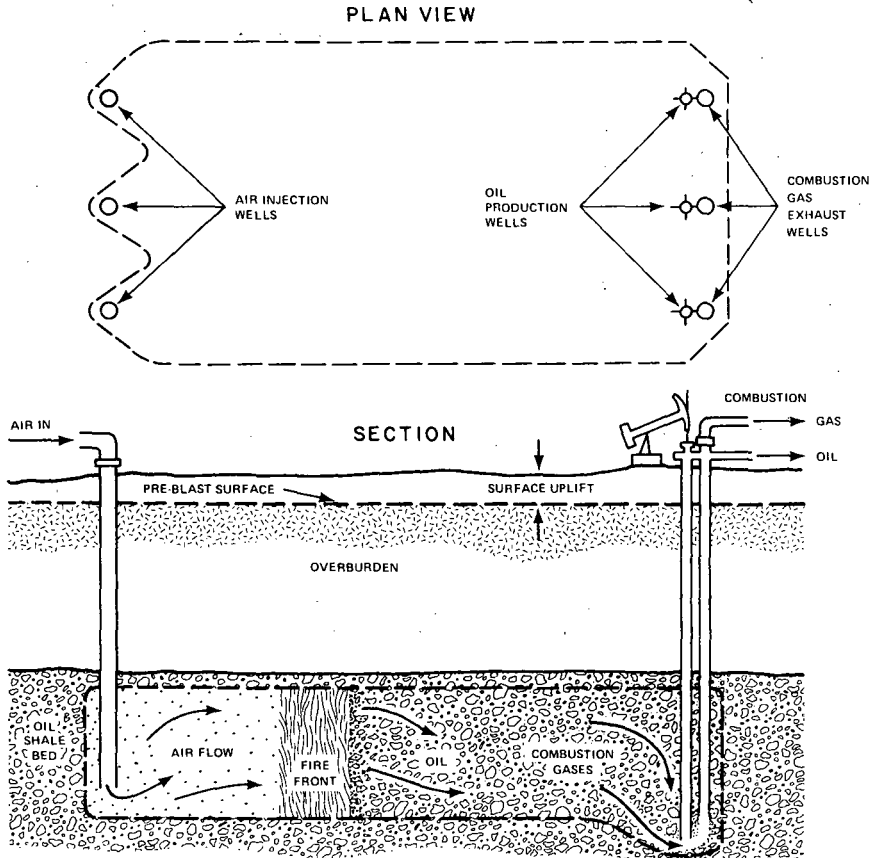


Figure 3. Schematic of the Geokinetics process.

### CHARACTERIZATION

The elemental abundances of toxic elements in raw and spent oil shales, shale oils, process waters and offgases from the above processes are reviewed. These abundances are compared with the elemental abundances of selected reference materials and with environmental quality standards in order to assess their significance.

## Raw Oil Shale

All of the selected processes use oil shale from the Green River Formation of the Piceance Basin of Colorado, Utah and Wyoming. Green River oil shale is a fine-grained sedimentary rock that contains ~20 wt % organic material known as kerogen. The inorganic portion is primarily dolomite and calcite with lesser amounts of quartz, analcime, Na-feldspar and K-feldspar. In addition, Mg-siderite, illite, pyrite and aragonite are frequently detected minerals [2, 3]. The toxic elements of interest may occur as substitution products in the major mineral phases; they may be organically bound or they may occur as minor mineral phases.

The elemental abundances of some toxic elements in feedstocks for five retorting processes are summarized in Table 2 and compared with Green River concentration ranges and average crustal rock abundances. The first column presents the range in elemental concentrations measured in 280 samples (555 m of core) of two core holes from the Naval Oil Shale Reserve No. 1 [2]. These are the most extensive data presently available on Green River oil shale and are presented here for comparison with specific feedstocks. These investigators found that the elemental compositions of two core holes from the Naval Oil Shale Reserve No. 1 were very similar even though the core holes were from the center and edge of the depositional basin and 10 km apart. This lateral uniformity is particularly important for environmental studies of MIS retorting because it means that several core holes can be well characterized and the results extrapolated to MIS retorts located throughout the formation. Giauque et al. [2] also found that the concentrations of most of the 57 elements they studied did not vary with depth by more than a factor of three or four in either of the core holes. However, variations of a factor of 10 or greater were observed for As, Cd, Hg, Mo, Se, B and F. Vertical variations in As, Se, Pb, Sb, Hg, Cu and Co for core hole 25, near the Logan Wash site, are shown in Figure 4. This figure demonstrates the vertical uniformity of each element throughout much of the core as well as a strong correlation among the seven elements.

The second and third columns of Table 2 present average elemental concentrations for the two core holes for the retorting horizon or the portion of the formation that is economically recoverable by MIS retorting. The composition of core hole 25 (118- 215-m depth) from the depositional edge of the basin approximates that of shale from the retorting horizon at Logan Wash (Occidental MIS retorts 3 and 6); the composition of core hole 15/16 (261- to 447-m depth) from the basin center represents shale from the retorting horizon of tracts C-a and C-b (MIS processes presently under development here). Column 4 summarizes the results of preliminary analyses by Wilkerson [23] for five samples of weathered raw shale from the Geokinetics site

Table 2. Elemental Abundances of Some Toxic Elements in Raw Oil Shale Charges to Retorting Processes and in Average Crustal Rocks (ppm)

	Range in Green River Oil Shale <sup>a</sup>	Retorting Horizon (118-215 m depth) of Logan Wash, CO (Core Hole 25 Depositional Basin) <sup>a</sup>	Retorting Horizon (261-447 m depth) at Tracts C-a and C-b, CO (Core Hole 15/16 from Center of Depositional Basin) <sup>a</sup>	Geokinetics True In Situ <sup>b</sup>	LLNL and LBNL Simulated In Situ Retorts <sup>c</sup>	Paraho Direct-Mode Retort <sup>d</sup>	TOSCO Modified Fischer Assay <sup>c</sup>	Crustal Abundance <sup>e</sup>	Concentration Ratio C <sub>RS</sub> /C <sub>CR</sub> (9)
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
As	5-134	39±19	42±23	43±23	42±1	44±1	75±2	1.8	26
B	25-250	82±32	74±38	-	108±11	94±2	80±8	10	8.8
Cd	0.2-1.4	0.61±0.25	-	-	0.72±0.07	0.64±0.03	1.1±0.1	0.2	3.8
Co	4-14	8.3±1.9	8.6±1.9	-	8.8±0.2	9.0±0.1	9.7±0.2	25	0.36
Cr	18-60	33±9	33±8	36±9	46±1	34±1	29±1	100	0.35
Cu	11-63	31±9	30±10	40±12	39±3	40±2	46±2	55	0.69
F	100-3200	1260±510	1340±630	-	990±20	-	1020±100	625	1.8
Hg	0.01-0.50	0.065±0.032	0.077±0.048	-	0.08±0.004	0.09±0.01	0.14±0.01	0.08	1.1
Mn	190-460	335±54	317±63	244±60	377±6	315±12	272±9	950	0.32
Mo	4-54	18±9	20±9	-	20±1	22±2	28±2	1.5	14
Ni	11-32	21±4	20±4	28±5	24±2	28±1	31±3	75	0.34
Pb	8-41	20±7	19±8	27±10	24±1	26±2	29±1	12.5	1.9
Sb	0.5-5.2	1.7±0.6	1.6±0.7	-	2.0±0.1	2.1±0.1	3.2±0.1	0.2	11
Se	0.5-12.3	1.6±0.6	2.0±1.0	1.5±0.3	2.5±0.3	2.0±0.1	4.3±0.3	0.05	46
V	29-203	95±36	94±30	<50-110	93±5	94±2	127±30	135	0.75
Zn	38-153	68±13	71±17	52±12	65±2	64±2	74±4	70	0.94

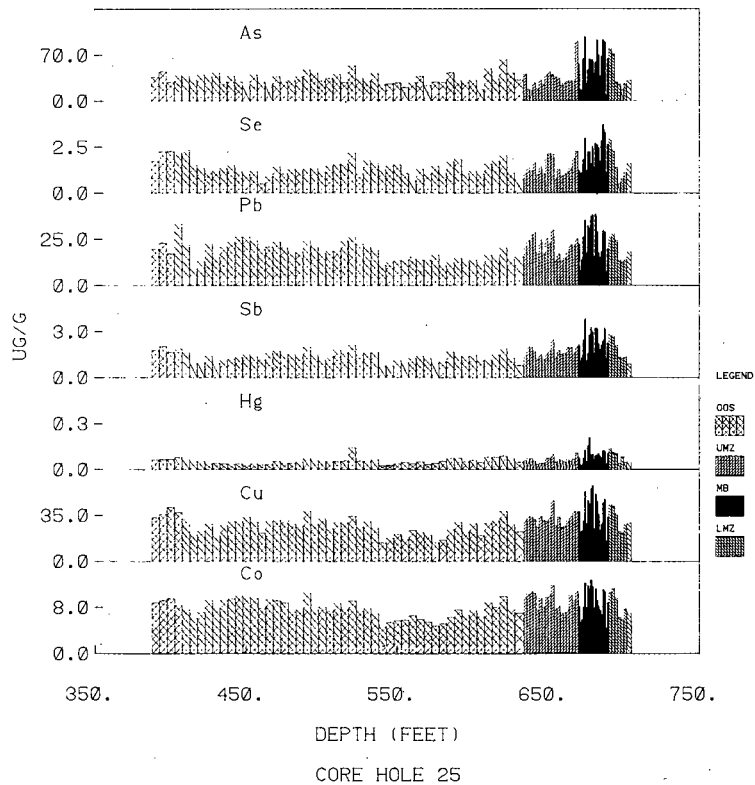
<sup>a</sup>Giauque et al. [2].

<sup>b</sup>Wilkerson [23].

<sup>c</sup>Fox et al. [20].

<sup>d</sup>Fruchter et al. [10, 11].

<sup>e</sup>Taylor [24].



**Figure 4.** Vertical variation in As, Se, Pb, Sb, Hg, Cu and Co throughout core hole 25 from the Naval Oil Shale Reserve No. 1. This core hole is near the depositional edge of the basin and approximates raw shales at the Logan Wash, Colorado site. (OOS = overlying oil shale; UMZ = Upper Mahogany Zone; MB = Mahogany Bed; LMZ = Lower Mahogany Zone) [2].



at Book Cliff, Utah. Columns 5 and 6 present the elemental concentrations in feedstock for the LLNL and LBNL simulated in situ and Paraho direct-mode retorts, respectively. Both of these feedstocks are from the Anvil Points Mine, Colorado. The two sets of values are within two standard deviations of each other for all elements. This is remarkable considering the different preretorting shale preparation, differences in sampling and analytical methodologies, and the possibility that the samples came from different horizons within the mine. Column 7 presents the elemental abundances in feedstock for the Fischer Assay retort runs discussed in this chapter. The samples are from the Dow Mine of Colony Development Co. Note that this shale differs from the others reported here. Column 8 summarizes the elemental concentration of average crustal rock as computed by Taylor [24]. These average abundances were calculated on the basis of a 1:1 mixture of granite and basalt abundances. Average crustal rock is used here as a reference material to identify elements which are enriched or depleted in oil shale relative to other rocks. This is achieved by using the concentration ratio (CR) which is summarized in column 9 and which is defined as:

$$CR = C_s/C_r$$

where  $C_s$  = the elemental concentration in the sample of interest, i.e. raw shale (RS), spent shale (SS), shale oil (SO)  
 $C_r$  = the concentration of the same element in a reference material, CR = crustal rock (CO = conventional oil)

The concentration ratios in column 9 represent the ratio of the average elemental abundances in the six raw shales presented in Table 2 (columns 2-7) to the crustal rock concentrations.

The data in Table 2 illustrate several important differences between Green River shales and average crustal rocks. The concentration ratios in column 9 indicate that the conventionally sulfide-forming elements As, Cd, Mo, Sb and Se as well as B are significantly enriched in Green River oil shales and that the elements Co, Cr, Mn and Ni are significantly depleted compared with average crustal rocks. The other elements, viz., Cu, F, Hg, Pb, V and Zn, are similar to average crustal rocks. This agrees with results previously reported by Fox [1] except that Cd was not reported as enriched in that study.

The high concentrations of the toxic elements As, B, Cd, Mo, Sb and Se could lead to environmental problems. The elements As, Cd and Se have been demonstrated to be released in significant quantities to oils, waters and gases during oil shale retorting [1, 11]. Boron and Mo are readily leached from spent shales [25] and thus may find their way into surface and groundwaters. All of these elements will occur in raw and spent shale-derived fugitive dust. This dust is viewed as a major environmental concern for oil shale development because high atmospheric dust concentrations could lead to violations of the Clean Air Act and contribute to worker and public health problems and ecological disturbances. Fugitive dust is discussed in a separate section of this chapter.

The chemical form of elements in oil shale is of critical importance because it controls the mobility of each element during retorting and leaching. Unfortunately, little work has been done in this area. The data which are available are summarized in Table 3. Desborough et al. [26] hypothesized the mineral residence of several toxic elements based on their occurrence in other crustal rocks. Giauque et al. [2, 3] investigated mineral residence by correlating mineral phases and elemental abundance data for 280 samples of oil shale. This work revealed that more than half of the 57 elements studied correlated well with the minerals Na-feldspar and K-feldspar while As, Cd, Hg, Mo and Se correlated with the organic fraction of the oil shale matrix. These investigators suggested that Co, Cu, Ni, Pb, Sb and Zn occurred as sulfides, which is consistent with findings by Saether et al. [27]. Saether et al. [28] demonstrated that F is associated with micaceous clay minerals, especially illite, in the Mahogany Zone.

Table 3. Postulated Residences of Some Toxic Trace Elements<sup>a</sup>

---

Sulfides

Co, Cu, Ni, Pb, Sb, Zn, As, Mo, Se, Hg

Illite

F

Feldspars and Mg-siderite

B, Cr, Mn, V

Organic Phase<sup>b</sup>

As, Mo, Se, Hg

Unknown

Cd

---

<sup>a</sup> Based on data presented by Giauque et al. [2], Saether et al. [27, 28], and Desborough et al. [26].

<sup>b</sup> Recent analyses show a strong correlation between these elements and total sulfur, which suggests a dual residence in sulfide minerals and/or in the organic phase.

### Spent Oil Shale

Spent oil shale is the solid residue that remains after the organic material has been removed by pyrolysis and combustion. The elemental compositions of raw and spent oil shale are similar for most elements, although the mineral compositions may vary considerably. Differences in the elemental and mineral composition of raw and spent shales are due to high-temperature mineral reactions and to the loss of organics and carbon dioxide from the shale matrix during retorting. The major mineral phases of spent shales vary, but they generally include survivors of the retorting process such as quartz and Na- and K-feldspars and the decomposition products periclase (MgO) and calcite ( $\text{CaCO}_3$ ). Synthesis products, which are the results of high-temperature mineral reactions, are also present in spent shales from in situ processes where maximum retorting temperatures may exceed  $1000^\circ\text{C}$ . Synthesis products identified to date include augite, mellilite, kalsilite and monticellite.

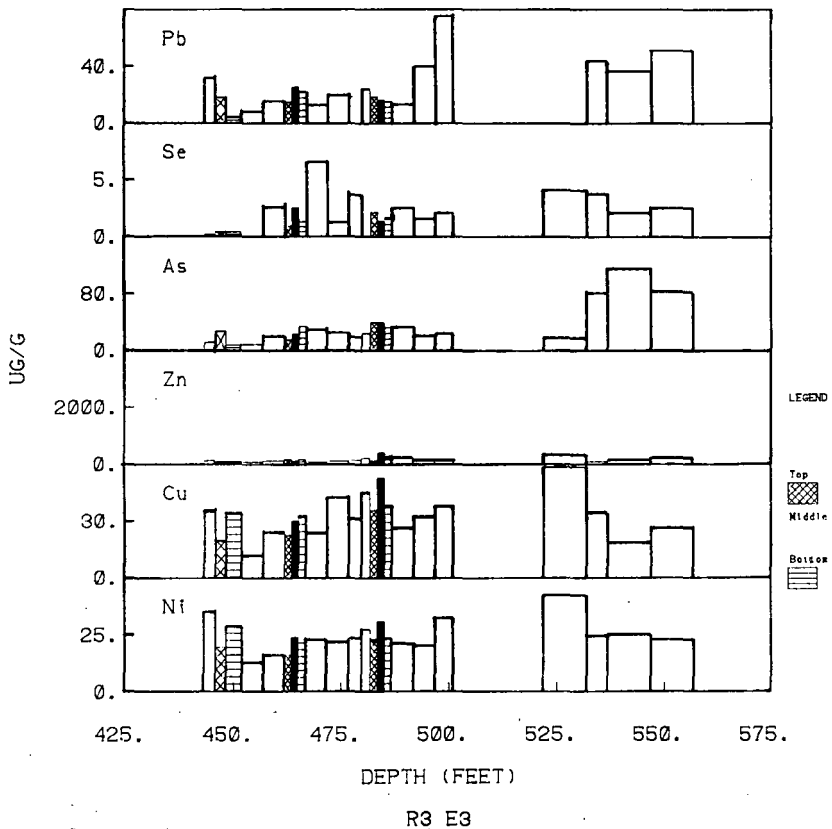
The elemental concentrations of nonvolatile elements are higher in spent shale than in raw shale because 20% or more of the oil shale is removed, primarily as volatilized organics and carbon dioxide, leaving behind ~100% of the nonvolatile elemental masses. On the other hand, the volatile elements, including Hg, Cd and, under some circumstances, Se, may be depleted in the spent shale relative to the raw shale due to their loss from the matrix [1, 29]. The elemental abundances of some toxic elements in the spent shale from the five retorting processes under investigation are summarized in Table 4 and are compared with the average crustal rock abundances presented previously. Variations in elemental abundances in spent shale from a core through Occidental Retort 3 are shown in Figure 5. These concentrations are not directly comparable to concentrations shown in Figure 4 because the vertical positions of the spent shale samples were not carefully controlled during coring.

Comparison of Table 4 and Table 2 shows that there is greater variability in elemental concentrations among the spent shales than among the raw shales. The increased variability is the result of retorting as well as the difficulties inherent in sampling spent shales, especially those from field in situ retorts. These difficulties include contamination, poor recovery during coring and nonuniform spent shale. These sampling difficulties preclude accurate assessments of the effects of in situ retorting processes as employed by Geokinetics and Occidental on trace element mobilization. For example, coring of Occidental Retort 3 at Logan Wash recovered <20% of the in-place material, and of that a majority came from highly localized zones within the retort. Additionally, the samples were contaminated by drilling fluids, and chemical changes occurred in the spent shale due to water leakage into the retort [14]. Nonuniform retorting, due to different porosity and permea-

Table 4. Comparison of Elemental Abundances of Some Toxic Elements in Spent Shale with Average Crustal Values (ppm)

	Occidental Retort 3 at Logan Wash (1)	Geokinetics True In Situ <sup>a</sup> (2)	LLNL Simulated In Situ Retort <sup>b</sup> (3)	Paraho Direct-Mode <sup>c</sup> (4)	TOSCO Modified Fischer Assay <sup>b</sup> (5)	Crustal Abundance <sup>d</sup> (6)	Concentration Ratio <sup>e</sup> C <sub>SS</sub> /C <sub>CA</sub> (7)
As	34 ± 24	80 ± 22	58 ± 1	59 ± 1	82 ± 3	1.8	37
B	252 ± 138 <sup>f</sup>	—	140 ± 15	107 ± 2	110 ± 9	10	12
Cd	—	—	0.77 ± 0.08	0.91 ± 0.04	1.28 ± 0.13	0.2	4.9
Co	—	—	11.9 ± 0.2	11.1 ± 0.2	11.5 ± 0.2	25	0.46
Cr	—	78 ± 41	50 ± 1	44 ± 1	36 ± 1	100	0.43
Cu	36 ± 11	86 ± 15	49 ± 2	56 ± 1	67 ± 5	55	1.0
F	—	—	980 ± 60	—	1420 ± 200	625	1.9
Hg	0.041 <sup>f</sup>	—	<0.01	0.035 ± 0.003	0.040 ± 0.001	0.08	0.47
Mn	—	316 ± 62	480 ± 10	396 ± 14	342 ± 10	950	0.43
Mo	10 ± 7 <sup>f</sup>	—	27 ± 1	34 ± 1	37 ± 2	1.5	22
Ni	25 ± 6	57 ± 19	38 ± 3	32 ± 2	38 ± 1	75	0.51
Pb	26 ± 14	40 ± 30	39 ± 2	36 ± 2	38 ± 3	12.5	3.0
Sb	—	—	2.9 ± 0.1	2.6 ± 1.5	3.6 ± 0.1	0.2	15
Se	—	—	1.6 ± 0.3	2.3 ± 0.1	5.1 ± 0.3	0.05	60
V	—	182 ± 42	128 ± 6	129 ± 6	161 ± 36	135	1.0
Zn	148 ± 87	91 ± 30	123 ± 3	82 ± 2	99 ± 4	70	1.5

<sup>a</sup>Wilkerson [23].<sup>b</sup>Fox et al. [20].<sup>c</sup>Fruchter et al. [11].<sup>d</sup>Taylor [24].<sup>e</sup>Excludes Occidental Retort 3 and Geokinetics samples because of sampling problems noted in the text.<sup>f</sup>Fruchter [12].



**Figure 5.** Variation in Pb, Se, As, Zn, Cu and Ni throughout core hole 3E3 taken through Occidental's Retort 3 at Logan Wash, Colorado. Large samples of core material were segregated into "top", "middle" and "bottom" samples as shown in the legend. The open bars were unsegregated.

bility distributions within in situ retorts, results in considerable heterogeneity in spent shales. Thus, large numbers of cores are required to obtain a representative sample. The required number is rarely available. Thus, elemental abundances in column 1 of Table 4 are not representative of the entire retorted horizon of retort 3 and cannot be reliably compared with elemental abundances for the raw shale reported in column 2 of Table 2. Similar difficulties exist with the Geokinetics data, and the values reported in column 2 of Table 4 cannot be reliably compared with the raw shale values reported in column 4 of Table 2. An extensive coring program at the Geokinetics site was recently completed by LETC using methods designed to mitigate some of these sampling problems. Detailed elemental characterization of the new cores is in progress at LBNL.

Other spent shales in Table 4, however, are comparable to the raw shales shown in Table 2. These other spent shales are from smaller-scale laboratory reactors in which retorting was closely controlled and sampling was carefully conducted. Because they are laboratory reactors, rather than large underground chambers of shale, sampling is considerably simplified; contamination from drilling fluids does not occur, 100% recovery of the spent shale is possible, and the spent shale is of a uniform composition. Additionally, the other samples in Table 4 (Paraho, LLNL, Fischer Assay) were the subject of a careful scientific investigation in which critical sampling parameters were controlled [11, 20].

The elemental concentration ratios presented in Table 4 are slightly higher than the corresponding ratios reported in Table 2 for raw shales, with the exception of the ratio for Hg. The Hg ratio is lower because Hg is volatilized during retorting, depleting it in spent shales relative to raw shales.

The elevated concentrations of As, B, Cd, Mo, Sb and Se in spent shales may pose some of the same hazards previously discussed for raw shales, namely release of these elements to the environment as a consequence of leaching and fugitive dust exposure and fallout. Preliminary investigations on the leachability of spent shale from Occidental Retort 3 indicate that the concentrations of F, B, Mo, As and Se in the initial leachates are high enough to warrant further study [14]. Static leaching experiments on 16 spent shale samples from Retort 3 revealed As concentrations ranging from 0.005 to 0.15 mg/L; B concentrations of <0.3-6.7 mg/L; Mo concentrations of 0.04-0.05 mg/L; and Se concentrations of <0.001-0.040 mg/L. The leachability of some elements may be significantly modified in spent shales, relative to raw shales, due to mineralogical changes that occur during retorting. Stollenwerk and Runnels [25] found that the amount of Mo and B leached from TOSCO II spent shale was significantly greater than the amount leached from the raw shale, but the amount of F was lower in the spent shale leachate than the raw shale leachate. There was no significant difference in the amounts of Se and As leached from raw and spent shales.

### Shale Oil

Shale oil is the hydrocarbon product produced by the condensation of vapors from the pyrolysis of oil shale. Typically, it is a black waxy liquid that has a high pour point. Shale oils produced by surface retorts such as Paraho or TOSCO retorts are different from in situ-produced oils. The nitrogen content of surface-produced oils usually ranges from 1.4 to 2.3% and the pour point ranges from 18 to 32°C. The nitrogen content of in situ-produced oils is 1.4-1.8% and the pour point may range from -1.1 to 21°C [1]. Other differences have also been noted in yields of distillation products, viscosity

and elemental abundances [16, 30, 31]. These differences are primarily due to differences in retort operations. Surface retorts typically use short rapid shale heatup, small shale particles, retorting temperatures of 500-700°C and continuous shale feed. In situ retorts, on the other hand, are batch reactors that typically employ slow shale heatup, low retorting rates, temperatures which can reach 1000°C, and larger particles. In in situ retorts, the relatively longer residence time of the oil in high temperature zones and the holdup of heavy components on the cooler shale ahead of the reaction front result in in situ oil cracking. Thus, in situ oils have a lower nitrogen and residuum content, a lower pour point and viscosity, and a higher light distillate content than surface oils.

Shale oils, in general, differ in some significant ways from crude oils. Relative to conventional crudes [32], shale oils have a high nitrogen content, a moderate sulfur content and a lower hydrogen content. Hydrocarbon composition is markedly different, and distillation yields vary accordingly. The refining of shale oil will produce less gasoline and more kerosene and diesel fuel than refining of an equivalent volume of crude oil. Since shale oil has a larger percentage of distillation products in the higher boiling fractions, its viscosity and pour point are higher. Another difference is that shale oil may contain process-derived inorganic solids and pyrolytic products [11, 16].

The elemental compositions of shale oils from the five processes studied here are compared with the elemental composition of average conventional crude in Table 5. This tabulation shows that shale oils from different processes vary considerably with respect to some elements. Fox [1, 30] investigated the effect of shale source and retort operating conditions on the elemental composition of 24 oils from three simulated in situ retorts and concluded that shale source and the retort type are the major determiners of elemental composition. On the other hand, retorting temperature and atmosphere did not significantly affect elemental composition of shale oils within the limits of experimental error. Fox also found elevated concentrations of Cu, Pb and Zn in oils produced in the LLNL simulated in situ retorts. The conclusion was drawn that these elevated concentrations were due to contamination from copper alloys used in the product collection system.

The concentration ratios in column 7 of Table 5 indicate that As, Co, Hg, Se and Zn are enriched in shale oils compared to conventional crude oils and that Cr, Cu, Mo, Ni and V are depleted. The elevated concentrations of As, Co, Hg, Se and Zn could result in both process and environmental problems, depending on the chemical form of the element and the use of the oil.

Shale oil may be directly combusted in oil-fired power plants, refined into gasoline, diesel fuel and other distillation products, or used as a feedstock for chemical production. Combustion of shale oil may volatilize greater quantities of Hg, As and Se than combustion of conventional crudes. Tests of

Table 5. Comparison of Elemental Abundances of Some Toxic Elements in Shale Oils with Conventional Crude Oils (ppm)

	Occidental Retort 6 <sup>a</sup> (1)	Geokinetics True In Situ <sup>a</sup> (2)	LLNL Simulated In Situ Retort <sup>a</sup> (3)	Paraho Direct-Mode <sup>a</sup> (4)	TOSCO Modified Fischer Assay (5)	Conventional Crude Oil <sup>b</sup> (6)	Concentration Ratio C <sub>SO</sub> /C <sub>CO</sub> (7)
As	15.1 ± 0.1	8.75 ± 0.09	14 ± 3	28.2 ± 0.1	20 ± 4	0.01	1720
B	—	—	—	—	—	—	—
Cd	<0.14	<0.06	0.025 ± 0.003	<0.17	<0.01	<0.01	—
Co	3.59 ± 0.02	1.84 ± 0.01	0.35 ± 0.08	1.32 ± 0.01	0.22 ± 0.03	0.2	7.3
Cr	0.033 ± 0.001	<0.01	0.14 ± 0.09	0.023 ± 0.005	0.41 ± 0.08	0.3	0.41
Cu	0.10 ± 0.01	<0.29	2.5 ± 0.2	0.05 ± 0.05	0.04 ± 0.01	0.14	0.45 <sup>d</sup>
F	—	—	—	—	—	—	—
Hg	0.06 <sup>c</sup>	0.12 <sup>c</sup>	0.22 ± 0.04	0.11 <sup>c</sup>	0.23 ± 0.02	0.07	2.1
Mn	0.0123 ± 0.0002	<2	0.039 ± 0.001	0.085 ± 0.001	0.08 ± 0.02	0.1	0.54
Mo	2.5 ± 0.1	3.0 ± 0.1	0.86 ± 0.26	0.85 ± 0.86	—	10	0.18
Ni	8.8 ± 0.4	3.8 ± 0.6	2.9 ± 0.4	3.0 ± 0.3	1.2 ± 0.6	10	0.39
Pb	<2	<2	1.5 ± 0.6	<2	0.03 ± 0.01	0.3	—
Sb	0.026 ± 0.001	0.016 ± 0.001	0.03 ± 0.01	0.046 ± 0.001	0.035 ± 0.003	—	—
Se	0.81 ± 0.01	0.80 ± 0.01	2.9 ± 0.3	1.20 ± 0.03	0.8 ± 0.1	0.17	7.7
V	0.45 ± 0.01	<6	0.29 ± 0.01	0.224 ± 0.003	1.2 ± 0.5	50	0.11
Zn	1.5 ± 0.1	3.4 ± 0.1	5.4 ± 1.5	2.0 ± 0.1	0.98 ± 0.40	0.25	8 <sup>d</sup>

<sup>a</sup>Fox [30].

<sup>b</sup>Bertine and Goldberg [33].

<sup>c</sup>Wilkerson [16].

<sup>d</sup>Excludes LLNL oil due to contamination.



a Paraho shale oil in a utility boiler equipped with a scrubber indicated that 21, 31 and 100% of the As, Pb and Hg, respectively, were emitted with the stack gases [34]. If these increased emissions are not controlled by stack gas cleaning processes such as desulfurization or electrostatic precipitation, elevated atmospheric and soil-column concentrations of these elements, particularly in the vicinity of the power plant, may result.

The high concentrations of As in shale oils are known to interfere with catalytic reactions during prerefining (hydrotreating) and with subsequent refinery operations [35, 36]. As a result, As must be removed from shale oil before it is refined. Proposed processes for As removal employ an absorbent [37] or an alumina guard bed [36]. The used absorbents will contain high concentrations of As and other toxic elements and probably will be classified as hazardous wastes necessitating special handling and disposal.

The fate of these trace elements in shale oils depends on their chemical form. There has been very little work done in this area. Shaw [38], in analyses of distillation fractions of a Rock Springs true in situ shale oil, found that the concentrations of Cr, Co, Mo, Mn, As and Se increased with the temperature range of the cut, but V was concentrated in the naphtha and residuum cuts. The elements concentrated in the residuum are probably associated with nonvolatile asphalt ends. This suggests that they would not be volatile during combustion. Some volatile compounds, however, are certain to exist in the lighter fractions.

In other work, Wilkerson [16] fractionated Paraho, Geokinetics, and Occidental shale oils using a solvent precipitation method. This work showed that most of the Ni, Co, Mo, Zn, V, Hg and Sb were present in the asphaltic fraction. The majority of the As was associated with the resin and n-pentane/methanol-soluble fractions which contain the nonpolar, lower-molecular-weight components of shale oil. Wilkerson postulated that inorganic forms of As in shale oils may include arsenic oxide ( $As_4O_6$ ) and/or metallic arsenic ( $As_2^0$  or  $As_4^0$ ). Alkaline extracts of shale oils in our laboratory suggest that methylarsonic acid may be present. Wilkerson [16] also postulated that Ni and Co may be present as porphyrins or multidentate mixed ligands.

### Process Waters

Oil shale retorting will generate effluents from conventional water uses, such as steam and power production, mining, and domestic and service consumption of water. Additionally, two process waters are produced during retorting. These process waters, known as retort water and gas condensate, are unique to the oil shale industry and will require special study and consideration by the industry because they are chemically complex and pose difficult waste treatment problems [39]. We will consider only the process waters,

and, of them, we will focus on retort waters. The other waters have been discussed previously [31].

The quantities, types and nature of waters produced during oil shale retorting depend on the process and the retort operating conditions. The sources of these waters are combustion, mineral dehydration, input steam and groundwater intrusion (in situ processes). Combined production of water ranges between 0.1 and 10 bbl  $H_2O$ /bbl oil [31]. Water production for surface processes is at the lower end of this range (0.1-0.5 bbl  $H_2O$ /bbl oil) and at the upper end for in situ processes (0.4-10 bbl  $H_2O$ /bbl oil) due to groundwater intrusion. Several types of waters are generated during retorting, as illustrated by the Occidental MIS process shown in Figure 6. In this process, water and oil are collected together in an underground sump at the bottom of the retort. These are pumped into a separator tank where the majority of the water, termed "retort water," is separated from the oil by decantation. The oil from this tank is then introduced into the heater-treater to remove any residual moisture. The oil is heated and the water, termed "heater-treater water," is collected by decantation. Both retort water and heater-treater water may then be introduced into a low-pressure boiler and a portion blown down to control solids within the boiler. This is termed "boiler blowdown water." Water condensed from the offgas stream is termed "gas condensate."

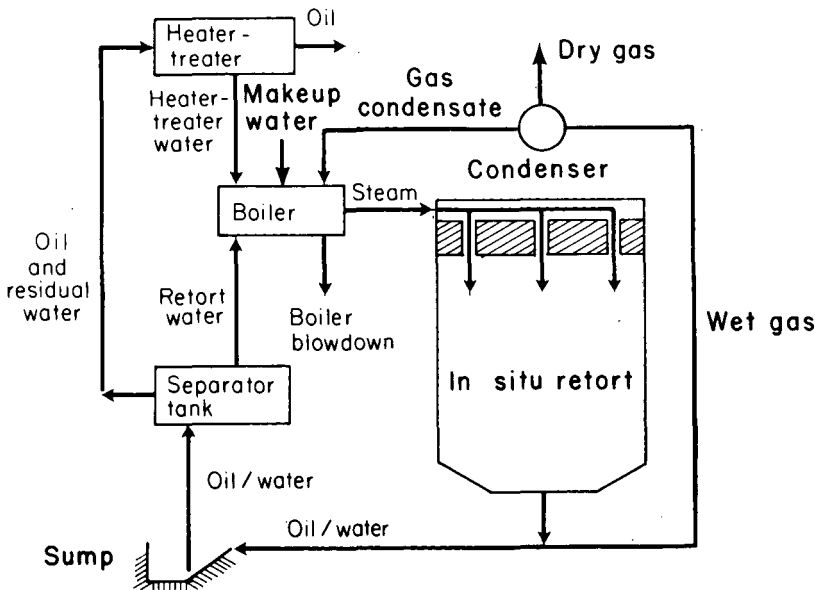


Figure 6. Schematic showing the production of wastewaters during the Occidental modified in situ process.

Table 6. Comparison of Elemental Abundances of Some Toxic Elements in Retort Waters with Water Quality Criteria (ppm)

	Occidental Retort 6 <sup>a</sup> (1)	Geokinetics True In Situ <sup>b</sup> (2)	LLNL Simulated In Situ Retort <sup>c</sup> (3)	Paraho Direct Mode <sup>d</sup> (4)	TOSCO Modified Fischer Assay (5)	Constraining Water Quality <sup>e</sup> Criteria (6)
As	1.1 ± 0.3	2.6 ± 3.9	2.6 ± 0.1	5.8 ± 1.0	8.0 ± 2.4	0.1 (D)
B	12.9 ± 0.4	61 ± 68	—	43 ± 6	—	0.75–2.0 (I)
Cd	—	0.084 ± 0.088	0.005 ± 0.0005	—	—	0.03–0.0004 (A)
Co	<0.02	0.56 ± 0.30	<0.03	0.032 ± 0.001	<0.12	0.05–5.0 (L, I)
Cr	<0.07	0.078 ± 0.039	0.39 ± 0.22	<0.060	<7.4	0.05 (D, A)
Cu	0.03 ± 0.01	0.21 ± 0.17	133 ± 6	0.66	<0.10	0.5 (L)
F	35 ± 1	35 ± 6	—	25	—	1.4–2.4 (D)
Hg	<0.02	0.0038 ± 0.011	0.085 ± 0.011	0.0023 ± 0.0001	—	0.00005 (A)
Mn	<0.04	0.94 ± 1.9	0.19 ± 0.03	0.17 ± 0.05	0.3 ± 0.1	0.05 (D)
Mo	0.3 ± 0.1	11.9 ± 8.7	—	0.15	0.13 ± 0.04	0.010–0.050 (I)
Ni	<0.02	1.6 ± 2.1	1.57 ± 0.10	0.54 ± 0.10	0.31 ± 0.08	0.20–2.0 (I)
Pb	<0.04	0.64 ± 0.92	1.15 ± 0.16	<0.40	<0.36	0.03 (A)
Sb	0.018 ± 0.008	0.011 ± 0.003	<0.07	0.020 ± 0.004	—	0.2 (A)
Se	0.04 ± 0.01	0.22 ± 0.47	1.1 ± 0.1	9.8 ± 1.1	3.1 ± 0.4	0.01 (D)
V	<0.04	0.43 ± 0.25	0.08 ± 0.01	0.044 ± 0.008	—	0.1 (L)
Zn	<0.1	0.095 ± 0.067	13.3 ± 0.6	0.41 ± 0.04	0.20 ± 0.07	2.0–10 (D, I)

<sup>a</sup>U.S. DOE [14].<sup>b</sup>Geokinetics [41].<sup>c</sup>Fox [1].<sup>d</sup>Fruchter et al. [10].<sup>e</sup>NAS [42]; D = domestic, I = irrigation, A = aquatic life, L = livestock watering.

The only process water for which there are abundant characterization data is retort water. The concentrations of some toxic elements in retort waters from five processes are presented in Table 6. This table shows significant differences among waters from the five processes. These differences have been hypothesized to be due to sampling and analytical problems [1]. In addition, the problems attendant with the analysis of retort waters are legendary [40]. Fox [1] concluded that water composition depends, among other things, on contact time between the oil and water and on operation of the product collection system. Variability also may be caused by changes in product water composition during retorting. Significant temporal variations in the concentrations of many constituents have been noted in unpublished data from several field in situ experiments. Because of these problems, the concentrations shown in Table 6 should not be construed as accurate representations of elemental abundances in waters from commercial processes. Considerable additional work is required in order to resolve the variability issue.

The data in Table 6 demonstrate that the concentrations of As, Se and Zn are elevated in surface process waters relative to in situ process waters. This difference was previously noted in work by the U.S. DOE [14] and was hypothesized to be due to operating conditions and to the fact that surface processes produce much less water, and thus soluble species partitioned from the oil would be more highly concentrated. Another noticeable feature of the data presented in Table 6 is the unusually high Mo value for Geokinetics retort water. A similar concentration was also observed in the U.S. DOE study; the source of this Mo is unknown. The high concentrations of Cr, Cu and Zn in the LLNL water are presumably due to contamination from copper alloys used in the product collection system [1].

The last column of Table 6 presents constraining water quality criteria. These criteria are compared with retort water concentrations to evaluate the significance of the release of this water to the environment. These water quality criteria were developed under the aegis of the National Research Council at the request of the U.S. Environmental Protection Agency. Water quality criteria are recommended concentrations that should be maintained in the main water mass to protect a specified water use. The "constraining" criteria in Table 6 are the most stringent among domestic supply, irrigation water, aquatic life or livestock watering.

Comparison of the five retort waters with constraining water quality criteria indicates that the concentration of As, B, F, Hg, Mn, Mo, Pb and Se exceed these criteria for most waters. The environmental significance of these concentrations depends on the projected use of the water. Some developers of surface processes presently plan to codispose of retort water and spent shale. Thus, some of these elements may be released to the environment through leaching or volatilization from the disposal pile. Other developers

may evaporate the retort water in surface ponds, creating an opportunity for loss of volatile species.

Only limited data exist for other types of process waters. Analyses of boiler blowdown water for the Occidental process have been reported by the U.S. DOE [14], and analyses of other Paraho effluents have been reported by Fruchter et al. [10].

The environmental significance of toxic elements in process waters depends on the chemical form of the element, since some chemical forms are highly toxic while others are benign. The classical case, of course, is methyl mercury, which is considerably more toxic than elemental Hg. Very few chemical speciation investigations have been performed due to the difficulty of identifying species in complex matrices. So far, the focus of speciation investigations has been on arsenicals because As is elevated in all shale products. The results of these investigations are summarized in Table 7. Fox et al. [15] found that the major arsenical in several in situ process waters was arsenate and that lesser but significant amounts of methylarsonic acid also were present. Other data [15] reveal that the major arsenicals in Paraho retort water are arsenite and arsenate. The presence of arsenite has been corroborated by researchers at Battelle Pacific Northwest Laboratory [10].

The potential presence of these arsenic species is significant from an industrial and public health standpoint. Arsenite is a known carcinogen [44]; the methylated form is low boiling and may be volatile under ambient conditions. Microorganisms are known to produce toxic gaseous arsenical products, such as arsine [45], from arsenate, arsenite, and mono- and dimethyl arsenate. Thus, these forms may escape into the atmosphere if the waters are evaporated or codisposed with spent shales.

### Offgases

The pyrolysis of oil shale produces from 70 to 14,000 scf of low-Btu gas per ton of shale retorted [1]. Surface processes produce less gas per ton of retorted shale than do the in situ processes, due to the lower temperatures required for surface retorting. The major constituents in these gases are CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub> and C<sub>2</sub> through C<sub>5</sub> hydrocarbons. Principal gaseous pollutants include H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>x</sub>, COS, thiophene and certain volatile trace elements [1, 11].

There are few direct offgas data available on the concentration of trace elements. This is primarily due to the difficulties of sampling and performing trace element analyses on a matrix of such complex and variable composition. For example, the standard EPA reference methods for sampling gaseous

Table 7. Tentatively Identified Arsenicals in Oil Shale Process Waters<sup>a</sup> [15]

	LLNL Simulated In Situ Retort Water	Occidental Retort 6			Geokinetics True In Situ Water	Paraho Direct- Mode Water
		Retort Water	Gas Condensate	Boiler Blowdown		
Arsenite ( $\text{AsO}_2^-$ )	---	---	---	---	---	(+)
Arsenate ( $\text{AsO}_4^{3-}$ )	(+)	(+)	---	(+)	(+)	(+)
Methylarsonic Acid ( $\text{CH}_3\text{AsO}(\text{OH})_2$ )	(+)	(+)	---	(+)	(+)	(+)
Dimethylarsinic Acid ( $(\text{CH}_3)_2\text{AsO}(\text{OH})$ )	---	---	---	---	---	---
Phenylarsonic Acid ( $\phi - \text{AsO}(\text{OH})_2$ )	---	---	---	---	---	---

<sup>a</sup> --- signifies that the species was looked for but not detected; (+) signifies that the species was tentatively identified by high-performance liquid chromatography coupled with atomic absorption spectroscopy using known retention times of authentic arsenicals.

Hg in stack gases [46] have been found to be unsuitable for sampling Hg in oil shale offgases during retorting experiments at LETC and LLNL [29, 47]. Attempts to use acid gas scrubber solutions to sample Hg in Paraho-direct recycle gas also have proven to be unsatisfactory [10].

Available data for direct measurements of total Hg and As and speciation measurements of these two elements in gases from the Paraho-direct and Occidental retort experiments are summarized in Table 8. Time-weighted average threshold limit values (TLV) for the workplace are included in Table 8 for comparison. The Au-amalgamation sampling technique was used for total Hg and has proven to be a reliable sampling method. The chemical forms of Hg and As were determined using the techniques of Braman and Johnson [48] and Johnson and Braman [49], respectively.

Arsenic speciation measurements indicate that the major forms of As in thermal oxidizer gas are gaseous arsenic trioxide ( $\text{As}_2\text{O}_3$ ) and particulate As. In the recycle gas, arsenic trioxide predominates. The estimated error

Table 8. Mercury and Arsenic Species in Paraho-direct and Occidental Retort 6 Offgas Compared to Time-Weighted Average Threshold Limit Values (TLV) ( $\mu\text{g}/\text{m}^3$ )<sup>a</sup>

	Paraho Direct-Mode		Occidental Retort 6 <sup>c</sup>	TLV for 40-hr Work Week <sup>d</sup>
	Thermal Oxidizer <sup>b</sup>	Recycle <sup>b</sup>		
<b>Mercury</b>				
Hg <sup>0</sup>	4.5-9.4	—	—	50
HgCl <sub>2</sub>	<0.1	—	—	50
CH <sub>3</sub> HgCl	<0.2	—	—	10
(CH <sub>3</sub> ) <sub>2</sub> HgCl	<0.1	—	—	10
Total Hg	4.5-12 (n=5) <sup>d</sup>	46-75	10-26 (n=13)	—
<b>Arsenic</b>				
As <sub>2</sub> O <sub>3</sub> (g)	12-36	112-149	<0.8-1.9	50
AsH <sub>3</sub>	<0.2-0.3	2	0.9-3.5	200
CH <sub>3</sub> AsH <sub>2</sub>	<0.2	3	—	—
(CH <sub>3</sub> ) <sub>2</sub> AsH	<0.2	1.0-1.7	<0.4	—
Other Organic As	<0.2	0.5	—	—
Particulate As	19 (n=1)	1.2 (n=1)	—	—
Total As	12-55	120-155	—	500

<sup>a</sup>Unless otherwise indicated in parentheses, two discrete samples were analyzed to determine the concentrations.

<sup>b</sup>Fruchter et al. [10].

<sup>c</sup>U.S. DOE [14].

<sup>d</sup>ACGIH [44].

in all of the Paraho-direct As data (Table 8) is  $\pm 50\%$ . The Occidental arsine ( $\text{AsH}_3$ ) values are near blank and reported as not significant by the authors. Considering the errors, only tentative identification of arsine and methyl- and dimethylarsine can be made in the recycle gas. Comparison of these values with workroom TLVs indicate that all reported concentrations except that of  $\text{As}_2\text{O}_3$  in the Paraho recycle gas are less than the TLVs. Arsenic trioxide is a human carcinogen [44] and could pose a worker health problem if recycle gas were vented in the workplace. Considering the limited data available, any general statements regarding the levels and chemical form of As and Hg in surface and MIS retort offgas are premature.

Mercury speciation measurements in the flared offgas (thermal oxidizer) show that only elemental Hg is emitted to the atmosphere. This is as expected since the vast majority of Hg compounds decompose to  $\text{Hg}^0$  at the high flare temperatures. Although Hg levels in the flared offgas are less than TLVs, additional characterization is necessary to determine the concentration, identity and stability of mercury compounds in the recycle and unflared offgases.

Recent work at LBNL suggests that organically bound Hg is the predominant chemical form of Hg vapor in the offgas from the LBNL retort. Mercury measurements were made with carbosive (activated carbon) columns upstream of and in series with Au-amalgam tubes. These carbosive columns selectively adsorb organic Hg to the exclusion of inorganic forms. The results suggest that organically bound Hg is the predominant chemical form of Hg. Additional experimentation is necessary to verify these observations and the specificity of carbosive columns for organic/inorganic Hg in oil shale offgas.

Measurements of total Hg in the offgases during simulated in situ retort experiments at LETC, LLNL, and LBNL have been made. At the LETC 10-ton retort, 10 discrete samples using Au-amalgam tubes were collected and analyzed. For the other retort experiments, continuous on-line analyses were made using Zeeman atomic absorption spectroscopy (ZAA). This method is described elsewhere [50]. Except for the 10-ton experiment, the reported Hg concentrations in Table 9 are orders of magnitude higher than those reported for Hg in Table 8. The discrepancy between offgas Hg concentrations measured at field retorts [9, 10, 14] and those measured by Fox et al. [29] and Girvin et al. [5, 50] are real and not thought to be due to differences in analytical techniques. The Au-amalgamation and the ZAA techniques generally agree to within  $\pm 20\%$  or better for the measurement of total Hg in LBNL retort offgas.

Two factors contribute to the difference between offgas Hg values reported in Tables 8 and 9: condensation and sampling time. First, during LBNL retort experiments, it has been found that  $\sim 50\%$  of the total Hg vapor originally present in the offgas stream is removed when offgases



Table 9. Measurements of Total Hg in the Offgas of Some Simulated In Situ Retorts ( $\mu\text{g}/\text{m}^3$ )

	Hg Concentration	Retort
Girvin et al. [5]	42-540	LLNL 6000-kg Run L-3
Fox et al. [29]	80-8000	LETC controlled state Run CS-69
Girvin et al. [6]	6-2200	LBNL retort Run LBNL-02
Fruchter et al. [9]	2-5	LETC 10-ton

contact cool ( $< 40^\circ \text{C}$ ) surfaces. This is presumably due to condensation, and, when the surface is stainless steel, subsequent amalgamation. It was found that stainless steel surfaces must be maintained at temperatures  $> 150^\circ \text{C}$  to prevent losses. The elimination of cool surfaces in contact with the offgas resulted in the recovery of 100% of the Hg originally present in the shale [47]. It has also been observed during LBNL, LLNL and LETC retort experiments that Hg vapor is almost totally removed from the offgas stream when passing through raw oil shale whose temperature is  $140^\circ \text{C}$  or less [29, 47].

These condensation opportunities may partially explain why Hg concentrations in Paraho and Occidental offgases are much lower than in offgases from simulated in situ retorts. At Paraho, the offgas passes sequentially through the cool raw oil shale entering the retort, an oil coalescer, an electrostatic precipitator, and finally through extensive plumbing before reaching the gas sampling point. Offgases from Occidental retort 6 contacted cool raw shale in the lower portion of the retort and a section of cool plumbing prior to reaching the point of sampling. In both cases, loss of Hg vapor to cold or cool surfaces may have resulted in the loss of Hg and thus the observation of lower concentrations in both the recycle gas and gas discharged to the atmosphere. This offers a de facto control technology but complicates comparison of data among investigators.

The second factor affecting the difference in observed Hg concentrations is the time during the oil shale retort experiment when sampling for Hg vapor is conducted. This factor will primarily affect batch-type processes, i.e., all of the in situ processes. The continuous ZAA Hg measurements by Fox et al. [29] and Girvin et al. [6] have shown that Hg emissions during simulated in situ retorting are nonuniform. During the final stage of retorting, when the last segment of raw shale exceeds  $200^\circ \text{C}$ , a pulse of Hg is observed in the offgas which is two to three orders of magnitude higher than concentrations

observed during the initial and intermediate stages of retorting. The Occidental measurements were not made during the final stage of the retorting process.

The mechanism responsible for this Hg pulse has been suggested by Fox et al. [29]; Hg originally present in raw shale is volatilized by the approaching pyrolysis front, swept ahead of the front by the offgas, and then condenses on a layer of cool raw shale. If this process continues as the front propagates down or through the retort bed, Hg becomes progressively more concentrated in the successive layers of raw shale. When the final layer is heated, a large pulse of Hg appears in the offgas. No measurements have been made during the final stages of field retorting experiments to verify the existence of a final Hg pulse. This has been due to limited sampling during field experiments that last many months.

Except for the two measurements of As presented above, direct quantitative measurements in the offgas of the other volatile toxic elements under study here have not been made. However, elemental mass balance measurements of product streams (excluding offgas) from simulated in situ retorting experiments at LETC and LLNL attributed mass deficiencies to the offgas [1]. On this basis, ~30% of the Cd in the raw shale may be volatilized into the offgas, and at retorting temperatures in excess of 900°C, a maximum of 1 and 13% of the original As and Se may be mobilized to the gas phase. It should be noted that the maximum retorting temperatures reached for the Paraho retort run discussed above was 750°C. For this temperature, As volatilization into the gas phase would be expected to be exceedingly low.

Cadmium was recently detected for the first time in oil shale offgases. The successful qualitative on-line measurement of Cd vapor in offgas was made by directly aspirating offgas from the LBNL retort into a conventional flame atomic absorption spectrometer. Significant quantities of Cd were volatilized at retort temperatures above 500°C. An effort is currently under way to make quantitative measurements using this technique.

As can be seen, a paucity of direct trace element offgas data exists, even for Hg. Mechanisms analogous to those affecting Hg may result in vapor phase losses to surfaces contacting offgases and nonuniform emission rates (pulse formation) during retorting for the other volatile elements, namely Cd, Se, Sb and As. The possibility that such mechanisms exist should be examined.

### **Fugitive Dust**

Fugitive dust and particulates, largely raw and spent shale fines and suspended soil material, will be produced by oil shale production. Activities that produce fugitive particulates include blasting to release the ore; raw and

spent shale loading, haulage, crushing, screening and stockpiling; loading and unloading of surface retorts; and disposal pile development. Particulates from these activities will have a chemical composition similar to that of raw and spent shales shown in Tables 2 and 4. Considerable dust is also produced by vehicular traffic and construction activities, because the soils in the oil shale region are light and disintegrate into a fine powder when disturbed during dry seasons. Additional particulate material may be produced by wind erosion of spent shale disposal piles and other waste dumps. The quantity of these emissions is roughly proportional to the amount of material handled and the areal extent of the plant and disposal pile. Emission quantity additionally depends on the particle size of the raw and spent shale and on mining methods. Surface mining and retorting produce higher particulate emissions than underground processes. Retorting processes that use a fine shale charge or produce a fine spent shale, such as Lurgi or TOSCO, would be expected to generate more particulates. Open pit mining operations, in which activities are exposed to the atmosphere, generate more fugitive particulates than underground mining methods.

The quantities and composition of fugitive dust at the Paraho semiworks plant have been investigated by Cotter et al. [51] and Fruchter et al. [10]. Some of these data are summarized in Table 10. These studies indicate that atmospheric dust concentrations in the mining, crushing and loading areas are significantly elevated above background levels ( $\sim 5 \text{ mg/m}^3$ ), ranging from 1 to  $35 \text{ mg/m}^3$ . Both studies observed a bimodal particle size distribution, consisting largely of particles  $>7 \mu\text{m}$  and  $<0.6 \mu\text{m}$  with relatively few particles in the size fractions between these limits. Cotter et al. [51] found 20–37% of the total loading was in the size range  $>8 \mu\text{m}$  and even greater percentages, 33–63%, in the  $<0.6 \mu\text{m}$  fraction. Therefore, respirable dust, defined as particles  $<3 \mu\text{m}$ , is a significant fraction of fugitive dust at the Paraho plant. Elemental analyses suggest that most of this material is raw or spent shale fines. However, Fruchter et al. [10] showed that As, Cr, Co, V and Sb were elevated in particles in the 1.1- to  $2.0\text{-}\mu\text{m}$  size fraction compared to raw and spent shales, suggesting another source such as thermal oxidizer emissions or diesel particulates. This fugitive dust could be inhaled by workers or transported away from the site and deposited in the surrounding countryside. The resultant health and environmental impacts have not been investigated.

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Table 10. Elemental Composition of Particulates Collected from the Paraho Semiworks Retort in November 1977 by Fruchter et al. [10]

	Particle Size ( $\mu\text{m}$ )	Elemental Concentration in Particulates ( $\text{ng}/\text{m}^3$ )				
		As	Co	Cr	Mn	Sb
Retort Site	>7.0	158 ± 9	24.2 ± 0.6	76 ± 4	610 ± 20	4.4 ± 0.5
	3.3-7.0	60 ± 4	9.8 ± 0.3	32 ± 2	193 ± 9	2.5 ± 0.3
	2.0-3.3	31 ± 2	5.8 ± 0.3	24 ± 2	98 ± 5	1.3 ± 0.3
	1.1-2.0	30 ± 2	5.2 ± 0.3	23 ± 2	76 ± 5	1.8 ± 0.3
	<1.1	159 ± 11	52.6 ± 1.4	280 ± 15	700 ± 30	13 ± 1.0
Crusher Site	>7.0	77 ± 11	11.0 ± 0.2	44 ± 1	326 ± 11	3.3 ± 0.7
	3.3-7.0	23 ± 4	4.7 ± 0.2	19 ± 1	101 ± 5	1.4 ± 0.3
	2.0-3.3	13 ± 2	2.3 ± 0.1	13.2 ± 0.8	46 ± 3	0.71 ± 0.25
	1.1-2.0	12 ± 2	2.0 ± 0.1	21 ± 1	37 ± 3	0.56 ± 0.21
	<1.1	254 ± 34	20.9 ± 0.6	146 ± 4	1070 ± 30	8.22 ± 1.8
Tailings Pile	>7.0	125 ± 20	20.7 ± 0.6	107 ± 4	605 ± 35	5.9 ± 1.3
	3.3-7.0	71 ± 12	12.1 ± 0.4	69 ± 3	260 ± 12	3.4 ± 0.8
	2.0-3.3	46 ± 8	7.9 ± 0.3	50 ± 3	169 ± 9	3.4 ± 0.8
	1.1-2.0	46 ± 8	8.2 ± 0.4	48 ± 3	150 ± 9	2.2 ± 0.6
	<1.1	301 ± 48	61.3 ± 1.5	378 ± 14	1360 ± 50	18.3 ± 3.9
Background Site	>7.0	1.56 ± 0.33	0.33 ± 0.02	1.89 ± 0.09	9.2 ± 0.4	0.066 ± 0.016
	3.3-7.0	0.64 ± 0.14	0.18 ± 0.01	1.81 ± 0.08	4.3 ± 0.2	0.046 ± 0.012
	2.0-3.3	0.52 ± 0.13	0.13 ± 0.01	1.46 ± 0.07	2.0 ± 0.2	0.030 ± 0.014
	1.1-2.0	0.43 ± 0.10	0.12 ± 0.01	1.42 ± 0.08	2.1 ± 0.2	0.057 ± 0.013
	<1.1	3.77 ± 0.83	0.81 ± 0.04	13.7 ± 0.3	16.2 ± 0.7	0.29 ± 0.04

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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