Source Characterization Studies at the Paraho Semiworks Oil Shale Retort

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May 1979

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ABSTRACT

In order to determine the redistribution of trace and major elements and species during aboveground oil shale retorting, the Pacific Northwest Laboratory carried out a comprehensive program for the sampling and analysis of feedstock, products, effluents, and ambient particulates from the Paraho Semiworks Retort. Samples were obtained during two periods in 1977 when the retort was operating in the direct mode. Careful attention was paid to obtaining samples that were as representative as possible and to preserving these samples until they could be analyzed. The analysis of some of the more unstable samples was performed on site.

To analyze samples for a large number of elements and to ensure accuracy of the results, researchers employed a multitechnique analytical approach. The techniques included instrumental neutron activation, x-ray fluorescence, various forms of atomic absorption spectroscopy, and dc arc plasma emission spectroscopy. The data were statistically analyzed to determine both the precision of each technique and the agreement between techniques.

The data were used to construct mass balances for 31 trace and major elements in various effluents, including the offgas. The computed mass balances indicated that ~1% or greater fractions of the As, Co, Hg, N, Ni, S, and Se were released during retorting and redistributed to the product oil, retort water, or product offgas. The fraction released for these seven elements ranged from ~1% for Co and Ni to 50 to 60% for Hg and N. Approximately 20% of the S and 5% each of the As and Se were released.

Ambient aerosols were found to be elevated near the retorting facility and associated crushing and retorted shale disposal sites. Approximately 50% of these particles were in the respirable range ($<5 \mu\text{m}$). The elevated dust loadings are presently very local, as indicated by relatively low aerosol loadings at background sites 100 to 200 m away. Because of the experimental nature of the present retort, state-of-the-art dust control measures have not been employed; this qualification should be considered in interpretation of the aerosol data.

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CHARACTERIZATION STUDIES AT THE PARAHO SEMIWORKS OIL SHALE RETORT

INTRODUCTION

Oil shale reserves of the Green River formation in Colorado, Utah and Wyoming have the potential to provide anywhere from 300 million to 2 trillion barrels of oil, depending on the various economic, technical and environmental assumptions made in the estimate. Even the lower very conservative figure amounts to more than five times the United States' proved petroleum reserves, and moderate estimates of 600-800 billion barrels compare favorably with both the United States' coal reserves and the entire world's proved reserves of petroleum. Thus, if the technological, economic and political barriers to the production of shale oil can be overcome, oil shale could become an important source of precious liquid hydrocarbons.

The source characterization studies detailed in this report, which were sponsored by the U.S. Department of Energy, Office of Health and Environmental Research, are intended to provide detailed and accurate information on the types and amounts of various substances which may be emitted to the environment from oil shale retorting processes, or which may find their way to the environment during subsequent portions of the shale oil cycle. Such information is vital to related health and environmental fate and effect studies. The data presented here are related specifically to one process, the Paraho direct heated Semiworks Retort at Anvil Points, Colorado. However, it is probable that many of these data will have considerable general validity for all types of oil shale retorting processes.

The objectives of this initial characterization study at Paraho were to (1) calculate a representative mass balance for a number of trace and major elements of potential environmental significance; 2) obtain information on the physical and chemical forms of certain elements emitted from the retort; 3) determine elemental distributions of particulates emitted from the crushing and retorting operations; 4) determine the classes of organic compounds, and,

in some cases, the specific organic compounds and their amounts in the product oil and water from the Paraho retort; and 5) to determine the effects, if any, of the operation of the pilot and semiworks retorts on the soil and groundwater immediately adjacent to the plant site. The latter two objectives are still ongoing at the time of this report. An additional important goal of the study was to find or develop and verify suitable analytical technology to meet these objectives.

DESCRIPTION OF THE PARAHO RETORT PROCESS

The Paraho surface retorting process has been described elsewhere (Jones 1976). It is presently operated by Development Engineering, Inc. (DEI) at Anvil Points, Colorado at the former U.S. Bureau of Mines site. The shale used in the process is obtained from a room and pillar mine in the Mahogany Zone of the Green River formation. The mine at Anvil Points is located at an elevation of about 2440 meters, some 600 meters above the present retort. For the present pilot and semiworks retorts, the shale is trucked about 9 kilometers down a haul road. A proposed commercial module would be located closer to the mine and shale would be handled with conveyors. At the processing site the mined shale is crushed and screened to between minus 7.6 cm and plus 0.6 cm. The crushed shale fraction (10-15%) less than 0.6 cm is not presently used in the retort.

DEI has recently operated two retorts at Anvil Points, a 0.77-m ID by 18-m-high pilot plant unit and a 2.6-m ID by 23-m semiworks retort. All of the studies detailed in this report were conducted on the semiworks retort. Both of the retorts can be operated in either a direct or indirect heated mode. All of the samples used in this study were obtained during direct heated operation.

In direct heated operation, illustrated in Figure 1, controlled combustion within the retort provides the heat necessary for retorting. The process is continuous and flows are countercurrent with the gas phase flowing upwards. The uniform downward flow of shale is controlled by a patented, hydraulically operated grate mechanism. Input raw shale is distributed evenly at the top by

FIGURE 1. Paraho Surface Retorting Process (Direct Mode)

a rotating distributor and is then preheated by rising hot gases in the mist formation zone. Next, the preheated shale passes through the retorting zone where the organic "kerogen" is decomposed into an oil mist, gas, and carbon residue (coke). The retorted shale then enters the combustion zone of the retort where the carbon residue and recycle gas serve as fuel for combustion. Input air is distributed evenly across the bed along with the recycle gas

in this retort zone. In the bottom of the retort, the shale is cooled by the incoming bottom recycle gas, giving its heat to this gas; the retorted shale then exits through the bottom of the retort and is conveyed to a storage site. The oil mist produced is carried out the top of the retort through the offgas collector and is separated from the gas by a coalescer and electrostatic precipitator. The product collected is an oil-water emulsion of about 5 wt% water. The emulsion produced during each shift is collected in a small gauging tank where it can be sampled. It is then pumped to a settling tank where the water is separated and drained, and the "dry" product oil is then pumped to storage.

SAMPLE COLLECTION

Sampling is critical to a program of this type because meaningful analytical results depend on the integrity and representativeness of the samples. Obtaining representative samples from each important process stream at an operating pilot plant presents a number of difficulties. Contamination of the samples is another potential problem during field sampling operations. Fortunately, the Paraho Semiworks Retort is well designed for the purposes of sampling, as discussed below. After consultation with DEI personnel, a sampling program was developed to achieve the desired results. The samples were collected mainly during two field trips, one for four days in August 1977 and one for three days in November 1977. Sample collection and necessary onsite analyses were performed using a PNL camper-mounted mobile laboratory. The types of samples collected may be divided into six categories:

- 1) solid samples
- 2) oil samples
- 3) water samples
- 4) gas samples
- 5) ambient particulate samples, and
- 6) baghouse fine samples.

SOLID SAMPLES

A sample was taken of both the raw feed shale and the retorted shale during each of the seven days at the plant site. The samples were obtained from the raw and retorted shale samplers installed in the semiworks retort by DEI. These systems consist of a timer-controlled flip gate mechanism which periodically removed a sample from the raw or retorted shale conveyor. The samples were then crushed to a powder in the sampling system and deposited in a container. Twenty-four-hour composites of about 20-25 kg were collected in this manner and then mixed and split into smaller samples. Some of the solid samples obtained were splits of samples taken by T. R. Wildeman of the Colorado School of Mines for his studies (Wildeman and Heistand 1979). The representatives of the Paraho raw and retorted shales have been studied in detail for various time periods by Wildeman and Heistand (1979) and found to be essentially constant for 24-hour composites.

OIL SAMPLES

Samples of product oil plus a small amount of product water were collected for each 24-hour period during the seven days at the plant site. The samples were taken from either the 65-barrel or 200-barrel collection tanks at the retort. Most of the samples were 1 liter in volume, but a 60-liter sample was taken on August 24, 1977. In addition, a 60-liter sample of the "dry" product oil was taken from the large separation tank during August 1977. The oil in this tank probably represented a 10- to 12-day production period, and it contained less than 1 wt% water. The small 1-liter samples were collected in Teflon bottles; the larger samples were collected in Teflon-lined stainless steel kegs. The containers were filled as full as possible to minimize headspace, and the headspace was purged with nitrogen. Nitrogen was not actually bubbled through the sample so as to minimize volatile loss. The samples were cooled immediately in an ice bath and transported to the laboratory packed in ice.

WATER SAMPLES

Samples of the product water, co-produced in the retort with the oil, were collected during each of the seven 24-hour sampling periods. Because

very little water is produced by the Paraho process (about 5% by weight), it was difficult to obtain large samples from the gauging tank. Approximately 1 liter of water was collected for each 24-hour period. In addition, one 60-liter product water sample was taken from one of the large separation tanks. The 1-liter samples were filtered through quartz wool to remove oil and grease. One 250-m ℓ aliquot was immediately frozen in dry ice to preserve the As species for later determination. Another 250-m ℓ aliquot was placed in an acid-leached glass bottle and acidified for Hg determination. The precipitate which formed upon acidification was saved for later analysis. Another 250-m ℓ aliquot was adjusted to pH 12 with Ultrex NaOH for B and Se analysis. The remainder of the sample was left untreated for other analyses. All the samples were placed in Teflon bottles and packed in ice for shipment to the laboratory. Values for Eh, pH, S⁼, and total dissolved Hg were determined immediately onsite.

GAS SAMPLES

Samples of gas from the retort were taken both from the recycle gas line and the thermal oxidizer flare stack. Gas samples were obtained from a point downstream from the thermal oxidizer using a quartz probe. Recycle gas samples were taken from a point downstream from the pressure side of the recycle compressor. A number of different samples were taken for various purposes as described below.

Bulk gas samples from each sample point were taken using evacuated, Teflon-lined stainless steel bottles. Gas volumes of 50 to 300 liters were scrubbed by water and NaOH impinger solutions at both gas sampling sites for trace metals. A 0.4-micron nucleopore filter was placed in front of the impinger trains to measure particulates and oil mist. Acid impinger solutions were also used as gas scrubbers at the thermal oxidizer. These acid impingers were tried on the recycle gas line, but proved rather unsatisfactory because of heavy sudsing. Gas samples for trace organic analysis were passed through small stainless steel tubes filled with Tenax resin.

A number of gas samples were also taken for speciation analysis. Samples of both thermal oxidizer and recycle gases were analyzed for sulfur, mercury, and arsenic species.

AMBIENT PARTICULATE SAMPLES

Ambient aerosol collection was conducted at the Paraho facility using HiVol samples and particle sizing cascade impactors so that both total elemental loadings and elemental distributions versus particle size could be determined. Collection sites were located adjacent to the major aerosol generating activities associated with the retorting facility including crushing, retorting, and tailings disposal. Aerosol sampling was also conducted at a "background" site considerably removed from onsite retorting activities.

Anderson "2000" impactors were employed for all particle sizing. The impactors were housed in air sampling shelters in order to minimize errors due to direct dust fall and to short-term wind effects. Whatman 41 filter paper was utilized for an impaction surface on all impaction stages and also as the backup filter.

Sampling was conducted during two periods, August 23-26 and November 15-17, 1977. Sampling was conducted during weather conditions varying from clear skies to broken clouds, generally with a gentle breeze of 1 to 5 mile/hr. The aerosol sampling was terminated during gusty winds and/or rain showers. The August data are subject to a slightly greater degree of uncertainty, since these were the first field samples taken and field procedures were being developed during this period. Some parameters, such as the optimum sampling interval to produce stage loadings suitable for analytical purposes without overloading and subsequent bounce-down, were uncertain before the August sampling period. Also improved accuracy in flow calibration and sampling volume was achieved during the November sampling with the addition of improved sampling equipment which contained flow controllers and allowed a better visual determination of flowrate during the sampling interval.

BAGHOUSE FINE SAMPLES

Samples were obtained from two dust-control baghouses installed in the plant. The raw shale fines were collected from a baghouse located where the raw shale conveyor leaves the raw shale storage bin. Samples from this baghouse were obtained by scraping the walls of the baghouse with a plastic scraper. Samples of the retorted shale fines were obtained from a conveyor which carries these fines from a baghouse at the bottom of the retort out to

the retorted shale pile for disposal. Because of the differences in volumes of material produced, the raw shale fines probably represent several days of operation, while the retorted shale fines represent several hours at most.

GENERAL SAMPLE PREPARATIONS

SOLID SAMPLES

Samples of the raw and retorted shale were received from the Paraho samplers as gravel-sized particles or smaller. These samples were further ground to pass a 140-mesh sieve using alumina jar mills. Further grinding was considered unnecessary for analytical purposes as it had the potential for causing significant contamination and alteration of the samples. The ground raw and retorted shale samples were blended in a polyethylene mixer and split, using a riffle splitter, into 50-g aliquots for analysis.

The baghouse fines were sieved in order to determine the size distribution of the particles, and each size fraction was analyzed separately. Subsamples of those fractions larger than 140 mesh were further ground for x-ray fluorescence (XRF) analyses, which require fine particles.

LIQUID SAMPLES

Oil samples were warmed to room temperature, shaken and sampled directly. They were not filtered.

The water samples were filtered at the site through quartz wool to remove oil and grease. No noticeable precipitate had formed in any samples except those that had been acidified. The acidified samples were further filtered at the laboratory. The other samples were shaken thoroughly and directly sampled. Further sample preparation for each analytical method will be described under the appropriate section.

AEROSOL SAMPLES

After the aerosol samples had been collected, the Anderson 2000 impactor was disassembled in a laboratory at the retort site, and the Whatman collection stages were cut into quarters and placed into polyethylene bags for return to PNL for subsequent subsampling of the impacted aerosol. Care was

taken to handle the Whatman stages by the edges only and to avoid contact with the impaction dots.

Upon return to PNL, the impacted aerosols from each stage were subsampled by excising approximately 1-cm circles centered about the visible impaction area. This area of interest was excised from the collection stage using surgical scissors and then placed into an acid-cleaned 2/5 dram polyethylene vial. Procedural blanks were prepared by excising identical areas from clean Whatman collection stages.

INORGANIC ANALYTICAL METHODS

THE MULTITECHNIQUE APPROACH

Many of the samples obtained from oil shale retorts are chemically and physically complex, creating the potential for matrix effects as well as other types of interferences in many of the commonly used methods for chemical analysis. Therefore, the techniques employed for inorganic analysis of the Paraho samples were chosen when possible for their relative freedom from matrix effects as well as their sensitivity and precision. Because no one method can now meet all these requirements for all elements of interest, a multitechnique approach was adopted. This multitechnique approach to inorganic analysis also provided an opportunity to assess the strengths and weaknesses of the various methods for different samples. The major techniques used included instrumental neutron activation analysis (INAA), energy dispersive x-ray fluorescence analysis (XRF), dc arc plasma emission spectroscopy, flame atomic absorption spectroscopy, and graphite furnace atomic absorption spectroscopy. Other techniques, including radiochemical neutron activation analysis, cold vapor atomic absorption spectroscopy, ion-selective electrodes, hydride generation, and various gas monitoring devices were used to supplement these techniques for specific elemental and speciation analyses. These methods are described in detail below.

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

The solid samples were crushed, mixed, and split as described above. Sample aliquots of about 0.1 to 0.5 grams were weighed into 2/5-dram

polyethylene vials, and the vials were heat sealed. Each 2/5-dram vial was then placed in a 2-dram polyethylene vial which was also heat sealed. Depending on the irradiation facility, liquid samples were either sealed in the 2/5-dram vials, placed directly into the 2-dram vials and then sealed in plastic bags, or placed in 10-ml screw-cup bottles.

Preparation of Standards

Standards (single or mixed elements), usually in liquid form, were prepared fresh from their stock solution. A known aliquot of the standard was weighed into a 2/5-dram vial. About 50 to 100 mg of Specpure MgO or SiO₂ were added to the vial either before or after irradiation to absorb the liquid standard, and the excess liquid was dried at low temperature. This was done to minimize the geometry effect during counting. Several U.S. Geological Survey standard rock samples including BCR-1, W-1, AGV-1, GSP-1 and PCC-1, and IAEA Standard Soil 5 were also included in each irradiation to provide additional analytical standards.

Sequential Irradiations

The neutron activation procedures used in this laboratory have been described elsewhere (Laul 1979). The basic parameters controlling the determination of elements by sequential INAA are: 1) neutron flux in a reactor, 2) irradiation times, 3) delay interval prior to counting, 4) half-life and γ -ray energy of a radionuclide, and 5) the resolution and efficiency of the detector. Table 1 outlines the irradiation parameters, radionuclide (isotope) produced for each element, half-life, γ -ray energy selected, and optimum decay interval used in the analysis of geological samples. Also listed in Table 1 are the possible γ -ray interferences from other radionuclides and interfering reactions from other elements.

The sequential INAA procedure consists of two irradiation periods and four counting intervals as delineated in Table 1. This scheme is routinely used in this laboratory for geological or other types of samples and is similar to the schemes used in other laboratories. The irradiated samples and standards are counted at an appropriate geometry (shelf position) to limit the counting dead time to less than 15% on a 130 cc Ge(Li) detector (FWHM 1.8 keV for 1332 keV γ) coupled to a 2048-channel analyzer. A pileup

TABLE 1. Instrumental Neutron Activation Analysis (n,γ) Process

TABLE I. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (n,γ) PROCESS				
ISOTOPE	HALF-LIFE	γ-ENERGY SELECTED (keV)	DECAY INTERVAL	POSSIBLE INTERFERENCE
I. ⁵¹ Ti	5.79 m	320	15 m	
²⁷ Mg	9.46 m	1014	↓	²⁷ Al(n,p)
⁵² V	3.75 m	1434		
²⁸ Al	2.32 m	1779		²⁸ Si(n,p)
⁴⁹ Ca	8.80 m	3084	↓	
¹⁶⁵ Dy	2.32 h	95	3-5 h	
⁵⁶ Mn	2.58 h	847	↓	⁵⁶ Fe(n,p)
²⁴ Na	15.0 h	1369		²⁴ Mg(n,p), ²⁷ Al(n,α)
II. ¹⁵³ Sm	46.8 h	103	5-7 d	
¹⁵² Eu	12.7 y	122	↓	
¹⁷⁷ Lu	6.74 d	208		^{177m} Lu(208)
²³⁹ Nb(U)	56.3 h	228		^{177m} Lu(229)
¹⁷⁵ Yb	4.21 d	396		
¹³¹ Ba	12.1 d	496		
¹⁴⁷ Nd	11.1 d	531		
¹⁴⁰ La	40.2 h	816, 1597		
²⁴ Na	15.0 h	1369, 1733		²⁴ Mg(n,p), ²⁷ Al(n,α)
⁴² K	12.4 h	1524	↓	
¹⁸² Ta	115 d	68, 1221	40-50 d	
¹⁵² Eu	12.7 y	122, 1408	↓	
¹⁴¹ Ce	32.5 d	146		⁵⁹ Fe(143)
¹⁶⁰ Tb	72.1 d	299		²³³ Pa(300)
²³³ Pa(Th)	27.0 d	312		
⁵¹ Cr	27.8 d	320		
¹⁸¹ Hf	42.5 d	482		
⁸⁵ Sr	64.0 d	514		
⁹⁵ Zr	65.5 d	757		¹⁵⁴ Eu(757)
¹³⁴ Cs	2.05 y	796		
⁵⁸ Co(Ni)	71.3 d	811		¹⁵² Eu(811)
⁴⁶ Sc	83.9 d	889, 1121		
⁸⁶ Rb	18.7 d	1078		
⁵⁹ Fe	45.6 d	1099, 1292		
⁶⁵ Zn	243.0 d	1116		¹⁵² Eu(1112), ⁴⁶ Sc(1121)
⁶⁰ Co	5.26 y	1173, 1332		
¹²⁴ Sb	60.3 d	1691	↓	

PARAMETERS { NEUTRON FLUX = 6×10^{12} n/cm²/sec
IRRADIATION I - 5 MINUTES
IRRADIATION II - 6 HOURS

rejector amplifier or a pulser is used in the system to minimize or account for the pulse losses (in high dead time cases).

Short Irradiations

Samples and standards (with Cu foil flux monitors) were individually irradiated at a flux of 1×10^{13} n/(cm²·s) for 5 min in the pneumatic facility ("rabbit" system) of the Washington State University reactor. After irradiation, the primary activity produced is that of ²⁸Al ($t_{1/2} = 2.3$ min), which decays rapidly compared with most of the other radionuclides. If the sample is counted immediately after irradiation, the ²⁸Al with its high activity and high γ -energy (1779 keV) would produce a very high Compton continuum, and thus decrease considerably the sensitivities of the other radionuclides. On the other hand, if 15 min or so decay is allowed, then the other radionuclides are more readily measured. Immediately after irradiation, the γ -activity ratio of raw shale ²⁸Al/⁵¹Ti is about 2400; after 15 min, the ratio is reduced to ~160. Thus, decay time is necessary to optimize the detection of other radionuclides.

After the irradiation, the 2/5-dram polyethylene vial containing the sample was transferred into a clean 2-dram polyethylene vial, and, after 15 min, the samples and standards were counted on the Ge(Li) system for 5 min each. A timer was installed in the counting system to yield the actual elapsed time during the count, which was later used to estimate the true decay correction factor for short-lived radionuclides. The elements Ti, Mg, V, Al, and Ca are measured in this counting interval. The major interfering reactions are ²⁸Si(n,p)²⁸Al and ²⁷Al(n,p)²⁷Mg. These interferences were evaluated and were found to amount to 20% Si = 0.14% Al, and 10% Al = 2.8% Mg. The oil shale samples had Si/Al ratios similar to the geological rock standards so the Al correction from Si was insignificant. The Mg correction from Al was significant in most of the solid samples, and therefore Mg concentrations by INAA were not reported.

Following the first counting interval, the irradiated samples were allowed to decay for 3 to 5 hr to let the short-lived radionuclides decay completely, and then the samples were again counted on the Ge(Li) system for 10 to 15 min.

each. The elements Dy, Mn, and Na are measured in the second counting. The major interferences are $^{56}\text{Fe}(n,p)^{56}\text{Mn}$, $^{24}\text{Mg}(n,p)^{24}\text{Na}$, and $^{27}\text{Al}(n,\alpha)^{24}\text{Na}$, respectively. The contribution to Mn from Fe was negligible. The contributions for Na are 7.0 ppm from 1% Mg and 5.0 ppm from 1% Al in the rabbit system. Thus, with 5 min of irradiation and two optimum decay intervals, it is possible to measure seven elements (Ti, V, Al, Ca, Dy, Mn, and Na) in the soil oil shale samples.

Long Irradiations

To determine the elements characterized by longer half-life isotopes, appropriate standards were irradiated at a thermal neutron flux of 1×10^{13} n/(cm².s) for 5 to 7 hr in the Washington State University or Oregon State University reactors. The samples were allowed to decay for 3 to 5 days to let the major ^{24}Na activity decay considerably. The irradiated samples were transferred into clean 2/5-dram polyethylene vials and each 2/5-dram vial was then placed in a 2-dram polyethylene vial. The samples and standards were then counted for 30 to 100 min each on a Ge(Li) detector system. Figure 2 shows a typical spectrum of the BCR-1 sample counted for 30 min after a 7-day decay interval. There are many radionuclides identified in the spectrum, but only short- and medium-lived radionuclides with selected γ -energies (Table 1) for elements Sm, Eu, Lu, U via ^{239}Np , Yb, Ba, Nd, La, Na, and K are measured in this counting interval. The element Na is also determined in the short irradiation and this provides an additional check on the Na value obtained in this counting from the long irradiation.

After the completion of the first count, the samples were allowed to decay for 40 to 50 days to let the short- and medium-lived activities decay completely or considerably. The samples and standards were then counted for 100 to 1000 min. The bottom part of Figure 2 shows a spectrum of the BCR-1 sample counted for 100 min after a 40-day decay period. Fifteen elements (Ta, Eu, Ce, Tb, $^{233}\text{Pa}(\text{Th})$, Cr, Hf, Ba, Sr, Cs, Rb, Fe, Zn, Co, and Sb) corresponding to the radionuclides (isotopes) and selected γ -ray energies listed in Table 1 are measured in this count.

FIGURE 2. Gamma-Ray Spectra of Neutron Irradiated USGS Standard Basalt After 7-Day and 40-Day Decay Intervals

After the completion of Ge(Li) counting, the samples and standards were later counted for 30 to 1000 min on a Ge(Li)-NaI(Tl) coincidence and non-coincidence counting system. Figure 3 displays spectra of coincidence and noncoincidence γ -rays of the BCR-1 standard counted for 30 min after a 50-day decay interval. The peak/Compton ratios and detection sensitivities for many elements such as Ce, Cr, Ba, Sr, Nd, Rb, Zn, and Sb are greatly increased in the noncoincidence spectrum. The 1116-keV peak of Zn is better resolved by the reduced peak tail of the 1121-keV peak of ^{46}Sc in the noncoincidence spectrum. The 146-keV peak of ^{141}Ce , unlike in normal Ge(Li) counting, contained only a small contribution from the 143-keV peak of ^{59}Fe . The element Ni, previously not measured in the normal Ge(Li) counting, was easily measured in the noncoincidence counting. Overall, the accuracy and relative precision for many elements was improved by a factor of about 3 by noncoincidence counting relative to the normal Ge(Li) counting. Sensitivity was improved by a factor of about ten.

Computer Processing for INAA

The computer code used to process gamma spectra in our laboratory is called CANGAS (Computer Analysis for Gamma-ray Spectrometry) and has been described elsewhere (Laul et al. 1979). CANGAS is based on a manual selection approach of a photopeak area and Compton background channels of the identified photopeaks of interest in a spectrum. The program first checks for any shift in the assigned peak center (channel) in an allowable shift range (1 to 6 channels) with an iterative maxima summing process and a peak symmetry value. A shift of 0.5 channels is allowed each iteration in the direction that causes the value of peak symmetry to decrease. Iterations continue until the peak symmetry value changes sign. At this iteration, the smaller absolute value between the two peak symmetry values determines the final peak shift, and thus the peak center. After locating the peak center, the program integrates the photopeak according to the assigned width in a reference library. The program also shifts the assigned Compton background channels according to the integral shift in the peak center and also allows an additional shift of one channel by a minimum summing iterative process.

X-RAY FLUORESCENCE ANALYSIS

Our group uses two XRF systems for rapid simultaneous elemental evaluation. The primary system is a KEVEX-810 multiple secondary unit; the other system is a PNL-built isotopic unit. These systems have been recently improved by the addition of several isotopic sources including 100-mCi isotopic sources of ^{55}Fe , ^{109}Cd , and ^{241}Am , as well as Zr and Ag secondary sources. The reason for using multiple sources is that the most efficient excitation of an element can be achieved by having the excitation energy or source energy slightly above that of the electron binding energy of the element being excited. These differences are illustrated in Figures 4 and 5.

Sample Preparation for XRF Analysis

Solids

Samples of from 0.2 to 1.5 g of powder (<140 mesh) are pelletized in a 3.2-cm-dia, 27,000-kg laboratory press. They are either pelletized directly

FIGURE 4. X-Ray Fluorescence Spectrum of a Spent Oil Shale Using a Zr Secondary Excitation Source

FIGURE 5. X-Ray Fluorescence Spectrum of a Spent Oil Shale Using a Ag Secondary Excitation Source

or are pelletized after first mixing with an equal weight of cellulose (TLC reagent grade, J. T. Baker).

Oils

A one-ml oil sample is pipetted onto a prepared slide with a 1/8-mil polypropylene seal on the flush side. The mounted sample is placed in a laminar flow hood and allowed to attain a highly viscous state. Normally about a day is required with a resultant 5 to 15% weight loss for most crude oils. The sample so prepared generates very little outgassing when exposed to vacuum in the x-ray system.

The analysis requires a 6-min x-ray exposure using a tungsten x-ray primary beam with a filtered Zr or Ag secondary source.

If there is a concern for loss of volatile inorganics, the sample can be processed in air, eliminating the evaporative step. This procedure, however, requires the use of a prepared multielement standard to compensate for the back-scattering and absorption caused by air. Sensitivities for the low Z elements are diminished by a factor of 5 or 6 for air compared to vacuum. Volatilization losses do not seem to be significant with most crude and shale oil samples.

Table 2 presents a comparison of neutron activation analysis (NAA) and XRF analysis of a crude oil from Wilmington, California, and a Paraho shale oil.

Comparison of these analyses shows that, except for the case of arsenic, the results are in good agreement, which provides an indication of the accuracy

TABLE 2. Comparison of Neutron Activation Analysis and X-Ray Fluorescence Analysis of a Crude Petroleum and a Crude Shale Oil

Elements, ppm	Wilmington Crude Petroleum			Paraho Oil Collected 8-25-78		
	Method			Method		
	NAA	XRF-Air	XRF-Vac	NAA	XRF-Air	XRF-Vac
10% Error						
As	0.25	0.08 ± 0.04	0.14 ± 0.07	31 ± 2	23 ± 2	19 ± 2
Br	<1	0.11 ± 0.06	0.27 ± 0.09	<0.2		<0.14
Ca			<10			245 ± 29
Cl	6		<126	3.0 ± 0.9		<140
Co	1.21	1.31 ± 0.2	1.79 ± 0.36	1.39 ± 0.08		1.44 ± 0.42
Cr	0.15	<1.0	<1.47			1.55 ± 0.66
Cu	<10	1.50 ± 0.2	0.48 ± 0.27	1.1 ± 0.04	0.83 ± 0.12	0.97 ± 0.23
Fe	32	37 ± 3	40 ± 4		59 ± 5	74 ± 8
Ga		<0.08	<0.14			<0.11
Hg		<0.3	<0.51			
K			<20			41 ± 15
Mn	<0.2	<0.38	<0.67	0.4 ± 0.05	0.45 ± 0.25	<0.51
Mo		<0.19		<3		
Nb		<0.17				
Ni	54	58 ± 4	62 ± 6		2.72 ± 0.20	2.76 ± 0.36
Pb		<0.4	<0.60		<0.40	<0.40
Rb		<0.13	<0.17		<0.19	<0.14
S, %	1.58		1.63	0.99 ± 0.08		0.89 ± 0.10
Se	0.37	0.37 ± 0.07	0.38 ± 0.10		0.92 ± 0.07	0.72 ± 0.12
Sr		<1.2	<1.6		<1.3	<1.2
Ti			<2.5	2.6		4.1 ± 1.9
V	47	46 ± 3	56 ± 6	0.29 ± 0.01		<1.29
Y		<0.14				
Zn	1.07	1.4 ± 0.1	1.7 ± 0.2	<0.70	0.57 ± 0.09	0.55 ± 0.13
Zr		<0.16				

of the XRF method. It is possible that some volatile forms of arsenic are lost during the XRF sample preparation. The XRF determination also provides data on a number of elements not easily obtainable by other methods.

Process Waters

We have developed and validated three x-ray fluorescence procedures for use in the analysis of oil shale waters, including process waters and impinger solutions. One method involves evaporation of a small volume (100 μ l) of solution into a 1-cm dia area and placing the sample into the constant flux area of the x-ray beam. This method is rapid but requires a homogeneous sample. It also presents difficulties with low Z elements when there is mass absorption due to organics.

Another method involves freezing the solution into a thin wafer and exposing it to x-rays under vacuum for a short period. This application has the advantage of no volatile loss. The primary disadvantage is the necessity of relatively high scattering resulting from the mass of water.

The most useful and versatile procedure is addition of a known weight of solution (10 to 50 g) to 50 mg of cellulose. The sample is evaporated into a laminar flow hood at ambient temperature, homogenized, and pressed into a weighed, 3.18-cm-dia wafer, and its weight is determined. Counting time is 60 min at 40 kV and 13.5 mA using a Zr or Ag secondary source. The resultant spectra are reduced using a computer program that corrects for peak overlap, mass absorption, and elemental enhancement. Differences in spectra using two of the techniques for the same process water sample are illustrated in Figures 6 and 7. Where comparison with determinations from other methods considered reliable were available, the agreement in the reported values was generally good with the difference between methods usually less than 10%.

Computer Processing for XRF

Data reduction of the multichannel analyzer output is accomplished by FORTRAN computer programs SAP and SAP3 (Nielson 1977a). The programs correct for absorption, particle size effects, enhancement, and energy overlaps. A direct peak analysis provides rapid determination of net peak areas and is background independent. Existing data reduction for libraries are for Zr

FIGURE 6. X-Ray Fluorescence Spectrum of Oil Shale Process Water Using Cellulose Water Technique

(15.747 keV) secondary source (Si to Sr) K electron, (Pb) L electron; Ag (22.105 keV) secondary source (K to Mo) K lines; and ^{241}Am (59.4 keV) isotopic source (Si to Nd) K lines. Development of libraries for ^{55}Fe (5.895 keV), ^{109}Cd (22.105 keV) and Ti (4.509 keV) are in progress.

The data reduction computer program, SAP3, developed by Nielson (1977a) was used to process the XRF spectra obtained from the Paraho samples. The SAP3 program was originally developed for use with pelletized solid samples, but was successfully applied in this instance to the oil and water samples after some minor modifications to the program.

The SAP3 program smooths spectral data, computes net peak areas, and computes elemental concentrations from a thin-film spectrometer calibration. It then performs peak overlap corrections and three matrix corrections for a) self absorption, b) particle size, and c) enhancement. Spectral analysis

FIGURE 7. X-Ray Fluorescence Spectrum of Oil Shale Process Water Using 1-cm Spot Technique

and corrections require no operator attention beyond entry of sample parameters such as weight, analysis livetime, and if particle size corrections are desired, the estimated mean particle size and density.

The SAP3 program is unique among other x-ray data reduction programs in two major aspects: its peak analysis method (Nielson 1977b) and its matrix correction method (Nielson 1977c). Peak analysis uses a modification of the Covell method which yields partial net peak areas which are independent of linear background and are proportional to the total net peak areas. The method is thus of particular advantage for x-ray fluorescence spectra, which are frequently too crowded for reliable background subtraction. The method has good precision and permits corrections for peak overlap using simple peak ratio (alpha) coefficients.

Matrix corrections rely on estimating an approximate light element ($Z \leq 13$) content of the sample from the incoherent and coherent scatter peaks after they

have been corrected for absorption and for scattering from the heavy ($Z \geq 13$) elements. The total sample absorption due to both light and heavy elements is iteratively computed and used in self absorption, particle size, and enhancement corrections. Since the corrections are based on the thin-sample x-ray calibration, repeated calibrations for specific sample types are avoided. Samples having average atomic numbers ranging from 5 to 13 have been successfully analyzed by SAP3. Details of the theory and description of the peak analysis and matrix correction methods have been reported by Nielson (1977b, 1977c).

Calibration for SAP3 uses thin uniform deposits (50 to 120 $\mu\text{g}/\text{cm}^2$) of single metals or binary compounds evaporated onto 0.013-mm mylar backings (Micromatter, Inc., Seattle, WA). Sensitivities determined from the foils are plotted as a function of x-ray energy, and the resulting curves are smoothed to establish the multielement thin-sample sensitivity curves. The thin standards are analyzed under identical conditions to those used for the samples. Peak overlap coefficients are also determined from these standards. Calibration of the scatter peaks relies on analysis of a standard reference material. The spectrum from this analysis is then analyzed with various scatter peak calibration constants until satisfactory results are obtained. The constants are then entered in the library for use in future analyses. The constants depend only on the instrumental geometry and excitation conditions.

DC ARC PLASMA EMISSION SPECTROSCOPY

Plasma emission spectroscopy is in routine use in our laboratory for sequential elemental analysis of aqueous and fused solid sampling in the oil shale characterization programs. The system in use is a Spectrospan III system employing a dc argon plasma excitation system and an ultrahigh resolution echelle grating spectrometer. The greatest value of the system has been for boron analysis; however, procedures have been tested and satisfactory results obtained in aqueous samples for the 32 elements shown in Table 3. Because of the very high temperature of the argon arc (6000 K), chemical interferences are minimal. Ionization interferences, on the other hand, are a problem and must

TABLE 3. DC Arc Plasma Emission Spectroscopy – Approximate Detection Limits for Elements in Aqueous Samples

<u>Elements with Detection Limits 1 to 5 ppb</u>	<u>Elements with Detection Limits 5 to 10 ppb</u>	<u>Elements with Detection Limits 10 to 100 ppb</u>	<u>Elements with Detection Limits 100 to 500 ppb</u>
Be	Li	K	Si
Na	Ti	Fe	P
Mg	Co	In	As
Ca	Ni	Au	Se
Sr	B	Pb	Sn
Ba	Ag	Tl	
V	Cd		
Cr			
Mn			
Cu			
Zn			
Mo			
Ag			
Al			

be corrected for in many cases by addition of Li buffer, matrix-matched standards, or the method of standard additions.

Sensitivity drift in the excitation source was a major problem with the instrument in its original form. An improved three-electrode excitation source has recently been retrofitted on our instrument. This source has been operated for up to 5 hr continuously without significant deterioration in the electrodes. Some increased sensitivity has been observed in the new source, but the main improvement has been its stability. Multi-element operation now appears to be a very desirable option with this technique. With suitable modification, the system can become capable of simultaneous determination of a group of 20 elements.

Sample Preparation

Aqueous samples that were homogeneous, including impinger solutions, were analyzed directly with no pretreatment. The powdered solid samples were fused

with a small amount of Ultrex sodium carbonate, and dissolved in Ultrex nitric acid. Approximately 3 g of Na_2CO_3 were used to fuse 500-mg samples of raw and retorted shale. Each fused sample was then dissolved in acid and diluted to 100 mL of solution.

ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption (AA) spectroscopy is a versatile technique that can be used to determine a number of major and minor elements in oil shale samples, including Li, Na, Mg, Al, Si, K, Ca, Fe, Cd, and Hg. Conventional flame atomic absorption was used to determine all of these elements except Hg, which was determined by flameless atomic absorption. We also experimented with the use of a graphite furnace AA technique for determinations of Cd directly in solid samples.

Conventional Flame Atomic Absorption

The instruments used were a Perkin Elmer 403 and an Instrumentation Laboratory Associates 257. Aqueous samples that were homogeneous, including impinger solutions, were aspirated directly. Powdered solid samples were fused with lithium metaborate, with a ratio of LiBO_2 /sample of 6:1.

Commercially prepared aqueous atomic absorption standards were used for most elements. A sample of U.S. Geological Survey standard rock BCR-1 prepared in a similar fashion to the solid raw and spent shale samples was also analyzed as a control.

Graphite Furnace Atomic Absorption

A new state-of-the-art graphite furnace atomic absorption system has recently been set up at our laboratory. The system is an Instrumentation Laboratory Associates Model 257 microprocessor-based spectrometer with D_2 arc background correction. The instrument is equipped with an IL 555B graphite furnace system and FASTAC autosampler. The system is capable of measuring a wide range of elements in both solids and liquids with sensitivities in the picogram range. One of the unique features of the instrument is the use of a tungsten resistance thermometer in contact with a graphite cuvette for direct temperature measurement from room temperature up to 3000°C . The temperature measurement is also used in a feedback circuit to control the heating rate.

Technique development is still under way with this new system; however, it has already been used successfully for the determination of cadmium in raw and retorted oil shale and NBS Standard (coal fly ash) 1633. For solid samples, a rectangular cuvette of pyrolytic graphite is used. One to two mg of sample is weighed out on pyrolytic graphite microboats and inserted into the cuvette. It was found that the samples could be charred up to 400°C without loss of Cd. Ramp atomization up to 1400°C removed all Cd from the Paraho samples. It was found that more highly sintered samples such as NBS fly ash required an atomization temperature of 2000°C for best sensitivity. Standardization was achieved simply by using solution standards dried on the microboats and analyzed under the same conditions using the peak area mode of the microprocessor. The value obtained for NBS fly ash was 1.44 ± 0.15 ppm Cd compared to the certified value of 1.45 ± 0.06 .

By careful temperature programming, it was possible to determine the minimum temperature at which cadmium was released from the sample. About 500°C appears to be the threshold for Cd release from small, finely-ground samples in an inert atmosphere. Under actual retorting conditions, Cd release may be more retarded because of larger feedstock size (1/2 to 3 in) and the presence of oxygen.

Flameless Atomic Absorption for Mercury Analysis

The procedure quantitatively separates Hg from 50 to 150-mg solid samples by a process of sample combustion and thermal decomposition. The separation train (Figure 8) channels Hg-free air to samples, which are subsequently heated to 950°C in an enveloping quartz tube. The high temperature and oxidizing conditions within the tube volatilize Hg from the sample matrix, and an underlying 3 to 4-cm layer of gold-coated quartz beads convert the evolved Hg to elemental mercury vapor (Hg^0). To separate Hg^0 from interfering organic vapors, the effluent sample gases are directed into an alumina column which selectively retains most of the organic vapors but passes Hg^0 . The Hg^0 is finally collected by amalgamation with a column of gold-coated glass beads maintained at room temperatures.

Following the amalgamation step, the column containing the trapped Hg is detached from the separation train and assembled into a flameless atomic absorption system. Here the amalgamated Hg is released by heating the gold-coated

glass beads to 500°C in a N₂ gas stream. The Hg⁰ is swept into a long-pathlength gas absorption cell where it is measured by atomic absorption at 254 nm.

The effectiveness of the procedure has been tested by determining Hg in NBS coal (S.R.M. #1632) and NBS orchard leaves (S.R.M. #1571). These standard reference materials provided known Hg concentrations in representative environmental matrices. The resulting analyses together with Hg analyses for selected coal and oil shale materials are given in Table 4. The data for the two standard reference materials are in reasonable agreement with NBS certified values.

FIGURE 8. Separation Train for Volatilizing Mercury from Sample Materials

TABLE 4. Determination of Hg in NBS Standards and Selected Coal and Oil Shale Materials

<u>Material</u>	<u>Total Hg Found, ppb</u>	<u>Mean Estimated Analytical Error, ppb</u>	<u>NBS Certified Value, ppb</u>
NBS Coal	93,92,93,95,90,97	93 ± 10	120 ± 20
NBS Orchard Leaves	154,168,164,174,147	161 ± 15	155 ± 15
Feed Coal	172,179,155,165,148	164 ± 20	
Solvent Refined Coal	19,16,20	18 ± 3	
Coal Mineral Residue	<5,<5,<5	<5	
Oil Shale (1)	268,274,263	268 ± 20	
Oil Shale (2)	107,101,80,100,98,97	97 ± 10	
Spent Shale	19,12,13,14	15 ± 4	
Shale Oil	153,202,177,138,203	175 ± 30	

BORON ANALYSIS

Boron analysis in oil shale materials presents a special challenge, since it cannot be determined by many of the multielement techniques employed in this study. Many procedures reported in the literature list interferences which make them inapplicable to these samples. After careful consideration, two primary, and quite independent techniques were selected for boron determinations. These techniques were a plasma emission spectroscopy method described earlier, and the Azomethine(H) colorimetric method. Some samples were also checked using a prompt gamma spectrometric method developed elsewhere (Gladney, Journey and Curtis 1976). Publications on the spectrophotometric determination of low-level boron (0.1 to 4 ppm) solutions, plant samples, and soil samples using Azomethine(H) suggested application of the method to oil shale samples. The method is selective and sensitive on geothermal waters, sea water, shale oil and oil shale process water, and suffers from very few interferences.

The procedure for clear solutions (groundwaters) is fairly straightforward. A 4 ml sample is pipetted into a 25-ml polyethylene bottle. It is important that polyethylene or quartz be used throughout to avoid contamination problems. One ml of a buffer washing solution containing ammonium acetate

(pH 4.5) and pentasodium DPTA is added followed by 1 mL of Azomethine(H) indicator. After thorough mixing, the solution is allowed to stand for 1 hr. The solution's absorbance at 415 nm is compared to that of standard boron solutions. A distilled water blank is also run through the procedure.

Liquid materials such as Na_2CO_3 , fused oil shale, shale oil and shale oil retort water which are not clear must be treated to remove the color without losing the boron. In cases where the color is due to organic compounds, the sample may be wet ashed or low-temperature ashed. During the ashing procedure, the pH must be kept high (8-9) to prevent volatilization of boric acid.

SPECIATION METHODS

Mercury Speciation - Product Gases

The total mercury concentration in the flared product gas was measured by using an in-stack quartz sampling probe and absorption tubes containing 80 to 100-mesh gold-coated beads. Samples of the effluent gas were pumped from the thermal oxidizer stack and passed through the gold-coated bead traps to remove total vapor mercury. Total mercury was measured in the recycle gas taken from the pressure side of the recycle compressor. The chemical forms of mercury in the flared gas stream were measured by pumping additional aliquots through selective sorption beds which absorb HgCl_2 , CH_3HgCl , Hg° and $(\text{CH}_3)_2\text{HgCl}$ (Braman and Johnson 1976). After collection, all traps containing mercury were analyzed by flameless atomic absorption spectrometry. The two measurements of total mercury in the recycle gas were 46 and 75 $\mu\text{g}/\text{m}^3$. The range of total mercury observed in the Paraho thermal oxidizer gas was 4.5 to 12 $\mu\text{g}/\text{m}^3$ (Table 5). The speciation measurements indicate that the mercury is emitted to the atmosphere as the metal (Hg°). This observation is to be expected as almost all mercury compounds decompose to Hg° at high temperatures.

Arsenic Speciation

Gas Samples

Figure 9 shows a schematic of the sampling train used for sampling offgases from the Paraho retort for arsenic species. The As traps are adapted from those developed by Johnson and Braman 1975. In this sampling train the oxidized forms

TABLE 5. Mercury and Mercury Species in the Paraho Thermal Oxidizer Gas

Date	Paraho Thermal Oxidizer Gas		
	Total Hg, $\mu\text{g}/\text{m}^3$	Hg Species, $\mu\text{g}/\text{m}^3$	
8-24-77	9 ± 3		
8-25-77	6.7 ± 0.8		
8-26-77	4.5 ± 1.3	as HgCl_2	<0.3
		as CH_3HgCl	<0.2
		as Hg^0	4.5
		as $(\text{CH}_3)_2\text{HgCl}$	<0.1
11-15-77	7.2 ± 0.9		
11-16-77	12 ± 2	as HgCl_2	<0.1
		as CH_3HgCl	<0.4
		as Hg^0	9.4
		as $(\text{CH}_3)_2\text{HgCl}$	<0.4

FIGURE 9. Arsenic Speciation Sampling Train

of As vapor are trapped in the NaOH impingers after passing through the filter. Arsine and methyl arsines in the gas pass through the impingers and are trapped on the silver-coated quartz or pyrex beads. Soft glass is avoided because of its high arsenic blank.

Arsenic on the filters was determined using XRF. Arsenic species in the impingers are determined by the plasma emission spectroscopy-hydride technique described below. Total arsenic in the impingers was determined by XRF.

Product Waters and Impinger Solutions

Inorganic As^{+3} , As^{+5} , and organic $(\text{CH}_3)_x\text{AsO}$ acids are reduced to corresponding arsines from aqueous solutions by successive addition of NaBH_4 . The reduction is pH dependent and associated to the pK_a of the acid. The gaseous arsines are entrained by a He-carrier gas and subsequently frozen out in a liquid nitrogen U-tube. Gradual warming of the U tube volatilizes the various arsines according to their boiling points and introduces them to a dc discharge system incorporating a monochromate set at the As emission line and peak height recording system (Figure 10). The combination of pH dependency and difference in boiling points provides the necessary properties for speciation and separation (Table 6).

Sulfur Speciation

Gases from process lines were fed either directly, or through volume dilution systems, into analytical instrumentation for measurements. Hydrogen sulfide levels were measured directly using two different analyzers. The

FIGURE 10. Arsenic Speciation Measurement System

TABLE 6. Speciation Properties for Arsenic Determinations (Braman et al. 1977)

Molecular Form	pKa	pH 1 Undissociated	pH 4 Undissociated	Reduction Product	Boiling Point, °C
As(III), HAsO_3	9.23	1.00	1.00	AsH_3	-55
As(V), H_3AsO_4	2.25	0.943	0.017	AsH_3	-55
Methylarsenic acid					
$\text{CH}_3\text{AsO}(\text{OH})_2$	2.60	0.995	0.038	CH_3AsH_2	2
Dimethylarsenic acid					
$(\text{CH}_3)_2\text{AsO}(\text{OH})$	6.19	1.00	1.00	$(\text{CH}_3)_2\text{AsH}$	35.6

mercaptans were measured potentiometrically in an Interscan sulfur analyzer. The values given for mercaptans should be considered preliminary, although the values for total sulfur (sulfide and mercaptans) should be accurate. Sulfur dioxide was determined by the lowering of potentiometric sulfur response when this species was selectively scrubbed from the process or diluted air stream. Results of these analyses at the Paraho Semiworks Retort are shown in Table 7.

TABLE 7. Sulfur Species at Paraho Semiworks Retort
(11/15/77-11/16/77)

THERMAL OXIDIZER - OFFGAS SAMPLE

11/15	$\text{SO}_2 = 276 \text{ ppm}$	Dilution technique	Interscan ^(a)
	$\text{SO}_2 = 256 \text{ ppm}$	Direct	Interscan
	$\text{H}_2\text{S} < 0.4 \text{ ppm}$	Dilution technique	Interscan
	$\text{RSH} < 0.4 \text{ ppm}$	Dilution technique	Interscan

RECYCLE GAS CONCENTRATION - OFFGAS SAMPLE

11/15	$\text{H}_2\text{S} + \text{RSH} = 2800 \text{ ppm}$	From 11/16 ratio	Interscan
11/16	$\text{H}_2\text{S} + \text{RSH} = 2400 \text{ ppm}$	Direct - dilution	Del-Mar Colorimeter

PROCESS WATER SAMPLE

11/15	Sulfur as $\text{S}^{=}$ = 9.9 ppm
	Total Sulfur = 4.6%

(a) Interscan sulfur analyzer, potentiometric measurement.

Sulfur speciation methods for the retort process waters are in a somewhat less developed state, as a number of widely recognized sulfur methods have been shown to be inapplicable to these complex waters. Table 7 also shows a sulfide analysis of a Paraho process water which we performed using a selective ion electrode, and total sulfur values obtained by neutron activation and XRF. The large differences indicate that the great majority of sulfur in this water sample is not in the form of sulfide. There have been suggestions that the bulk of the sulfur may be present as a combination of sulfur dioxide, sulfur, and thiosulfate, but we have been unable to confirm these suggestions. Work on this aspect of sulfur speciation using ion chromatography is continuing.

INORGANIC DATA FOR THE PARAHO SEMIWORKS RETORT

The complete trace and major element data for Paraho samples analyzed using the multitechnique approach described in the preceding sections are shown in Appendices A-E. Some speciation data can be found in the analytical sections describing these measurements. Interpretation of these data in terms of elemental balances for the retort, a statistical treatment of the data, and a summary of the data are described in subsequent sections of this report.

ANALYSIS OF AUGUST 24, 1977 SAMPLES

Special attention was given to the analysis of samples collected on August 24, 1977, particularly the raw and retorted shale. There were several purposes behind this additional effort. First, a multitechnique intercomparison was carried out to enable objective assessment of the accuracy of the analytical data. The August 24 raw shale in particular has been rigorously characterized for some 50 elements. A large quantity (15 to 20 kg) of this material has been archived and will eventually be made available to other workers in the field as an analytical reference material. The data given in this report combined with additional analyses provided by colleagues at Lawrence Berkeley Laboratory will form the basis for standardization of the material. In addition, a more limited analysis has been carried out on two lots to verify the homogeneity of the material. Finally, the August 24, 1977 samples have been chosen as representative samples for a material balance study for several selected elements of interest.

Data Analysis

Tables 8 and 9 give the complete analytical results for analysis of August 24, 1977 raw and retorted shale for 50 elements. In many cases several techniques were used and it is possible to intercompare results. In general, six replicate samples were analyzed by each analytical technique. The analytical errors shown in Tables 8 and 9 are thus derived from the precision of six analyses. In a few cases only a single determination was made. These include the radiochemical measurement for Cd, Se, Zn, and U, and the graphite furnace AA determination of Cd. The element analyses by the LECO Corporation shown in Table 10 are the result of triplicate determinations. To reduce the data to a form suitable for graphical representation, a simple computer code was used to perform the following operations:

- 1) A minimum error of 2% was assigned to all data. Any data with a reported error less than 2% were set equal to 2%.
- 2) An error-weighted average of the data was computed for each element.
- 3) If more than two analyses were reported, Chauvenet's criterion was then applied and, if necessary, the worst outlier rejected. A new error-weighted average was then computed. This procedure was only followed once per element for each sample because of the small size of each data set. Very few points were actually rejected in this manner. Those which were rejected are noted with an asterisk in Tables 8 and 9.
- 4) Once an appropriate average value was determined a percentage deviation of each individual value from the mean for that element was computed. These values together with the appropriate percentage standard deviation for each point are plotted in Figures 11 and 12. This is a convenient format for viewing all of the data at once. Only elements which were analyzed by more than one reliable technique are plotted; individual determination rejected by Chauvenet's criterion (step 3) are omitted.
- 5) Additionally, a percent root mean squared deviation is computed for each group of data (shown at top of Figures 11 and 12) and a chi-square test was applied to test the validity of the error analysis.

TABLE 8. Multielement Analysis of Paraho-Feedstock Shale Collected 8/24/77
(in ppm except as noted)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Al (%)	3.89 $\pm$ 0.14			3.78 $\pm$ 0.08	3.69 $\pm$ 0.11			3.77 $\pm$ 0.06
As	48.0 $\pm$ 0.7		41.6 $\pm$ 5					44.3 $\pm$ 0.6
B				94 $\pm$ 2				94 $\pm$ 2
Ba	483 $\pm$ 34			515 $\pm$ 8				512 $\pm$ 10
Br	0.57 $\pm$ 0.13							0.57 $\pm$ 0.13
Ca (%)	10.4 $\pm$ 0.5		10.7 $\pm$ 0.5	9.9 $\pm$ 0.1	11.0 $\pm$ 0.4*			10.1 $\pm$ 0.2
Cd		0.64 $\pm$ 0.03				0.61 $\pm$ 0.08		0.64 $\pm$ 0.03
Ce	43.1 $\pm$ 0.9							43.1 $\pm$ 0.9
Co	9.0 $\pm$ 0.1							9.0 $\pm$ 0.1
Cr	36.7 $\pm$ 1.8		39.7 $\pm$ 9.3	33.8 $\pm$ 0.6				34.2 $\pm$ 0.6
Cs	3.84 $\pm$ 0.22							3.84 $\pm$ 0.22
Cu			40.3 $\pm$ 2.3	40.0 $\pm$ 5.5				40.3 $\pm$ 2.1
Dy	2.4 $\pm$ 0.4							2.4 $\pm$ 0.4
Eu	0.60 $\pm$ 0.02							0.60 $\pm$ 0.02
Fe (%)	2.08 $\pm$ 0.04		2.02 $\pm$ 0.10	2.01 $\pm$ 0.04	2.14 $\pm$ 0.04			2.07 $\pm$ 0.02
Ga			8.4 $\pm$ 0.8					8.4 $\pm$ 0.8
Hf	1.75 $\pm$ 0.05							1.75 $\pm$ 0.05
Hg							0.089 $\pm$ 0.005	0.089 $\pm$ 0.005
Ho	0.67 $\pm$ 0.11							0.67 $\pm$ 0.11
K (%)	1.69 $\pm$ 0.11		1.66 $\pm$ 0.02	1.79 $\pm$ 0.03*	1.55 $\pm$ 0.03			1.61 $\pm$ 0.02
La	20.6 $\pm$ 0.7							20.6 $\pm$ 0.7
Lu	0.28 $\pm$ 0.03							0.28 $\pm$ 0.03
Mg (%)				3.42 $\pm$ 0.05	3.59 $\pm$ 0.3			3.46 $\pm$ 0.06
Mn	312 $\pm$ 20		319 $\pm$ 20	314 $\pm$ 22				315 $\pm$ 12
Mo			24 $\pm$ 2.5	20.9 $\pm$ 1.9				22.0 $\pm$ 1.5

TABLE 8. (contd)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Na (%)	1.68 $\pm$ 0.01				1.73 $\pm$ 0.07			1.69 $\pm$ 0.03
Nb			8.0 $\pm$ 0.7					8.0 $\pm$ 0.7
Nd	20.4 $\pm$ 2.1							20.4 $\pm$ 2.1
Ni	23.0 $\pm$ 5.3		24.2 $\pm$ 1.2*	27.6 $\pm$ 0.6				27.5 $\pm$ 0.6
Pb			26.5 $\pm$ 2.1					26.5 $\pm$ 2.1
Rb	74.9 $\pm$ 2.3		74.0 $\pm$ 2.7					74.5 $\pm$ 1.8
S			5730 $\pm$ 500					5730 $\pm$ 500
Sb	2.09 $\pm$ 0.08							2.09 $\pm$ 0.08
Sc	5.77 $\pm$ 0.16							5.77 $\pm$ 0.16
Se	2.1 $\pm$ 0.2	2.0 $\pm$ 0.1						2.03 $\pm$ 0.09
Si (%)			14.1 $\pm$ 0.7		15.2 $\pm$ 0.1			15.0 $\pm$ 0.3
Sm	3.10 $\pm$ 0.3							3.10 $\pm$ 0.3
Sr	674 $\pm$ 24		678 $\pm$ 21	712 $\pm$ 14				696 $\pm$ 11
Ta	0.55 $\pm$ 0.02							0.55 $\pm$ 0.02
Tb	0.37 $\pm$ 0.03							0.37 $\pm$ 0.03
Th	6.33 $\pm$ 0.13							6.33 $\pm$ 0.13
Ti (%)	0.18 $\pm$ 0.02		0.17 $\pm$ 0.02		0.18 $\pm$ 0.01			0.18 $\pm$ 0.01
U	4.2 $\pm$ 0.3	4.6 $\pm$ 0.2						4.5 $\pm$ 0.2
V	86 $\pm$ 6		95 $\pm$ 6	96 $\pm$ 3				94.2 $\pm$ 2.4
Y			14 $\pm$ 1					14 $\pm$ 1
Yb	1.26 $\pm$ 0.11							1.26 $\pm$ 0.11
Zn	67.2 $\pm$ 3.7	63 $\pm$ 3	62.6 $\pm$ 2.3	73.2 $\pm$ 4.0*				63.6 $\pm$ 1.6
Zr				36.2 $\pm$ 1.3				36.2 $\pm$ 1.3

*Deleted from error weighted average.

INAA - Instrumental Neutron Activation Analysis

RCAA - Radiochemical Neutron Activation Analysis

XRF - X-Ray Fluorescence Analysis

PES - Plasma Emission Spectroscopy (Sodium Carbonate Fusion)

FAA - Conventional Flame Atomic Absorption (Lithium Metaborate Fusion)

GFAA - Graphite Furnace Atomic Absorption

CVAA - Cold Vapor Atomic Absorption

TABLE 9. Multielement Analysis of Paraho Retorted Shale Collected 8/24/77
(in ppm except as noted)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Al (%)	4.83 ± 0.05*			4.46 ± 0.05	4.56 ± 0.17			4.48 ± .08
As	59.2 ± 0.9		59.8 ± 1.9					59.4 ± 1.0
B				107 ± 2				107 ± 2
Ba	593 ± 13			613 ± 12				604 ± 9
Br	0.80 ± 0.18							0.80 ± 0.18
Ca (%)	13.1 ± 0.5		13.9 ± 0.7	11.1 ± 0.2	13.2 ± 0.2			13.3 ± 0.2
Cd		0.90 ± 0.04				0.99 ± 0.13		0.91 ± 0.04
Ce	51.5 ± 1.5							51.5 ± 1.5
Co	11.1 ± 0.2							11.1 ± 0.2
Cr	44.3 ± 0.9		49.6 ± 8.9	41.0 ± 3.8				44.2 ± 0.9
Cs	4.68 ± 0.21							4.68 ± 0.21
Cu			56.3 ± 1.0	46.9 ± 5.3				55.9 ± 1.1
Dy	3.5 ± 0.2							3.5 ± 0.2
Eu	0.73 ± 0.02							0.73 ± .02
Fe (%)	2.42 ± 0.04		2.56 ± 0.13	2.35 ± 0.03	2.47 ± 0.08			2.40 ± 0.030
Ga			11.6 ± 1.2					11.6 ± 1.2
Hf	2.11 ± 0.03							2.11 ± 0.03
Hg							0.035 ± 0.003	0.035 ± 0.003
Ho	0.88 ± 0.04							0.88 ± 0.04
K (%)	1.98 ± 0.20		1.94 ± 0.05	2.11 ± 0.05*	1.81 ± 0.03			1.86 ± 0.03
La	24.7 ± 0.3							24.7 ± 0.3
Lu	0.35 ± 0.03							0.35 ± 0.03
Mg (%)				3.88 ± 0.03	4.32 ± 0.09			4.07 ± 0.06
Mn	388 ± 23		420 ± 24	374 ± 28				396 ± 14
Mo			32.7 ± 1.4	41.3 ± 3.9				33.7 ± 1.3

TABLE 9. (contd)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Na (%)	2.15 $\pm$ 0.03				2.24 $\pm$ 0.03			2.19 $\pm$ 0.03
Nb			9.2 $\pm$ 1.5					9.2 $\pm$ 1.5
Nd	22.3 $\pm$ 1.1							22.3 $\pm$ 1.1
Ni	29.7 $\pm$ 4.6		32.1 $\pm$ 3.9	32.4 $\pm$ 1.8				32.1 $\pm$ 1.5
Pb			36.2 $\pm$ 2.0					36.2 $\pm$ 2.0
Rb	89.9 $\pm$ 4.1		88 $\pm$ 2					88.4 $\pm$ 1.8
S			6780 $\pm$ 620					6780 $\pm$ 620
Sb	2.63 $\pm$ 0.15							2.63 $\pm$ 1.5
Sc	6.84 $\pm$ 0.15							6.84 $\pm$ 0.15
Se		2.3 $\pm$ 0.1						2.3 $\pm$ 0.1
Si (%)			17.8 $\pm$ 1.3		18.2 $\pm$ 0.3			18.2 $\pm$ 0.4
Sm	3.68 $\pm$ 0.07							3.68 $\pm$ 0.07
Sr	820 $\pm$ 26*		866 $\pm$ 7	892 $\pm$ 14				879 $\pm$ 12
Ta	0.65 $\pm$ 0.02							0.65 $\pm$ 0.02
Tb	0.42 $\pm$ 0.04							0.42 $\pm$ 0.04
Th	7.55 $\pm$ 0.10							7.55 $\pm$ 0.10
Ti (%)	0.21 $\pm$ 0.04		0.24 $\pm$ 0.01		0.20 $\pm$ 0.03			0.24 $\pm$ 0.01
U	5.3 $\pm$ 0.2	4.9 $\pm$ 0.2						5.10 $\pm$ 0.14
V	111 $\pm$ 13		139 $\pm$ 19	133 $\pm$ 7				129 $\pm$ 6
Y			16.4 $\pm$ 0.9					16.4 $\pm$ 0.9
Yb	1.61 $\pm$ 0.13							1.61 $\pm$ 0.13
Zn	89.2 $\pm$ 3.0	77 $\pm$ 4	86.2 $\pm$ 5.5	93.6 $\pm$ 5.3*				82.3 $\pm$ 2.2
Zr				36.2 $\pm$ 1.3				36.2 $\pm$ 1.3

*Deleted from error weighted average.

INAA - Instrumental Neutron Activation Analysis

RCAA - Radiochemical Neutron Activation Analysis

XRF - X-Ray Fluorescence Analysis

PES - Plasma Emission Spectroscopy (Sodium Carbonate Fusion)

FAA - Conventional Flame Atomic Absorption (Lithium Metaborate Fusion)

GFAA - Graphite Furnace Atomic Absorption

CVAA - Cold Vapor Atomic Absorption

TABLE 10. Major Element Concentrations in Paraho Raw and Retorted Shale Collected August 24, 1977(a)

<u>Element)</u>	<u>Raw</u>	<u>Retorted</u>	<u>Retorted/Raw</u>
Hydrogen (%)	1.50 $\pm$ 0.03	0.167 $\pm$ 0.004	0.111 $\pm$ 0.002
Carbon (%)	15.5 $\pm$ 0.16	6.11 $\pm$ 0.04	0.394 $\pm$ 0.005
Nitrogen (%)	0.66 $\pm$ 0.10	0.298 $\pm$ 0.004	0.45 $\pm$ 0.017
Oxygen (%)	39.6 $\pm$ 1.7	50.7 $\pm$ 1.7	1.18 $\pm$ 0.09
Sulfur (ppm)	6000 $\pm$ 240	5830 $\pm$ 250	0.97 $\pm$ 0.06

(a) Analysis by LECO Corporation.

A number of observations can be drawn from Figures 11 and 12. Agreement between analytical methods is in general quite good, and in almost all cases error bars overlap. One notable exception is the determination of As in the raw shale by instrumental neutron activation and XRF. This is only noticeable since both methods have good precision. Even in this case the disagreement is only 10-15%. A wide range of precision is evident illustrating the advantages of using several different analytical techniques for multielement analysis.

Retorted/Raw Element Ratios

The ratio of an element in the retorted shale to the same element in raw shale is useful because it may be used in assessing a material balance. Furthermore, any systematic analytical errors should tend to cancel when a ratio is computed. To test that premise, the ratio was calculated in a number of different ways. Table 11 shows the elemental ratios calculated from the data in Tables 8 and 9 with errors propagated quadratically. An error-weighted average of the data for each element is given in the last column of Table 11. Those data are then shown graphically in Figure 13. Table 12 provides a summary of the average ratio calculated for each technique with suspected volatile elements such as As, Cd, Se, S, and Hg deliberately omitted. An overall unweighted average was computed for the best data on approximately 20 nonvolatile elements yielding a ratio of 1.20 ± 0.02 . The loss of raw shale mass expected simply from the Fischer assay should yield mineral phase element enrichments of only about 1.10 in the retorted shale. The additional 10% enrichment observed for

FIGURE 11a. Relative Performance of Analytical Techniques Used in the Multielement Analysis of Paraho Raw Oil Shale (8-24-77)

FIGURE 11b. Relative Performance of Analytical Techniques Used in the Multielement Analysis of Paraho Raw Oil Shale (8-24-77)

FIGURE 12a. Relative Performance of Analytical Techniques Used in the Multielement Analysis of Paraho Retorted Shale (8-24-77)

FIGURE 12b. Relative Performance of Analytical Techniques Used in the Multielement Analysis of Paraho Retorted Shale (8-24-77)

TABLE 11. Ratio of Elements in Retorted Shale to Elements in Raw Shale

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Al	1.24 $\pm$ 0.05			1.18 $\pm$ 0.03	1.24 $\pm$ 0.06			1.24 $\pm$ 0.024
As	1.23 $\pm$ 0.03		1.44 $\pm$ 0.05					1.29 $\pm$ 0.03
B				1.14 $\pm$ 0.03				1.14 $\pm$ 0.03
Ba	1.23 $\pm$ 0.09			1.19 $\pm$ 0.03				1.19 $\pm$ 0.03
Br	1.40 $\pm$ 0.45							1.40 $\pm$ 0.45
Ca	1.26 $\pm$ 0.08		1.30 $\pm$ 0.09	1.12 $\pm$ 0.02*	1.20 $\pm$ 0.05			1.23 $\pm$ 0.04
Cd		1.41 $\pm$ 0.09				1.62 $\pm$ 0.30		1.43 $\pm$ 0.09
Ce	1.20 $\pm$ 0.04							1.20 $\pm$ 0.04
Co	1.23 $\pm$ 0.03							1.23 $\pm$ 0.03
Cr	1.21 $\pm$ 0.02		1.21 $\pm$ 0.06	1.21 $\pm$ 0.11				1.21 $\pm$ 0.03
Cs	1.22 $\pm$ 0.09							1.22 $\pm$ 0.09
Cu			1.40 $\pm$ 0.08	1.17 $\pm$ 0.21				1.37 $\pm$ 0.08
Dy	1.45 $\pm$ 0.26							1.45 $\pm$ 0.26
Eu	1.22 $\pm$ 0.05							1.22 $\pm$ 0.05
Fe	1.16 $\pm$ 0.03		1.27 $\pm$ 0.09	1.17 $\pm$ 0.03	1.15 $\pm$ 0.04			1.17 $\pm$ 0.02
Ga			1.38 $\pm$ 0.19					1.38 $\pm$ 0.19
Hf	1.21 $\pm$ 0.04							1.21 $\pm$ 0.04
Hg							0.39 $\pm$ 0.04	.67 $\pm$ 0.09
Ho	1.31 $\pm$ 0.22							1.31 $\pm$ 0.22
K	1.17 $\pm$ 0.15		1.17 $\pm$ 0.03	1.18 $\pm$ 0.03	1.17 $\pm$ 0.03			1.17 $\pm$ 0.02
La	1.20 $\pm$ 0.02							1.20 $\pm$ 0.02
Lu	1.25 $\pm$ 0.17							1.25 $\pm$ 0.17
Mg				1.13 $\pm$ 0.02	1.20 $\pm$ 0.05			1.14 $\pm$ 0.02
Mn	1.24 $\pm$ 0.11		1.32 $\pm$ 0.11	1.19 $\pm$ 0.12				1.24 $\pm$ 0.07
Mo			1.36 $\pm$ 0.15	1.98 $\pm$ 0.26*				1.33 $\pm$ 0.15

TABLE 11. (contd)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Na	1.28 $\pm$ 0.02				1.29 $\pm$ 0.06			1.28 $\pm$ 0.02
Nb			1.15 $\pm$ 0.21					1.15 $\pm$ 0.21
Nd	1.09 $\pm$ 0.12							1.09 $\pm$ 0.12
Ni	1.29 $\pm$ 0.36		1.33 $\pm$ 0.17	1.17 $\pm$ 0.07				1.20 $\pm$ 0.06
Pb			1.37 $\pm$ 0.13					1.37 $\pm$ 0.13
Rb	1.20 $\pm$ 0.07		1.19 $\pm$ 0.05					1.19 $\pm$ 0.04
S			1.18 $\pm$ 0.15					1.18 $\pm$ 0.15
Sb	1.26 $\pm$ 0.09							1.26 $\pm$ 0.09
Sc	1.19 $\pm$ 0.04							1.19 $\pm$ 0.04
Se		1.15 $\pm$ 0.08	1.26 $\pm$ 0.37					1.16 $\pm$ 0.08
Si			1.26 $\pm$ 0.04		1.20 $\pm$ 0.02			1.20 $\pm$ 0.02
Sm	1.19 $\pm$ 0.03							1.19 $\pm$ 0.03
Sr	1.22 $\pm$ 0.06		1.28 $\pm$ 0.04	1.25 $\pm$ 0.03				1.26 $\pm$ 0.02
Ta	1.18 $\pm$ 0.06							1.18 $\pm$ 0.06
Tb	1.14 $\pm$ 0.14							1.14 $\pm$ 0.14
Th	1.19 $\pm$ 0.03							1.19 $\pm$ 0.03
Ti	1.17 $\pm$ 0.26		1.41 $\pm$ 0.18		1.11 $\pm$ 0.17			1.33 $\pm$ 0.15
U	1.26 $\pm$ 0.10	1.07 $\pm$ 0.06						1.08 $\pm$ 0.05
V	1.29 $\pm$ 0.18		1.46 $\pm$ 0.22	1.39 $\pm$ 0.08				1.38 $\pm$ 0.07
Y			1.17 $\pm$ 0.11					1.17 $\pm$ 0.11
Yb	1.28 $\pm$ 0.15							1.28 $\pm$ 0.15
Zn	1.25 $\pm$ 0.08	1.22 $\pm$ 0.09	1.38 $\pm$ 0.10	1.18 $\pm$ 0.10				1.26 $\pm$ 0.05
Zr			1.16 $\pm$ 0.08	1.00 $\pm$ 0.10				1.10 $\pm$ 0.06

*Deleted from error weighted average.

INAA - Instrumental Neutron Activation Analysis

RCAA - Radiochemical Neutron Activation Analysis

XRF - X-Ray Fluorescence Analysis

PES - Plasma Emission Spectroscopy (Sodium Carbonate Fusion)

FAA - Conventional Flame Atomic Absorption (Lithium Metaborate Fusion)

GFAA - Graphite Furnace Atomic Absorption

CVAA - Cold Vapor Atomic Absorption

FIGURE 13. Ratio of Elements in Retorted Shale to Elements in Raw Shale Compared to the Average Enrichment for Nonvolatile Elements

TABLE 12. Retorted/Raw Shale Ratio Summary for Nonvolatile Elements. Paraho Oil Shale Collection 8-24-77.

Method	Error Weighted Average	Unweighted Average Error <5%
INAA	1.20 ± 0.01 (32) ^(a)	1.20 ± 0.02 (14)
XRF	1.24 ± 0.02 (20)	1.21 ± 0.05 (4)
PES	1.17 ± 0.01 (15)	1.18 ± 0.04 (8)
FAA	1.19 ± 0.01 (8)	1.21 ± 0.05 (7)
Overall	---	1.20 ± 0.019 (33)

(a) Number in () is number of measurements used in average.

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

FAA = Conventional Flame Atomic Absorption

the Paraho combustive retorting process is evidently due to unaccounted-for water and gas losses and to CO₂ loss through thermal decomposition of dolomite and calcite.

The dashed lines shown in Figure 13 show the limits of the average ratio computed above (1.20 ± 0.02). Mercury is clearly being released and redistributed into products other than the retorted shale. At the maximum retorting temperature (~600°C), the mercury should be quantitatively removed. The mercury found on the retorted shale has probably been recondensed from the recycle gas. Sulfur is presumably also lost; however, that is not determinable from the XRF analysis because of poor precision. Cadmium actually seems to show a small additional enrichment in the retorted shale. Cadmium has been shown to be mobilized somewhat during in-situ retorting (Fox et al. 1977). Graphite furnace atomic absorption studies in our laboratory on raw and retorted shale show volatilization of cadmium at 500-600°C, in the same range as the maximum temperature reached in the Paraho process. Some of the cadmium may thus be redistributed by the recycle gas during retort operations. Temperature fluctuation during

retort operation may account for a nonequilibrium excess. Clearly more work is needed on cadmium since its behavior is very sensitive to retorting conditions.

Samples were sent to the LECO Corporation for analysis of the known volatile major elements (C, H, N, O, and S). Those data are shown in Table 10 and the ratios plotted in Figure 14, with the dashed lines as the average for nonvolatile elements. The LECO data do show some loss of sulfur and the expected large losses of hydrogen, carbon, and nitrogen. Oxygen oddly enough agrees with the ratio for nonvolatiles. Evidently some of the oxygen lost as CO_2 is being compensated for by oxidation reactions (on pyrite, for example).

ELEMENTAL MASS BALANCES FOR THE PARAHO SEMIWORKS RETORT

Mass balances for 31 elements have been completed for the Paraho semiworks retort as operated during direct mode retorting. The relative distribution of

FIGURE 14. Ratio of Elements in Retorted Shale to Elements in Raw Shale Compared to the Average Enrichment for Nonvolatile Elements

elements among the products and effluents was determined from: 1) accurate, high-precision measurements of each element in the raw shale, retorted shale, product oil, product water, and product gas and 2) the calculated equilibrium material balance between the mass of feedstock and product materials.

The detailed chemical analyses obtained from samples collected on August 24, 1977 were used to compute the elemental mass balances described here. In the few cases where chemical characterization data were not available for this collection date, data from other days were substituted. It is assumed that such substitutions are reasonable and that the computed mass balance of each affected element is valid for the date of interest. This assumption is supported by reported feedstock variation studies (Wildeman and Heistand 1979) and by data given in Table 13, which summarizes elemental abundances in the feedstock and products for seven days during August and November 1977. The overall uniform comparison between the data of different days suggests that the input and redistribution of elements were rather constant during the time of this study.

Calculation of the Semiworks Material Balance for August 24, 1977

Table 14 tabulates the pertinent retorting parameters and physical characteristics of the products produced during this study. All but three of the parameters and physical characteristics were provided by DEI plant management. The mass flowrate of the retorted shale and product gas, and the average molecular weight of the product gas were computed from experimental data by PNL.

The material balance for the semiworks retort per ton unit time may be expressed by the general equation

$$\text{MASS(M) INPUTS} = \text{MASS OUTPUTS} \quad (1)$$

For routine operation in the direct mode, this relationship is

$$M_{\text{raw shale}} + M_{\text{process air}} = M_{\text{retorted shale}} + M_{\text{product oil}} + M_{\text{product water}} + M_{\text{product gas}} \quad (2)$$

TABLE 13. Elemental Abundances in the Feedstock, Products, and Effluents of the Paraho Semiworks Retort (Direct Mode)

		Date (1977)						
Material		8-23	8-24	8-25	8-26	11-15	11-16	11-17
Al	raw shale (%)	3.90	3.77	3.69	3.79	3.72	3.84	3.93
	retorted shale (%)	4.57	4.83	4.60	4.61	4.70	4.51	4.65
	product oil (ppm)	11	16	22	10	7	3	18
	product water (ppm)	N.D. (a)	<0.4	0.3	N.D.	<1	<2	0.4
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	<70	N.D.	N.D.	N.D.	N.D.	N.D.
As	raw shale (ppm)	44	44	44	45	43	44	44
	retorted shale (ppm)	53	59	62	62	69	67	61
	product oil (ppm)	27	31	30	29	35	36	37
	product water (ppm)	N.D.	5.7	4.1	4.4	17.4	13.6	5.9
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	[155] (b)	N.D.	N.D.	N.D.	155	120
B	raw shale (ppm)	105	94	111	106	80	86	83
	retorted shale (ppm)	123	107	134	113	96	98	101
	product oil (ppm)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	product water (ppm)	N.D.	43	2.1	13	43	36	16
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	<30	N.D.	N.D.	N.D.	N.D.	N.D.
Ba	raw shale (ppm)	480	510	N.D.	N.D.	500	510	570
	retorted shale (ppm)	600	600	580	560	760	710	740
	product oil (ppm)	N.D.	[<2]	N.D.	N.D.	<2	<3	<3
	product water (ppm)	N.D.	[<1]	N.D.	<1	<3	<3	<3
	product gas ($\mu\text{g}/\text{m}^3$)	<3000	[<700]	<4000	<4000	<900	<700	<800
C	raw shale (%)	N.D.	15.5	N.D.	N.D.	N.D.	N.D.	N.D.
	retorted shale (%)	N.D.	6.1	N.D.	N.D.	N.D.	N.D.	N.D.
	product oil (%)	N.D.	86.0	N.D.	N.D.	N.D.	N.D.	N.D.
	product water (%)	N.D.	2.5	N.D.	N.D.	N.D.	N.D.	N.D.
	product gas (g/m^3)	146	[146]	N.D.	N.D.	N.D.	N.D.	N.D.

(a) Not Determined.

(b) Brackets indicate value was substituted from a different day.

TABLE 13. (contd)

		Date (1977)						
	Material	8-23	8-24	8-25	8-26	11-15	11-16	11-17
Ca	raw shale (%)	11.1	10.1	11.2	11.5	10.5	10.7	10.9
	retorted shale (%)	13.8	13.3	14.3	14.1	13.9	13.6	13.9
	product oil (ppm)	42	[42]	48	N.D.	N.D.	34	N.D.
	product water (ppm)	N.D.	38	36	33	43	42	41
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	<400	N.D.	N.D.	N.D.	N.D.	N.D.
Co	raw shale (ppm)	8.5	9.0	N.D.	N.D.	8.1	7.9	7.8
	retorted shale (ppm)	11.3	11.1	9.6	9.7	10.9	10.8	10.4
	product oil (ppm)	1.05	0.93	1.39	1.01	1.35	1.30	1.19
	product water (ppm)	N.D.	0.03	0.13	0.11	0.37	0.30	0.19
	product gas ($\mu\text{g}/\text{m}^3$)	<7	[<2]	<10	<10	<5	<2	<3
Cr	raw shale (ppm)	30	34	33	N.D.	35	34	37
	retorted shale (ppm)	40	44	41	43	N.D.	N.D.	N.D.
	product oil (ppm)	<0.03	<0.05	N.D.	<0.03	<0.1	<0.2	<0.1
	product water (ppm)	N.D.	<0.06	<0.04	<0.04	<0.1	<0.1	<0.1
	product gas ($\mu\text{g}/\text{m}^3$)	<7	<7	<10	<10	<50	<20	<60
Cu	raw shale (ppm)	42	40	41	41	40	39	38
	retorted shale (ppm)	52	56	52	52	55	61	60
	product oil (ppm)	0.71	0.42	0.72	0.48	0.44	0.40	0.36
	product water (ppm)	N.D.	0.7	0.8	0.5	6.8	10	<0.5
	product gas ($\mu\text{g}/\text{m}^3$)	<30	<5	<40	<40	<40	<100	<30
Fe	raw shale (%)	2.07	2.07	1.98	2.06	2.15	2.11	2.18
	retorted shale (%)	2.50	2.40	2.46	2.46	2.58	2.56	2.56
	product oil (ppm)	50	49	59	53	70	59	57
	product water (ppm)	N.D.	1.5	2.2	1.8	1.9	1.9	3.8
	product gas ($\mu\text{g}/\text{m}^3$)	<100	<20	<500	<6000	<4000	<2000	N.D.
H	raw shale (%)	N.D.	1.50	N.D.	N.D.	N.D.	N.D.	N.D.
	retorted shale (%)	N.D.	0.17	N.D.	N.D.	N.D.	N.D.	N.D.
	product oil (%)	N.D.	11.7	N.D.	N.D.	N.D.	N.D.	N.D.
	product water (%)	N.D.	10.5	N.D.	N.D.	N.D.	N.D.	N.D.
	product gas (g/m^3)	26.7	[26.7)	N.D.	N.D.	N.D.	N.D.	N.D.

TABLE 13. (contd)

		Date (1977)						
Material		8-23	8-24	8-25	8-26	11-15	11-16	11-17
Hg	raw shale (ppb)	84	89	85	89	96	95	104
	retorted shale (ppb)	21	35	34	30	21	25	25
	product oil (ppb)	N.D.	300	N.D.	N.D.	N.D.	N.D.	N.D.
	product water (ppb)	N.D.	2.3	5.8	N.D.	5.6	6.3	<400
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	[75]	N.D.	N.D.	46	75	N.D.
K	raw shale (%)	1.52	1.61	1.50	1.60	1.70	1.56	1.65
	retorted shale (%)	1.77	1.86	1.81	1.84	1.91	2.01	2.02
	product oil (ppm)	N.D.	<100]	N.D.	N.D.	N.D.	N.D.	<100
	product water (ppm)	N.D.	<20	<20	<20	<30	<30	<10
	product gas ($\mu\text{g}/\text{m}^3$)	<500	<2000	<2000	<3000	<2000	N.D.	<500
Mg	raw shale (%)	3.70	3.46	3.68	3.48	3.58	3.75	3.70
	retorted shale (%)	4.31	4.32	4.27	4.18	4.38	4.47	4.55
	product oil (ppm)	12	25	53	18	<7	6	18
	product water (ppm)	N.D.	490	240	230	870	790	320
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	<90	N.D.	N.D.	N.D.	N.D.	N.D.
Mn	raw shale (ppm)	322	315	290	323	330	329	330
	retorted shale (ppm)	402	396	384	383	420	430	420
	product oil (ppm)	0.15	0.21	0.40	0.20	0.12	0.41	0.22
	product water (ppm)	N.D.	0.18	0.44	0.39	0.12	0.12	0.46
	product gas ($\mu\text{g}/\text{m}^3$)	<100	<20	<50	<100	<100	N.D.	<100
Mo	raw shale (ppm)	21	22	N.D.	23	23	22	22
	retorted shale (ppm)	35	31	32	30	32	35	33
	product oil (ppm)	N.D.	<2	N.D.	N.D.	N.D.	N.D.	N.D.
	product water (ppm)	N.D.	0.15	0.07	0.07	0.51	0.43	0.07
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	<40	N.D.	N.D.	N.D.	N.D.	N.D.
N	raw shale (%)	N.D.	0.66	N.D.	N.D.	N.D.	N.D.	N.D.
	retorted shale (%)	N.D.	0.30	N.D.	N.D.	N.D.	N.D.	N.D.
	product oil (%)	N.D.	2.39	N.D.	N.D.	N.D.	2.60	N.D.
	product water (%)	N.D.	2.3	N.D.	N.D.	N.D.	N.D.	N.D.
	product gas (g/m^3)	N.D.	5.4	N.D.	N.D.	N.D.	5.4(a)	N.D.

(a) N as NH_3

TABLE 13. (contd)

		Date (1977)						
Material		8-23	8-24	8-25	8-26	11-15	11-16	11-17
Na	raw shale (%)	1.72	1.69	1.67	1.63	1.71	1.77	1.72
	retorted shale (%)	2.21	2.19	2.25	2.18	2.30	2.28	2.29
	product oil (ppm)	3.6	4.3	7.4	6.2	3.2	1.3	3.5
	product water (ppm)	N.D.	111	107	97	335	316	72
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	[<60]	N.D.	N.D.	<1000	<60	N.D.
Ni	raw shale (ppm)	23	28	27	28	23	24	28
	retorted shale (ppm)	33	32	34	36	33	36	33
	product oil (ppm)	2.71	2.74	2.72	2.73	2.99	2.61	2.69
	product water (ppm)	N.D.	0.54	0.23	0.22	0.37	0.40	0.38
	product gas ($\mu\text{g}/\text{m}^3$)	<60	<5	<50	N.D.	<1	<200	<100
Pb	raw shale (ppm)	21	27	27	27	23	23	23
	retorted shale (ppm)	33	35	32	32	33	35	32
	product oil (ppm)	<0.3	<0.3	<0.4	<0.3	<0.3	<0.3	N.D.
	product water (ppm)	N.D.	<0.4	<0.2	<0.2	<0.3	<0.3	<0.3
	product gas ($\mu\text{g}/\text{m}^3$)	<100	<70	<200	<200	<100	<300	<100
Rb	raw shale (ppm)	67	75	67	71	75	72	72
	retorted shale (ppm)	82	88	86	81	88	87	87
	product oil (ppm)	<0.1	<0.1	<0.2	<0.1	<0.1	<0.5	<0.6
	product water (ppm)	N.D.	0.14	<0.1	<0.2	0.32	0.34	0.08
	product gas ($\mu\text{g}/\text{m}^3$)	<50	<10	<80	<200	<40	<10	<40
S	raw shale (%)	N.D.	0.60	N.D.	N.D.	N.D.	N.D.	N.D.
	retorted shale (%)	N.D.	0.58	N.D.	N.D.	N.D.	N.D.	N.D.
	product oil (%)	0.73	0.74	0.99	0.74	0.67	0.74	0.78
	product water (%)	N.D.	3.9	1.7	N.D.	4.8	4.6	2.2
	product gas (g/m^3)	N.D.	[3.4]	N.D.	N.D.	4.0	3.4	N.D.
Sb	raw shale (ppm)	2.0	2.1	N.D.	N.D.	2.2	2.0	2.1
	retorted shale (ppm)	3.1	2.6	2.7	2.6	3.2	2.7	2.8
	product oil (ppm)	0.035	0.028	N.D.	0.038	0.052	0.050	<0.03
	product water (ppm)	N.D.	0.020	0.019	0.010	<0.02	<0.02	<0.06
	product gas ($\mu\text{g}/\text{m}^3$)	<20	[<3]	<20	<20	<9	<5	<3

TABLE 13. (contd)

		Date (1977)						
Material		8-23	8-24	8-25	8-26	11-15	11-16	11-17
Se	raw shale (ppm)	N.D.	2.0	2.0	1.7	2.8	2.2	2.0
	retorted shale (ppm)	3.1	2.3	2.9	3.3	4.0	2.9	2.9
	product oil (ppm)	0.84	0.91	N.D.	0.98	0.98	0.64	0.77
	product water (ppm)	N.D.	9.8	3.7	3.7	6.7	7.1	4.1
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	<70	N.D.	N.D.	N.D.	N.D.	N.D.
Si	raw shale (%)	15.1	15.0	14.7	14.5	15.5	15.5	15.5
	retorted shale (%)	18.2	18.2	17.8	17.9	18.3	18.4	18.5
	product oil (ppm)	55	[55]	N.D.	N.D.	N.D.	44	N.D.
	product water (ppm)	N.D.	41	24	23	35	24	39
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	<600	N.D.	N.D.	N.D.	N.D.	N.D.
Sr	raw shale (ppm)	710	700	680	720	720	740	740
	retorted shale (ppm)	860	880	840	840	860	880	890
	product oil (ppm)	<1	<1	<1	<1	<1	<1	N.D.
	product water (ppm)	N.D.	0.85	0.41	0.50	0.80	0.85	0.43
	product gas ($\mu\text{g}/\text{m}^3$)	<600	<90	<400	<800	<200	<800	<300
Th	raw shale (ppm)	6.4	6.3	N.D.	N.D.	6.1	6.5	6.5
	retorted shale (ppm)	7.1	7.6	6.8	6.4	7.8	7.4	7.8
	product oil (ppm)	0.008	0.009	N.D.	0.008	<0.01	0.021	<0.01
	product water (ppm)	N.D.	[<0.01]	N.D.	<0.01	<0.01	<0.01	<0.01
	product gas ($\mu\text{g}/\text{m}^3$)	<200	[<2]	<200	<200	<3	<2	<2
Ti	raw shale (%)	0.20	0.18	0.20	0.19	0.18	0.17	0.18
	retorted shale (%)	0.25	0.24	0.23	0.22	0.21	0.24	0.21
	product oil (ppm)	N.D.	[2.6]	2.6	N.D.	N.D.	N.D.	N.D.
	product water (ppm)	N.D.	5.1	<1	1.4	<3	10	2.8
	product gas ($\mu\text{g}/\text{m}^3$)	N.D.	<70	N.D.	N.D.	N.D.	N.D.	N.D.
U	raw shale (ppm)	4.5	4.5	N.D.	N.D.	N.D.	N.D.	N.D.
	retorted shale (ppm)	5.6	5.1	5.0	4.9	N.D.	N.D.	N.D.
	product oil (ppm)	N.D.	[<0.03]	N.D.	<0.03	<0.07	<0.09	<0.08
	product water (ppm)	N.D.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.05
	product gas ($\mu\text{g}/\text{m}^3$)	<40	<40	<50	<50	<20	N.D.	<3

TABLE 13. (contd)

		Date (1977)						
Material		8-23	8-24	8-25	8-26	11-15	11-16	11-17
V.	raw shale (ppm)	84	94	N.D.	N.D.	86	65	81
	retorted shale (ppm)	108	115	109	112	102	105	99
	product oil (ppm)	0.19	0.25	0.29	0.24	0.21	0.20	0.31
	product water (ppm)	N.D.	0.045	0.020	<0.01	0.090	0.077	0.020
	product gas ($\mu\text{g}/\text{m}^3$)	<300	<40	N.D.	<400	<100	N.D.	<100
Zn	raw shale (ppm)	66	64	67	70	66	64	64
	retorted shale (ppm)	86	82	85	88	86	92	86
	product oil (ppm)	0.53	0.41	0.57	0.27	0.25	0.34	0.28
	product water (ppm)	N.D.	0.41	0.31	1.06	0.85	7.5	0.08
	product gas ($\mu\text{g}/\text{m}^3$)	<200	[<20]	<100	<100	<20	N.D.	<30

Mass of Raw Shale, Process Air, Product Oil, and Product Water

The material balance for August 24 was calculated by solving for each term in Equation 2. Four of the terms were determined directly from the retorting data given in Table 14. Expressed as mass flowrates per hour, the terms are:

$$\begin{aligned} M_{\text{raw shale}} &= 10.5 \text{ ton/hr} \\ M_{\text{process air}} &= 2.04 \text{ ton/hr} \\ M_{\text{product oil}} &= 0.880 \text{ ton/hr} \\ M_{\text{product water}} &= 0.0404 \text{ ton/hr} \end{aligned}$$

TABLE 14. Retorting Parameters for the Paraho Semiworks Retort (Direct Mode)

Parameter	Date (1977)						
	8-23	8-24	8-25	8-26	11-15	11-16	11-17
Fischer Assay (FA), GPT oil	23.8	23.8	25.5	25.6	27.7	24.8	25.1
Oil Yield, %FA ⁽¹⁾ (wet)	95.8	95.8	95.8	95.8	94.7	94.7	94.7
Oil Yield, %FA (dry)		91.0					
Oil Density, °API ⁽²⁾	21.2	21.2	21.2	21.2	21.3	21.3	21.3
Pourpoint, °F ⁽³⁾	85	85	85	85	85	85	85
Wt % Water in Oil	4.4	4.6	4.0 ⁽⁴⁾	4.0 ⁽⁴⁾	4.0 ⁽⁴⁾	4.0 ⁽⁴⁾	4.0 ⁽⁴⁾
Raw Shale Rate, T/H	10.6	10.5	10.8	11.0	11.0	11.2	10.8
Process Air Rate, MSCF/T		4.8					
Retorted Shale Rate, T/H		8.75 ⁽⁵⁾					
Product Gas Rate, MSCF/T	7.1	7.2	6.9	6.8	7.0	6.8	7.3
Average Molecular Wt of Product Gas, g/mole		27.2 ⁽⁵⁾					

(1) +2% error

(2) Measured once during each 14-day period

(3) Measured during each transfer to permanent storage (usually every third operating day)

(4) Annual mean value

(5) PNL determined value

Mass of Retorted Shale

The mass of the retorted shale was calculated from the enrichment of "non-volatile" elements in the retorted shale relative to their abundances in the raw shale. During retorting, mass is lost from the feedstock shale due to kerogen decomposition, water loss, and to partial decomposition of the carbonate minerals. The nonvolatile elements associated with the mineral phase thus become enriched in the retorted shale. The ratio of element abundance in retorted shale to element abundance in raw shale gives the elemental enrichment factor (EEF). The reciprocal of the EEF is the fraction of raw shale mass transferred to the retorted shale. The EEFs for approximately 20 nonvolatile elements, as determined from representative samples of August 24 raw and retorted shale, are summarized in Table 12. To minimize the uncertainty due to analytical errors, only those elements which could be measured with a high degree of accuracy and precision (<5%) were considered. The average EEF determined from 33 analyses is 1.20 ± 0.02 . The mass of retorted shale produced per hour is then

$$\begin{aligned} M_{\text{retorted shale}} &= (M_{\text{raw shale}})(1/\text{EEF}) \\ &= (10.5 \text{ ton/hr})(1/1.20) \\ &= 8.75 \text{ ton/hr} \end{aligned} \quad (3)$$

Mass of Product Gas

The mass of the product gas may be calculated by: 1) difference, as all other terms in Equation 2 are now known, or 2) the given product gas volume (Table 14) and the experimentally measured specific gravity of the gas. Since our analysis of the product gas was essentially a "dry" measurement, any average molecular weight determined would be too high because of loss of water vapor (reportedly about 18% by volume). The mass of the product gas per hour by method (1) is then

$$\begin{aligned} M_{\text{product gas}} &= (M_{\text{raw shale}} + M_{\text{process air}}) - (M_{\text{retorted shale}} \\ &\quad + M_{\text{product oil}} + M_{\text{product water}}) \\ &= (10.5 + 2.04) - (8.75 + 0.880 + 0.0404) \\ &= 2.87 \text{ ton/hr} \end{aligned} \quad (4)$$

Average Molecular Weight of Product Gas

The average molecular weight of the product gas was calculated from the mass flowrate computed above and from the volume flowrate given in Table 14. For each ton of input raw shale, the mass and volume (V) of product gas produced are 0.273 ton and 7200 standard cubic feet, respectively. The average molecular weight of the product gas is then

$$\begin{aligned}\text{Average Molecular Weight} &= (M_{\text{product gas}})(V_{\text{product gas}}/22.4\ell)^{-1} \quad (5) \\ &= \frac{(0.273 \text{ ton})(9.072 \times 10^5 \text{ g/ton})}{(7200 \text{ SCF})(28.32\ell/\text{SCF})(1 \text{ mole}/22.4\ell)} \\ &= 27.2 \text{ g/mole}\end{aligned}$$

The completed material balance for the Paraho Semiworks Retort, normalized to each ton of input raw shale, is shown in Figure 15. Assuming the input of

FIGURE 15. Retorting Parameters and Material Balance Flowrates for the Paraho Semiworks Retort as Operated on August 24, 1977

each element to be entirely with the raw shale (process air contribution zero),^(a) the material balance of Figure 15 may be reduced to reflect only those terms which relate the mass of the raw shale to the mass of the products. Thus, one ton of input raw shale corresponds to the production of 0.833 ton of retorted shale, 0.0838 ton of product oil, 0.00385 ton of product water, and 0.273 ton of product gas. This relationship and the abundance data in Table 13 were used to determine each element's mass distribution among the products. The resulting mass balances for 31 elements are summarized in Table 15.

Redistribution of Elements Among the Products

The redistribution of elements from the raw shale may be characterized by three general categories. The first category (I) includes the elements which remain almost totally with the retorted shale and have partitioning coefficients of less than 0.01% for the product oil, product water, and product gas. This group includes the elements Al, Ba, Ca, Cr, K, Mg, Mn, Na, Rb, Si, and Sr. The second category (II) includes elements that have a cumulative partitioning coefficient (products other than retorted shale) of from 0.01 to approximately 5%: As, B, Co, Cu, Fe, Ni, Sb, Se, Th, Ti, V, and Zn. Although they were not observed in the product oil or gas, three additional elements, Mo, Pb, and U, cannot be ruled out as members of this group because of their detection limits (see Table 15). The third category (III) includes elements that have greater than 10% of their mass redistributed into products other than the retorted shale. This group includes the major elements C, H, N, and S, and the volatile heavy metal Hg.

The redistribution of category I elements into the product oil is primarily in the form of raw and/or retorted shale fines. This statement is based on data in Table 16, which tabulates the partitioning coefficients for all elements detected in the product oil. The partitioning coefficients for the mineral

(a) The input process air is assumed to contain only O_2 and N_2 . The element 0 was not considered in the redistribution of elements from the feedstock shale. The process air N is assumed to be unreactive and appears quantitatively in the product gas as N_2 . The N from the feedstock shale is assumed to be in other chemical forms in the products and effluents (e.g., NH_3 in the product gas) and, therefore, distinguishable from the process air N_2 .

TABLE 15. Elemental Mass Balances for the Paraho Semiworks Retort During Direct Mode Retorting

	Elemental Abundance In Raw Shale, ppm	% Element Redistributed into Products and Effluents (August 24, 1977)				Imbalance (%)
		Retorted Shale	Product Oil	Product Water	Product Gas	
Al	37,700	106.7	<0.01	<0.01	<0.01	+ 6.7
As	44	111.7	5.90	0.05	0.08	+17.7
B	94	94.8	N.D. ⁽¹⁾	0.18	<0.01	- 5.0
Ba	510	98.0	<0.03	<0.01	<0.03	- 2.0
C	155,000	32.8	46.5	0.06	21.1	+ 0.5
Ca	101,000	109.7	<0.01	<0.01	<0.01	+ 9.7
Co	9.0	102.7	0.87	<0.01	<0.02	+ 3.6
Cr	34	107.8	<0.01	<0.01	<0.01	+ 7.8
Cu	40	116.6	0.09	<0.01	<0.01	+16.7
Fe	20,700	96.6	0.02	<0.01	<0.01	- 3.4
H	15,000	9.4	65.4	2.7	40.0	+17.5
Hg	0.089	32.8	28.2	0.01	23.0	-16.0
K	16,100	96.2	<0.05	<0.01	<0.01	- 3.8
Mg	34,600	104.0	<0.01	<0.01	<0.01	+ 4.0
Mn	315	104.7	<0.01	<0.01	<0.01	+ 4.7
Mo	22	117.4	<0.8	<0.01	<0.04	+17.4
N	6,600	37.9	30.3	1.3	17.9	-12.6
Na	16,900	107.9	<0.01	<0.01	<0.01	+ 7.9
Ni	28	95.2	0.82	<0.01	<0.01	- 4.0
Pb	27	108.0	<0.09	<0.01	<0.06	+ 8.0
Rb	75	97.7	<0.01	<0.01	<0.01	- 2.3
S	6,000	80.9	10.4	2.5	12.7	+ 6.5
Sb	2.1	103.1	0.11	<0.01	<0.03	+ 3.2
Se	2.0	95.8	3.81	1.88	<0.8	+ 1.5
Si	150,000	101.1	<0.01	<0.01	<0.01	+ 1.1
Sr	700	104.7	<0.01	<0.01	<0.01	+ 4.7
Th	6.3	100.5	0.01	<0.01	<0.01	+ 0.5
Ti	1,800	111.1	0.01	<0.01	<0.01	+11.1
U	4.5	94.4	<0.06	<0.01	<0.02	- 5.5
V	94	101.9	0.02	<0.01	<0.01	+ 1.9
Zn	64	106.7	0.05	<0.01	<0.01	+ 6.7

(1) Not Determined.

TABLE 16. Percentage of Elements Transferred from Feedstock
Raw Shale to Product Oil (8-24-77)

Element	Abundance In Raw Shale, ppm	Abundance In Product Oil, ppm	% Element Transferred from Raw Shale to Product Oil
H	15,000	117,000	65.4
C	155,000	860,000	46.5
N	6,600	23,900	30.3
S	6,000	7,400	10.4
Hg	0.089	0.30	28.2
As	44	31	5.9
Se	2.0	0.91	3.8
Co	9.0	0.93	0.87
Ni	28	2.74	0.82
Sb	2.1	0.028	0.11
Cu	40	0.42	0.088
Zn	64	0.41	0.054
V	94	0.25	0.022
Fe	20,700	49	0.020
Th	6.3	0.009	0.012
Ti	1,800	2.6	0.012
Mg	34,600	25	0.0061
Mn	315	0.21	0.0056
Al	37,700	16	0.0036
Ca	101,000	42	0.0035
Si	150,000	55	0.0031
Na	16,900	4.3	0.0021

elements Al, Ca, Mg, Mn, Na, and Si ranged from 0.0021 to 0.0061% with a mean and relative standard deviation of $0.0040 \pm 0.0015\%$. The small but essentially equal fractions of these six elements in the product oil indicate that they are most likely being redistributed together as shale particulate matter.

If the base level of elements associated with shale particulates in the product oil is set equal to the mean value calculated above (0.0040%) plus two standard deviations (0.0030%), it is reasonable to conclude that elements with partitioning coefficients exceeding the sum (0.007%) are present in additional chemical forms. Analytical errors or sample contamination may invalidate this statement for a few elements which are close to the 0.007% limit (e.g., Ti and Th); however, for elements with partitioning coefficients of 0.02% or greater (e.g., Fe), this difference is considered to be real. The elements of category II are probably redistributed as volatile metallic or organometallic compounds. This statement is supported by other mass balance studies (Fox et al. 1977; Shendriker and Faudel 1978) and by investigations which report that As and Fe cannot be removed from Paraho shale oil by filtering through 15-micron filters (Sullivan et al. 1977). An additional explanation is that very fine-grained and insoluble trace minerals, chemically unlike the shale fines, are being preferentially precipitated or transported into the product oil.

The observed redistribution of category III elements into the product oil ranges from 10.4% for S to 65.4% for H. A significant fraction (30.3%) of the trace element Hg was observed to partition into the product oil. This partitioning coefficient agrees well with others reported for Hg in various oil shale retorting processes (Fox et al. 1977) and in laboratory retorting studies (Donnell and Shaw 1977).

The abundances and partitioning coefficients for elements detected in the product water are summarized in Table 17. Because the August 24 water sample was collected from one of the small gauging tanks, it represented product water which had only recently been co-produced by the retorting process. Other more "aged" product waters were collected on August 26 and November 15 and 16 from the large settling tanks used for oil-water separation. The product water obtained from these tanks is typically several days older than water in the gauging tanks.

TABLE 17. Percentage of Elements Transferred from Feedstock
Raw Shale to Product Water (8-24-77)

Element	Abundance In Raw Shale, ppm	Abundance in Product Water, ppm	% Element Transferred from Raw Shale to Product Water
H	15,000	105,000	2.7
S	6,000	39,000	2.5
Se	2.0	9.8	1.9
N	6,600	23,000	1.3
B	94	43	0.18
C	155,000	25,000	0.062
As	44	5.7	0.050
Hg	0.089	0.0023	0.010
Ni	28	0.54	0.0074
Cu	40	0.70	0.0067
Mg	34,600	490	0.0055
Sb	2.1	0.020	0.0037
Mo	22	0.15	0.0026
Na	16,900	111	0.0025
Zn	64	0.41	0.0025
Co	9.0	0.03	0.0013
Ti	1,800	5.1	0.0011
Rb	75	0.14	0.00072
Sr	700	0.85	0.00048
Mn	315	0.18	0.00022
V	94	0.045	0.00018
Ca	101,000	38	0.00015
Si	150,000	41	0.00011
Fe	20,700	1.5	0.000028

A comparison between the elemental abundances of each product water type is given in Table 18. Several elements (As, B, Co, Mg, Mo, Na, Sb, S, Se, and V) are observed to be two to three times more concentrated in the product waters originating from the large settling tanks. These increased levels are believed to be due to the more complete separation between the organic and aqueous phases. This explanation is especially fitting when considering the mass differences between the two products (see Figure 15). Even the smallest additional element separation from the product oil will be magnified by approximately 20 to 25 times in the product water. The anomalously high values for Cu and Zn in the aged product waters (approximately 10 times the gauging tank abundances) may reflect other factors such as corrosion from the storage tanks.

The partitioning coefficients for S and Se in the August 24 product water are 2.5 and 1.9%, respectively. This rather close agreement may be related to the elements' chemical similarities. The total S measured in the product water was 3.9%; however, the $S^{=}$ levels were only a few ppm. About 0.05% of the raw shale arsenic was observed to partition into the product water. The chemical form of the arsenic in the product water was about 50% As^{+3} and 50% As^{+5} . No methyl or dimethyl arsenic was detected (see Appendix D).

The abundances and partitioning coefficients for elements detected in the product gas are summarized in Table 19. Significant fractions of the elements S, C, H, Hg, N, and S are released from the raw shale and redistributed into the product gas. In addition, a small fraction of the As (0.08%) was also observed to partition into the gas. The element hydrogen is redistributed in the gas chiefly as water vapor, H_2 , CH_4 , and other hydrocarbon gases. Carbon is redistributed as hydrocarbon gases, as CO and CO_2 from combustion, and as CO_2 from decomposition of the carbonate minerals. Nitrogen is redistributed chiefly as NH_3 in the gas phase.

The partitioning coefficient for total sulfur redistributed into the product gas was observed to be 12.7%. The partitioning coefficient for Hg in the product gas was observed to be 23.0%. The chemical form is assumed to be elemental mercury vapor (Hg^0) as organic forms should be condensed with the product oil. The small fraction of arsenic in the product gas was primarily inorganic As_2O_3 vapor. Only a small quantity of arsine or methylated arsine was detected (see Appendix D).

TABLE 18. Comparison Between Elemental Abundance in Gauging Tank and Settling Tank Product Waters

Element (ppm unless noted)	Product Water From Gauging Tanks				Product Water From Settling Tanks		
	8-24	8-25	8-26	11-17	9-26	11-15	11-16
Al	<0.4	0.3	N.D. ^(a)	0.4	0.7	<1	<2
As	5.7	4.1	4.4	5.9	10.9	17.4	13.6
B	43	2.1	13	16	41	43	36
Ba	N.D.	N.D.	<1	<3	N.D.	<3	<3
C(%)	2.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ca	38	36	33	41	64	43	42
Co	0.03	0.13	0.11	0.19	0.35	0.37	0.30
Cr	<0.06	<0.04	<0.04	<0.1	0.13	<0.1	<0.1
Cu	0.7	0.8	0.5	<0.5	21	6.8	10
Fe	1.5	2.2	1.8	3.8	4.2	1.9	1.9
H(%)	10.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Hg(ppb)	2.3	5.8	N.D.	<400	<500	5.6	6.3
K	<20	<20	<20	<10	65	<30	<30
Mg	490	240	230	320	960	870	790
Mn	0.18	0.44	0.39	0.46	0.31	0.12	0.12
Mo	0.15	0.07	0.07	0.07	0.53	0.51	0.43
N(%)	2.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Na	111	107	97	72	396	335	316
Ni	0.54	0.23	0.22	0.38	0.41	0.37	0.40
Pb	<0.4	<0.2	<0.2	<0.3	<0.3	<0.3	<0.3
Rb	0.14	<0.1	<0.2	0.08	0.41	0.32	0.34
S(%)	3.9	1.7	N.D.	2.2	5.1	4.8	4.6
Sb	0.020	0.019	0.010	<0.06	0.034	<0.02	<0.02
Se	9.8	3.7	3.7	4.1	6.4	6.7	7.1
Si	41	24	23	39	24	35	24
Sr	0.85	0.41	0.50	0.43	1.1	0.80	0.85
Th	<0.01	N.D.	<0.01	<0.01	N.D.	<0.01	<0.01
Ti	5.1	<1	1.4	2.8	6.0	<3	10
U	<0.1	<0.1	<0.1	<0.05	<0.1	<0.1	<0.1
V	0.045	0.020	<0.01	0.020	0.094	0.090	0.077
Zn	0.41	0.31	1.06	0.08	5.0	0.85	7.5

(a) Not determined.

TABLE 19. Percentage of Elements Transferred from Feedstock Raw Shale to Product Gas (8-24-77)

<u>Element</u>	<u>Abundance in Raw Shale, ppm</u>	<u>Abundance in Product Gas</u>	<u>%Element Transferred from Raw Shale to Product Gas</u>
H	15,000	26.7 (g/m ³)	40.0
C	155,000	146 (g/m ³)	21.1
N	6,600	5.4 (g/m ³)(a)	17.9
S	6,000	3.4 (g/m ³)	12.7
<hr/>			
Hg	0.089	75 (μg/m ³)	23.0
As	44	155 (μg/m ³)	0.079

(a) N as NH₃

RESULTS OF AMBIENT PARTICULATE SAMPLING

The total dust loading in both August and November, indicated by the summation column, shows that the retorting, crushing, and disposal process generate large amounts of aerosol. Total dust loadings for aluminum are generally greater than 100 μg·m⁻³, indicating a total aerosol level of approximately 2·mg m⁻³ if the aluminum concentration is assumed to be 4 to 6 percent in the ambient aerosols (that found in raw or spent shale).

Aerosol sampling intervals must be kept short in such a heavily dust-laden environment to minimize overloading of any stages and subsequent bounce down. This raises questions concerning the representativeness of sampling; however, the fact that the total loadings appear very similar in August and November indicate the samples obtained are probably fairly representative.

The compositions of the aerosols collected appear similar to those which would be expected from entrainment of raw or spent shale particles. This can be observed by comparison of the elemental ratios of raw or retorted shale with those of the aerosol. The composition at the background site also reflects entrainment of shale-related material although total dust or aerosol loadings are approximately 50 times lower. The background site was only 1-2 hundred yards removed from the retorting facility, indicating that the heavy aerosol

loadings associated with the shale processing are only a local feature on the scale presently being employed.

The activities on site generate particles at both ends of the particle size spectrum ($>7\text{ }\mu\text{m}$ and $<1.2\text{ }\mu\text{m}$) with relatively few particles in the size fractions between. In the November samples, greater than 20% of the total loading for most elements was in the size range greater than $7\text{ }\mu\text{m}$. An even larger percentage, often 50% or larger, was found in the fraction less than $1.1\text{ }\mu\text{m}$. Therefore, the respirable fraction, defined as those particles in size fractions less than $3.3\text{ }\mu\text{m}$ for our samples, is generally also greater than 50% of the total particulate matter present.

For selected elements, including As, Cr, V, Sb, and Co, elemental distributions on the lower impactor stages appear dissimilar to those which would be expected from entrainment of shale-related material. If these are real, and the low analytical blank observed indicates this to be the case, other source(s) must be found. One potential source of fine particles enriched in volatile or semivolatile elements as observed might be the thermal oxidizer associated with the retort, which was sampled in November and did show elevations of some of these same elements in the particulates obtained (see Appendix E). Other sources might be diesel combustion on the site and/or nearby associated with the interstate highway construction; and finally, mining and blasting activities associated with the mine or again, the highway construction occurring locally during the periods of sampling.

The retorting facility with associated crushing and tailings disposal has very elevated local dust loadings with greatest abundances of large ($>7\text{ }\mu\text{m}$) and fine ($<1.1\text{ }\mu\text{m}$) particulates. A very substantial fraction ($>50\%$) of these particulate loadings appears to be in the respirable range $<5\text{ }\mu\text{m}$. At present the elevated dust loadings associated with the facility are extremely local as indicated by much lower aerosol loadings at a nearby background site.

One must keep in mind the aerosol data generated from the Paraho facility are extremely site specific. The purpose of the retorting operation on the

present pilot-plant scale is to prove the feasibility of a specific engineering process for aboveground retorting of oil shale. This has been done using, in many cases, outmoded or outdated pieces of equipment. Consequently, dust control has been of relatively minor concern at the present time and justifiably so. Extrapolation of aerosol data from the present facility to commercial scale is impossible, since dust control technology would necessarily be applied on such a scale and improved and modern equipment would also be utilized. However, at a larger retort facility further dust control may prove necessary as well as desirable from the standpoints of occupational safety, occupational health, and general environmental contamination.

SUMMARY AND CONCLUSIONS

Inorganic analysis of solid, liquid, particulate, and gaseous samples from the Paraho Semiworks Retort was completed using a multitechnique approach. Most of the techniques used instrumental methods, so that interferences from chemically complex matrices could be minimized. In many cases, analytical techniques were altered or improved in order to make them applicable to oil shale samples.

The techniques employed for most of the analyses were a combination of instrumental neutron activation, energy dispersive x-ray fluorescence, flame atomic absorption spectroscopy and dc plasma emission spectroscopy. Additional analyses were performed by graphite furnace atomic absorption, cold vapor atomic absorption, and radiochemical activation. The data were statistically analyzed to determine the precision of each method and to see how closely the various techniques compared. Better than 10% comparisons between two or more of the techniques were obtained for analyses of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Rb, Si, U, V and Zn. Better than 20% comparisons were obtained for Cd, Cr, Mo and Ti. Systematic differences of about 15-20% between x-ray fluorescence and neutron activation determinations of arsenic were noted, with the neutron activation being generally higher. The environmentally interesting elements B, Hg, and Se could be reliably determined by only one method, so intercomparisons could not be made. Fluorine could not be reliably determined by any technique (selective ion electrode, colorimetry) that we tried.

The data were also used to construct mass balances for 31 trace and major elements in the various effluents, including the offgas for the Paraho retort operating in the direct mode. The computed mass balances show that approximately 1% or greater fractions of the As, Co, Hg, N, Ni, S and Se are released during retorting and are redistributed to the product shale oil, retort water, or product offgas. The fraction for these seven elements ranged from 1% for Co and Ni to 50 to 60% for Hg and N.

Approximately 20% of the S and 5% of the As and Se are released. The mass balance redistribution during retorting for Al, Fe, Mg, V and Zn was observed to be no greater than 0.05%. These mass balance figures are generally in agreement with previous mass balance studies made for a limited number of elements on laboratory-scale or smaller pilot retorts (Fox et al. 1977, Shendrikar and Faudel 1978, Wildeman 1977, Fruchter et al. 1978). Thus, the mass balances reported here for the Paraho Retort may have some general validity for other types of oil shale retorting technologies.

The ambient particulate samples showed a bimodal size distribution, consisting largely of particles greater than 7 μm and less than 1.1 μm . Although most of the elemental concentrations in the aerosols can be accounted for if raw or retorted shale is considered to be the source, the elements As, Cr, Co, V, and Sb are elevated in the 1.1 to 2.0- μm size fraction. This enrichment appears to indicate a second source of particulates in the air. Other possible sources include thermal oxidizer effluents, activities such as diesel combustion, blasting, and local highway construction, and/or emissions from vegetation.

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APPENDIX A
PARAHO SEMIWORKS RETORT - DIRECT MODE
DAILY FEEDSTOCK AND EFFLUENT SAMPLES

**TABLE A.1. Paraho Semiworks Retort - Direct Mode
Raw Oil Shale
Collected 8-23-77 (in ppm except as noted)**

Element	INAA	XRF	PES	AA	CVAA
Al (%)	3.89 ± 0.08			3.91 ± 0.04	
As	50 ± 1	37 ± 3			
B			105 ± 5		
Ba	580 ± 70	480 ± 30			
Br	<0.7	1.1			
Ca (%)	10.9 ± 1.2	11.0 ± 0.8		11.4 ± 0.2	
Co	8.5 ± 0.2				
Cr	30 ± 5	28 ± 8			
Cu		42 ± 4			
Eu	0.73 ± 0.05				
Fe (%)	2.06 ± 0.05	2.06 ± 0.14		2.10 ± 0.11	
Ga		9 ± 1			
Hg					0.084 ± 0.004
K (%)		1.54 ± 0.12		1.49 ± 0.06	
La	19.5 ± 0.3	17 ± 4			
Lu	0.38 ± 0.06				
Mg (%)				3.70 ± 0.03	
Mn	313 ± 15	330 ± 25		403 ± 23	
Mo		21 ± 2			
Na (%)	1.77 ± 0.02			1.65 ± 0.09	
Nb		10 ± 2			
Ni		23 ± 3			
Pb		21 ± 3			
Rb		67 ± 5			
Sb	2.0 ± 0.2				
Sc	6.1 ± 0.1				
Se		3.1 ± 6			
Si (%)		13.8 ± 1.6		15.1 ± 0.6	
Sm	3.5 ± 0.1				
Sr		710 ± 60			
Th	6.4 ± 0.2				
Ti (%)	0.18 ± 0.02	0.21 ± 0.01		0.20 ± 0.01	
U	4.5 ± 1.1				
V	84 ± 6				
Y		14 ± 2			
Zn		66 ± 5			
Zr		62 ± 4			

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
PES = DC-Coupled Plasma Emission Spectroscopy
AA = Atomic Absorption Analysis
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE A.2. Paraho Semiworks Retort - Direct Mode
Raw Oil Shale
Collected 8-24-77 (in ppm except as noted)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Al (%)	3.89 $\pm$ 0.14			3.78 $\pm$ 0.08	3.69 $\pm$ 0.11			3.77 $\pm$ 0.06
As	48.0 $\pm$ 0.7		41.6 $\pm$ 5					44.3 $\pm$ 0.6
B				94 $\pm$ 2				94 $\pm$ 2
Ba	483 $\pm$ 34			515 $\pm$ 8				512 $\pm$ 10
Br	0.57 $\pm$ 0.13							0.57 $\pm$ 0.13
Ca (%)	10.4 $\pm$ 0.5		10.7 $\pm$ 0.5	9.9 $\pm$ 0.1	11.0 $\pm$ 0.4*			10.1 $\pm$ 0.2
Cd		0.64 $\pm$ 0.03				0.61 $\pm$ 0.08		0.64 $\pm$ 0.03
Ce	43.1 $\pm$ 0.9							43.1 $\pm$ 0.9
Co	9.0 $\pm$ 0.1							9.0 $\pm$ 0.1
Cr	36.7 $\pm$ 1.8		39.7 $\pm$ 9.3	33.8 $\pm$ 0.6				34.2 $\pm$ 0.6
Cs	3.84 $\pm$ 0.22							3.84 $\pm$ 0.22
Cu			40.3 $\pm$ 2.3	40.0 $\pm$ 5.5				40.3 $\pm$ 2.1
Dy	2.4 $\pm$ 0.4							2.4 $\pm$ 0.4
Eu	0.60 $\pm$ 0.02							0.60 $\pm$ 0.02
Fe (%)	2.08 $\pm$ 0.04		2.02 $\pm$ 0.10	2.01 $\pm$ 0.04	2.14 $\pm$ 0.04			2.07 $\pm$ 0.02
Ga			8.4 $\pm$ 0.8					8.4 $\pm$ 0.8
Hf	1.75 $\pm$ 0.05							1.75 $\pm$ 0.05
Hg							0.089 $\pm$ 0.005	0.089 $\pm$ 0.005
Ho	0.67 $\pm$ 0.11							0.67 $\pm$ 0.11
K (%)	1.69 $\pm$ 0.11		1.66 $\pm$ 0.02	1.79 $\pm$ 0.03*	1.55 $\pm$ 0.03			1.61 $\pm$ 0.02
La	20.6 $\pm$ 0.7							20.6 $\pm$ 0.7
Lu	0.28 $\pm$ 0.03							0.28 $\pm$ 0.03
Mg (%)				3.42 $\pm$ 0.05	3.59 $\pm$ 0.3			3.46 $\pm$ 0.06
Mn	312 $\pm$ 20		319 $\pm$ 20	314 $\pm$ 22				315 $\pm$ 12
Mo			24 $\pm$ 2.5	20.9 $\pm$ 1.9				22.0 $\pm$ 1.5

TABLE A.2. Paraho Semiworks Retort - Direct Mode
Raw Oil Shale
Collected 8-24-77 (in ppm except as noted)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Na (%)	1.68 $\pm$ 0.01				1.73 $\pm$ 0.07			1.69 $\pm$ 0.03
Nb			8.0 $\pm$ 0.7					8.0 $\pm$ 0.7
Nd	20.4 $\pm$ 2.1							20.4 $\pm$ 2.1
Ni	23.0 $\pm$ 5.3		24.2 $\pm$ 1.2*	27.6 $\pm$ 0.6				27.5 $\pm$ 0.6
Pb			26.5 $\pm$ 2.1					26.5 $\pm$ 2.1
Rb	74.9 $\pm$ 2.3		74.0 $\pm$ 2.7					74.5 $\pm$ 1.8
S			5730 $\pm$ 500					5730 $\pm$ 500
Sb	2.09 $\pm$ 0.08							2.09 $\pm$ 0.08
Sc	5.77 $\pm$ 0.16							5.77 $\pm$ 0.16
Se	2.1 $\pm$ 0.2	2.0 $\pm$ 0.1						2.03 $\pm$ 0.09
Si (%)			14.1 $\pm$ 0.7		15.2 $\pm$ 0.1			15.0 $\pm$ 0.3
Sm	3.10 $\pm$ 0.3							3.10 $\pm$ 0.3
Sr	674 $\pm$ 24		678 $\pm$ 21	712 $\pm$ 14				696 $\pm$ 11
Ta	0.55 $\pm$ 0.02							0.55 $\pm$ 0.02
Tb	0.37 $\pm$ 0.03							0.37 $\pm$ 0.03
Th	6.33 $\pm$ 0.13							6.33 $\pm$ 0.13
Ti (%)	0.18 $\pm$ 0.02		0.17 $\pm$ 0.02		0.18 $\pm$ 0.01			0.18 $\pm$ 0.01
U	4.2 $\pm$ 0.3	4.6 $\pm$ 0.2						4.5 $\pm$ 0.2
V	86 $\pm$ 6		95 $\pm$ 6	96 $\pm$ 3				94.2 $\pm$ 2.4
Y			14 $\pm$ 1					14 $\pm$ 1
Yb	1.26 $\pm$ 0.11							1.26 $\pm$ 0.11
Zn	67.2 $\pm$ 3.7	63 $\pm$ 3	62.6 $\pm$ 2.3	73.2 $\pm$ 4.0*				63.6 $\pm$ 1.6
Zr				36.2 $\pm$ 1.3				36.2 $\pm$ 1.3

*Deleted from error weighted average.

INAA - Instrumental Neutron Activation Analysis

RCAA - Radiochemical Neutron Activation Analysis

XRF - X-Ray Fluorescence Analysis

PES - Plasma Emission Spectroscopy (Sodium Carbonate Fusion)

FAA - Conventional Flame Atomic Absorption (Lithium Metaborate Fusion)

GFAA - Graphite Furnace Atomic Absorption

CVAA - Cold Vapor Atomic Absorption

TABLE A.3. Paraho Semiworks Retort – Direct Mode
Raw Oil Shale
Collected 8-25-77 (in ppm except as noted)

Element	XPF	PES	AA	CVAA
Al (%)			3.69	
As	42 ± 4			
B		111		
Ba	<1			
Ca (%)	10.6 ± 0.7		11.1	
Cr	33 ± 10			
Cu	41 ± 4			
Fe (%)	1.91 ± 0.13		2.05	
Ga	9 ± 1			
Hg				0.085 ± 0.004
K (%)	1.52 ± 0.10		1.48	
Mg (%)			3.68	
Mn	290 ± 22		441	
Na (%)			1.67	
Ni	27 ± 3			
Pb	27 ± 2			
Rb	67 ± 5			
Se	2.0 ± 0.4			
Si (%)	12.9 ± 1.4		14.7	
Sr	680 ± 50			
Ti (%)	0.20 ± 0.01		0.20	
Zn	67 ± 5			

XRF = X-ray Fluorescence (Energy Dispersion)
PES = DC-Coupled Plasma Emission Spectroscopy
AA = Atomic Absorption Analysis
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE A.4. Paraho Semiworks Retort - Direct Mode
Raw Oil Shale
Collected 8-26-77 (in ppm except as noted)

Element	XRF	PES	AA	CVAA
Al (%)			3.79	
As	42 ± 4			
B		106 ± 6		
Br	<1			
Ca (%)	11.7 ± 0.8		11.3	
Cr	50 ± 10			
Cu	41 ± 4			
Fe (%)	2.03 ± 0.14		2.08	
Ga	9 ± 1			
Hg				0.089 ± 0.004
K (%)	1.68 ± 0.13		1.51	
Mg (%)			3.48	
Mn	320 ± 25		325	
Mo	23 ± 2			
Na (%)			1.63	
Nb	8 ± 1			
Ni	28 ± 3			
Pb	27 ± 2			
Rb	71 ± 5			
Se	1.7 ± 5			
Si (%)	14.1 ± 1.6		14.5	
Sr	720 ± 50			
Ti (%)	0.18 ± 0.01		0.20	
Y	14 ± 2			
Zn	70 ± 5			
Zr	60 ± 9			

XRF = X-ray Fluorescence (Energy Dispersion)
PES = DC-Coupled Plasma Emission Spectroscopy
AA = Atomic Absorption Analysis
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE A.5. Paraho Semiworks Retort – Direct Mode
Raw Oil Shale
Collected 11-15-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al (%)	3.69 ± 0.06			3.75	
As	47 ± 1	39 ± 4			
B			80 ± 8		
Ba	500 ± 50				
Br	<1				
Ca (%)	9.5 ± 1.2	11.1 ± 0.8		10.9	
Co		8.1 ± 0.3			
Cr	35 ± 4				
Cu		40 ± 4			
Eu	0.60 ± 0.05				
Fe (%)	2.14 ± 0.03	2.16 ± 0.15		2.15	
Ga		8 ± 1			
Hf	1.7 ± 0.2				
Hg					0.096 ± 0.005
K (%)	1.7 ± 0.2	1.7 ± 0.1		1.61	
La	20 ± 1				
Mg (%)				3.58	
Mn	288 ± 25	330 ± 30		390	
Mo		23 ± 2			
Na (%)	1.78 ± 0.02			1.73	
Nb		5 ± 1			
Ni		23 ± 2			
Pb		23 ± 3			
Rb		75 ± 5			
Sb	2.2 ± 0.2				
Sc	6.0 ± 0.1				
Se		2.8 ± 0.5			
Si (%)		15.4 ± 1.6		15.1	
Sm	3.0 ± 0.4				
Sr		720 ± 60			
Th	6.1 ± 0.2				
Ti (%)	0.17 ± 0.04	0.19 ± 0.02			
V	86 ± 8				
Y		13 ± 2			
Zn		66 ± 5			
Zr		63 ± 9			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE A.6. Paraho Semiworks Retort - Direct Mode
Raw Oil Shale
Collected 11-16-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al (%)	3.65 ± 0.05			4.03	
As	44 ± 1	43 ± 4			
B			86 ± 9		
Ba	510 ± 60				
Br	<1				
Ca (%)	9.6 ± 1.2	10.4 ± 0.7		10.9	
Co	7.9 ± 0.2				
Cr	34 ± 4				
Cu		39 ± 4			
Eu	0.66 ± 0.05				
Fe (%)	2.06 ± 0.03	2.14 ± 0.14		2.13	
Ga		8 ± 1			
Hf	2.0 ± 0.2				
Hg					0.095 ± 0.005
K (%)	1.5 ± 0.2	1.7 ± 0.2		1.49	
La	20 ± 1				
Mg (%)				3.75	
Mn	308 ± 24	350 ± 30		380	
Mo		22 ± 2			
Na (%)	1.79 ± .02			1.80	
Nb		6 ± 1			
Ni		24 ± 2			
Pb		23 ± 3			
Rb		72 ± 5			
Sb	2.0 ± 0.2				
Sc	5.6 ± 0.1				
Se		2.2 ± 0.5			
Si (%)		15.5 ± 1.5		15.5	
Sm	3.0 ± 0.4				
Sr		740 ± 60			
Th	6.5 ± 0.2				
Ti (%)	0.16 ± 0.04	0.17 ± 0.03			
V	65 ± 7				
Y		12 ± 2			
Zn		64 ± 5			
Zr		63 ± 9			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE A.7. Paraho Semiworks Retort - Direct Mode
Raw Oil Shale
Collected 11-17-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al (%)	3.91 ± 0.05			3.95	
As	45 ± 1	43 ± 4			
B			83 ± 9		
Ba	570 ± 50				
Br	<1				
Ca (%)	12.1 ± 1.4	10.9 ± 0.8		10.9	
Co	7.8 ± 0.2				
Cr	37 ± 2				
Cu		38 ± 3			
Eu	0.68 ± 0.07				
Fe (%)	2.16 ± 0.03	2.21 ± 0.14		2.17	
Ga		8 ± 1			
Hf	1.7 ± 0.2				
Hg					0.104 ± 0.005
K (%)	1.7 ± 0.1	1.7 ± 0.2		1.56	
La	21 ± 1				
Mg (%)				3.70	
Mn	317 ± 25	360 ± 30		400	
Mo		22 ± 2			
Na (%)	1.75 ± .02			1.74	
Nb		6 ± 1			
Ni		28 ± 2			
Pb		23 ± 3			
Rb		72 ± 5			
Si (%)		15.3 ± 1.5		15.5	
Sm	3.2 ± 0.4				
Sr	740 ± 50				
Th	6.5 ± 0.2				
Ti (%)	0.11 ± 0.04	0.18 ± 0.02			
V	81 ± 7				
Y		12 ± 2			
Zn		64 ± 6			
Zr		64 ± 9			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE B.1. Paraho Semiworks Retort - Direct Mode
Retorted Oil Shale
Collected 8-23-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al (%)	4.63 ± 0.09			4.50	
As		53 ± 5			
B			123 ± 5		
Ba	640 ± 100	600 ± 30	570 ± 15	600 ± 100	
Br	<0.7	<1.1			
Ca (%)	13.6 ± 2.0	13.8 ± 1.0		13.9	
Co	11.3 ± 0.3				
Cr	42 ± 6	30 ± 12	48 ± 5		
Cu		52 ± 5			
Eu	0.80 ± 0.06				
Fe (%)	2.51 ± 0.05	2.53 ± 0.17		2.46	
Ga		11 ± 1			
Hg					0.021 ± 0.002
K (%)		1.78 ± 0.14		1.76	
La	24.6 ± 0.4	26 ± 4			
Lu	0.42 ± 0.07				
Mg (%)				4.31	
Mn	399 ± 31	412 ± 25	395 ± 15	500 ± 40	
Mo		35 ± 2			
Na (%)	2.36 ± 0.01			2.20	
Nb		15 ± 4			
Ni		33 ± 3			
Pb		33 ± 3			
Rb		32 ± 6			
Sb	3.1 ± 0.3				
Sc	7.6 ± 0.1				
Se		3.1 ± 0.6			
Si (%)		14.6 ± 1.8		18.2	
Sm	4.4 ± 0.1				
Sr		900 ± 60	811 ± 30		
Th	7.1 ± 0.2				
Ti (%)	0.25 ± 0.04	0.25 ± 0.02		0.17 ± 0.04	
U	5.6 ± 0.14				
V	101 ± 10		114 ± 4		
Y		16 ± 2			
Zn		86 ± 6			
Zr		74 ± 11			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE B.2. Paraho Semiworks Retort - Direct Mode
Retorted Oil Shale
Collected 8-24-77 (in ppm except as noted)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Al (%)	4.83 $\pm$ 0.05*			4.46 $\pm$ 0.05	4.56 $\pm$ 0.17			4.48 $\pm$.08
As	59.2 $\pm$ 0.9		59.8 $\pm$ 1.9					59.4 $\pm$ 1.0
B				107 $\pm$ 2				107 $\pm$ 2
Ba	593 $\pm$ 13			613 $\pm$ 12				604 $\pm$ 9
Br	0.80 $\pm$ 0.18							0.80 $\pm$ 0.18
Ca (%)	13.1 $\pm$ 0.5		13.9 $\pm$ 0.7	11.1 $\pm$ 0.2	13.2 $\pm$ 0.2			13.3 $\pm$ 0.2
Cd		0.90 $\pm$ 0.04				0.99 $\pm$ 0.13		0.91 $\pm$ 0.04
Ce	51.5 $\pm$ 1.5							51.5 $\pm$ 1.5
Co	11.1 $\pm$ 0.2							11.1 $\pm$ 0.2
Cr	44.3 $\pm$ 0.9		49.6 $\pm$ 8.9	41.0 $\pm$ 3.8				44.2 $\pm$ 0.9
Cs	4.68 $\pm$ 0.21							4.68 $\pm$ 0.21
Cu			56.3 $\pm$ 1.0	46.9 $\pm$ 5.3				55.9 $\pm$ 1.1
Dy	3.5 $\pm$ 0.2							3.5 $\pm$ 0.2
Eu	0.73 $\pm$ 0.02							0.73 $\pm$.02
Fe (%)	2.42 $\pm$ 0.04		2.56 $\pm$ 0.13	2.35 $\pm$ 0.03	2.47 $\pm$ 0.08			2.40 $\pm$ 0.030
Ga			11.6 $\pm$ 1.2					11.6 $\pm$ 1.2
Hf	2.11 $\pm$ 0.03							2.11 $\pm$ 0.03
Hg							0.035 $\pm$ 0.003	0.035 $\pm$ 0.003
Ho	0.88 $\pm$ 0.04							0.88 $\pm$ 0.04
K (%)	1.98 $\pm$ 0.20		1.94 $\pm$ 0.05	2.11 $\pm$ 0.05*	1.81 $\pm$ 0.03			1.86 $\pm$ 0.03
La	24.7 $\pm$ 0.3							24.7 $\pm$ 0.3
Lu	0.35 $\pm$ 0.03							0.35 $\pm$ 0.03
Mg (%)				3.88 $\pm$ 0.03	4.32 $\pm$ 0.09			4.07 $\pm$ 0.06
Mn	388 $\pm$ 23		420 $\pm$ 24	374 $\pm$ 28				396 $\pm$ 14
Mo			32.7 $\pm$ 1.4	41.3 $\pm$ 3.9				33.7 $\pm$ 1.3

TABLE B.2. Paraho Semiworks Retort - Direct Mode
Retorted Oil Shale
Collected 8-24-77 (in ppm except as noted).

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Na (%)	2.15 $\pm$ 0.03				2.24 $\pm$ 0.03			2.19 $\pm$ 0.03
Nb			9.2 $\pm$ 1.5					9.2 $\pm$ 1.5
Nd	22.3 $\pm$ 1.1							22.3 $\pm$ 1.1
Ni	29.7 $\pm$ 4.6		32.1 $\pm$ 3.9	32.4 $\pm$ 1.8				32.1 $\pm$ 1.5
Pb			36.2 $\pm$ 2.0					36.2 $\pm$ 2.0
Rb	89.9 $\pm$ 4.1		88 $\pm$ 2					88.4 $\pm$ 1.8
S			6780 $\pm$ 620					6780 $\pm$ 620
Sb	2.63 $\pm$ 0.15							2.63 $\pm$ 1.5
Sc	6.84 $\pm$ 0.15							6.84 $\pm$ 0.15
Se		2.3 $\pm$ 0.1						2.3 $\pm$ 0.1
Si (%)			17.8 $\pm$ 1.3		18.2 $\pm$ 0.3			18.2 $\pm$ 0.4
Sm	3.68 $\pm$ 0.07							3.68 $\pm$ 0.07
Sr	820 $\pm$ 26*		866 $\pm$ 7	892 $\pm$ 14				879 $\pm$ 12
Ta	0.65 $\pm$ 0.02							0.65 $\pm$ 0.02
Tb	0.42 $\pm$ 0.04							0.42 $\pm$ 0.04
Th	7.55 $\pm$ 0.10							7.55 $\pm$ 0.10
Ti (%)	0.21 $\pm$ 0.04		0.24 $\pm$ 0.01		0.20 $\pm$ 0.03			0.24 $\pm$ 0.01
U	5.3 $\pm$ 0.2	4.9 $\pm$ 0.2						5.10 $\pm$ 0.14
V	111 $\pm$ 13		139 $\pm$ 19	133 $\pm$ 7				129 $\pm$ 6
Y			16.4 $\pm$ 0.9					16.4 $\pm$ 0.9
Yb	1.61 $\pm$ 0.13							1.61 $\pm$ 0.13
Zn	89.2 $\pm$ 3.0	77 $\pm$ 4	86.2 $\pm$ 5.5	93.6 $\pm$ 5.3*				82.3 $\pm$ 2.2
Zr				36.2 $\pm$ 1.3				36.2 $\pm$ 1.3

*Deleted from error weighted average.

INAA = Instrumental Neutron Analysis

RCAA = Radiochemical Neutron Activation Analysis

XRF = X-Ray Fluorescence Analysis

PES = Plasma Emission Spectroscopy (Sodium Carbonate Fusion)

FAA = Conventional Flame Atomic Absorption (Lithium Metaborate Fusion)

GFAA = Graphite Furnace Atomic Absorption

CVAA = Cold Vapor Atomic Absorption

**TABLE B.3. Paraho Semiworks Retort – Direct Mode
Retorted Oil Shale
Collected 8-25-77 (in ppm except as noted)**

Element	INAA	XRF	PES	AA	CVAA
Al (%)	4.74 ± 0.09			4.46	
As	64 ± 1	59 ± 5			
B			134 ± 4		
Ba	600 ± 70	540 ± 30	496 ± 15	600 ± 100	
Br	<0.7	<1			
Ca (%)	12.6 ± 2.0	14.4 ± 1.0		14.1	
Co	9.6 ± 0.3				
Cr	36 ± 6	40 ± 17	45 ± 6		
Cu		52 ± 5			
Eu	0.71 ± 0.05				
Fe (%)	2.51 ± 0.06	2.58 ± 0.18		2.29	
Ga		12 ± 1			
Hg					0.034 ± 0.002
K (%)		1.86 ± 0.14		1.76	
La	21.7 ± 0.3	20 ± 4			
Lu	0.40 ± 0.06				
Mg (%)				4.27	
Mn	373 ± 31	395 ± 30	434 ± 15	463 ± 40	
Mo		32 ± 2			
Na (%)	2.27 ± 0.04			2.28	
Nb		10 ± 1			
Ni		34 ± 4			
Pb		32 ± 3			
Rb		86 ± 6			
Sb	2.7 ± 0.2				
Sc	7.0 ± 0.1				
Se		2.9 ± 0.5			
Si (%)		16.3 ± 1.8		17.8	
Sm	4.0 ± 0.2				
Sr		840 ± 60	731 ± 28		
Th	6.8 ± 0.2				
Ti (%)	0.18 ± 0.04	0.25 ± 0.02		0.20 ± 0.04	
U	5.0 ± 1.2				
V	96 ± 10		122 ± 5		
Y		15 ± 2			
Zn		85 ± 6			
Zr		67 ± 10			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE B. 4. Paraho Semiworks Retored - Direct Mode
Retorted Oil Shale
Collected 8-26-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al (%)	4.85 ± 0.09			4.37	
As	65 ± 1	58 ± 6			
B			113 ± 3		
Ba	660 ± 80	560 ± 30	510 ± 15	500 ± 100	
Br	<0.7	<1			
Ca (%)	14.2 ± 2.0	14.5 ± 1.0		13.6	
Co	9.7 ± 0.3				
Cr	36 ± 5	40 ± 9	54 ± 5		
Cu		52 ± 5			
Eu	0.68 ± 0.05				
Fe (%)	2.42 ± 0.01	2.57 ± 0.18		2.38	
Ga		11 ± 1			
Hg					0.030 ± 0.002
K (%)		1.86 ± 0.15		1.81	
La	22.1 ± 0.3	25 ± 4			
Lu	0.45 ± 0.03				
Mg (%)				4.18	
Mn	366 ± 31	440 ± 10	399 ± 15	500 ± 40	
Mo		30 ± 2			
Na (%)	2.22 ± 0.02			2.17	
Nb		7 ± 1			
Ni		36 ± 3			
Pb		32 ± 3			
Rb		81 ± 6			
Sb	2.6 ± 0.2				
Sc	7.1 ± 0.1				
Se		3.3 ± 0.6			
Si (%)		16.9 ± 1.9		17.9	
Sm	4.1 ± 0.1				
Sr		840 ± 60	783 ± 30		
Th	6.4 ± 0.2				
Ti (%)	0.22 ± 0.04	0.24 ± 0.02		0.19 ± 0.04	
U	4.9 ± 1.0				
V	111 ± 10		113 ± 4		
Y		15 ± 2			
Zn		88 ± 7			
Zr		71 ± 11			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE B.5. Paraho Semiworks Retort - Direct Mode
Retorted Oil Shale
Collected 11-15-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al (%)	4.74 ± 0.07			4.55	
As	70 ± 1	67 ± 5			
B			90 ± 9		
Ba	760 ± 80				
Br	<1				
Ca (%)	14.5 ± 1.6	13.6 ± 0.9		13.7	
Co	10.9 ± 0.4				
Cr	36 ± 5				
Cu		55 ± 5			
Eu	0.84 ± 0.09				
Fe (%)	2.55 ± 0.05	2.66 ± 0.17		2.44	
Ga		13 ± 1			
Hf	2.0 ± 0.2				
Hg					0.021 ± 0.002
K (%)	1.9 ± 0.2	2.0 ± 0.2		1.32	
La	26 ± 1				
Mg (%)				4.38	
Mn	374 ± 28	420 ± 30		460	
Mo		32 ± 2			
Na (%)	2.54 ± .02			2.31	
Nb		8 ± 1			
Ni		36 ± 4			
Pb		33 ± 3			
Rh		88 ± 6			
Sb	3.2 ± 0.4				
Sc	7.1 ± 0.1				
Se		4.0 ± 0.6			
Si (%)		17.2 ± 1.7		18.3	
Sm	3.3 ± 0.4				
Sr		860 ± 60			
Th	7.8 ± 0.3				
Ti (%)	0.20 ± 0.05	0.22 ± 0.02			
V	102 ± 9				
Y		15 ± 2			
Zn		86 ± 6			
Zr		66 ± 10			

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
PES = DC-Coupled Plasma Emission Spectroscopy
AA = Atomic Absorption Analysis
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE B.6. Paraho Semiwork Sretort - Direct Mode
Retorted Oil Shale
Collected 11-16-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al (%)	4.45 ± 0.06			4.57	
As	67 ± 4	66 ± 4			
B			98 ± 10		
Ba	710 ± 70				
Br	<1				
Ca (%)	11.7 ± 1.3	13.7 ± 0.9		13.4	
Co	10.8 ± 0.4				
Cr	35 ± 5				
Cu		61 ± 5			
Eu	0.83 ± 0.08				
Fe (%)	2.48 ± 0.04	2.74 ± 0.18		2.46	
Ga		10 ± 1			
Hf	2.0 ± 0.2				
Hg					0.025 ± 0.002
K (%)		2.2 ± 0.2		1.32	
La	25 ± 1				
Mg (%)				4.49	
Mn	310 ± 26	430 ± 30		460	
Mo		35 ± 2			
Na (%)	2.40 ± .02			2.27	
Nb		6 ± 1			
Ni		36 ± 3			
Pb		35 ± 3			
Rb		87 ± 6			
Sb	2.7 ± 0.3				
Sc	6.8 ± 0.1				
Se		2.9 ± 0.5			
Si (%)		17.0 ± 1.7		18.4	
Sm	3.6 ± 0.4				
Sr		880 ± 60			
Th	7.4 ± 0.3				
Ti (%)	0.24 ± 0.04	0.23 ± 0.02			
V	105 ± 8				
Y		16 ± 2			
Zn		92 ± 7			
Zr		75 ± 11			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE B.7. Paraho Semiworks - Direct Mode
Retorted Oil Shale
Collected 11-22-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al (%)	4.62 ± 0.07			4.68	
As	61 ± 1	50 ± 5			
B			101 ± 10		
Ba	740 ± 50				
Br	<1				
Ca (%)	11.8 ± 1.4	14.0 ± 0.9		13.8	
Co	10.4 ± 0.4				
Cr	38 ± 5				
Cu		60 ± 5			
Eu	0.80 ± 0.08				
Fe (%)	2.50 ± 0.03	2.73 ± 0.18		2.46	
Ga		12 ± 1			
Hf	2.3 ± 0.3				
Hg					0.025 ± 0.002
K (%)	2.2 ± 0.2	2.1 ± 0.2		1.76	
La	25 ± 1				
Mg (%)				4.55	
Mn	367 ± 27	440 ± 30		440	
Mo		33 ± 2			
Na (%)	2.35 ± .04			2.28	
Ni		33 ± 3			
Pb		32 ± 3			
Rb		87 ± 6			
Sb	2.8 ± 0.3				
Sc	7.0 ± 0.1				
Se		2.9 ± 0.5			
Si (%)		18.7 ± 1.7		18.5	
Sm	3.9 ± 0.4				
Sr		890 ± 60			
Th	7.8 ± 0.2				
Ti (%)	0.19 ± 0.04	0.22 ± 0.02			
V	99 ± 8				
Y		15 ± 2			
Zn		86 ± 6			
Zr		72 ± 11			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE C.1. Paraho Semiworks Retort - Direct Mode
Product Oil
Collected 8-23-77 (in ppm except as noted)

Element	INAA	XRF	AA
Al	10.3 $\pm$ 0.6		12 $\pm$ 2
As	28.0 $\pm$ 0.3	23 $\pm$ 2	
Br	<0.06		
Ca			42 $\pm$ 1
Cl	0.6 $\pm$ 0.2		
Co	1.05 $\pm$ 0.03		
Cr	<0.03		
Cu	<0.5	0.71 $\pm$ 0.15	<0.2
Fe	44 $\pm$ 2	52 $\pm$ 5	53 $\pm$ 1
Mg	14 $\pm$ 1		9 $\pm$ 1
Mn	0.15 $\pm$ 0.02	<0.3	
Na	3.43 $\pm$ 0.06		
Ni	2.58 $\pm$ 0.05	2.83 $\pm$ 0.22	
Pb		<0.3	
Rb	0.04 $\pm$ 0.020	<0.1	
S (%)	0.73 $\pm$ 0.07		
Sb	0.035 $\pm$ 0.004		
Sc	0.0031 $\pm$ 0.0002		
Se	0.91 $\pm$ 0.01	0.77 $\pm$ 0.07	
Si			55 $\pm$ 6
Sr		<1	
Th	0.008 $\pm$ 0.001		
V	0.190 $\pm$ 0.010	<0.9	
Zn	0.46 $\pm$ 0.01	0.59 $\pm$ 0.08	

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
AA = Atomic Absorption Analysis
Analyses by Pacific Northwest Laboratory

TABLE C.2. Paraho Semiworks Retort - Direct Mode
Product Oil
Collected 8-24-77 (in ppm except as noted)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>
Al	16.0 $\pm$ 0.3	
As	30.5 $\pm$ 0.3	24 $\pm$ 2
Br	<0.1	
Cl	<0.7	
Co	0.93 $\pm$ 0.03	0.91 $\pm$ 0.35
Cr	<0.05	
Cu	0.42 $\pm$ 0.13	
Fe	42 $\pm$ 2	56 $\pm$ 5
Mg	25 $\pm$ 5	
Mn	0.21 $\pm$ 0.02	<0.3
Na	4.07 $\pm$ 0.08	
Ni	2.72 $\pm$ 0.08	2.75 $\pm$ 0.20
Pb		<0.3
Rb		<0.1
S (%)	0.74 $\pm$ 0.05	
Sb	0.028 $\pm$ 0.004	
Sc	0.0029 $\pm$ 0.0003	
Se	0.99 $\pm$ 0.01	0.82 $\pm$ 0.07
Sr		<1
Th	0.009 $\pm$ 0.001	
V	0.25 $\pm$ 0.01	<0.60
Zn	0.41 $\pm$ 0.01	0.41 $\pm$ 0.08

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
Analyses by Pacific Northwest Laboratory

TABLE C.3. Paraho Semiworks Setort - Direct Mode
Product Oil
Collected 8-25-77 (in ppm except as noted)

Element	INAA	XRF
Al	22.2 ± 0.5	
As	37 ± 1	23 ± 2
Br	<0.2	
Cl	<2	
Co		0.57 ± 0.25
Cu	<0.9	0.33 ± 0.12
Fe		59 ± 5
Mg	18 ± 9	
Mn	0.36 ± 0.05	0.45 ± 0.25
Na	7.4 ± 1.5	
Ni		2.72 ± 0.20
Pb		<0.4
Rb		<0.2
S (%)	0.99 ± 0.08	
Se		0.92 ± 0.07
Sr		<1
V	0.280 ± 0.010	<1
Zn		0.57 ± 0.08

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
Analyses by Pacific Northwest Laboratory

TABLE C.4. Paraho Semiworks Retort - Direct Mode
Product Oil
Collected 8-26-77 (in ppm except as noted)

Element	INAA	XRF
Al	10.3 $\pm$ 0.2	
As	26.6 $\pm$ 0.3	22 $\pm$ 2
Br	<0.1	
Cl	0.6 $\pm$ 0.3	
Co		1.01 $\pm$ 0.03
Cr	<0.03	
Cu	<0.4	0.48 $\pm$ 0.15
Fe	43 $\pm$ 2	63 $\pm$ 5
Mg	18 $\pm$ 5	
Mn	0.20 $\pm$ 0.02	<0.3
Na	6.98 $\pm$ 0.08	
Ni	2.67 $\pm$ 0.05	2.79 $\pm$ 0.20
Pb		<0.3
Rb	0.070 $\pm$ 0.015	<0.1
S (%)	0.74 $\pm$ 0.08	
Sb	0.038 $\pm$ 0.004	
Sc	0.0031 $\pm$ 0.0002	
Se	1.02 $\pm$ 0.01	0.93 $\pm$ 0.07
Sr		<1
Th	0.008 $\pm$ 0.001	
V	0.240 $\pm$ 0.005	
Zn	0.25 $\pm$ 0.01	0.28 $\pm$ 0.07

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
Analyses by Pacific Northwest Laboratory

TABLE C.5. Paraho Semiworks Retort - Direct Mode
Product Oil-Holding Tank
Collected 8-25-77 (in ppm except as noted)

<u>Element</u>	<u>INAA</u>
Al	5.4 ± 0.3
As	28.9 ± 0.2
Br	<0.06
Cl	<0.7
Co	1.02 ± 0.03
Cr	<0.03
Cu	<0.3
Fe	43 ± 2
Mg	<7
Mn	0.090 ± 0.005
Na	3.08 ± 0.06
Ni	2.57 ± 0.03
Rb	0.05 ± 0.02
S (%)	0.82 ± 0.06
Sb	0.039 ± 0.004
Sc	0.0015 ± 0.0003
Se	0.96 ± 0.01
Th	<0.003
V	0.22 ± 0.01
Zn	0.43 ± 0.01

INAA = Instrumental Neutron Activation Analysis
Analyses by Pacific Northwest Laboratory

TABLE C.6. Paraho Semiworks Retort - Direct Mode
Product Oil
Collected 11-15-77 (in ppm except as noted)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>
Al	6.9 ± 0.4	
As	36.8 ± 0.2	25 ± 2
Ba	<2	
Br	<0.1	
Cl	<0.4	
Co	1.40 ± 0.04	1.29 ± 0.22
Cr	<0.1	
Cu	<0.5	0.44 ± 0.15
Fe	78 ± 6	62 ± 5
Hf	<0.007	
Mg	<7	
Mn	0.116 ± 0.017	0.48 ± 0.22
Na	3.85 ± 0.07	
Ni	2.93 ± 0.15	3.05 ± 0.23
Pb		<0.3
Rb	<0.4	<0.1
S (%)	0.67 ± 0.06	
Sb		0.052 ± 0.009
Sc	0.0027 ± 0.0008	
Se	1.02 ± 0.03	0.94 ± 0.09
Sr		<1
Th	<0.007	
U	<0.07	
V	0.21 ± 0.01	<0.82
Zn	0.22 ± 0.02	0.27 ± 0.07

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
Analyses by Pacific Northwest Laboratory

TABLE C.7. Paraho Semiworks Retort - Direct Mode
Product Oil
Collected 11-16-77 (in ppm except as noted)

Element	INAA	XRF	AA
Al	3.0 ± 0.2		
As	39.9 ± .2	24 ± 2	
Ba	<3		
Br	<0.06	<0.02	
Ca			34 ± 1
Cl	<0.06		
Co	1.25 ± 0.04	1.31 ± 0.22	
Cr	<0.1		<0.2
Cu	0.3 ± 0.1	0.65 ± 0.15	
Fe	51 ± 7	63 ± 5	64 ± 1
Hf	<0.009		
Mg	<7		6 ± 1
Mn	0.080 ± 0.015	0.47 ± 0.22	0.69 ± 0.1
Na			
Ni	1.03 ± .04	2.53 ± 0.22	
Pb		<0.3	
Rb	<0.5	<0.1	
S (%)	0.74 ± 0.05		
Sb	0.05 ± 0.01		
Sc	0.07 ± 0.0004		
Se	0.69 ± 0.04	0.58 ± 0.07	
Si			44 ± 1
Sr		<1	
Th	0.21 ± 0.004		
U	<0.09		
V	0.20 ± 0.05		
Zn	0.30 ± 0.03	0.38 ± 0.07	

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE C.8. Paraho Semiworks Retort - Direct Mode
Product Oil
Collected 11-21-77 (in ppm except as noted)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>
Al	18.0 $\pm$ 0.9	
As	39.2 $\pm$.2	24 $\pm$ 2
Ba	<3	
Cl	<0.7	
Co	1.24 $\pm$ 0.05	1.14 $\pm$ 0.15
Cr	<0.1	
Cu	<0.5	0.36 $\pm$ 0.13
Fe	62 $\pm$ 10	51 $\pm$ 4
Hf	<0.01	
Mg	18 $\pm$ 5	
Mn	0.22 $\pm$ 0.03	<0.3
Na	1.17 $\pm$.04	
Ni	2.45 $\pm$ 0.15	2.93 $\pm$ 0.22
Rb	<0.5	
S (%)	0.78 $\pm$ 0.06	
Sb	<0.03	
Sc	<0.002	
Se	0.95 $\pm$ 0.04	0.58 $\pm$ 0.07
Th	<0.01	
U	<0.08	
V	0.31 $\pm$ 0.01	
Zn	0.25 $\pm$ 0.04	0.31 $\pm$ 0.07

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

Analyses by Pacific Northwest Laboratory

TABLE D.1. Paraho Semiworks Retort - Direct Mode
Product Water
Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA	ISE
Al	<0.4					
As	5.63 ± 0.04	4.9 ± 0.3	6.9			
B			43 ± 6			
Ba			0.33			
Br	<0.05	<0.1				
Ca			12.1	38.4		
Cl	36 ± 1					
Co	0.032 ± 0.001	<0.30				
Cr	<0.060	<0.80				
Cu	<1	0.7 ± 0.1		0.66		
F						25
Fe	<3	1.5 ± 0.3				
Ga		<100				
Hg		<0.40			0.0023 ± 0.0001	
K	38 ± 7			17		
Li			1.70	1.25		
Mg	460 ± 20		612	520		
Mn	0.13 ± 0.04		0.16	0.22		
Mo		<0.14	0.15			
Na	115 ± 1					
Ni	0.530 ± 0.100	0.540 ± 0.120				
P			1.95			
Pb		<0.40				
Rb	0.150 ± 0.040	0.120 ± 0.040				
S (%)	3.9 ± 0.2					
Sb	0.020 ± 0.004					
Se	9.5 ± 0.6	8.8 ± 0.5	11			
Si			37	44		
Sr	1.10 ± 0.20	0.60 ± 0.06	0.80			
Ti		6.1 ± 1.2				
U	<0.10	<0.20				
V	0.045 ± 0.008	<1.0	0.042			
Zn	0.44 ± 0.08	0.36 ± 0.09	0.15	0.42		
Zr		<0.10				

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

ISE = Ion Specific Electrode

Analyses by Pacific Northwest Laboratory

TABLE D.2. Paraho Semiworks Retort - Direct Mode
Product Water
Collected 8-23-77 (in ppm except as noted)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>	<u>PES</u>	<u>AA</u>	<u>CVAA</u>	<u>ISE</u>
Al	0.26 ± 0.06					
As	4.40 ± 0.03	3.8 ± 0.2	3.1			
B			2.1			
Br	<0.05	<0.1				
Ca				35.9		
Cl	65 ± 1					
Co	0.130 ± 0.010	<0.2				
Cr	<0.041	<0.4				
Cu	0.8 ± 0.2	0.8 ± 0.1		0.91		
F						1.4
Fe	1.8 ± 0.2			2.6		
Ga		<0.08				
Hg		<0.3			0.0058 ± 0.0002	
K		<20		8		
La				0.58		
Mg	220 ± 10			258		
Mn	0.41 ± 0.05			0.47		
Mo		0.110 ± 0.050	0.030			
Na	105 ± 1			112		
Ni	0.270 ± 0.090	0.190 ± 0.070				
P			1.90 ± 0.2			
Pb		<0.2				
Rb	<0.10	<0.06				
S (%)	1.7 ± 0.1					
Sb	0.019 ± 0.004					
Se	4.0 ± 0.2	3.4 ± 0.2	1.6			
Si			2.2	26		
Sr	0.42 ± 0.10	0.39 ± 0.04				
Ti		<1				
U	<0.1	<0.1				
V	0.24 ± 0.003	<0.6	0.015			
Zn	0.39 ± 0.08	0.39 ± 0.07	0.24	0.21		
Zr		<0.08				

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
PES = DC-Coupled Plasma Emission Spectroscopy
AA = Atomic Absorption Analysis
CVAA = Cold Vapor Atomic Absorption
ISE = Ion specific Electrode
Analyses by Pacific Northwest Laboratory

TABLE D.3. Paraho Semiworks Retort - Direct Mode
Product Water
Collected 8-26-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	ISE
As	5.00 ± 0.04	3.9 ± 0.2	4.3		
B			12		
Ba	0.8				
Br	<0.05	<0.1			
Ca				33.4	
Co	0.11 ± 0.01				
Cr	0.040 ± 0.004				
Cu		0.5 ± 0.1		0.53	
F					10
Fe	<3	1.5 ± 0.2		2.1	
Ga		<0.08			
Hf	<0.005				
Hg		0.3			
K	<20			8	
Li				0.51	
Mg				234	
Mn				0.39	
Mo		<0.1	0.066		
Na	92.7 ± 0.4			100	
Ni	0.240 ± 0.080	0.200 ± 0.100			
P			0.83 ± 0.11		
Pb		<0.2			
Rb	0.20	0.080 ± 0.030			
Sb	10 ± 2	0.010 ± 0.002			
Se	4.0 ± 0.2	3.4 ± 0.2	3.8		
Si			19	26	
Sr	0.67 ± 0.10	0.33 ± 0.04			
Th	0.008 ± 0.001				
Ti		1.4 ± 0.5			
U		<0.1	<0.10		
V			0.017		
Zn	1.26 ± 0.10	0.87 ± 0.09	1.08	1.02	
Zr		<0.08			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

ISE = Ion Specific Electrode

Analyses by Pacific Northwest Laboratory

TABLE D.4. Paraho Semiworks Retort - Direct Mode
Product Water-Holding Tank
Collected 8-26-77 (in ppm except as noted)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>	<u>PES</u>	<u>AA</u>	<u>ISE</u>
Al	0.67 ± 0.17				
As	14.0 ± 0.1	10.9 ± 0.7	11		
B			41		
Br	0.27 ± 0.04	<13			
Ca				64.4	
Cd			0.36		
Cl	83 ± 3	<400			
Co	0.35 ± 0.01	<1			
Cr	0.13 ± 0.03				
Cu	24 ± 1	15.3 ± 1.0		24	
F					52
Fe	7 ± 1	3.7 ± 0.4		4.7	
Ga		<0.1			
Hg		<0.5			
K	70 ± 11			60	
Li				2.3	
Mg	940 ± 20			974	
Mn	0.34 ± 0.13			0.27	
Mo		0.46 ± 0.08	0.59		
Na	400 ± 10			444	
Ni	0.41 ± 0.01				
Pb			0.69		
Rb	0.39 ± 0.08	0.43 ± 0.05			
S (%)	5.1 ± 0.3				
Sb	0.034 ± 0.005				
Se	6.2 ± 0.1	5.3 ± 0.3	6.6		
Si			23	24	
Sr	2.0 ± 0.3	1.06 ± 0.08			
Ti		6.0 ± 1.5			
U	<0.1	<0.2			
V	0.090 ± 0.007		0.097		
Zn	6.5 ± 0.2	4.0 ± 0.3	4.51		
Zr		<0.1			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

ISE = Ion Specific Electrode

Analyses by Pacific Northwest Laboratory

TABLE D.5. Paraho Semiworks Retort - Direct Mode
Product Water
Collected 11-15-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al	<1				
As		15.1 ± 0.9	18		
B	20 ± 2		43		
Ba	<3				
Br	<0.02	<0.1			
Ca				43	
Cl	62 ± 3				
Co	0.37 ± 0.020	<0.4			
Cr	<0.1	<1			
Cu	7.3 ± 1.3	5.5 ± 0.4		7.6	
F					36
Fe	<5	1.9 ± 0.3			
Ga		0.15 ± 0.07			
Hf	<0.008				
Hg		0.5			0.0056 ± 0.0005
K	<25			48	
Li				2.1	
Mg	800 ± 20			936	
Mn	<0.2	<0.5		0.12	
Mo		0.52 ± 0.08	0.50		
Na	330 ± 1			370	
Ni		0.372 ± 0.13			
P			1.5 ± 0.2		
Pb		<0.3	0.72		
Rb	0.31 ± 0.05	0.32 ± 0.05			
S (%)	4.3 ± 0.3				
Sb	<0.02				
Se	6.58 ± 0.18	6.8 ± 0.4	12		
Si			34	35	
Sr	0.72 ± 0.18	0.37 ± 0.07			
Th	<0.01				
Ti		<3			
U	<0.09	<0.2			
V	0.084 ± 0.017		<2	0.095	
Zn	0.73 ± 0.03	0.8 ± 0.1	1.01	0.37	
Zr			<0.1		

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE D.6. Paraho Semiworks Retort - Direct Mode
Product Water
Collected 11-16-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al	<2				
As	16 ± 2	10.8 ± 0.7	13		
B			36		
Ba			0.110 ± 0.006		
Br	<0.4	<0.1			
Ca			15	42	
Cl	71 ± 3				
Co	0.30 ± 0.05	<0.4			
Cr	<0.1	<0.9			
Cu	11.8 ± 1.5	7.7 ± 0.5		10.4	
F					33
Fe	<7	1.9 ± 0.3			
Ga		<0.2			
Hg	<0.008			0.0063 ± 0.006	
K	<30			45	
Li			2.6 ± 0.1	1.9	
Mg	740 ± 20		867 ± 35	848	
Mn	<0.2		0.091 ± 0.005	0.12	
Mo		0.430 ± 0.080	0.40		
Na	300 ± 1			354	
Ni		400 ± 130			
P			0.43 ± 0.05		
Pb		<0.30	1.15		
Rb	0.360 ± 0.060	0.320 ± 0.050			
S (%)	4.6 ± 0.3				
Sb	<0.02				
Se	6.44 ± 0.18	6.5 ± 0.4	8.3		
Si			20	28	
Sr		0.85 ± 0.07	1.22 ± 0.05		
Th	<0.002				
Ti		10 ± 2			
U	<0.08	<2			
V	0.077 ± 0.019	<1	0.077		
Zn	7.0 ± 0.1	6.7 ± 0.4	7.5	8.6	
Zr		<100			

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE D.7. Paraho Semiworks Retort - Direct Mode
Catchment Pond Water
Collected 11-16-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	CVAA
Al	<0.8				
As	1.6 ± .1	1.2 ± 0.1	1.7		
B			0.76		
Ba	<1		0.19 ± 0.01		
Br	<0.3				
Ca			70 ± 3	198	
Cl	223 ± 5				
Co	<0.008	<0.1			
Cr		<0.2			
Cu	<2	<0.5		<0.02	
F					2.5
Fe	<5	<1		2.1	
Ga		<0.07			
Hf	<0.004				
Hg		<0.3			
K	<30			24	
Li			0.41 ± 0.04	0.39	
Mg	70 ± 20		101 ± 4	84	
Mn	<0.3	0.38 ± 0.09	0.19 ± 0.01	0.22	
Mo		<0.08	0.13		
Na	357 ± 1			366	
Ni		<0.09			
P			<0.2		
Pb		<0.2			
Rb		<0.06			
S (%)	0.14 ± 0.04				
Sb	<0.01				
Se		<0.07	<0.2		
Si			7.0	11	
Sr	1.34 ± 0.13	1.3 ± 0.1	2.1 ± 0.1		
Th	<0.003				
Ti		2.0 ± 0.3			
U	<0.1	<0.1			
V	<0.03	<0.3	0.013		
Zn		<0.2	0.024		
Zr		<0.07			

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
PES = DC-Coupled Plasma Emission Spectroscopy
AA = Atomic Absorption Analysis
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE D.8. Paraho Semiworks Retort - Direct Mode
Product Water
Collected 11-17-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA	
Al	0.4 ± 0.1				
As	6.5 ± .3	4.9 ± 0.3	5.6		
B			16		
Ba	<3				
Br	0.2 ± 0.1	<0.1			
Ca				41	
Cl	16 ± 1				
Co	0.19 ± 0.01	<0.2			
Cr	<0.1	<0.5			
Cu	<0.3	<0.5			
F					16
Fe	<7	2.1 ± 0.3		5.4	
Ga		<0.1			
Hf	<0.01				
Hg		<0.4			
K	<10				
Mg	320 ± 20				
Mn	0.34 ± 0.05			0.57	
Mo		<0.1	0.073		
Na	70 ± 1				
Ni		0.38 ± 0.09			
P			1.24 ± 0.2		
Pb		<0.3	0.69		
Rb		0.080 ± 0.040			
S (%)	2.2 ± 0.1				
Sb	<0.06				
Se	4.06 ± 0.12	4.2 ± 0.3	3.3		
Si			36	41	
Sr	0.50 ± 0.05	0.36 ± 0.05			
Th	<0.01				
Ti		2.3 ± 0.7			
U	<0.05	<0.2			
V	0.022 ± 0.002		0.018		
Zn	0.07 ± 0.01	<0.2	0.12	0.064	
Zr		<0.1			

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
PES = DC-Coupled Plasma Emission Spectroscopy
AA = Atomic Absorption Analysis

TABLE E.1. Paraho Semiworks Retort - Direct Mode
Recycle Gas
Collected 8-23-77 (in $\mu\text{g}/\text{m}^3$)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>
Ba	<3000	
Co	<7	<60
Cr	<7	<100
Cu		<30
Fe		<100
Ga		<30
K		<2000
La	<5	
Mn		<100
Ni		<60
Pb		<100
Rb	<200	<50
Sb	<20	
Sc	<1	
Sr		<600
Th	<200	
U	<40	
V		<300
Zn	<300	<200

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
Analyses by Pacific Northwest Laboratory

TABLE E.2. Paraho Semiworks Retort - Direct Mode
Recycle Gas
Collected 8-24-77 (in $\mu\text{g}/\text{m}^3$)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>	<u>PES</u>	<u>CVAA</u>
Al			<70	
B			<30	
Ba	<3000			
Ca		<400		
Co	<30	<10		
Cr	<7	<30		
Cu		<5		
Fe		<20		
Ga		<5		
Hg				<20
K		<500		
La	<5			
Mg			<90	
Mn		<20		
Mo			<40	
Ni		<5		
Pb		<70		
Rb		<10		
Sb	<20			
Sc	<0.7			
Se			<70	
Si			<600	
Sr		<90		
Th	<200			
Ti		<70		
U	<40			
V		<40		
Zn		<5		

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

**TABLE E.3. Paraho Semiworks Retort - Direct Mode
Recycle Gas
Collected 8-25-77 (in $\mu\text{g}/\text{m}^3$)**

<u>Element</u>	<u>INAA</u>	<u>XRF</u>
Ba	<4000	
Co	<10	<50
Cr	<10	<20
Cu		<40
Fe		<500
Ga		<30
K		<2000
La	<7	
Mn		<50
Ni		<50
Pb		<200
Rb	<200	<80
Sb	<20	
Sc	<1	
Sr		<400
Th	<200	
U	<50	
V		<400
Zn	<200	<100

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
Analyses by Pacific Northwest Laboratory

TABLE E.4. Paraho Semiworks Retort - Direct Mode
Recycle Gas
Collected 8-26-77 (in $\mu\text{g}/\text{m}^3$)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>
Ba	<4000	
Co	<10	
Cr	<10	
Cu		<40
Fe	<6000	
Ga		<40
K		<3000
La	<7	
Mn		<100
Pb		<200
Rb	<200	<100
Sb	<20	
Sc	<1	
Sm		<800
Th	<200	
U	<50	
V		<400
Zn	<100	<200

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
Analyses by Pacific Northwest Laboratory

TABLE E.5. Paraho Semiworks Retort - Direct Mode
Recycle Gas
Collected 11-15-77 (in ppm except as noted)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>	<u>CVAA</u>
Ba	<900		
Co	<5		
Cr	<50		
Cu		<40	
Fe	<4000		
Ga		<20	
Hg			46 ± 5
K	<2000		
La	<6		
Mn		<100	
Na	<1000		
Ni		<1	
Pb		<100	
Rb	<100	<40	
Sb	<9		
Sc	<0.3		
Sr		<200	
Th	<3		
U	<20		
V		<100	
Zn		<20	

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

**TABLE E.6. Paraho Semiworks Retort - Direct Mode
Recycle Gas
Collected 11-16-77 (in $\mu\text{g}/\text{m}^3$)**

Element	INAA	XRF	Hydride Generation	CVAA
As			155 $\pm$ 30	
Ba	<700			
Co	<2			
Cr	<20			
Cu		<100		
Fe	<2000			
Ga		<80		
Hg				75 $\pm$ 15
La	<0.4			
Na	<60			
Ni		<200		
Pb		<300		
Rb	<10			
Sb	<5			
Sc	<0.2			
Sr		<800		
Th	<2			
U	<2			
Y		<100		
Zr		<200		

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE E.7. Paraho Semiworks Retort - Direct Mode
Recycle Gas
Collected 11-17-77 (in $\mu\text{g}/\text{m}^3$)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>	<u>Hydride Generation</u>
As			120 $\pm$ 35
Ba	<800		
Co	<3	<60	
Cr	<60	<100	
Cu		<30	
Ga		<20	
K	<800	<500	
La	<3		
Mn		<100	
Ni		<100	
Pb		<100	
Rb	<100	<40	
Sb	<3		
Sc	<0.3		
Sr		<300	
Th	<2		
U	<3		
V		<100	
Zn		<30	

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
Analyses by Pacific Northwest Laboratory

TABLE F.1. Paraho Semiworks Retort - Direct Mode
Thermal Oxidizer Gas
Collected 8-24-77 (in $\mu\text{g}/\text{m}^3$)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>	<u>CVAA</u>
Ba	<1000		
Co	<3	<30	
Cr	<3	<50	
Cu		<20	
Fe	<2000		
Ga		<10	
Hg		<40	9 $\pm$ 3
K		<2000	
La	<2		
Mn		<50	
Ni		<20	
Pb		<50	
Rb	<60	<20	
Sb	<6		
Sc	<0.3		
Sr		<200	
Th	<60		
Ti		<200	
U	<20		
V		<100	
Zn	<100	<100	

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE F.2. Paraho Semiworks Retort - Direct Mode
Thermal Oxidizer Gas
Collected 8-25-77 (in $\mu\text{g}/\text{m}^3$)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>	<u>CVAA</u>
Ba	<1000		
Ca		<2000	
Co	<3		
Cr	<3		
Cu		<20	
Fe		<30	
Ga		<10	
Hg		<40	6.7 $\pm$ 0.8
K		<2000	
La	<2		
Mn		<30	
Ni		<20	
Pb		<50	
Rb	<60	<20	
Sb	<6		
Sc	<0.3		
Sr		<200	
Th	<60		
U	<20		
V		<100	
Zn	<100	<50	

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE F.3. Paraho Semiworks Retort - Direct Mode
Thermal Oxidizer Gas
Collected 8-26-77 (in $\mu\text{g}/\text{m}^3$)

<u>Element</u>	<u>INAA</u>	<u>XRF</u>	<u>CVAA</u>
Ba	<2000		
Ca		<20	
Co	<7		
Cr	<7	<40	
Fe		<20	
Ga		<6	
Hg			4.5 $\pm$ 1.3
K		<600	
La	<5		
Mn		<20	
Ni		<20	
Pb		<30	
Rb		<20	
Sb	<10		
Sc	<0.7		
Sr		<60	
Th	<100		
Ti		<60	
U	<40		
Y		<50	
Zn	<100	<60	

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE F.4. Paraho Retort - Direct Mode
Thermal Oxidizer Gas
Collected 11-15-77 (in $\mu\text{g}/\text{m}^3$)

<u>Element</u>	<u>INAA</u>	<u>CVAA</u>
Ba	<800	
Co	<3	
Cr	<30	
Fe	<2000	
Hg		7.2 ± 0.9
K	<600	
La	<0.5	
Na	<200	
Rb	<60	
Sb	<7	
Sc	<0.2	
Th	<2	
U	<2	

INAA = Instrumental Neutron Activation Analysis

CVAA = Cold Vapor Atomic Absorption

Analyses by Pacific Northwest Laboratory

TABLE F.5. Paraho Semiworks Retort - Direct Mode
Thermal Oxidizer Gas
Collected 11-16-77 (in $\mu\text{g}/\text{m}^3$)

Element	INAA	XRF	Hydride Generation	CVAA
As			13 $\pm$ 4	
Ba	<800			
Co	<4	<40		
Cr	<100	<40		
F		<10		
Fe		<20		
Hg				12 $\pm$ 2
K		<1000		
La	<1			
Mn		<100		
Ni		<60		
Pb		<80		
Rb	<60	<30		
Sb	<6			
Sc	<0.2			
Sr		<200		
Th	<2			
U	<3			
V		<100		
Zn		<10		

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
CVAA = Cold Vapor Atomic Absorption
Analyses by Pacific Northwest Laboratory

TABLE F.6. Paraho Semiworks Retort - Direct Mode
Thermal Oxidizer Gas
Collected 11-17-77 (in $\mu\text{g}/\text{m}^3$)

Element	INAA	XRF	Hydride Generation
As			55 $\pm$ 8
Ba	<1000		
Co	<3		
Cr	<100	<100	
Cu		<20	
Fe		<500	
Ga		<20	
K		<100	
La	<2		
Ni		<70	
Pb		<50	
Rb	<100	<20	
Sb	<4		
Sc	<0.5		
Sr		<200	
Th	<2		
U	<3		
V		<70	
Zn		<30	

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

Analyses by Pacific Northwest Laboratory

APPENDIX B
PARAHO SEMIWORKS RETORT - DIRECT MODE
BAGHOUSE FINES SAMPLES

TABLE B.1

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Raw Shale Baghouse Fines - 140-200 Mesh
 Batch 03, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA
Al (%)				3.75
As	48 ± 1	43 ± 4		
B			104 ± 9	
Ba	480 ± 60	540 ± 30		
Br	<0.7	<1		
Ca (%)		11.6 ± 0.8		11.4
Co	7.7 ± 0.2			
Cr	26 ± 4	41 ± 12		
Cu		44 ± 4		
Eu	0.58 ± 0.03			
Fe (%)	1.85 ± 0.05	2.07 ± 0.14		1.94
Ga		10 ± 1		
K (%)		1.54 ± 0.12		1.42
La	17.7 ± 0.2	15 ± 4		
Lu	0.31 ± 0.05			
Mg (%)				3.44
Mn		340 ± 25		349
Mo		29 ± 2		
Na (%)	1.58 ± 0.01			1.70
Nb		8 ± 1		
Ni		28 ± 3		
Pb		30 ± 3		
Rb		65 ± 5		
Sb	1.9 ± 0.2			
Sc	5.4 ± 0.1			
Se	3.1 ± 0.1	2.3 ± 0.5		
Si (%)		13.6 ± 1.7		15.0
Sr		710 ± 50		
Th	5.5 ± 0.2			
Ti (%)		0.19 ± 0.01		0.18
U	4.2 ± 1.0			
Y		12 ± 2		
Zn		80 ± 6		
Zr		63 ± 9		

INAA = Instrumental Neutron Activation Analysis
 XRF = X-ray Fluorescence (Energy Dispersion)
 PES = DC-Coupled Plasma Emission Spectroscopy
 AA = Atomic Absorption Analysis
 Analyses by Pacific Northwest Laboratory

TABLE B.2

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Raw Shale Baghouse Fines - 140-200 Mesh
 Batch 03, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	AA
Al (%)			3.59
As	50 ± 1	43 ± 4	
Ba	500 ± 80		
Br	<0.7	<1	
Ca (%)		9 ± 0.6	9.7
Co	9.4 ± 0.3		
Cr	29 ± 4	35 ± 9	
Cu		47 ± 4	
Eu	0.54 ± 0.05		
Fe (%)	1.57 ± 0.05	1.65 ± 0.11	1.75
Ga		9 ± 1	
K (%)		1.41 ± 0.10	1.41
La	17.1 ± 0.3		
Lu	0.29 ± 0.04		
Mg (%)			3.09
Mn		250 ± 20	315
Mo		36 ± 2	
Na (%)	1.92 ± 0.02		1.98
Nb		9 ± 1	
Ni		30 ± 3	
Pb		33 ± 2	
Rb		76 ± 5	
Sb	2.4 ± 0.3		
Sc	4.9 ± 0.1		
Se		2.8 ± 0.5	
Si (%)		13.3 ± 1.4	14.1
Sm	3.2 ± 0.1		
Sr		630 ± 50	
Th	5.0 ± 0.2		
Ti (%)		0.18 ± 0.01	0.19
U	4.0 ± 1.0		
Y		14 ± 2	
Zn		83 ± 6	
Zr		75 ± 10	

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE B.3

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Raw Shale Baghouse Fines - >140 Mesh
 Batch 03, Collected 8-24-77 (in ppm except as noted)

Element	INAA	AA
Al (%)		3.45
As	59 $\pm$ 1	
Ba	725 $\pm$ 100	
Br	<0.7	
Ca (%)		8.8
Co	11.5 $\pm$ 0.4	
Cr	58 $\pm$ 9	
Eu	0.61 $\pm$ 0.09	
Fe (%)	1.97 $\pm$ 0.05	1.24
K (%)		1.36
La	20.2 $\pm$ 0.4	
Lu	0.34 $\pm$ 0.05	
Mg (%)		2.99
Mn		294
Na (%)	2.19 $\pm$ 0.02	1.92
Sb	3.3 $\pm$ 0.4	
Sc	5.7 $\pm$ 0.1	
Si (%)		13.7
Sm	3.9 $\pm$ 0.1	
Th	6.8 $\pm$ 0.5	
Ti (%)		0.22
U	6.4 $\pm$ 1.2	

INAA = Instrumental Neutron Activation Analysis
 XRF = X-ray Fluorescence (Energy Dispersion)
 PES = DC-Coupled Plasma Emission Spectroscopy
 AA = Atomic Absorption Analysis
 Analyses by Pacific Northwest Laboratory

TABLE B.4

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Raw Shale Baghouse Fines - 200-325 Mesh
 Batch 03, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	AA
Al (%)			3.79
As	44 ± 1	41 ± 4	
Ba	550 ± 80	540 ± 30	
Br	<0.7	<1	
Ca (%)		9.7 ± 0.7	9.7
Co	9.7 ± 0.2		
Cr	33 ± 5	48 ± 12	
Cu		42 ± 4	
Eu	0.57 ± 0.04		
Fe (%)	1.74 ± 0.05	1.81 ± 0.12	1.97
Ga		8 ± 1	
K (%)		1.48 ± 0.11	1.44
La	18.4 ± 0.3	19 ± 4	
Lu	0.27 ± 0.04		
Mg (%)			3.14
Mn		280 ± 22	378
Mo		30 ± 2	
Na (%)	2.14 ± 0.02		2.02
Nb		9 ± 1	
Ni		30 ± 3	
Pb		29 ± 3	
Rb		68 ± 5	
Sb	2.3 ± 0.2		
Sc	5.4 ± 0.1		
Se		2.1 ± 0.5	
Si (%)		12.6 ± 1.7	15.8
Sm	3.3 ± 0.02		
Sr		630 ± 50	
Th	5.7 ± 0.2		
Ti (%)		0.23 ± 0.02	0.19
U	3.9 ± 1.0		
Y		13 ± 2	
Zn		74 ± 6	
Zr		66 ± 9	

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE B.5

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Retorted Shale Baghouse Fines - <325 Mesh
 Batch 02, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA
Al (%)				4.23
As	158 ± 2	109 ± 9		
Ba	800 ± 90	520 ± 30	501 ± 15	600 ± 100
Br	<0.7	<1		
Ca (%)		15.2 ± 1.1		14
Co	20 ± 0.4			
Cr	51 ± 7	44 ± 13	49 ± 5	
Cu		69 ± 6		
Fe (%)	2.75 ± 0.05	2.60 ± 0.18		2.27
Ga		10 ± 1		
K (%)		1.68 ± 0.13		1.58
La	31.2 ± 0.4	30 ± 4		
Lu	0.47 ± 0.08			
Mg (%)				4.53
Mn		470 ± 35	416 ± 15	520 ± 40
Mo		52 ± 3		
Na (%)	3.31 ± 0.14			2.47
Nb		7 ± 1		
Ni		51 ± 4		
Pb		37 ± 4		
Rb		89 ± 6		
Sb	5.2 ± 0.4			
Sc	9.6 ± 0.1			
Se		2.9 ± 0.5		
Si (%)		17.8 ± 1.8		17.8
Sm	5.4 ± 0.1			
Sr		870 ± 70	815 ± 35	
Th	8.7 ± 0.3			
Ti (%)		0.25 ± 0.02		0.19 ± 0.04
U	8.3 ± 1.9			
V			132 ± 5	
Y		12 ± 2		
Zn		115 ± 8		
Zr		63 ± 10		

INAA = Instrumental Neutron Activation Analysis
 XRF = X-ray Fluorescence (Energy Dispersion)
 PES = DC-Coupled Plasma Emission Spectroscopy
 AA = Atomic Absorption Analysis
 Analyses by Pacific Northwest Laboratory

TABLE B.6

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Raw Shale Baghouse Fines - <325 Mesh
 Batch 03, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	AA
Al (%)			3.80
As	51 $\pm$ 1	42 $\pm$ 4	
Ba	720 $\pm$ 100	680 $\pm$ 40	
Br	<0.7	<1	
Ca (%)		10.9 $\pm$ 0.8	11.2
Co	8.5 $\pm$ 0.2		
Cr	40 $\pm$ 6	28 $\pm$ 11	
Cu		35 $\pm$ 3	
Eu	0.67 $\pm$ 0.04		
Fe (%)	2.01 $\pm$ 0.05	1.95 $\pm$ 0.13	2.12
Ga		8 $\pm$ 1	
K (%)		1.54 $\pm$ 0.12	1.41
La	19.7 $\pm$ 0.3	23 $\pm$ 4	
Lu	0.28 $\pm$ 0.04		
Mg (%)			3.36
Mn		320 $\pm$ 24	420
Mo		30 $\pm$ 2	
Na (%)	2.36 $\pm$ 0.02		2.10
Nb		8 $\pm$ 1	
Ni		29 $\pm$ 3	
Pb		36 $\pm$ 3	
Rb		69 $\pm$ 5	
Sb	2.7 $\pm$ 0.3		
Sc	6.1 $\pm$ 0.1		
Se		2.4 $\pm$ 0.5	
Si (%)		13.5 $\pm$ 1.7	15.6
Sm	3.2 $\pm$ 0.1		
Sr		760 $\pm$ 60	
Th	5.7 $\pm$ 0.2		
Ti (%)		0.19 $\pm$ 0.01	0.20
U	4.5 $\pm$ 1.1		
Y		12 $\pm$ 2	
Zn		77 $\pm$ 6	
Zr		70 $\pm$ 10	

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE B.7

PARAHO SEMIWORKS RETORT - DIRECT MODE

Retorted Shale Baghouse Fines

Bulk, Unscreened, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA
Al (%)				4.52 ± 0.12
As	108 ± 2	104 ± 8		
B			105 ± 10	
Ba	610 ± 70	590 ± 30	474 ± 7	580 ± 30
Br	<0.7	<1		
Ca (%)		13.8 ± 0.9		12.8 ± 0.2
Co	14.3 ± 0.3			
Cr	36 ± 6	34 ± 12	46 ± 10	
Cu		70 ± 6		
Eu	0.69 ± 0.05			
Fe (%)	2.27 ± 0.05	2.56 ± 0.18		2.39 ± 0.03
Ga		13 ± 1		
K (%)		1.66 ± 0.13		1.65 ± 0.01
La	21.5 ± 0.3	26 ± 4		
Lu	0.39 ± 0.06			
Mg (%)				4.30 ± 0.03
Mn		400 ± 30	408 ± 22	450 ± 40
Mo		53 ± 3		
Na (%)	2.55 ± 0.02			2.65 ± 0.02
Nb		8 ± 1		
Ni		46 ± 3		
Pb		42 ± 4		
Rb		91 ± 6		
Sb	3.5 ± 0.3			
Sc	6.5 ± 0.1			
Se		3.8 ± 0.6		
Si (%)		16.5 ± 1.7		17.8 ± 0.3
Sm	3.7 ± 0.1			
Sr		830 ± 60	735 ± 20	
Th	6.6 ± 0.6			
Ti (%)		0.26 ± 0.02		0.19 ± 0.01
U	5.0 ± 1.2			
V			143 ± 3	
Y		15 ± 2		
Zn		103 ± 8		
Zr		69 ± 10		

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE B.8

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Retorted Shale Baghouse Fines - > 20 Mesh
 Batch 02, Collected 8-24-77 (in ppm except as noted)

Element	XRF	PES	AA
Al (%)			4.37
As	40 ± 3		
Ba			600 ± 100
Br	<1		
Ca (%)	13.8 ± 1		13.1
Cr	47 ± 13	65 ± 7	
Cu	39 ± 4		
Fe (%)	3.5 ± 0.24		3.72
Ga	11.9 ± 1.2		
K (%)	2.38 ± 0.18		2.40
Mg (%)			4.36
Mn	494 ± 37	482 ± 20	540 ± 40
Mo	17 ± 2		
Na (%)			1.44
Nb	10 ± 1		
Ni	37 ± 3		
Pb	19 ± 3		
Rb	90 ± 6		
Se	2.8 ± 0.5		
Si (%)	17.1 ± 1.8		18.1
Sr	770 ± 50		
Ti (%)	0.26 ± 0.02		0.21 ± 0.04
Y	16 ± 2		
Zn	73 ± 5		
Zr	77 ± 10		

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE B.9

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Retorted Shale Baghouse Fines - 20-40 Mesh
 Batch 02, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA
Al (%)				4.19
As	50 ± 1	45 ± 4		
Ba	650 ± 70		495 ± 30	600 ± 100
Br	<0.7	<1		
Ca (%)		14.2 ± 1.0		13.5
Co	9.8 ± 0.2			
Cr	39 ± 6	50 ± 13	57 ± 6	
Cu		41 ± 4		
Eu	0.83 ± 0.05			
Fe (%)	2.64 ± 0.05	2.96 ± 0.20		2.65
Ga		12.1 ± 1.2		
K (%)		2.24 ± 0.17		2.02
La	24.2 ± 0.4			
Lu	0.45 ± 0.07			
Mg (%)				4.41
Mn		440 ± 30	428 ± 20	500 ± 40
Mo		22 ± 2		
Na (%)	1.78 ± 0.02			1.80
Nb		9 ± 1		
Ni		30 ± 3		
Pb		3.7 ± 4		
Rb		90 ± 6		
Sb	2.2 ± 0.2			
Sc	8.1 ± 0.1			
Se		3.6 ± 0.6		
Si (%)		16.8 ± 1.7		17.8
Sm	4.3 ± 0.1			
Sr		870 ± 60	753 ± 20	
Th	6.8 ± 0.2			
Ti (%)		0.27 ± 0.02		0.20 ± 0.04
U	4.5 ± 1.0			
V			114 ± 4	
Y		15.5 ± 2.0		
Zn		77 ± 6		
Zr		66 ± 10		

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE B.10

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Retorted Shale Baghouse Fines - 40-70 Mesh
 Batch 02, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	AA
Al (%)			4.50
As	79 ± 1	71 ± 6	
Ba	790 ± 90	600 ± 30	600 ± 100
Br	<0.7	<1	
Ca (%)		13.2 ± 0.9	12.3
Co	13.9 ± 0.2		
Cr		35 ± 12	
Cs	42 ± 6		
Cu		58 ± 5	
Eu	0.66 ± 0.06		
Fe (%)	2.72 ± 0.05	2.72 ± 0.19	2.86
Ga		11 ± 1	
K (%)		1.98 ± 0.15	1.95
La	23.6 ± 0.4	30 ± 4	
Lu	0.45 ± 0.07		
Mg (%)			4.26
Mn		380 ± 30	500 ± 40
Mo		37 ± 3	
Na (%)	2.14 ± 0.02		2.17
Nb		11 ± 1	
Ni		37 ± 3	
Pb		37 ± 4	
Rb		95 ± 6	
Sb	2.8 ± 0.2		
Sc	7.4 ± 0.1		
Se		3.7 ± 0.6	
Si (%)		17.2 ± 1.7	18.4
Sr		830 ± 60	
Th	6.9 ± 0.2		
Ti (%)		0.26 ± 0.02	0.22 ± 0.04
U	5.2 ± 1.2		
Y		15 ± 2	
Zn		87 ± 6	
Zr		85 ± 11	

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE B.11

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Retorted Shale Baghouse Fines - 70-140 Mesh
 Batch 02, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA
Al (%)				4.46
As	117 ± 2	108 ± 8		
Ba	570 ± 70	560 ± 30	478 ± 15	600 ± 100
Br	<0.7	<1		
Ca (%)		12.5 ± 0.9		11.5
Co	17.8 ± 0.4			
Cr	45 ± 7	55 ± 13	53 ± 5	
Cs		<6		
Cu		72 ± 7		
Eu	0.74 ± 0.06			
Fe (%)	2.55 ± 0.05	2.59 ± 0.2		2.51
Ga		12.4 ± 1.3		
K (%)		1.73 ± 0.13		1.74
La	23.9 ± 0.3	23 ± 4		
Lu	0.38 ± 0.07			
Mg (%)				4.21
Mn		390 ± 30	387 ± 15	440 ± 40
Mo		60 ± 4		
Na (%)	2.54 ± 0.02			2.57
Nb		10 ± 1		
Ni		52 ± 4		
Pb		48 ± 4		
Rb		108 ± 8		
Sb	3.6 ± 0.2	2.7 ± 2		
Sc	7.2 ± 0.1			
Se		3.4 ± 0.5		
Si (%)		18.6 ± 1.8		19.2
Sm	4.2 ± 0.1			
Sr		800 ± 60	671 ± 25	
Th	6.8 ± 0.2			
Ti (%)			0.27 ± 0.02	0.21 ± 0.04
U	6.3 ± 1.4			
V		108 ± 40	150 ± 6	
Y		16 ± 1.9		
Zn		110 ± 8		
Zr		70 ± 10		

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE B.12

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Retorted Shale Baghouse Fines - 140-200 Mesh
 Batch 02, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	AA
Al (%)			4.59
As	117 ± 2	107 ± 8	
Ba	640 ± 70	550 ± 30	500 ± 100
Br	<0.7	<1	
Ca (%)		13.2 ± 0.9	11.9
Co	17.0 ± 0.4		
Cr	36 ± 5	57 ± 13	
Cu		72 ± 6	
Eu	0.71 ± 0.05		
Fe (%)	2.54 ± 0.04	2.82 ± 0.20	2.59
Ga		12 ± 1	
K (%)		1.85 ± 0.13	1.67
La	24.0 ± 0.3	22 ± 4	
Lu	0.41 ± 0.07		
Mg (%)			4.15
Mn		410 ± 30	450 ± 40
Mo		47 ± 3	
Na (%)	2.76 ± 0.02		2.77
Nb		9 ± 1	
Ni		47 ± 4	
Pb		44 ± 4	
Rb		90 ± 6	
Sb	3.5 ± 0.3		
Sc	6.8 ± 0.1		
Se		3.1 ± 0.5	
Si (%)		17.2 ± 1.7	19.1
Sm	4.1 ± 0.1		
Sr		760 ± 50	
Th	6.2 ± 0.2		
Ti (%)		0.28 ± 0.02	0.22 ± 0.04
U	5.8 ± 1.3		
Y		12 ± 2	
Zn		109 ± 8	
Zr		67 ± 10	

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

TABLE B.13

PARAHO SEMIWORKS RETORT - DIRECT MODE
 Retorted Shale Baghouse Fines - 200-325 Mesh
 Batch 02, Collected 8-24-77 (in ppm except as noted)

Element	INAA	XRF	PES	AA
Al (%)				4.50
As	118 ± 2	103 ± 8		
Ba	660 ± 80		486 ± 15	600 ± 100
Br	<0.7	<1		
Ca (%)		13.7 ± 0.9		12.8
Co	15.5 ± 0.4			
Cr	36 ± 5	42 ± 12	46 ± 5	
Cu		67 ± 8		
Eu	0.79 ± 0.06			
Fe (%)	2.40 ± 0.04	2.39 ± 0.17		2.42
Ga		10 ± 1		
K (%)		1.60 ± 0.12		1.60
La	23.2 ± 0.4			
Lu	0.43 ± 0.07			
Mg (%)				4.25
Mn		400 ± 30	388 ± 16	460 ± 40
Mo		53 ± 3		
Na (%)	2.74 ± 0.02			2.48
Nb		8 ± 1		
Ni		40 ± 4		
Pb		42 ± 4		
Rb		95 ± 6		
Sb	3.7 ± 0.3			
Sc	6.9 ± 0.1			
Se		2.8 ± 0.5		
Si (%)		17.3 ± 1.7		18.5
Sm	4.1 ± 0.1			
Sr		860 ± 70	753 ± 30	
Th	6.6 ± 0.2			
Ti (%)		0.25 ± 0.02		0.20 ± 0.04
U	6 ± 1.4			
V			132 ± 5	
Y		15 ± 2		
Zn		101 ± 7		
Zr		75 ± 11		

INAA = Instrumental Neutron Activation Analysis

XRF = X-ray Fluorescence (Energy Dispersion)

PES = DC-Coupled Plasma Emission Spectroscopy

AA = Atomic Absorption Analysis

Analyses by Pacific Northwest Laboratory

APPENDIX C
PARAHO SEMIWORKS RETORT - DIRECT MODE
AMBIENT PARTICULATES

TABLE C.1

IRRADIATION AND COUNTING PROCEDURES FOR AEROSOLS

<u>Irradiation Interval/ Neutron Flux^(a)</u>	<u>Decay Interval</u>	<u>Count Interval</u>	<u>Instrumentation</u>	<u>Elements Determined</u>
0.5-1 min/ 1×10^{13}	10 min	5 min	Ge(Li)	Al, Cl, Cu, Mg, Mn, Na, Ti, V
6-8 hrs/ 5×10^{12}	4-7 days	10 min	Ge(Li) or Anti-Coincidence Shielded Ge(Li)	{ As, Ba, Ca, K, La, Na, Sm
	~30 days	100-1,000 min		
				Ce, Co, Cr, Cs, Eu, Fe, Hf, Ni, Rb, Sb, Sc, Se, Sr, Ta, Th, Sr

^(a) Neutrons/(cm².s)

TABLE C.2

PARAHO SEMIWORKS RETORT - DIRECT MODE
ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - AUGUST 1977

	Particle Size	Al $\mu\text{g}/\text{m}^3$	As ng/m^3	Ca $\mu\text{g}/\text{m}^3$	Co ng/m^3
TAILINGS PILE 8-24-77	>2.5	22.3 $\pm$ 0.7	58 $\pm$ 1	76 $\pm$ 8	6.0 $\pm$ 0.1
	1.5 - 2.5	9.3 $\pm$ 0.3	23.1 $\pm$ 0.6	39 $\pm$ 5	5.0 $\pm$ 0.1
	1.1 - 1.5	7.8 $\pm$ 0.3	17.9 $\pm$ 0.6	30 $\pm$ 4	4.1 $\pm$ 0.1
	0.8 - 1.1	5.7 $\pm$ 0.2	14.4 $\pm$ 0.5	<9	3.7 $\pm$ 0.1
	<0.8	87 $\pm$ 4	162 $\pm$ 4	240 $\pm$ 20	34.8 $\pm$ 0.3
	Σ	132 $\pm$ 4	275 $\pm$ 4	390 $\pm$ 20	53.6 $\pm$ 0.3
TAILINGS PILE 8-25-77	>6.8	170 $\pm$ 5	420 $\pm$ 13	550 $\pm$ 60	62 $\pm$ 1
	4.1 - 6.8	31 $\pm$ 1	114 $\pm$ 6	94 $\pm$ 12	18.0 $\pm$ 0.2
	3.0 - 4.1	10.5 $\pm$ 0.4	35 $\pm$ 1	36 $\pm$ 7	7.2 $\pm$ 0.2
	2.0 - 3.0	6.0 $\pm$ 0.3	19.2 $\pm$ 0.8	25 $\pm$ 6	5.31 $\pm$ 0.14
	<2.0	37 $\pm$ 1	124 $\pm$ 5	110 $\pm$ 10	18.3 $\pm$ 0.3
	Σ	255 $\pm$ 5	712 $\pm$ 15	820 $\pm$ 60	111 $\pm$ 1
RETORT AREA 8-24-77	>6.8	146 $\pm$ 4	260 $\pm$ 10	450 $\pm$ 40	42.4 $\pm$ 0.5
	4.1 - 6.8	23.0 $\pm$ 0.7	60 $\pm$ 1	57 $\pm$ 9	9.4 $\pm$ 0.2
	3.0 - 4.1	7.9 $\pm$ 0.4	26.9 $\pm$ 0.9	<14	3.8 $\pm$ 0.1
	2.0 - 3.0	4.7 $\pm$ 0.3	13.2 $\pm$ 0.7	<13	2.6 $\pm$ 0.1
	<2.0	42 $\pm$ 1	75 $\pm$ 3	110 $\pm$ 10	15.2 $\pm$ 0.3
	Σ	224 $\pm$ 4	435 $\pm$ 11	620 $\pm$ 40	73.4 $\pm$ 0.6
RETORT AREA 8-25-77	>6.8	546 $\pm$ 8	2420 $\pm$ 50	1760 $\pm$ 80	351 $\pm$ 2
	4.1 - 6.8	182 $\pm$ 5	655 $\pm$ 15	660 $\pm$ 50	110 $\pm$ 1
	3.0 - 4.1	59 $\pm$ 2	239 $\pm$ 4	240 $\pm$ 30	40.6 $\pm$ 0.5
	2.0 - 3.0	21.9 $\pm$ 0.8	113 $\pm$ 3	65 $\pm$ 12	18.0 $\pm$ 0.3
	<2.0	111 $\pm$ 3	356 $\pm$ 9	340 $\pm$ 30	64.3 $\pm$ 0.5
	Σ	920 $\pm$ 10	3780 $\pm$ 50	4070 $\pm$ 100	584 $\pm$ 2
CRUSHER AREA 8-24-77	>2.5	30.0 $\pm$ 0.8	70 $\pm$ 2	91 $\pm$ 9	13.1 $\pm$ 0.2
	1.5 - 2.5	8.5 $\pm$ 0.3	15.8 $\pm$ 0.8	28 $\pm$ 4	3.47 $\pm$ 0.07
	1.1 - 1.5	5.8 $\pm$ 0.2	12.0 $\pm$ 0.7	13 $\pm$ 2	2.42 $\pm$ 0.06
	0.8 - 1.1	5.6 $\pm$ 0.2	11.6 $\pm$ 0.6	14 $\pm$ 2	2.22 $\pm$ 0.05
	<0.8	106 $\pm$ 3	168 $\pm$ 5	280 $\pm$ 20	33.5 $\pm$ 0.3
	Σ	156 $\pm$ 3	278 $\pm$ 6	430 $\pm$ 20	54.7 $\pm$ 0.2

TABLE C. (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE
ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - AUGUST 1977

	Particle Size	Cr ng/m ³	Cs ng/m ³	Fe μg/m ³	K μg/m ³
TAILINGS PILE 8-24-77	>2.5	31 ± 1	1.2 ± 0.1	10.6 ± 0.1	8.7 ± 0.9
	1.5 - 2.5	28 ± 1	0.98 ± 0.12	7.17 ± 0.09	3.9 ± 0.4
	1.1 - 1.5	20 ± 1	0.82 ± 0.11	6.17 ± 0.08	2.7 ± 0.3
	0.8 - 1.1	20 ± 1	0.66 ± 0.09	5.22 ± 0.08	2.1 ± 0.2
	<0.8	147 ± 2	8.5 ± 1.0	54.2 ± 0.4	24 ± 3
	Σ	246 ± 2	12.2 ± 1.0	83.4 ± 0.4	41 ± 3
TAILINGS PILE 8-25-77	>6.8	177 ± 4	13 ± 1	81.5 ± 0.8	68 ± 13
	4.1 - 6.8	58 ± 1	2.8 ± 0.3	18.0 ± 0.2	17 ± 3
	3.0 - 4.1	37 ± 1	1.19 ± 0.15	6.93 ± 0.14	5.1 ± 1.0
	2.0 - 3.0	58 ± 1	0.81 ± 0.11	4.69 ± 0.12	3.2 ± 0.6
	<2.0	189 ± 2	3.7 ± 0.4	20.3 ± 0.2	16 ± 3
	Σ	519 ± 5	22 ± 1	131 ± 1	109 ± 14
RETORT AREA 8-24-77	>6.8	137 ± 3	10 ± 1	62.9 ± 0.5	57 ± 11
	4.1 - 6.8	48 ± 1	1.90 ± 0.25	11.5 ± 0.2	14 ± 3
	3.0 - 4.1	30.8 ± 0.9	0.88 ± 0.13	4.53 ± 0.12	6.4 ± 1.3
	2.0 - 3.0	22.7 ± 0.8	0.44 ± 0.08	3.18 ± 0.10	2.9 ± 0.6
	<2.0	194 ± 3	4.2 ± 0.6	22.5 ± 0.4	20 ± 4
	Σ	433 ± 4	17 ± 1	105 ± 1	100 ± 12
RETORT AREA 8-25-77	>6.8	1010 ± 20	91 ± 12	508 ± 2	490 ± 80
	4.1 - 6.8	336 ± 6	24 ± 3	123 ± 1	120 ± 20
	3.0 - 4.1	127 ± 3	8.2 ± 1.1	38.1 ± 0.5	40 ± 6
	2.0 - 3.0	80.8 ± 2.4	3.4 ± 0.5	16.0 ± 0.3	17 ± 3
	<2.0	372 ± 6	16 ± 2	74.9 ± 0.6	58 ± 9
	Σ	1930 ± 20	143 ± 12	760 ± 2	725 ± 80
CRUSHER AREA 8-24-77	>2.5	43 ± 1	3.9 ± 0.4	18.0 ± 0.2	13 ± 3
	1.5 - 2.5	16.4 ± 0.5	1.1 ± 0.1	4.71 ± 0.07	2.6 ± 0.7
	1.1 - 1.5	11.1 ± 0.4	0.84 ± 0.09	3.74 ± 0.07	2.3 ± 0.6
	0.8 - 1.1	12.6 ± 0.4	0.85 ± 0.01	3.71 ± 0.06	2.1 ± 0.6
	<0.8	142 ± 2	15 ± 1	57.5 ± 0.4	40 ± 11
	Σ	225 ± 1	22 ± 1	87.7 ± 0.4	60 ± 11

TABLE C.2 (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE
ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - AUGUST 1977

	Particle Size	La ng/m ³	Mg μg/m ³	Mn ng/m ³	Na μg/m ³
TAILINGS PILE 8-24-77	>2.5	15 ± 1	31 ± 5	280 ± 10	12.4 ± 0.2
	1.5 - 2.5	5.9 ± 0.5	19 ± 3	120 ± 10	5.5 ± 0.1
	1.1 - 1.5	4.7 ± 0.4	17 ± 3	90 ± 10	4.2 ± 0.1
	0.8 - 1.1	3.4 ± 0.4	13 ± 3	70 ± 10	3.5 ± 0.1
	<0.8	48 ± 4	94 ± 14	930 ± 30	48 ± 1
	Σ	77 ± 4	174 ± 16	1490 ± 40	74 ± 1
TAILINGS PILE 8-25-77	>6.8	97 ± 10	250 ± 40	1900 ± 60	76 ± 1
	4.1 - 6.8	36 ± 4	43 ± 9	390 ± 10	15.2 ± 0.3
	3.0 - 4.1	8.6 ± 0.9	15 ± 6	130 ± 10	5.1 ± 0.1
	2.0 - 3.0	5.0 ± 0.7	8 ± 7	94 ± 6	4.0 ± 0.1
	<2.0	34 ± 4	42 ± 9	450 ± 10	22.3 ± 0.4
	Σ	181 ± 12	360 ± 40	2960 ± 90	123 ± 1
RETORT AREA 8-24-77	>6.8	67 ± 6	180 ± 20	1630 ± 40	70 ± 1
	4.1 - 6.8	15 ± 1	39 ± 9	290 ± 10	12.6 ± 0.2
	3.0 - 4.1	7.1 ± 0.7	19 ± 6	77 ± 7	6.4 ± 0.1
	2.0 - 3.0	3.4 ± 0.5	<10	52 ± 5	4.0 ± 0.1
	<2.0	25 ± 2	29 ± 9	440 ± 10	27 ± 1
	Σ	118 ± 6	270 ± 20	2490 ± 40	120 ± 1
RETORT AREA 8-25-77	>6.8	480 ± 30	760 ± 40	6440 ± 90	486 ± 9
	4.1 - 6.8	133 ± 10	300 ± 40	2290 ± 60	78 ± 1
	3.0 - 4.1	50 ± 2	96 ± 19	760 ± 30	24.8 ± 0.4
	2.0 - 3.0	25 ± 2	19 ± 12	320 ± 20	12.9 ± 0.3
	<2.0	70 ± 6	180 ± 20	1360 ± 40	61 ± 1
	Σ	758 ± 32	1360 ± 60	1170 ± 120	663 ± 9
CRUSHER AREA 8-24-77	>2.5	22 ± 2	41 ± 5	350 ± 10	15.2 ± 0.3
	1.5 - 2.5	4.8 ± 0.9	12 ± 3	98 ± 4	3.8 ± 0.1
	1.1 - 1.5	3.8 ± 0.6	10 ± 2	62 ± 3	3.3 ± 0.1
	0.8 - 1.1	3.5 ± 0.7	7.1 ± 2.2	63 ± 3	3.3 ± 0.1
	<0.8	54 ± 5	93 ± 14	1030 ± 30	59 ± 1
	Σ	88 ± 6	160 ± 15	1600 ± 30	85 ± 1

TABLE C.2 (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE
 ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - AUGUST 1977

	Particle Size	Ni ng/m ³	Rb ng/m ³	Sb ng/m ³	Sc ng/m ³
TAILINGS PILE 8-24-77	>2.5	11 ± 5	23 ± 3	1.5 ± 0.2	2.46 ± 0.01
	1.5 - 2.5	21 ± 6	18 ± 2	1.5 ± 0.2	1.96 ± 0.01
	1.1 - 1.5	15 ± 5	15 ± 2	1.0 ± 0.2	1.63 ± 0.01
	0.8 - 1.1	11 ± 4	12 ± 2	1.0 ± 0.17	1.34 ± 0.01
	<0.8	90 ± 22	130 ± 15	10.2 ± 1.4	14.4 ± 0.1
	Σ	148 ± 24	198 ± 16	15.2 ± 1.5	21.8 ± 0.1
TAILINGS PILE 8-25-77	>6.8	570 ± 90	240 ± 30	12 ± 1	25.7 ± 0.2
	4.1 - 6.8	550 ± 70	52 ± 6	3.2 ± 0.4	6.15 ± 0.05
	3.0 - 4.1	84 ± 14	14 ± 3	1.3 ± 0.2	2.34 ± 0.03
	2.0 - 3.0	100 ± 15	18 ± 3	1.1 ± 0.2	1.56 ± 0.01
	<2.0	170 ± 30	52 ± 7	4.4 ± 0.5	6.34 ± 0.05
	Σ	1470 ± 120	380 ± 30	22 ± 1	42.1 ± 0.2
RETORT AREA 8-24-77	>6.8	370 ± 90	150 ± 20	8.4 ± 1.0	19.2 ± 0.1
	4.1 - 6.8	61 ± 23	35 ± 6	2.0 ± 0.3	3.81 ± 0.03
	3.0 - 4.1	55 ± 16	13 ± 3	1.1 ± 0.2	1.52 ± 0.02
	2.0 - 3.0	54 ± 16	11 ± 3	0.53 ± 0.15	1.03 ± 0.01
	<2.0	290 ± 80	50 ± 10	4.7 ± 0.7	7.11 ± 0.05
	Σ	830 ± 120	260 ± 20	16.8 ± 1.3	32.7 ± 0.1
RETORT AREA 8-25-77	>6.8	1100 ± 200	1200 ± 200	73 ± 9	158 ± 1
	4.1 - 6.8	500 ± 100	340 ± 60	22 ± 3	41.2 ± 0.1
	3.0 - 4.1	150 ± 40	110 ± 20	8.0 ± 1.1	13.4 ± 0.1
	2.0 - 3.0	130 ± 30	44 ± 10	3.8 ± 0.6	5.89 ± 0.04
	<2.0	260 ± 60	200 ± 40	12.1 ± 1.6	23.7 ± 0.1
	Σ	2140 ± 240	1890 ± 240	119 ± 10	242 ± 2
CRUSHER AREA 8-24-77	>2.5	47 ± 14	56 ± 10	3.2 ± 0.4	5.63 ± 0.02
	1.5 - 2.5	27 ± 7	14 ± 3	0.86 ± 0.13	1.50 ± 0.01
	1.1 - 1.5	18 ± 6	9.1 ± 2.2	0.60 ± 0.10	1.11 ± 0.01
	0.8 - 1.1	7 ± 4	11 ± 2	0.66 ± 0.11	1.03 ± 0.01
	<0.8	100 ± 30	160 ± 20	8.5 ± 1.0	16.4 ± 0.1
	Σ	199 ± 30	250 ± 20	13.8 ± 1.0	25.7 ± 0.1

TABLE C.2 (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE

ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - AUGUST 1977

	Particle Size	Sm ng/m ³	Sr ng/m ³	Th ng/m ³	Ti ng/m ³
TAILINGS PILE 8-24-77	>2.5	3.8 ± 0.2	270 ± 30	2.8 ± 0.1	1.9 ± 0.4
	1.5 - 2.5	1.8 ± 0.1	200 ± 30	2.3 ± 0.1	0.75 ± 0.22
	1.1 - 1.5	1.3 ± 0.1	160 ± 20	1.9 ± 0.1	0.62 ± 0.20
	0.8 - 1.1	1.3 ± 0.1	150 ± 20	1.6 ± 0.1	0.46 ± 0.18
	<0.8	14.0 ± 0.7	1430 ± 160	14.8 ± 0.4	5.0 ± 1.0
	Σ	22.2 ± 0.8	2210 ± 170	23.4 ± 0.4	8.7 ± 1.1
TAILINGS PILE 8-25-77	>6.8	16 ± 1	3300 ± 420	26.9 ± 0.7	9.3 ± 2.5
	4.1 - 6.8	6.6 ± 0.6	1030 ± 130	7.9 ± 0.2	3.1 ± 0.6
	3.0 - 4.1	2.0 ± 0.1	430 ± 60	2.9 ± 0.1	2.1 ± 0.4
	2.0 - 3.0	1.24 ± 0.08	75 ± 18	1.92 ± 0.01	0.63 ± 0.40
	<2.0	5.2 ± 0.5	790 ± 110	6.6 ± 0.2	3.0 ± 0.5
	Σ	31 ± 1	5630 ± 460	46.2 ± 0.7	18.1 ± 2.7
RETORT AREA 8-24-77	>6.8	14 ± 1	1670 ± 180	22.9 ± 0.8	8.6 ± 1.4
	4.1 - 6.8	4.1 ± 0.2	380 ± 40	5.6 ± 0.2	1.8 ± 0.5
	3.0 - 4.1	2.0 ± 0.1	220 ± 30	2.29 ± 0.11	0.62 ± 0.37
	2.0 - 3.0	1.22 ± 0.09	72 ± 14	1.42 ± 0.09	0.96 ± 0.37
	<2.0	7.9 ± 0.5	990 ± 110	7.9 ± 0.4	2.6 ± 0.6
	Σ	29 ± 1	3330 ± 220	40.1 ± 0.9	14.6 ± 1.7
RETORT AREA 8-25-77	>6.8	99 ± 3	22700 ± 3500	166 ± 6	31.8 ± 2.6
	4.1 - 6.8	29 ± 1	5900 ± 900	57 ± 2	15.2 ± 2.2
	3.0 - 4.1	13.1 ± 0.4	1700 ± 300	20.8 ± 0.8	7.1 ± 1.2
	2.0 - 3.0	6.33 ± 0.23	1600 ± 300	8.79 ± 0.39	3.4 ± 0.8
	<2.0	15.6 ± 0.7	7000 ± 1100	30.1 ± 1.2	7.1 ± 1.3
	Σ	163 ± 3	38900 ± 3800	283 ± 6	65 ± 4
CRUSHER AREA 8-24-77	>2.5	3.9 ± 0.3	570 ± 50	5.9 ± 0.2	2.2 ± 0.4
	1.5 - 2.5	0.93 ± 0.10	130 ± 10	1.56 ± 0.05	0.67 ± 0.18
	1.1 - 1.5	0.66 ± 0.08	150 ± 20	1.07 ± 0.04	0.49 ± 0.14
	0.8 - 1.1	0.73 ± 0.08	62 ± 9	1.06 ± 0.04	0.37 ± 0.14
	<0.8	12.7 ± 0.4	1480 ± 130	14.7 ± 0.4	0.52 ± 1.0
	Σ	18.9 ± 0.5	2390 ± 140	24.3 ± 0.4	4.3 ± 1.1

TABLE C.2 (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE

ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - AUGUST 1977

	Particle Size	V ng/m ³
TAILINGS PILE 8-24-77	>2.5	92 ± 7
	1.5 - 2.5	38 ± 4
	1.1 - 1.5	35 ± 4
	0.8 - 1.1	24 ± 2
	<0.8	300 ± 19
	Σ	490 ± 20
TAILINGS PILE 8-25-77	>6.8	670 ± 50
	4.1 - 6.8	140 ± 10
	3.0 - 4.1	37 ± 6
	2.0 - 3.0	26 ± 6
	<2.0	130 ± 10
	Σ	1000 ± 50
RETORT AREA 8-24-77	>6.8	430 ± 30
	4.1 - 6.8	81 ± 7
	3.0 - 4.1	27 ± 7
	2.0 - 3.0	13 ± 5
	<2.0	151 ± 13
	Σ	700 ± 30
RETORT AREA 8-25-77	>6.8	1880 ± 50
	4.1 - 6.8	770 ± 40
	3.0 - 4.1	290 ± 20
	2.0 - 3.0	130 ± 10
	<2.0	440 ± 30
	Σ	3510 ± 70
CRUSHER AREA 8-24-77	>2.5	74 ± 7
	1.5 - 2.5	26 ± 3
	1.1 - 1.5	22 ± 3
	0.8 - 1.1	14 ± 3
	<0.8	322 ± 18
	Σ	460 ± 20

TABLE C.3

PARAHO SEMIWORKS RETORT - DIRECT MODE

ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - NOVEMBER 1977

	Particle Size	Al $\mu\text{g}/\text{m}^3$	As ng/m^3	Ca $\mu\text{g}/\text{m}^3$	Ce ng/m^3
RETORT SITE 11-16-77	>7.0	59.2 ± 2.1	158 ± 9	205 ± 47	64 ± 4
	3.3 - 7.0	17.0 ± 0.7	60 ± 4	68 ± 9	23 ± 2
	2.0 - 3.3	8.3 ± 0.40	31 ± 2	80 ± 12	14 ± 1
	1.1 - 2.0	6.32 ± 0.34	30 ± 2	33 ± 5	14 ± 1
	<1.1	63.4 ± 2.4	159 ± 11	205 ± 25	109 ± 7
	Σ	154 ± 3	438 ± 15	590 ± 60	224 ± 8
CRUSHER SITE 11-16-77	>7.0	32.8 ± 1.1	77 ± 11	96 ± 11	33 ± 1
	3.3 - 7.0	9.55 ± 0.39	23 ± 4	25 ± 4	14 ± 1
	2.0 - 3.3	4.07 ± 0.22	13 ± 2	<6	6.5 ± 0.4
	1.1 - 2.0	2.93 ± 0.18	12 ± 2	10 ± 2	6.0 ± 0.4
	<1.1	106 ± 4	254 ± 34	310 ± 30	74 ± 3
	Σ	155 ± 4	384 ± 36	440 ± 30	134 ± 3
TAILINGS PILE 11-16-77	>7.0	60.6 ± 2.8	125 ± 20	<110	60 ± 3
	3.3 - 7.0	23.8 ± 1.0	71 ± 12	89 ± 12	35 ± 2
	2.0 - 3.3	14.1 ± 0.7	46 ± 8	56 ± 9	22 ± 1
	1.1 - 2.0	13.7 ± 0.7	46 ± 8	51 ± 9	21 ± 1
	<1.1	138 ± 5	301 ± 48	440 ± 50	152 ± 8
	Σ	251 ± 6	589 ± 55	640 ± 50	290 ± 9
BACKGROUND SITE 11-17-77	>7.0	1.00 ± 0.04	1.56 ± 0.33	2.6 ± 0.3	1.28 ± 0.06
	3.3 - 7.0	0.447 ± 0.020	0.64 ± 0.14	1.1 ± 0.2	0.57 ± 0.04
	2.0 - 3.3	0.242 ± 0.014	0.52 ± 0.13	0.65 ± 0.14	0.036 ± 0.04
	1.1 - 2.0	0.178 ± 0.012	0.43 ± 0.10	0.49 ± 0.12	0.035 ± 0.030
	<1.1	1.64 ± 0.07	3.77 ± 0.83	4.3 ± 0.7	2.0 ± 0.1
	Σ	3.53 ± 0.09	6.92 ± 0.92	9.1 ± 0.8	3.9 ± 0.1

TABLE C (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE
ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - NOVEMBER 1977

	Particle Size	Co ng/m ³	Cr ng/m ³	Cs ng/m ³	Eu ng/m ³
RETORT SITE 11-16-77	>7.0	24.2 ± 0.6	76 ± 4	3.8 ± 0.4	1.14 ± 0.12
	3.3 - 7.0	9.8 ± 0.3	32 ± 2	1.6 ± 0.2	0.44 ± 0.07
	2.0 - 3.3	5.8 ± 0.3	24 ± 2	0.99 ± 0.17	0.21 ± 0.07
	1.1 - 2.0	5.2 ± 0.3	23 ± 2	0.70 ± 0.16	0.26 ± 0.06
	<1.1	52.6 ± 1.4	280 ± 15	5.8 ± 0.7	1.63 ± 0.24
	Σ	98 ± 2	435 ± 16	12.9 ± 0.9	3.7 ± 0.3
CRUSHER SITE 11-16-77	>7.0	11.0 ± 0.2	44 ± 1	2.5 ± 0.6	0.59 ± 0.05
	3.3 - 7.0	4.7 ± 0.2	19 ± 1	0.94 ± 0.23	0.24 ± 0.03
	2.0 - 3.3	2.3 ± 0.1	13.2 ± 0.8	0.38 ± 0.11	0.12 ± 0.03
	1.1 - 2.0	2.0 ± 0.1	21 ± 1	0.51 ± 0.13	0.14 ± 0.03
	<1.1	20.9 ± 0.6	146 ± 4	4.7 ± 1.2	1.51 ± 0.13
	Σ	41 ± 1	243 ± 4	9.0 ± 1.4	2.6 ± 0.1
TAILINGS PILE 11-16-77	>7.0	20.7 ± 0.6	107 ± 4	4.3 ± 1.7	0.96 ± 0.11
	3.3 - 7.0	12.1 ± 0.4	69 ± 3	2.7 ± 1.1	0.59 ± 0.09
	2.0 - 3.3	7.9 ± 0.3	50 ± 3	2.1 ± 0.8	0.48 ± 0.09
	1.1 - 2.0	8.2 ± 0.4	48 ± 3	1.4 ± 0.6	0.38 ± 0.08
	<1.1	61.3 ± 1.5	378 ± 14	15 ± 6	2.63 ± 0.30
	Σ	110 ± 2	652 ± 15	26 ± 6	5.0 ± 0.4
BACKGROUND SITE 11-17-77	>7.0	0.33 ± 0.02	1.89 ± 0.09	0.11 ± 0.03	0.023 ± 0.004
	3.3 - 7.0	0.18 ± 0.01	1.81 ± 0.08	0.050 ± 0.014	0.015 ± 0.003
	2.0 - 3.3	0.13 ± 0.01	1.46 ± 0.07	0.032 ± 0.010	<0.006
	1.1 - 2.0	0.12 ± 0.01	1.42 ± 0.08	0.033 ± 0.010	0.014 ± 0.003
	<1.1	0.81 ± 0.04	13.7 ± 0.3	0.20 ± 0.05	0.037 ± 0.008
	Σ	1.54 ± 0.05	20.4 ± 0.3	0.43 ± 0.06	—

TABLE C.3 (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE

ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - NOVEMBER 1977

	Particle Size	Fe $\mu\text{g}/\text{m}^3$	Hf ng/m^3	K $\mu\text{g}/\text{m}^3$	La ng/m^3
RETORT SITE 11-16-77	>7.0	31.9 ± 0.5	2.6 ± 0.4	23 ± 1	40 ± 5
	3.3 - 7.0	10.6 ± 0.3	0.83 ± 0.19	8.7 ± 0.8	18 ± 3
	2.0 - 3.3	6.2 ± 0.2	0.77 ± 0.16	4.5 ± 0.6	9.6 ± 2.4
	1.1 - 2.0	5.5 ± 0.2	0.37 ± 0.13	2.4 ± 0.6	10 ± 4
	<1.1	42.3 ± 1.0	1.9 ± 0.6	21 ± 3	51 ± 9
	Σ	96.5 ± 1.2	6.5 ± 0.8	60 ± 3	129 ± 12
CRUSHER SITE 11-16-77	>7.0	16.4 ± 0.2	1.3 ± 0.2	15 ± 1	23 ± 3
	3.3 - 7.0	5.5 ± 0.2	0.52 ± 0.09	6.7 ± 0.5	9.7 ± 1.7
	2.0 - 3.3	2.5 ± 0.1	0.13 ± 0.07	1.7 ± 0.4	4.0 ± 1.3
	1.1 - 2.0	2.3 ± 0.1	0.26 ± 0.07	1.5 ± 0.4	4.3 ± 1.5
	<1.1	31.0 ± 0.6	2.8 ± 0.4	42 ± 3	69 ± 10
	Σ	57.7 ± 0.7	5.0 ± 0.5	67 ± 3	110 ± 11
TAILINGS PILE 11-16-77	>7.0	27.4 ± 0.6	2.7 ± 0.5	26 ± 2	51 ± 7
	3.3 - 7.0	15.5 ± 0.4	1.4 ± 0.3	13 ± 2	17 ± 5
	2.0 - 3.3	9.3 ± 0.3	0.73 ± 0.26	9.6 ± 1.6	14 ± 4
	1.1 - 2.0	9.5 ± 0.3	0.90 ± 0.24	4.8 ± 1.3	17 ± 4
	<1.1	76.4 ± 1.6	7.3 ± 1.2	61 ± 6	113 ± 17
	Σ	138 ± 2	13 ± 1	114 ± 7	212 ± 20
BACKGROUND SITE 11-17-77	>7.0	0.60 ± 0.02	0.068 ± 0.011	0.33 ± 0.06	0.63 ± 0.15
	3.3 - 7.0	0.30 ± 0.01	0.022 ± 0.009	0.23 ± 0.04	0.47 ± 0.10
	2.0 - 3.3	0.196 ± 0.010	0.028 ± 0.007	0.088 ± 0.023	0.20 ± 0.07
	1.1 - 2.0	0.164 ± 0.010	0.018 ± 0.007	0.062 ± 0.021	0.18 ± 0.06
	<1.1	1.05 ± 0.04	0.11 ± 0.03	0.57 ± 0.11	0.66 ± 0.22
	Σ	2.31 ± 0.05	0.25 ± 0.03	1.28 ± 0.14	2.14 ± 0.30

TABLE C.3 (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE

ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - NOVEMBER 1977

	Particle Size	Mg $\mu\text{g}/\text{m}^3$	Mn ng/m^3	Na $\mu\text{g}/\text{m}^3$	Sb ng/m^3
RETORT SITE 11-16-77	>7.0	68 $\pm$ 24	610 $\pm$ 20	32.5 $\pm$ 0.7	4.4 $\pm$ 0.5
	3.3 - 7.0	32 $\pm$ 6	193 $\pm$ 9	8.7 $\pm$ 0.3	2.5 $\pm$ 0.3
	2.0 - 3.3	19 $\pm$ 5	98 $\pm$ 5	4.3 $\pm$ 0.24	1.3 $\pm$ 0.3
	1.1 - 2.0	<8	76 $\pm$ 5	3.0 $\pm$ 0.2	1.8 $\pm$ 0.3
	<1.1	106 $\pm$ 15	700 $\pm$ 30	33.6 $\pm$ 1.0	13 $\pm$ 1.0
	Σ	225 $\pm$ 29	1680 $\pm$ 40	82 $\pm$ 1	23 $\pm$ 1
CRUSHER SITE 11-16-77	>7.0	53 $\pm$ 6	326 $\pm$ 11	15.1 $\pm$ 0.2	3.3 $\pm$ 0.7
	3.3 - 7.0	14 $\pm$ 3	101 $\pm$ 5	3.6 $\pm$ 0.1	1.4 $\pm$ 0.3
	2.0 - 3.3	11 $\pm$ 3	46 $\pm$ 3	1.48 $\pm$ 0.07	0.71 $\pm$ 0.25
	1.1 - 2.0	6.7 $\pm$ 2.9	37 $\pm$ 3	1.32 $\pm$ 0.07	0.56 $\pm$ 0.21
	<1.1	124 $\pm$ 16	1070 $\pm$ 30	52 $\pm$ 1	8.2 $\pm$ 1.8
	Σ	209 $\pm$ 18	1580 $\pm$ 30	74 $\pm$ 1	14 $\pm$ 2
TAILINGS PILE 11-16-77	>7.0	86 $\pm$ 27	605 $\pm$ 35	28.2 $\pm$ 1.1	5.9 $\pm$ 1.3
	3.3 - 7.0	37 $\pm$ 9	260 $\pm$ 12	18.4 $\pm$ 0.7	3.4 $\pm$ 0.8
	2.0 - 3.3	33 $\pm$ 8	169 $\pm$ 9	8.32 $\pm$ 0.56	3.4 $\pm$ 0.8
	1.1 - 2.0	20 $\pm$ 9	150 $\pm$ 9	6.90 $\pm$ 0.52	2.2 $\pm$ 0.6
	<1.1	180 $\pm$ 30	1360 $\pm$ 50	80 $\pm$ 2	18.3 $\pm$ 3.9
	Σ	360 $\pm$ 40	2540 $\pm$ 60	137 $\pm$ 3	33 $\pm$ 4
BACKGROUND SITE 11-17-77	>7.0	1.18 $\pm$ 0.25	9.2 $\pm$ 0.4	0.40 $\pm$ 0.03	0.066 $\pm$ 0.016
	3.3 - 7.0	0.59 $\pm$ 0.18	4.3 $\pm$ 0.2	0.14 $\pm$ 0.03	0.046 $\pm$ 0.012
	2.0 - 3.3	0.75 $\pm$ 0.21	2.0 $\pm$ 0.2	0.083 $\pm$ 0.013	0.030 $\pm$ 0.014
	1.1 - 2.0	0.35 $\pm$ 0.18	2.1 $\pm$ 0.2	0.072 $\pm$ 0.012	0.057 $\pm$ 0.013
	<1.1	2.5 $\pm$ 0.5	16.2 $\pm$ 0.7	0.82 $\pm$ 0.06	0.29 $\pm$ 0.04
	Σ	5.4 $\pm$ 0.6	33.8 $\pm$ 0.9	1.52 $\pm$ 0.07	0.49 $\pm$ 0.05

TABLE C.3 (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE

ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - NOVEMBER 1977

	Particle Size	Sc ng/m ³	Se ng/m ³	Sm ng/m ³	Ta ng/m ³
RETORT SITE 11-16-77	>7.0	10.0 ± 0.1	<3.1	6.3 ± 0.5	0.97 ± 0.22
	3.3 - 7.0	3.40 ± 0.05	<5.0	3.1 ± 0.3	0.60 ± 0.15
	2.0 - 3.3	1.96 ± 0.04	<2.0	1.4 ± 0.2	0.33 ± 0.14
	1.1 - 2.0	1.71 ± 0.03	<1.6	1.3 ± 0.2	0.29 ± 0.12
	<1.1	11.4 ± 0.2	<7.0	16.3 ± 1.3	1.41 ± 0.43
	Σ	28.5 ± 0.2	—	28.4 ± 1.5	3.6 ± 0.5
CRUSHER SITE 11-16-77	>7.0	4.94 ± 0.03	<1.6	3.6 ± 0.3	0.57 ± 0.11
	3.3 - 7.0	1.68 ± 0.02	<1.0	1.2 ± 0.2	0.23 ± 0.07
	2.0 - 3.3	0.82 ± 0.01	<0.8	0.99 ± 0.15	0.17 ± 0.05
	1.1 - 2.0	0.68 ± 0.01	<0.8	1.7 ± 0.2	0.19 ± 0.06
	<1.1	8.97 ± 0.08	<2.0	14.7 ± 1.7	1.1 ± 0.3
	Σ	17.1 ± 0.09	—	22.2 ± 1.8	2.3 ± 0.3
TAILINGS PILE 11-16-77	>7.0	8.45 ± 0.08	<3.1	6.3 ± 0.6	0.98 ± 0.23
	3.3 - 7.0	4.64 ± 0.06	<2.8	4.4 ± 0.5	0.60 ± 0.20
	2.0 - 3.3	3.06 ± 0.05	<2.5	3.5 ± 0.4	0.42 ± 0.17
	1.1 - 2.0	2.88 ± 0.04	<2.4	3.1 ± 0.4	0.55 ± 0.18
	<1.1	23.3 ± 0.2	<9.0	17.5 ± 1.7	6.4 ± 0.9
	Σ	42.3 ± 0.2	—	34.8 ± 2.0	9.0 ± 1.0
BACKGROUND SITE 11-17-77	>7.0	0.182 ± 0.002	<0.08	0.13 ± 0.01	0.019 ± 0.007
	3.3 - 7.0	0.085 ± 0.001	<0.07	0.060 ± 0.006	<0.012
	2.0 - 3.3	0.052 ± 0.001	<0.07	0.050 ± 0.006	<0.011
	1.1 - 2.0	0.048 ± 0.001	<0.07	0.039 ± 0.004	<0.012
	<1.1	0.264 ± 0.004	<0.02	0.18 ± 0.02	0.061 ± 0.019
	Σ	0.63 ± 0.005	—	0.46 ± 0.02	—

TABLE C.3 (CONTINUED)

PARAHO SEMIWORKS RETORT - DIRECT MODE
 ELEMENTAL COMPOSITION VERSUS PARTICLE SIZE OF AEROSOLS - NOVEMBER 1977

	Particle Size	Th ng/m ³	Ti μg/m ³	V ng/m ³
RETORT SITE 11-16-77	>7.0	9.9 ± 1.1	2.5 ± 0.7	213 ± 14
	3.3 - 7.0	3.9 ± 0.4	1.9 ± 0.4	67 ± 7
	2.0 - 3.3	2.1 ± 0.3	0.81 ± 0.24	34 ± 4
	1.1 - 2.0	2.3 ± 0.3	0.96 ± 0.24	40 ± 5
	<1.1	10.8 ± 1.2	4.3 ± 0.9	244 ± 21
	Σ	29 ± 2	10.5 ± 1.3	598 ± 27
CRUSHER SITE 11-16-77	>7.0	5.6 ± 0.3	2.0 ± 0.4	109 ± 8
	3.3 - 7.0	2.5 ± 0.2	0.46 ± 0.17	39 ± 4
	2.0 - 3.3	1.03 ± 0.08	0.37 ± 0.16	16 ± 3
	1.1 - 2.0	1.09 ± 0.09	0.63 ± 0.16	14 ± 3
	<1.1	9.8 ± 0.6	6.1 ± 1.0	330 ± 23
	Σ	20 ± 1	9.6 ± 1.1	508 ± 25
TAILINGS PILE 11-16-77	>7.0	9.3 ± 0.9	6.1 ± 1.7	259 ± 31
	3.3 - 7.0	6.2 ± 0.6	2.1 ± 0.5	79 ± 10
	2.0 - 3.3	4.3 ± 0.4	1.9 ± 0.4	51 ± 9
	1.1 - 2.0	4.1 ± 0.4	1.3 ± 0.4	55 ± 7
	<1.1	23 ± 2	8.6 ± 1.8	460 ± 40
	Σ	47 ± 2	20 ± 3	909 ± 50
BACKGROUND SITE 11-17-77	>7.0	0.21 ± 0.01	0.079 ± 0.016	3.4 ± 0.3
	3.3 - 7.0	0.11 ± 0.01	0.034 ± 0.010	0.9 ± 0.2
	2.0 - 3.3	0.059 ± 0.007	0.035 ± 0.010	1.0 ± 0.2
	1.1 - 2.0	0.059 ± 0.007	0.037 ± 0.010	1.5 ± 0.2
	<1.1	0.31 ± 0.03	0.096 ± 0.029	7.5 ± 0.7
	Σ	0.75 ± 0.03	0.28 ± 0.04	14.3 ± 0.8

APPENDIX D
PARAHO SEMIWORKS RETORT - DIRECT MODE
SPECIATION MEASUREMENTS

PARAHO SEMIWORKS RETORT - DIRECT MODE

ARSENIC SPECIATION
PROCESS WATER (µg/ml)

		<u>As⁺³</u>	<u>As⁺⁵</u>	<u>Methyl Arsenic</u>	<u>Dimethyl Arsenic</u>	<u>Total</u>
8-24-77	@1115	2.4	3.1	<0.06	<0.06	5.5
8-25-77	@ AM	1.1	1.1	<0.06	<0.06	2.2
8-26-77	@0900	1.9	2.1	<0.06	<0.06	4.0

PARAHO SEMIWORKS RETORT - DIRECT MODE

ARSENIC SPECIATION
($\mu\text{g}/\text{m}^3$)

	<u>Particulate As</u> <u>0.5 μ Fluoropore</u>	<u>Vapor</u> <u>As₂O₃</u>	<u>Organic</u> <u>As</u>	<u>AsH₃</u>	<u>Methyl</u> <u>Arsine</u>	<u>Di-Methyl</u> <u>Arsine</u>	<u>Other</u> <u>Organic</u> <u>Arsine</u>	<u>Total</u> <u>Arsenic</u> <u>($\mu\text{g}/\text{m}^3$)</u>
Est error = $\pm 50\%$								
11-16-77								
Recycle gas	Did not filter	149	<12	1.8	2.8	1.0	0.5	155
Thermal oxidizer	Did not filter	12	<12	0.3	<0.2	<0.2	<0.2	12.3
11-17-77								
Recycle gas	1.2	112	<12	2	3	1.7	0.5	120
Thermal oxidizer	19	36	<12	<0.2	<0.2	<0.2	<0.2	55

PARAHO SEMIWORKS RETORT - DIRECT MODE

MERCURY SPECIATION MEASUREMENT -
THERMAL OXIDIZER

<u>Date</u>	<u>Paraho Thermal Oxidizer Gas</u>		
	<u>Total Hg, $\mu\text{g}/\text{m}^3$</u>	<u>Hg Species, $\mu\text{g}/\text{m}^3$</u>	
8-24-77	9 ± 3		
8-25-77	6.7 ± 0.8		
8-26-77	4.5 ± 1.3	as HgCl_2	<0.3
		as CH_3HgCl	<0.2
		as Hg°	4.5
		as $(\text{CH}_3)_2\text{HgCl}$	<0.1
11-15-77	7.2 ± 0.9		
11-16-77	12 ± 2	as HgCl_2	<0.1
		as CH_3HgCl	<0.4
		as Hg°	9.4
		as $(\text{CH}_3)_2\text{HgCl}$	<0.4

PARAHO SEMIWORKS RETORT - DIRECT MODE

SULFUR SPECIES AND CARBON MONOXIDE
Nov. 15, 1977 - Nov. 16, 1977

THERMAL OXIDIZER

11/15	SO ₂ = 276 ppm	Dilution technique	Interscan*
	SO ₂ = 256 ppm	Direct	Interscan
	H ₂ S < 0.4 ppm	Dilution technique	Interscan
Mercaptans	< 0.4 ppm	Dilution technique	Interscan
	CO Est. 1840 ppm	Assume 20:1 sensitivity	
		Remaining CO dilution	Interscan
	CO Est. 1400 ppm	Direct	Interscan

RECYCLE GAS CONCENTRATION

11/15	H ₂ S + RSH = 2800 ppm	From 11/16 ratio	Interscan
	CO = 21400 ppm	20:1 sensitivity estimate	Interscan
11/16	H ₂ S + RSH = 2400 ppm	Direct - dilution	Del-Mar Colorimeter
	CO = 16040 ppm	20:1 sensitivity estimate	Interscan

* Potentiometric

APPENDIX E
PARAHO SEMIWORKS RETORT - DIRECT MODE
MISCELLANEOUS ANALYSES

PARAHO SEMIWORKS RETORT - DIRECT MODE

Major Element Concentrations in Paraho Raw and Retorted Shale Collected August 24, 1977(a)

<u>Element)</u>	<u>Raw</u>	<u>Retorted</u>	<u>Retorted/Raw</u>
Hydrogen (%)	1.50 ± 0.03	0.167 ± 0.004	0.111 ± 0.002
Carbon (%)	15.5 ± 0.16	6.11 ± 0.04	0.394 ± 0.005
Nitrogen (%)	0.66 ± 0.10	0.298 ± 0.004	0.45 ± 0.017
Oxygen (%)	39.6 ± 1.7	50.7 ± 1.7	1.18 ± 0.09
Sulfur (ppm)	6000 ± 240	5830 ± 250	0.97 ± 0.06

(a) Analysis by LECO Corporation.

PARAHO SEMIWORK RETORT - DIRECT MODE

XRD ANALYSES

	<u>Sample Number</u>	<u>Mineral</u>	<u>Estimated Wt%, ±10%</u>
Paraho Raw Shale Baghouse Fines 8-24-77	1	Dolomite	45
		Quartz	25
		Calcite	15
		Feldspar	10
		Analcime	5
Paraho Raw Shale 8-23-77	2	Dolomite	50
		Quartz	25
		Analcime	10
		Calcite	5
		Feldspar	5
Paraho Retorted Shale Baghouse Fines* 8-24-77	3	Quartz	30
		Calcite	25
		Feldspar	20
		Dolomite	15
		Analcime	15
Paraho Retorted Shale 8-23-77*	4	Illite	5
		Quartz	35
		Dolomite	25
		Calcite	20
		Analcime	10
		Feldspar	10
		Illite	5

* Some of the Mg present in the dolomite in the raw shale is unaccounted for in our analyses of the retorted shale. It is probably present as amorphous MgO, which would not show up on XRD.

PARAHO SEMIWORKS RETORT - DIRECT MODE

SULFUR, NITROGEN, CARBON AND HYDROGEN ANALYSES*

		<u>% S</u>	<u>% N</u>	<u>% C</u>	<u>% H</u>
Paraho Crude Oil	1	0.91	2.10	86.00	11.73
8-24-77	2	0.88	2.40		
	3	0.81	2.67		
Paraho Crude Oil		0.81	2.60		
11-16-77					
Prudhoe Bay Crude	1	1.42	0.23		
	2	1.46	0.23		
Wilmington, CA Crude		2.04	0.71		

* Analyses by Schwarzkopf Laboratories, Woodside, New York.

PARAHO SEMIWORKS RETORT - DIRECT MODE

Elemental Analysis of Thermal Oxidizer Dust
by Instrumental Neutron Activation Analysis
(all values $\mu\text{g/g}$ unless noted)

Element	Dust Collected 11-16-77	Retorted Shale (8-24-77)	Ratio Dust/Retorted
Al (%)	2.92 ± 0.08	4.83 ± 0.10	0.60
As	520 ± 10	59 ± 1	8.81
Ba	430 ± 50	600 ± 10	0.72
Br	2.8 ± 0.31	0.80 ± 0.20	3.50
Ca (%)	10.6 ± 0.9	13.3 ± 0.2	0.80
Ce	51.0 ± 0.7	52 ± 2	0.98
Cs	2.8 ± 0.2	4.7 ± 0.2	0.60
Fe (%)	1.91 ± 0.02	2.40 ± 0.03	0.80
Hg	4.2 ± 0.1	0.030 ± 0.003	140
K (%)	1.4 ± 0.3	1.86 ± 0.03	0.75
La	26.0 ± 0.5	24.7 ± 0.3	1.05
Lu	0.29 ± 0.02	0.35 ± 0.03	0.83
Mn	380 ± 40	396 ± 14	0.96
Na (%)	1.35 ± 0.01	2.19 ± 0.03	0.62
Nd	27 ± 3	22 ± 1	1.23
Rb	86 ± 6	88 ± 2	0.98
Sb	5.0 ± 0.3	2.6 ± 0.2	1.92
Se	41.0 ± 0.8	2.3 ± 0.1	17.8
Sr	730 ± 20	880 ± 10	0.83
Ta	0.70 ± 0.06	0.65 ± 0.02	1.08
Tb	0.48 ± 0.05	0.42 ± 0.04	1.14
Th	8.9 ± 0.4	7.6 ± 0.1	1.17
Ti (%)	0.21 ± 0.05	0.24 ± 0.01	0.88
U	7.0 ± 1.0	5.1 ± 0.1	1.37
V	140 ± 10	130 ± 6	1.08
Yb	1.4 ± 0.2	1.6 ± 0.1	0.88
Zn	120 ± 3	82 ± 3	1.46

PARAHO SEMIWORKS RETORT - DIRECT MODE

Eh,pH AND S⁼ IN FRESH RETORT WATER SAMPLES

11-15-77 Eh = -125 mV
 pH = 8.50 at 20°C
 S⁼ = 9.9 ppm*

11-16-77 Eh = -92 mV
 pH = 8.55 at 20°C

11-17-77 Eh = -162 mV
 pH = 8.60 at 20°C
 S⁼ = 1.2 ppm*

* Sulfide measured with ion specific electrode by method of standard subtraction.

PARAHO SEMIWORKS RETORT - DIRECT MODE

TOTAL STACK PARTICULATES
(0.45 Nucleopore Filters)

	<u>Recycle Gas Line*</u>	<u>Thermal Oxidizer</u>
8-24-77	2.4 mg/m ³ (0.60m ³ total)	<0.8 mg/m ³ (0.20 m ³ total)
11-15-77	2.5 mg/m ³ (0.18 m ³ total)	120 mg/m ³ (0.20 m ³ total)
11-16-77	4.2 mg/m ³ (0.060 m ³ total)	160 mg/m ³ (0.20 m ³ total)
11-17-77	1.5 mg/m ³ (0.12 m ³ total)	70 mg/m ³ (7.0 m ³ total)

*Not isokinetically sampled.

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