

Trace Element Variations in an
Oil-Shale Retorting Operation

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Experiments were conducted jointly between Colorado School of Mines (CSM) and Development Engineering, Inc. (DEI) using raw shale feed to the Paraho Semi-Works retort. (1,2) A schematic diagram of the 10-1/2 foot O.D. Semi-Works retort is shown in Figure 1. The Direct Mode operation, where combustion occurs within the retort to provide necessary heat, is portrayed in this schematic diagram. Operations are continuous and flows are countercurrent. Gases flow upward. The downward flow of shale is controlled by a hydraulically-operated grate mechanism. Shale is distributed evenly across the top of the bed by a rotating distributor. Here, the shale is 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 oil, gas, and coke. The coke remaining on the retorted shale serves as fuel in the combustion zone. Air is distributed evenly across the bed in an air-gas mixture in this zone. In the lower section of the retort, the shale is cooled by bottom recycle gas and this gas, in turn, is preheated before entering the combustion zone. The oil, as a stable mist, is carried out the top of the retort through the off-gas collector and is separated from the gas in a coalescer-electrostatic precipitator system.

In the Indirect Mode operation, the gas blower is replaced by an external heater. The middle and upper recycle gas is passed through this heater to provide heat needed for retorting. In this mode, the product gas is not diluted with products of combustion and nitrogen from the air, and the carbon remaining on the retorted shale is not utilized.

Uniform flow of solids and gases within the retort is essential in order to maintain a continuous operation and a high efficiency. In the Paraho Semi-Works retort, the bottom grate, the air-gas distributors, and the rotating shale distributor are designed to assure uniform flows. In addition, the raw shale feed is carefully screened and handled to a uniform feed. Feedstock for the retort consists of + 1/2 inch to - 3 inch nominal size. Fines and non-uniform shale size can result in gas channeling, high pressure drops, and uneven bed temperatures. These problems cause low oil yields and could, eventually, result in a retort shutdown. In addition to providing good operations and high efficiencies within the retort, the resulting lump-size retorted shale reduces considerably the environmental impact caused by dusting.

Although lump-size feed improves retort operation, minimizes environmental impacts, and reduces crushing costs, this feed creates problems in securing a representative sample for laboratory analysis. A raw

shale sampling system was designed to meet the accepted criteria for sampling this lump-size, non-homogeneous material. (3) A diagram of the Paraho sampling system is shown in Figure 2. A motorized gate diverts flow from the retort at preset intervals (usually 30-50 minutes). Approximately 200 pounds of material is taken in a single cut. The sample is crushed to -3/4 inch and passed through a four-stage splitter. The retained sample is crushed to - 1/4 inch and passed through a second four-stage splitter. This system provides a 24-hour composite laboratory sample (20-30 lbs, - 1/4 inch) from the 2 1/2-4 tons of the lump material sampled from the raw shale feed. An examination of the Paraho raw shale sampling system showed it to be unbiased. (4) Careful analyses of the grade (gallons oil/ton shale) indicated no significant differences between reject streams A and B and the laboratory sample. This laboratory sample was used in the studies presented in this paper.

Sampling Program

The objective of this research is to determine the concentrations of trace elements in the Paraho oil-shale feedstock and to study the fate of those trace elements during retorting. Elements of particular interest are B, F, As, Se, and Mo (5). In this regard, sampling the Paraho feedstock presents a problem. Lumps of rock -3 inches to +1/2 inch in size is not an ideal size of sample. One or two lumps is all that would be needed for most analyses, but that can hardly be considered representative. However, if the Paraho sampler were used to secure a sample, the amount would be about 6 kg. The sample is obviously physically heterogeneous. Does this also mean that it will be chemically heterogeneous? In addition, mining, hauling, crushing and retorting are a continuous operation at Anvil Points, little stockpiling is done. Does this mean that feedstock sampled on one day will differ significantly from that used in the retort on another day? Fundamental sampling questions such as this require a sampling program that is based on a strong foundation of statistical theory.

The statistical model followed in the sampling was a hierarchical or nested analysis of variance (6,7). In this case, one month of 30 days in which the retort was operating was subdivided or nested into 24 hour, 8 hour, and 1 hour periods. Of these 30 days, 6 were chosen as test days. Samples were taken on each of the three 8 hour periods. Then, on one randomly chosen 8 hour shift, eight 1 hour samples of oil shale feedstock were taken. This nested sampling design is shown in Figure 3. Now, for some constituent, such as iron, if all the samples were the same then

$$\text{concentration of Fe}_i = \mu_{\text{Fe}} \quad (1)$$

where μ_{Fe} is the mean of Fe concentrations and i designates the i^{th} sample. This is not the case. There can be a deviation or error due to the time in which the sample was taken and the imprecision of the analysis. So the equation 1 becomes

$$\% \text{Fe}_{ijkm} = \mu_{\text{Fe}} + \alpha_i + \beta_{ij} + \gamma_{ijk} + \delta_{ijkm} \quad (2)$$

Mean + 24 hr + 8 hr + 1 hr + analysis

where i designates the retort day and α_i is the deviation from the mean due to the sample being taken on that day. Similarly, β_{ij} represents the deviation due to the sample being taken in the j^{th} 8 hr shift of the i^{th} day, γ_{ijk} means the same for the 1 hr period; and δ_{ijkm} is the error for the analysis. By carefully setting up a nested sampling design and randomly selecting the sampling periods, an estimate of magnitude of the error or deviation for each time

period can be obtained. Certainly, if more periods were sampled, the estimates of error would be better, but the design choice is such that a minimum of samples yields meaningful estimates on all the error parameters.

One can not actually determine the errors and deviations; but if the sampling design is properly constructed, estimates of the errors can be estimated (6,7). Such an estimate is called a variance, the variance equation corresponding to equation 2 is

$$s_{Fe}^2 = s_{\alpha}^2 + s_{\beta}^2 + s_{\gamma}^2 + s_{\delta}^2 \quad (3)$$

These variances are similar to estimates of the standard deviation but in this case, the variance is partitioned among several components. The partitioning of the variance allows the following questions to be answered:

1. Is the mean of all the samples representative of the whole retort month or is there a trend over the month?
2. Is there significant scatter in any one of the 24 hr; 8 hr; or 1 hr time periods?
3. Are the analytical procedures precise enough or do they contribute to most of the scatter in the concentration values?

Analysis Program

DEI performed the Fischer assay analyses by a procedure that has been described previously (4). The precision of the analyses has been determined to be 2% relative standard deviation for the oil yield and 15% and 20% relative standard deviation for the water yield and gas plus loss yield. All 70 oil shale feedstock samples that were collected were analyzed for oil yield.

The elemental analyses were done by energy dispersive x-ray fluorescence (EXRF) analysis. The details of the analytical procedure have been previously published (8,9). In this procedure, four samples were chosen for analysis in each of the six hourly sample sections and three of the eight hour shift samples were analyzed for each day for a total of 37 samples. Also, duplicates of eight samples were analyzed to determine the variance of the analysis procedure. The relative standard deviation for the analysis for each element is listed in Table I. They range from above 10% for light elements to below 5% for heavier elements. These results are typical of the precision of the EXRF method. Comparison of analyses of NBS standard coal (SRM 1632) and round robin analyses done on oil shales show the accuracy of the analyses to be within $\pm 10\%$ (10,11). K and Se concentrations do not compare well with other analytical methods; the results are aberrant by about 30%.

Results and Conclusions

In Table I, the results for the Fischer assays and EXRF analyses are listed. The average, mean, range, standard deviation of the mean, and relative standard deviation of the mean are based on all samples. The average analysis relative standard deviation is based on the variations found in the eight samples for which multiple analyses were performed. The percent of variance for 24 hr, 8 hr, 1 hr and analysis level is determined from the analysis of variance program. The meaning of the variances requires an explanation.

For each level (i) analytical, 1 hour, 8 hour, 24 hour, and analysis,

a variance S_i^2 is determined for each element. Then, the percent of total variance for the level for the concentration of Fe is:

$$\% (S_{Fe})_i^2 = \left(\frac{(S_{Fe})_i^2}{\sum_{i,j,k,m} (S_{Fe})_n^2} \right) \times 100$$

This parameter measures where the majority of the variation lies for each concentration in the 4 level sampling scheme design. For example, for oil yield, the % variance is greatest on the 24 hr level, the value being 63%. This implies that the samples taken on the 1 hr and 8 hr periods each day did not change significantly with respect to the day-to-day changes. Thus, the samples taken on one day are appreciably different from the samples taken on other days. The 24 hr averages for oil yield for the 6 days were 23.8, 25.8, 30.4, 24.5, 31.2, and 26.9 gallons per ton respectively. The daily variation is readily apparent. For day 3 where the 24 hr average is 25.8, the 8 hr oil yields are 25.2, 26.7, and 25.4 gpt and the 1 hr oil yields are 25.5, 22.4, 27.8, 21.2, 26.7, 27.4, 25.3, and 25.0 gpt. These results are about typical. The tight range of the 8 hr samples is obvious; the 1 hr samples range a bit more but not as much as the daily averages. The percent of variance for the 1 hr level is 37%. Thus, the percent of variance is a measure of how much scatter there is in the concentration of a substance at each level.

The first conclusion that appears from the results in Table I is that the oil yield measurably changed from day to day. The percent of variance is 63% for the daily level, 0% for the 8 hr level, and 37% for the 1 hr level. The oil yield is a reasonable measure of the organic content of the shale. So, this implies that for the retort month there were measurable differences from day to day in the organic content. This also implies that an average organic content for the month is probably not meaningful, but that a daily average for organic content can be reasonably estimated.

The elemental concentration results show these samples to be quite interesting. A geochemist would expect concentration ranges for trace elements to range by about a factor of 10 over a section of a formation. Here the range is only a factor of 2. For some elements like Rb and Sr, the relative standard deviation over all the samples is less than 10%. For most of the elements, the analytical precision is at 10% or less. This can be considered to be quite respectable for a multi-element analytical technique. Nevertheless, for Ca, Mn, Fe, Cu, and Se the analytical precision contributions most of the error as can be seen by the percent of variance for the analysis for these elements. This implies that more precise techniques should be used to obtain the concentrations of these elements in oil shale. Finding techniques with uniform precision significantly below 10% is difficult. For none of the elements does the daily or 8 hr percent of variance exceed 33%. This implies that a representative sample for the retort month for the inorganic elements can be calculated. The grand mean for each element represents a reasonable average for the whole month. For the elements listed, the results are not statistically different from those of other laboratories who were conducting other experiments at Anvil Points at the same time. So thus, the mean concentration values for the elements represent an accurate estimate of the feedstock that month within the constraints of the analytical scheme and the sampling design.

The contrast in conclusions for the organic and inorganic portions of the oil shale feedstock is obvious. Since great care was taken in the consideration of the sampling design, one has to conclude that this difference is real. To test this further, the concentration of all the substances listed in Table I for all the samples analyzed were tested by a linear correlation program. The results for the correlation coefficients are listed in Table II. None of the coefficients relating the oil yield to the elements rises above 0.5. This also shows the basic dissimilarity between organic and inorganic portions of this oil shale.

Several implications arise from this organic and inorganic difference. The primary conclusion is that on a production level none of the above elements vary in the same general way as the organic content of the oil shale. This conclusion allows the situation of variability in layers in the formation; but if there is mining, then hauling and crushing blend out any variations. This conclusion also will allow the possibility of some minor amount of an element such as As or Pb to be associated with the organic portion of the shale but the majority of amount of that element cannot be associated with organics in the shale. Another implication of this dicotomy is that the results of analyses on the organic content which would typically be performed by an oil analysis laboratory will not yield information about the inorganic elements. This implication means that specific analyses for the inorganic elements will have to be made if their concentrations are of interest. Fortunately, the results shown for Table I for the inorganic elements show the feedstock to be quite uniform. This means that careful analysis of a sample taken once a week will yield more information on elemental concentrations than less accurate analyses taken on samples collected every hour or every shift.

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Table I. Concentration parameters of Paraho oil shale. The sampling period is from August 23, 1977 through September 20, 1977.

| Substance | Conc. Unit | Grand Mean | Grand Standard Deviation | Grand Rel. Std. Dev. % | Range | Avg. Analysis Rel. Dev. % | % OF VARIANCE | | | |
|------------|------------|------------|--------------------------|------------------------|----------|---------------------------|---------------|------------|------------|----|
| | | | | | | | 24 hr Level | 8 hr Level | 1 hr Level | |
| Oil | gpt | 27.0 | 3.2 | 11.9 | 22-39 | 2 | 63 | 0 | 37 | - |
| Water | gpt | 4.4 | 1.7 | 39 | 1.6-11.4 | 15 | 0 | 93 | 7 | - |
| Gas & Loss | gpt | 2.2 | 0.6 | 28 | 1.0-3.7 | 20 | 0 | 26 | 74 | - |
| Ca | % | 12.3 | 1.5 | 12 | 7.2-15 | 13 | 3 | 0 | 0 | 97 |
| Mn | ppm | 313 | 34 | 11 | 191-380 | 10 | 12 | 0 | 0 | 88 |
| Fe | % | 2.13 | 0.21 | 10 | 12.2-25 | 9.2 | 6 | 0 | 0 | 94 |
| Ni | ppm | 32 | 3 | 9.5 | 18-36 | 6.6 | 0 | 0 | 55 | 45 |
| Cu | ppm | 35 | 4 | 10.1 | 20-40 | 6.6 | 8 | 22 | 2 | 68 |
| Zn | ppm | 83 | 24 | 29 | 40-180 | 9.8 | 14 | 0 | 68 | 18 |
| Ga | ppm | 7.0 | 0.8 | 12 | 4-8 | 7.6 | 18 | 0 | 32 | 50 |
| As | ppm | 44 | 5.6 | 13 | 26-58 | 8.7 | 25 | 0 | 23 | 52 |
| Se | ppm | 1.5 | 0.26 | 17 | 1.0-2.3 | 15 | 7 | 0 | 0 | 93 |
| Rb | ppm | 80 | 6 | 7.4 | 45-85 | 1.7 | 24 | 0 | 73 | 3 |
| Sr | ppm | 770 | 66 | 8.6 | 410-830 | 2.2 | 32 | 0 | 62 | 6 |
| Y | ppm | 12 | 1.2 | 10.6 | 6.2-14 | 4.9 | 8 | 0 | 49 | 43 |
| Zr | ppm | 56 | 14 | 25 | 26-120 | 8.3 | 10 | 0 | 80 | 10 |
| Nb | ppm | 5.7 | 0.5 | 9.7 | 3.3-6.6 | 2.4 | 19 | 0 | 72 | 9 |
| Mo | ppm | 23 | 2.5 | 10.8 | 13-28 | 2.3 | 0 | 0 | 89 | 11 |
| Ba | ppm | 480 | 67 | 14 | 240-670 | 1.7 | 14 | 0 | 84 | 2 |
| Pb | ppm | 24 | 3.1 | 13 | 15-35 | 3.2 | 0 | 26 | 65 | 9 |

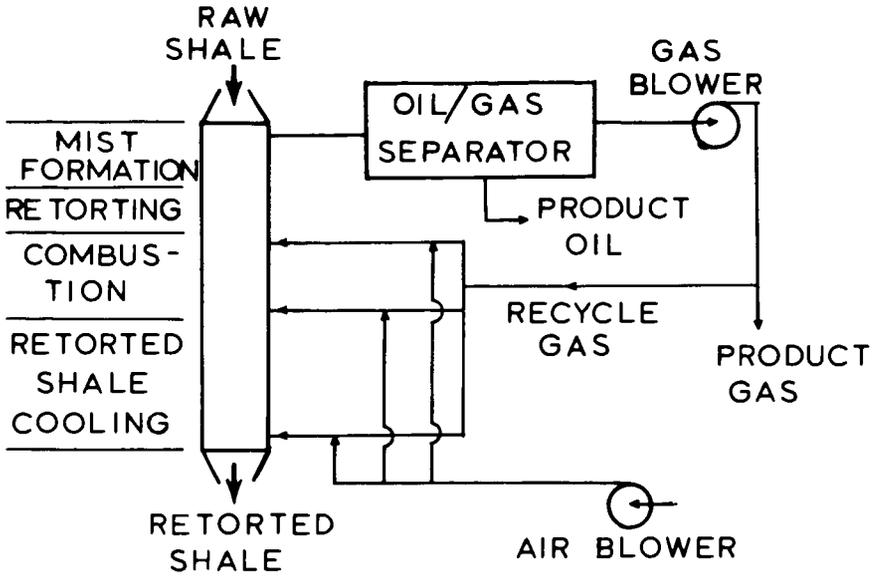


FIGURE 1. SCHEMATIC OF PARAHO RETORT FOR THE DIRECT HEATED MODE.

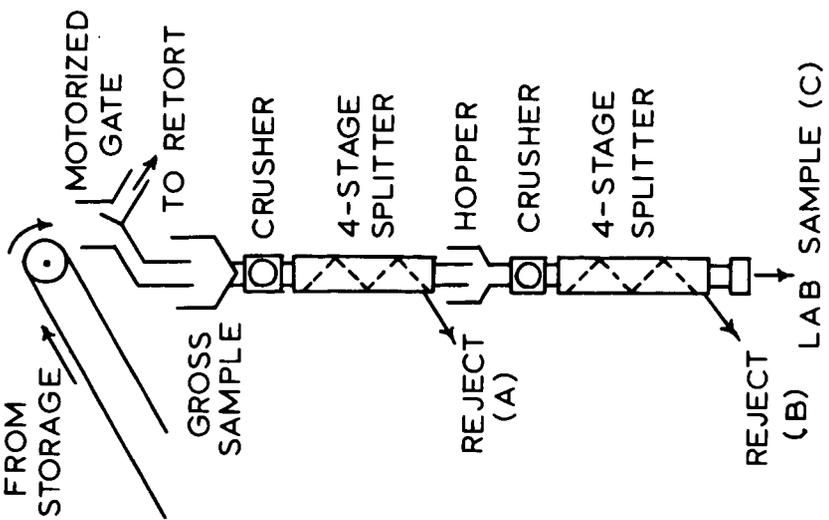


FIGURE 2. FEEDSTOCK SAMPLING SYSTEM FOR THE PARAHO RETORT.

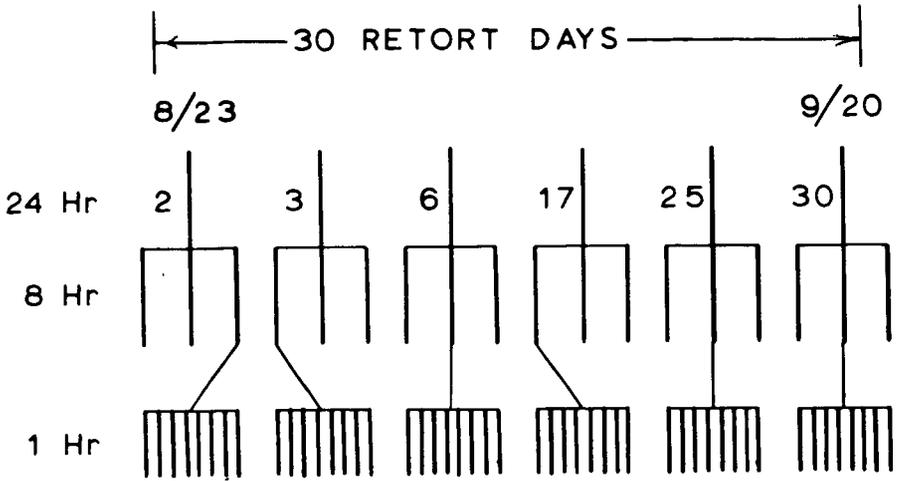


FIGURE 3 TIME NESTED PARAHO SAMPLING DESIGN.