

FINAL REPORT

THE USE OF PULSEWAVE TECHNOLOGY AS A KEROGEN BENEFICIATION TECHNIQUE IN OIL SHALE PROCESSING

Small Business Technology Transfer Research Grant No. DE-
FG02-04ER86195

Summary

The purpose of this research project was to identify and quantify the benefits of an innovative process (the “Pulsewave” process) that allows for the clean removal of the desirable organic material, primarily kerogen, from raw oil shale ore prior to the retorting process, and does so without significantly altering the chemistry of either component. This beneficiation process would allow for kerogen to be retorted as a nearly pure phase as compared to current technologies that retort the raw oil shale ore in its entirety.

Pulsewave, LLC, the recipient of this STTR Grant, obtained oil shale samples from the Mahogany Zone of the Parachute Creek Member of the Green River Formation in Rio Blanco County, Colorado. These samples were then processed at Pulsewave’s facility in Denver, Colorado, which resulted in the substantial liberation of kerogen from the mineral matrix of the shale. The processed material containing both the liberated kerogen and inert shale mineral matter were then sent to Dr. John Crelling at the Coal Research Institute at Southern Illinois University, where the liberated kerogen was separated from the mineral matrix by float/sink and Density Gradient Centrifuge methods. Finally, the separated kerogen was sent to Western Research Institute in Laramie, Wyoming, Pulsewave’s research partner in this Phase 1 research project, where the clean kerogen and its Fischer Assay products were tested for liquids yield, heteroatom content and other properties by a series of analyses.

The results of this research clearly demonstrate that kerogen can be liberated from oil shale by the Pulsewave process. By producing this relatively clean stream of kerogen for processing, it was demonstrated that the oil yield was increased significantly over raw oil shale (149.1 gal/ton for highly purified kerogen concentrate vs. 32.3 gal/ton for the raw oil shale used for this study), and an analysis of the oil product determined that it is substantially the same as shale oils produced by conventional retorting. In addition to increasing the shale oil yield from the raw feedstock, the production of this relatively clean kerogen phase by the Pulsewave process could significantly lower handling and processing costs and decrease the amount of pollution normally associated with conventional oil shale retorting operations.

Introduction

Oil shale is a fine-grained sedimentary rock containing abundant organic material that can be refined into synthetic crude oil and its products. Approximately 35% of the world's known oil shale reserves are contained in the Green River formation that covers an area of approximately 17,000 square miles in western Colorado, eastern Utah and southwestern Wyoming (State of Utah, 1980). Estimates for this reserve vary but indicate as much as 1.2 trillion barrels of oil could be in place in this formation, or enough oil to meet the internal demand of the United States for over a century at current consumption rates (Duncan and Swanson, 1965, and Duncan, 1981). In spite of this, there has not been an active full-scale oil shale project in the United States since 1991, due in large part to the start-up and operational costs associated with such a project and the negative environmental impact of oil shale mining.

Unlike conventional petroleum deposits that are pumped out of the ground in liquid form, in its natural state oil shale contains no liquid hydrocarbons. The hydrocarbon component of oil shale is an organic solid, primarily kerogen with a few percent bitumen (Himus, 1951) that is encased in a shale matrix and must be heated (retorted) in order to produce synthetic crude oil. Retorting is the process of heating the shale to a temperature of approximately 900-degrees F, at which point the organic component decomposes into gas, condensable oil and a solid residue (Nowacki, 1981). There are two major methods of processing oil shale: those in which the organics are retorted from the shale while it is still in the ground (*in situ*), and those in which the shale is mined and the ore is crushed and retorted above-ground (*ex situ*) (Lewis, 1984, and Russell, 1990).

The *in situ* method of processing oil shale usually entails the creation of a major void space in the shale by fracturing it with explosives, hydraulic pressure, or even by removing some of the shale by underground mining (Ranney, 1979). Heat is then applied by the injection of a hot fluid medium or by internal combustion created within the void spaces in the rock. At present, this method has several associated problems, including low recovery efficiencies, difficulty in creating the required void space, surface subsidence and a serious potential for the contamination of adjacent or nearby aquifers by soluble organic material and inorganic salts that are released by the *in situ* retorting process (Keller, 1985, and Tyner, 1984).

The *ex situ* method of surface mining or underground mining is attractive because it can recover up to 90% of the oil shale reserves (Keller, 1985). In this method, the shale is mined, crushed in a mill and retorted to recover the volatile organic products.

The environmental effects of *ex situ* oil shale mining and processing are complex and profound. Under current oil shale processing technology, blocks of mined ore are run through a jaw mill or ball mill to reduce it to a manageable size. Due to the small particle size of the desirable organic material in oil shale, the organic material is not separated from the shale matrix by this process (Nowacki, 1981). The fragments of oil shale are then retorted whole in order to process the organic material into a condensable liquid or vapor stream (Russell, 1990). After retorting the hydrocarbons from raw oil shale, the

retorted or spent shale is a highly alkaline solid that occupies a volume 20 to 30% greater than its original state, due primarily to an increase in pore space (Ranney, 1979). The porosity of raw oil shale is generally less than 10%, while the porosity of retorted shale porosity of retorted shale could be as high as 40%. Approximately 50 to 80% of this spent shale may be returned to and disposed of in the mine where it was extracted, but because of the increase in volume in retorted shale the remaining fraction will have to be taken to aboveground disposal sites (Earnest, 1977, Keller, 1985, and Peterson, 1978). In addition to adding significantly to the cost of operating an oil shale project, this processing and disposal method creates environmental problems related to the location of the disposal site, the effects of spent shale leachates at the disposal site, problems with the direct vegetation of the waste site due to high pH and water soluble salts, stabilization of the spent shale, and groundwater pollution in aquifers near the underground (mine) disposal site (Chappell, 1978, Fox, 1984, and Welles, 1984).

Pulsewave, LLC is a privately held firm involved in proprietary research aimed at mating its recently developed and patented resonance disintegration technology with potential commercial applications in several areas of materials science including the energy and mineral industries. In 2000, Pulsewave began research into the application of resonance disintegration technology as a method of liberating organic material from raw oil shale ore. This research led to the development of an innovative process that allows for the clean removal of the desirable kerogen and other organic material from raw oil shale ore prior to the retorting process, and does so without significantly altering the chemistry of either component. Kerogen, loosely defined, is the solid organic component of sedimentary rocks. Given sufficient time and suitable geologic conditions, this material can be converted to valuable liquid or gaseous fossil energy resources such as crude oil and natural gas. The Pulsewave beneficiation process would allow for kerogen to be retorted as a nearly pure phase as compared to current technologies that retort the raw oil shale ore in its entirety.

The technology behind the Pulsewave milling machine provides for the selective differentiation and fragmentation of particles in complex multi-phase materials such as oil shale, as opposed to the simple crushing and micronizing that result from conventional milling methods. This results in materials being fragmented from within rather than being crushed by impact or grinding. Therefore, materials will tend to cleave along the internal planes of their structure that are the most susceptible to separation, and in the case of the components in oil shale, that is apparently the boundary between particles of mineral matter and particles of the more elastic kerogen. This process produces a “cleaner” component particle than conventional milling because of the elimination of the smearing that normally accompanies the physical crushing of a material. The Pulsewave procedure processes raw oil shale to produce a finely divided material and then separates this material into a kerogen concentrate and a mineral fraction. The produced kerogen concentrate is available for other downstream processing to produce a shale oil product. This kerogen beneficiation offers several benefits to the oil shale industry, including but are not limited to the following:

Company Confidential/Proprietary Pulsewave LLC

- The pre-retort removal of the undesirable shale matrix would substantially reduce the leachable solids and toxic water that are produced by retorting raw oil shale ore. The Pulsewave process does not significantly alter the chemistry of the shale matrix, only the particle size, and therefore does not mobilize the toxic elements or compounds that are chemically bound and relatively stable in the raw ore. Essentially, the processed shale should be basically the same material as that which was present to begin with, thereby facilitating its handling and disposal.
- If the organic and mineral matter fractions of the oil shale were separated before the retorting process, the mineral matter fraction would not undergo expansion due to high heat (“popcorn” effect). Thus it could be returned *in total* to the site where it was originally mined with no need for accommodation of an increased volume of waste material.
- The source of many of the pollutants in the gaseous emissions from a retort facility would be removed from the retort process, resulting in cleaner “off gas” from these facilities.
- The micronized shale waste that would result from the Pulsewave process would be so small in particle diameter that it could easily be transported to the disposal site (i.e., underground mine) by hydraulic means and packed into place at high density. In addition, fine-grained oil shale particles such as those that have been produced by the Pulsewave process have a tendency to be self-cementing and the resulting material tends to have a very low permeability, thus reducing the potential for groundwater flow through the material in an underground disposal site (Peterson, 1978).
- By removing the organic matter from the mineral matrix prior to the retorting process, the energy necessary to retort the resulting clean kerogen phase would be considerably less than that required to retort raw oil shale. Carbonate minerals are a major component of many oil shales, including the Green River formation of the western US and these minerals decompose endothermically and react with other minerals in oil shale at approximately the same temperature required for kerogen conversion (Chappell, 1988, and Keller, 1985). The heat requirement for these reactions is large, and therefore they consume a significant amount of the energy during a conventional retorting operation.
- With the shale matrix removed, the relatively clean kerogen phase generated at or nearby to the mining site could be blended with locally produced crude oils and transported via pipeline to an off-site refinery or retorting facility, resulting in lower processing costs and environmental exposure.

The combination of any of these perceived benefits could significantly reduce the costs associated with processing oil shale into shale oil and also mitigate the negative environmental impact of extracting and processing oil shale. The focus of this DOE

STTR Research Grant was to perform controlled experiments and analyses that would verify and quantify the benefits of applying the Pulsewave technology to oil shale processing as indicated above. It was felt that the large-scale introduction of this technology would offer significant improvements in the cost and handling of oil shale ore and the associated retorting process, and would mitigate many of the environmental problems associated with retorted shale.

Project Objectives

The objective of this proposal was to identify and quantify some of the benefits of an innovative technology that will allow for the effective separation of the shale matrix from the desirable organic material in oil shale *prior* to the retorting process. Prior to submitting the application for this STTR, Pulsewave had already demonstrated the successful liberation of kerogen from its encasing oil shale matrix by processing bulk oil shale in their resonance disintegration machine. This Phase I research was intended to demonstrate the efficacy and efficiency of the Pulsewave process for liberating desirable organic material from its oil shale matrix, and to characterize and quantify the benefits of this process in terms of converting the separated organic material, the environmental benefits of producing and converting a clean kerogen phase, and the heteroatom content of the resultant shale oil.

Research Procedure and Results

A substantial portion of the research for this Phase I project took place at three different locations. The actual Pulsewave processing took place at Pulsewave's Centennial, Colorado facility, a 12,000 square-foot building which houses three Pulsewave Resonance Disintegration machines in addition to general laboratory facilities, a sample storage room and several offices for support staff.. Western Research Institute (WRI), of Laramie, Wyoming was Pulsewave's partner in this Phase I research effort and performed most of the analyses of the clean kerogen produced by Pulsewave. WRI is a nonprofit technology research and development organization, serving industry and government with expertise in energy, environment, and highway materials. WRI's main headquarters are located on the campus of the University of Wyoming in Laramie, Wyoming. This facility houses administration and 42 laboratories. In addition to the main facility, WRI operates a 22-acre Advanced Technology Center (ATC) north of Laramie. The ATC contains 14 buildings with laboratories, pilot facilities, shops, and offices. The pilot-plant facilities include 22,000 square feet of combustion, mild gasification, and in situ remediation laboratories, a 5,400-square-foot gas turbine pilot facility, a 7,000-square-foot waste management laboratory complex and a new facility for the production of fuels by bioprocessing. Dr. John Crelling, a Subcontractor to this research, supported this research through use of the facilities of the Coal Characterization Laboratory and Maceral Separation Laboratory at Southern Illinois University. Dr. Crelling separated the liberated keorgen from the micronized matrix in order to provide WRI a clean kerogen sample for analysis. The equipment made available to this project

through Dr. Crelling's lab included an Automated Fraction Collectors, a Beckman J2-21M Centrifuge, a Mettler/Parr DMA46 Density Meter, and Leitz and Zeiss microscopes and digital cameras capable of petrographic analysis and digital imagery in both reflected and fluorescent light.

Sampling and Pulsewave Processing Procedures

Mr. Gerald Daub, a Consulting Geologist from Grand Junction, Colorado, collected 4 55-gallon drums of oil shale samples from the Mahogany Zone of the Parachute Creek Member of the Green River Formation in Rio Blanco County, Colorado.

Photomicrographs of a control sample of this oil shale were taken and Figure 1 below is one of these that clearly shows *in situ* kerogen encased in the mineral matter matrix.

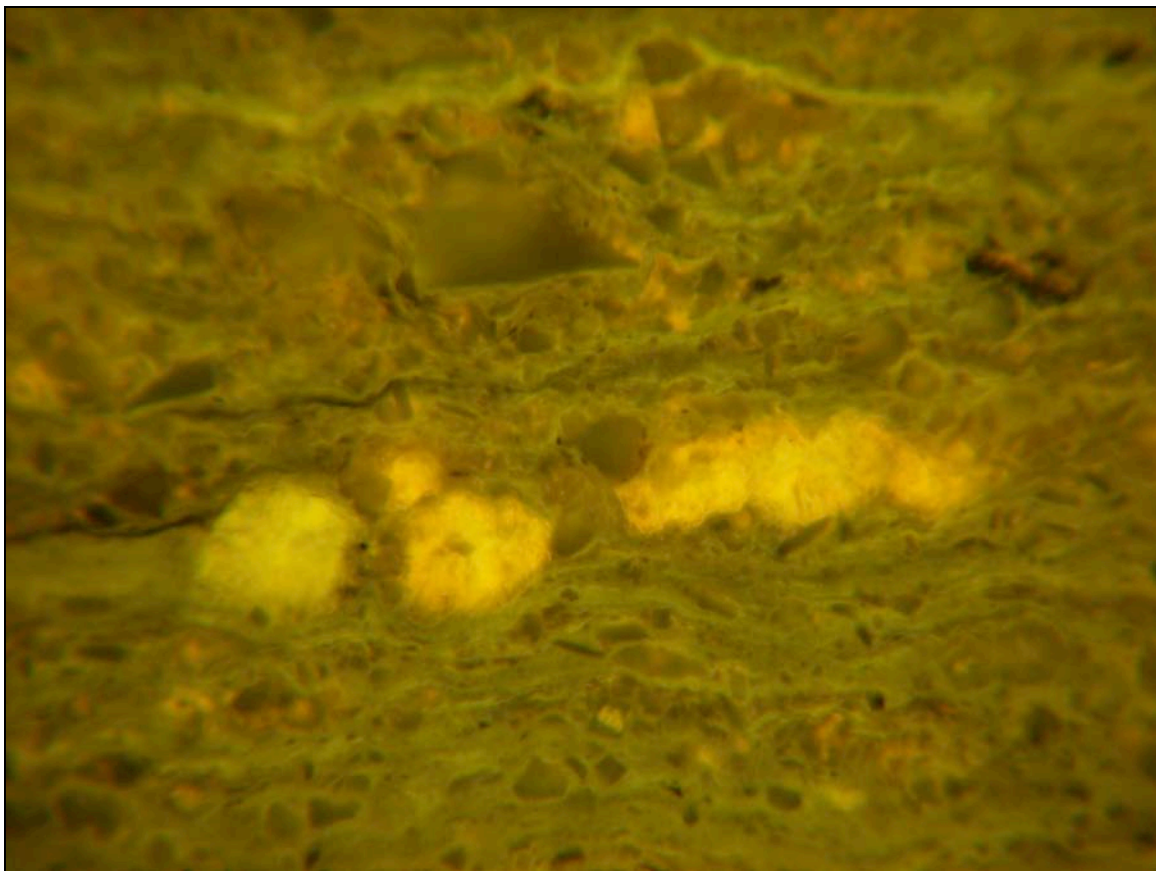


Fig. 1. Photomicrograph of *in situ* keorgen particles in Green River oil shale matrix. The yellow material is the kerogen. (~ 450x)

These samples were shipped to Pulsewave's Centennial facility where they were crushed to approximately 2" size in order to be processed though the machine. This feed material was then processed through the Pulsewave machine and the output material was measured for particle size in Pulsewave's Malvern Laser Diffraction particle size analyzer and was microscopically examined to access the degree of kerogen liberation.

This process was repeated several times in order to find the optimum machine settings for reducing the material and liberating the organics from the mineral matrix. Polished section mounts were made of this material and photomicrographs were taken, including Figure 2 below, which shows cleanly liberated kerogen and mineral matter particles.

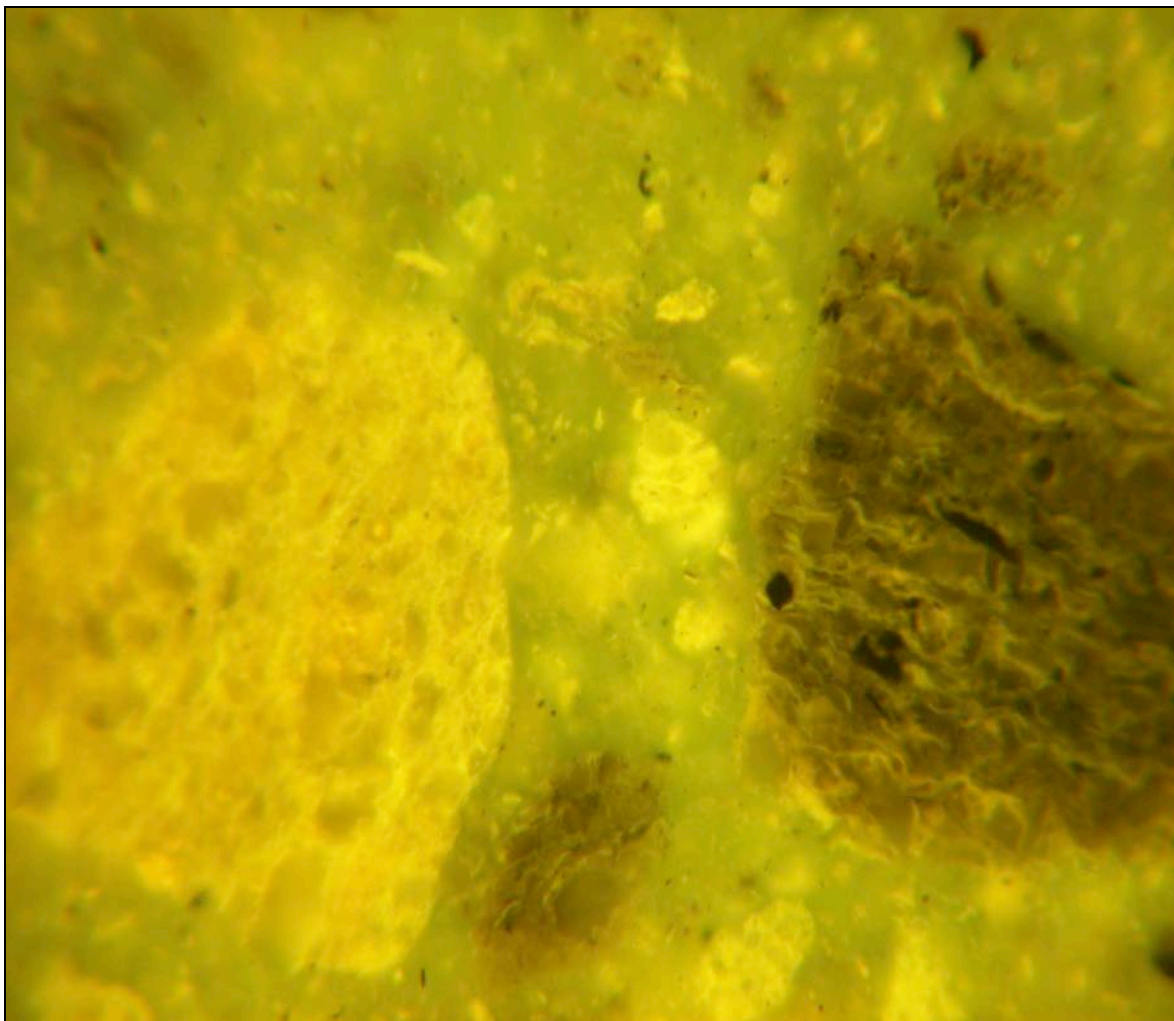


Fig. 2. Photomicrograph of Pulsewave-processed Green River oil shale product showing cleanly liberated kerogen particles (yellow) and particles of mineral matter (gray-brown). The green background is an epoxy mounting medium. (~450x)

Based on microscopy it was determined that a machine setting that resulted in the reduction of the oil shale product to a $d(0.5)$ of 12.053 μm resulted in the greatest degree of kerogen liberation. Figure 3 below is a summary of the Malvern particle size analysis of this material.

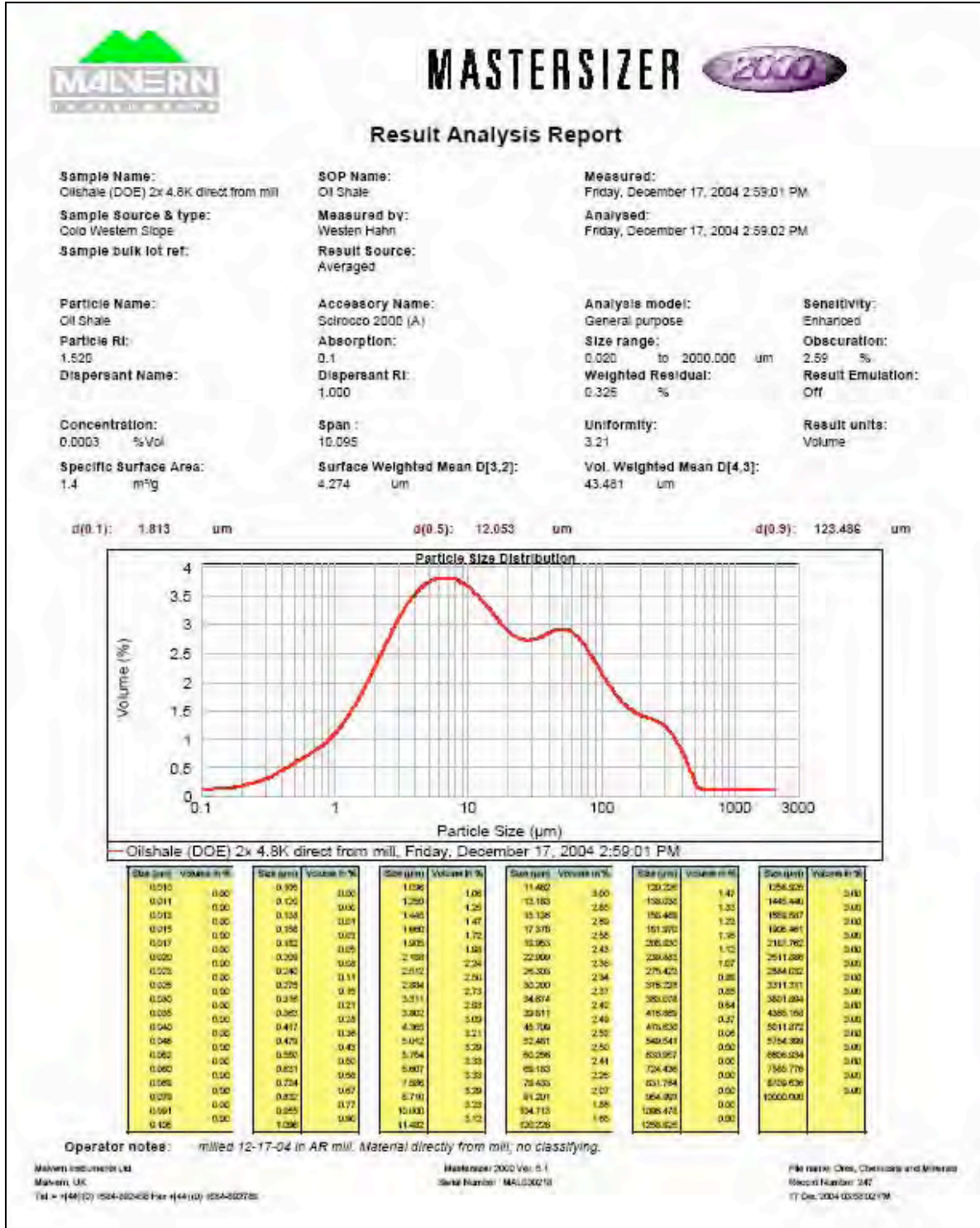


Fig. 3. Particle size analysis of the Pulsewave-processed oil shale product.

Separation of organic and mineral phases

The separation of the liberated kerogen took place at the Coal Research Institute at Southern Illinois University under the auspices of Dr. John Crelling. Two samples were prepared using different density separation points – 1.4 g/ml (initial kerogen concentrate) and 1.25 g/ml (highly purified kerogen concentrate). This was accomplished by sink/float and ultimately Density Gradient Centrifuge techniques (Crelling, 1994). This objective was established to determine the potential quality of a kerogen concentrate prepared from Pulsewave-processed shale, and efforts focused on ensuring that the desired float (kerogen) fraction satisfied the desired criteria. No effort was made to re-separate the sink fraction to maximize the separation since this would have greatly increased the amount of time/effort involved and it was never envisioned that the laboratory procedures used would serve as a useful model for a large scale separation procedure. Hence the ensuing data in the next portion of this report mentioning that the sink fraction still contains organic material are neither surprising nor significant. Figure 4 below is a density profile showing the density of the initial kerogen concentrate produced by Dr. Crelling’s methods and shows a clear concentration of material in the 1.2-1.4 g/ml range.

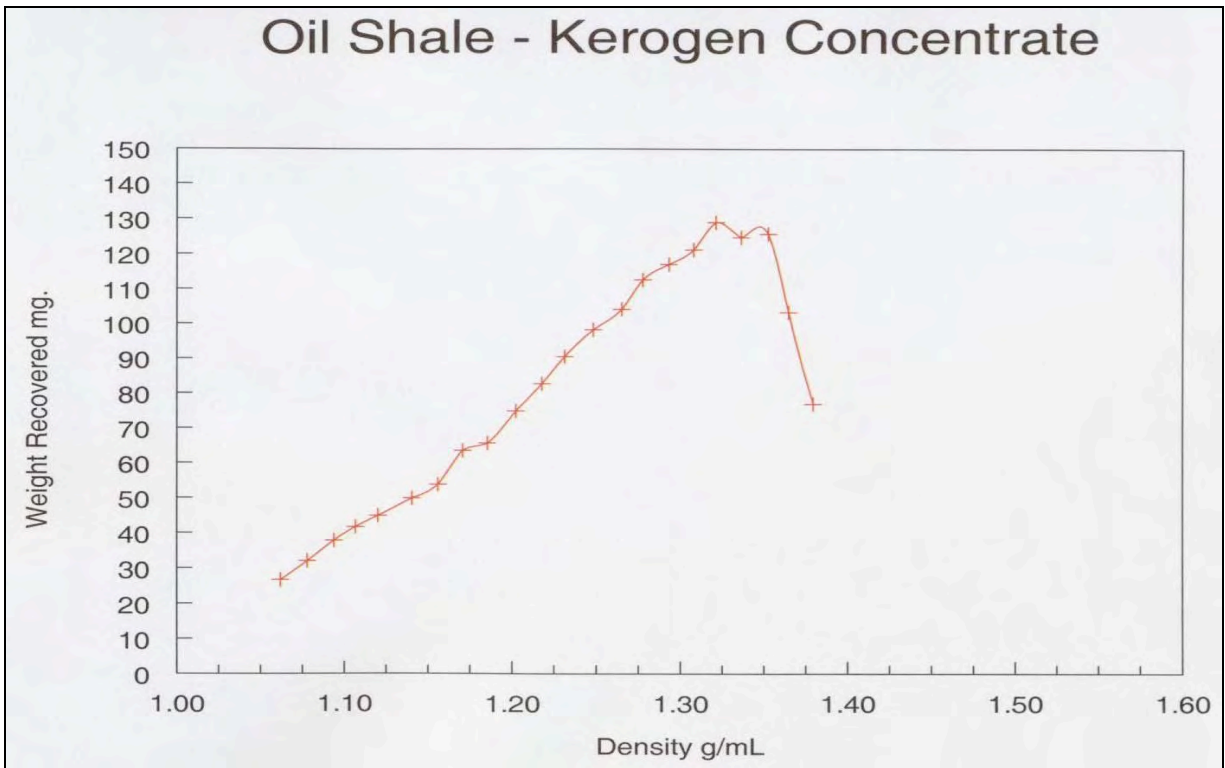


Figure 4. Density profile for the separated kerogen concentrate.

Pyrolysis-Gas Chromatographic-Mass Spectrometric Analysis

Pyrolytic techniques are widely used for investigation of sedimentary organic materials, including oil shales and coals. Pyrolysis coupled with Gas Chromatography and Mass Spectrometry, (Py-GC-MS) is one of the more common of these techniques and is used to provide information on the nature of the volatile and semi-volatile products released by thermal treatment of the organic matter. Although not identical to retorting, this process produces a product functionally equivalent to the primary oil produced by conventional dry retorting (such as Fischer assay) and directly provides information on the composition and characteristics of the produced oil.

Preliminary Py-GC-MS analyses were conducted on both the raw oil shale and the Pulsewave-produced kerogen concentrate at Southern Illinois University. SIU is equipped with one of the most sophisticated Py-GC-MS systems in the world. The system consists of state-of-the-art customized pyrolysis equipment that provides accurate temperature and heating-rate control and is stable with a variety of non conventional derivative reagents, a conventional high-end chromatographic system, and both mass spectrometric and matrix isolation Fourier Transformation IR detection for analysis and identification of individual compounds. This combination of instrumentation is the only system of its type in existence. Results of these analyses are illustrated in Figures 5 and 6 below. These figures illustrate the overall distribution of all products and the distribution of straight chain aliphatic materials in the total pyrolysis oil.

The pyrolysis oils generated from both samples are composed primarily straight chain aliphatic materials and light (single ring) aromatic species. Minor branched aliphatics, including phytane, are also present, but are much less significant overall than straight chain materials. Oxygenated products are not significant, although some evidence for aliphatic carboxylic acids was observed. These data are fairly typical of Py-GC-MS data for algal derived kerogens.

Overall, these data suggest that concentration of the kerogen by removal of the majority of the mineral matter from the comminuted shale does not significantly affect the gross nature or “quality” of the shale oil produced by conventional pyrolysis. Only minor quantitative differences were observed between the pyrolysis products derived from these samples. That is, the nature of the products observed is identical in both samples, but minor differences in the relative distributions of individual compounds are observed.

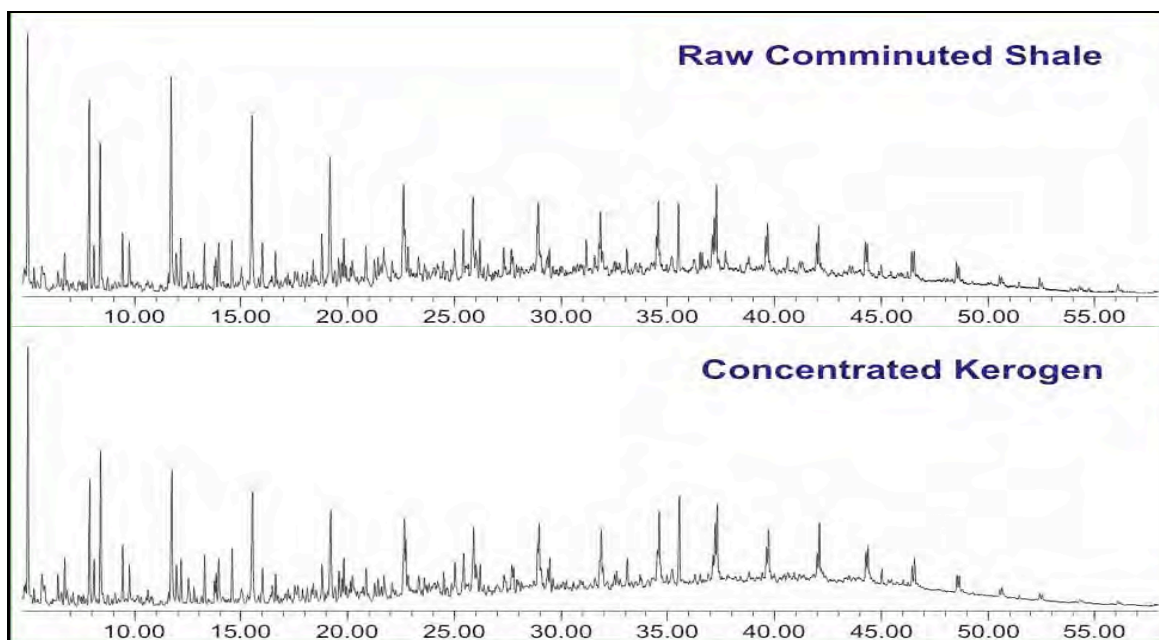


Figure 5. Total Ion Chromatograms for pyrolysis products of unseparated and Pulsewave-concentrated oil shale kerogen. Plots are detector response (Y axis) vs. time (x axis). Peaks indicate the presence of discrete compounds, which can be identified on the basis of their individual mass spectra.

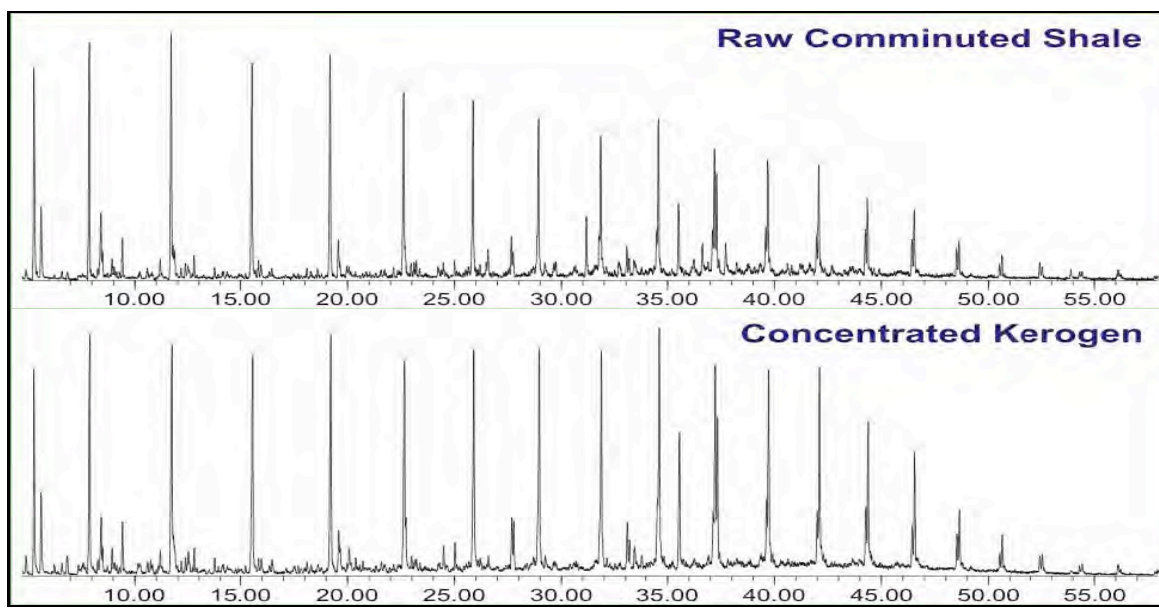


Figure 6. Distribution of n-alkyl products ($m/z=99+m/z=97$) observed in pyrolysis products of unseparated and Pulsewave-concentrated oil shale kerogen. Data are a subset of the data illustrated in Figure 5.

Material Balance Fischer Assay Experiments

After the raw oil shale ore had been micronized by the Pulsewave process and the organic separated from the mineral matrix, the samples of initial kerogen concentrate and highly purified kerogen concentrate were sent to Western Research for Fischer Assay analysis. These material balance Fischer Assay experiments were conducted in retorts patterned after the Lawrence Livermore material balance Fischer Assay retorts and the procedure used was that defined by Lawrence Livermore National Laboratory (Singleton et. al. 1982). The Lawrence Livermore design was selected over the Bureau of Mines Fischer Assay retort because the former design allows more efficient collection of the oil and shows a higher oil yield.

The retorting experiments were conducted by placing a known mass of the oil shale sample in the retort, sealing the retort, purging it with nitrogen and checking for leaks. The loaded retort was heated under an autogenous atmosphere from ambient temperature to 500°C at a rate of 12°C/minute and allowed to soak at 500°C for 30 minutes. The shale oil was condensed and collected in a cold finger submersed in an ice bath. The pressure rise of the system was measured and recorded and the gas production calculated. A sample of the produced gas was analyzed for permanent gases, hydrocarbon components and hydrogen sulfide using a Hewlett Packard 5840 gas chromatograph equipped with a thermal conductivity detector.

After completion of each experiment, the liquid and solid products were collected and the recovered mass determined and used for the material balance calculation. Samples of the raw and retorted oil shale and the shale oils were submitted to Huffman Laboratories of Golden, Colorado for analysis. The shale oil samples were subjected to elemental analysis to include: carbon, hydrogen, nitrogen, sulfur, arsenic, iron and mercury. The raw and retorted oil shale samples were subjected to the same analysis plus analysis to determine carbonate carbon.

Table 1 provides the results from the material balance Fischer Assay. The results presented in the table include the mass of oil shale used for the experiment, the oil yield (gallons/ton), the mass of oil recovered, the mass of gas produced, the mass of retorted shale, the mass balance closure, and the density of the shale oil. The mass balance closures for the experiments range from 99.4 to 103.3%. These material balance closures are considered good except for the value of 103.3%. This value is higher than normally observed for this type of experiment and is believed to be due to experimental errors associated with the smaller mass of the kerogen concentrate used for the experiment.

The average oil yield for the raw processed oil shale is 32.1 gal/ton and compares favorably with the value of 32.3 gal/ton reported by Gerry Daub for the raw oil shale used for this study. The agreement of the oil yield values from two different laboratories provides a level of confidence in the methods used for the analyses.

Sample	Mass Sample Used for Fischer Assay (g)	Oil Yield (gal/ton)	Mass of Oil (g)	Mass of Gas (g)	Mass of Retorted Oil Shale (g)	Mass Balance (%)	Oil Density (g/cc)
Raw Processed Oil Shale	50.0	33.1	6.408	1.4	41.6	100.2	0.927
Raw Processed Oil Shale	50.0	31.0	6.048	1.5	41.7	100.3	0.936
Initial Sink Concentrate	50.0	21.2	4.183	1.5	42.8	99.4	0.944
Initial Sink Concentrate	50.0	20.4	4.032	1.1	43.7	100.1	0.947
Initial Kerogen Concentrate	10.0	58.8	2.295	0.6	7.0	101.2	0.935
Initial Kerogen Concentrate	10.0	63.5	2.508	0.6	7.1	103.3	0.946
Initial Kerogen Concentrate	20.0	58.7	4.610	1.0	14.1	100.5	0.941
Highly Purified Kerogen Concentrate	10.6	146.1	6.020	0.8	3.3	99.0	0.935
Highly Purified Kerogen Concentrate	10.0	152.1	5.910	0.9	3.0	100.5	0.935

Table 1. Results of material balance Fischer Assay of the oil shale samples.

The average oil yield for the sink concentrate and the initial kerogen concentrate are 20.8 and 60.3 gal/ton respectively. The material balance Fischer Assay of the kerogen concentrate was performed in triplicate. The first two analyses were conducted using 10 grams of the kerogen concentrate. The third experiment was conducted using 20 grams. The third experiment was performed using the larger mass of oil shale to minimize experimental errors associated with using a small mass of the kerogen concentrate, which produced one experiment with a material balance closure of 103.3%. If the experiment using 10 grams of kerogen concentrate that has a mass balance closure of 103.3% is removed from the calculation of the average oil yield, then the average oil yield for the kerogen concentrate is 58.8 gal/ton.

As compared to the oil yield for the processed oil shale (32.1 gal/ton), **the initial kerogen concentrate shows an increase in oil yield to 60.3 gal/ton and demonstrates beneficiation of the kerogen with the process.** However, the oil yield of the sink concentrate only decrease to 20.8 gal/ton and indicates there is a significant amount of kerogen remaining in the sink concentrate that does not report to the kerogen concentrate during the separation step of the process.

The oil yield for the two Fischer Assay experiments of the highly purified kerogen concentrate averaged **149.1 gal/ton. This is a significant increase as compared with either the processed oil shale (32.1 gal/ton) or the initial kerogen concentrate (60.3 gal/ton).** The sink concentrate obtained from generation of the highly purified kerogen

concentrate was not subjected to Fischer Assay analysis. Therefore, the yield of kerogen reporting to the highly purified kerogen concentrate has not been established.

Table 2 provides the composition of the gas produced during the material balance Fischer Assay experiments. These gas analyses are typical of the gas composition produced from Fischer Assay retorting of oil shale. Hydrogen is the most abundant species and methane is the most abundant hydrocarbon gas. Carbon dioxide is present in significant concentration as a result of decomposition of the carbonate minerals in the oil shale. The hydrogen sulfide concentration is low. There are no strong correlations between the gas composition and the processing to produce the sink and kerogen samples.

Species	Raw Processed Oil Shale	Raw Sink Concentrate	Raw Kerogen Concentrate	Highly Purified Kerogen Concentrate
Hydrogen	34.9	32.7	32.7	33.6
Methane	21.5	22.2	30.6	33.1
Carbon dioxide	20.9	21.5	29.7	25.8
Ethylene	2.4	2.3	1.0	1.0
Ethane	7.4	14.5	3.0	3.3
Hydrogen sulfide	0.1	0.2	0.1	0.1
Propylene	3.2	0.0	0.0	0.0
Propane	1.6	2.0	0.9	1.0
Carbon monoxide	2.7	0.0	0.0	0.0

Table 2. Composition of produced gases from Fischer Assay retorting of the oil shale samples.

Hydroretorting Experiments

Conversion of the kerogen concentrate to oil using classical thermal retorting processes, such as Fischer Assay, may not be the best technical option for processing the recovered kerogen because these technologies are designed to process materials with high mineral content. Since the kerogen concentrate is primarily the free organic material, hydroretorting may offer the opportunity to recover higher oil yields than would be expected from conventional retorting. This retorting approach has been shown to increase the oil yield and product quality for both eastern and western oil shales found in the United States (Feldkirchmer and Janka, 1979 and Dyni et. al., 1989).

Samples of the raw processed oil shale and the Pulsewave-produced kerogen concentrate were subjected to hydroretorting in a U-tube reactor system assembled for this study by Western Research Institute. The system is composed of the U-tube reactor formed from ¼-inch (id) stainless steel tubing, a condenser, a liquid product collection chamber and a backpressure regulator. The reactor was heated in a fluidized bed sand bath. The experiments were conducted by adding 2.5 to 5 grams of sample to the U-tube reactor,

attaching the reactor to the system, and hydrotreating the sample at 475°C for 30 minutes at a hydrogen pressure of 2000 psig using a flow rate of 100 cc/min. At the end of each experiment, the retorted shale and the liquid product were collected. The water was separated from the collected oil by centrifugation. The condenser and associated lines were washed with toluene until there was no color. The solvent was removed by rotary evaporation and the mass of shale oil in the lines was determined and added to the mass of condensate oil to obtain the total mass of liquid product. The oil yield was calculated based on the recovery of the available organic carbon in each sample.

The shale oil product collected as a condensate for the hydrotreating of the kerogen concentrate sample congealed at the ice bath temperatures used for product collection. When warmed to room temperature, the shale oil was fluid. This observation implies the oil recovered from hydrotreating the kerogen concentrate is composed of a higher concentration of high carbon number normal paraffins than the oil produced from hydrotreating the raw processed oil shale. Recovery of the solid material from the reactor showed the material was tightly compacted. As the material was removed from the inlet to the outlet of the reactor tube the material became progressively more oil wet, indicating retorting was not completed during the time frame of the experiment.

The results from the hydrotreating experiments are summarized in Table 3. The results presented in the table include: the mass of each sample used for the experiment, the mass of shale oil recovered, the mass of water separated from the oil and the mass of residual solids collected from the reactor. The yield of condensable oil calculated for hydrotreating the raw processed oil shale was 62.1% of the organic carbon content and the total gas production was 11.1% of the total mass of oil shale. The oil yield obtained for the raw kerogen concentrate was 88.5% of the available organic carbon and 14.5% reporting to the gaseous product.

	Raw Oil Processed Shale	Kerogen Concentrate
<u>Reactants</u>		
Mass Feedstock (g)	4.800	2.497
<u>Products</u>		
Mass Oil		
Mass Collected Oil (g)	0.521	0.632
Mass Water (g)	0.092	0.062
Mass Solids (g)	3.653	1.443
Total Products (g)	4.265	2.138
Loss to Gas (%)	11.1	14.5
Oil Yield (% organic carbon)	62.1	88.5

Table 3. The results from hydrotreating the raw processed oil shale and kerogen concentrate samples.

Heteroatom Analysis

The oils from retorting each of the oil shale materials was combined to produce a composite sample for each feedstock to ensure sufficient sample for the heteroatom analyses conducted by Huffman Laboratories of Golden, Colorado. Table 4 provides the elemental composition of the shale oils produced from the Fischer Assay retorting of the three samples. The carbon and hydrogen content of the oils is typical for shale oils and hence the H/C atomic ratio is also typical. There is no trend in the sulfur concentration as a function of the processing steps used to produce the oil shale feedstocks. A trend is noted in the nitrogen distribution. The nitrogen concentration is related to the oil yield of the oil shale. Samples with higher oil yield exhibit higher concentrations of nitrogen in the produced shale oil. Therefore, the shale oil produced from the kerogen concentrate has a higher concentration of nitrogen (2.11%) than the oil produced from the sink concentrate (1.69%), which is in line with data from previously reported studies that have shown the nitrogen in oil shale from the Mahogany zone is all organically bound. For this reason, the correlation of increasing nitrogen content in the produced oil with increased oil shale grade is expected.

Sample	Carbon (wt%)	Hydrogen (wt%)	Sulfur (wt%)	Nitrogen (wt%)	Arsenic (ppm)	Iron (ppm)	Mercury (ppm)
Shale Oil from Processed Oil Shale	81.74	11.60	0.81	1.89	13	35	0.08
Shale Oil from Sink Concentrate	84.04	11.48	0.54	1.69	13	28	0.08
Shale Oil from Kerogen Concentrate	83.46	10.90	0.64	2.11	8.2	41	0.07

Table 4. Elemental composition of shale oils produced by Fischer Assay retorting.

The values for arsenic and mercury are relatively constant among the three oil samples. There does not appear to be a clear trend with respect to the processing received by the different oil shale samples prior to retorting. There is a slight decrease in the arsenic concentration in the kerogen concentrate and a weak trend observed for iron. The iron concentration increases slightly with increased oil yield. The significance of this trend is not well understood. The results for arsenic, iron, and mercury do not show a significant change in distribution as a result of the processing and separation steps.

There is not a clear demonstration of the separation of the metal ions evaluated during this study. The failure to identify clear separation of these ions is due in part to the relatively high concentration of kerogen remaining in the sink concentrate. As mentioned above, the emphasis in these experiments was on the quality control of the float (kerogen) material as opposed to producing a clean sink fraction. Therefore, additional efforts are needed to optimize the separation step of the process in order to fully define the baseline and benefits of Pulsewave processing with regard to the heteroatom content of the processed material versus the raw oil shale.

Estimate of Technical and Economic Feasibility

This Phase 1 research effort has demonstrated that the Pulsewave process is effective in liberating kerogen from the mineral matrix in oil shale and in concentrating this kerogen. Table 5 below is an estimate of the kerogen beneficiation achieved in this Phase 1 research using the Pulsewave kerogen beneficiation process. The results of this Phase 1 research effort demonstrate both the technical feasibility of being able to separate the kerogen from the mineral matrix and that high Fischer Assay oil yields can be achieved from this resulting kerogen concentrate.

Sample	Sample Mass (g)	Calculated Mass Organic Carbon in Provided Samples (g)	Calculated Mass Kerogen in Provided Samples (g)	Estimated Percent of Kerogen in Provided Samples	Estimated Percent of Mineral in Provided Samples
Raw Processed Oil Shale	750	112.1	138.5	18	82
Raw Sink Concentrate	220	60.5	74.7	14	86
Raw Kerogen Concentrate	530	62.3	77.0	35	65
Highly Purified Kerogen Concentrate	25.6	15.9	19.7	77	23

Table 5. Estimate of the kerogen beneficiation from the PulseWave process.

Evaluation of the oil recovery data for the Fischer Assays and the hydroretorting experiments show that there was a significantly higher oil yield for the kerogen concentrate than for the raw processed oil shale. Furthermore, the results of the Pyrolysis-Gas Chromatographic-Mass Spectrometric Analysis indicate that shale oil produced from the Pulsewave-concentrated kerogen product would be chemically similar to those produced by conventional retort of the bulk raw oil shale. These results demonstrate that the kerogen concentrate produced by the Pulsewave technology is more amenable to processing than the raw oil shale and this implies that processing approaches that are more sophisticated than simple pyrolysis may be more beneficial for the kerogen concentrate.

Although not directly measured in this Phase 1 research, the environmental benefits of the pre-retort removal of the mineral matter from the desirable organic matter are obvious. If the kerogen and the mineral matter fractions of the oil shale were separated before the retorting process, the mineral matter fraction would not undergo expansion due to high heat (“popcorn” effect) and thus it could be returned *in total* to the site where it was originally mined with no need for an aboveground disposal site. This would obviously negate all of the adverse consequences of handling and disposing of retorted shale waste. Since the Pulsewave process does not alter the chemistry of the shale matrix, only the particle size, the process therefore does not mobilize toxic elements or compounds that are chemically bound and stable in the raw ore. Essentially, the

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Pulsewave-processed shale should be basically the same material as that which was present underground to begin with. Thus, retuning it to a surface or underground mine should introduce no hazard to the groundwater system.

Clearly, the Pulsewave kerogen liberation process has demonstrated that it is a viable alternative to conventional oil shale processing and retorting. It is Pulsewave's intention to further develop and refine this process and market it to companies involved in oil shale operations. Potential customers for the Pulsewave technology would most likely be the super-major oil companies that retain large blocks of domestic oil shale reserves; in the Piceance Creek Basin in western Colorado, site of the richest and most easily recoverable oil shale deposits, several of the large multi-national oil companies still own the mining rights to extensive oil shale deposits. From the mid-1980's through 2001 Exxon-Mobil, Phillips Petroleum, Unocal and other major companies applied for and received several patents for new oil shale recovery technologies. These facts indicate a commitment by major oil companies to exploiting these deposits under more favorable pricing conditions; Pulsewave, LLC would hope to facilitate any renewed period of industry oil shale activity by introducing the Pulsewave oil shale processing technology to industry.

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