

THE BENEFICIATION OF GREEN RIVER OIL SHALE BY PELLETIZATION

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BACKGROUND

Green River shale is a sedimentary, highly laminated, fine textured rock composed mainly of the minerals dolomite, calcite, quartz, feldspar, clay and frequently, pyrite. A minor portion, less than 50 percent by weight and averaging about 10 percent, consists of kerogen, a solid organic, highly cross-linked polymeric substance, polycyclic in nature, with an appreciable hetero-atom content. Oil shale, unlike tar sands and gilsonite, is largely insoluble in organic solvents. However, it exhibits a striking tendency to imbibe and swell in the presence of organic liquids. Kerogen can be converted by pyrolysis to liquid and gaseous fuels and to a carbonaceous residue.

The high mineral content of oil shale imposes a huge heat demand upon a thermal upgrading process and calls for very large processing facilities. A reduction in the mineral content of the feed by an ore beneficiation step can strongly influence the process economics and may also afford the ancillary advantage of a decreased volume of contaminated, possibly biologically harmful retort tailings. A process for the beneficiation of Green River shale was investigated which yields kerogen-enriched oleophilic pellets and a dispersion in water of most of the mineral matter. The study was restricted to two shale samples, one consisting of core material from the Marathon lease and another from the Dow-Colony surface lease.

There exist a number of familiar procedures for effecting mineral separations, including sink-float methods based on density differences and froth flotation based on wettability. Because of the tendency of kerogen to swell and soften in the presence of organic liquids and thus possibly to mobilize trapped mineral particles, and because most minerals are water-wetted and thus extractable with water, we investigated a liquid-liquid (oil-water) pelletization method.

Several related procedures for upgrading shales have been described in the literature. Generally these were developed as an adjunct to chemical analysis of kerogen - to reduce interference by minerals and to avoid the risk of oxidation of the organic matter by severe chemical deashing.

A South African shale, Torbanite,⁽¹⁾ was ground with water in a porcelain ball mill. Oil (unspecified) was added in sufficient quantity to form a paste with the organic-rich fraction and grinding was continued. Mineral matter became suspended in the aqueous phase and this was discarded. The oily paste was solvent washed, dried and analyzed. The ash content was reduced from an original value of less than 40 percent to a value of about 10 percent.

A new Brunswick oil shale containing 58 percent mineral matter⁽²⁾ was processed in a similar way except that it was preground in a heavy gas-oil prior to the introduction of water. Following a 16-hour grinding period, the dried, enriched material had a mineral content of 34 percent.

Green River oil shale⁽³⁾ was treated with 5 percent acetic acid to remove carbonate minerals prior to grinding in a water, n-octane system. The aqueous mineral suspension was removed and replaced repeatedly with fresh water until no mineral matter was observable in the water. Analysis of the residue indicated that the mineral content was reduced from an initial 75 percent to 16 percent.

These procedures resemble the process for coal purification described in 1922 by W. E. Trent.⁽⁴⁾ It comprised fine grinding of coal to a 100/200 mesh size, sufficient to detach the mineral particles from the coal, then agitating with an organic, water insoluble liquid possessing a "selective affinity" for the coal. The process produced an "amalgam" of coal and organic liquid and rejected the inorganic gangue as aqueous slurry.

Recently, similar methods have been applied to the separation of tar from Alberta tar sands.⁽⁵⁾

EXPERIMENTAL

Procedure

The laboratory work described here was performed with two shale samples; one consisted of material from cores taken at a depth of 1830-1860 feet from the Marathon lease and the second in the form of rock fragments from the Colony mine (Dow property).

For the beneficiation we used a porcelain ball mill, the 5.5 gallon size with a 1.5-inch type grinding medium (Burundum of cylindrical form). The mill was charged with 10 pounds of grinding medium, 400-800 ml of water, 100-200 grams of shale (pulverized earlier to pass through a 100 mesh screen) and 50-100 cc of organic liquid binding agent (heptane). The mill was rotated for an hour. Typically, after about 10 minutes of operation, a kerogen-enriched fraction in the form of discrete flakes or pellets began to separate. Depending on the density of the binding agent and the degree of beneficiation, these would either float or sink in the aqueous suspension of gangue. After a one-hour milling cycle, the aqueous gangue dispersion was removed and replaced with fresh water. A small sample, 0.2-0.3 grams, of the enriched pellets was recovered for analysis and the milling operation repeated for as many cycles as deemed necessary. Both gangue and kerogen-enriched pellets were dried under vacuum at 70-80°C (see Plate I). The size of the enriched pellets is a function of the quantity of added organic binding agent. An insufficient quantity of binding agent yields pellets too small for easy separation from the gangue suspension by means of coarse sieves. An excess of binder results in the formation of a voluminous, soft kerogen paste which entrains gangue. The optimum condition described above yields pellets roughly 1 cm in diameter. The kerogen content was determined as weight loss by plasma ashing. (We used two plasma ashing devices: International Plasma Corporation, Model 1003B-248AN and LFE Corporation, Low Temperatures Asher, No. LTA-600.) Since the plasma combustion temperature does not exceed 50°C we avoid the mineral decomposition (especially carbonates) encountered during high temperature combustion.

Results

The results of a typical beneficiation experiment with Marathon lease material is shown in Figure 1. This entailed four one-hour milling cycles, the aqueous mineral dispersion being removed and replaced with fresh water after each cycle. Kerogen contents for both the organic-rich pellets (oleophilic) and the water dispersible mineral gangue (hydrophilic) are shown. The Figure also shows the results of two single cycle experiments.

The Marathon sample was obtained from a depth of more than 1800 feet. Since an ore beneficiation step would be more appropriate for a minable, shallow formation, we also tested samples from the Dow-Colony (Parachute Creek) mine. Starting with particles in the 8 to 10 sieve size range, the material was milled in water until 90 percent passed through a 100 mesh screen. Organic binder was added to the aqueous slurry and the process was continued as described above. Results of duplicate experiments are shown in Figure 2. The beneficiation obtained with this Dow-Colony shale is less favorable than that with Marathon lease material.

Particle Size of Shale Minerals

Analysis of oil shale surfaces by the scanning electron microscope prior to and following low temperature ashing reveals that the mineral matter occurs in the form of fine, discrete particles within a continuous kerogen matrix.

Figure 3 shows size distributions of inorganic mineral particles obtained by low temperature ashing of unprocessed oil shales. These minerals have mean particle diameters (50 percent frequency level) of 5-6 microns.

Minerals Distribution and Beneficiation

X-ray diffraction analysis of the products of the beneficiation of Dow-Colony shale is shown in Table 1. It is clear that the oleophilic extract (pellets) retains or concentrates the carbonates (dolomite, calcite, aragonite), particularly the dolomite. The hydrophilic gangue consists mainly of feldspar and quartz. Since silica, silicates and carbonates, in a clean condition, are water wetted the above results would indicate that the beneficiation procedure renders at least a portion of the carbonates oil-wet. The mechanism for the wettability reversal of the carbonate may reside in the adsorption, by the carbonate minerals, of certain carboxylic constituents of the shale - the bitumens. Bitumens are a solvent-extractable high molecular weight component of oil shale. They are rich in carboxylic functional groups - containing about 35 percent of fatty acids, resinous acids, polymer acids and benzenoid acids(6) (see below). Their dissolution in the added organic binder would make them accessible to the carbonates. Carboxylic acids are the most commonly utilized "collectors" for carbonate minerals in froth flotation processes. They adsorb strongly and decrease the water wettability of calcium carbonate thus facilitating its separation from a hydrophilic gangue with the gas phase. Similarly, in the pelletization process, the action of the adsorbed bitumen constituents on the carbonate mineral particles renders them largely inseparable from the oleophilic kerogen. Where pyrite is present, one would expect that, due to its inherent oil wettability, it too would accumulate in the oleophilic pellets.

Determination of Bitumens

Samples of pulverized Dow-Colony oil shale were extracted both at room temperature and by Soxhlet refluxing with n-heptane and with toluene. Solvent was stripped from the extract under vacuum and the acid numbers of the tar-like residual bitumens were determined. Results for duplicate samples are shown in Table 2. We note that significant quantities of carboxylic acids are indeed extracted.

Table 1
MINERAL DISTRIBUTION FOLLOWING BENEFICIATION STEPS
DOW-COLONY SAMPLE
(Estimated Weight Percent in Crystalline
Portion - X-ray Diffraction)

	Untreated	Kerogen Extract (Oleophilic Pellets)	Gangue (Hydrophilic)
Calcite	10	10	5
Dolomite	65	83	20
Aragonite	5	5	-
Quartz	10	1	20
Feldspar	10	1	52
Dawsonite	-	-	3

Table 2
EXTRACTION OF BITUMEN FROM DOW-COLONY SHALE

Solvent	Bitumen Recovered % of Shale	Acid Number, MgKOH/gram
Toluene, Room Temp.	0.7	9.2, 9.5
Heptane, Room Temp.	0.9	3.6, 2.6
Toluene, Soxhlet	1.5	12.7, 18.8
Heptane, Soxhlet	1.6	19.2, 13.1

Mineral Contents of Marathon and Dow-Colony Lease Shales

In view of the above, one would anticipate difficulty in upgrading by this method, shales containing large quantities of carbonate mineral (dolomite, calcite, aragonite) and/or pyrite (FeS₂). In Table 3 we show the mineral distributions, determined by X-ray diffraction, for samples from the Marathon and Dow-Colony leases. The sums of the weights percent of the carbonates and pyrites in the Marathon samples lie between 30 and 35 percent whereas in the Dow-Colony samples, they lie between 47 and 80 percent. This supports the finding that superior upgrading is accomplished with the Marathon lease shale.

Table 3
MINERAL CONSTITUENTS OF MARATHON LEASE
AND DOW-COLONY MINE SHALE SAMPLES
(Estimated Weight Percent in Crystalline Portion)

	Marathon Lease		Dow-Colony		
Calcite	-	-	10	10	10
Dolomite	35	30	27	40	65
Aragonite	-	-	-	-	5
Pyrite	-	-	10	10	-
Quartz	15	20	12	10	10
Feldspar	15	20	25	15	10
Analcite	-	-	3	10	-
Dawsonite	20	15	5	-	-
Nahcolite	10	10	-	-	-
Clay	-	-	5	-	-
Unidentified	5	5	3	5	-

THE MECHANISM OF BENEFICIATION

Kerogen, as noted earlier, is a polymeric substance that can imbibe large quantities of organic liquids. This is accompanied by swelling and a slight softening of the matrix. Such gross swelling, as well as exfoliation, under the influence of various organic liquids can be observed visually with raw oil shale. We suggest that this swelling and softening of the kerogen is a key element in the beneficiation scheme described here. During the milling process the inorganic mineral particles are not ejected via a comminution of a brittle matrix (chopped out of the

kerogen, so to speak) but are instead worked out of the softened kerogen mass by a deforming and kneading process. The kerogen particles introduced initially become fused rather than bridged by pendular rings of binding agent as in coal pelletization. After drying, the gangue disintegrates into its component small particles but the kerogen pellets dry to a hard brittle mass exhibiting no evidence of the presence of discrete small particles.

Chemical Additives

In an effort to improve the ore upgrading process - to increase the level of carbonate minerals rejection - we studied the effect of chemical additives.

1. Flotation depressants: It was indicated earlier that the release of oil soluble carboxylic acids may be responsible for the retention of carbonates by the kerogen-organic binder pellets. Chemical flotation depressants are sometimes applied to overcome the collecting tendency of fatty acids and thus to increase the water wettability of the carbonate particles.⁽⁷⁾ The introduction of such flotation depressants, including sodium oxalate, chromium nitrate, copper nitrate, ferric sulfate and aluminum nitrate failed to improve the beneficiation process described here.

2. Sodium bicarbonate: Marathon lease samples which exhibit high levels of beneficiation also contain nahcolite (NaHCO_3). The beneficiation process thus operates at an elevated pH. To investigate the effect of high pH on Dow-Colony shale, experiments were performed with added sodium bicarbonate and sodium hydroxide. No improvement in kerogen enrichment was obtained.

3. Surfactants and dispersants: A selection of typical commercial surface active agents, both anionic and nonionic, were tested to determine whether beneficial interfacial or wetting conditions could be obtained. These agents included:

Triton X-100 (nonionic, ethoxylated octyl phenol)
Phuronic F68 (nonionic, ethylene oxide - propylene oxide
condensation product)
NEODOL[®] 25-7, 25-9, 25-30, 25-45 (nonionic, linear primary
alcohol ethoxylates)
NEODOL[®] 25-3S (anionic, sulfated form of NEODOL[®] 25-3).

Several dispersants too were checked, including:

Marasperse N22 and CB (lignosulfonates)
Guartec (industrial grade guar gum)

This approach also was unrewarding.

Product Assay

Fischer Assays were performed with samples of Marathon lease material, with both raw shale and with the beneficiated pellets. Spent shale (char) from the assay was subjected to heat value analysis (Btu content). Results are shown in Table 5.

Table 5
FISCHER ASSAYS
MARATHON LEASE SHALE

	Raw Shale	Beneficiated Product
Oil, gal/ton	44.3	154.2
Oil, % by weight	16.6	57.4
Water, gal/ton	6.4	2.5
Water, % by weight	2.7	1.0
Spent Shale (char), % by weight	74.4	33.0
Gas + Loss, % by weight	6.3	8.6
Btu/lb of char	693	5,352

DISCUSSION

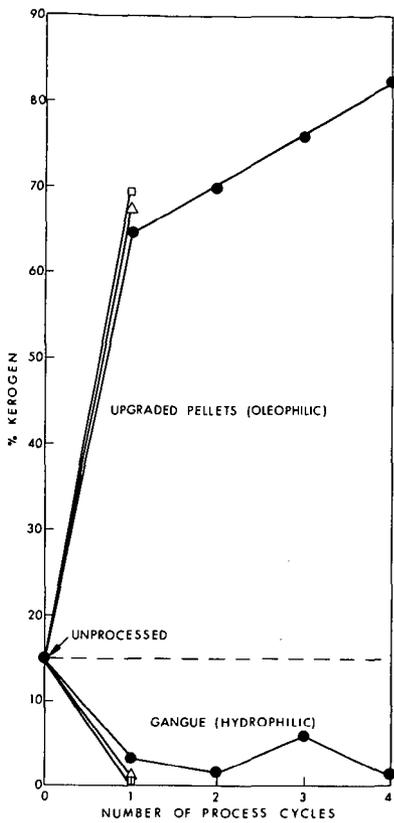
Two shale samples were studied - one from the Marathon lease (cores) and the other from the Dow-Colony mine. Clearly, the latter is the more relevant to an ore beneficiation process. The result obtained with this material is less favorable than that achieved with the Marathon cores. Still the increase in kerogen content from a value of 21 percent for the raw material to 62 percent for the upgraded pellets represents a rejection of 83 percent of the mineral matter (neglecting a small loss of kerogen to the gangue). This can mean a sizable decrease in the heat demand of a retorting process. There may also be an ancillary environmental benefit. The rejected inorganic gangue contains only a small residue of kerogen, in unmodified form. This is no more damaging chemically than the original oil shale. The residue, char, from the retorting of the enriched pellets has a sufficiently high Btu content (Table 5) and low minerals content to be useful as a process fuel. Its ash would be free of organic matter and low in silica dust. Thus the returns to the environment from a process involving ore beneficiation, retorting of the kerogen-enriched pellets and char burning would be free of organic pyrolysis products.

The laboratory experiments were performed batchwise in small ball mills. A larger scale operation would call for continuous processing, probably in a rod mill. At present the procedure does not appear to be economically feasible. A major cost is that of the initial comminution of the shale. Because the material possesses a very unfavorable grindability work index, this step requires an excessive power outlay. Furthermore, the process calls for a large quantity of organic binding agent, the recovery of which too is very costly. Whether means can be devised for improving the economics must await further investigation.

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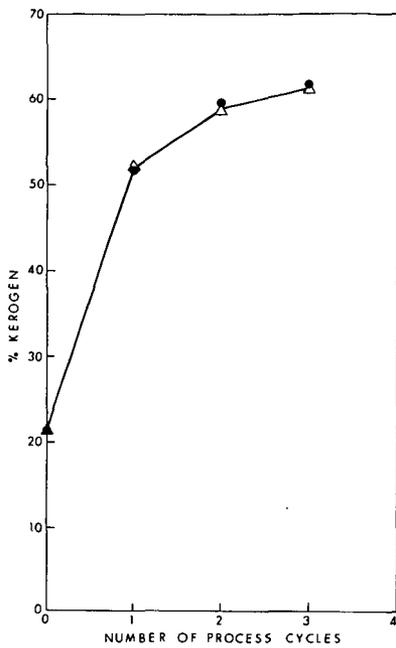
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Fig. 1 The recovery of Marathon Lease kerogen as a function of number of beneficiation cycles. (Kerogen determined as weight loss on low temperature ashing)



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Fig. 2 The beneficiation of Dow-Colony shale.

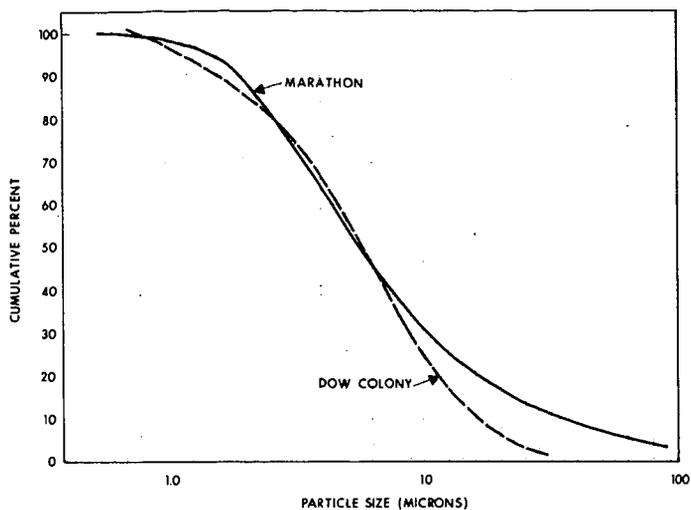


Fig. 3 Cumulative particle size distribution of the mineral constituents of oil shales (from low temperature ashing). Particle size by Coulter counter.

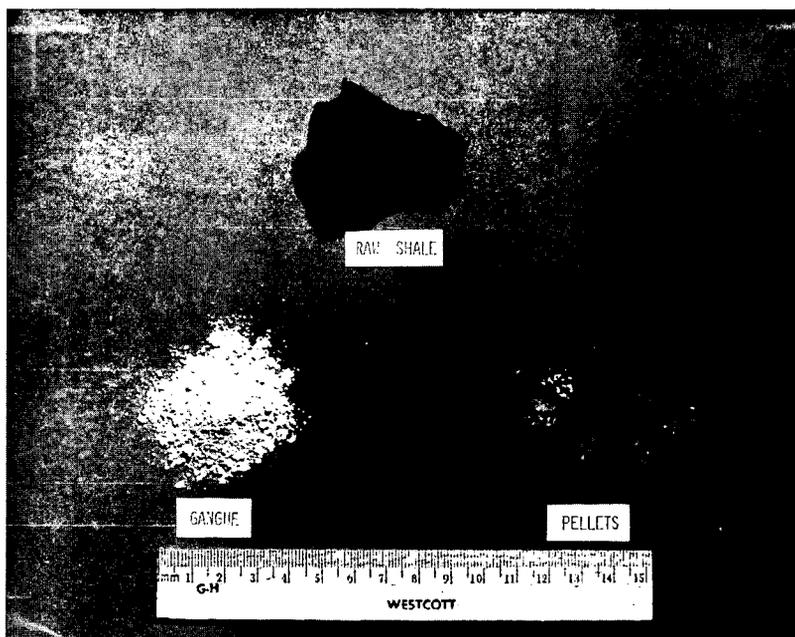


PLATE 1

The Beneficiation Products of Green River Oil Shale