

## BENEFICIATION OF WATER-SENSITIVE EASTERN OIL SHALES

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### INTRODUCTION

Development of the eastern oil shale deposits of the US has been considered of secondary importance when compared with the development of the western shale. The usual reason given for this assessment is the low oil yield of the eastern shales. For example, a typical eastern shale containing 12% organic carbon yields about 12-14 gallons per ton (G/T); in comparison a western shale with the same organic carbon percent yields about 28 G/T. Thus for eastern shales to be considered as an attractive alternative source of liquid fuels a higher yield of oil has to be achieved.

Techniques are known by which an oil shale may be beneficiated so as to increase the amount of oil that is generated by retorting. One such technique described for eastern shales is froth flotation.

Beneficiation by grinding and froth flotation is a well established procedure in the mineral dressing industry. Large scale ore beneficiation facilities have been developed and are commercially applied.

In froth flotation advantage is taken of the difference between the specific gravity of the organic and inorganic components in the shale. Thus if the organic-rich portion of the shale which has a lower density than the inorganic portion could be disengaged from the organic-poor portion, the two portions will exhibit a specific gravity difference that may allow for their separation by flotation.

Unlike western shale which has essentially a layered structure of magnesium and calcium marlstones interspaced with organic-rich kerogen, eastern shale has essentially a matrix structure. This matrix is typically composed of particles of quartzite, clay, organic-rich kerogen and pyrite. To achieve the separation of the organic-rich from the organic-poor components of an eastern shale, it is thus necessary to reduce the shale matrix to its components which could then be separated by flotation.

For eastern shales, size reduction by grinding (1) can bring about the separation of the desirable organic from the inorganic components of the shale. This has also been achieved by persistent milling in a rod mill (1), ball mill, or a rod and ball mill (2,3). It has also been reported (1-6) that the finer the particles, the more successful is the beneficiation. The grinding or milling process is a major contributor to the

cost of beneficiation. It has been estimated (7) that 45% of the cost of beneficiation accrues to the grinding step with energy the major component.

Although water has been used for dust control and lubrication during grinding, it has not been used as the main medium for size reduction. Earlier work at Mobil (8) has shown that when a water slurry of an eastern shale is stirred, the shale particles crumble and lose their shape and size. This suggested the use of agitated water slurries of the shale as a means of size reduction and flotation.

## EXPERIMENTAL

### Apparatus

The beneficiation apparatus consisted of two components, a flotation cell and a circulating pump. Figure 1 depicts the flotation cell used. A TEEL pump manufactured by Dayton Electric Co., Model IP 810, equipped with 2 1/4 inch diameter flexible impeller driven by a 1/4 HP electric motor was used to circulate the shale and reduce its size. The outlet of the flotation cell was attached to the inlet of the impeller pump and the pump outlet was attached to the inlet of the flotation cell. A 1/2 inch 25 micron frit was used to support the shale slurry and to supply the frothing gas.

A DuPont thermogravimetric analyzer (TGA) was used to determine the weight loss; heat up rate was 10°C/min. Air or argon was used to sweep the volatiles during thermal decomposition of the kerogen.

### Procedure

In a typical experiment about 750ml of water was placed in the flotation cell and the pump started. About 50g of 8-mesh shale was then added to the circulating water and the slurry was allowed to circulate for 30-60 minutes.

About 0.1g of sodium dodecylbenzenesulfonate was then added to the slurry and the mixture circulated for 10 minutes. Flotation gas was then turned on to generate a foam with small bubbles and the flow adjusted so as to achieve a steady flow of foam at the foam outlet of the flotation cell.

Samples of the foam were collected at predetermined intervals. Each sample was filtered, Büchner, and the collected solid washed well, and dried to constant weight at room temperature at a pressure of about 0.05 mm Hg, weighed and analyzed.

In TG analyses care was taken to use an amount of shale that gave a uniform layer of shale on the TGA balance. Usually a 20-25 mg sample was satisfactory.

## RESULTS AND DISCUSSION

### Shale Particle Size Reduction

Earlier work on eastern shale at Mobil (8) has shown that some shales are friable when wet. It was observed, for example,

that when a slurry of 8-mesh New Albany shale was stirred gently, most of the shale became smaller than the original 8-mesh size. It was clear that wet New Albany shales yield and crumble under the impact of the Teflon blade of a glass stirrer. This observation suggested to us the use of an impeller slurry pump as a means of size reduction. It was reasoned that when the impeller struck the wet shale particles, they would break down and crumble.

After several experiments with different impellers it was concluded that the impact of the impeller on the wet shale reduced the particle size of the shale but the particle size was not small enough to bring about flotation. However, when a slurry pump equipped with a flexible impeller was used, the shale size was sufficiently reduced for its flotation. This size reduction was brought about by the scraping action of the flexible impeller over the wet shale. As the impeller moved in its housing, the shale particles were trapped by the flexible vanes and scraped over the metal surface of the impeller housing; this scraping action brought about the size reduction.

### Shale Flotation

Several attempts were made to apply the sink/float procedure (9) for beneficiating the shale particles generated by the action of the impeller pump. The fine shale was mixed with brines of various densities and allowed to segregate into lighter and heavier portions. Brines containing calcium chloride or calcium bromide with densities in the range of 1.05-1.64 g/cc were used. In all sink/float attempts little or no beneficiation took place.

The same brines were also used as the liquid medium of the shale slurry and circulated by the impeller pump followed by flotation. Although size reduction was affected, little or no beneficiation took place. In one example a brine with a density of 1.105 g/cc produced a small fraction containing 41% more carbon than the raw shale; organic carbon was increased from 12.83% to 18.10% by weight.

After the unsuccessful experiments with the various brines a slurry composed of 50g, 8-mesh shale and 750 ml water containing 0.013% by weight (0.1g) sodium dodecylbenzenesulfonate was circulated and was successfully beneficiated. The shale used in all these studies was a well characterized New Albany shale containing little or no carbonate carbon. Table 1 presents the elemental analyses of the raw shale and shows the yields of products obtained in the Fischer assay and selected properties and elemental composition of the oil and spent shale. The carbon content of the oil represents a 33% conversion of the carbon of the raw shale to oil. This level of carbon conversion is typical of eastern shales (10) and serves to illustrate the need for beneficiation.

Table 2 shows the elemental analyses and amounts of the beneficiated fractions of the New Albany shale studied. About 17% by wt of the shale has over 32% by weight carbon, a 2.5 fold carbon beneficiation. This 17% fraction contains 45% of the total carbon contained in the 50g sample. About 5% of the

sample remained unground and essentially had the same composition as that of the raw shale. About 95% of the fractions collected by flotation passed a 200 mesh screen, however the fractions with the high carbon content had a "waxy" feel and were difficult to sieve. These particles stuck to the sieve opening and an accurate measure of their mesh size distribution could not be made. It is estimated that over 25% would pass a 325 mesh sieve.

The leanest fraction was a finely ground portion of the shale that remained in the flotation cell upon termination of the experiment and was separated from the 8-mesh residue by sieving. This finely ground residue passed a 200 mesh sieve and had a 3% by wt. carbon content.

#### Estimate of Oil Yield by TGA

Since these experiments were carried out on 50g samples of shale, Fischer assay (FA) yields could not be determined on any of the beneficiated shale fractions. Although all beneficiated fractions were analysed for carbon and hydrogen content, Table 2, it was considered necessary to estimate their oil yield potential.

It has been shown (11) that small samples, 1 or 2 mg, could be used in thermal decomposition studies for comparing the oil generating potential of shales. Also, thermogravimetric (TG) analysis techniques have been used to compare shales by determining relative weight loss profiles (12,13). Weight loss from three shales of known FA yield, including the shale used in this study, was determined by TGA, Table 3. The New Albany shales have similar weight loss in TGA and have FA yields consistent with such weight loss. Also the western shale which is known to produce more oil per percent organic carbon than the eastern shales shows the same trend in the TGA.

By combining elemental analyses of the beneficiated shale fractions with their TGA weight loss and using the data for shales with known FA yields an estimate of the FA yields of the fractions could be made, Table 4. The two fractions with the highest carbon contents also have the highest weight loss in argon. Weight loss in air was also determined, Table 5, and shows that the raw shale and the unground residue have the same weight loss. Considering the elemental composition and the TGA weight loss in argon of both samples, it was concluded that the unground residue is unbeneficiated shale. The recovered unground material was similar in appearance to the raw shale and crumbled when wet. It was reasoned that this material must have been trapped at the bottom of the flotation cell and was not carried into the pump housing where size reduction takes place.

TGA weight loss in air when compared to weight loss in argon is one measure of how well carbon conversion to oil takes place during thermal decomposition of a kerogen. A spent shale with a high char content will lose that char by oxidation when air is the sweep gas. A high char content is an indication of poor organic carbon conversion to oil. The beneficiated fractions do not generate char to the same extent as the raw shale. Whereas

the weight loss in argon of the raw shale is 36% of that in air, that of the beneficiated fractions is 65%. It is possible that the inorganic matrix, in the raw shale, especially the pyrite, contributes to the inefficient conversion of the kerogen to oil.

Although the sulfur content of the beneficiated shale increases relative to that of the raw shale, the ratio of carbon to sulfur is higher, 5.22 vs. 2.69, and that of sulfur to hydrogen is lower 2.30 vs 3.38. Pyrite in shales is a hydrogen consumer (14) and competes with carbon for the available hydrogen during thermal conversion of kerogen to product oil. Shales containing pyrite are known to produce significant amounts of hydrogen sulfide (15).

#### CONCLUSIONS

A new approach to size reduction followed by froth flotation to beneficiate water-sensitive eastern shales coupled with thermogravimetric analysis has been investigated. Organic-rich fractions with 3.5 times the oil generating capacity of the raw shale were prepared by this procedure. It is suggested that this procedure be used as a screening test for the applicability of flotation to the beneficiation of shales.

#### REFERENCES

1. H. S. Hanna and W. E. Lamont, AIChE 1982 Summer National Meeting, August 1982, Cleveland, Paper No. 35A.
2. U.S. D.O.E. Contract ET 78 Col 2628, December 31, 1982.
3. P. H. Fahstrom, 12th Oil Shale Symposium, Golden, Colorado, April 1979.
4. News Feature, Chemical Engineering, February 22, 1982, p. 37.
5. Synthetic Fuels Report, September 1982, p. 2-10.
6. Synthetic Fuels Report, June 1983, p. 2-28.
7. J. D. Miller, U.S. Patent No. 4,279,743, July 21, 1981.
8. C. A. Audeh, J. J. Dickert and P. E. Fowles, U.S. Patent 4,466,882, August 24, 1984.
9. C. J. Vadovic ACS Symposium Series #230, 1983, p. 385.
10. A. M. Rubel and T. T. Coburn, 1981 Eastern Oil Shale Symposium Proceedings, Lexington, Kentucky, November, 1984, p. 21.
11. J. W. Reasoner, L. Sturgeon, K. Naples and M. Margolis, 1981 Eastern Oil Shale Symposium Proceedings, Lexington, Kentucky, November, 1981, p. 11.
12. R. A. Addington, J. P. Humphrey, and E. M. Piper, 1983, IGT Symposium Synthetic Fuels from Oil Shale and Tar Sands, Louisville, Kentucky, May 17-19, 1983, P. 497.

13. M. Nakamura, R. Matsumotu, M. Sasaki, N. Yamagucki and N. Hirai, *ibid*, p. 167.
14. M. R. Abadi and R. W. Mickelson, AIChE 91st National Meeting, August, 1981, Detroit, Paper No. 16B.
15. C. A. Audeh, ACS, Division of Petroleum Chemistry, Inc. Preprints, Vol. 29, No. 1, p. 19.

Table I

Properties and Yields of Products Obtained by Fischer Assay Retorting a New Albany Raw Shale

Yields	
Oil, G/T	13.0
Oil, %wt	5.0
Spent Shale, %wt	90.2
Gas, liters/100 g	1.67
H <sub>2</sub> S, liters/100 g (%wt)	0.53(0.81)
Total Gas, liters/100 g	2.20
Water, %wt	1.9
Oil Properties	
Gravity, °API	22.6
Specific Gravity, 60/60°F	0.9182
Viscosity at 40°C, cS	8.94
Viscosity at 40°C, SUS	51.0
Carbon, %wt	85.26
Hydrogen, %wt	10.87
Nitrogen, %wt	1.13
Sulfur, %wt	1.62
Raw Shale Analysis, %wt	
Carbon	12.83
Hydrogen	1.41
Nitrogen	0.40
Sulfur	4.77
Ash	77.4
Spent Shale Analysis, %	
Carbon	8.05
Hydrogen	0.47
Nitrogen	0.34
Sulfur	3.78
Ash	86.6

Table II  
 Yields and Elemental Analyses of Beneficiated  
 New Albany Oil Shale Fractions

Fraction No	Weight	% Wt	C	H	N	S
Raw Shale	50	100	12.83	1.41	0.40	4.77
1	2.8	5.6	32.20	2.74	0.83	6.30
2	6.0	12.0	33.01	2.70	0.78	6.19
3	16.0	32.0	9.69	0.56	0.26	2.82
4	20.0	40.0	7.19	0.37	0.18	2.58
Residue (ground)	2.7	5.4	3.04	0.33	0.06	1.27
Unground Residue	2.6	5.2	11.85	0.83	0.34	5.48

Table III  
 Fischer Assay Yield and Thermogravimetric Weight Loss in  
 Argon in the 210-510°C Temperature Range of 3 Shales

Shale Sample	Carbon %wt	TGA Wt Loss % wt		Fischer Assay Oil Yield G/T
		Oil	Water	
Colorado	12.1	10.5	1.0	27.8
New Albany 1	11.8	4.3	2.5	11.1
New Albany 2	12.8	5.0	2.1	13.0

Table IV  
 Thermogravimetric Weight Loss in Argon in the 210-510°C  
 Temperature Range of Beneficiated  
 New Albany Oil Shale Fractions

<u>Fraction No</u>	<u>Loss, % Weight</u>	<u>G/T</u>
Raw Shale	6.5	13.0
1	22.0	45.0
2	22.0	45.0
3	4.0	8.0
4	3.0	6.0
Residue (ground)	1.0	-
Unground Residue	5.0	11.0

Table V

Thermogravimetric Weight Loss in Air of Beneficiated  
New Albany Oil Shale Fractions

<u>Fraction No</u>	<u>Loss, % Weight</u>
Raw Shale	18.3
1	34.0
2	34.0
3	5.0
4	5.0
Unground Residue	18.0

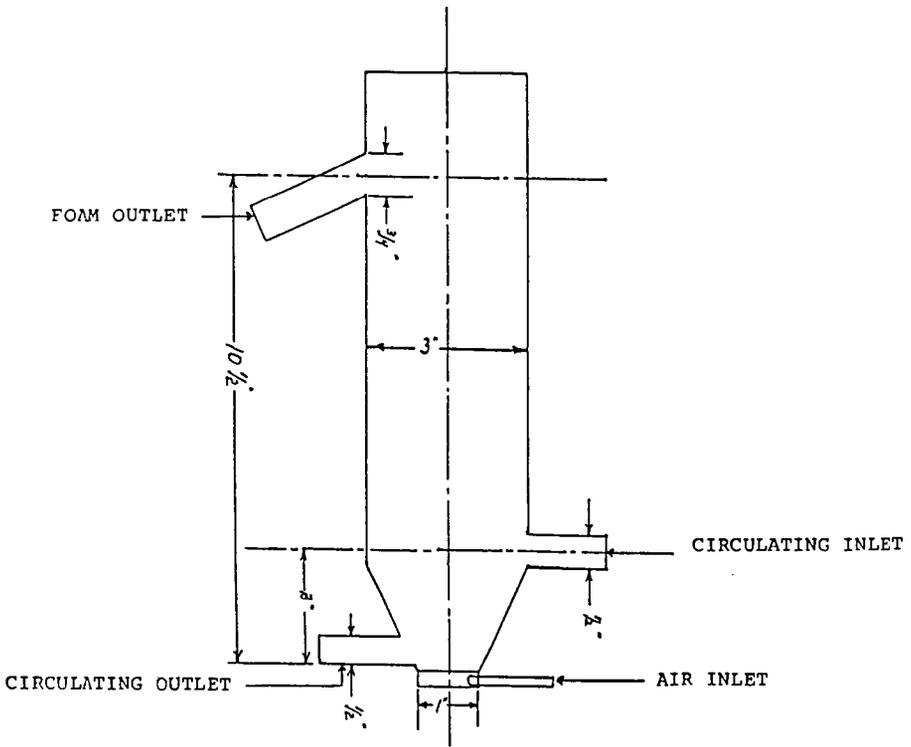


FIGURE 1

FLOTATION CELL