BENEFICIATION OF U.S. OIL SHALES BY FROTH FLOTATION

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ABSTRACT

A bench-scale study of the beneficiation of western and eastern oil shales was conducted using ball mill grinding and froth flotation techniques. The liberation of organic and inorganic particles required reducing the particles to about 10-20 μm. Ball mill grinding energies were estimated to be about 50 kwh/ton for the western "Anvil Points" shale (13.5 wt% organics, 24 GPT) and 30 kwh/ton for the eastern "Antrim" shale (8 wt% organics, 7 GPT) for reduction to 20 μm. Froth flotation can increase the organic content of Anvil Points shale to about 27 wt% (50 GPT) at about 80% recovery. Froth flotation of finely ground Antrim shale produced concentrates containing 21 wt% organics (23 GPT) with 90% recovery. Higher grades of concentrates at lower recoveries can be obtained with additional stages of grinding and froth flotation. The separation efficiencies for the Anvil Points and Antrim shales were found to be 52% and 60% at the optimum conditions.

INTRODUCTION

Beneficiation, or upgrading, or kerogen concentration of oil shales has been recently proposed by many investigators as a potential method of reducing the costs of retorting oil shale.[1,2] U.S. oil shales typically contain four to six times as much ash-forming minerals as they contain oil-forming kerogen. Hence a large amount of inorganic minerals also need to be heated along with the kerogen during retorting. Capital and operating costs associated with retorting can be reduced by using an oil shale feed containing higher ratio of kerogen-to-ash forming minerals. Selective mining of thin, high grade oil shale zones is expensive and may not be practical in large scale mining. Beneficiation methods can use low grade ores and can produce a consistent high grade material for retorting. Further, the inorganic mineral components rejected by the beneficiation methods can be disposed in a more environmentally acceptable manner than the ashes from the retorting step.

Froth flotation is an important and versatile mineral processing method in metallurgical industry for concentrating valuable minerals. It is being extensively used for upgrading sulfide ores of copper, lead, zinc, and molybdenum, and oxide ores of iron, and is also used in the separation of phosphates from carbonates. Modern froth flotation plants that can handle 25,000 to 100,000 tons per day are used in the copper industry.[3]

In the froth flotation process the ore is crushed and wet ground to a size where the valuable mineral is liberated as a discrete particle from the rest of the ore. The ground slurry of liberated particles in water is then subjected to agitation in a flotation cell with the injection of a constant swarm of bubbles. The minerals, whose surfaces are hydrophobic, attach themselves to the bubbles. The bubbles and attached minerals rise as a froth out of the flotation cell. The hydrophilic gangue minerals remain in the slurry. Kerogen, the valuable constituent of the oil shale, is relatively hydrophobic and can attach to air bubbles during froth flotation without addition of surface modifying chemical agents. However, bubble attachment can be enhanced by adding chemicals such as kerosene and diesel oils.

The application of froth flotation for upgrading the oil shale from Green River formation (Mahagony zone) was investigated by Fahlstrom[1] and by Tsai and Lumpkin.[4] Fahlstrom reported that this oil shale can be ground to below 20 μm (80% passing) with an energy input of 20-45 kwh/ton. The ground shale, containing 16.3 wt% organic, was upgraded by froth flotation to a concentrate containing 52-60 wt% at an organic recovery of 95%. No results were reported on the beneficiation of coarser particle sizes.

Tsai and Lumpkin studied the froth flotation of oil shale from Anvil Points and Logan Wash using particle sizes ranging from 1000 to 44 μm. The separation efficiency reached a maximum at particle sizes from 500 to 150 μm, and they found that the shale can be upgraded from 28 GPT to 42 GPT recovery of 75% (Logan Wash shale for 38 to 50 GPT; 80% organic recovery). Experiments with subsieve particles, if performed, were not reported by Tsai and Lumpkin.

The University of Alabama's Mineral Resource Institute investigated the froth flotation of eastern Devonian shales.[5] They reported that grinding the shale to a particle size of 10-30 μm and subsequent froth flotation upgraded the shale from 10 GPT to 24 GPT.

At SRI International we have been investigating the froth flotation of U.S. oil shales (both western and eastern) in a study funded by the U.S. Department of Energy. In this paper we report the results of using this technique on a western shale from the Green River formation (Anvil Points shale) and on an eastern Devonian shale from Michigan Antrim formation (Antrim shale).

EXPERIMENTAL METHODS AND PROCEDURE

The western oil shale used in this study was obtained from the Anvil Points stockpile. This "Anvil Points" shale had an organic content of 13.5 wt% (24 GPT). The ash-forming minerals consisted of carbonates (calcite and dolomites), feldspars, quartz, and clays. Table 1 summarizes the relevant characteristics of this shale.

The eastern Devonian shale used in this investigation was from the Michigan Antrim formation, and was obtained from National Gypsum Company, Alpena, MI. This "Antrim" shale had an organic content of 8 wt% (7 GPT). The inorganic minerals consisted of quartz, illite, kaolinite with small amounts of pyrite, and marcasite. Carbonate minerals such as calcite and dolomite were absent in this shale. Table 2 summarizes the relevant properties of this shale. About 2 tons of each shale was procured for this study.

About 200 kg of each shale was crushed in a jaw crusher followed by crushing in a hammermill to a size below 6 mm. The crushed shales were split into batches of ~4 kg each using a riffle splitter. The shales were then ground in a 14-inch diameter porcelain ball mill using 3.8-cm-diameter alumina balls as grinding medium. The amount of solids during grinding was kept at 60% by weight. Figure 1 illustrates the beneficiation procedure.

Preliminary froth flotation experiments were performed in a laboratory flotation cell (Booth type) of about 3-liter capacity. A No. 7 Denver flotation cell (28-liter capacity) was also used. Generally, the results from both cells were very similar except that the laboratory cells required a somewhat higher quantity of frother agent than the Denver cell.

The products (concentrate and tailings) from the flotation were filtered in a pressure filter and dried at 80°C. The organic content of the shales was determined by thermogravimetric (TGA) analysis at a heating rate of 10°C/min in air. A typical TGA curve is shown in Figure 2. The weight loss between 250°C and 600°C was taken to be equivalent to the organic content of the shale. Specimens were also sent out to analytical laboratories for Fisher assay analysis. A linear correlation was found between the organic content and the Fischer assay as shown in Figure 3, and the correlation for Anvil Points shale was found to be very similar to the one reported by Stanfield.[6]

RESULTS AND DISCUSSION

Grinding Studies

The ball mill grindability of the two oil shales was determined by the comparative method suggested by Berry and Bruce.[7] Dolomite mineral with a Bond work index of 11.3 was used as the reference ore. Dolomite and the oil shales were ground in the ball mill under identical conditions of ball load, percent solids, rotation speed, etc. By comparing the product distribution, we calculated the Bond work indices for the oil shales, and the indices were found to be 13.6 and 23 for the Antrim and Anvil Points shales respectively. Because the comparative method is reliable only for materials with similar work indices, the work index value is

Table 1

REVELENT CHARACTERISTICS OF WESTERN MAHOGANY SHALE
USED IN FROTH FLOTATION BENEFICIATION

Formation	Green River (Mahagony Zone)
Source	Anvil Points Stockpile
Density	2.15
Fischer assay (g cm^{-3})	24
Organic content (GPT)	13.5
Inorganic minerals (wt%)	86.5
Estimated mineral composition (wt%)	
Carbonates	48
Feldspars	21
Quartz	13
Clays, illites	13
Analcite	4
Pyrites	1

Table 2

RELEVANT CHARACTERISTICS OF EASTERN DEVONIAN SHALE
USED IN FROTH FLOTATION

Formation	Michigan Antrim
Source	National Gypsum Company, Alpene, MI
Density	2.2
Fischer assay (g cm^{-3})	7
Organic content (GPT)	8.0
Inorganic minerals (wt%)	92.0
Estimated mineral composition (wt%)	
Quartz	65
Illite	25
Kaolinite	8
Marcasite	2
Pyrite	1

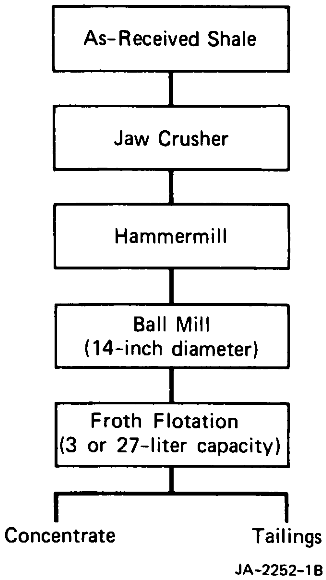

Figure 1. Oil Shale Beneficiation Procedure

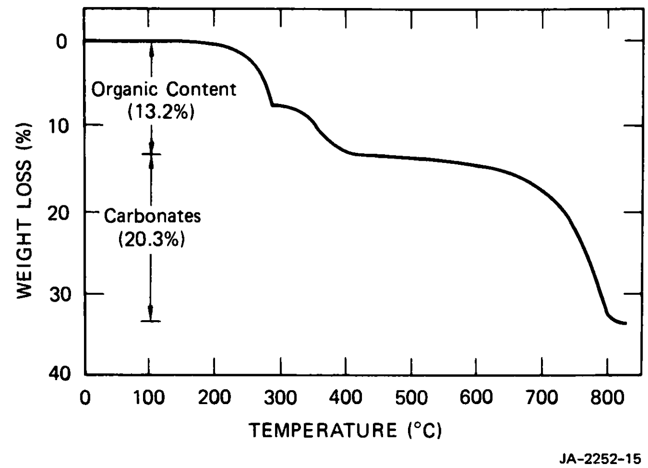

Figure 2. TGA Curve of Anvil Points Shale (heating rate of 10^{o}C/min)

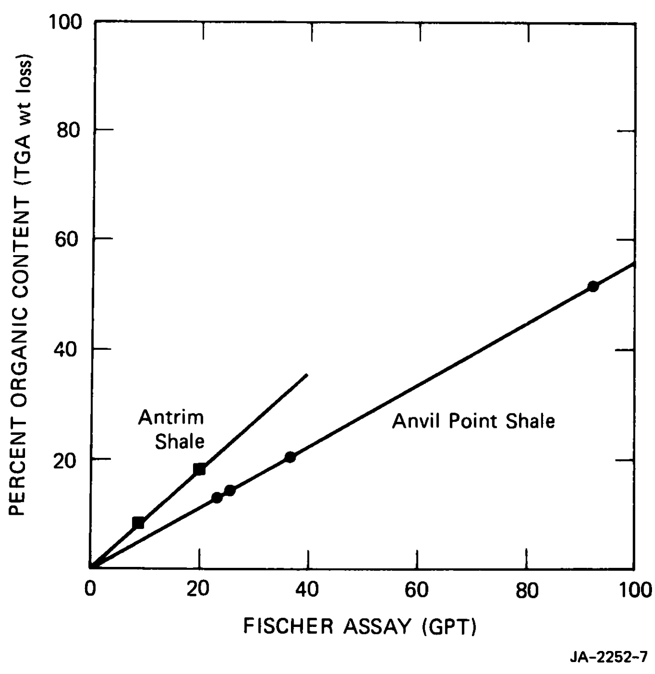

Figure 3. Correlation of Organic Content With Fischer Assay Yield

more reliable for Antrim shale than for the Anvil Points shale. However, the value for the Anvil Points shale is similar to the one* reported by Fahlstrom[1] for the shales from Green River formation. Figure 4 illustrates the input grinding energies calculated to obtain different particle sizes (80% passing size).

For the flotation studies, the oil shales were first crushed in a hammermill and then ground in the ball mill for various periods of time. The product particle size distribution was obtained by sieving and by Coulter counter technique (for subsieve ranges). About 35 and 85 minutes were required, respectively, to grind the Antrim and Anvil Points shales to a particle size (80% passing) below 270 mesh (53 μm). Figures 5 and 6 illustrate the subsieve particle size distribution of the two shales as a function of ball milling time.

Flotation Studies: Anvil Points Shale

Preliminary flotation studies were conducted with different frothers, such as pine oil, amyl alcohol, and N-octyl alcohol, and different collectors, such as kerosene and No. 2 diesel oil. No significant changes in either concentrate organic content or in organic recovery was found with these different reagents. Hence pine oil and kerosene were used as frother and collector respectively. No collector reagent was necessary, for particle sizes below 200 μm and above this size increasing quantities of kerosene (up to 6 lbs/ton) were necessary for flotation as the particle size was increased.

The froth flotation behavior of Anvil Points shale in the size range of 50 to 500 μm is illustrated in Figure 7. We define the efficiency of the flotation for separating organics and inorganics by the term

Separation efficiency =
organic recovery x mineral rejection/100.

Organic recovery is the percentage of organics in the feed shale recovered in the concentrate and mineral rejection is 100 minus the percentage of minerals in the feed shale appeared in the concentrate. Both the recovery of organic and the concentrate organic content are accounted for in the separation efficiency term.

As seen in Figure 7, the separation efficiency does not appear to be dependent on the particle size. This is not surprising because the particle size needed to liberate the inorganic mineral grains is in the range of 10-20 μm. The results observed in this study are similar to those reported by Tsai and Lumpkin, except that the flotation behavior of particles in the range of 50-100 μm is similar to the coarser particles; Tsai and Lumpkin observed a decrease in the separation efficiency in this particle size range.

The effect of ball milling time on the concentrate grade, organic recovery, and the separation efficiency is shown in Figure 8. The organic recovery increases sharply after about 2 hours of ball milling time. At this stage of grinding 90% of the ground particles were below 53 μm, and thus substantial liberation of inorganic minerals has been achieved. Between 2 and 8 hours of ball milling time the organic content of concentrate steadily increases, while the organic recovery remains constant. This is likely to be due to reduction in the mean particle size of the ground shale. Beyond 8 hours the mean particle size did not change significantly, and this is reflected in the flotation behavior.

The separation efficiency increases from about 27% after one hour of grinding to about 52% after 8 hours of grinding. The observed efficiency is considerably smaller than the ~80% observed by Fahlstrom.[1]

The difficulty in separating the organic kerogen from the inorganic minerals even after fine grinding is probably caused by the association between kerogen and the inorganic minerals. The x-ray diffraction spectra of the "as-received" oil shale, two concentrate grades and the flotation

*Fahlstrom did not report any specific values of Bond work indices for Green River oil shales. From the reported grinding energies versus product particle size, we estimate the Bond work index to be between 10 and 19.

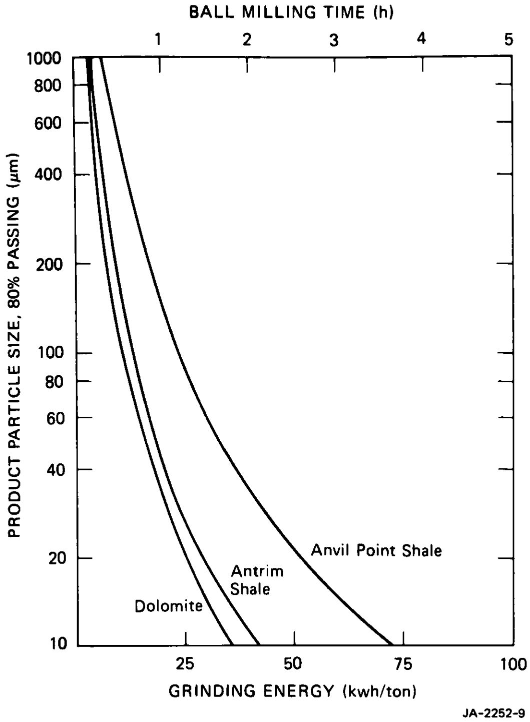

Figure 4. Ball Mill Product Size as a Function of Grinding Energy

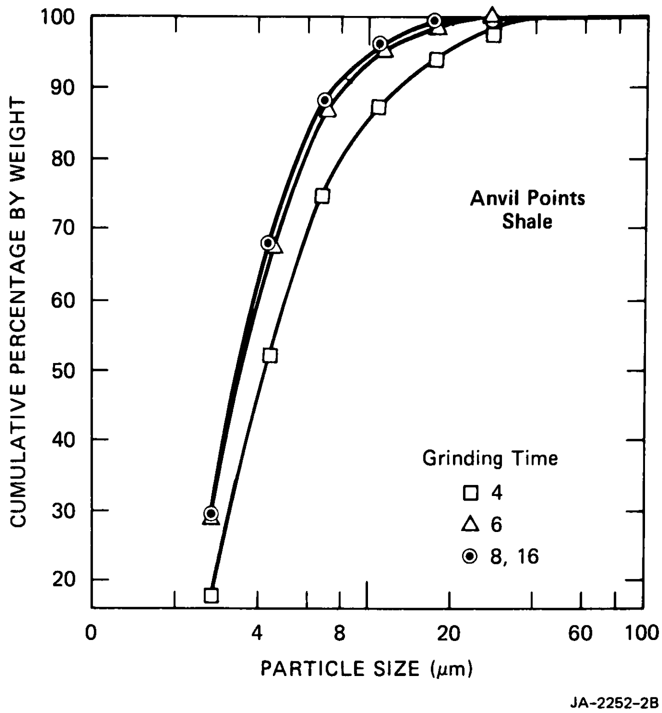

Figure 5. Particle Size Distribution as a Function of Grinding Time (Anvil Points Shale)

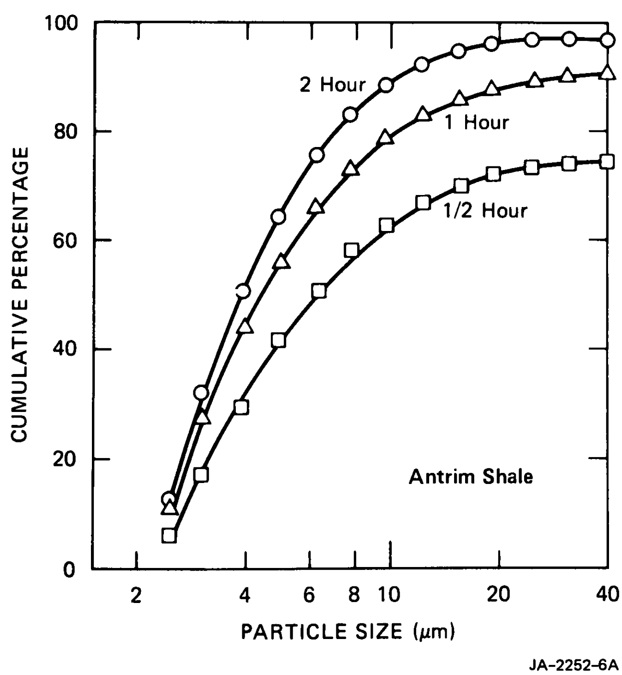

Figure 6. Particle Size Distribution as a Function of Grinding Time (Antrim Shale)

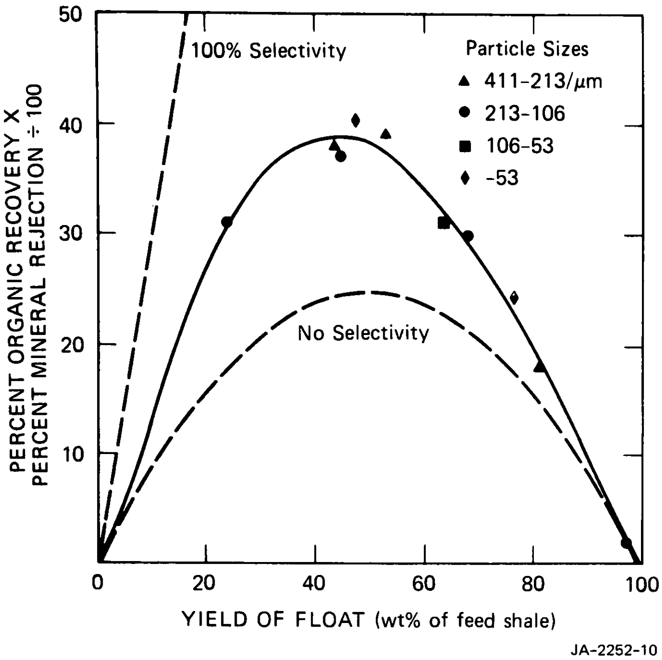

Figure 7. Effect of Particle Size on the Separation Efficiency During Flotation of Anvil Points Shale

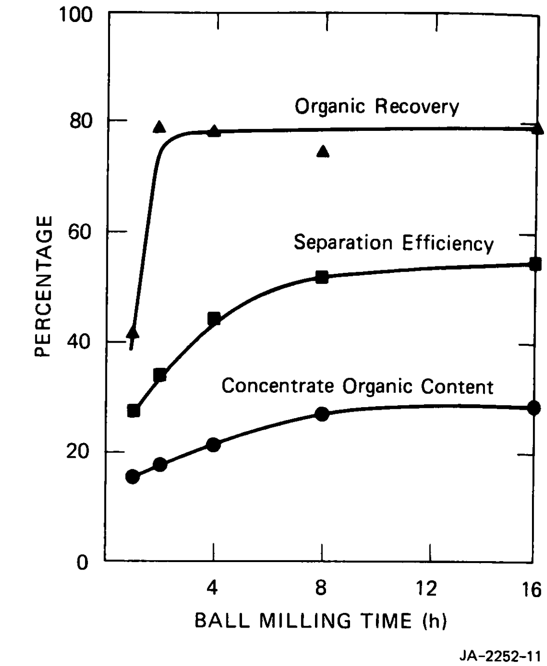

Figure 8. Effect of Grinding Time on the Flotation of Anvil Points Shale

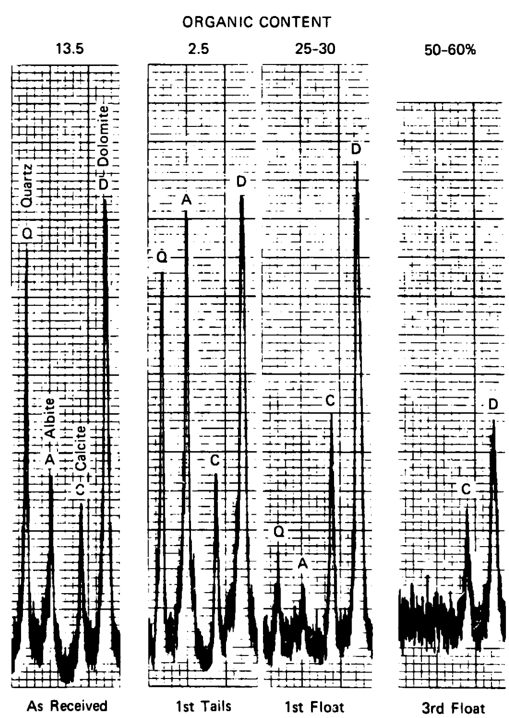

Figure 9. X-ray Diffraction Spectra of Anvil Points Shale (Feed, Concentrates and Tailings)

tailings are shown in Figure 9. The minerals quartz and albite are easily separated during the froth flotation. However calcite and dolomite tend to float with the kerogen.* This may be caused by either a strong bond between the kerogen and the carbonate minerals or caused by a coating of an organic compound over the carbonate minerals. Jeong and Kobylinski,[8] using spectroscopic (FTIR and NMR) studies, hypothesized that chemical bonding may be possible between carbonate minerals, olefins, and branched paraffins. Even a monolayer of a hydrophobic organic coating will cause the carbonates to attach themselves to the air bubbles.

It may also be possible that the organic phase in the oil shale is "smeared" over the carbonate minerals during grinding. This smearing effect is suggested by the observation that when the oil shale is ground with additional dolomite and then subjected to flotation, the concentrate contained a significant quantity of the added dolomite.**

The effect of temperature during flotation on the separation efficiency is shown in Figure 10. The recovery of organics increased at elevated temperatures. However the grade of the concentrate increased slightly from 5°C to 20°C, and above ambient temperature it steadily decreased.

Additional upgrading of kerogen is possible by grinding and flotation of the concentrate. Regrinding and reflotation of concentrate is not uncommon in minerals beneficiation. Table 3 lists the grade of the concentrate as a function of flotation stages. Between each stage the concentrate was ground in a 6-inch ball mill for 4 hours. The mean particle size did not change significantly during regrinding. At the end of four stages, the organic content of the final concentrate was increased by a factor of 3.5 over the original oil shale.

Flotation Studies: Michigan Antrim Shale

The Antrim shale used was low in organics (8 wt%) and contained no carbonates. Hence the flotation behavior can be expected to be significantly different from that of the Anvil Points shale.

The flotation characteristics of the Antrim shale as a function of ball mill grinding time are shown in Figure 11. The recovery of organics increased from 55% after 30 minutes of grinding to about 85% after 2 hours of grinding. The organic content slightly decreased with increasing grinding time. As we noted earlier, 80% of particles were below 53 μm after 35 minutes of grinding, and a 2-hour grind resulted in 80% of the particles below 7 μm. Hence it appears that liberation of organic particles requires reduction to about 10 μm.

Figure 12 illustrates the effect of solids concentration of the froth flotation feed on the separation efficiency. The grade of the concentrate decreases with increasing solids concentration, while the recovery of organics increases at high solids concentration. Hence separation efficiency is at a maximum around 6% solids concentration, although at 12% the separation efficiency is not reduced significantly.

As we noted earlier, different frothing agents such as pine oil, amyl alcohol, and n-octyl alcohol did not change the flotation behavior. The effect of pine oil (added in pounds per ton) on the grade of concentrate and the organic recovery is shown in Figure 13. Increasing the pine oil increases the recovery but decreases the organic content of the concentrate. The separation efficiency appears to be at maximum at about 1 lb/ton, even though at 0.5 lb/ton the separation efficiency is not significantly different from that at 1 lb/ton. However, at 2 lbs/ton the separation efficiency is significantly reduced.

As in the case of the Anvil Points shale, the organic content of the Antrim shale concentrate can be increased by regrinding and froth flotation as shown in Table 4. The grade of the concentrate increases from about 19% to 30% after one additional stage, and after the third stage it increases to 37%. At each stage of froth flotation, 80-90% of

* The calcite and dolomite minerals alone by themselves do not float under the conditions employed in this study.

** However when dolomite is added during flotation, the added dolomite remained in the tailings.

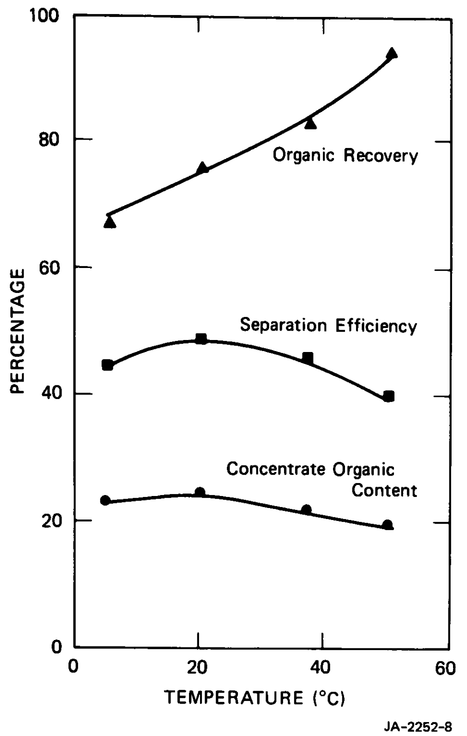

Figure 10. Effect of Temperature on the Flotation of Anvil Points Shale

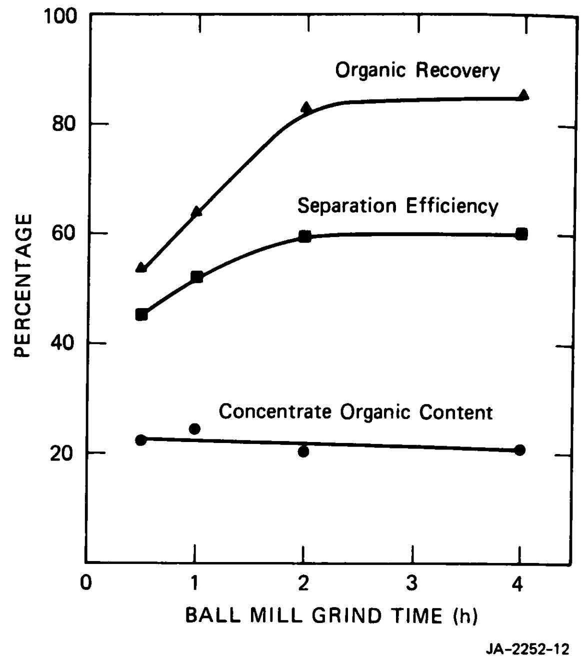

Figure 11. Effect of Grinding Time on the Flotation of Antrim Shale (Pine Oil Addition 1 lb/ton, 6% Solids in Flotation Feed)

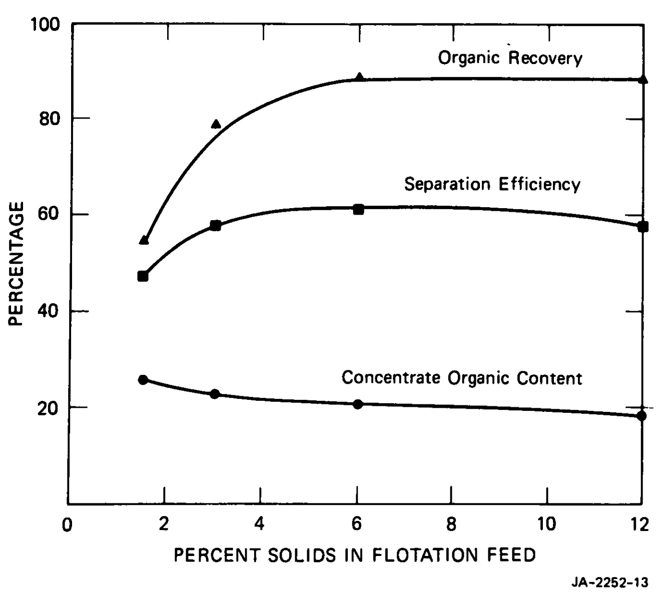

Figure 12. Effect of Percent Solids on Flotation of Antrim Shale (4-hr Grinding, 1 lb/ton Pine Oil Addition)

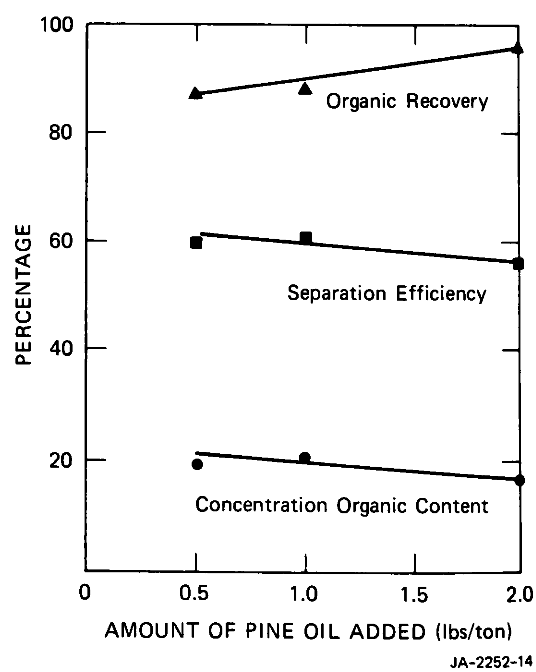

Figure 13. Effect of Frother Addition on the Flotation of Antrim Shale (4-hr Grinding, 6% Solids in Flotation Feed)

Table 3

CONCENTRATE GRADE AND KEROGEN RECOVERY AS A FUNCTION OF FLOTATION STAGES*

Stage Number	Median Particle Size (μm)	Percent Solids Grinding	Percent Solids Flotation	Grade of Concentrate (% Organics)	Cumulative Recovery (%)
1	15	63.5	11.0	23.8	89
2	12	48.0	5.3	35.0	65
3	12	29.0	5.3	42.0	54
4	15	20.0	3.7	48.4	47

*Percentage of organics of feed shale = 14.2.

Table 4

CONCENTRATE GRADE AND ORGANIC RECOVERY AS A FUNCTION OF FLOTATION STAGES

Stage Number	Median Particle Size (μm)	Percent Solids Grinding	Percent Solids Flotation	Grade of Concentrate (% Organics)	Cumulative Recovery (%)
1	4	63	5	19.0	82.1
2	4	20	2	30.0	74.2
3	4	15	2	37.1	66.8

*Percentage of organics of feed shale = 8.0.

organics are recovered; the overall recovery is at 67% after three stages of froth flotation. Although the organic content of the concentrate increases at each stage of regrinding and flotation, the separation efficiency does not change significantly.

CONCLUSIONS

Froth flotation techniques can be used to beneficiate oil shales from Green River formation (Anvil Points shale) and Michigan Antrim formation (Antrim shale). It is estimated that 50 and 30 kwh/ton of ball mill grinding energies were required to reduce the particle sizes of Anvil Points shale and Antrim shale respectively to below 20 μm. Froth flotation of ground Anvil Points shale increased the organic content from 13.5 wt% (24 GPT) to 27 wt% (50 GPT) with about 80% organics recovered in the concentrate. Three additional stages of grinding and flotation produced a final concentrate containing 48.4 wt% organics (90 GPT); however, the cumulative organic recovery was only 47%. The Antrim shale was upgraded in a single stage of grinding and flotation from 8.0 wt% organics (7 GPT) to 21 wt% organics (23 GPT). Two additional stages of grinding and flotation increased the grade of concentrate (38 wt%, 43 GPT) but decreased the recovery (67%). Grinding the concentrates did not significantly change the particle sizes. The separation efficiencies during flotation were found to be about 52% and 60% at the optimum conditions for Anvil Points and Antrim shales respectively. Technical and economic aspects of an oil shale beneficiation process based on froth flotation need to be assessed in light of the above experimental results.

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