JOINT SYMPOSIUM ON OIL SHALE, TAR SANDS, AND RELATED MATERIAL
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AND THE DIVISION OF WATER, AIR, AND WASTE CHEMISTRY
AMERICAN CHEMICAL SOCIETY
SAN FRANCISCO MEETING, April 2-5, 1968

USE OF CARBONIC ACID TO CONCENTRATE KEROGEN IN OIL SHALE

By

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INTRODUCTION

Research to determine the characteristics of the bonding energy between kerogen and the mineral constituents of oil shale is being conducted at the Bartlesville Petroleum Research Center. A major problem encountered in this research is the separation of unaltered kerogen from the mineral constituents. The major mineral constituents in the oil shale are dolomite, calcite, quartz, and feldspars. Minor amounts of illite, pyrite, and analcite are usually present (5). The term kerogen as used in this paper means all of the organic material.

The ideal method for separating kerogen from the mineral matter in oil shale should fulfill several requirements. First, the kerogen should not be altered chemically during the process. Second, the method should yield enough material for elemental analysis and degradation studies. Finally, the kerogen concentrate should be fully representative of the organic material in the oil shale.

Both physical and chemical methods have been used for concentrating kerogen from the mineral matter (1). Physical methods include gravity techniques and methods based on wettability differences. Chemical methods include digestion in various acids such as acetic (2), hydrochloric and/or hydrofluoric.

This paper describes a method using carbonic acid to concentrate the organic material in oil shale. Carbonic acid is a weak acid formed when carbon dioxide dissolves in water. Carbonic acid was selected because it should be too weak to alter the kerogen, yet does dissolve carbonates such as calcite and dolomite. It ionizes mainly into H^+ and HCO_3^- and dissolves carbonates by converting them to the soluble bicarbonates.

APPARATUS

The apparatus used in this study is shown in Figure 1. The stainless steel cylinder is prepared from 4-inch tubing. The glass liner is a 1-liter beaker with the lip sawed off. The tubing for water and carbon dioxide is 1/8-inch plastic and enters the system through fittings that are drilled out so the tubing goes all the way through. A piece of fine (Whatman #42) filter paper is attached to the face of the fritted glass filter. This is removed after each run and a new piece applied. The only metal that the solution contacts is the stainless steel valves.

EXPERIMENTAL PROCEDURE

Two samples of oil shale from the Rifle, Colorado, area were selected for use in this study. The Fischer Assay Analysis of these samples by the Laramie Petroleum Research Center is shown in the following table.

TABLE 1.--Fischer Assay Analysis of Colorado Oil Shale Samples

	Weight-percent				Gallons per ton	
Sample Number	Oil	Water	Spent Shale	Gas Loss	Oil	Water
1	6.8	1.3	90.0	2.0	18.0	3.0
2	15.25	1.6	79.5	3.7	40.8	7.7

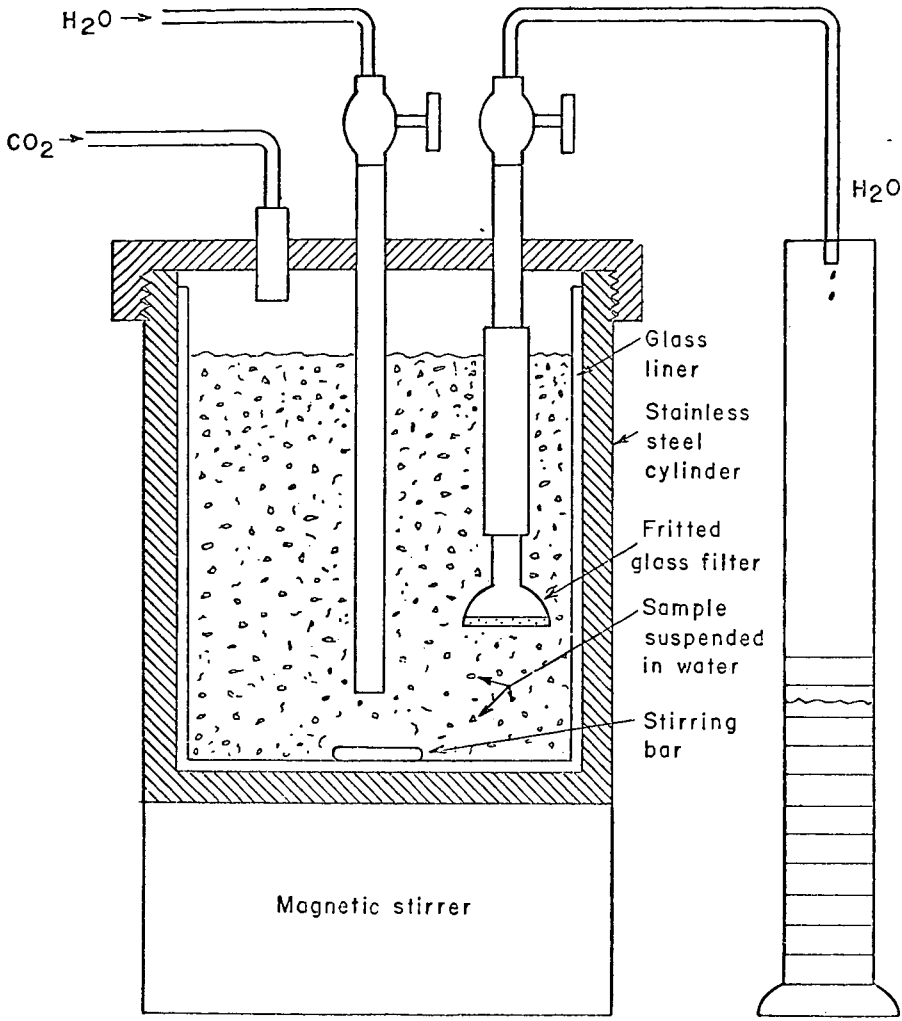

FIGURE 1.-Apparatus for Digestion of Oil Shale in Water Saturated With Carbon Dioxide.

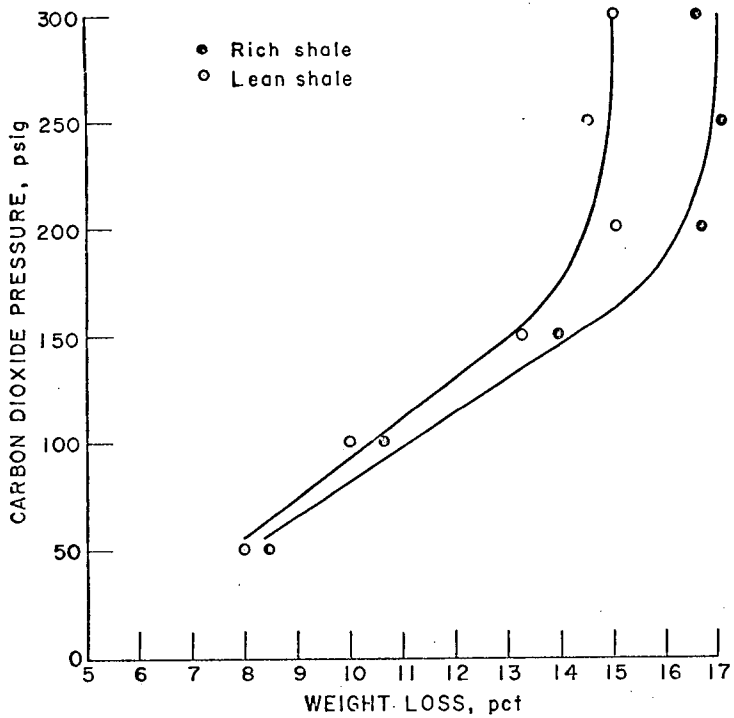

FIGURE 2.-Effect of Carbon Dioxide Pressure on the Soluble Material in Oil Shale.

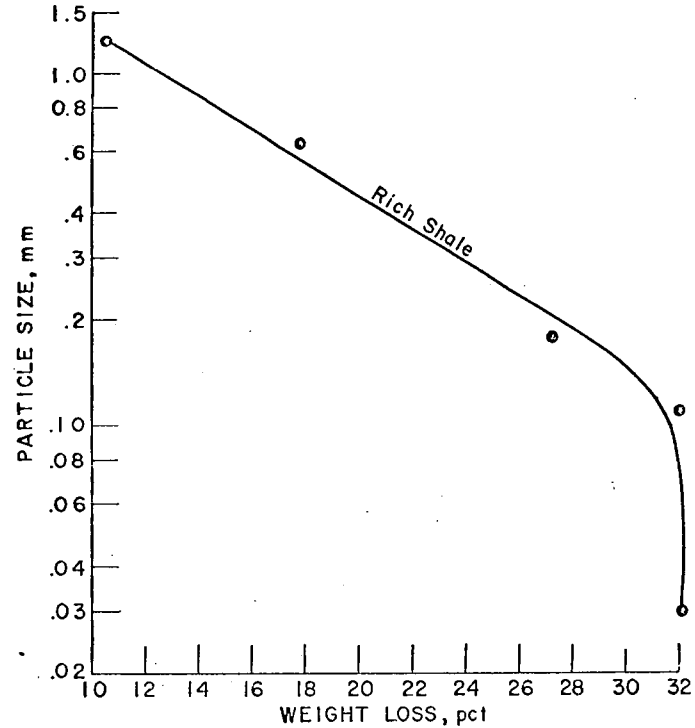

FIGURE 3.-Effect of Particle Size on the Carbonic Acid Soluble Material in Oil Shale.

Sample Number 1 is a lean, light yellowish brown oil shale. Sample Number 2 is a rich, dark brown oil shale. About 200 grams of each oil shale was crushed in a jaw crusher and ground with mortar and pestle till all the sample passed through a 200-mesh screen. The samples were vacuum dried (80°C) for 3 days to remove all the free water and stored in air-tight containers.

Samples of oil shale were weighted into the glass liner of the apparatus in Figure 1. Distilled water was added and the sample stirred in contact with air until water wet. The glass liner was placed in the stainless steel cylinder and assembly of the apparatus was completed. Carbon dioxide pressure was applied discharging the solution from the system through the filter. The system was flushed with carbon dioxide before more distilled water was pumped in under pressure. A batch technique was used so the system was stirred under pressure from 2 hours to overnight before solution was discharged through the filter. Calcium and magnesium were determined in the effluent water by titrating with EDTA (ethylenediaminetetraacetic acid). When no further calcium or magnesium were detected in the effluent, extraction was complete. Wet chemical analysis using hydrochloric acid was carried out on the oil shale after treatment by carbonic acid. The analysis confirmed that some iron and aluminum and all the calcium and magnesium had been removed.

Both oil shales were treated with hydrochloric acid for comparison with the carbonic acid treatment. A batch technique was used with overnight standing at low heat (70°C).

The total carbon and hydrogen in all samples was determined by combustion analysis. Mineral carbon (carbonates) was determined by treating the sample with acid to evolve carbon dioxide. Organic carbon was determined by difference.

RESULTS AND DISCUSSION

The effect of carbon dioxide pressure on the removal of soluble minerals in oil shale was determined first. Samples of both shales were suspended in 800 milliliters of distilled water, placed under carbon dioxide pressure, and stirred for 8 hours. Each sample weighed 2 grams. An aliquot of 300 milliliters was discharged through the filter under pressure. This was evaporated to dryness at low heat (95°C) and weighed to determine total solids. This data was used to calculate weight loss. This procedure was repeated for various pressures from 50 to 300 psig. The weight loss increased with increasing pressure up to 200 psig where it leveled off as shown in Figure 2. The pH of water saturated with CO_2 levels off at 3.3 in this region (3). Optimum pressure is, therefore, 200 psig, and this pressure was used for successive experiments.

A slight discrepancy is observed in the results in that the higher weight loss occurred in the oil shale with the lower carbonate content. Obviously, other minerals are being dissolved that are more soluble than the carbonates, under these conditions. Chemical analysis revealed the presence of gypsum ($CaSO_4$) which is more soluble under these conditions (4).

The effect of particle size on the removal of soluble minerals in oil shale was determined next. A sample of each oil shale was crushed and sieved. The weight loss in carbonic acid was determined for each particle size. For the rich shale weight loss increased with decreasing particle size from 1.25 mm (10 mesh) to 0.10 mm (150 mesh) where it leveled off as shown in Figure 3. Optimum particle size is therefore 150 mesh or finer. Samples used in all other experiments were finer than 200 mesh. For the lean oil shale, particle size did not affect weight loss over the indicated range. The effect of particle size on the rich shale is probably caused by the occlusion of carbonates by kerogen. The lean shale is low in kerogen, and therefore very little occlusion can occur.

At optimum conditions, carbonic acid removed about 90% as much material as was removed with hydrochloric acid. The results of both treatments are shown in Table 2.

TABLE 2.--Weight Loss of Shales Under Optimum Conditions

Sample	Weight Loss, Percent	
	HCl	H_2CO_3
Rich oil shale	36.2	32.1
Lean oil shale	57.6	53.4

These data show that a substantial portion of the mineral matter was removed from oil shales by the carbonic acid. Analysis of the samples treated with carbonic acid revealed that all the calcium and magnesium had been removed. It was noted also that no carbon dioxide evolved when the sample was subsequently treated with hydrochloric acid. Therefore, carbonic acid is as effective as hydrochloric acid in removing calcite, dolomite. and other carbonates and

other calcium and magnesium minerals. Chemical analysis revealed that excess weight loss in hydrochloric acid was caused by the dissolving of more aluminum and iron compounds.

The organic carbon and hydrogen contents of all samples, determined by combustion analysis, are shown in Table 3.

TABLE 3.--Combustion Analysis of Treated Oil Shales

Sample Description	Organic Carbon, Percent	Hydrogen, Percent	C/H
Lean Oil Shale	6.40	1.10	5.91
Treated with HCl	14.44 (6.12)[a]	2.44 (1.04)	5.92
Treated with H_2CO_3	13.44 (6.26)	2.26 (1.05)	5.94
Rich Oil Shale	17.8	2.47	7.21
Treated with HCl	27.4 (17.5)	3.82 (2.44)	7.17
Treated with H_2CO_3	25.6 (17.4)	3.57 (2.42)	7.22

a/ Numbers in parentheses are based on the original oil shale.

The organic carbon content of the original oil shales is subject to an error of 0.4% carbon, while the treated samples are accurate to within 0.1% carbon. The organic carbon content of the original oil shale is subject to a larger error because it is determined by difference. The inorganic carbon content is high (24% CO_2 for lean shale and 11% CO_2 for rich shale) compared to the organic carbon content in the original samples. The inorganic carbon content is also subject to a larger experimental error. The results show that within experimental error organic carbon content and the carbon-to-hydrogen ratio are not affected by treatment with either acid. Both of these facts indicate that the kerogen is unaltered by treatment with either acid. However, the color of the sample of oil shale treated with hydrochloric acid was darker than the sample treated with carbonic acid, which indicates that hydrochloric acid may have reacted with the kerogen.

Treatment with carbonic acid is a very good first step in separating the organic material from the mineral matrix of oil shale. Further concentration can be obtained by physical means. Centrifuging the sample treated with carbonic acid in a saturated aqueous solution of calcium chloride yields a concentrate containing 85% to 90% of the organic material with an ash content of less than 30%. Centrifuging the original sample yielded only 15% of the kerogen and an ash content of 50%.

CONCLUSIONS

All the mineral carbonates such as calcite and dolomite can be removed from an oil shale by treatment with carbonic acid. Optimum conditions for removal are a carbon dioxide pressure of 200 psig and oil shale particles smaller than 0.10 mm (150 mesh). The organic carbon content of the oil shale is not affected by carbonic acid. The lack of color change in the product also indicates the organic material is unaltered by carbonic acid. Analyses can be performed on this concentrate without interference from inorganic carbon.

ACKNOWLEDGMENTS

This paper is based on research conducted at the Bureau of Mines, Bartlesville Petroleum Research Center, Bartlesville, Oklahoma, in cooperation with the Bureau of Mines, Laramie Petroleum Research Center, Laramie, Wyoming.

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