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A STUDY OF POSSIBILITIES FOR THE RECOVERY OF OIL AND URANIUM FROM THE CHATTANOOGA SHALE

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ABSTRACT

At present no commercial method has been developed to recover either oil or uranium from the Chattanooga Shale. In this study, samples of shale were retorted to remove oil and leached to remove uranium. The processes were carried out in both possible orders. After this treatment, analyses were performed to determine the possibilities for a commercially feasible process to recover both resources. Results point to a good probability that such a process can be developed.

INTRODUCTION

Although the Chattanooga Shale has been known for several decades to contain kerogen (a substance which yields oil upon heating) and uranium, no economically feasible process for the recovery of either has yet been developed. The need for energy self-sufficiency and work done in recent years, however, are making Chattanooga Shale commercially more attractive than it has been. This study concerns itself with the recovery of these resources and deals specifically with the possibilities of recovering both from the same volume of shale.

STRATIGRAPHY AND DESCRIPTION

The Chattanooga Shale is part of a sequence of late Devonian to early Mississippian black shales which covers most of the East Central United States and portions of Canada. The Chattanooga itself covers most of Northern Alabama, Middle Tennessee, much of Kentucky, and parts of Indiana and Ohio. It is composed of fine grains of inorganic material, principally quartz, feldspar, and pyrite, which are bound together by a complex clay-organic matrix. The Chattanooga is divided into two main layers: the Gassaway (upper) member and the Dowelltown (lower) member. The shale is overlain in part by the Fort Payne Chert and the Maury Formation. A stratigraphic equivalent of the Fort Payne is the New Providence Shale which covers most of Kentucky and portions of Northern Tennessee (Mutschler, et. al., 1976).

COLLECTION

Samples for this study were obtained from an outcrop at Crocker Springs in Northern Davidson County, Tennessee. Because this study was of resource recovery and not resource distribution or content, one locality was used to provide the entire supply of shale used in the laboratory.

METHOD

The material collected was divided into separate samples and designated in the following manner: A—raw shale used as a control; B1, B2, B3—three samples to be retorted first and then leached; and C1, C2, C3—three samples to be leached first and then retorted.

The three samples in the B series were crushed to small chunks and retorted until nothing more was produced at a temperature range of 450°C to 520°C. The spent shale from the three retorts was then mixed and pulverized to a fine powder in a ball mill. A small sample was taken for analysis and two batches, each containing approximately 50g of shale were removed and designated B4 and B5.

The oils produced from B1, B2, and B3 were separated from the retort water, weighed, and measured for volume. Gases produced were collected over water and volumes measured.

The samples in the C series, each weighing about 50g, were leached in the following manner: C1—refluxed for 4 hours with 10% sulfuric acid in a liquid to solid ratio of 3 ml/g; C2—refluxed for two hours with 10% sulfuric acid in a liquid to solid ratio of 1.5 ml/g, filtered, and repeated with fresh acid; C3—treated the same as C2 except that the first and second refluxes had liquid to solid ratios of 1 ml/g and 2 ml/g, respectively.

Sample B4 was leached in the same manner as sample C1 and sample B5 was treated in the same manner as sample C2. Small amounts of samples B4, B5, C1, C2, and C3 were removed for analysis. The remainder of the C series was combined and retorted.

One gram of samples A, B (mixture after retorting), B4, B5, C1, C2, and C3 were analyzed for apparent uranium content using a semiquantitative paper chromatographic method (Thompson and Lakin, 1957).

The leach liquor of each of the leachings of C1, C2, C3, B4, and B5 was neutralized to a pH of 5 with barium hydroxide to precipitate the excess sulfate from the acid, filtered, evaporated to about 20 ml from an original volume of 150 ml, and filtered again. The leach liquors were combined to give a total volume of about 100 ml. The resulting mixture was then extracted with 10 ml of a .1M solution of di(2-ethyl-hexyl) phosphoric acid dissolved in kerosine which was .05M in respect to tributylphosphine oxide (Blake, et. al., 1958). The extraction was carried out with a phase ratio of 1:1, the same 10 ml of extractant being used with each 10 ml of leach liquor.

The extractant was then back-extracted (stripped) with about 2 ml of an aqueous sodium carbonate solution. The resulting solution was then checked with a gamma counter to detect uranium by the gamma radiations present in the decay of U^{238} (Weast, 1975).

RESULTS AND DISCUSSION

Table 1 shows the results of the retorts. The oil produced from the retorting of the B series came off at an average rate of about 7.3 gallons of oil per ton of shale. Samples which had been allowed to sit for several weeks between the time that they were crushed and the time they were retorted gave a lower yield than those which were retorted immediately after being crushed. The oil produced had an average density of .91 g/ml, was black, and not very viscous. It also contained much sulfur and was very corrosive. Some gas was produced and sample B3 yielded gas at a rate of 60 cubic feet per ton of shale. This gas contained a large amount of hydrogen sulfide. Finally, highly contaminated water at a rate of 20-30 gallons per ton and some elemental sulfur were produced during retorting.

TABLE 1. *Oil yield showing the effect of prior leaching.*

Sample	B1	B2	B3	C Mix
Mass (g)	509	493	485	147
Oil Yield (ml)	15.0	15.5	15.3	2
Oil Yield Rate (gal/ton)	7.07	7.55	7.57	3.27
Oil Density (g/ml)	.919	.906	----	----
Gas Yield (ml)	----	----	900	----
Gas Yield Rate (ft^3/ton)	----	----	59.6	----

Table 2 shows the results of the uranium analysis. There are two noticeable trends in the efficiencies of the leachings: (1) Retorting markedly reduces subsequent uranium removal, and (2) Multistage leachings increase the uranium removal for the same total liquid to solid ratio.

The decrease in uranium removal after retorting is apparently due to a decrease in permeability of the shale. This was also seen in the apparent decrease in uranium content in the mixed retorted material of sample B from the raw shale in sample A. Conversely, shale leached first suffers a large decrease in oil yield.

TABLE 2. *The effect of retorting on uranium removal.*

Sample	A	B Mix	C1	C2	C3	B4	B5
Uranium Content Raw Shale (ppm)	38*	----	----	----	----	----	----
U Content after Reflux (ppm)	----	33.3*	----	----	----	----	----
Liquid/Solid Ratio, 1st Reflux (ml/g)	----	----	3.0	1.5	1.0	3.0	1.5
Time of 1st Reflux (min)	----	----	240	120	120	240	120
Liquid/Solid Ratio, 2nd Reflux (ml/g)	----	----	----	1.5	2.0	----	1.5
Time of 2nd Reflux (min)	----	----	----	120	120	----	120
Total Liquid/Solid Ratio (ml/g)	----	----	3.0	3.0	3.0	3.0	3.0
Total Reflux Time (min)	----	----	240	240	240	240	240
Uranium Content after Reflux (ppm)	----	----	15*	6*	12	16*	14*
% of Total Uranium Removed	----	----	61	84	68	58	64

The decrease in efficiencies of single stage leaching is apparently due to the presence of contaminants in the shale which leach out immediately upon contact with the acid. These contaminants compete with the more refractory uranyl ions for sulfate, hence decreasing the removal of the uranyl. The multistage leachings overcome this problem by removing the contaminated acid and replacing it with fresh acid (Pollara, et. al., 1958).

The use of the synergistic combination of di(2-ethylhexyl)-phosphoric acid and tributylphosphine oxide in kerosine worked very well in this investigation. The only problem encountered was the formation of an emulsion during the extraction which was very hard to break up.

Although no accurate quantitative analysis of the uranium in the final concentrate was performed, the gamma counter did detect a consistent gamma increase commensurate with a high level of uranium.

There have been three methods of uranium removal discussed widely in the literature: (1) Batch leaching, (2) Countercurrant decantation, and (3) Oxygen pressure leaching (Pollara, et. al., 1958). Of these three, the best for the removal of uranium in a joint recovery process would be countercurrent decantation. Batch leaching is a single stage process, which is not efficient in the removal of uranium. Oxygen pressure leaching, which utilizes the oxidation of pyrite in the shale to produce sulfuric acid is unsuitable for joint recovery processes because it oxidizes the kerogen in unretorted shale, and the sulfur required would not be present if the shale were already retorted. Countercurrent leaching, on the other hand, is a multistage process which has already been shown to work well on the Chattanooga Shale (Pollara, et. al., 1958).

The development of processes is not the only hindrance to commercial utilization of the Chattanooga. In addition, there are environmental factors, such as wastewater and spent shale from processing, mining considerations such as the strength and thickness of overlying rock and ventilation of the mine shafts. All of these factors increase the expense of development. Costs may, however, be offset by marketing byproducts from the shale, such as sulfur, vanadium, and building materials containing spent shale.

CONCLUSION

It is probably a feasible idea to recover both oil and uranium from the same volume of shale. The processes used would differ somewhat, depending on which product is considered most valuable. The most important material would be removed first, as there is a consistent tendency for the second resource recovered to be diminished.

The dialkyl phosphoric acid extraction (DAPEX) process used in this research is a commercial process and could be applied to the shale in a joint recovery process. The specific reagents are especially suited to the low concentration shale leach liquors, showing an extraction coefficient of about 7000 (Blake, et. al., 1958).

More work must be done before widescale use of the Chattanooga Shale for its resources is realized. Recently, Illinois Gases Technology, Chicago, has developed a distillation method in a hydrogen atmosphere which reportedly causes much greater oil yields than have been previously possible (Maher, Pers. Corr, 1981). It is hoped that research like this will soon make the Chattanooga Shale a viable and useable resource.