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Quarterly Report

Contract No. AT 30-1-Gen-202

SECTION I

RECOVERY OF URANIUM FROM SHALES

(A. E. Bearse, Supervisor)

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March 15, 1949

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SECTION I

RECOVERY OF URANIUM FROM SHALES

(A. E. Bearse, Supervisor)

INTRODUCTION

Section I of this report is concerned with the problem of recovering uranium from domestic shales, which have been found to contain up to a maximum of 0.01 per cent of uranium. The work discussed was carried out during the period December 15, 1948, to March 15, 1949, under Contract No. AT 30-1-Gen-202.

Other sections of this report deal with related problems which have a direct bearing on the development of a uranium recovery process based on shale as the raw material. Section II describes briefly the program that is just getting started on identification of the mode of occurrence of uranium in shales, and Section III relates to the problem of recovering fuel values from the shale, as a step in the preparation of the shale for leaching.

Previous work on the uranium recovery project has been summarized in the following Battelle reports:

BMI-JDS-101, January 15, 1948

BMI-JDS-130, June 30, 1948

BMI-JDS-141, September 15, 1948

BMI-JDS-156, December 15, 1948

The status of the investigation as of December 15, 1948, was presented in considerable detail in the last of these reports. Briefly, it was shown

that about 65 per cent of the uranium in the shale can be obtained in solution by leaching roasted shale with dilute sulphuric acid. Methods have been found for precipitating nearly all of the dissolved uranium from the leach liquors to give a low-grade cake containing about 0.7 per cent of uranium. Upgrading the initial precipitate to 1.5 per cent of uranium by a caustic soda treatment was described.

In the preceding report (BMI-JDS-156), the following steps were indicated to be of interest in the tentative process for recovering uranium from shales:

- (1) Recovery of fuel values by retorting.
- (2) Roasting of the retorted product by one of several alternative techniques.
- (3) Agitation leaching of the roasted shale at room temperature with dilute acid, preferably with sulphuric acid obtained from the oxides of sulphur given off during the roasting operation.
- (4) Precipitation of uranium from the acid leach liquors (after reduction of ferric to ferrous iron) by controlled neutralization.
- (5) Subsequent upgrading of the initial precipitate by one of several possible methods under investigation.

No significant change in the above tentative process is indicated as a result of the recent work.

During the quarter, a considerable amount of detailed information has been obtained on the various steps involved. The scale of roasting operations has been increased by the use of a rotary kiln, with the objects of evaluating this type of equipment and of providing larger

amounts of roasted shale for leaching studies. A systematic study of leaching variables has been carried out to aid in determining the optimum conditions for maximum uranium extraction, while at the same time obtaining the lowest practical level of contaminants in the pregnant liquors. Additional data are presented on the recovery of uranium from the leach liquors.

SUMMARY

Roasting studies have been continued, employing both a small, single-hearth Herreshoff roaster and a rotary kiln. Additional data have been secured on the effect of roasting time and temperature on extraction of uranium and extraneous elements by dilute sulphuric acid. These data indicate that a considerable improvement in ratios of contaminants to uranium in leach solutions may be attained by use of the maximum roasting temperatures consistent with satisfactory uranium recovery. Evidence is that the effect of roasting time on contaminant ratios is of minor significance.

The effect of particle size (of the raw shale roasted) on uranium extraction is shown to be negligible, when the exothermic reaction is not allowed to carry the shale to excessive temperatures. Results indicate, however, that the particle size of the shale fed to the roaster may be of importance in connection with the time of roasting required.

Preliminary results from the initial rotary kiln tests indicate that this type of equipment is suitable for the roasting of shale and that the level of uranium extraction attainable by leaching (60-65 per cent)

is comparable to that secured with other types of roasting equipment. Optimum roasting times and temperatures are similar to those found in earlier tests on other types of smaller scale equipment. Work is continuing to evaluate more completely the effects of the main variables, as well as to increase production rates. The kiln is proving to be of special value in providing the quantities of roasted shale required for the leaching and recovery studies now in progress, since no other equipment now in operation has the necessary capacity. Recent shipments of shale from the Sligo adit have provided an adequate supply of the raw material for the immediate future for the recovery work.

Work has also been initiated on the problem of recovering the oxides of sulphur from the kiln stack gases, although no conclusive results have as yet been obtained. Some work on the application of the well-known autoxidation process for the production of dilute sulphuric acid from gases of low SO_2 concentration has been started.

A two-stage fluo-solids roaster, on a somewhat larger scale than previous bench-scale units, is being constructed, and test work is scheduled to begin shortly. Provisions are being included in this unit to enrich the roaster gas between stages with either air or oxygen also, to recycle any desired portion of the roaster gases from the second stage.

A comprehensive investigation of leaching variables is in progress, using a relatively large amount of shale roasted under uniform conditions. It is believed that a sufficiently ample supply of roasted material exists

to permit extensive leaching studies without the necessity arising of introducing additional and different roasted shales, as has been necessary in similar leaching investigations in the past.

Leaching variables under investigation are: temperature, particle size, sulphuric acid concentration, pulp density, and leaching time. Available results indicate that the lowest feasible leaching temperatures result in the minimum ratios of contaminants to uranium in solution. Fortunately, leaching temperature, over the range of 45°F. to 180°F. (7°C. to 82°C.), exerts no significant effect on uranium extraction. The results of the particle size, time, and acid concentration studies do not yet warrant definite conclusions.

Attempts to increase over-all uranium extractions on a poorly roasted shale, by leaching previously leached residues with strong mineral acids at elevated temperatures, increased the extraction of uranium, although ultimate extractions were no higher than is considered normal for a well-roasted shale.

Evidence has been developed to indicate that more consistent results may be attained when the primary ammonia precipitation of uranium from leach solutions is performed at elevated temperatures (160°F. or 71°C.). The success of this precipitation has an important bearing on future upgrading treatments. Lack of uniform results in the early recovery studies has confused the evaluation of the secondary treatments.

Caustic soda and several carbonates have been investigated as possible aids in upgrading the primary ammonia precipitate. Caustic

soda has shown some promise in removing the aluminum from the uranium precipitate; but unfortunately, losses of uranium to the caustic solution have ranged from 10 to 40 per cent. The use of carbonates to dissolve the uranium from the primary precipitate appear more promising than the caustic soda treatment, removals of from 80-90 per cent having been secured. Means of increasing this to quantitative removal are currently being considered.

EXPERIMENTAL DETAILS AND DISCUSSION OF RESULTS

Description of Shale Samples

Five new samples of shale have been received since the previous quarterly report (BMI-JDS-156, December 15, 1948). One of these was a five-ton sample from a road cut; two were ten-ton samples from the Sligo adit; and two were small "channel" samples from the side walls of the adit.

A composite sample of the five-ton batch (No. 1207-113; U.S.G.S. No. R-C2-213) has been assayed and contains 0.0097 per cent of uranium, which is even higher than the 0.0092 per cent found for the preliminary sample from the same location (No. 1207-109; U.S.G.S. No. R-C2-113). The sulphur content of this sample is also high, amounting to 8.6 per cent. Approximately two tons of it was immediately crushed, ground, and screened to minus 6-mesh size.

The first of the ten-ton shipments (No. 1207-116; U.S.G.S. No. IC-201-111) was secured from the 43-48-foot level in the adit; this

shipment has been set aside for future needs. The second ten-ton (U.S.G.S. No. LC-201-113; BMI No. 1207-117) (from the 89-95-foot level) was subjected to primary crushing to minus 3/4-inch size, and the resultant pile was sampled so that a 1/8 cut of approximately one ton was secured. This 1/8 cut was ground and screened to minus 6 mesh and representative samples were taken for petrographic and phase separation studies. Although complete analytical results are not yet available, preliminary reports indicate that the uranium content of these ten-ton samples exceeds the 0.008 per cent level. Uranium recovery studies on these adit samples should show whether there are any significant differences in behavior between unweathered shale and shale obtained from outcrops, which may have been subjected to weathering.

Two small (20-pound) "channel" samples from the side walls of the adit have also been received and are being analyzed in order to serve as checks on the larger samples. No analytical results are as yet available on these.

Analytical results are now at hand on Shale No. 1207-112, receipt of which was noted in the previous quarterly report (BMI-JDS-156). This was a one-ton sample, consisting of a number of individual samples from different horizons of the top black, from 0 to 5.0 feet. Analysis of a composite of the upper 2.6 feet revealed that the uranium content was 0.0083; the sulphur content 7.4 per cent; and the loss on ignition 24.0 per cent. The uranium content of the lower 2.4 feet was somewhat lower, amounting to 0.0071 per cent. Representative samples of the various levels

have been saved; the bulk of the shipment is to be thoroughly mixed and used as a roaster feed.

Roasting and Retorting Studies

The principal effort continues to be devoted towards developing methods and equipment satisfactory for roasting shale on an increasingly larger scale, without the necessity of resorting to impractically long roasting times.

The preliminary phases of the studies with a small-scale, single-hearth Herreshoff-type roaster have now been concluded, although there are still minor questions and anomalies arising from the earlier work which appear to merit further investigation as time permits. It is also planned to continue to employ the Herreshoff as a control tool to aid in evaluating the results secured on different shales with the rotary kiln.

Currently, the main endeavor is to investigate the feasibility of a rotary kiln type of roaster for the roasting of shale. A 12-inch by 12-foot gas-fired rotary kiln has been assembled and preliminary test work initiated.

Studies have also been continued on investigating the possibility of utilizing fluo-solids techniques for roasting. Earlier small-scale tests indicated some promise, although it appeared that the scale of operations was too small to develop conclusively all of the inherent possibilities of this type of equipment. In order to surmount this

difficulty, a slightly larger two-stage bench scale fluo-solids roaster is now being constructed. Test work is expected to be commenced in the near future on this larger equipment.

Various exploratory studies have also been conducted, including treatment of roasted shale with sulphur trioxide. Only preliminary results on these studies are available, and no conclusions are warranted at this time.

Hearth Roasting

Results of earlier experiments on a small (13-inch diameter) single hearth Herreshoff-type roaster have been described in the previous quarterly report (BMI-JDS-156). Similar test procedures have been followed in the current studies, which have extended hearth roasting to several other shale samples. Other tests have been conducted on the effects of different variables in roasting procedure on uranium extraction and on contaminant ratios in the leach liquor. Additional results, unavailable at the time of the previous quarterly report, are also presented. In addition, the Herreshoff has been utilized during recent months as a semi-production unit for the production of uniformly roasted shale for leaching and recovery studies.

Effect of Roasting Time and Temperature on Uranium Extraction. The previous quarterly report presented evidence that uranium extraction decreased markedly at observed furnace bed temperatures above 950°F. (510°C.).

[In the same report, it was also shown that the actual shale temperature under these conditions was in the 1050-1100°F. (565-600°C.) range.]

Further time-temperature tests on other shale samples tend to confirm the existence of an optimum roasting temperature range, above which uranium extraction decreases excessively as roasting temperatures are increased. These data are presented in Tables 1 and 2 for Shales No. 1090-4 and No. 1207-111. A graphical presentation is given in Figure 1.

The series of tests on Shale No. 1207-111 is not sufficiently extensive to illustrate the marked decrease in uranium extraction at roasting temperatures above 950°F. (510°C.) (bed temperature), although it serves to illustrate the breadth of the optimum temperature range. These tests, however, were made primarily to select the optimum roasting temperature for preparing larger amounts of this roasted shale for leaching studies, and only those temperatures believed to be in the general range were investigated.

Effect of Gas Firing on Uranium Extraction. In order to simulate more closely plant conditions, a series of time-temperature tests similar to the previous series was conducted, in which the "Globar" elements were replaced by two small blast-type gas burners. Other conditions were maintained as before, with the exception of the air flow rate, which arbitrarily was increased 50 per cent to compensate for the increased air requirements.

TABLE 1. EFFECT OF ROASTING TIME AND TEMPERATURE ON EXTRACTION OF URANIUM FROM SHALE ROASTED IN A SINGLE-HEARTH FURNACE.

Shale Used: No. 1207-111 (0.0083 per cent uranium)

Screen Analysis:	<u>Mesh</u>	<u>Per Cent</u>
	+4	3
	-50	13
	-100	7
	-325	3

Roasting Conditions: 1500 grams of raw shale roasted at temperatures indicated with an air flow of 20 liters/minute. Fifty-gram samples withdrawn at hourly intervals.

Leaching Conditions: Fifty-gram sample in 200 ml. of 2 per cent sulphuric acid for three hours at room temperature, with agitation.

Roasting Time, Hours	Uranium Extracted, Per Cent				
	Roasting Temperature, °F. (1)				
	750	795	840	885	930
2	48	41	65	58	63
3	55	56	70	61	64
4	65	59	70	64	69
5	67	68	70	60	67
6	63	-	-	-	-

(1) Temperature of furnace bed; actual shale temperature was higher by about 100-150°F.

TABLE 2. EFFECT OF ROASTING TIME AND TEMPERATURE ON EXTRACTION OF URANIUM FROM SHALE ROASTED IN A SINGLE-HEARTH FURNACE

Shale Used: 1090-4A (0.0061 per cent uranium)

Screen Analysis:	<u>Mesh</u>	<u>Per Cent</u>
	+4	2
	-30	26
	-100	10
	-200	5

Roasting Conditions: 1500 grams of raw shale roasted at temperature indicated with an air flow of 20 liters/minute.
Fifty-gram samples withdrawn at hourly intervals.

Leaching Conditions: Fifty-gram sample in 200 ml. of 2 per cent sulphuric acid at room temperature for 3 hours, with agitation.

Roasting Time, Hours	Uranium Extracted, Per Cent				
	Roasting Temperature, °F. (1)				
	840	930	1020	1110	1200
2	56	53	48	27	20
3	54	-	43	29	19
4	59	-	48	31	19
5	61	59	45	30	21
6	56	-	49	27	19
8	51	56	44	26	19

(1) Temperature of furnace bed; actual shale temperature was higher by about 100-150°F.

FIGURE 1. EFFECT OF ROASTING TEMPERATURE ON EXTRACTION OF URANIUM FROM TWO SHALES BY TWO PER CENT SULPHURIC ACID

The same general type of time-temperature relationship was found to exist in this series of tests, and the usual marked decrease in extraction of uranium by 2 per cent sulphuric acid after roasting at bed temperatures above 950°F. (510°C.) was again noted. The data are shown in Table 3 and are graphically presented in Figure 2. The curve resulting from the earlier series on the same shale with "Globar" heating is also plotted.

Although there appears to be a slightly lower uranium extraction with gas firing, the difference is only of the same order as the possible analytical error. The weight of other evidence points toward comparable extractions, irrespective of the method of heating. However, the 50 per cent increase in air flow rate may be a contributing factor toward a real difference. Further experimental work is indicated to confirm this possibility. Dust losses may be considerably higher with gas firing than with electrical heating.

Effect of Particle Size of Raw Shale on Uranium Extraction after Roasting. One series of tests was conducted to determine the effect of the particle size of the shale (before roasting) on uranium extraction and on length of roasting time required. These studies covered the range minus 16 and plus 30 mesh down to minus 70 and plus 200 mesh. Earlier small-scale roasting studies had indicated that particle size of the raw shale exerted no significant effect on uranium extraction by acid leaching. A more recent series of Herreshoff roasts indicated that finer

TABLE 3. EFFECT OF ROASTING TIME AND TEMPERATURE ON EXTRACTION OF URANIUM FROM SHALE ROASTED IN A HEARTH FURNACE WITH GAS FIRING

Shale Used: No. 1207-107 (0.0086 per cent uranium)

Screen Analysis:	<u>Mesh</u>	<u>Per Cent</u>
	-4	100
	-50	36
	-100	19
	-325	5

Roasting Conditions: 1500 grams of raw shale roasted at temperatures indicated with an air flow of 30 liters/minute. Fifty-gram samples withdrawn at hourly intervals.

Leaching Conditions: Fifty-gram samples leached for 3 hours at room temperature with 2 per cent sulphuric acid and agitation.

Roasting Time, Hours	Uranium Extracted, Per Cent						
	Roasting Temperature, °F. (1)						
	795	840	885	930	975	1020	1110
1	24	14	21	22	22	19	17
2	45	43	49	47	40	33	23
3	52	46	54	47	42	33	26
4	50	49	54	50	42	32	25
5	52	49	53	47	44	35	24
6	55	49	-	48	42	33	22

(1) Temperature of furnace bed; actual shale temperature was higher by about 100-150°F.

FIGURE 2. COMPARISON OF EFFECTS OF GAS FIRING AND ELECTRICAL HEATING ON EXTRACTION OF URANIUM BY TWO PER CENT SULPHURIC ACID FROM SHALE ROASTED IN A HERRESHOFF TYPE FURNACE

particle size resulted in lowered uranium extraction. However, there was reason to believe that in this latter series, the more vigorous and more rapid exothermic reaction of the finely ground shale resulted in the attainment of shale temperatures exceeding the known safe limits for satisfactory uranium extraction. Therefore, a lower roasting temperature was selected for the current study, so that even in the event of a considerable temperature rise, the optimum temperatures would not be exceeded. The results of the series, presented in Table 4, confirm the original conclusion that particle size of the raw shale prior to roasting did not significantly affect the extraction of uranium. The present data indicate that the time required for roasting at a furnace bed temperature of 795°F. (425°C.) is substantially reduced when finer particle sizes are used. Whereas the minus 16- and plus 30-mesh shale required 3 hours to attain maximum extraction; the minus 30- and minus 70-mesh shales attained maximum extraction in only 2 hours.

Effect of Roasting Conditions on Amounts of Contaminants Dissolved.

The effect of roasting conditions (as well as the effects of leaching conditions) on the amounts of contaminants dissolved along with the uranium has been noted earlier. However, these early results were on small-scale tests, the reproducibility of which was questionable. The roasted samples resulting from the various Herreshoff roaster studies afforded an opportunity to secure additional data on contaminants, and a number of selected samples were analyzed for iron and aluminum, two of the principal metallic

TABLE 4. EFFECT OF ROASTING TIME AND PARTICLE SIZE OF RAW SHALE ON EXTRACTION OF URANIUM AFTER ROASTING IN A SINGLE-HEARTH FURNACE

Shale Used: No. 1207-107 (0.0086 per cent uranium)

Roasting Conditions: 1500 grams of raw shale was roasted at 795°F. (425°C.) (1) with an air flow of 20 liters/minute; 50-gram samples were withdrawn at hourly intervals.

Leaching Conditions: Fifty-gram samples in 200 ml. of 2 per cent sulphuric acid for three hours at room temperature, with agitation.

Roasting Time, Hours	Uranium Extracted, Per Cent		
	Particle Size Before Roasting		
	-16 +30 Mesh	-30 +50 Mesh	-70 +200 Mesh
1	14	16	25
2	35	45	50
3	48	44	52
4	47	48	52
5	48	44	48
6	48	42	51

(1) Temperature of furnace bed.

contaminants. Since all samples selected were subjected to an identical leaching procedure, leaching conditions were not a factor in these tests.

Analytical results are presented for three different shale samples, including one roasted with gas-firing. A bed temperature range of 795-1110°F. (425-600°C.) and a time range of from 2-5 hours were covered by these results. The results are tabulated in Tables 5, 6, and 7 and are graphically presented in Figures 3, 4, and 5.

Roasting temperature was by far the most significant variable, particularly with respect to the relative amounts of iron dissolved, up to an observed bed temperature of about 950°F. (510°C.). Since the extraction of uranium decreased rapidly above this temperature, the lack of additional change in the ratio of iron to uranium in solution is of little importance beyond 950°F. (510°C.).

Roasting temperature did not appear to exert a significant effect on the ratio of aluminum to uranium in solution in the case of Shales 1090-4 and 1207-101B. There is some question on the tests on Shale 1207-111, but pending confirmatory analytical results, these results can be discounted. The evidence is in agreement that, if any change exists, it is toward a decreasing ratio as the roasting temperature is increased.

The general conclusion can be drawn that roasting should be carried out at the highest temperature consistent with satisfactory uranium extraction, in order to minimize the relative amounts of iron and aluminum carried into solution with the uranium. Due to the difficulties in measuring the actual shale temperature in the various units of equipment used

TABLE 5. EFFECT OF ROASTING TIME AND TEMPERATURE ON THE WEIGHT RATIOS OF IRON AND ALUMINUM TO URANIUM IN LEACH SOLUTION(1)

Shale Used: No. 1207-101B (0.0065 per cent uranium)

Screen Analysis:	<u>Mesh</u>	<u>Per Cent</u>
	-4	100
	-100	11
	-325	3

Roasting Conditions: 1500 grams of raw shale roasted at temperatures indicated with an air flow of 20 liters/minute; 50-gram samples withdrawn at hourly intervals.

Leaching Conditions: Fifty-gram samples in 200 ml. of 2 per cent sulphuric acid for three hours at room temperature, with agitation.

Roasting Temp., °F.(2)	Time of Roast, Hours								
	3			4			5		
	<u>Weight Ratios</u>		Uranium Extracted, Per Cent	<u>Weight Ratios</u>		Uranium Extracted, Per Cent	<u>Weight Ratios</u>		Uranium Extracted, Per Cent
	<u>Fe</u> <u>U</u>	<u>Al</u> <u>U</u>		<u>Fe</u> <u>U</u>	<u>Al</u> <u>U</u>		<u>Fe</u> <u>U</u>	<u>Al</u> <u>U</u>	
750				122	46	54			
795	90	36	66	91	39	66	92	39	62
840				86	41	62			
885				40	35	61			
930				17	33	60			

- (1) Shale roasted in a single-hearth Herreshoff-type furnace heated by "Global" elements.
 (2) Temperature of furnace bed.

TABLE 6. EFFECT OF ROASTING TIME AND TEMPERATURE ON THE WEIGHT RATIOS OF IRON AND ALUMINUM TO URANIUM IN LEACH SOLUTION(1)

Shale Used: No. 1207-107 (0.0086 per cent uranium)

Screen Analysis: Mesh Per Cent

-4	100
-50	36
-100	19
-325	5

Roasting Conditions: 1500 grams of raw shale roasted at temperatures indicated with an air flow of 30 liters/minute; 50-gram samples withdrawn at hourly intervals.

Leaching Conditions: Fifty-gram samples of 200 ml. of 2 per cent sulphuric acid for three hours at room temperature with agitation.

Roasting Temp., °F. (2)	Time of Roast, Hours											
	2			3			4			5		
	<u>Wt. Ratios</u>		Uranium Extracted, Per Cent	<u>Wt. Ratios</u>		Uranium Extracted, Per Cent	<u>Wt. Ratios</u>		Uranium Extracted, Per Cent	<u>Wt. Ratios</u>		Uranium Extracted, Per Cent
	<u>Fe</u> U	<u>Al</u> U		<u>Fe</u> U	<u>Al</u> U		<u>Fe</u> U	<u>Al</u> U		<u>Fe</u> U	<u>Al</u> U	
795				40	46	52						
840				5	36	46						
885	21	37	49	19	34	54	13	36	54	11	30	53
930				8	46	47						
975				7	40	42						
1020				9	38	33						
1110				8	43	26						

(1) Shale roasted in a single-hearth Herreshoff-type furnace heated by gas firing.

(2) Temperature of furnace bed.

TABLE 7. EFFECT OF ROASTING TIME AND TEMPERATURE ON THE WEIGHT RATIOS OF IRON AND ALUMINUM IN LEACH SOLUTION⁽¹⁾

Shale Used: No. 1207-111 (0.0083 per cent uranium)

Screen Analysis: Mesh Per Cent

+4	3
-50	13
-100	7
-325	3

Roasting Conditions: 1500 grams of raw shale roasted at temperatures indicated with an air flow of 20 liters/minute; 50-gram samples withdrawn at hourly intervals.

Leaching Conditions: 50-gram samples in 200 ml. of 2 per cent sulphuric acid for 3 hours at room temperature with agitation.

Roasting Temp., °F. (2)	Time of Roast, Hours											
	2			3			4			5		
	<u>Wt. Ratios</u>		Uranium Extracted, Per Cent	<u>Wt. Ratios</u>		Uranium Extracted, Per Cent	<u>Wt. Ratios</u>		Uranium Extracted, Per Cent	<u>Wt. Ratios</u>		Uranium Extracted, Per Cent
	<u>Fe</u> U	<u>Al</u> U		<u>Fe</u> U	<u>Al</u> U		<u>Fe</u> U	<u>Al</u> U		<u>Fe</u> U	<u>Al</u> U	
750							67	52	67			
795							66	73	68			
840	48	68	65	45	60	70	45	63	70	42	59	70
885							16	63	60			
930							7	30	67			

(1) Shale roasted in a single-hearth Herreshoff-type furnace heated by "Globar" elements.

(2) Temperature of furnace bed.

FIGURE 3. EFFECT OF ROASTING TEMPERATURE ON EXTRACTION OF URANIUM AND ON WEIGHT RATIOS OF ALUMINUM TO URANIUM IN TWO PER CENT SULPHURIC ACID LEACH SOLUTION

FIGURE 4 EFFECT OF ROASTING TEMPERATURE ON EXTRACTION OF URANIUM AND ON WEIGHT RATIOS OF IRON TO URANIUM IN TWO PER CENT SULPHURIC ACID LEACH SOLUTION

-30-

FIGURE 5. EFFECT OF ROASTING TIME ON WEIGHT RATIOS OF IRON AND ALUMINUM TO URANIUM IN TWO PER CENT SULPHURIC ACID LEACH SOLUTIONS

in all tests to date, the optimum roasting temperature can not be precisely fixed. The best estimate at present is that it lies in the range of 1000-1200°F. (540-650°C.) for a normal oxidizing roast as currently practiced.

Roasting in a Rotary Kiln

A 12-inch-diameter by 12-foot-length rotary kiln was secured and assembled; and preliminary test work on it has been conducted. The kiln is lined with a Corhart Electrocast lining, and small (1 inch) flights are integral parts of the lining refractories. The kiln is countercurrently gas fired, using a Maxon Premix burner. Some difficulty has been experienced in operating it at low demand rates.

Figure 6 is a schematic sketch of the rotary kiln as finally set up, also showing the location of thermocouples. Five thermocouple wells were inserted in the kiln proper, each extending about 1/2 inch beyond the refractory lining. Thermocouple jacks were utilized to permit spot readings as the kiln rotated. A sixth thermocouple was located in the stack to record stack gas temperatures. The pitch of the kiln was established at approximately 0.4 inch per foot, and all tests to date have been at this pitch.

The effects of temperature, particle size, and time of residence on the extraction of uranium and on capacity have been investigated in a qualitative way, but the interdependence of the principal variables has prevented the securing of precise data on the effects of the individual variables.

FIGURE 6. SCHEMATIC ELEVATION OF 12-INCH x 12-FOOT ROTARY KILN

It was discovered early in the work that the heat losses from the kiln were so great as to prevent maintenance of the desired temperatures over its length. To alleviate this condition, 3 inches of rock wool insulation was applied to the kiln and to the exit breeching. Although the improvement in temperature gradient gained in this way was considerable, the gradient was still greater than desired.

A technique has been devised to reduce this temperature gradient further and to include a greater portion of the kiln length within the desired temperature range. It consists essentially of overheating the feed end of the kiln, prior to commencing a run, to a temperature that provides earlier initiation of the exothermic reaction obtained in roasting shale. This results in a higher temperature over the middle portion of the kiln. As soon as this is obtained, the rate of gas input is reduced, thereby reducing the temperature of the firing end to within permissible limits. As long as raw shale is being introduced, this equilibrium can apparently be maintained. Such an equilibrium would probably be attained eventually with continuous operation; and the above method was primarily to attain it in the relatively short (8 to 12 hour) experimental runs.

A graphical plot of equilibrium temperatures is shown in Figure 7; Curve (3) illustrates the temperature gradient attained where the exothermic reaction is utilized to supply a portion of the heat in the middle of the kiln.

FIGURE 7. VARIATIONS IN TEMPERATURE OVER LENGTH OF 12-INCH x 12-FOOT ROTARY KILN

Examination of the temperature curves disclose that the shale is slow to reach the desired roasting temperature of 1000-1100°F. (540-595°C.) even when advantage is taken of the exothermic reaction. It would appear that only approximately 50 per cent of the length of the kiln is effective roasting length; further that about one-half of the time of residence of the shale within the kiln is devoted solely to heating up, without much roasting occurring.

Feed rates of from 8 to 17 pounds per hour have been employed, and maximum temperatures have been held in the range of 1000-1100°F. (540-595°C.). Residence times have ranged from 3 to 8 hours.

Preliminary analytical results of the rotary kiln experiments indicate that uranium extractions of from 55-65 per cent can be attained by leaching with dilute sulphuric acid after roasting under optimum conditions. The levels of uranium extraction attainable with the rotary kiln compare favorably with those obtained on the earlier Herreshoff and tube furnace tests. However, throughput rates have been lower than anticipated, due partially to the short effective roasting time, which it is hoped can be increased.

Data on the first series of tests are presented in Table 8. All of these tests were made with Shale No. 1090-4; recent ones have been on Shale No. 1207-113, but no data are presented on these in the absence of any analytical results. The first several runs were made with ore ground to approximately minus 4 mesh. It was observed that the larger particles were incompletely roasted, even when the finer particles appeared

TABLE 8. RESULTS OBTAINED ON ROASTING SHALE IN A 12-INCH BY 12-FOOT ROTARY KILN

Shale Used: No. 1090-4 (0.0061 per cent uranium)

Kiln Pitch: 0.4 in./ft.

Run No.	Shale Size	Rotation, R.P.M.	Approximate Residence Time, Hours	Average Temperature		Feed Rate, Lbs./Hr.	Uranium Extraction, Per Cent(1)	Visual Appearance of Roasted Shale
				#1 T.C.	#5 T.C.			
4244-1	-4M	0.33	3	1020	390	-	42	Incompletely roasted
4244-2	-4M	0.16	4	1105	550	8	30	Ditto
4244-5	-4M	0.16	4	1110	660	15.4	28	"
4244-8	-4M	0.15	5	1245	625	15.4	43	"
4244-9	-4M	0.15	5	1110	660	15.4	51	"
4244-10	-6M	0.16	5	1100	570	17.3	51	"
4244-12	-6M	0.16	5	1045	660	17.3	30-60	"
4244-13	-6M	0.12	5	1110	730	10.9	60.64	Completely roasted
4244-14	-6M	0.12	8	1075	645	10.9	62-67(2)	Ditto
4244-15	-6M	0.13	5.5	1045	660	12.1	49	Incompletely roasted
4244-16	-6M	0.16	4	970	735	14.7	60-67(2)	Completely roasted

(1) Fifty-gram samples leached in 200 ml. of 2 per cent sulphuric acid for 3 hours at room temperature. Extraction based on solution analysis only except as noted.

(2) Sixty-seven per cent extraction on basis of solution; 60 or 62 per cent on basis of uranium balance.

to be completely roasted. Accordingly, the plus 6-mesh portion of this shale was screened out and all subsequent tests were conducted on minus 6-mesh shale.

Both rate of feed and speed of rotation govern the time of residence and the depth of the shale bed within the kiln. Each of these was varied in an endeavor to obtain complete roasting in the minimum length of time. Due to the interdependence of the two variables, as well as to the fact that temperatures were not entirely reproducible, only tentative conclusions may be drawn at this time. On the basis of the preliminary results, it appears that shale can be roasted in approximately four hours where the temperature range is from 735-970°F. (390-520°C.).

It was frequently noted, during the course of an 8- to 12-hour test, that the first and last product to issue from the kiln appeared to be completely roasted, while that from the middle of the run often did not so appear. The presumption is that true equilibrium conditions existed only during the middle portion of the run, and more exact studies will necessitate either longer, or perhaps even continuous, operations.

The kiln is finding a valuable application in providing larger amounts of roasted shale for leaching and uranium recovery studies.

Recovery of Oxides of Sulphur from Roaster Gases. It has been assumed that a treatment process eventually developed on Chattanooga Shale will be self-sufficient in sulphur requirements for the leaching operation. The sulphur content of raw shale (generally above 6 per cent for shales of satisfactory uranium content) lends support to this assumption. Evidence

has been secured that, under the usual roasting conditions, the bulk of the sulphur is driven off during the roasting operation.

As a part of the rotary kiln studies, some attention is being given to the problem of sulphur recovery, also to the feasibility of the well-known autoxidation process for the production of dilute sulphuric acid from sulphur dioxide, as applied to shale roaster gases.

Equipment for determination of the sulphur dioxide and trioxide content of the stack gases from the rotary kiln is being assembled. Preliminary Orsat analyses have indicated that excess air is several hundred per cent greater than required, which connotes excessive dilution of the stack gases produced to date.

Several preliminary tests in which the roaster gases were absorbed in water, have been conducted, with rather disappointing results. The lowest pH values so far obtained have been 1.7-1.8, which is indicative of rather dilute (less than 1 per cent) acid, and also of inefficient absorption.

Roasting in a Fluidized Bed

Close contact has been maintained with the group in the Fuel Division which is investigating the various aspects of fuel recovery from shale by retorting and roasting in a fluidized bed. In the previous quarterly report (BMI-JDS-156) evidence was presented to indicate that this shale can be roasted by fluo-solids techniques although certain mechanical difficulties have been encountered. Either raw shale or previously retorted shale may be autogenously roasted, employing recycled roaster gases (enriched with either air or oxygen as the fluidizing medium.

Results to date on small-scale equipment have shown that a simple removal of combustibles (which can be done rapidly) is not sufficient to solubilize a high percentage of the uranium. The sulphating reaction is quite apparently a relatively slow one, and neither the batch or continuous fluidization roasts in small-scale equipment have provided the necessary reaction time. A two-stage continuous fluidization roaster, consisting of two reactors 4 inches in diameter and 24 inches long, is now being constructed to permit larger scale roasts and to provide longer residence times. It is being designed to have a capacity of 5 to 6 pounds of raw shale per hour and to provide an average roasting time of 2 to 3 hours. Provisions are being made to add air or oxygen between the stages.

Leaching Studies

Leaching work has usually been associated with roasting procedures in an attempt to secure a maximum recovery of uranium. As a result, the study of leaching variables has been made on a large number of roasts, which have been processed under a variety of conditions. To eliminate this variation in the roasted shale for this work, a 10-pound lot and a 50-pound lot of Shale No. 1207-111 were accumulated from various 3.3-pound samples roasted at a hearth temperature of 840°F. (450°C.) in a Herreshoff furnace. These two lots of roasted shale were thoroughly mixed by rolling and split to provide (1) a head sample and (2) samples for experimental work, which would be uniform in composition. In this way, the variables due to raw material and roasting conditions were reduced to a minimum.

Using this carefully prepared roasted shale, a series of experiments has been run using as leaching variables temperature, pulp density, particle size of the roasted ore, time, and acid concentration. The factors investigated were extraction of uranium and dissolution of contaminants, principally iron and aluminum.

Effect of Temperature

Carefully selected samples were prepared as described above and were leached with 2 per cent sulphuric acid at temperatures from 45°F. to 180°F. (7°C. to 82°C.). The results of these experiments are given in Table 9 and Figure 8. Examination of these data shows that the temperature of leaching had little effect on the extraction of uranium but had a large effect on the amount of contaminants dissolved. The ratio of iron and aluminum to uranium was doubled between 45°F. (7°C.) and 85°F. (29°C.) and was increased four-fold between 85°F. (29°C.) and 180°F. (82°C.). This makes a total increase of eight-fold over the range investigated, showing the importance of maintaining a low leaching temperature.

Since the process immediately preceding leaching is a roasting operation, it is apparent that methods of cooling the calcines will be important.

Effect of Pulp Density

It is necessary to know the optimum conditions and the effect of pulp density on the leaching step. Well-mixed samples of roasted shale were leached with 2 per cent sulphuric acid at pulp densities ranging from

TABLE 9. EFFECT OF TEMPERATURE ON THE LEACHING OF ROASTED SHALE

Shale Used: No. 1207-111 (0.0083 per cent uranium prior to roasting).

Roasting Conditions: Herreshoff roasted at a hearth temperature of 850°F. Samples from 10-pound lot, mixed by rolling.

Screen Analysis: Mesh	Per Cent
-4	100
-30	43
-200	15

Leaching Conditions: 100 grams of shale leached with 200 ml. of 2 per cent H_2SO_4 for 1/2 hour. Leach made in constant-temperature bath.

Temp., °F.	Final pH	Uranium Extracted		Total Uranium Found, mg./100 g. of Roasted Shale	Wt. Ratio of Contaminants to Uranium in Solution	
		mg./100 g. of Roasted Shale	Per Cent(1)		Al	Fe
45	0.9	5.4	57	9.6	7:1	15:1
65	0.9	5.5	50	11.0	11:1	20:1
85	1.0	5.6	55	10.2	16:1	27:1
140	1.7	6.0	59(2)	-	43:1	73:1
180	1.7	5.6	56	10.0	62:1	91:1

(1) Per cent extraction based on total uranium found in the extract and residue.

(2) Based on average of total uranium found in extracts and residues from other experiments in this series.

FIGURE 8. EFFECT OF LEACHING TEMPERATURE ON DISSOLUTION OF URANIUM, IRON, AND ALUMINUM FROM ROASTED SHALE NO. 1207-111 BY TWO PER CENT SULPHURIC ACID

1:1 to 1:20 (ratios of solid to solution) as shown in Table 10 and Figure 9. These data indicate that there may be a slight increase in uranium extraction down to a pulp density of about 1:5 when leaching for one-half hour. At pulp densities lower than this, although the uranium recovery did not change appreciably, the contaminant ratio increases. This may have been due, in part, to differences in pH. On the basis of this series of experiments, it appears that a pulp density of about 1:5 will give the maximum extraction of uranium. Additional work on other controlled lots of roasted shale must be done to confirm this result.

Effect of Particle Size

A series of runs was made to determine if there was a relation between particle size and the dissolution of uranium, iron, and aluminum. This work was divided into two parts, the one using the particles as delivered to the leaching unit, the other selecting a single range of particle size (minus 16 mesh and plus 30 mesh) of roasted shale and grinding this sample to produce the finer screen fractions. The latter work is incomplete and will be reported later.

The results of leaching various particle sizes of roasted shale with 2 per cent sulphuric acid are given in Table 11. Examination of these results shows that there may be a difference between the roasted shale which is coarser than 20 mesh and that finer than 20 mesh. No explanation for the low result for minus 325-mesh material can be offered at this time. The ball-milled sample, which contained all of the particle

TABLE 10. EFFECT OF PULP DENSITY ON THE LEACHING OF ROASTED SHALE

Shale Used: No. 1207-111 (0.0083 per cent uranium before roasting),

Roasting Conditions: Herreshoff roasted for 5 hours at a hearth temperature of 850°F. Sample from 10-pound lot well mixed by rolling.

Screen Analysis:	<u>Mesh</u>	<u>Per Cent</u>
	-4	100
	-30	43
	-200	15

Leaching Conditions: 100 grams of shale leached with 100 ml. of 2 per cent H_2SO_4 at 85°F. for 1/2 hour.

Wt. Ratio of Roasted Ore to Lixiviant	Final pH	<u>Uranium Extracted</u>		Total Uranium Found, mg./100 g. of Roasted Ore	<u>Wt. Ratio of Contaminants to Uranium in Solution</u>	
		mg./100 g. of Roasted Ore	Per Cent (1)		Al	Fe
1:1	1.1	4.9	54	9.2	20:1	11:1
1:2	0.9	6.5	57	11.3	19:1	12:1
1:3	1.0	6.2	57	11.0	23:1	16:1
1:5	0.9	5.7	62	9.2	23:1	18:1
1:10	0.7	6.4	62	10.2	26:1	21:1
1:20	0.7	5.9	63	9.4	29:1	25:1

(1) Per cent extraction based on total uranium found in the extract and residue.

FIGURE 9. EFFECT OF PULP DENSITY ON LEACHING OF ROASTED SHALE NO. 1207-111 WITH TWO PER CENT SULPHURIC ACID

TABLE 11. EFFECT OF PARTICLE SIZE OF ROASTED SHALE ON LEACHING

Shale Used: No. 1207-111 (0.0083 per cent uranium before roasting).

Roasting Conditions: Herreshoff roasted at a hearth temperature of 850°F. for 5 hours. Sample from 10-pound lot mixed by rolling.

Leaching Conditions: Roasted shale screened to particle size indicated. Indicated weight of ore leached with 200 ml. of 2 per cent H_2SO_4 for 2 hours at 85°F.

Shale Mesh Size ⁽¹⁾	Wt. of Shale, g.	Final pH	Uranium Extracted		Total Uranium Found, mg./100 g. of Roasted Shale	Wt. Ratio of Contaminants to Uranium in Solution	
			mg./100 g. of Roasted Shale	Per Cent ⁽²⁾		Al	Fe
-4 +10	91.5	0.8	5.7	59	9.7	35:1	24:1
-10 +20	100.0	0.9	6.1	61	10.0	36:1	24:1
-20 +65	100.0	0.9	6.7	68	9.9	34:1	23:1
-65 +100	40.6	0.9	6.4	64 ⁽³⁾	10.1	53:1 ⁽³⁾	47:1 ⁽³⁾
-100 +200	49.9	1.0	6.4	69 ⁽³⁾	9.4	46:1 ⁽³⁾	40:1 ⁽³⁾
-200 +325	28.6	0.9	-	-	-	43:1 ⁽³⁾	43:1 ⁽³⁾
-325	100.0	1.1	5.0	57	8.8	45:1	31:1
Ball Milled	100.0	1.7	6.4	71	9.1	73:1	30:1

(1) Tyler screen scale.

(2) Per cent extraction based on total uranium found in the extract and residue.

(3) Since the pulp densities of these leaches are different, the uranium extraction and the contaminant ratios may not be comparable to other values.

sizes of the original roasted shale and is largely minus 325 mesh, gave an exceptionally high extraction. Further work must be done to clarify these results.

Effect of Leaching Time and Acid Concentration

The results of the experimental work on the effect of time of leaching and acid concentration on roasted shale, have been inconsistent. This work is being continued and will be reported when the variations in the results have been reconciled.

Acid Treatment of Leach Residues

The residue from a leaching experiment was treated with various mineral acids. Roasted shale No. 1207-103A and B, which was used, had given poor extractions in normal leaching. A well-mixed portion of this residue was treated with 0.4N and 4.0N sulphuric, hydrochloric, and nitric acids at 85°F. (29°C.) and 180°F. (82°C.). The results, shown in Table 12, indicate that for the same acid strength, the mineral acids were of about equal efficiency in extracting the uranium present. The higher temperature, particularly with high acid concentration, gave the best recovery. Even with the 4N HNO_3 , only 35 per cent of the uranium in the residue was extracted, which gave a total recovery of 58 per cent for the two leaches. It does not appear that strong acid treatment of this roasted shale would increase the recovery of uranium above levels attainable with dilute acid on a well-roasted shale.

TABLE 12. ACID TREATMENT OF RESIDUE FROM SULPHURIC ACID LEACH OF SHALES NO. 1207-103A AND -103B

Shale Used: Residue from leaching roasted shale 1207-103A and B with 2 per cent H_2SO_4 . The uranium extraction of this ore was only 2.6 mg./100 g. and the uranium content of the residue was 4.8 mg./100 g. indicating a roasted head sample of 7.4 mg./100 g.

Leaching Conditions: 100 g. of leach residue was treated with 200 ml. of the indicated acid for 1/2 hour at the indicated temperature.

Lixiviant	Normality	Weight Per Cent	Leaching Temperature, °F.	Uranium Extraction, Per Cent(1)	Total Uranium Extraction, Per Cent(2)
H_2SO_4	0.4	2	85	8	41
H_2SO_4	0.4	2	180	17	46
H_2SO_4	4.0	18	85	10	42
H_2SO_4	4.0	18	180	29	54
HNO_3	0.4	2	85	10	42
HNO_3	0.4	2	180	15	45
HNO_3	4.0	23	85	14	44
HNO_3	4.0	23	180	35	58
HCl	0.4	2	85	9	42
HCl	0.4	2	180	17	46
HCl	4.0	14	85	13	43
HCl	4.0	14	180	29	54

See Page 49 for Footnotes.

TABLE 12. (CONTINUED)

Footnotes

- (1) Per cent extraction based on head analysis of 4.8 mg./100 g. for the residue from the initial leach.
- (2) Total per cent extraction includes both the initial extraction by 2 per cent H_2SO_4 and the extraction by the acid indicated in the table.

Filter Cake Washing Tests

A laboratory filtration experiment was run in order to learn something of the filtering characteristics of leach slurries. A 1:1 pulp-density slurry was made using dried leach residues and a 25 gram per liter sodium chloride solution. The chloride ion was titrated to indicate the washing efficiency. A six-inch-diameter laboratory filter disc was used as the filter plate.

The results of three experimental runs are shown in Table 13. With filter cakes of 1/8 inch in thickness, the water retention was about 37 per cent. After washing the cake twice, with water equivalent to 2/3 of the volume of the filtrate, the washing efficiency was found to be about 96 per cent, or about 80 per cent per wash. Washing efficiency of 80 per cent per stage of washing is a value which is frequently used in design work. It is realized that the use of dried residues and added electrolyte may have affected the results.

Using this 80 per cent value for washing efficiency, a filter with three stages of washing should recover over 99 per cent of the solution in the filter cake.

Filtration studies will be continued on a vacuum filter of test-plant size.

Recovery of Uranium from Sulphuric Acid Leach Solutions

Recovery by Precipitation at Controlled pH

An ammonia precipitation procedure has been selected to provide the primary precipitates required for the upgrading investigation.

TABLE 13. FILTERING CHARACTERISTICS OF A ROASTED SHALE SLURRY AS DETERMINED IN THE LABORATORY

Slurry Composition: A 1:1 mixture of dried leach residues and 25 g./l. NaCl solution.

	<u>Experiment Number</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Time of filter disc immersion, seconds	60	60	90
Filter cake thickness, inches	1/8	1/8	1/8+
Water in cake, per cent	36	37	38
Filtrate volume, ml.	67	66	86
First wash, ml.	40	20	43
Second wash, ml.	44	40	56
NaCl in cake, grams	0.56	0.47	0.62
NaCl in residue, grams	0.021	0.082	0.041
Washing efficiency, per cent	96	83	92
Washing efficiency per wash, per cent (calculated)	80	60	72

Essentially, it involves the procedure, previously described, consisting of reduction of the ferric iron with sulphur dioxide, digestion at 180-200°F. (80-95°C.) and precipitation with dilute (<3 per cent) ammonia to a pH of about 5.5. A high-temperature glass electrode has been secured and the ammonia precipitations are now performed hot. This latter modification promises more reproducible results, as well as improving slightly the physical character of the precipitate. It is planned to repeat some of the earlier work in order to secure comparable data on hot precipitation, as well as to investigate further the causes of some of the previous erratic results.

Upgrading of Primary Precipitate

Treatment of the primary precipitate from uranium leach solutions with caustic soda has shown some promise in removing aluminum from the primary precipitate. The highest uranium concentrations obtained in ignited residues from such treatment have been between two and three per cent, whereas the primary precipitate was in the 0.5-1.0 per cent range, initially. However, losses of uranium to the sodium hydroxide solution have been excessive and erratic, ranging from 10-43 per cent of the uranium originally present in the leach solution, as is shown in Table 14.

Examination of Tables 14 and 15, which present the data from the upgrading tests, indicates a considerable lack of uniformity with respect to the uranium left in the filtrate from the primary ammonia precipitation.

TABLE 14. SODIUM HYDROXIDE TREATMENT OF PRIMARY AMMONIA PRECIPITATES

Leach Solution No. (1)	Vol., ml.	pH Ammonia Pptn. (2)	Temp., °F.	Time, Hours	Vol. of Caustic Soln., ml.	Grams of NaOH	Ammonia Filt.	Caustic Filt.	Ignited Residue	Uranium Conc. in Ignited Residue, Per Cent	Total Uranium Found mg. %
4015-10	50	5.7	160-180	2-3	50	0.65	25	20	55	1.2	2.7 93
4015-10	50	5.9	Ditto	0.5	50	0.5	5	20	75	1.8	2.7 93
4015-10	50	5.9	"	1.0	50	0.5	4	43	53	1.4	2.6 89
4015-10	50	5.7	"	1.0	50	0.5	5	41	54	2.3	2.9 100
4015-10	50	6.3	"	1.0	50	0.5	1	29	70	1.6	2.8 97
4015-10	50	5.8	"	1.0	50	0.5	6	38	56	1.3	2.7 93
4015-42	50	5.8	"	1.0	75	1.5	2	10	88	2.2	12.9 96
4017-330	25	6.0	"	1.0	50	0.75	1	33	66	2.2	6.1 101
4017-330	25	6.0	"	1.0	50	0.5	11	20	69	2.8	5.6 93

(1) Analytical Data on Leach Solutions Used

Leach Soln. No.	mg. Per Liter			Weight Ratio		
	Uranium	Iron	Aluminum	Fe:U	Al:U	pH
4015-10	58	4,240	2,560	73:1	44:1	1.3
4015-42	270	20,500	20,500	76:1	37:1	1.2
4017-330	240	2,910	2,910	12:1	30:1	1.2

(2) pH measured before digestion of ammonia precipitate.

(3) Expressed as per cent of total uranium found.

TABLE 15. CARBONATE TREATMENT OF PRIMARY AMMONIA PRECIPITATES

Procedure: Fifty-ml. samples of leach solution 4015-10 (containing 2.9 mg. of uranium) were precipitated with ammonia and the precipitate was leached with 50 ml. of a 2 per cent solution of the indicated carbonate at the temperature shown.

<u>Ammonia Precipitation</u>			<u>Carbonate Leach</u>			<u>Uranium in Carbonate Filtrate</u>		<u>Uranium in Ignited Residue</u>			<u>Total Uranium Found</u>	
pH(1)	<u>Uranium in Filtrate</u>		Carb. Used	Time, Hours	Temp., °F.	mg.	Per Cent(2)	mg.	Per Cent of Total(2)	Conc. Per Cent	mg.	Per Cent
5.8	0.5	16	Na ₂ CO ₃	1	190-200	2.6	81	0.1	3	0.04	3.2	110
5.9	0.1	3	Na ₂ CO ₃	1	190-200	2.6	90	0.2	7	0.06	2.9	100
6.1	0.5	18	NaHCO ₃	16	60-70	0.2	7	2.1	75	0.55	2.8	97
5.9	0.2	7	(NH ₄) ₂ CO ₃	16	60-70	0.7	26	1.8	67	0.49	2.7	93

(1) pH measured before digestion of ammonia precipitate.

(2) Expressed as per cent of total uranium found.

More recent data indicate that these erratic results were caused by two principal factors: (1) a faulty pH meter and (2) the slowly attained equilibrium between the ammonia precipitate and the mother liquor. This latter factor results in apparent pH values higher than the ultimately reached values. Similar drifts in pH have been observed in the work on carnotites (see Report BMI-JDS-160, December 31, 1948). In one test made to investigate this phenomenon, a leach solution neutralized to an apparent pH of 6.2 at 85°F. (29°C.) dropped to a pH of 4.9 after a one-hour digestion at 160°F. (71°C.). As noted earlier, it is believed that hot precipitation will largely overcome this difficulty and will produce more consistent and reproducible results. Interpretation of the results of the various secondary treatment tests described in this report is quite difficult when the results of the primary precipitations are obviously erratic.

Preliminary results on removal of uranium from the primary precipitate with carbonate solutions are shown in Table 15. A 2-per cent solution of carbonate appeared to be quite effective, removing from 80 to 90 per cent of the uranium when contacted with the precipitate for one hour at 190-195°F. (90°C.). Two per cent solutions of ammonium carbonate and sodium bicarbonate (at room temperature) dissolved only a little uranium, even with a leaching time of 16 hours.

Metal balances for both series of experiments were fairly good, ranging from 89 to 110 per cent. The average of all of the values shown in Tables 14 and 15 is 96 per cent of the uranium entering, on the basis of the head analyses.

The carbonates appear to offer considerable promise, and intensive effort is planned on their use. The minimum quantities and concentrations required for effective uranium removal remain to be determined. The possibility of increasing the uranium removal by means of stronger solutions, or by countercurrent leaching, also merits further investigation; as does the use of pressure leaching, at least in the case of ammonium carbonate.

Bloating of Leached Shale*

With the object of developing a possible market for leached shale residues several preliminary bloating tests were carried out. In bloating, gases developed during heating are entrapped, forming cells which increase the insulating properties of the material.

Bloating tests were conducted on residues from several leaching experiments on roasted shale. Five-gram samples were weighed out in Alundum boats and heated to temperatures of 2250°F., 2300°F., 2350°F., 2400°F., and 2450°F. in a platinum-wound, resistance-tube furnace. The rate of temperature rise was about 500°F. per hour. Bloating occurred between 2300°F. (1260°C.) and 2450°F. (1345°C.), with the most pronounced bloating taking place between 2350°F. (1290°C.) and 2450°F. (1345°C.).

* This work was carried out by E. R. Hunt and A. E. Pavlish.

PLANS FOR FUTURE WORK

The investigation on the rotary kiln is to be continued, with particular attention devoted to increasing the capacity and to a more exact evaluation of the variables affecting the operation of the kiln. Demands of the leaching and recovery studies for increasingly larger quantities of roasted shale will probably necessitate placing the kiln operations on a practically continuous basis during certain periods. In connection with the rotary kiln, some attention will be devoted to the problem of recovery of sulphur oxides from the roaster gases, and to the problem of conversion of these gases to sulphuric acid.

Fluo-solids retorting and roasting studies will be continued in order to obtain a definitive answer as to whether this process is adaptable to shale.

The leaching investigation will seek to clarify some of the anomalies and inconsistent results of the current tests; and subsequent to this, to extend the tests to other samples of roasted shale. The possibility of a leach-roast-leach procedure to improve over-all uranium extraction is to be investigated further, as several preliminary tests have indicated possibilities in this direction.

Uranium enrichment of the sulphuric acid leach solutions is scheduled to receive additional attention, particularly as regards the problem of contaminant ratios in such enriched solutions. Much of this work may fit in with the preparation of the enriched leach solutions required for the recovery studies. Efforts will be made to scale up

the leaching operation; in this connection, a test-plant-size, continuous, drum-type, vacuum filter will be used.

The primary ammonia precipitation is to be investigated further in order to define more exactly the variables affecting this precipitation and to make possible more reproducible results. It is expected that the use of lime and magnesia will also be investigated in this connection.

The various methods of secondary treatment of the primary uranium precipitate, particularly those involving carbonates, will be intensively investigated to determine the limits of upgrading that may be accomplished with these methods.

Notebook References

<u>Book No.</u>	<u>Pages</u>
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3754	55-56, 60-68
3859	60-61
4015	8-82
4017	31-76
4094	33-70
4118	1-8
4188	4-8
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Quarterly Report

Contract No. AT-30-1-Gen-202

SECTION II

IDENTIFICATION OF THE MODE OF OCCURRENCE
OF URANIUM IN SHALES

(H. R. Nelson, Supervisor)

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March 15, 1949

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IDENTIFICATION OF THE MODE OF OCCURRENCE
OF URANIUM IN SHALES

Work has been started on identification of the mode of occurrence of uranium in shale. The initial part of the investigation, now in progress, is the concentration of the various mineral phases of the shale. These include pyrite, clay, quartz, and organic matter. The new 10-ton lot of black Tennessee shale from the Sligo adit, BMI No. 1207-117 (USGS No. LC-201-113), has been selected for major study and a representative sample, 700-800 lbs., was obtained thereof. A cut of this sample has been sent to the USGS laboratory in Washington. Samples were also selected for petrographic study to aid in the choice of means for concentrating the various phases.

Preliminary fractionation by Infrasizing and flotation work is now in progress. It appears that there is some liberation of the mineral phases in the Infrasizer cone 5 cut. The average particle size of this fraction is about 20 to 30 microns. All flotation and fractionation work is being followed by petrographic study.

Concentrates of the various phases, when obtained, will be analyzed chemically and studied by means of X-ray diffraction for identification. Phases whose chemical analyses show an increased concentration of uranium will then be studied by physico-chemical methods to determine possible modes of occurrence of the uranium.

Knowledge of the mode of occurrence of the uranium should be of value in directing the course of the extraction studies toward more complete removal of the uranium from the shale.

The technique of thermal analysis can be applied to minerals or materials which undergo some transformation as they are heated. This transformation may be the loss of water, decomposition, or an actual change in crystal structure. Changes are detected by a differential thermocouple.⁽¹⁾ One bead of the thermocouple is inserted in an inert material which does not show an exothermic or endothermic reaction in the temperature range under test. At a constant heating rate, any reaction in the sample in which heat is evolved or absorbed will be evidenced as a reading on the differential thermocouple. This technique should be of use in identifying the constituents of the shales under study.

Results have been obtained on three different shale samples. Sample 1207-113 was a portion of head sample from the 5-ton lot, Sample 4017-473 was a portion of 1090-4 ore, while Sample 4188-9 was the same as the preceding one except that it had been calcined for 15 hours at 700°F. (370°C.), 1-1/2 hours at 800°F. (430°C.), and 1-1/2 hours at 900°F. (480°C.).

Figure 10 shows that the two raw shale samples show endothermic reactions near 1050°F. (565°C.) and 1475°F. (800°C.). The exothermic peak at the initial portion of the curves is thought to be from combustion

(1) Multiple Differential Thermal Analysis, Paul F. Kerr and J. L. Kulp, Am. Mineralogist 33, 387 (1948)

FIGURE 10. THERMAL ANALYSIS RESULTS FOR SHALES AND VARIOUS MINERALS

of organic material in the shale. The endothermic reactions mentioned above have not yet been identified as to shale constituent. Figure 10 includes curves for halloysite, montmorillonite, quartz, and beidellite as taken from the literature.⁽¹⁾⁽²⁾ Halloysite and quartz show minima at 1090°F. (590°C.) which is near that for the shale at 1050°F. (565°C.), but further work with pure constituents should be done before definite conclusions are drawn. It is interesting that this reaction is absent in the calcined sample. The high-temperature reaction at 1475°F. (800°C.) is still evident after the calcining.

(1) See preceding page.

(2) Differential Thermal Method for Identification of Clay Minerals, F. H. Norton, J. Am. Ceramic Soc. 22, 54 (1949).

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Section III

Recovery of Fuel Values from Oil Shale

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March 15, 1949

SECTION III
RECOVERY OF FUEL VALUES FROM OIL SHALE

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SECTION III

RECOVERY OF FUEL VALUES FROM OIL SHALE

INTRODUCTION

This phase of the research program in progress at Battelle is concerned with the development of economic processes for the recovery of fuel values from Chattanooga shale, which has a carbon content of the order of 15-20 per cent, and therefore has some potential fuel value. This section reviews progress on the problem of fuel recovery from the beginning of active work through March 15, 1949. Emphasis of the program is on an engineering study of the application of known processes to this shale, in the interest of obtaining a practical solution as rapidly as possible. Concurrently, however, a program of research into the fundamental structure and chemical properties of the organic material in the shale is also being conducted, with the expectation that the basic information obtained will be of value in understanding and improving the procedures developed in the engineering study. Part I of this section deals with the investigation of the methods of fuel recovery, and only discusses the chemical and other characteristics of the shale insofar as these properties seem to be immediately pertinent in the selection and development of a practical fuel recovery process. Part II of this section describes the fundamental studies, discussing the chemical and physical properties of the shale which are known, and the methods being used in obtaining further information.

PART I. ENGINEERING STUDIES OF RECOVERY OF FUEL VALUES FROM OIL SHALE

SUMMARY

The engineering research planned, or in progress, to develop processes for fuel recovery deals with three basic operations, (1) distillation, to convert the solid kerogen in the shale to oil and gas, (2) chemical reaction of the carbon with steam, to produce "water gas", and (3) direct combustion of carbonaceous residues to recover useful energy in the form of heat.

Recovery of fuel values must be accomplished with the limitation that the shale cannot be subjected to a temperature above approximately 600°C. (1100°F.) without interfering with subsequent uranium extraction. The fluidized bed has been adopted as the means of carrying out these three types of processes, distillation, gasification, and combustion, principally because the fluid-solids system has been shown in other industrial operations to be capable of producing high rates of heat transfer and chemical reaction with remarkably good temperature control, and thus, the limitation on maximum temperature can be observed easily. Operations are being conducted in both bench-scale and pilot-scale units.

A number of bench-scale tests have been completed. They indicate that approximately 45 per cent of the carbon in the shale can be removed by distillation at temperatures safely below the limit for optimum uranium recovery. The most economical time-temperature combination for distillation has not yet been determined, and is the immediate objective

of further bench-scale work. Likewise, the bench-scale work indicates that the carbon can be burned off completely within the safe temperature limits, but a more complete time-temperature pattern is needed here also.

Gasification through reaction with steam or carbon dioxide to produce a mobile fuel does not appear to be a very hopeful possibility because a temperature above the allowable maximum is normally required to produce an appreciable rate of reaction. Bench-scale tests will, nevertheless, be made.

The pilot-scale unit has been built to obtain engineering data on the operations which look promising in the small bench unit. The equipment is designed for continuous-process operation with complete collection of products, and is instrumented to give rather complete data on flow of materials to and from the column, and process conditions of temperature and pressure, with the intention that the data can be projected to plant requirements.

The first series of tests in the pilot-scale unit have investigated distillation of the shale at 538°C (1000°F.) in an atmosphere of steam. Operation has been repeatedly halted by formation of extremely dense cakes of ore and condensate, and complete material balances have not yet been obtained. One operation did, however, produce gas which, when scrubbed free of CO₂, would have a heating value of approximately 830 Btu per cubic foot. This will, of course, be a product of commercial value if continuous operation produces it in appreciable volume.

Operations in the engineering study will be continued at both the bench and pilot levels. Hypothetical plant layouts are being drawn up on the basis of the bench-scale results already obtained, and equipment requirements and capacity will be specified as rapidly as experimental data are obtained.

PROBLEMS RELATED TO RECOVERY OF FUEL VALUES FROM OIL SHALE

The organic carbon and hydrogen present in oil shale are combined in the form of a substance known as kerogen. Kerogen is somewhat analogous to the carbonaceous matter of bituminous coal, in that it appears to be a complex mixture consisting principally of hydrocarbons of unknown individual composition and structure. Like the carbonaceous content of coal, kerogen exists as a solid material, which is irreversibly decomposed by the application of heat into a mixture of gases, liquids, and a carbonaceous residue. Utilization of the organic material in the shale as a fuel is made possible by means of four general methods of recovery, which are (1) solvent extraction, (2) gasification by chemical reaction to form combustible products, (3) destructive distillation, and (4) direct combustion to release heat energy.

The economic recovery of a large proportion of the organic material by solvent extraction does not at present appear promising, and primary consideration is being given in the present study to the latter

three methods. Final selection of any one, or of some combination, of the three methods must be based not only on the amounts of fuel and heat energy obtainable, but also on the necessity of leaving the shale residue in the optimum condition for subsequent recovery of the uranium content. Two requirements for optimum uranium recovery are tentatively recognized: (1) The shale residue should preferably be devoid of carbon deposited in the inorganic matrix, and of any oily residue on the surface, which might interfere with leaching by dilute acid solutions. (2) Any fuel recovery procedure must not permit the shale to reach a temperature exceeding approximately 600°C. (1100°F.).

As soon as methods of uranium recovery are definitely established, and procedures for fuel recovery concordant with the established methods are developed, then the selection of an integrated process for fuel recovery can be made on economic grounds. The collection of experimental data on fuel recovery processes, and the economic analysis of these data, are the objectives of the engineering research described in this section.

Selection of Fuel Recovery Methods for Experimental Investigation

The four general methods which might be applied in the recovery of fuel values have already been listed. The advantages and disadvantages of each method were evaluated prior to the inauguration of experimental work, as outlined in the following paragraphs.

Solvent extraction can be carried out below the maximum temperature limitation set by the necessity for maximum uranium recovery. However, as will be shown in the part of this section on fundamental investigations, solvent extraction of the kerogen has produced very low yields, reflecting unfavorably on the practicality of the process. Also, solvent extraction is almost certain to leave the shale soaked with an oily material, which would be detrimental to the later recovery of uranium compounds by leaching with water solutions. There is the possibility of removing this oily residue by burning, but this would in turn impose an additional step on the process. Unless some major improvement in solvent-extraction yields should develop, it appears unlikely that this method will be applicable.

Destructive distillation is a promising procedure for fuel recovery. An assay of the shale, by the standard laboratory method developed at the Bureau of Mines, shows that a portion of the kerogen is converted to oily products. Another part of the kerogen remains as "fixed carbon" in the shale, and the objective of research on distillation is to determine the conditions under which the largest proportion of the kerogen is converted to desirable liquid and gaseous products.

Gasification by chemical reaction must convert the carbon of the kerogen into either hydrocarbons or carbon monoxide, if combustible products are to be obtained. The production of hydrocarbons requires hydrogenation, and the production of hydrogen for use in the process is

a major technical and economic problem, involving usually the generation of water gas. Water gas must then be subjected to the "water gas shift" reaction, $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$, followed by scrubbing out of the carbon dioxide to leave the desired hydrogen. The integrated process, including the final hydrogenation step, would require a heavy capital investment, and it appears unlikely that it will prove of interest unless the technology of uranium production should dictate otherwise.

Production of carbon monoxide from the carbon in the shale could be done directly by oxidation either with carbon dioxide or with steam. Either of these methods would be quite adaptable were it not for the limitation against temperature exceeding 600°C . (1100°F .). It appears likely that the rate of the oxidation reaction would be uneconomically slow at this temperature, although checks will be made in each case by bench-scale test.

Combustion of the raw shale or of the carbonaceous residue in the shale after retorting, using either air or oxygen, appears feasible, but the process must be limited to the maximum temperature of 600°C . (1100°F .), and the resulting heat energy will be of relatively low potential. The problem becomes one of restraining the rate of the reaction or of dissipating the evolved heat so rapidly that the temperature of the shale does not exceed the maximum limit.

A fluidized reaction bed has been selected as the most promising means of carrying out the recovery operations discussed above. In such a bed, the shale particles are suspended in an upward-flowing stream of gas, whose velocity is adjusted to maintain the particles in suspension but to minimize entrainment and carry-over. Temperatures within the bed are uniform and can be controlled with precision. Because of the intimate mixing obtained by the "boiling" action, rates of chemical reaction and of heat transfer are high. The raw shale must be crushed or ground, and sized, but such an operation must be carried out prior to the water leach in any event, and therefore the fuel recovery process should not be charged with the entire expense of preparation. Large amounts of shale can be handled and transported economically in the fluidized state. This method has been investigated for oil recovery from other shales on a pilot-plant scale¹.

EXPERIMENTAL WORK

Experimental work is being conducted in two fluidizing columns, with the first emphasis being placed on destructive distillation of the shale to produce oily products. One column is as small as can be conveniently built while still maintaining proper conditions for fluidization; it is used for exploratory studies and treats the shale in batches of one to two pounds. For convenience, these are termed bench-scale tests. The

¹References at end of Part I, Section III.

other column is designed for continuous processing of shale on a pilot-plant scale, although it can, of course, be used for batch treatments if desired.

Bench-Scale Equipment

The initial experiments were conducted in an electrically heated Pyrex glass column, three inches in diameter and 48 inches high. Observation slots were provided to permit examination of the fluidized bed, and means were available for measuring the internal temperature and the approximate rate of flow of the fluidizing medium. Although several tests were completed successfully, frequent breakage of the glass column occurred. A steel bench-scale column, 4 inches in diameter, is being constructed, which will be equipped with viewing ports, and means for measurement and control of temperature, pressure, and flow of fluidizing gases.

Bench-Scale Tests

Table 16 shows the size distribution of the ground shale used in bench-scale tests. Table 17 presents the experimental results. Uranium extractions were determined by leaching the shale with dilute sulphuric acid after roasting in a tube furnace.

TABLE 16. SCREEN ANALYSIS OF SHALE¹

	Runs Nos. 1 and 2	Runs Nos. 3 and 4
	Per Cent	
On 16	3.0	0.0
30	28.3	0.0
50	32.8	70.0
80	16.4	30.0
100	5.8	0.0
140	8.0	0.0
200	3.2	0.0
Past 200	2.4	0.0
Total	100.0	100.0

1. Battelle Sample No. 1090-4.

TABLE 17. BENCH-SCALE TREATMENT OF SHALE IN A FLUIDIZED BED
Conditions and Effects of Treatment^{1,2}

	Material				
	Original Sample	Samples After Test Runs			
		Test 1	Test 2	Test 3	Test 4
Pretreatment	-	-	Fluidized in steam for 30 minutes at 800°F.		
<u>Fluidized test conditions</u>					
Fluidizing medium	-	Steam	Steam	Air and Steam	Air
Test duration, min.	-	30	20	63	45
Bed temperature, °F.	-	800	1100	1100	To 1585 (avg.1350)
Steam flow rate, lb per sq ft per hr,	-	-	43.2	-	-
and feet per second	-	-	0.76	-	-
<u>Analysis of treated samples</u>					
Total carbon	14.6	8.3	8.0	0.3	0.1
Total sulfur	4.8	4.7	2.2	0.3	0.3
Pyritic sulfur	3.7	3.7	0.7	0.05	0.05
Loss on ignition	22.0	15.8	12.8	2.3	1.1
Uranium yield, by extraction, per cent	58	64	54	44	23

1. Battelle Sample No. 1090-4.

2. Batch weight, one pound for each test.

Test 1 was a treatment by fluidization in steam at 430°C. (800°F.) for 30 minutes, which resulted in a reduction of total carbon from 14.6 to 8.3 per cent, no change in the sulfur content, and a reduction of the loss on ignition of the treated sample from 22 to 16 per cent.

In view of the small reduction in carbon content achieved in Test 1, each succeeding test was preceded by a pretreatment which was a duplication of Test 1. In Test 2, the sample was fluidized in steam at 600°C. (1100°F.) for 20 minutes. Here again carbon loss was moderate, but the sulfur content of the shale, particularly the pyritic sulfur, was sharply reduced. In Test 3, likewise made at 600°C. (1100°F.), air was added to the fluidizing steam in an amount sufficient to release enough heat of combustion from the shale to maintain the bed and column at the temperature of 600°C. (1100°F.). This was continued until the temperature of the bed fell steadily even with increasing amounts of air, which required a period of 63 minutes in addition to the 30 minutes of steam pretreatment. This test resulted in almost complete removal of combustible material from the shale as shown by the determinations for carbon, sulfur, and the loss on ignition at the treated sample. Recovery of the uranium after this treatment, 44 per cent, was appreciably lower than in the tests using steam alone as the fluidizing medium. In Test 4, air alone was used as the fluidizing medium after the 30-minute pretreatment in steam, and the temperature of the bed was allowed to rise with

the only control being that a steady amount of air was supplied to keep the bed in a uniform state of fluidization. The temperature rose to 863°C. (1585°F.), and complete removal of combustible matter was attained in 45 minutes. The uranium recovery fell to 23 per cent, which supports the tentative conclusion that 600°C. (1100°F.) is the maximum temperature to which the uranium-bearing shale can safely be preheated without adversely affecting recovery of the uranium.

Interpretation of the Bench-Scale Data

Comparison of Tests 1 and 2 shows that increasing the bed temperature from 425°C. to 600°C. (800°F. to 1100°F.) and increasing the total time of treatment when fluidizing in superheated steam did not increase significantly the extent of carbon removal from the shale. This implies that as much carbonaceous fuel can be recovered in the form of gas and oil at 425°C. (800°F.) as at 600°C. (1100°F.), and in fact, suggests that the optimum distillation can be achieved with both lower temperatures and shorter residence time, both of which are highly desirable from the viewpoint of process economics. Some further bench-scale testing will, therefore, be devoted to finding the minimum process requirements for recovering the maximum amount of distillation products. Calculation has also shown that Tests 1 and 2 both removed approximately 45 per cent of the carbon, whereas the standard Fischer Assay method of evaluating oils by a distillation in laboratory scale equipment removes

as a maximum only about 30 per cent of the carbon. The Fischer Assay method involves heating the shale from room temperature to 482°C. (900°F.) slowly and steadily over a period of 40 minutes, while in these bench-scale tests the shale was heated quite rapidly by being dropped directly into the fluidizing column. This suggests possible increases in the oil and gas yields through what might be called "flash" distillation, or rapid passage through a column operating at an even higher temperature than has previously been considered allowable. This procedure will also be investigated in connection with the tests for optimum temperature and residence time in distillation.

A further indication from these tests is, of course, that more drastic treatment than distillation in steam must be adopted if carbon removal is to be complete. Controlled combustion and gasification by reaction with steam will be studied as soon as the new steel column is in operation.

Test 3 shows that controlled combustion is technically feasible in that all of the carbon was burned out of the ore at a temperature of 600°C. (1100°F.). This complete removal required approximately one hour for the one-pound batch sample, but it is believed that a higher rate of combustion could be allowed in a steady-flow operation where a portion of the heat released could be absorbed in heating freshly added shale. The problem of controlled combustion will receive further attention in early tests in both the bench- and pilot-scale columns. The temperature

at which controlled combustion can be conducted apparently must also be reviewed, as the uranium recovery after this one test fell to 44 per cent.

Test 4 is of particular interest because it shows the result of allowing combustion to go on without restraint in the bed of fluidized shale. The only controlled condition was that a steady air flow sufficient for smooth fluidization was maintained, and the temperature reached a level well above the permissible maximum. Consequently, the uranium extraction fell to 23 per cent.

Comparison of the results of tests such as 3 and 4 may provide information on what features of the system control the combustion which takes place. Each shale sample contained 0.08 lb. of carbon at the start of combustion. The air rate in each test averaged 0.34 feet per second. At this linear rate of flow in a tube of approximately 2.8 inches inside diameter, 0.00925 mol of oxygen passed through the tube per hour. The rate of carbon combustion, on the assumption that there was 0.08 lb. carbon to be removed, was $\frac{0.08}{12} \times \frac{60}{63} = 0.0063$ mol per hour during the 63-minute run. Inasmuch as carbon and oxygen combine mol for mol in the combustion process, an average excess of 50 per cent of oxygen was available for combustion; therefore, the combustion was not smothered for lack of oxygen in the fluidizing atmosphere.

Another indication of interest can be obtained by comparing the apparent rates of combustion at the different temperatures of Runs 3 and 4. Approximately the same amount of carbon was burned in the two

tests, and since this operation required 63 minutes in Test 3 and only 45 minutes in Test 4, it can be said that the rate of combustion in Test 4 was $63/45 = 1.4$ times that of Test 3.

The average temperature of the bed in Test 4 approximated 730°C. (1350°F.). If the rate of reaction were controlled by the rates of diffusion of gases, the rate might be expected to increase with the square root of the temperature, which would indicate that the rate in Test 4 should have been $(1350/1100)^{1/2} = 1.12$ times that of Test 3. The actual ratio of rates was 1.4, as shown above. This agreement is not sufficiently close to allow a conclusion on whether the rate of diffusion of oxygen to the carbon surface or the rate of reaction at the surface is the rate-controlling step. However, the temperature is falling into a range in which reaction rate may well control. This question may be of direct importance in selection of a combustion gas from oxygen, air, or some other mixture of oxygen and nitrogen, and the results from future tests will be analyzed carefully with this possibility in mind.

PILOT-SCALE STUDIES

Pilot-Scale Equipment

Construction of a pilot-scale unit has been carried on concurrently with the bench-scale studies. Figure 11 is a photograph of the unit when near completion, and Figure 12 is a schematic diagram of the system.

FIGURE 11. PILOT-SCALE EQUIPMENT FOR RECOVERY OF SHALE OIL FROM A FLUIDIZED BED

FIGURE 12. SCHEMATIC DIAGRAM OF PILOT-SCALE UNIT FOR TREATMENT OF SHALE IN FLUIDIZED BED

The pilot-scale column proper is a section of 6-inch pipe, 10 feet in length, topped by a disengaging section one foot in diameter, in which a portion of the fines carried by the column effluent are dropped out.

The column is wound with resistance-wire heating elements, and is pierced at frequent intervals for pressure taps, thermocouple insertions, and for direct observation of the bed. Fresh shale is fed continuously to the column from the hopper at the left of Figure 12, and the spent shale is withdrawn at the same rate through the draw-off standpipe, allowing continuous operation of the column. The fluidizing medium enters at the bottom of the column, and passes upward through the mass of crushed shale, which it maintains in the characteristic boiling motion of the fluidized bed. The fluidizing medium plus distillation or decomposition products from the shale pass out through the top of the column and through the auxiliary units for separation into the various components. Fines carried from the disengaging section are separated from the gas-vapor stream in the cyclone separators. The gas-vapor mixture then passes to the jacketed "hot" condenser, the temperature of which will be controlled to obtain separation of higher boiling oils. The "cold" condenser will be water cooled and is expected to remove the lower boiling oils and the steam, while noncondensable gases will pass to the gas holder.

Preliminary Tests of Pilot-Scale Equipment

Shakedown tests of the pilot-scale equipment showed that good fluidization of the bed of crushed shale could be maintained in an atmosphere of superheated steam supplied at the rate indicated by the bench-scale test: 43 pounds of steam per square foot per hour, with a linear velocity of approximately 0.8 feet per second. Plugging of the feeding system by shale and condensed steam blocked first attempts at steady operation. Equipment is being installed to allow use of either nitrogen or recycled shale gas as the fluidizing medium to obtain data on the type and amounts of oils and gases which can be produced by distillation. The use of steam as the fluidizing medium for the retorting operation has the advantage that there will not be dilution of the gaseous products, and it may be attempted again after the more urgent work of establishing operation and producing the first fuel products for study is accomplished.

Operation in the tests was not sufficiently prolonged to produce oil for measurement or analysis, but the gas holder was filled with a mixture with the average composition.

<u>Gas</u>	<u>Per Cent</u>
Acid gases*	44.0
Carbon monoxide	6.2
Illuminants	2.0
Hydrogen	10.8
Methane	19.7
Oxygen	4.0
Nitrogen	13.3
	<u>100.0</u>

*Gases absorbed in strong caustic solution; carbon dioxide, sulfur dioxide, hydrogen sulfide.

This preliminary analysis shows a calculated heating value of approximately 320 Btu per cubic foot "as collected". If the acid gases were removed by scrubbing, and the oxygen and nitrogen were eliminated through prevention of air leakage, the heating value would approximate 830 Btu per cubic foot. Such a product in appreciable volume would, of course, be a good gaseous fuel.

FUTURE WORK

Work will be continued on the distillation of the shale and the combustion of residual carbon as indicated in the body of the section.

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PART II. STUDIES OF THE FUNDAMENTAL PROPERTIES OF OIL SHALE

INTRODUCTION

It has been stated that the fluidized retorting of oil shale in an atmosphere of steam, air, or inert gas appears to be the method most immediately and easily applicable to the recovery of a portion of the fuel values from Chattanooga oil shale. The work described in Part I of this section was accordingly initiated to collect the engineering information necessary for estimates of costs and for selection of optimum conditions of operation. A considerable portion of the planning for the engineering phases of the research has been based upon the probability of certain similarities between the Chattanooga shale and the Green River shale of Colorado. This has been necessary because of the scarcity of information on the properties of the organic matter in Chattanooga shale. Fortunately the activities of the Bureau of Mines with respect to the exploitation of Green River shale in recent years have provided much information of potential value, and their continued program can be expected to provide much additional data¹.

Nevertheless, there are certain evident differences between the two shales, which make it advisable that the fundamental properties of the organic content of Chattanooga shale be studied, both to determine

¹References at end of Part II, Section III.

the basis for these differences, and to indicate wherein the two shales are similar. As soon as similarities are established, large bodies of Bureau of Mines data will become available for study in relation to the Chattanooga shale, and much laboratory work may be avoided. A precise delineation of differences between the two shales with reference to their fuel values may also point the way to novel methods of treatment for the recovery of liquid fuels, which will be of economic interest.

The nature of the problem dictates that these fundamental studies shall be of exploratory nature for some time, until sufficient background is obtained on the nature and characteristics of the organic content of Chattanooga shale. Of present interest are a number of general fields in which information will be sought. These include a study of the manner in which the organic material of the shale, known as kerogen, is laid down in the inorganic matrix, the rate and extent of conversion of the kerogen to soluble bitumens by heating to various temperatures, the mode and extent of decomposition of the bitumens to form liquid and gaseous products at higher temperatures, and the composition of the resulting products. The following sections review the work in progress and discuss the future program.

SUMMARY

Seeking information as to the physical and chemical "make-up" of the shale, various types of investigations have been carried out.

Demineralization of the shale with hydrofluoric acid and hydrochloric acid has successfully reduced the ash content from 78.2 per cent ash to 29.2 per cent ash. Analysis of the kerogen obtained from this demineralization substantiates the belief that the inorganic material remaining in the kerogen is iron pyrites. Attempts at a gravity separation of the pyrites from the kerogen failed. Microscopic study of the kerogen shows the inorganic material to be "locked" with the organic constituents and a sink-float separation would be almost impossible.

Chlorination of the shale produced mixtures of sulfur chlorides rather than the anticipated liquid organic chlorides useful as solvents for the organic components of the shale.

Chattanooga shale has been subjected to heat treatment for various periods of time in an effort to determine optimum conditions for the conversion of the organic constituents of the shale into bitumen. Carbon tetrachloride solutions of the bitumen extracts have been analyzed chromatographically and spectrophotometrically, in an attempt to isolate the components of the bitumen and determine their structure. As yet, no conclusive results have been obtained from the chromatography experiments, but they will be continued and it is believed that definite results will be obtained soon.

SHALE COMPOSITION

All the tests reported in Part II were conducted on samples of shale from Lot S-100-46 of the U.S.G.S. which has been given the Battelle designation 1090-4. Ultimate analyses of this lot have been reported previously, but are repeated here for convenience.

Inorganic Analysis

	<u>Per Cent</u>
L.O.I.	22.0
SiO ₂	48.6
Na ₂ O-K ₂ O	3.4
CaO	0.21
Al ₂ O ₃	10.4
MgO	0.78
Fe ₂ O ₃	9.86
S	5.3
P ₂ O ₅	0.27
CO ₂	0.1

Organic Analysis

	<u>Per Cent</u>
Carbon	14.6
Hydrogen	1.8
Nitrogen	0.41

By means of the modified Fischer assay developed by the Bureau of Mines, it was determined that the yield of liquid products for this sample was 9.6 gallons per ton of ore, and the yield of water was 7.2 gallons per ton. The loss in weight of the shale on retorting minus the weight of recovered oil and water gives a value reported as 'weight of gas plus loss'. The gas plus loss of Chattanooga shale sample 1090-4 was determined to be 4.2 per cent.

There are several methods of determining the organic content of oil shale. In certain cases, the Bureau of Mines reports the organic

content equal to the loss on ignition minus carbon dioxide and water. This method gives a value of approximately 19 per cent for Chattanooga shale. However, in the heat treatment studies reported later, the percentage of organic matter in shale is given by Maier and Zimmerly² of the University of Utah as the total percentage of carbon and hydrogen present. In comparing the results obtained by heat treatment of Chattanooga shale with those obtained by Maier and Zimmerly, this method of calculating organic content is used. The ultimate analyses of Chattanooga shale gives 14.6 per cent carbon and 1.8 per cent hydrogen or a total of 16.4 per cent organic matter.

COMPARISON OF CHATTANOOGA SHALE WITH COLORADO SHALE

The most significant difference between the Chattanooga shale and the Green River formation of Colorado is, of course, the fact that uranium is completely absent from the Green River shale. Another difference of interest to this phase of the investigation is the lesser amount of liquid products obtained from the Chattanooga shale by ordinary retorting methods compared to the amount obtained from Colorado shale containing an equivalent amount of organic material. The Colorado shale may vary in organic content over a wide range, but the yield of liquid products bears a direct relation to the contained organic matter. Figure 13 shows unpublished data from the Bureau of Mines illustrating this relationship. It can be seen that a Colorado shale of 19 per cent

FIGURE 13. FISCHER ASSAY VS. ORGANIC CONTENT OF RAW SHALE

organic matter gives a yield of 35 gallons per ton by the modified Fischer assay method developed by the Bureau of Mines³. This assay is a method of determining the liquid yield by a standardized retorting procedure. In comparison, the assay for the Chattanooga shale having an equivalent organic content shows a liquid yield of only 9.6 gallons per ton. One of the objectives of this research is the determination of the reasons for this difference, and the development of recovery methods which will give a greater yield of liquid products. Such methods must, of course, leave the shale in a condition for subsequent recovery of the uranium.

SEPARATION OF KEROGEN FROM SHALE

In order to study the chemical and physical properties of kerogen, the organic material distributed throughout the inorganic matrix of the shale, it appeared desirable to separate a substantial quantity of the kerogen from the inorganic constituents of the shale.

Solution of Inorganic Matrix by Acids

Partial demineralization of the shale was accomplished by a method used by the Bureau of Mines³ on a Colorado shale yielding 35 gallons of oil per ton of shale. A sample of Chattanooga shale containing 78.2 per cent ash was pulverized to a screen size of 60 to 100 mesh.

The pulverized shale was moistened with 80 per cent ethanol, treated with concentrated hydrochloric acid until no further reaction was apparent, washed by decantation with water, and the residue was allowed to dry in air. The partially extracted shale was transferred to copper dishes, excess hydrofluoric acid was added, and the mixture was heated on a steam bath until nearly dry. This treatment with hydrofluoric acid was repeated four times until no further reaction took place. The residue was then treated again with hydrochloric acid and washed with hot water until no additional mineral matter could be extracted. At this point, the ash content was found to be 29.3 per cent by weight of the insoluble residue. When the residue was subjected to further treatment with hydrofluoric and hydrochloric acids, the ash content was decreased by only 0.1 per cent, and it was concluded that further treatment would be ineffective.

A typical data record from the Bureau of Mines report³ shows that like treatment of Colorado shale of original ash content equal to 69.3 per cent produced a kerogen-rich residue with an ash content of 16.3 per cent.

The bulk of the insoluble inorganic material remaining after acid extraction is believed to be iron pyrites, because analysis of the impure kerogen showed it to contain iron and sulfur in the correct ratio for FeS_2 (16.9 per cent Fe; 20.1 per cent S). Furthermore, the ash

obtained from ignition of the kerogen was ferromagnetic and was insoluble in nitric acid, indicating that it was probably iron oxide (Fe_3O_4) resulting from oxidation of the iron pyrites.

Attempted Gravity Separation of Iron Pyrites From Kerogen

The specific gravity of kerogen is approximately 1, and that of pyrite is approximately 4.3. Therefore, it seemed possible that a gravity separation might be used to remove the pyrite and obtain pure kerogen. Such a separation was accomplished with Colorado shale by the Bureau of Mines, which reported that, when no further acid treatment was possible, the metal sulfides were almost entirely removed by allowing them to settle in a large quantity of water and decanting off the kerogen. By this method the ash content of the kerogen from Colorado shale was reduced from 16.3 per cent to 1.3 per cent. No separation was obtained when a similar procedure was tried on the kerogen obtained from the Chattanooga shale. The tests were extended to include other liquids, chloroform (sp.g. 1.49), carbon tetrachloride (sp.g. 1.59), and methyl iodide (sp.g. 2.28), but no separation was obtained.

A microscopic study of the kerogen-rich residue showed the residual inorganic material to be "locked" in the organic material in such a manner that a sink-float method of separation would be long and tedious, if not impossible.

It has been thought that a finer grinding of the shale to perhaps 100 to 200 mesh, before demineralization, might make a gravity

separation of the acid-insoluble inorganic material from the organic material feasible, as the kerogen might be present as finer particles, which would be more likely to float in the liquid being used for separation. Some of the shale has been ground to -100 mesh (25 per cent -200 mesh) and the preliminary acid extraction procedure is in progress.

EXTRACTION OF KEROGEN BY SOLVENTS

Extraction With Organic Solvents

Several investigators have attempted to extract kerogen from raw shale by the use of organic solvents, but none has reported much success. J. W. McKinney⁴ extracted shale with alcohol, ether, carbon disulfide, acetone, chloroform, carbon tetrachloride, benzene, and pyridine. The best result was obtained with benzene, but this solvent extracted only 3.2 net per cent. The Bureau of Mines³ digested 35- and 60-gallon Colorado shale for 20 days, using each of the following solvents: ethyl alcohol, methyl alcohol, ethyl ether, chloroform, carbon disulfide, carbon tetrachloride, benzol, petroleum, gasoline, turpentine, and pyridine.

All of these solvents were found to be ineffective, dissolving less than 5 per cent of the total kerogen. They concluded that none of the common solvents could be used to make a complete extraction of kerogen from the inorganic matrix.

Despite the low yields from solvent extraction of other shales, it seemed necessary to establish definitely whether or not solvent extraction might be feasible for the removal of kerogen from Chattanooga shale. Accordingly, a sample was digested with ethyl alcohol for several days, the extract was evaporated, and the amount of organic matter remaining as a residue was determined. Less than 2 per cent of the original shale was recovered. In another phase of the work, reported in a later paragraph, carbon tetrachloride was found to extract less than 1 per cent of the organic matter from the shale. In view of these results and those reported by the Bureau of Mines, it was decided that further attempts at solvent extraction would be unprofitable.

Hydrotropic Extraction

In a further attempt to find some means of purification of the kerogen obtained by demineralization of the shale, a hydrotropic extraction was attempted. Hydrotropic salts will greatly increase the solubility of many organic compounds in water, when the salts are present in concentrations above 25 per cent. In this investigation, a mixture of sodium xylene sulfonates (marketed under the trade name of Naxionate) was used as a hydrotrope. A 2.00-gram sample of the kerogen residue containing 29.3 per cent ash was added to 100 ml. of a 40 per cent solution of sodium xylene sulfonate in water, and the undissolved portion was filtered off. Dilution of the filtrate to bring the sodium xylene

sulfonate concentration down to less than 25 per cent precipitated the solute, and it was recovered by filtration. The reprecipitated solids were found to weigh 0.20 g., which was 10.0 per cent by weight of the impure kerogen. The unextracted residue was found to have an ash content of 30.0 per cent, which represents an increase of 0.7 per cent. Within the limits of experimental error, this seems to justify the conclusion that a part of the kerogen was dissolved in the concentrated sodium xylene sulfonate solution and was recovered on dilution.

It was thought that perhaps the Naxonate treatment had released the "locked" inorganic material from the organic materials in the kerogen and that further treatment with hydrofluoric acid might extract more of the inorganic material. However, it was found that treatment of the residue from this extraction with hydrofluoric acid and hydrochloric acid, and then washing with water did not decrease the ash content below the original 30.0 per cent by weight.

PRODUCTION OF SOLVENT FROM SHALE

It is very likely that complex organic compounds of the type probably present in the kerogen would be soluble only in solvents which possess some structural similarity to the kerogen molecules. The preparation of a liquid solvent from the kerogen with a minimum of disruption or rearrangement of the molecular structure was, therefore, attempted.