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RECOVERY OF URANIUM FROM NORTH
DAKOTA LIGNITES

Final Report

By

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July 31, 1950

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ABSTRACT

The mineralogy of a North Dakota lignite sample was studied, and an estimated mineralogical composition is presented. Results of a series of float-sink tests of raw lignite are included. Chemical analyses of several samples of North Dakota lignite are presented.

Recovery of uranium from a sample of North Dakota lignite (0.013 per cent of uranium) by hydrometallurgical methods was investigated briefly. Uranium extractions of 80-99 per cent were obtained with a sulfuric acid leach of lignite ash; acid consumption was approximately 850 lbs./lb. of uranium extracted. Uranium extractions from lignite ash with a carbonate leach were from 65-75 per cent; sodium carbonate consumption was approximately 1000 lbs./lb. of unbeneficiated ash. This was reduced to about 300 lbs./lb. of uranium extracted when most of the sulfate was removed from the lignite before leaching.

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INTRODUCTION

Among the low-grade (<0.1 per cent) domestic uranium ores which may represent a potential source of uranium at some future date are certain lignites occurring in North Dakota and Wyoming. Present knowledge of these lignites is very scant as to extent, potential tonnages, or the feasibility of recovering uranium from them. Additional information is needed in order to properly evaluate this source with respect to other low-grade domestic uranium ores. Further information on the amenability of lignite to extraction of the uranium is desirable in order to guide future decisions on the geological effort to be expended.

The reserves of lignite in North Dakota reach astronomical figures; they have been estimated as upwards of 500,000,000,000 tons. However, most of these probably do not contain significant percentages of uranium. Limited reconnaissance by the U. S. Geological Survey⁽¹⁾ has indicated inferred reserves of uranium-bearing lignites of the order of 23,000,000 tons, in the limited areas investigated. The weighted average uranium content was estimated to be 0.007 per cent.

In order that information on uranium recovery might keep pace with the accumulating geological data, a limited investigation was undertaken on methods of recovering uranium from lignite. Included in this study was an investigation of the mineralogy of North Dakota lignite; also included was a brief examination of the possibilities of beneficiation of lignite by ore-dressing methods.

(1) "Reconnaissance for Trace Elements in North Dakota and Eastern Montana. Preliminary Report - Lignite", Donald G. Wyant, U. S. Geological Survey, Trace Elements Investigation No. 61, November, 1949.

The work described in this report was carried out under Contract W-38-094-Eng-27 during the period October 1, 1949, to May 31, 1950, as part of a larger program on the recovery of uranium from low-grade raw materials.

SUMMARY

Eleven samples of North Dakota lignite were received from the U. S. Geological Survey during the course of the investigation. The extraction test work was, however, restricted to one sample, a lignite from Sentinel Butte, which was the first, and largest, sample received. Analyses made of other samples indicated that the Sentinel Butte sample (Lignite No. 1090-500) could probably be considered as nearly a "typical lignite" as any. Due to extremely wide variations in chemical analysis, a "typical lignite" appeared to be almost a hypothetical case. However, nothing in the data indicated that widely dissimilar results might be expected from any of the other samples submitted.

Study of the mineralogy of Lignite No. 1090-500 indicated that gypsum was the major inorganic mineral present, plus a substantial fraction of iron oxides. Chemical analysis of other lignite samples confirmed that these two were among the major inorganic constituents; in some, the Fe_2O_3 content was greater than the gypsum content. Also present were analcite and jarosite, as well as minor amounts of dolomite and quartz. The mineralogical study showed that the uranium was not associated with the inorganic minerals, but was primarily associated with the organic, carbonaceous, fraction. No uranium mineral was identified.

The nature of lignite made leaching the preferred choice for an extractive method. Cursory attention was given to extraction of the uranium directly from raw lignite. The results of this work showed that, although uranium extractions in the 70-80 per cent range could be obtained, a vigorous attack with strong mineral acid was required. Sodium carbonate was not a feasible reagent for raw lignite, due to its reaction with the organic phase to produce an unfilterable slurry. When lignite was subjected to retorting*, uranium extraction was negligible, even under vigorous attack with strong mineral acids.

Since the North Dakota lignites studied had ash contents ranging from about 25 to 35 per cent of the (dry) raw lignite, roasting appeared to offer a means of concentrating and upgrading the uranium, thereby providing more favorable conditions for maximum uranium extraction. In addition, the reduction in mass could reduce greatly the size of the leaching plant required. Most of the experimental work was, therefore, conducted on lignite ash. The uranium content of the ash of four of the higher grade lignite samples ranged from 0.029 to 0.086 per cent. The uranium content of the ash from Lignite No. 1090-500 was 0.051 per cent.

The uranium could be quantitatively extracted from lignite ash by leaching with strong (20 per cent) sulfuric acid, which also gave uranium extractions of 70-80 per cent from raw lignite. Losses in weight on leaching the ash were about 20 to 25 per cent, indicating some selectivity. Under more moderate conditions, uranium extractions of 80

* A process similar to that employed on oil shale.

to 90 per cent were readily obtained on the ash. However, measurements of approximate acid consumption during leaching revealed that sulfuric acid was being consumed at the rate of about 850-900 pounds per pound of uranium extracted. Although the identity of the acid-consuming constituents was not definitely determined, evidence pointed to the Fe_2O_3 and/or MgO content of the ash as the controlling factor. Studies of beneficiation of the raw lignite by physical methods, prior to roasting, indicated that no appreciable improvements in acid consumption were possible. Apparently the major acid-consuming constituents were rejected only in proportion to the uranium rejected. No practicable method of reducing acid consumption was discovered. On the basis of the observed data, recovery of the uranium by an acid leach would be a technically feasible, but costly, process, in terms of reagent costs alone.

Due to the strongly alkaline nature of lignite ash, it seemed probable that a sodium carbonate leach would be more economical than an acid leach. The initial sodium carbonate leaches indicated that the alkalinity was, in fact, too high, and actually appeared to be suppressing uranium extraction. Addition of sodium bicarbonate or carbon dioxide to the leach solution was successful in materially increasing uranium extraction, presumably through carbonation of the alkalies present to their respective carbonates, thus lowering the pH to the desired level. With the aid of this technique, extraction of uranium was increased to the 65-75 per cent range.

Several roasting and leaching variations aimed, respectively, at reducing the alkalinity and increasing the uranium extraction were of

little significance. Included in these were: roasting with iron pyrites and/or sodium chloride; quenching of the roasted ash; and the addition of oxidizing agents to the leach. Subjecting leach residues to a second carbonate leach resulted in only negligible extraction of additional uranium.

Sodium carbonate consumption was calculated to exceed 950-1000 pounds per pound of uranium extracted, on ash from unbeneficiated lignite, based on sulfate analyses of the pregnant liquor. Since this value represents only that portion of the sodium carbonate consumed through reaction with the calcium sulfate present in the ash, it is undoubtedly somewhat below the true value. Other minor constituents, such as alumina, would increase this figure. The high sulfate content of lignite is objectionable for two reasons: each pound of sulfate consumes slightly more than one pound of sodium carbonate; and high concentrations of sodium sulfate in the leach liquor apparently have an adverse effect on uranium extraction.

The effect of reducing the sulfate content of lignite ash was investigated. In one method, gypsum was largely eliminated from raw lignite, before roasting, by a series of water leaches. Although this technique was feasible in the laboratory, the very low solubility of gypsum appears to limit the practical application of this method, since tremendous quantities of water would be required.

Removal of sulfate by water leaching was definitely beneficial. Upon leaching lignite ash from the above test, in which 74 per cent of the sulfate had been removed, uranium extraction was 77 per cent, and sodium carbonate consumption was reduced to approximately 300 pounds per pound of uranium extracted.

Removal of gypsum from raw lignite by conventional ore-dressing methods was also investigated. Float-sink tests indicated that 60 per cent of the gypsum could be rejected with a uranium recovery of about 90 per cent. Carbonate leaching tests on several of the float-sink fractions showed sodium carbonate consumption was reduced to the 250-350 pounds range. Further tests, cyclic or semi-cyclic in nature, would be required to evaluate the effect of sodium sulfate build-up on carbonate consumption and uranium extraction. The evidence of the single-stage leaching tests described above suggests that sodium sulfate in the leach liquors may be a major problem, under conditions other than those of complete, or nearly complete, removal of the gypsum.

The over-all conclusion drawn was the same as that for acid leaching; recovery of uranium by carbonate leaching would be a technically feasible, but costly, process, in terms of reagent costs.

Molybdenum is a possible by-product of uranium recovery from lignite. The molybdenum assay of ash from Lignite No. 1090-500 was 0.11 per cent, or about twice the uranium content. Analyses of a number of pregnant liquors from various uranium-extraction tests indicated that there was a reasonable possibility that molybdenum could be extracted along with the uranium, particularly when a carbonate leach was used. Additional study would be required to evaluate definitely the feasibility of molybdenum recovery. Such work should be a part of any future study of the recovery of uranium from lignite.

Although the problem of recovering uranium from the lignite leach liquors was not investigated, it is believed that the use of

anion-exchange resins would be successful. This belief is based on the earlier work carried out at Battelle on the recovery of uranium from shales*.

Since the study of North Dakota lignites was primarily in the nature of a preliminary survey, the conclusions drawn are based only on limited data. However, it is believed that the generalized conclusions reached are fundamentally correct, and that more intensive study would result in changes in degree only, unless low-ash lignites containing uranium are found.

EXPERIMENTAL WORK AND DISCUSSION OF RESULTS

Lignite Samples

During the investigation of uranium recovery from lignites, eleven samples of North Dakota lignite and five samples of Wyoming lignite were supplied by the U. S. Geological Survey. Not all of these samples were of sufficient uranium content to warrant extensive investigation, although a number of them were analyzed in order to develop background information.

Identifying information on the North Dakota lignite samples is contained in Table 1. Comparative analyses for several of these are shown in Table 2. It will be noted that gypsum is a predominant component of these uranium-bearing lignites, as evidenced by the high CaO and sulfate sulfur contents.

* BMI-JDS-210 and -210A, September 30, 1949.

TABLE 1. NORTH DAKOTA LIGNITE SAMPLES

U.S.G.S. Field No.	B.M.I. No.	Wt., Lbs.	Uranium, Per Cent			Moisture, Per Cent, As Rec'd. (B.M.I.)	Ash, Per Cent, As Rec'd. (B.M.I.)	Sample Represents
			As Rec'd. (U.S.G.S.)	Ash (U.S.G.S.)	(B.M.I.)			
---	1090-500	550	---	---	0.051	35.0	16.4	Exposed face of a 6-ft. bed from a road cut in Sentinel Butte.
HB-10-26	1090-501	65	0.009	0.015	0.029	27.2	27.4	Similar to 1090-500, except taken from a 3-ft. bed 80 ft. lower in Butte.
DW-54-272	1090-502	16	0.011	0.06	0.055	16.7	28.8	Lignite 3.1 ft. thick from Black Butte.
DW-49-270	1090-503	25	0.024	0.11	0.086	14.6	30.8	Lignite 2.1 ft. thick from Small Butte, 1 mile east of Black Butte.
EPB-10-78 -79 -80	1090-504	92	0.006	0.016	0.011	15.2	20.2	Lignite 7.1 ft. thick from Bullion Butte.
EPB-14-81 -82 -83	1090-505	105	0.006	0.016	0.020	13.1	48.6	Lignite 4.5 ft. thick from Bullion Butte.
EPB-2-12 -13 -14	---	80	0.001	0.004	-	-	-	Lignite bed 15 ft. thick from Bullion Butte.

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TABLE 1. (CONTINUED)

U.S.G.S. Field No.	B.M.I. No.	Wt., Lbs.	Uranium, Per Cent			Moisture, Per Cent, As Rec'd. (B.M.I.)	Ash, Per Cent,		Sample Represents
			As Rec'd. (U.S.G.S.)	Ash (U.S.G.S.)	(B.M.I.)		As Rec'd. (B.M.I.)	(B.M.I.)	
EPB-3-72 } -73 } -74 }	-	105	0.002	0.006	-	-	-	-	Lignite bed 15 ft. thick (same bed as EPB-2-12) Bullion Butte.
EPB-9-75 } -76 } -77 }	-	83	0.002	0.006	-	-	-	-	Lignite bed 20 ft. thick (same bed as EPB-2-12) Bullion Butte.
HB-14-40	-	53	0.001	-	-	-	-	-	Lignite 3 ft. thick from Freyburg, North Dakota.
HB-16a-47 } -48 }	-	136	0.001	-	-	-	-	-	Lignite taken from mine on east side of Sentinel Butte. Thickness - 20 ft.

TABLE 2. COMPARISON OF SAMPLES OF NORTH DAKOTA LIGNITES

	Chemical Analyses (Calculated to an Ash Basis), Per Cent			
	Lignite No.			
	1090-500	1090-501	1090-502	1090-503
Uranium	0.051	0.029	0.055	0.086
Fe ₂ O ₃	16.6	24.5	33.0	31.1
Al ₂ O ₃	7.5	3.4	4.2	4.3
CaO	24.9	10.1	8.0	6.5
SiO ₂	12.3	20.9	21.1	22.7
Sulfate sulfur (as SO ₃)	20.8	25.6	13.9	18.7
Total sulfur (as SO ₃)	24.9	28.8	18.1	22.8
Ash (dry basis), per cent	25.3	37.5	34.8	36.0

A more detailed analysis of Lignite No. 1090-500, upon which the experimental work was conducted, is presented in Table 3. In Table 4 is shown a comparison of this lignite with the ash from a typical commercial lignite, such as is mined in North Dakota for fuel. Lignite No. 1090-500 is much higher in calcium sulfate than commercial lignite, and is correspondingly lower in SiO_2 . The iron content is also higher than is indicated for commercial lignite.

Identifying information on several samples of Wyoming lignite received is presented in Table 5. These were small samples, and were not employed for experimental work, although they were analyzed for uranium. The uranium content of these samples suggests that the Wyoming lignite samples were of generally lower grade than North Dakota lignites, although these Wyoming samples may not be typical.

Mineralogy of North Dakota Lignite

Estimated Mineral Composition

The approximate mineral composition of Lignite No. 1090-500 was determined from petrographic examinations and chemical and X-ray diffraction analyses. Fractions of the head sample, hand-picked products, and float-sink products were examined and analyzed. The estimated mineral composition is shown in Table 6. No uranium mineral was found.

Association of Uranium

Microscopic examinations were made on hand-picked specimens of various minerals in the head sample. The predominant mineral in these

TABLE 3. ANALYSIS OF LIGNITE NO. 1090-500

Component	Chemical Analysis, Per Cent	
	Dry Basis	Ash Basis (Calc.)
Uranium	0.013	0.051
SiO ₂	3.11	12.3
Fe ₂ O ₃	4.2	16.6
Al ₂ O ₃	1.9	7.5
MoO ₃	0.041	0.17
CaO	6.3	24.9
MgO	0.86	3.4
Na ₂ O	1.49	5.9
K ₂ O	0.08	0.3
CO ₂	0.36	1.4
P ₂ O ₅	0.06	0.2
SO ₄ ⁼ sulfur (as SO ₃)	5.3	20.8
Total sulfur (as SO ₃)	6.3	24.9
Total carbon	49.8	-
Volatile matter	49.3	-
Ash	25.3	-

Component	Spectrographic Analysis, (Ash Basis) Per Cent
MoO ₃	0.1-0.5
TiO ₂	0.1-1.0
MnO ₂	0.05-0.5

Others Less Than 0.1 Per Cent

Cu, Cr, V, Zr, B, Yt, Yb

TABLE 4. COMPARISON OF LIGNITE NO. 1090-500 AND A COMMERCIAL NORTH DAKOTA LIGNITE

Component	Chemical Analysis, Per Cent (Ash Basis)	
	1090-500(1)	Commercial Lignite(2)
SiO ₂	12.3	38.6
Fe ₂ O ₃	16.6	9.3
Al ₂ O ₃	7.5	16.7
CaO	24.9	13.4
MgO	3.4	4.0
Na ₂ O	5.9	8.7
K ₂ O	0.3	0.8
Total S (as SO ₃)	24.9	5.6
CO ₂	1.4	2.1
TiO ₂	(3)	0.8
	97.2	100.0

(1) Calculated from analysis of dry raw lignite.

(2) U. S. Bureau of Mines, Technical Paper No. 207, page 23.

(3) Spectrographic analysis indicated 0.1-1.0 per cent TiO₂ in 1090-500 ash.

TABLE 5. WYOMING LIGNITE SAMPLES

U.S.G.S. Field No.	B.M.I. No.	Wt., Oz.	Uranium, Per Cent			Ash, Per Cent, As Received		Sample Represents
			As Rec'd. (U.S.G.S.)	Ash (U.S.G.S.) (B.M.I.)		(U.S.G.S.)	(B.M.I.)	
DW-103-297	1090-506	10	0.004	-	0.020	-	25.2	Composite of lignite seams from carbonaceous clay and lignite bed. Total 0.9 ft.
WNS-1-1	1090-507	12	0.008	-	0.019	-	37.3	Lignite and carbonaceous clay from 10-ft. outcrop.
WNS-4-6	1090-508	12	0.004	-	0.007	-	74.2(1)	Lignite from 15-ft. bed of carbonaceous clay and lignite.
WNS-11-5	1090-509	12	0.004	0.008	0.009	47.3	49.4	Composite of lignite and clay bed; 5 ft. of 10 ft.
WNS-13-18	1090-510	11	0.002	0.018	0.020	9.1	9.2	Composite of 6-ft. bed; high-quality lignite seam.

(1) In appearance, this sample very much resembled Chattanooga shale.

TABLE 6. ESTIMATED MINERAL COMPOSITION OF LIGNITE NO. 1090-500

Constituent	Formula	Estimated Per Cent
Organic material	C, H ₂ , O ₂ , N ₂	76
Gypsum	CaSO ₄ •2H ₂ O	12
Analcite	NaAlSi ₂ O ₆ •H ₂ O	4
Jarosite	K ₄ Fe ₆ (OH) ₁₂ (SO ₄) ₄	3
Iron oxides	Fe ₂ O ₃ , etc.	3
Dolomite	Ca, Mg(CO ₃) ₂	0.5
Quartz	SiO ₂	0.5
Others (includes clay, zircon, tourmaline)		1.5
		100.0

hand specimens was from 10 to 100 times more abundant than in the head sample. Consequently, if the uranium were associated with any of these minerals, the uranium assay of that specimen should have been appreciably greater than the assay of the head sample. As shown by Table 7, the uranium is not associated with any of the principal inorganic minerals in the lignite. Analyses of several float-sink products, which were greatly concentrated, are presented in Table 8. In the first product listed (Sink 2.23 - Float 2.33), the analcite has been concentrated about 15-fold. However, the uranium assay is lower than in the heads. Altogether, 19 float-sink products were analyzed. In none, however, was a marked concentration of uranium found. The conclusion is that the uranium is associated primarily (but not exclusively) with the organic material. The form in which the uranium occurs is not known.

Liberation of Minerals

Screened size fractions of the head sample were examined to determine the degree of liberation of the inorganic from the organic materials. Liberation of the inorganic minerals started in the 20- to 28-mesh fraction, and was estimated to be 75 per cent complete in the 270- to 325-mesh size range. On the basis of chemical analyses, the liberation in the 270- to 325-mesh size range was not significantly better than it was in the 48- to 65-mesh size range. This is illustrated by a comparison of the chemical analyses of the 48- to 65-mesh and 200- to 325-mesh materials that floated in a liquid of 1.60 density:

TABLE 7. PRINCIPAL MINERALS AND URANIUM ASSAYS OF HAND-PICKED SAMPLES FROM LIGNITE NO. 1090-500

Fraction	Mineral	Estimated Per Cent of Mineral in Fraction	Uranium Assay, Per Cent ⁽¹⁾
Heads	-	-	0.0085
11-4	Quartz	35	
	Analcite	30	
	Carbonaceous	25	0.0013
	Others	10	
11-3	Gypsum	60	
	Carbonaceous	20	
	Jarosite	15	0.0017
	Analcite	5	
11-5	Jarosite	45	
	Carbonaceous	25	
	Gypsum	20	0.0031
	Analcite	10	
11-10	Jarosite	65	
	Gypsum	20	0.0042
	Carbonaceous	15	
11-6	Magnetite, Hematite, Goethite, Limonite	60	
	Gypsum	40	0.0048
11-8(2)	Carbonaceous (shiny, splintery)	85	
	Others	15	0.0072

- (1) Assay on air-dried samples; not corrected for surface moisture or water of hydration.
- (2) Carbonaceous material of a somewhat different appearance; this fraction represented a very small part of the heads.

TABLE 8. MINERAL ANALYSIS AND URANIUM ASSAY OF SOME FLOAT-SINK PRODUCTS FROM LIGNITE NO. 1090-500

Gravity	Product		Mineral Composition		Uranium Assay, Per Cent
	Split	Mesh Size	Mineral	Per Cent	
Sink	2.23	-48 +100	Analcite	60	0.0069
Float	2.33		Carbonaceous	30	
			Gypsum	10	
Sink	2.52	-200 +325	Anhydrite ⁽¹⁾	50	0.0023
			Magnetite,		
			Ilmenite	20	
			Carbonaceous	20	0.0039
Sink	2.96	-325	Magnetite,		
			Ilmenite	60	
			Jarosite	25	
			Limonite		
			Hematite	15	
			Zircon		

(1) Samples were dried at 105-110°C. before analysis, dehydrating the gypsum to anhydrite.

<u>Mesh</u>	<u>U</u>	<u>CaO</u>	<u>Fe₂O₃</u>	<u>MgO</u>	<u>Al₂O₃</u>	<u>SiO₂</u>	<u>C</u>
-48 +65	0.012	2.5	1.3	1.0	0.62	0.57	56.9
-200 +325	0.010	2.4	1.5	1.0	0.46	0.35	57.7

Leaching Studies

Leaching of Raw and Retorted Lignite

The possibility of extracting uranium directly from raw or retorted lignite was investigated briefly. The results of the test work on raw lignite indicated that the uranium could be extracted, with moderate effectiveness, as shown by the results in Table 9. Acid consumption appeared to be high, probably equally as high as for lignite ash, per unit of uranium extracted. A relatively fine particle size was essential for maximum extraction; the application of heat was also quite advantageous. Prime disadvantages of leaching raw lignite are the low uranium content of the solids and the large bulk of material to be handled.

The extraction of uranium from retorted lignite was negligible, even under vigorous attack by strong mineral acids. The lignite was retorted for 20 hours at 1100°F. The maximum uranium extraction obtained under any of the experimental conditions was less than 5 per cent. In this respect, the experience on lignite closely paralleled that on Chattanooga shales, where retorted material was invariably the least amenable to leaching. The results from the preliminary leaching tests on retorted lignite indicated no promise and no further investigation was conducted.

TABLE 9. EXTRACTION OF URANIUM FROM RAW LIGNITE

Lignite Used: No. 1090-500 (0.013 per cent uranium)

Screen Analysis:	<u>Coarse Lignite</u>		<u>Fine Lignite</u>	
	<u>Mesh</u>	<u>Per Cent</u>	<u>Mesh</u>	<u>Per Cent</u>
	+12	25	-100	100
	-12 +100	52	-200	94
	-100	23		

Leaching Procedure: 50 grams of raw lignite leached in indicated lixiviant at 20 per cent pulp density for 2 hours at indicated temperature.

Lixiviant	Leaching Temp., °F.	Wt. Loss, Per Cent	Filtrate pH	Uranium Extracted, Per Cent(1)
<u>Coarse Lignite</u>				
2% H ₂ SO ₄ (0.4N)	70-80	5	1.8	3
2-1/2% HNO ₃ (0.4N)	70-80	9	1.6	2
1-1/2% HCl (0.4N)	70-80	8	1.5	2
20% H ₂ SO ₄ (4N)	70-80	8	<0	66
26% HNO ₃ (4N)	70-80	18	<0	55
16% HCl (4N)	70-80	19	<0	51
5% Na ₂ CO ₃	70-80	Slurry unfilterable		
15% Na ₂ CO ₃	70-80	Slurry unfilterable		
<u>Fine Lignite</u>				
5% H ₂ SO ₄	70-80	7	-	35
10% H ₂ SO ₄	70-80	10	-	47
20% H ₂ SO ₄	70-80	9	-	66
5% H ₂ SO ₄	180-190	11	0.9	43
10% H ₂ SO ₄	180-190	15	0.4	62

TABLE 9. (CONTINUED)

Lixiviant	Leaching Temp., °F.	Wt. Loss, Per Cent	Filtrate pH	Uranium Extracted, Per Cent(1)
20% H ₂ SO ₄	180-190	15	<0	79
26% HNO ₃	180-190	40	<0	82
16% HCl	180-190	27	<0	78

(1) Per cent extracted based on total uranium found.

Leaching of Lignite Ash

Acid Leaches. The temperature at which the lignite was roasted had some effect on the extraction of uranium by a subsequent acid leach. A roasting temperature of 1500°F. was at the borderline of incipient fusion, and the refractoriness of the ash roasted at furnace temperatures above this adversely affected uranium extractions. As indicated by the data in Table 10, there appeared to be no appreciable differences in extraction in the roasting-temperature range of 900-1200°F. More detailed study would be required to fix the permissible maximum roasting temperature.

The effects of leaching time and temperature were found to be minor over the ranges investigated, as illustrated by Table 11. As between a 10 per cent and 20 per cent sulfuric acid lixiviant, the higher acid strength produced slightly higher uranium extractions, although it will be noted that the loss in weight on leaching was approximately doubled. This suggests that dissolution of undesired components was the chief result of the increase in acid concentration. Acid consumption was so high in leaching lignite ash that the starting acid concentrations were rather meaningless. The indications were that the primary requisite was to supply sufficient acid to maintain the lixiviant at about pH 2.5 or under. The following data are illustrative:

<u>Starting Acid</u> <u>Concentration,</u> <u>Wt. Per Cent.</u>	<u>Pulp</u> <u>Density,</u> <u>Per Cent</u>	<u>Acid Added,</u> <u>Lbs./Ton of</u> <u>Ash</u>	<u>Wt. Loss on</u> <u>Leaching,</u> <u>Per Cent</u>	<u>Filtrate</u> <u>pH</u>	<u>Uranium</u> <u>Extracted</u> <u>Per Cent</u>
5	5	1900	21	0.8	92
10	20	1600	19	0.5	94
20	20	800	12	2.2	86

TABLE 10. EFFECT OF ROASTING TEMPERATURE ON EXTRACTION OF URANIUM FROM LIGNITE ASH

Lignite Used: No. 1090-500 (0.013 per cent uranium).

Screen Analysis: Minus 1/4" before roasting; ground to minus 100 mesh before leaching.

Roasting Procedure: 1.0-kilogram portions of dry lignite were roasted for 3-5 hours in a single-hearth laboratory Herreshoff roaster.

Leaching Procedure: Ash samples were leached for 2 hours at 180-190°F. at a pulp density of 20 per cent in 20 per cent H₂SO₄.

Roasting		Leaching Wt. Loss, Per Cent	Filtrate pH	Uranium Extracted, Per Cent(1)
Temp., °F.	Time, Hrs.			
900	5	26	0.6	99
900	5	26	0.6	98
1000	4	24	0.6	95
1100	4	21	0.5	97
1200	4	19	0.5	95
1500(2)	3	13	0.6	90
1800(2)	2	18	0.5	77

(1) Per cent extracted based on total uranium found.

(2) Incipient fusion at these temperatures.

TABLE 11. EFFECT OF LEACHING TIME AND TEMPERATURE ON EXTRACTION OF URANIUM FROM LIGNITE ASH

Lignite Used: No. 1090-500 (0.051 per cent uranium - ash basis)

Screen Analysis: Minus 1/4" before roasting; ground to minus 100 mesh before leaching.

Roasting Procedure: 1.0-kilogram batches of dry lignite were roasted for about 5 hours at 900°F. in a small single-hearth Herreshoff roaster. Composite made of seven such batches.

Temp., °F.	Leaching Time, Hrs.	Pulp Density, Per Cent	Wt. Loss, Per Cent	Filtrate pH	Uranium Extracted, Per Cent (1)
<u>20% H₂SO₄</u>					
180-190	2.0	20	26	0.6	99
180-190	2.0	20	26	0.6	98
70-80	2.0	20	19	0.5	94
<u>10% H₂SO₄</u>					
180-190	2.0	20	12	2.0	92
70-80	2.0	20	12	2.2	86
70-80	1.0	20	13	1.5	88
70-80	0.25	20	11	1.5	84

(1) Per cent extracted based on total uranium found.

In order to obtain an approximate value of the acid consumption in leaching lignite ash, one four-stage cyclic test was conducted, with the results shown in Table 12. The leaching was carried out at a pH of 2.2, and it was noted that, under these conditions, acid consumption appeared to level off after the first stage. Disregarding the acid content of the pregnant liquor, the consumption averaged about 900 lbs./lb. of uranium extracted. With an estimated credit for the acid remaining in the pregnant liquor, this value was estimated to be approximately 850 lbs/lb. of uranium extracted.

The acid-consuming constituents are evidently not water-soluble compounds. In two tests, lignite ash was slurried with water six times before being subjected to an acid leach. Although the loss in weight from the water leaching was 16-17 per cent, there was no appreciable reduction in acid consumption. It is surmised that the water leaches were removing gypsum, primarily.

Carbonate Leaches. The alkaline nature of lignite ash (a water slurry of ash normally exhibited a pH in excess of 11) suggested that a sodium carbonate leach might be preferable to an acid leach. Preliminary tests with a sodium carbonate lixiviant showed that only from 25 to 50 per cent of the uranium was being extracted. Further investigation brought out the fact that the pH's of these leach solutions were over 13. Since strong alkalies, such as NaOH and $\text{Ca}(\text{OH})_2$, are used to precipitate uranium from sodium carbonate solutions, it appeared probable that it was the alkalies present that were producing this high pH, and suppressing uranium extraction. If this were the case, addition of sodium bicarbonate

TABLE 12. FOUR-CYCLE LEACH OF LIGNITE ASH WITH SULFURIC ACID

Lignite Used: No. 1090-500 ash (0.051 per cent uranium - ash basis)

Procedure: 15 grams of ash was leached with sulphuric acid solution for 1 hour at 70-80°F. and at 20 per cent pulp density. The pH was maintained at 2.2 by the addition of sulphuric acid. The filtrate was used to leach the subsequent batch of lignite ash.

	Cycle Number			
	I	II	III	IV
H ₂ SO ₄ added, grams	6.0	4.8	4.8	4.9
Final pH of leach	1.5-1.8*	2.1	2.2	2.2
Weight loss, per cent	10	7	9	9
Residue, per cent of uranium	0.005	0.007	0.008	0.008
Uranium extraction, per cent	89	85	82	82

Total uranium extracted, mg.	22.9
Over-all uranium extraction, per cent	85
Pregnant liquor conc., mg. U/liter	350
H ₂ SO ₄ added, grams	20.5
Available H ₂ SO ₄ in pregnant liquor, grams (estimated)	<u>1.0</u>
Net H ₂ SO ₄ consumption, grams	19.5
Net H ₂ SO ₄ consumption, lbs./ton ash	650
Net H ₂ SO ₄ consumption, lbs./lb. U extracted	850

* Estimated.

or carbon dioxide (in order to convert the alkalies to their carbonates) would then be expected to reduce the pH and improve uranium extraction. As shown by Table 13, the addition of either increased uranium extractions to the 65 to 75 per cent level.

In practice, carbon dioxide would no doubt be the more economical reagent. Roasting of the lignite would produce carbon dioxide far in excess of the quantities required for leaching. Whether flue gases, containing from 10-15 per cent of CO_2 , would be as effective as pure CO_2 would require additional study. No measurements were made of the amount of carbon dioxide required. However, the results of several 2-hour leaches with 15 per cent Na_2CO_3 and CO_2 , which are presented below, indicated that large excesses of CO_2 were used in the laboratory tests:

<u>Length of Time CO_2 Was Added</u>	<u>Filtrate pH</u>	<u>Uranium Extracted, Per Cent</u>
First 0.5 hour	9.6	72
First 1.0 hour	9.4	70
Entire 2.0 hours	9.3	72
Last 1.0 hour	9.3	60
Last 0.5 hour	9.7	56

The effects of roasting temperature were not investigated in connection with uranium extraction by carbonate leaches. It was presumed that no major differences existed from the results observed earlier for acid leaches. Most of the carbonate studies were conducted on ash roasted at furnace temperatures of approximately 900°F.

In the early stages of the investigation of carbonate leaching of lignite ash, there were some indications that rapid quenching of the

TABLE 13. EXTRACTION OF URANIUM FROM LIGNITE ASH BY CARBONATE
LEACH SOLUTIONS

Lignite Used: No. 1090-500 ash (0.051 per cent uranium)

Screen Analysis: Standard (cf. Table 11).

Roasting Procedure: Standard (cf. Table 11).

Leaching Procedure: Samples of lignite ash were leached for 2 hours
at temperatures and pulp densities shown.

Lixiviant Used, Conc., Wt. Per Cent	Pulp Density Per Cent	Wt. Loss, Per Cent	Filtrate pH	Uranium Extracted, Per Cent ⁽¹⁾
<u>70-80°F. Leaches</u>				
15% Na ₂ CO ₃	10	12	>13	55
15% Na ₂ CO ₃ + CO ₂ (2)	10	8	9.1	74
15% Na ₂ CO ₃ + CO ₂ (2)	10	11	8.4	74
10% Na ₂ CO ₃ + CO ₂ (2)	10	12	9.5	67
10% Na ₂ CO ₃ + CO ₂ (2)	5	11	9.9	73
8% NaHCO ₃	5	10	7.9	50
<u>180-190°F. Leaches</u>				
15% Na ₂ CO ₃	10	9	13	49
15% Na ₂ CO ₃ + CO ₂ (2)	10	7	9.3	72
15% Na ₂ CO ₃ + 5% NaHCO ₃	10	6	10.4	70

(1) Per cent extracted on basis of total uranium found.

(2) CO₂ bubbled into slurry throughout leach.

ash from the roaster improved its amenability to a sodium carbonate leach. Earlier work on another contract on the recovery of uranium from carnotite ores had shown that quenching was desirable. However, upon further investigation, it was concluded that no substantial increase in uranium extraction resulted when lignite ash was quenched. A group of typical results is shown in Table 14.

Data recently reported by investigators at the Massachusetts Institute of Technology indicated that a multi-stage leach definitely improved uranium extraction from Rand ore precipitates. Tests of this procedure on lignite ash produced only minor improvements in extraction of the uranium. In two tests, in which uranium extractions of 70 to 75 per cent were obtained by a single leach, a re-leach of the residues with fresh carbonate solution extracted only an additional 4 to 7 per cent of the uranium. Total extraction in both cases was less than 80 per cent.

Investigation of the sodium carbonate consumption during leaching disclosed that it was quite high, in spite of the alkaline nature of the ash. Study of the data indicated that the primary cause of the high consumption was the high sulfate content of the lignite. As shown by the results of several single-stage leaches (Table 15), the sulfate present in the lignite ash was virtually quantitatively removed. The reaction of Na_2CO_3 and CaSO_4 to form Na_2SO_4 (in solution) and a precipitate of CaCO_3 theoretically results in the loss of 1.1 pounds of sodium carbonate for every pound of sulfate reacting. This would not be the total consumption; minor contaminants, particularly alumina, would consume additional sodium carbonate. On the basis of the tests shown, the sulfate alone accounts for approximately 1000 pounds of sodium carbonate per

TABLE 14. EFFECT OF QUENCHING OF LIGNITE ASH ON THE EXTRACTION OF URANIUM BY CARBONATE LEACHES

Lignite Used: No. 1090-500 (0.051 per cent uranium, ash basis).

Screen Analysis: Standard (cf. Table 11).

Roasting Procedure: Unquenched ash was roasted under standard conditions in a Herreshoff roaster (cf. Table 11). Quenched ash was roasted in a tube furnace at about 900°F. for 6 hours.

Lixiviant	Treatment	Temp., °F.	Wt. Loss, Per Cent	Filtrate pH	Uranium Extracted, Per Cent (1)
15% Na ₂ CO ₃ (2)	Quenched	70-80	7	10.2	63
15% Na ₂ CO ₃ (2)	Quenched	180-190	10	9.5	79
15% Na ₂ CO ₃ (2)	Unquenched	180-190	7	9.3	72
5% Na ₂ CO ₃ } 5% NaHCO ₃ }	Quenched	180-190	10	10.0	76
5% Na ₂ CO ₃ } 5% NaHCO ₃ }	Unquenched	180-190	8	9.7	71
10% Na ₂ CO ₃ } 5% NaHCO ₃ }	Quenched	180-190	5	10.2	76
10% Na ₂ CO ₃ } 5% NaHCO ₃ }	Unquenched	180-190	8	10.2	80

(1) Per cent extracted on basis of total uranium found.

(2) CO₂ bubbled into slurry throughout leach.

TABLE 15. APPROXIMATION OF Na_2CO_3 CONSUMPTION WITH AN ALKALINE LEACH

Ten grams of No. 1090-500 ash leached two hours at room temperature, at 10 per cent solids.

	10% Na_2CO_3 + CO_2	10% Na_2CO_3 + 5% NaHCO_3
Ash, g.	10.0	10.0
$\text{SO}_4^{=}$ assay, per cent	29.7	29.7
Na_2CO_3 in, g.	9.0	9.0
NaHCO_3 in, g.	-	4.5
Uranium in, mg.	5.1	5.1
Uranium extracted, mg.	3.4	3.2
Uranium extracted, per cent	67	63
<u>Residue</u>		
Wt., g.	8.8	9.4
Wt. loss, per cent	12	6
CO_2 assay, per cent	20.5	21.4
Na_2CO_3 equivalent, g.	4.05	4.84
<u>Filtrate</u>		
pH	9.5	10.4
$\text{SO}_4^{=}$ extracted, per cent	99	97
$\text{SO}_4^{=}$ assay, g.	2.94	2.88
Na_2CO_3 equivalent, g.	3.25	3.18
<u>Na_2CO_3 Consumed by Ca SO_4</u>		
Lbs./ton ash	650	640
Lbs./lb. of uranium extracted	960	1000

pound of uranium extracted. Another disadvantage is the rapid increase in the Na_2SO_4 content of the leach solution. It has been reported that high concentrations of Na_2SO_4 in carbonate leach solutions have an adverse effect on uranium extraction.

Results of a four-stage cyclic leach test, summarized in Table 16, indicated that uranium extraction decreased as the test progressed, even though ample quantities of sodium carbonate and bicarbonate were supplied. The Na_2SO_4 concentration was at the same time increasing rapidly, reaching a level of over 180 grams/liter in four cycles. Sufficient Na_2SO_4 was formed that, if the test had been conducted at a pulp density of 30 per cent, the filtrate from the fourth cycle would have been virtually saturated with respect to Na_2SO_4 . It is surmised that the high concentration of sodium sulfate in solution was largely responsible for the decreased uranium extraction. In this test, sodium carbonate consumption (based on sulfate analyses) was again about 1000 pounds/pound of uranium extracted.

Since calcium sulfate has a slight solubility, one way of removing it from the lignite or lignite ash is to leach it with water. In raw lignite, it is present as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); roasting converts it to anhydrite (CaSO_4). Of the two, gypsum is the more rapidly soluble, and leaching would preferably be carried out on the raw lignite.

The possibility of reducing the sulfate content of raw lignite was investigated briefly in the laboratory. In one test, in which minus 12-mesh raw lignite was subjected to an agitation leach with distilled water, at a pulp density of 10 per cent, 90 per cent of the sulfate was eliminated. In another test, minus 12-mesh raw lignite was given a five-stage percolation leach, at a pulp density of $33\frac{1}{3}$ per cent. The

TABLE 16. FOUR-CYCLE LEACH OF LIGNITE ASH WITH SODIUM CARBONATE-SODIUM BICARBONATE SOLUTION

Lignite Used: No. 1090-500 ash (0.051 per cent uranium).

Screen Analysis: Standard (cf. Table 11).

Roasting Procedure: Standard (cf. Table 11).

Leaching Procedure: 15-gram samples of lignite ash were leached with an aqueous 10 per cent sodium carbonate-5 per cent sodium bicarbonate solution for 2 hours at 70-80°F. and at a pulp density of about 10 per cent. Additional reagents were added to the filtrates from each cycle and the adjusted filtrate used to leach the next batch of ash.

	Cycle Number			
	I	II	III	IV
Na ₂ CO ₃ added, g.	13.5	3.4	3.4	3.4
NaHCO ₃ added, g.	6.8	4.1	4.1	4.1
Filtrate pH	9.0*	9.4	8.9	9.0
Wt. loss, per cent	3	-8(1)	-3(1)	8
Uranium assay residue, per cent	0.013	0.016	0.016	0.028
Uranium extracted, per cent ⁽²⁾	71	60	62	40
Over-all uranium extracted, per cent ⁽²⁾				59
Uranium conc. in pregnant liquor, mg./liter				130
Over-all sulfate extraction, per cent				83
Conc. of Na ₂ SO ₄ in pregnant liquor, g./liter				182
Lbs. of Na ₂ CO ₃ consumed/lb. of uranium extracted (based on sulfate)				1040

(1) Weight gain, partly as a result of incomplete dissolution of the added carbonates.

(2) Per cent extracted based on total uranium found.

* Estimated.

contact time was 72 hours for the first stage and 24 hours/stage thereafter. Over-all removal of sulfate, after five stages, was about 60 per cent. Extraction of uranium was negligible. However, due to the limited solubility of gypsum, tremendous quantities of water are required to obtain effective reduction of the sulfate content by a leaching method. Removal by conventional ore-dressing methods, described elsewhere in this report, would probably be a more practical manner in which to reduce the sulfate content of lignite.

Tests on the effect of prior removal of gypsum on sodium carbonate consumption showed that material reductions resulted when the bulk of the gypsum was removed. The results of one test are shown in Table 17. In this experiment, about 75 per cent of the gypsum was leached from the raw lignite by a two-stage water leach before roasting. A 15 per cent $\text{Na}_2\text{CO}_3\text{-CO}_2$ leach extracted 77 per cent of the uranium from the ash. On the basis of sulfate analyses of the leach solution, sodium carbonate consumption in this test was approximately 300 lbs./lb. of uranium extracted. This compares with consumption figures from previous tests, in which no sulfate was removed, of approximately 1000 lbs./lb. of uranium extracted. It will be noted that, even at a pulp density of 20 per cent, the sulfate content of the leach liquor was 55 g./liter, as Na_2SO_4 . At a pulp density of 40 per cent, the equivalent figure was 155 g./liter. It is surmised that the high sulfate concentration was at least partially responsible for the reduced uranium extraction in the latter case.

Miscellaneous Leaching Tests. Several tests were conducted in which NaN_3 or KClO_3 was added to a sulfuric acid leach of lignite ash.

TABLE 17. EXTRACTION OF URANIUM FROM LIGNITE ASH WITH A REDUCED SULFATE CONTENT

Lignite Used: No. 1090-500 (0.051 per cent uranium, ash basis).

Raw Leach: 1000 grams of minus 12-mesh raw lignite was leached twice at 70-80°F. with distilled water, with agitation, at a pulp density of 20 per cent. 74 per cent of sulfate was removed.

Roasting: Dried residue from raw leach roasted for 6 hours at 900°F. in Herreshoff single-hearth roaster.

Ash Leach: Samples of ash from roaster were leached for 2 hours at 70-80°F. in a 15% $\text{Na}_2\text{CO}_3\text{-CO}_2$ solution.

	Per Cent Pulp Density	
	20	40
Filtrate pH	8.5	8.0
Uranium extracted, per cent ⁽¹⁾	77	53
Sulfate extracted, per cent ⁽²⁾	93	93
Sulfate in leach solution, g. Na_2SO_4 /l.	55	150
Sodium carbonate equivalent of sulfate in solution, lbs./lb. of uranium extracted	290	450

(1) Per cent extracted based on total uranium found.

(2) Per cent extracted of sulfate remaining in ash.

No effects attributable to the oxidizing agents were observed. Uranium extractions duplicated those of the control tests, within experimental error.

The effect of adding iron pyrites and/or sodium chloride to lignite before roasting on the subsequent extraction was investigated briefly. The addition of iron pyrites was found to reduce the sulfuric acid consumption only slightly. However, in these tests, the sulfuric acid equivalent of the iron pyrites added was far in excess of the apparent savings in acid. The addition of sodium chloride to the roast was without apparent effect on subsequent leaching, whether with acid or carbonate solutions. Presumably, the roasting temperature of 900-1000°F. was too low to produce a true chloridizing roast.

Beneficiation of Lignite

The laboratory investigation on leaching of uranium from lignite ash showed that, although the uranium was readily extracted, reagent consumption was excessive, owing to the gangue minerals associated with the uranium. In order to determine the feasibility of rejecting some of these inorganic minerals before leaching, a float-sink analysis of Lignite No. 1090-500 was made. Besides serving this major purpose, this work was also useful in the study of the mineralogy of lignite and the association of the uranium. These latter two subjects have been discussed in the preceding pages.

The float-sink tests were carried out on a minus 48-mesh fraction of the head sample, which was further split on a 100-mesh and a 325-mesh screen. The -48 +100 and -100 +325 mesh fractions were split

in carbon tetrachloride and acetylene tetrabromide solutions of specific gravities 1.60, 2.40, and 2.52. Some intermediate splits were made at 2.25 and 2.33 on one fraction to obtain a concentrated fraction of analcite (sp. gr. 2.3). Analcite is a zeolite-type mineral, and was suspected of being a carrier for the uranium.

The minus 325-mesh fraction was split only at 2.96 specific gravity. Therefore, in calculating the theoretical quantities of the mineral portions that could be rejected by physical means of concentration, the minus 325-mesh fraction was not taken into account. This would not introduce a serious error, because the uranium analysis and mineralogical composition of the minus 325-mesh fraction were not appreciably different from the plus 325-mesh fraction. Also, the minus 325-mesh fraction represented only about 25 per cent of the head sample, and the liberation of the minerals was more complete in this fraction due to its finer size.

An estimation of the percentages of the total inorganic constituents that could be rejected by physical means and corresponding uranium recoveries is shown in Figure 1. The data are plotted for CaO and Fe₂O₃ separately and for the combined CaO, Fe₂O₃, Al₂O₃, MgO, and SiO₂. When 50 per cent of the total inorganic minerals was rejected, the recovery of uranium was about 90 per cent. If larger percentages of the inorganic minerals were rejected, the recovery of uranium fell off rapidly.

Table 18 presents calculated analyses of some of the "concentrate" products in comparison with the head analysis. These products are typical of the best results that could be expected from physical methods of concentration.

FIGURE 1. CURVES SHOWING RECOVERY OF URANIUM AND VARIOUS PERCENTAGES OF INORGANIC CONSTITUENTS REJECTED

TABLE 18. CALCULATED ANALYSIS OF VARIOUS CONCENTRATES FROM FLOAT-SINK ANALYSIS OF LIGNITE NO. 1090-500

Products	Wt., %	Assay, Per Cent							Distribution, Per Cent					
		U	CaO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	Ash	U	CaO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO
Combined float 1.60	56	0.0124	1.4	1.4	0.48	0.56	1.0	9.5	54	21	18	16	16	47
Combined float 2.40 ⁽¹⁾	86	0.0137	3.1	2.5	2.9	1.6	1.1	15.5	92	40	51	82	69	81
Combined float 2.52 ⁽²⁾	94	0.0135	5.7	3.5	3.0	1.8	1.3	-	99	75	78	96	87	99
Composite heads ⁽³⁾	100	0.0128	6.5	4.2	3.0	2.0	1.2	26	100	100	100	100	100	100

(1) Includes float 1.60 and sink 1.60 - float 2.40 products.

(2) Includes float 1.60, sink 1.60 - float 2.40, and sink 2.40 - float 2.52 products.

(3) The minus 325-mesh fraction, which assayed approximately the same as the plus 325-mesh fraction, was not included in the calculation.

In order to determine if reductions in reagent consumption proportional to the amount of inorganic constituents rejected could be realized, sulfuric acid and sodium carbonate leaches were performed on certain of the float-sink products.

Acid Leaches of Beneficiated Lignite

The results of several sulfuric acid leaching tests are presented in Table 19. Since all of the tests were made on ashed material, consumption of acid was computed on the basis of pounds of acid per pound of uranium extracted. The quantity of acid used in each test was that required to reduce the pH of the slurry to 2.0. The amount of unreacted acid remaining in solution at the end of the leach was not measured; however, this value should have been reasonably constant for all tests.

It is evident from these results that the saving in acid was not proportional to the amount of total inorganic constituents rejected, nor was it proportional to the amount of either CaO or Fe_2O_3 rejected. A possible explanation of this may be that MgO was also one of the major acid consuming constituents. The analyses indicated that the ratio of MgO to uranium was not appreciably different in the float-sink products from that in the heads. Spectrographic analysis of a leach solution from another sample which was analogous to Sample No. 1, in a similar test, indicated that appreciable quantities of Mg were present. Another possible explanation might be that the major acid-consuming constituents are the fractions of the inorganic minerals which are intimately associated with the uranium-bearing organic fraction, and consequently not rejected with the major amounts of inorganic minerals. The conclusions were that beneficiation of the lignite would not be an economic method of reducing acid consumption.

TABLE 19. RESULTS OF SULFURIC ACID LEACHING TESTS ON ASH FROM BENEFICIATED LIGNITE

Lignite No. 1090-500 beneficiated by gravity separation of raw lignite. Specific gravity fractions roasted at approximately 900-1000°F. and leached.

Sample No.	Product		Chemical Analysis, Per Cent (Raw Basis)							
	Split	Mesh	U	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	MgO	Ash	
1	Float 1.60	-65 +200	0.013	1.5	0.49	0.40	2.5	1.0	9.5	
2	Sink 1.60 Float 2.40	-100 +200	0.016	4.6	2.2	4.0	4.0	1.3	24.	
3	Head	-65	0.0102	4.6	1.7	3.2	6.2	1.1	26	

Sample No.	Chemical Analysis, Per Cent (Calc. to Ash Basis)						
	U	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	MgO	Total
1	0.137	16	5.2	4.2	26	11	62
2	0.066	19.	9.1	17	17	5.4	67
3	0.0394	18	6.6	12	24	4.2	65

Leach Results on Titrating With 1N (5 Per Cent) H₂SO₄ to pH 2.0

Sample No.	Uranium Extracted, Per Cent	Lbs. H ₂ SO ₄ /Lb. U Extracted
1	87	740
2	97	830
3	79	840
4(1)	88	860
5(1)	87	880

(1) Samples No. 4 and No. 5 were composite samples analogous to head (Sample No. 3).

Sodium Carbonate Leaches of Beneficiated Lignite

The results of sodium carbonate leaching on the same samples are shown in Table 20. Because of the difficulty in determining the free Na_2CO_3 in the resultant leach liquor, the quantity of Na_2CO_3 consumed during the leaching operation was not obtained directly. As in the other sodium carbonate leaching tests, consumption was calculated on the basis of sulfate solubilized. On this basis, the best product (float 1.60 fraction) had a sodium carbonate consumption of only about one-fourth that of the head sample. The uranium extraction was also appreciably higher than that obtained on the head sample, although this was the result of a single, unconfirmed, test.

In order to determine more accurately the over-all reduction in carbonate consumption and increases in uranium recovery, cyclic or semi-cyclic tests on larger samples of beneficiated lignite would be required. The effects of sodium sulfate build-up in the leach solution on carbonate consumption, and especially on uranium recovery, also require further study.

By-Product Possibilities

Perhaps the most promising by-product possibility from lignite is molybdenum. Chemical analysis of the composite sample of Lignite No. 1090-500 showed that the ash contained 0.11 per cent of molybdenum (0.041 per cent in dry raw lignite). This is slightly greater than twice the uranium content; one ton of ash would contain approximately 1.0 pound of uranium and approximately 2.2 pounds of molybdenum.

TABLE 20. RESULTS OF CARBONATE LEACH TESTS ON ASH FROM BENEFICIATED LIGNITE

Sample No.	Product		CaO in Ash, Per Cent (2)	Pregnant Solution		Lbs. Na ₂ CO ₃ / Lb. U Extracted	Uranium Extracted, Per Cent
	Split	Wt. Sample, Grams		SO ₄ , Total mg.	Equivalent Na ₂ CO ₃ , mg.		
1	Float 1.60	2.40	26.3	470	520	220	84
2	Sink 1.60 Float 2.40	4.80	16.6	670	740	320	72
3	Head	5.0	23.9	1650	1820	960	71
4(3)		5.0	24.9	1465	1620	850	72
5(3)		5.0	24.9	1510	1670	835	77

- (1) Portions of similarly numbered samples from sulfuric acid leach tests (Table 19).
- (2) Calculated from analysis of raw lignite.
- (3) Composite samples analogous to No. 3.

Although none of the experimental work was directed especially toward molybdenum recovery, analyses for molybdenum were made on various leach solutions resulting from a number of the uranium-extraction tests. These results are shown in Table 21, in comparison with the corresponding uranium extraction obtained. Molybdenum appears to be less amenable to an acid leach, and more amenable to a sodium carbonate leach, than is the uranium. Earlier work in connection with an investigation of shale* had indicated that molybdenum was also readily recovered from leach solutions, accompanying the uranium when the uranium was recovered by means of anion exchange.

Enormous quantities of salt cake (sodium sulfate) could be readily recovered, if the demand warranted. In view of the low unit value of this material, and the presumed location of any recovery plant at the mine, the feasibility of recovering sodium sulfate appears dubious.

Power and carbon dioxide are other by-product possibilities. Lignite is reported to average approximately 6000 B.T.U./lb. on an as-received basis. A plant recovering uranium from lignite by means of a roast-leach process would undoubtedly be self-sufficient in heat and power, and presumably could produce quantities of surplus power. Carbon dioxide could be recovered from the flue gases, if a need for it existed.

RECOMMENDATIONS FOR FUTURE WORK

Reduction of reagent consumption is perhaps the most important phase of the lignite problem. Any future work should include this as one of its major objectives.

* BMI-JDS-210 and -210A.

TABLE 21. EXTRACTION OF MOLYBDENUM FROM LIGNITE ASH

Lignite Used: No. 1090-500 (0.013 per cent uranium - raw basis).

Screen Analysis: Standard (cf. Table 11).

Roasting Procedure: Dry lignite roasted for six hours at 900°F.

Leaching Procedure: Leached for two hours under conditions shown.

Lixiviant	Temp., °F.	Pulp Density, Per Cent	Wt. Loss, %	Filtrate pH	Extracted, Per Cent	
					U (1)	Mo (2)
<u>Acid Leaches</u>						
5% H ₂ SO ₄	70-80	5	21	0.8	92	47
10% H ₂ SO ₄	70-80	20	12	2.2	86	5
10% H ₂ SO ₄	180-190	20	12	2.0	92	3
20% H ₂ SO ₄	180-190	20	26	0.6	98	112
<u>Carbonate Leaches</u>						
10% Na ₂ CO ₃ + CO ₂	180-190	5	9	11.1	81	87
5% Na ₂ CO ₃ + CO ₂	180-190	5	8	8.0	64	87
5% Na ₂ CO ₃ + 5% NaHCO ₃	180-190	10	9	10.2	76	87
10% Na ₂ CO ₃ + 5% NaHCO ₃	180-190	20	9	10.7	71	118
10% Na ₂ CO ₃ + CO ₂	180-190	20	9	10.2	65	85

(1) Per cent extracted on basis of total metal found.

(2) Per cent extracted on basis of solution and head analyses.

Beneficiation of lignite by physical concentration methods is another phase closely related to the above. This was not intensively explored in the current work and should receive further attention.

Any future work should include a wider selection of samples than it was possible to examine in the preliminary investigation.

If additional work is carried out, the problem of recovering uranium from the leach liquors will need attention. Presumably, anion-exchange resins would be used.

A P P E N D I X

Notebook References

The data upon which this report was based are contained in the following Laboratory Record Books:

<u>Number</u>	<u>Pages</u>
4278	25-52
4924	1-40; 49-57
4859	1-100
5098	1-100

Battelle Reports

The investigation of uranium recovery from lignite has also been reported in the following Monthly Progress Reports.

<u>Report No.</u>	<u>Date</u>
BMI-JDS-218	November, 1949
BMI-JDS-220	December, 1949
BMI-JDS-222	January, 1950
BMI-JDS-226	February, 1950
BMI-JDS-228	March, 1950