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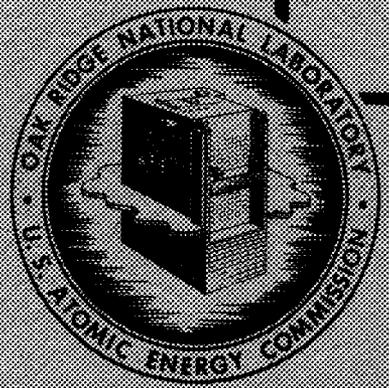
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Metallurgy - Raw Materials

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MATERIALS CHEMISTRY DIVISION
URANIUM CHEMISTRY OF RAW
MATERIALS SECTION
PROGRESS REPORT
Recovery of Uranium from Lignites
October 1, 1952 to March 31, 1953



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URANIUM CHEMISTRY OF RAW MATERIALS SECTION

PROGRESS REPORT

Recovery of Uranium from Lignites

October 1, 1952 to March 31, 1953

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June 1, 1953

JUL 23 1953

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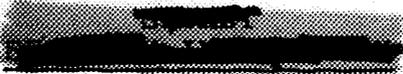
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INTRODUCTION

During the latter part of January several new samples of uraniferous Dakota lignite were received from the Bureau of Mines at Grand Forks, North Dakota. Since that time, most of the work has been devoted to studies of these more representative samples. Investigations are being made of the recovery of uranium (and molybdenum) from raw lignite, lignite char and various types of lignite ash. The experimental data obtained thus far are presented and discussed in the following sections.



SAMPLE DESCRIPTIONS

Several new lignite samples have been received from the Slim Buttes region of Harding County, S. Dakota. These samples were collected during the quartering of five bulk samples, as shown by the following data supplied by the Bureau of Mines, University Station, Grand Forks, N. Dakota.

<u>Locality</u>	<u>Location</u>	<u>Approx. Thickness of Lignite Sampled</u>	<u>Bulk Sample Designation</u>	<u>Drum Sample</u>
<u>West Side of Slim Buttes</u>				
83 (Auger hole)	SESW-1-17N-7E	Upper 4.0 of 5.5'	No. 1	No. 95 No. 119 No. 109
84 (Mendenhall mine)	NWSE-1-17N-7E	Upper 5.0 of 8.5'	No. 2	No. 103
93 (Auger hole)	SWNE-36-18N-7E	Upper 5 of 7.0'	No. 3	No. 97 No. 101
<u>East Side of Slim Buttes</u>				
82 (surface section)	SENE-8(?) -17N-8E	4.8'	No. 4	No. 92 No. 121
81 (surface section)	SWSE-8-17N-8E	5.2'	No. 5	No. 86 No. 141

These samples are identified by the drum numbers throughout this report.

Except for Nos. 92 and 121, the samples were uniform in appearance. These two, however, were dry at the top of the drum, soggy in the middle, and nearly a slurry at the bottom.

Proximate analyses of the new samples are given in Table 1. For comparison, the analyses of the older samples

Table 1

PROXIMATE ANALYSES OF LIGNITE SAMPLES

Lignite No.	Water %	Ash %	Fixed Carbon %	Volatile Matter %	U in		Mo in	
					Raw Lignite %	Ash %	Raw Lignite %	Ash %
ND-1-2 (a)	38.2	18.9	18.9	24.0	0.02		0.058	
	(b) 4.0	29.4	29.4	37.2				
	(c) -----	30.6	30.6	38.8	0.03	0.105	0.093	0.305
	(d) -----	-----	44.0	56.0				
ND-1-3 (a)	40.0	17.5	24.5	18.0	0.024			
	(b) 5.0	27.8	38.6	28.4				
	(c) -----	29.3	40.8	29.9	0.040	0.137		
	(d) -----	-----	57.8	42.2				
ND-1-4 (a)	40.5	14.5	14.5	30.5	0.031			
	(b) 6.0	22.9	22.9	48.2				
	(c) -----	24.3	24.3	51.4	0.052	0.214		
	(d) -----	-----	32.1	67.9				
86 (a)	40.0	27.2	17.6	15.2	0.004		0.038	
	(c) -----	45.2	29.3	25.3	0.007	0.016	0.064	0.14
	(d) -----	-----	53.7	46.3				
92 (a)	48.8*	12.3	14.8	24.1	0.006		0.022	
	(b) 6.7	22.3	27.0	44.0				
	(c) -----	24.0	28.8	47.2	0.012	0.048	0.043	0.18
	(d) -----	-----	37.9	62.1				
95 (a)	40.0	20.0	21.7	18.3	0.018		0.034	
	(c) -----	33.4	30.4	36.2	0.030	0.090	0.057	0.17
97 (a)	44.0	13.5	22.6	19.9	0.006		0.011	
	(c) -----	24.1	40.4	35.5	0.010	0.043	0.019	0.08

Table 1 (Cont'd.)

PROXIMATE ANALYSES OF LIGNITE SAMPLES

Lignite No.	Water %	Ash %	Fixed Carbon %	Volatile Matter %	U in		Mo in	
					Raw Lignite %	Ash %	Raw Lignite %	Ash %
101 (a)	46.7	11.0	19.9	22.4	0.009		0.030	
(c)	----	20.6	37.3	42.1	0.017	0.08	0.056	0.27
103 (a)	41.3	14.2	23.7	20.8	0.009		0.026	
(c)	----	24.2	40.4	35.4	0.015	0.062	0.044	0.18
109 (a)	38.6	18.3	23.1	20.0	0.013			
(b)	8.0	27.4	34.6	30.0				
(c)	----	29.8	37.6	32.6	0.021	0.069		
(d)	----	----	54.4	45.6				
121 (a)	46.5*	16.8	16.7	20.0	0.007		0.024	
(c)	----	31.4	31.2	37.4	0.013	0.042	0.044	0.14
141 (a)	42.7	11.8	23.2	22.3	0.004			
(c)	----	20.6	40.5	38.9	0.008	0.038		
(d)	----	----	47.9	52.1				

(a) Refers to material as received.

(b) Refers to air-dried material.

(c) Refers to water-free material.

(d) Refers to carbonaceous material, free of ash and water.

Water content determined by xylene method.

*Nos. 92 and 121: Average of water contents in samples from top, middle, and bottom of drum.

(ND-1, batches 2 to 4) which were used in previous investigations are also included. The water contents of the samples were determined by the xylene method, and the volatile matter by use of a Fischer retort at 525°C. Most of the uranium values are average values as obtained from (1) direct analyses of the raw lignites, (2) analyses of the ashes and (3) analyses of the pregnant liquors and tailings from leaching tests.

It may be noted that the group of east-side lignite samples run generally lower in uranium content than those from the west side - 0.007 to 0.013 as compared with 0.010 to 0.030 (dry basis). Indeed, some of the concentrations on "as received" basis are so low that any uranium recovery process would carry a sizeable mining cost. Other general differences in composition and reaction between the east-side and the west-side samples are noted below. On basis of the information so far available about these samples, it is not possible to state whether the characteristics shown are general for the lignite beds in the two regions, or perhaps reflect differences in sampling. Note, for example, that the east-side samples are indicated to be from surface section, while the west-side samples are from auger hole or mine.

The approximate percentages of major inorganic constituents in the new Dakota lignite samples are given in Table 2. All of the values in the table are calculated to a water-free basis. The most striking variation among the samples is in the sulfate content, the east-side samples as a group running lower than those from the west side.

In view of these differences in the lignite compositions, as well as variations showing up in preliminary recovery studies (see below), brief microscopic examinations of the new lignite batches were made by Dr. T. N. McVay. Comments made by Dr. McVay are listed in Table 3. For these studies, all of the lignite samples were ashed at 500°C. Although gypsum would be converted to anhydrite by this treatment, the latter is also easily recognized.

The microscopic observations agree well with the analytical data in that the gypsum content was noted to be low in all samples which were reported to be low in sulfate. In several cases, the amount of uncombined silica, as quartz, was limited. The low sulfate concentrations for some of the samples also require that the jarosite contents be small.

Table 2
MAJOR INORGANIC CONSTITUENTS IN LIGNITE SAMPLES
(Moisture free basis)*

Lignite No.	<u>R₂O₃</u>	<u>RO</u>	<u>R₂O</u>	<u>SiO₂</u>	Sulfate as <u>SO₃</u>	Total Sulfur as <u>SO₃</u>
86	14.3	2.5	2.2	22.0	3.3	4.0
92	11.7	3.9	1.0	14.4	0.3	1.4
95	11.7	3.0	1.0	12.0	6.3	8.0
97	6.4	2.9	2.3	8.9	4.6	7.9
101	5.4	3.8	2.1	5.3	5.8	7.1
103	6.6**	5.3	1.2	8.3	8.9	11.4
109	10.3	4.9	0.8	8.0	8.1	10.0
121	10.6	2.8	1.3	14.3	0.4	1.5
141	4.9**	2.6	3.1	6.6	2.9	4.0

*Calculated using water contents determined by xylene method.

**Fe₂O₃ + Al₂O₃.

Table 3
OBSERVATIONS FROM MICROSCOPIC EXAMINATION
OF ASHED SAMPLES

Lignite No.

86	Gypsum, clay minerals and grains colored red by iron oxide. As all samples contained some red colored grains, this description will not be repeated.
92	Very little quartz or gypsum.
121	Contains quartz but a minor amount of gypsum. Considerable clay.
141	Contains some gypsum.
95	Large amount of gypsum and one large piece of clay.
97	Similar to No. 95.
101	Large amount of gypsum.
103	Similar to No. 101.
General	Carbonate minerals were not found in any of the samples

DIRECT TREATMENT OF RAW LIGNITES

Very preliminary studies of direct uranium extractions from raw lignite (ND-1) were reported previously.⁽²⁾ Additional and more extensive studies are now being made with the new lignite samples aimed at an eventual general evaluation of the possibilities for direct treatment.

Leaching with Acids

Extraction results from direct acid leaching of lignite No. 109 are given in Tables 4 and 5. All samples used in these tests were prepared by riffing a portion of air dried (4-5% moisture) lignite which had been ground to minus 14 mesh. Leachings were conducted for different times and temperatures using various concentrations of acid at a pulp density of 20%.

Upon contacting the raw lignite at room temperature for 16 hours (see Table 4), about 75% of the uranium could be extracted if the acids were used in sufficient excess. Sulfuric, nitric and hydrochloric acids were about equal in their effect, whereas the extractions with phosphoric acid were somewhat lower. When the leaching temperature was increased to 80°C, about 85% of the uranium could be extracted during a four-hour contact (see Table 5). In these tests, the effectiveness of phosphoric acid was similar to that of nitric and hydrochloric, with sulfuric acid possibly showing some signs of superiority.

Though the quantities of acid required for solubilization of the uranium from raw lignite are large, an important consideration in a cyclic process is the amount of this acid that is actually consumed (neutralized) during the contact period. Using the method of J. C. Ingles,⁽³⁾ measurements of these quantities have been made on six different batches of raw lignite, the results from which are reported in Table 6. For these tests, each batch of air-dried lignite was leached with 5% and 12.5% H₂SO₄ solutions at a pulp density of 20% and at a temperature of 80°C. With the more dilute acid solutions, the consumption of acid by the various batches varied from 90 to 210 lbs of acid/ton. With the more concentrated acid, the variation was between 120 and 260 lbs/ton. The largest consumption of acid was given by No. 92, an east-side lignite, with No. 86, another east-side sample, intermediate.

Other experiments with acid leaching are being made to obtain further information concerning optimum process conditions, the elements other than uranium which are dis-

Table 4

DIRECT LEACHING OF RAW LIGNITE AT ROOM TEMPERATURE

Test No.	Kind	Acid		Filtration* Rate Gals./ft ² /hr	Final pH of Liquor	Wt. Loss from Leaching (%)	Tailings (air-dried) (% U)	Percent U Extn.
		Pounds per ton Lignite	Percent in Solution					
LS- 1	H ₂ SO ₄	100	1.25	1.2	1.45	7.6	0.012	42
LS- 2	"	200	2.5	1.3	1.13	7.2	0.010	51
LS- 3	"	400	5.0	1.3	0.75	7.6	0.009	52
LS- 4	"	800	10.0	1.3	0.55	9.1	0.006	71
LS- 5	"	1600	20.0	1.3	0.22	9.6	0.004	77
LS- 6	HNO ₃	100	1.25	1.3	1.55	8.1	0.025	13
LS- 7	"	200	2.5	1.2	1.00	9.7	0.017	30
LS- 8	"	400	5.0	1.1	0.65	13.8	0.013	48
LS- 9	"	800	10.0	2.5	0.30	17.9	0.011	57
LS-10	"	1600	20.0	2.5	0.0	23.4	0.005	77
LS-11	H ₃ PO ₄	100	1.25	0.8	2.02	3.8	0.013	34
LS-12	"	200	2.5	0.8	1.84	5.7	0.015	39
LS-13	"	400	5.0	0.7	1.63	7.2	0.014	47
LS-14	"	800	10.0	1.0	1.28	7.2	0.011	46
LS-15	"	1600	20.0	1.3	0.94	9.0	0.008	68
LS-39	HCl	100	1.25	2.5	1.06	5.7	0.020	19
LS-40	"	200	2.5	2.5	0.66	7.4	0.019	31
LS-41	"	400	5.0	4.3	0.43	13.0	0.014	47
LS-42	"	800	10.0	3.4	0.10	16.4	0.011	59
LS-43	"	1600	20.0	2.5	<0.0	17.8	0.008	73

Lignite No. 109, air dried; H₂O content, 5%; U content, 0.020%.

Leach conditions: Pulp density, 20%; time, 16 hrs.

*Filtration rates are shown for comparative purposes only. Measurements were made using a 7 cm Buchner type funnel. Final cake thickness was usually about 1/2 in.

Table 5

DIRECT LEACHING OF RAW LIGNITE AT 80°C

Test No.	Kind	Acid		Filtration* Rate Gals./ft ² /hr	Final pH of Liquor	Wt. Loss from Leaching (%)	Tailings (air-dried) (% U)	Percent U Extn.
		Pounds per ton Lignite	Percent in Solution					
LS-17	H ₂ SO ₄	100	1.25	7.1	1.35	10.0	0.010	56
LS-18	"	200	2.5	6.0	1.12	11.2	0.010	60
LS-19	"	400	5.0	9.9	0.80	12.8	0.004	83
LS-20	"	800	10.0	9.9	0.52	15.9	0.004	85
LS-21	"	1600	20.0	9.9	0.20	20.0	0.001	94
LS-23	HNO ₃	100	1.25	8.9	1.48	9.3	0.016	28
LS-24	"	200	2.5	9.9	1.02	13.7	0.011	48
LS-25	"	400	5.0	8.7	0.70	17.5	0.009	60
LS-26	"	800	10.0	10.4	0.40	25.2	0.006	78
LS-27	"	1600	20.0	10.3	0.08	29.1	0.004	86
LS-28	H ₃ PO ₄	100	1.25	5.2	1.85	10.0	0.011	53
LS-29	"	200	2.5	5.9	1.70	11.7	0.008	62
LS-30	"	400	5.0	5.8	1.55	11.2	0.006	69
LS-31	"	800	10.0	4.2	1.25	11.2	0.004	82
LS-32	"	1600	20.0	4.9	0.94	10.2	0.003	86
LS-33	HCl	100	1.25	5.3	1.12	8.5	0.010	50
LS-34	"	200	2.5	9.7	0.72	14.9	0.009	61
LS-35	"	400	5.0	15.9	0.44	19.2	0.008	69
LS-36	"	800	10.0	12.7	<0.0	22.9	0.006	73
LS-37	"	1600	20.0	6.5	<<0.0	19.7	0.003	85

Lignite No. 109, air dried; H₂O content, 5%; U content, 0.020%.
Leach conditions: Pulp density, 20%; time, 4 hrs.

*See Table 4.

Table 6

ACID CONSUMPTION BY RAW AIR-DRIED LIGNITE

<u>Test No.</u>	<u>Lignite No.</u>	<u>Moisture in Lignite (%)</u>	<u>H₂SO₄ Added</u>		<u>Final pH</u>		<u>Acid Consumption lbs./ton</u>
			<u>Pounds per ton Lignite</u>	<u>Percent in Solution</u>	<u>Liquor</u>	<u>Wash</u>	
LS-61	86	21	400	5.0	0.85	1.20	120
LS-62			1000	12.5	0.30	0.80	170
LS-63	92	27	400	5.0	0.70	1.30	210
LS-64			1000	12.5	0.30	1.05	260
LS-65	95	20	400	5.0	0.75	1.28	110
LS-66			1000	12.5	0.40	1.40	140
LS-67	97	20	400	5.0	0.85	1.48	90
LS-68			1000	12.5	0.42	1.00	120
LS-69	101	23	400	5.0	0.96	1.45	110
LS-70			1000	12.5	0.65	1.20	150
LS-71	103	24	400	5.0	0.80	1.10	110
LS-72			1000	12.5	0.60	1.10	160

Leach conditions: Pulp density, 20%; time, 4 hrs.; Temp. 80°C.
 Acid consumption data were obtained by free-acid titration.

solved during leaching, the consumption of acid by these elements as well as by the organic matter, etc. Completion of these tests should permit an evaluation of a direct acid process including acid recovery and recycle.

Leaching with Ammonium Carbonate

Previous tests⁽²⁾ in which batch ND-1 lignite was treated with solutions of ammonium carbonate showed appreciable dissolution of uranium, but the resultant slurries were extremely difficult to filter. Present experience with No. 109 has been the same.

Since the filtration difficulties apparently arise from reactions with organic matter, other tests have been made in which the lignite (ND-1) was heated to burn off the more volatile organic materials prior to the leaching treatment. The results from these experiments are shown below. About two-thirds of the uranium could be extracted from the lignite by this treatment, and filtration of the slurries was rapid. Further tests with other lignite samples will be conducted.

<u>Burning Time^a</u> <u>(Min. at 800°C)</u>	<u>Residue</u> <u>(% of Head)</u>	<u>Carbon</u> <u>(% of Residue)</u>	<u>U Ext'n.^b</u> <u>(%)</u>	<u>Tails</u> <u>(% U)</u>
60	19	.3	66	.054
30	25	19	66	.047
0	31	21.5	46 ^c	.058

- a) Raw lignite placed in furnace at 400°C and heated rapidly (15-20 min.) to 800°C. Bed depth, 1/8 - 3/16 in., 0.7 lbs lignite/sq.ft.
- b) Leached using 25 g ash (-100 mesh), 20 g (NH₄)₂CO₃ and 100 ml H₂O for 2 hrs at 80°C and 40 psi. One hour cooling period in autoclave.
- c) Low uranium material balance.
-

Leaching with Ammonium Phosphate

Previous tests⁽²⁾ with dihydrogen ammonium phosphate have shown a partial (20%) solubilization of uranium from

raw ND-1 lignite. Further experiments with this reagent, using lignite No. 109, are described in Table 7. In these tests, the uranium again was partially solubilized. However, under the most rigorous condition tested, the maximum extraction was only 40%.

Leaching with Non-Aqueous Solvents

Several preliminary experiments were made of the extraction of uranium from raw lignite (dried at 50-60°C) with solutions of organophosphorus compounds in carbon tetrachloride or naphtha. The results are shown in Tables 8, 9, and 10. In the absence of mineral acid (Table 8), uranium extraction by 0.1M dialkylphosphinic or dialkylphosphoric acid was negligible. A significant fraction of the uranium was extracted when a small amount of concentrated sulfuric acid was added to the extraction slurry, and the extraction was improved when concentrated nitric acid was used instead of sulfuric (Table 9). Similar tests with a neutral reagent (tributyl phosphate) and nitric acid are shown in Table 10. In this set of tests, uranium extraction improved with increased quantity of nitric acid and with increased extraction time. It may be noted that the quantity of nitric acid used to obtain 65% uranium extraction was considerably lower than that required for similar extractions in aqueous acid leaching (see Table 4).

Further studies of the application of non-aqueous leaching to lignites are being made, using different extraction reagents and diluents (with and without acidulation) under a variety of process conditions.

RECOVERY OF URANIUM FROM CHAR

Several samples of lignite char have been prepared by treating portions of ND-1 lignite for 2 hours at 500°C in a small Fischer retort. After grinding the products to minus 100 mesh, a series of leaching tests was conducted using solutions of ammonium carbonate and various mineral acids. The experimental conditions and results are described in Table 11.

As shown by the data, all extractions of uranium from the lignite char were quite low. Acid leaching with oxidants present, e.g., hot nitric acid, potassium permanganate, and hydrogen peroxide were no more effective than those using simple solutions of sulfuric and hydrochloric acids.

Table 7

LEACHING OF RAW LIGNITE WITH $\text{NH}_4\text{H}_2\text{PO}_4$

Test No.	$\text{NH}_4\text{H}_2\text{PO}_4$ Added		Temp. of Leach °C	Filtration* Rate Gals./ft ² /hr	Final pH of Liquor	Tailings (air-dried) (% U)	Percent U Extn.
	Pounds per ton Lignite	Percent in Solution					
LS-44	400	5	25	1.8	2.82	0.019	6
LS-45	800	10	"	1.2	2.90	0.017	11
LS-46	1200	15	"	1.5	3.00	0.018	13
LS-47	1600	20	"	1.6	3.04	0.018	20
LS-48	400	5	80	5.7	2.70	0.019	15
LS-49	800	10	"	5.7	2.84	0.017	31
LS-50	1200	15	"	4.6	2.92	0.012	32
LS-51	1600	20	"	6.3	2.95	0.012	40

Lignite No. 109, air dried; H_2O content, 5%; U content, 0.020%.

Leach conditions: Pulp density, 20%; time, 16 hrs at 25°C and 4 hrs at 80°C.

*See Table 4.

Table 8

EXTRACTION OF URANIUM FROM LIGNITE WITH
ORGANOPHOSPHORUS REAGENTS

<u>Exp. No.</u>	<u>Reagent</u>	<u>Diluent</u>	<u>Extraction Time, Hr.</u>	<u>U Extn. (%)</u>
LC-3- 1	Di(2-ethylhexyl)phosphinic Acid	CCl ₄	1/4	<1
- 2	" " " " "	CCl ₄	2	<1
- 3	" " " " "	Naphtha*	1/4	<1
- 7	Dibutylphosphoric Acid	CCl ₄	1/4	<1
- 8	" " " " "	CCl ₄	2	<1
- 9	" " " " "	Naphtha*	1/4	<1
-10	Diethylphosphoric Acid	CCl ₄	1/4	<1
-11	" " " " "	CCl ₄	2	1.1
-12	" " " " "	Naphtha*	1/4	<1

Procedure: 15 g samples of lignite were stirred with 45 ml of organic diluent, 0.10M in the indicated reagent. The slurry was filtered and the cake washed with fresh diluent.

Lignite (ND-1, batch 3) oven dried at 50-60°C for 16 hrs. (Head analysis 430 ppm.)

*Boiling range of 90-120°C.

Table 9

EXTRACTION OF URANIUM WITH DI(2-ETHYLHEXYL)PHOSPHINIC ACID
IN ORGANIC DILUENT WITH HNO₃ OR H₂SO₄ ADDED

<u>Exp. No.</u>	<u>Lbs H₂SO₄</u> <u>per ton of</u> <u>Dry Lignite</u>	<u>Lbs HNO₃</u> <u>per ton of</u> <u>Dry Lignite</u>	<u>U Extraction, %</u>
LC-4-1	50	---	4.6
-2	100	---	8.6
-3	---	50	20
-4	---	100	44

Procedure: 15 g of lignite, 45 ml of CCl₄, and conc. acid were stirred for 2 hours, filtered, and the cake washed with CCl₄.

Lignite (ND-1, batch 3) oven dried at 50-60°C for 16 hrs. (Head analysis 430 ppm.)

Table 10

EXTRACTION OF URANIUM BY TBP IN CCl₄ WITH ADDED HNO₃

Exp. No.	1st Extraction		2nd Extraction		Total Lbs HNO ₃ per ton Dry Lignite	Extraction Time, Hr.	U Extraction, (%)		
	Volume of Organic	Lbs HNO ₃ per ton Dry Lignite	Volume of Organic	Lbs HNO ₃ per ton Dry Lignite			1st	2nd	Total
LC-6-1	45 ml	100	--	---	100	1/2	--	--	24
-2	45	100	45	100	200	1/2 (each)	21	25	46
-3	45	200	--	---	200	1/2	--	--	51
-4	45	200	--	---	200	2	--	--	65
-5	90	200	--	---	200	1/2	--	--	36

Procedure: 15 g samples of lignite, CCl₄ containing 10% TBP (wt/volume basis), and conc. HNO₃ were stirred for the indicated period of time, filtered, and the cake washed with CCl₄. In LC-6-2, the residue was extracted with fresh organic solution and HNO₃ as before.

Lignite (ND-1, batch 3) oven dried at 50-60°C for 16 hrs. (Head analysis 430 ppm.)

Addition of oxidants to the ammonium carbonate solutions also failed to improve the extractions.

In the latter part of Table 11, tests are shown in which several char samples, prepared at different temperatures, were given an oxidizing roast at 500°C prior to leaching. This treatment, it may be observed, produced a carbon-free ash from which 80% of uranium could be extracted by water alone, even when the previous retorting operation had been carried out at a temperature as high as 800°C. In this respect, the chars have acted much the same as the raw lignite. Reference to Table 4, ORNL-1384,⁽¹⁾ shows similar extractions from ND-1 samples which had been ashed directly at 500°C.

RECOVERY FROM LOW TEMPERATURE ASH

Acid and carbonate leaching of low temperature lignite ash from batch ND-1 has been discussed in previous reports.^(1,2) These and other methods for treating low temperature ash are now being examined using the new lignite samples from the Slim Buttes area.

The ash samples for these tests were prepared by spreading raw lignite in a thin bed on a tray in a muffle furnace at a specified temperature (usually 800°C), or at a lower temperature with a brief heat-up period to the specified temperature. Although it is certain that the temperature of the burning lignite exceeded that of the furnace, the ash samples are designated in the following sections by the furnace temperature. Measurements with an imbedded thermocouple during burning in thin beds (3/16 to 1/4 inch) at a furnace temperature of 800°C showed average bed temperatures approaching a maximum of 900°; some particles probably reached higher temperatures. With similar samples burned by a standardized procedure, "800° ash" can be considered a reasonably definite and reproducible material, although its relationship to a given fire-box temperature in a large furnace remains to be established.

Leaching with Acid

In previous tests with low temperature ND-1 ash, 75-80% of the uranium could be extracted by acid leaching. The consumption of sulfuric acid as determined by free-acid titration was about 200 lbs/ton of ash.

Table 11

URANIUM EXTRACTION FROM LIGNITE CHAR

(ND-1)

Test No.	Retort Temp. °C	Leach			Filtrate pH	U Extn. (%)
		Agent	Amount of Agent lb/ton	Oxidant Added to Leach		
L-37	500	5% H ₂ SO ₄	250	---	3.05	9
L-38	500	5% H ₂ SO ₄	500	---	1.32	33
L-45	500	5% H ₂ SO ₄	1000	---	0.82	8
L-50	500	5% HNO ₃	1000	---	1.0	15
L-51	500	5% HCl	1000	---	0.4	9
L-46	500	5% H ₂ SO ₄	500	1 g KMnO ₄ /10 g Char	1.55	10
L-47	500	5% HCl	500	excess of H ₂ O ₂	1.00	7
L-40	500	20% (NH ₄) ₂ CO ₃	8000	---	----	2
L-41	500	20% (NH ₄) ₂ CO ₃	"	O ₂ gas	----	4
L-48	500	20% (NH ₄) ₂ CO ₃	"	1 g KMnO ₄ /10 g Char	8.85	5
L-49	500	20% (NH ₄) ₂ CO ₃	"	1 g (NH ₄) ₂ S ₂ O ₈ /10 g Char	8.83	6
L-39	500	H ₂ O (10% pulp density)		Oxid. roast at 500°	2.8	86
L-42	600	H ₂ O " " "		Same	2.55	81
L-43	700	H ₂ O " " "		Same	2.60	82
L-44	800	H ₂ O " " "		Same	2.80	84

With the new lignites (see Table 12), similar extractions have been obtained from samples 109, 92, 103, 101, 97, 95, and 121, and somewhat lower extractions (65-70%) were obtained from samples 141 and 86. These latter lignites are also lower in uranium content. The quantities of acid consumed during leaching were in most cases higher and in several cases considerably higher than those experienced with the ND-1 sample. The approximate quantities of acid consumed by each sample under conditions selected for nearly maximum uranium recovery may be listed as follows:

Lignite No.	Uranium Content (%)	H ₂ SO ₄ Consumed (lbs/ton of Ash)	U Ext'n. (%)	H ₂ SO ₄ Consumed (lbs/lb of U Dissolved)
86	.017	510	71	2125
92	.048	1000	80	1300
121	.042	1000	80	1480
141	.038	760	66	1520
95	.090	210	79	150
97	.043	400	77	600
101	.080	410	80	320
103	.062	290	80	295
109	.069	300	80	275

The metal cations contributing to the consumption of acid have so far been determined in only one test, using No. 92. The quantities of these elements dissolved along with their equivalent quantities of sulfuric acid are listed immediately below. In this particular experiment, the ash was treated for 4 hours at 80°C with 1000 lbs H₂SO₄/ton at a 9% pulp density.

Table 12

ACID LEACHING OF LIGNITE ASH

Test No. LA-	Lignite No.	Leach		Original H ₂ SO ₄ in Leach		Filtrate pH	% Uranium Ext'd.	Ash Tailing (% U)	Acid Consumed	
		Temp.	Pulp Density (%)	Lbs/ton Dry Lignite	Lbs/ton Ash				Lbs/ton Dry Lignite	Lbs/ton Ash
187	109	R.T.	40	45	150	2.6	68	.024	45	150
188		"	33	60	200	1.5	75	.020	51	170
189		"	25	90	300	0.9	75	.019	54	180
184		80°C	40	45	150	3.4	73	.022	45	150
185		"	33	60	200	3.1	73	.023	60	200
186		"	25	90	300	1.7	82	.016	90	300
190		"	22	105	350	1.0	80	.015	87	290
191		"	19	120	400	0.8	81	.017	90	300
192		"	9	300	1000	0.2	81	.016	104	345
221	103	R.T.	33	48	200	1.5	66	.020	42	175
245		80°C	22	84	350	---	82	.014	71	295
222		"	22	84	350	1.2	79	.015	68	285
219		"	17	120	500	0.7	73	.015	74	310
220		"	9	240	1000	0.3	76	.015	86	360
224	101	R.T.	33	42	200	3.5	*	----	---	---
226		"	17	105	500	1.0	70	.030	74	350
225		80°C	22	74	350	2.3	71	.027	74	350
227		"	17	105	500	1.2	78	.026	87	415
246		"	17	105	500	---	80	.020	86	410
240	95	R.T.	25	99	300	0.9	74	.023	68	205
229		"	17	165	500	0.6	79	.022	69	210

Table 12 (Cont'd.)

ACID LEACHING OF LIGNITE ASH

22

Test No. LA-	Lignite No.	Leach		Original H ₂ SO ₄ in Leach		Filtrate pH	% Uranium Ext'd.	Ash Tailing (% U)	Acid Consumed	
		Temp.	Pulp Density (%)	Lbs/ton Dry Lignite	Lbs/ton Ash				Lbs/ton Dry Lignite	Lbs/ton Ash
239	95	80°C	19	132	400	1.3	80	.018	117	355
230		"	17	165	500	0.9	84	.017	119	360
233	97	R.T.	17	120	500	1.1	77	.009	96	400
234		80°C	17	120	500	1.4	75	.009	108	450
247		"	17	120	500	---	82	.008	108	450
241	86	R.T.	17	225	500	0.7	56	.009	126	280
242		80°C	15	270	600	1.0	64	.007	203	450
235		"	9	450	1000	0.6	71	.005	230	510
206	92	R.T.	33	48	200	4.8	1	.045	---	**
207		"	25	72	300	3.6	39	.028	---	**
211		"	17	120	500	3.3	52	.023	---	**
238		"	9	240	1000	1.2	70	.013	222	925
208		80°C	25	72	300	3.7	49	.021	---	**
209		"	22	84	350	3.4	52	.020	---	**
210		"	19	96	400	3.4	58	.017	---	**
212		"	9	240	1000	2.3	80	.011	---	**
216		"	6	360	1500	0.9	80	.008	295	1230
248	121	R.T.	9	314	1000	1.3	79	.010	279	890
236		80°C	9	314	1000	2.6	80	.010	---	**
249		"	6	471	1500	1.1	88	.006	391	1245

Table 12 (Cont'd.)

ACID LEACHING OF LIGNITE ASH

Test No. LA-	Lignite No.	Leach		Original H ₂ SO ₄ in Leach		Filtrate pH	% Uranium Ext'd.	Ash Tailing (% U)	Acid Consumed	
		Temp.	Pulp Density (%)	Lbs/ton Dry Lignite	Lbs/ton Ash				Lbs/ton Dry Lignite	Lbs/ton Ash
213	141	R.T.	17	105	500	3.2	32	.021	---	**
243		"	9	210	1000	1.0	67	.016	161	765
244		80°C	9	210	1000	---	70	.014	182	865
214		"	9	210	1000	1.2	61	.018	184	875
217		"	6	315	1500	0.7	61	.017	197	940

Ash: Raw lignite roasted at a furnace temperature of 800°C for 1 1/2 hrs.
Ash ground to -100M.

Leach Conditions: Ash agitated with 5% H₂SO₄ for 4 hrs at room temperature (R.T.) or 80°C.

Acid Consumption: Obtained by free-acid titration.

*Wash of cake would not filter - sample discarded.

**Assumed all acid used up - no titration made.

<u>Metal Cation</u>	<u>Quantity Ext'd. (lbs/ton of Ash)</u>	<u>Equivalent H₂SO₄ (lbs/ton of Ash)</u>
Fe	17	45
Al	131	715
Ca	20	50
Mg	6	25
Na	23	50
K	4	5
	Total	890

Aluminum compounds, obviously, were by far the largest consumers of acid in the test described. Qualitative observations suggest that this will also be true for other batches studied, though a firm conclusion must await the completion of several additional analyses. In previous tests with No. 92, the total consumptions of acid have been about 1000 lbs/ton of ash as measured by titration (see Table 12). The calculated consumption of 890 lbs/ton shown above is in good agreement with previous measurements considering that the recent test was made with limited excess acid and that no allowance was made for consumption by calcium minerals which reacted but remained in the residue as calcium sulfate.

From general inspection of the data, it is apparent that samples from the east side of Slim Buttes are more basic and, hence, greater consumers of acid than those from the west side. In a qualitative way, this difference between the groups might be predicted from a comparison of their mineral and chemical compositions (Table 2 and 3). It has been shown that the ash from east-side samples is composed mainly of clay minerals and is less diluted by inert constituents such as gypsum and quartz.

In considering the west-side samples separately, it may be observed that the acid consumptions are reasonably moderate in terms of uranium extracted and are probably within reach of process application. It may also be possible to lower the consumptions listed above by closer control of temperature and concentration during the leaching and/or by accepting a somewhat lower percent extraction (see Table 12). The condition finally established would be governed by the optimum balance between mining, burning and reagent cost.

At the present time, additional studies of uranium extraction from ash are being made which will permit a more thorough evaluation of the general process. Measurements pertinent to the reformation and recycle of acids through thermal decomposition of the heavy metal salts will be included in these tests. Molybdenum extractions in direct

acid leaching of the new ash samples have not been reported and these are being checked. In previous tests with ND-1 ash, the solubilization of molybdenum during acid leaching was quite low ($\sim 10\%$).

Leaching with Ammonium Carbonate

In previous work with low temperature ash from lignite sample ND-1, uranium extractions of 65-75% have been achieved by leaching with solutions of ammonium carbonate. From incomplete tests, it is indicated that similar extractions might be expected from the new west-side lignite, whereas extractions from the east-side samples may be somewhat lower. These data will be reported at a later date.

Ammonium Bisulfate Roast - Ammonium Carbonate Leach

From the preceding discussions, it is apparent that rather large quantities of reagents have been required in attaining reasonable extractions of uranium from some of the samples of lignite ash. In view of this, it is of interest to consider processes in which a fairly simple regeneration and recycle of reagents might be permitted.

As a possible approach to such a process, preliminary experiments have been made in which low temperature lignite ash was first roasted with ammonium bisulfate, to "open up" the semirefractory material, and then leached with a solution of ammonium carbonate, to solubilize the uranium and molybdenum as well as to separate these elements from unwanted constituents such as aluminum and iron. Presumably, this process would be self-sufficient in sulfate, from gypsum, and in carbon dioxide, from lignite burning, while recycle of the ammonium carbonate can be expected by simple boiling of the leach liquors. Almost all of the uranium will precipitate during this operation, and the sulfate will remain in the end liquors as ammonium sulfate. A cyclic process would require the recovery of the latter by crystallization, and the regeneration of ammonium bisulfate and ammonia by thermal decomposition. Surplus ammonium sulfate could probably be sold on the open market.

Extraction results are presented in Table 13. In many of these tests, the calcines were leached with water prior to the leach with ammonium carbonate. This was done to obtain as much information as possible concerning the reactions occurring during the roast but without detracting from the application of the data to ammonium carbonate leaching since the water-soluble uranium and molybdenum compounds would be expected to report to the ammonium carbonate solution.

Table 13AMMONIUM BISULFATE, AMMONIUM CARBONATE TREATMENT

Run No.	Lignite No. (Ash)	Bake Temp. (°C)	1st Leach		2nd Leach		Tailings		Total Ext'n. (%)	
			U Ext'd. (%)	Mo Ext'd. (%)	U Ext'd. (%)	Mo Ext'd. (%)	% U	% Mo	U	Mo
1104	109	300	--	--	72	52	0.013	0.06	72	52
1107	141	310	43	50	18	24	0.02	0.06	61	74
1108	92	350	60	52	21	23	0.012	0.06	81	75
1109	95	350	76	56	5	18	0.03	0.08	81	74
1110	97	350	68	80	11	3	0.012	0.02	79	83
1111	86	325	61	71	9	4	0.005	0.04	70	75
1112	121	325	54	62	20	9	0.011	0.04	74	71
1113	101	360	85	30	3	45	0.04	0.07	88	75

Ash Formation: Burned at a furnace temp. of 800°C for 2 hrs.

Roast Conditions: 2000 lbs of NH_4HSO_4 /ton of ash for 2 hrs at temp. shown.

Leach Conditions: 1st leach - water at 20% pulp density for 1 hour at room temperature.
2nd leach - 1200 lbs of $(\text{NH}_4)_2\text{CO}_3$ /ton of ash at a pulp density of 20% for 1 hour at room temperature. Solution pH was 8.2.

As shown in Table 13, all of the lignites tested have responded quite well to the roast-leach treatment. The extractions of uranium and molybdenum were appreciably higher than those obtained by treating the ash directly with a solution of ammonium carbonate. It may also be noted, however, that ratios of reagents to lignite (ash), as used in these tests, were rather high. Though most of the reagents may be regenerated, the size of the recycle operation in itself would be great.

Further tests are being made to establish the minimum reagent requirements. The separation of molybdenum from the process liquors will also be considered.

RECOVERY FROM HIGH TEMPERATURE ASH

The previous work with lignite ash has been concerned with material formed at a low (ca. 800°C) burning temperature. However, in the event that uraniumiferous lignite were to be used as a power plant fuel, the burning temperature would obviously be maintained at the highest acceptable level.

As the new lignite samples have become available, studies of the extraction possibilities from the higher temperature ash have been started. Experience thus far has shown that lignite burned at about 1100°C will produce an ash which may be fritted but is not yet molten. Current experiments are being made, therefore, with ash samples heated to this temperature range. The tests described below, made with ash samples so prepared, are only preliminary to a more thorough study of high temperature ashes. The heating periods used so far, for example, are probably in considerable excess of those to be expected in actual operation and may be an important factor in the extent of uranium re-fractorization. Indeed, partial data would indicate that the uranium availability may be unaffected if the heating time is very brief. This and other process variables are being examined in current tests and will be described in a later report.

Acid Leaching

Preliminary survey tests have been made with several different high temperature ash samples to determine the availability of the contained uranium to simple acid treatment. The leach conditions and results are shown in Table 14. Although the extractions varied considerably from batch to

Table 14
ACID LEACHING OF HIGH TEMPERATURE ASH

<u>Run No.</u>	<u>Lignite No. (Ash)</u>	<u>Time at 1100°C* (min.)</u>	<u>Acid** Used</u>	<u>Leach Time (hrs)</u>	<u>Leach Temp. °C</u>	<u>Final pH</u>	<u>U Ext'n. (%)</u>
1201	109	45	5% H ₂ SO ₄	8	60	---	65
1202	109	45	" "	3	85	---	55
1203	141	15	" "	4	85	---	65
1205	92	15	" "	4	85	1.1	60
1207	92	15	" "	4	85	1.0	64
1206	86	15	" "	4	85	---	23
LA160	ND-1-3	90	5% HNO ₃	6	80	0.8	59
LA161	ND-1-3	90	5% HCl	6	80	0.5	58
LA105	ND-1-3	90	5% H ₂ SO ₄	6	80	0.9	53

*Samples were prepared by ashing lignite at a furnace temperature of 800°C and then heating at 1100°C for the indicated times.

**All leachings were made at a 10% pulp density.

batch, the general effect of increased temperature (for rather long periods of time) was to decrease the availability of the uranium (compare Table 14 with Table 12). Substitution of nitric or hydrochloric acid for sulfuric acid gave no significant improvement in uranium extraction from ND-1 ash.

Ammonium Carbonate Leach

Experiments in which high temperature ash samples were leached with solutions of ammonium carbonate are shown in Table 15. These results are similar to those previously obtained with ND-1 lignite in that all extractions were quite low.

Ammonium Bisulfate Roast, Ammonium Carbonate Leach

Several samples of high temperature ash, formed under various conditions, have been subjected to the bisulfate roast, carbonate leach treatment. As in acid leaching, the uranium extractions from high temperature ash were considerably lower than those from low temperature ash which had been treated by the same procedure (compare Tables 16 and 13).

Fluoride, Sulfate, Carbonate Treatment

As mentioned above in discussion of the ammonium bisulfate, ammonium carbonate treatment of low temperature ash, it is pertinent to consider the application of those reagents which give the possibility of fairly simple regeneration and recycle. The bisulfate, carbonate treatment in itself has not been particularly effective on the more refractory high temperature ash (see above). Better extractions have been attained, however, by using a modification of this treatment in which the ash has been given a previous low temperature bake with ammonium bifluoride.

As mentioned above, such a process should be self-sufficient in sulfate and carbon dioxide, whereas the consumption of ammonia would be determined by the efficiency of the recycle operations. Fluorine, though rather formidable in original cost, also offers the opportunity for regeneration and recycle. In this case, fluorine would be given off during the roast as silicon tetrafluoride and excess ammonium bifluoride. If these gases are washed with dilute aqueous ammonia, hydrated silica will be precipitated,⁽⁴⁾ leaving a solution of ammonium fluoride which can be evaporated to dryness to form ammonia and ammonium bifluoride. Fluorides

Table 15
AMMONIUM CARBONATE EXTRACTIONS OF
HIGH TEMPERATURE ASH

<u>Lignite No.</u> <u>(Ash)</u>	<u>% Uranium Extraction</u> <u>(NH₄)₂CO₃ Leach</u>	
	<u>Room Temp.</u> <u>and</u> <u>Pressure</u>	<u>Temp. 80°C</u> <u>Pressure 35 psi</u>
86	12	10
92	8	32
95	8	11
97	5	5
101	11	11
103	3	7
109	21	34
121	8	14
141	8	3

Ash samples: High temperature ash prepared by heating 800°C ash for 1 hr at 1100°C in an oxidizing temperature.

Leaching: 15% (NH₄)₂CO₃ solutions used under the conditions shown such that the total reagent quantity was 3000 lbs/ton of ash.

Table 16

AMMONIUM BISULFATE, AMMONIUM CARBONATE TREATMENT
OF HIGH TEMPERATURE ASH

Run No.	Lignite No.	Ash Preparation		% U Ext'd.		Total % Ext'n.		Remarks
		Temp. (°C)	Time (min.)	1st Leach	2nd Leach	U	Mo	
1101	109	1100	60	18	18	36	35	} Magnetic, partly reduced ash.
1102	109	"	60	27	7	34	--	
1105	109	"	45	--	54	54	23	Completely oxidized ash.
1106	ND-1-3	"	15	--	39	39	--	" "
1114	86	"	15	23	4	27	77	" "
1115	92	"	15	38	22	60	75	" "
1116	92	"	60	54	14	68	--	" "
1117	92	1150	60	44	1	45	--	Partly sintered ash.

Ash formation: Ash originally prepared at a furnace temperature of 800°C and then treated under the conditions shown.

Roasting: 2 hours at 350°C.

Leaching: 1st leach - water at 20% pulp density for 1 hour at room temperature.
2nd leach - 1200 lbs of (NH₄)₂CO₃/ton of ash at a pulp density of 20% for 1 hour at room temperature.

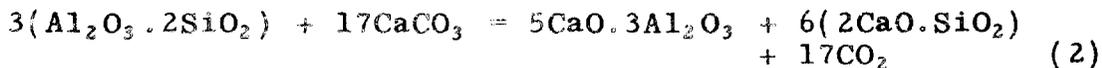
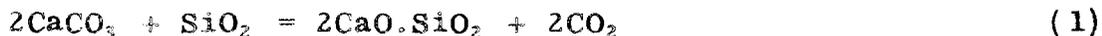
retained by the ash after the bifluoride treatment would presumably be decomposed in the subsequent roast with ammonium bisulfate and be recoverable from the off gases.

Extraction results as obtained from tests with five different lignite samples are reported in Table 17. Under the best conditions, extractions of about 90% of the uranium and 85% of the molybdenum have been obtained, high extraction being favored by low baking temperatures. Fluoride volatilization was favored by passing air or steam over the roasting mass.

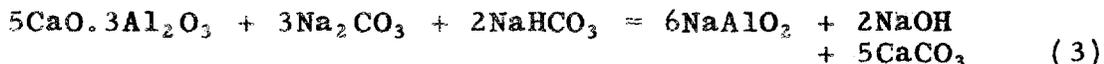
As in the previous case with low temperature ash, however, the quantities of reagents used, though amenable to recycle, are still quite large. Additional tests are being made with lower reagent quantities and also with admixed reagents in a single baking step.

Extractions from Lime and Lime-Soda Sinters

Cursory tests have been made in which the high temperature ash was roasted with lime or a lime-soda mixture and the resulting sinter was leached with sodium carbonate-bicarbonate solution. By analogy with the Pedersen and related processes, the lime, silica, and alumina can be expected to react under certain conditions according to equations (1) and (2).



Reaction (3) would take place during a subsequent carbonate leach.



It seemed possible that dissolution and transformation of aluminum and other constituents in this manner might leave the uranium mechanically exposed and hence more available to carbonate leaching.

The lignite ash used in the tests was prepared by burning a portion of batch No. ND-1-3 at a furnace temper-

Table 17

BIFLUORIDE-BISULFATE-CARBONATE TREATMENTOF HIGH TEMPERATURE ASH

Test No.	Lignite No. (Ash)	Bake ^a			Uranium Distribution, %				Mo Ext'd. %	F Volatilized + Dissolved % ^b
		NH ₄ HF ₂ Lbs/ton	(NH ₄) ₂ SO ₄ Lbs/ton	°C	Water Leach	(NH ₄) ₂ CO ₃ Leach	Total Ext'd.	Tails		
1015	ND-1-2	1200		600		66	66	34		
1022	ND-1-2	3000		600		82	82	18		
1027	109	2400	1200	275,350	60	25	85	15		83
1032	109	1200	2400	275,350		88	88	12		85
1050	86	2400	1200	250,350	88	3	91	9	96	92
1052	141	2400	1200	250,350	85	5	90	10	76	92
1055	109	2400		250	53					
			1600	350	26	17	96	4	72	
1056	109 ^c	2400		250	48					
			1600	350	36	8	92	8	58	
1058	109	2400		250	61	21				
			1600	390	1	6	89	11	96	99
1060	109 ^d	2000		275		12				
			2000	400		18		2		100
1057	92	2400		250	41	30				
			1600	390	7	9	87	13	85	98
1059	92	1600		250	31	33				
			2400	390	18	11	93	7	81	99
1061	92 ^d	2000		275		6				
			2000	400		13		4		99

Table 17 (Cont'd.)
BIFLUORIDE-BISULFATE-CARBONATE TREATMENT
OF HIGH TEMPERATURE ASH

High temperature ash prepared by heating 800°C ash at 1100°C, in an oxidizing atmosphere except as noted.

- a) Baked for 1 to 2 hours. Tests 1027 to 1052: 1.5 hours at each temperature without interruption; reagents mixed. Tests 1055 and ff.: Baked with bifluoride, leached, baked with bisulfate, re-leached.
- b) Calculated: Fluoride added minus fluoride found in tailings.
- c) Test 1056: Heated at 1100°C under reducing conditions.
- d) Tests 1060 and 1061: Baked under a current of steam.

ature of 800°C followed by calcination for about one hour at 1100°C. It was then ground to minus 100 mesh, mixed with CaCO₃ or a CaCO₃-Na₂CO₃ mixture and roasted in a high temperature furnace. After cooling, the sinter was leached with ten times its weight of a solution containing 10% Na₂CO₃ and 5% NaHCO₃ for 4 hours at 80°C. The results from these tests are given in Table 18.

It is apparent from the data that carbonate leaching can be improved by the lime sinter operation, but so far a maximum uranium extraction of only 50% has been achieved. It is further indicated that the temperature range, within which good extractions might be achieved, is rather limited (see tests LA-101, LA-99, and LA-95). The same seems to hold true for the composition of the sinter. Even if better recoveries could be obtained, the additional complication of variable feed compositions would probably make such a process extremely difficult if not impossible to control. Further work with lime sintering is not contemplated at this time.

Chloridizing Roast

In tests with high temperature ash from lignite ND-1, uranium extractions have been increased appreciably (from 55 to 75%) by roasting with NaCl prior to acid leaching. A one-hour roast at 850°C with 9% NaCl was nearly optimum for the process. Recent tests, however, made under the same conditions but with a different lignite sample, have not shown any significant benefit from the chloridizing roast. Further survey experiments with other lignite samples are in progress.

COMPOSITIONS OF VARIOUS FRACTIONS FROM RAW AND ASHED LIGNITES

Screen Analyses of Lignite Ash

Screen analyses have been performed on samples of ND-1 lignite which had been ashed at furnace temperatures of 500°C, 800°C, and 1000°C. The three samples received a thorough wet screening on a 325 mesh screen, and the fractions were filtered and dried. After drying, the +325 mesh material was screened (for 15 to 20 minutes in a Ro-Tap) using 10, 20, 35, 65, 100, 200, and 325 mesh screens. The fraction on each screen was weighed, ground through 80 mesh and submitted for uranium and molybdenum analyses. Results are shown in Tables 19, 20, and 21.

Table 18
EXTRACTION FROM LIME SINTERS

Test No.	Roast Agent		Roast		Description of Sinter	Filtrate pH	Uranium Extraction %
	CaCO ₃ (gms)	Na ₂ CO ₃ (gms)	Time (hrs)	Temp. (°F)			
LA-124	None		None			9.4	5
LA- 92	4	--	1	2500	Brittle, black glass	9.8	3
LA- 94	4	--	1	2200	Extremely hard	9.9	20
LA-101	4	--	1	2150	Hard	9.9	22
-102	4	1	"	"	Very hard	9.8	32
JB- 9	2	--	1	2100		9.7	33
-10	3	--	1	"		9.7	32
LA- 99	4	--	1	"	Medium	9.8	49
-100	4	1	1	"	"	9.8	53
JB-11	6	--	1	"		9.8	23
-12	4	--	1/2	"		9.8	24
-13	4	--	2	"		9.7	34
LA-97	2	--	1	2000	Soft	9.9	7
-95	4	--	"	"	"	10.0	5
-98	6	--	"	"	"	10.2	4

10 gms of ash per test.

Sinters leached with sodium carbonate-bicarbonate solution.

Table 19
SCREEN ANALYSIS 500°C ASH

Screen (Mesh)	Analysis		Wt. % Ret.	Cumul. Wt. % Ret.	% Distribution		Cumul. % Dist.	
	U	Mo			U	Mo	U	Mo
+10	0.0039	0.034	8.3	8.3	0.61	1.01	0.61	1.01
+20	0.0026	0.043	9.8	18.1	0.48	1.51	1.09	2.52
+35	0.0036	0.132	10.0	28.1	0.68	4.73	1.77	7.25
+65	0.0044	0.206	8.3	36.4	0.69	6.14	2.46	13.39
+100	0.0090	0.248	3.7	40.1	0.63	3.29	3.09	16.68
+200	0.0130	0.123	5.7	45.8	1.40	2.52	4.43	19.20
+325	0.0210	0.219	4.6	50.4	1.83	3.12	6.26	22.32
-325 (dry)	0.043	0.290	2.0	52.4	1.63	2.08	7.89	24.40
-325 (wet)	0.102	0.443	47.6	100.0	92.11	75.60	100.0	100.0
Totals			100.0*		100.0**	100.0		

*Normalized for loss of water-soluble components during wet screening.

**Uranium metallurgical balance corresponds to a head uranium content of 0.053%. Normal ash contains about 0.16% U; therefore, about 68% of the total uranium was water soluble.

Table 20
SCREEN ANALYSIS 800°C ASH

Screen (Mesh)	Analysis		Wt. % Ret.	Cumul. Wt. % Ret.	% Distribution		Cumul. % Dist.	
	U	Mo			U	Mo	U	Mo
+10	0.015	0.083	9.7	9.7	1.21	3.74	1.21	3.74
+20	0.034	0.11	11.3	21.0	3.19	5.79	4.40	9.53
+35	0.105	0.17	13.7	34.7	11.96	10.83	16.36	20.36
+65	0.144	0.24	13.6	48.3	16.25	15.18	32.61	35.54
+100	0.124	0.23	7.0	55.3	7.23	7.50	39.84	43.04
+200	0.143	0.28	9.6	64.9	11.40	12.95	51.24	55.99
+325	0.137	0.27	7.0	71.9	7.97	8.80	59.21	64.79
-325 (dry)	0.174	0.26	2.5	74.4	3.62	3.03	62.83	67.82
-325 (wet)	0.175	0.27	25.6	100.0	37.20	32.20	100.0	100.0
Totals			<u>100.0</u>		<u>100.0</u>	<u>100.0</u>		

Table 21

SCREEN ANALYSIS 1000°C ASH

<u>Screen (Mesh)</u>	<u>Analysis</u>		<u>Wt. % Ret.</u>	<u>Cumul. Wt. % Ret.</u>	<u>% Distribution</u>		<u>Cumul. % Dist.</u>	
	<u>U</u>	<u>Mo</u>			<u>U</u>	<u>Mo</u>	<u>U</u>	<u>Mo</u>
+10	0.06	0.13	12.5	12.5	4.36	5.81	4.36	5.81
+20	0.16	0.21	24.2	36.7	22.50	18.24	26.86	24.05
+35	0.20	0.24	21.5	58.2	25.00	18.54	51.86	42.59
+65	0.20	0.29	17.6	75.8	20.45	18.34	72.31	60.93
+100	0.20	0.34	7.0	82.8	8.14	8.54	80.45	69.47
+200	0.18	0.38	8.2	91.0	8.62	11.48	89.07	80.95
+325	0.20	0.51	4.1	95.1	4.78	7.50	93.85	88.45
-325 (dry)	0.16	0.60	1.4	96.5	1.28	3.01	95.13	91.46
-325 (wet)	0.24	0.68	3.5	100.0	4.87	8.54	100.00	100.00
Totals			<u>100.0</u>		<u>100.00</u>	<u>100.00</u>		

Since part of the uranium in the 500°C ash is water soluble, the screening of this ash was also performed using dry material only. These results are shown in Table 22.

The data illustrate that both the uranium and molybdenum tend to concentrate in the fine sizes, especially in the 500°C ash. With increasing temperature, increasing percentages of both elements appear in the coarse sizes. At 1000°C, the ash has aggregated and reacted to such an extent that only 20% of the uranium and 30% of the molybdenum are found in the material passing 100 mesh.

Analyses and Leachings of Air Classified Ash

In a previous report,⁽²⁾ partial analyses were given of 500°C, 800°C, and 1000°C ash (ND-1) samples which had been air classified in a Roller Particle Size Analyzer. Using the same separation method, other samples have been prepared recently from similar batches of ash. A portion of each of these new samples was submitted for molybdenum, iron, uranium, sulfate and silica determinations. The remainder of each sample was then subjected to a standard sulfuric acid leach to determine whether there were notable differences between the fractions in the availability of contained uranium.

The chemical composition of the various samples are listed in Table 23. In Table 24, tests are described in which each of the classified samples was given two consecutive leachings at 80°C for 4-6 hours with 5% solutions of H₂SO₄ (1000 lb/ton). Also included in the table are results from the leaching of cuts of the 500°C ash fractions with pure water.

It may be observed from the data that the uranium extractions in percent were essentially the same for all fractions of an ash which had been formed at a given furnace temperature. This means, of course, that the tailings from the relatively rich fine fractions were correspondingly greater in uranium concentration than those from the lean coarse fractions (Column 7, Table 24).

In agreement with previous experience, when the burning temperature was increased the average uranium extraction from each series of samples decreased. Also, more of the ash was found in the coarse fractions, and the uranium became more evenly distributed. For example, in tests with 1000°C ash, the uranium contents of the sized samples were comparatively similar, and the uranium concentrations in the process tailings were also similar, but in all cases were at a higher level than those obtained from ash formed at lower temperatures.

Table 22

DRY SCREEN ANALYSIS OF 500°C ASH

Screen (Mesh)	Analysis		Wt. % Ret.	Cumul. Wt. % Ret.	% Distribution		Cumul. % Dist.	
	U	Mo			U	Mo	U	Mo
+10	0.0043	0.17	8.44	8.44	0.28	4.15	0.28	4.15
+20	0.0048	0.13	13.85	22.29	0.52	5.22	0.80	9.37
+35	0.014	0.17	12.24	34.53	1.38	6.08	2.18	15.45
+65	0.129	0.32	15.90	50.43	16.03	14.75	18.2	30.20
+100	0.170	0.43	7.44	57.87	9.89	9.28	28.10	39.48
+200	0.210	0.46	13.10	70.97	21.50	17.48	49.60	56.96
+325	0.220	0.49	16.93	87.90	29.16	24.10	78.76	81.06
-325	0.225	0.54	<u>12.10</u>	100.0	<u>21.30</u>	<u>18.95</u>	100.0	100.0
Totals			100.0		100.0	100.0		

Table 23

DATA FROM AIR CLASSIFICATION OF LIGNITE ASH

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Sample	% of Total Wt.	U		Mo*		Fe		SiO ₂		SO ₄	
		%	% of Total	%	% of Total	%	% of Total	%	% of Total	%	% of Total
<u>Ash burned at 500°C (Av. head - 0.14% U)</u>											
Residue (coarse)	12	.007	0.6	.11	5	6.3	4	53.4	28	20.4	9
1 1/8" chamber	10	.017	1.2	.15	5	7.4	4	40.1	18	27.2	10
2 1/4" chamber	37	.110	30	.26	32	14.2	27	20.3	33	34.2	47
9" chamber	41	.230	68	.42	58	29.9	65	12.0	21	22.6	34
<u>Ash burned at 800°C (Av. head - 0.15% U)</u>											
Residue (coarse)	36	.034	8	.25	26	11.0	20	36.4	49	21.4	41
1 1/8" chamber	18	.110	13	.29	15	15.6	15	31.5	22	17.6	18
2 1/4" chamber	29	.210	40	.42	35	23.4	36	19.1	21	19.1	30
9" chamber	17	.350	39	.48	24	32.0	29	12.1	8	12.0	11
<u>Ash burned at 1000°C (Av. head - 0.17% U)</u>											
Residue (coarse)	54	.15	47	.25	42	16.9	45	36.7	62	6.1	42
1 1/8" chamber	14	.16	13	.35	15	19.0	13	30.3	13	7.7	14
2 1/4" chamber	21	.18	22	.45	29	21.2	26	24.2	19	11.6	31
9" chamber	11	.30	18	.42	14	30.5	16	18.3	6	9.5	13

*Mo - densitometric spectrographic analysis ($\pm 10\%$).

Table 24

SULFURIC ACID LEACH OF AIR CLASSIFIED LIGNITE ASH

Sample	Weight Distribution %	% U	% Distribution U Heads	% U Extraction		Tail Analysis % U	% Distribution U Tails
				1st Leach	1st + 2nd Leach		
<u>Ash burned at 500°C (Av. head - 0.14% U)</u>							
Residue (coarse)	12	.007	0.6	55*	--	.004	1
1 1/8" chamber	10	.017	1.2	71*	--	.006	1
2 1/4" chamber	37	.110	30	70*	--	.035	29
9" chamber	41	.230	68	76*	--	.075	69
Weighted Average: Tail analysis, % U = .045; % extraction = 69							
Residue (coarse)	12	.007	0.6	77	85	.002	1
1 1/8" chamber	10	.017	1.2	91	93	.002	1
2 1/4" chamber	37	.110	30	93	96	.010	19
9" chamber	41	.230	68	86	93	.038	79
Weighted Average: Tail analysis - 1 leach, % U = .020; % extraction = 86 2 leaches, % U = .013; % extraction = 91							
<u>Ash burned at 800°C (Av. head - 0.15% U)</u>							
Residue (coarse)	36	.034	8	75	78	.010	12
1 1/8" chamber	18	.110	13	81	84	.025	15
2 1/4" chamber	29	.210	40	83	85	.045	43
9" chamber	17	.350	39	87	89	.053	30
Weighted Average: Tail analysis - 1 leach, % U = .034; % extraction = 78 2 leaches, % U = .030; % extraction = 80							

Table 24 (Cont'd.)

SULFURIC ACID LEACH OF AIR CLASSIFIED LIGNITE ASH

Sample	Weight Distribution %	% U	% Distribution U Heads	% U Extraction		Tail Analysis % U	% Distribution U Tails
				Ist Leach	Ist + 2nd Leach		
<u>Ash burned at 1000°C (Av. head - 0.17% U)</u>							
Residue (coarse)	54	.15	47	56	62	.057	53
1 1/8" chamber	14	.16	13	56	62	.061	15
2 1/4" chamber	21	.18	22	62	67	.059	20
9" chamber	11	.30	18	76	81	.059	12

Weighted Average: Tail analysis - 1 leach, % U = .069; % extraction = 60
 2 leaches, % U = .058; % extraction = 67

Leach Conditions: 1st leach - 10 ml 5% H₂SO₄ per g ash for 6 hrs at 80°C.
 2nd leach - 10 ml 5% H₂SO₄ per g ash for 4 hrs at 80°C.

*H₂O leach only - 10 ml H₂O per g ash for 6 hrs at room temperature.

Qualitatively, it is suggested that the uranium, held originally in the lignite by organic matter, upon burning becomes an inherent part of the rather uniform fine ash fraction. With increasing burning temperatures, the uranium becomes refractorized, presumably due to physical or chemical interaction with the fine mineral constituents. Simultaneously, the fine particles begin to aggregate, distributing more and more to the coarser fractions as the temperature and time of heating increase. Thus, in any particular series of sized samples, the uranium would be contained in the same form, i.e., in a matrix which chemically is fairly uniform in composition and properties. The difference in the uranium concentrations of different fractions (either heads or tailings) would be attributed to differences in the extent of dilution by constituents barren of uranium.

Uranium Content of Mineral Fractions

Three (ca. 20 g) samples of organic-rich material were hand-picked from a large batch of oven-dried lignite. Each sample was carefully weighed, ashed at a furnace temperature of 500°C, reweighed, and then submitted for wet chemical analyses of uranium, molybdenum, titanium, aluminum, calcium, iron and silicon. A densitometric spectrographic analysis was also obtained on molybdenum along with a semiquantitative analysis of other trace metallic constituents.

A sample of ash obtained from normal lignite was submitted for analyses along with the hand-picked samples as a basis for comparison.

Previous work^(1,2) has shown a definite concentration of uranium in the organic-rich fraction. The purpose of these tests was to determine whether the uranium was associated with the organic matter itself, or associated with some trace metallic constituent, which also tended to concentrate in the organic-rich fraction. Results for the normal lignite ash and the three hand-picked samples are shown in Table 25.

From the ash contents of the hand-picked fractions (15%) and the normal lignite sample (34%), any element associated uniformly with the organic material should have been concentrated by a factor of approximately 3 (ashed basis). The uranium concentration was increased to a greater extent than this, while other elements changed as follows:

Table 25

COMPARISON OF SPECTROGRAPHIC AND CHEMICAL
ANALYSES OF ASHED HAND-PICKED LIGNITE SAMPLES

Element	Spectrographic ^a				Chemical			
	Normal	Hand-picked Samples			Normal	Hand-picked Samples		
	Ash	No. 1	No. 2	No. 3	Ash	No. 1	No. 2	No. 3
Ag	<.04	<.04	<.04	<.04	----	----	----	----
Al	----	----	----	----	5.5	10.0	9.3	9.0
B	.03	.07	.07	.07	----	----	----	----
Ba	.15	.08	.15	.15	----	----	----	----
Be	<.001T	.002	.002	.002	----	----	----	----
Ca	----	----	----	----	7.8	0.73	0.77	0.69
Co	<.04	<.04	<.04	<.04	----	----	----	----
Cr	<.04T	<.04T	<.04T	<.04T	----	----	----	----
Cu	<.04T	<.04T	<.04T	<.04T	----	----	----	----
Fe	----	----	----	----	17.6	24.3	23.8	25.1
K	.3	.08	.08	.08	----	----	----	----
Li	.01	.01	.01	.01	----	----	----	----
Mg	1	2	2	2	----	----	----	----
Mn	.04	.08	.08	.08	----	----	----	----
Mo	.30 ^b	.58 ^b	.62 ^b	.68 ^b	0.29	0.57	0.54	0.63
Na	.8	1	1	1	----	----	----	----
Ni	<.08T	<.08T	<.08T	<.08T	----	----	----	----
Pb	<.04	<.04	<.04	<.04	----	----	----	----
Si	----	----	----	----	10.4	5.9	6.2	6.1
Sn	<.04	<.04	<.04	<.04	----	----	----	----
Ti	----	----	----	----	0.31	0.41	0.42	0.40
U	----	----	----	----	0.16 ^c	0.62 ^d	0.78 ^d	0.59 ^d
V	<.04	<.04	<.04	<.04	----	----	----	----
Zn	<.3	<.3	<.3	<.3	----	----	----	----
Zr	<.08	<.08	<.08	<.08	----	----	----	----
Ash	----	----	----	----	34.2	14.7	14.05	15.3

a) Spectrographic results (with exception of Mo) are semi-quantitative estimates which were obtained for use as a guide to chemical analysis and should not be interpreted or construed to be precise quantitative determinations.

b) Ash was dissolved for Mo determination. Precision is $\pm 10\%$ of the amount present.

c) Std. error $\pm 20\%$.

d) Std. error $\pm 5\%$.

Calcium, ca.	x0.094
Silicon	0.58
Titanium	1.3
Iron	1.4
Aluminum	1.7
Molybdenum	2.0
Potassium	0.3
Lithium	1
Sodium	1
Magnesium	2
Manganese	2
Beryllium	2

These changes probably resulted from the preferential rejection of the coarser particles of gypsum, quartz, jarosite, and lumps of clay. On basis of the measured changes of the elements in these minerals, the elements which were more uniformly distributed should have been concentrated by a factor of about 1.9, in agreement with the factor of 2.0 found for molybdenum and also indicated for magnesium, manganese, and beryllium.

The uranium was concentrated in the three ashed samples by factors of x3.9, x4.9, and x3.7, as compared with factors of x3.0, x3.2, and x2.9 to be expected from the change in ash contents, if the uranium were uniformly distributed in the organic material. These differences are beyond the standard error for the analyses (Table 25), and suggest that the uranium was actually concentrated in the type of organic particles which were also low in ash.

Correlation of Uranium with Magnetic Material in Reduced Ash

When lignite is burned under reducing conditions at high temperatures, a black ash is formed which contains appreciable quantities of magnetic material (probably magnetite). A sample of such an ash (obtained by burning lignite No. 109 at a furnace temperature of 800°C, then heating it at 1100°C in a closed muffle) has been separated with a hand magnet into five fractions. The weights and uranium contents were as follows:

	<u>Non- Magnetic</u>	<u>Slightly Magnetic</u>	<u>Middlings</u>	<u>Strongly Magnetic</u>	<u>Most Magnetic</u>
wt, g:	0.785	0.630	1.058	1.011	0.262
U, mg/g:	0.28	0.32	0.69	1.20	~1*
U, mg:	0.22	0.20	0.73	1.22	0.2-0.3

*From material balance: Analytical sample lost.

Other ash samples are being similarly studied.

Sulfate in Lignite Ash

When lignite is ashed, sulfate is lost from the material through both decomposition and reduction. The extent of these losses from lignite ND-1, burned under several different conditions, are shown below.

<u>Furnace Temp.</u> °C	<u>Time</u> (hrs)	<u>SO₄ in Ash</u> (%)
		(37)**
500*	16	30
800	2	22
900	1	20
1000	0.75	18
1000	1.75	14
1100	1	11

*Placed in furnace at 500°C - others were placed in furnace at 400°C and temperature raised to that indicated.

**Calculated from head analysis.

ANALYSIS OF USGS SAMPLES

Eight batches of coal and shale have been sent to the Oak Ridge National Laboratory by the U. S. Geological Survey. Chemical analyses of these samples are reported in Table 26.

Four of the samples, from the La Ventana Mesa, New Mexico, were described as follows:

USGS 88-90: A composite sample of siltstone, impure shaly coal, and carbonaceous clay.

USGS 473-6: A composite sample of subbituminous and impure shaly coal.

USGS 477: A composite sample of uranium-bearing carbonaceous shale, and subbituminous coal.

USGS 490-1: A sample of subbituminous coal.

Table 26

COMPARISON OF HEAD ANALYSES OF USGS COAL AND
SHALE SAMPLES ON "AS-RECEIVED" BASIS

Analysis	USGS- 88-90	USGS- 477	USGS- 473-6	USGS- 490-1	USGS- FC	USGS- GC	USGS- Wyo-1	USGS- Wyo-2
Loss at 110°C	4.0	19.4	26.5	27.9	2.3	6.0	28.9	29.2
Volatile matter	17.1	30.7	27.3	34.6	25.4	14.7	37.6	35.1
Total carbon	5.1	20.1	21.2	32.8	21.4	6.6	34.3	29.2
Nitrogen	0.3	0.7	0.6	0.9	0.3	0.2	1.2	1.1
Total sulfur, (S)	1.3	0.9	0.3	1.7	2.5	---	0.9	1.0
Sulfate sulfur, (SO ₂)	3.3	1.3	<0.03	3.5	2.3	5.8	1.1	1.4
Carbonate, (CO ₂)	0.12	0.17	0.20	0.04	8.7	0.19	0.09	0.09
Ash	82.4	43.8	34.8	19.4	61.2	81.6	13.95	20.0
Uranium	0.11	0.4	0.08	0.055	0.037	0.071	.004	.005
SiO ₂	46.4	20.5	13.5	4.1	27.9	54.4	5.1	8.2
K ₂ O	4.2	0.7	0.09	0.05	0.5	5.1		
Na ₂ O	0.3	0.3	0.14	0.06	0.13	0.4		
CaO	1.5	3.8	5.2	2.7	12.9	4.1	1.3	1.3
MgO	1.5	1.2	1.6	0.3	1.1	0.2	0.3	0.3
Fe ₂ O ₃	9.9	6.1	1.8	3.8	3.9	1.6	1.3	1.9
Al ₂ O ₃	12.2	6.2	10.1	4.07	9.2	8.7		5.2
MoO ₃	0.05	---	---	---	---	---	---	---

Two samples were received from Idaho. One was a uranium-bearing carbonaceous shale from the Goose Creek District, Cassia County, and the other was a uranium-bearing coal from the Fall Creek District, Bonneville County. These samples have been designated as USGS-GC and USGS-FC, respectively.

Little is known of two other subbituminous coal samples received from Wamsutter, Wyoming. These have been designated as USGS-Wyo-1 and USGS-Wyo-2, respectively.

SUMMARY

Current studies are being made of several new lignite samples from the Slim Buttes region of Harding County, South Dakota. General differences in composition and reaction between the east Slim Buttes samples and those from the west side have been noted. It is not known whether these differences are general for the lignite beds in the two regions or whether they are the result of variations in sampling. The east-side samples were indicated to be from surface section and the west-side samples from auger hole or mine.

Reasonable extractions of uranium have been obtained by direct acid leaching of raw lignite. The acid requirements for this treatment have been rather high, especially for the east-side samples. Preliminary tests indicate that more efficient utilization of acid is achieved by using limited amounts of concentrated nitric acid in the presence of an organic extractant, e.g., TBP in CCl_4 .

Solubilization of uranium from raw lignite has been obtained by leaching with ammonium carbonate solution, but the resulting slurry was almost impossible to filter. When the more volatile matter was burned from ND-1 lignite prior to leaching, 65% of the uranium was extracted into an ammonium carbonate solution and filtration of the slurry was rapid.

Acceptable extractions of uranium from lignite char (retorted 2 hrs at 500°C) have not been obtained by any of the methods employed thus far.

Satisfactory extractions of uranium (75-80%) have been obtained from most samples of low temperature lignite ash by simple acid leaching. Consumptions of acid by the west Slim Buttes samples were moderate and within reach of process application whereas the consumption by the east-side samples were quite large.

Reasonable extractions from low temperature ash by ammonium carbonate leaching have also been indicated. Extractions of both uranium and molybdenum may be increased by baking the ash with ammonium bisulfate prior to the ammonium carbonate leach.

Treatment of lignite ash for extended periods at a high temperature causes partial refractorization of the uranium. To obtain extractions from this material that are comparable to those from low temperature ash a process has been devised which employs consecutively an ammonium bifluoride roast, an ammonium bisulfate roast and an ammonium carbonate leach. The reagents used in this process would presumably be amenable to recycle.

In other preliminary tests with high temperature lignite ash, it has been shown that the uranium in the ash does not become refractory if the heating periods are brief. Since the time required for refractorization is apparently longer than the anticipated retention time of the lignite particles in the hottest zone of some furnaces, it is suggested that uranium recovery from certain types of high temperature ash might be achieved by simple leaching methods. Further tests of this possibility are being made.

Studies of lignite fractions have been continued to determine the association of the uranium in the lignite and in the ash. Analysis of hand-picked lignite particles which were low in ash content indicated that only the uranium (of several elements checked by chemical or spectrographic analysis) was concentrated along with the organic material. Size analysis of ash samples prepared at different furnace temperatures indicated that at low temperatures the uranium was associated preferentially with the fine fractions, while at higher temperatures the distribution was more nearly uniform, presumably because of aggregation of the uraniumiferous fines. Magnetic separation of a reduced, high-temperature ash showed concentration of uranium with the magnetic fraction (presumably magnetite).

REFERENCES

- 1) "Progress Report Uranium Chemistry of Raw Materials Section, April 1, 1952 to June 30, 1952"; ORNL - Y-12, ORNL-1384, October 16, 1952.
- 2) "Progress Report Uranium Chemistry of Raw Materials Section; Part I, Uranium from Lignites; July 1, 1952 to September 30, 1952"; ORNL - Y-12, ORNL-1446, November 13, 1952.
- 3) Ingles, J. C., "Determination of Free Acid in Leach Liquors," Dept. of Mines and Technical Surveys (Canada), NP-1598, March 18, 1950.
- 4) Hileman, A., Am. J. Sci., (4) 22, 332 (1906).