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MATERIALS CHEMISTRY DIVISION

PROGRESS REPORT

LABORATORY RECORDS 1954

URANIUM CHEMISTRY OF RAW MATERIALS SECTION

Inv 55

Part I

Uranium From Lignites

JULY 1, 1952 to SEPTEMBER 30, 1952

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PROGRESS REPORT

URANIUM CHEMISTRY OF RAW MATERIALS SECTION

Part I. Uranium from Lignites

July 1, 1952 to September 30, 1952

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November 13, 1952

OAK RIDGE NATIONAL LABORATORY

Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation

Oak Ridge, Tennessee

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URANIUM CHEMISTRY OF RAW MATERIALS

INTRODUCTION AND SUMMARY

The studies of uraniferous lignites which have been made during the last quarter may be included in the following categories: (1) chemical processing of raw lignite, (2) chemical processing of lignite ash formed at low and intermediate temperatures, (3) chemical processing of lignite ash formed at high temperatures, (4) uranium content of the mineral and organic constituents of lignite and (5) concentration of uranium from raw and roasted lignite by physical methods. Work on the extraction of uranium from chars as formed during low and high temperature retorting operations has been started.

Further tests with 500°C ash from sample ND-1 have confirmed previous work, showing extractions up to 75% of the uranium by water leaching.

Treatment of ash formed at intermediate temperatures (~800°C) with solutions of ammonium carbonate has continued to show promise in that 75% of the uranium and 50% of the molybdenum can be consistently extracted from the sample on hand. Ammonium sulfate has been recovered from the solutions in a "free flowing", marketable form. Similar extractions of the uranium from this ash can also be obtained by treating with solutions of dilute acid. The consumptions of acid in these cases have been about 200 lbs. H_2SO_4/ton of ash.

About 70-75% of the uranium can be extracted from sample ND-1 by treating the raw lignite with solutions of 5% H_2SO_4. Tentative measurements show the acid comsumption to be around 140 lbs./ton of dried lignite.

Quenching of high temperature (1000°C) ash has not improved extractions from this material with ammonium carbonate. Other tests with high temperature ash and with lignite chars are incomplete.

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Examination of hand-picked, organic-rich lignite samples has again demonstrated the association of uranium with the organic material. Within the limit of the accuracy of the method used, correlation was not detected between the uranium concentration and that of any of the trace elements.

Attempts to concentrate the uranium by air classification of raw lignite were unsuccessful. Air classification of low temperature (500°C) ash placed almost all of the uranium with the fine, less than five micron, fraction. With ash formed at higher temperatures (800°C and 1000°C), the uranium concentrations of the finest particles were greatest, but appreciable amounts were also retained in the coarse fractions.

Encouraging results were obtained from a flotation test in which the gangue constituents were floated from the carbonaceous material.

Erratum

The "fixed" carbon analysis reported for lignite ND-1 on page 89 of ORNL-1308 is not correct. Tentative rechecks on this sample would place the fixed carbon above 20%. The B.T.U. values reported on page 14 of ORNL-1384 are also being checked.

CHEMICAL PROCESSING

Two methods were described previously for treating lignite ash which had been formed at temperatures below the point of incipient fusion. These are: (1) leaching 800°C ash with $(NH_4)_2CO_3$, including the recycle of NH_3, the utilization of CO_2 from stack gases, and possible production of $(NH_4)_2SO_4$, MoO_3 and uranium as products, and (2) controlled burning of the lignite at 500°C to form an acidic ash which will yield uranium to a water leach. Both of these methods, especially the first, have received further study and the results from this work are reported below.

Tests with 500°C lignite ash have confirmed previous work showing extraction of 75% of the uranium by water leaching.

The ammonium carbonate process has continued to show promise in that 75% of the uranium and 50% of the molybdenum can be consistently extracted from the lignite sample on hand. Uranium has been precipitated from the leach liquors by simply distilling off the excess $(NH_4)_2CO_3$. Ammonium sulfate has been recovered from the solutions in a crystalline, "free-flowing", marketable form. Further tests of this process will be made with lignite sample ND-1 but other, perhaps more representative, samples are needed to see if the same recoveries can be maintained.

Other methods for approaching the lignite-uranium problem have also been considered during the quarter. These are: (1) extraction of uranium by direct treatment of raw lignite, (2) extraction of uranium by acid leaching of 800°C ash, (3) removal of uranium from a high temperature refractory ash as formed in the production of power by direct burning, and (4) extraction of uranium from lignite chars as formed during various retorting operations. Preliminary test data from the first two of these studies are reported below.

Reasonable extractions of uranium are obtained by direct acid leaching of raw lignite sample ND-1 when the contacting acid is sufficiently concentrated ($\sim$5% H_2SO_4). Tentative measurements would show the acid consumption for this sample to be about 140 lbs. H_2SO_4/ton of raw dried lignite under conditions such that the uranium extraction is about 70%. Reasonable uranium extractions (70%) have also been obtained by ammonium carbonate leaching, but the resultant slurries are extremely hard to filter.

As shown last quarter,[1] 75% of the uranium can also be extracted from a 800°C ash of ND-1 by leaching with sulfuric acid solutions. Tentative measurements in this case have

shown consumptions of about 200 lbs. of H_2SO_4/ton of ash, i.e., equivalent to 60 lbs./ton of original raw dried lignite. This value and that given above for raw lignite are both much lower than reported by BMI[2] for a different sample of Dakota lignite.

Work with a high temperature ash (1000-1150°C) has been started but most of the test results are incomplete. Quenching of 1000°C ash has not proved beneficial to uranium extractions into ammonium carbonate solutions.

Direct Leaching of Raw Lignite with Acids, Bases and Salts

Leaching with Acid

Preliminary data from direct leaching of raw lignite sample ND-1 with sulfuric acid are presented in Tables 1, 2 and 3. When the original acid concentration was 5-9% and the pulp density was about 20%, extractions of 75% of the uranium were obtained. The leach solutions were, in all cases, discolored by an undetermined quantity of organic matter.

Acid Consumption: The acid consumed during leaching with 5% H_2SO_4 at a 25% pulp density has been tentatively measured at 140 lbs./ton of dried lignite for sample ND-1. This is a much lower quantity than reported for the sample studied sometime ago at Battelle.[2] Apparently, the sample there contained appreciable quantities of reactive bases such as dolomite.

Uranium in Leached Tailings: Although the percentage extractions of uranium from batch ND-1 are satisfactory, the uranium content of this batch is greater than the probable average for uraniferous lignite and the leached tailings carry appreciable concentrations of uranium, especially on an ash basis. The reason for the relative unavailability of about 25% of the uranium content is not known at this time. Certainly, as soon as possible, other lignite samples of lower initial uranium content should be examined to determine whether the uranium left in the tailings is proportionally lower and the same extraction can be maintained or whether the amount of uranium left in the tailings is much the same, so that the efficiency of the extractions would be seriously reduced.

Filtration: The filterability of the lignite slurries is dependent upon the quantity of acid used in the leach. When the acid was either insufficient or in large excess filtration was very slow. With intermediate quantities, e.g., 200 lbs. of H_2SO_4/ton of lignite at an initial concentration of 5%,

Table 1

DIRECT LEACHING OF RAW LIGNITE

Test No.	Leach Agent	Filtrate pH	Original H_2SO_4 lb./ton Raw Lignite	% Uranium Extracted	Tailing (%U) Raw Basis	Tailing (%U) Ash Basis
L-4	5% NaCl	2.8		0	.022	.110
5	20% "	2.8		0	.022	.110
18	5% $MgCl_2$	3.1		0	.024	.120
19	20% "	3.0		0	.022	.110
22	5% $CaCl_2$	2.9		0	.022	.110
23	20% "	2.6		0	.020	.100
14	5% Na_2SO_4	3.5		0	.022	.110
15	20% "	3.5		5	.020	.100
16	5% $NH_4H_2PO_4$	3.1		8	.018	.090
17	20% "	3.3		27	.016	.080
6	5% $(NH_4)_2CO_3$	7.8		67	.008	.040
26	1.25% H_2SO_4 *	2.0	50	15	.017	.092
27	2.5% " *	1.4	100	28	.013	.071
1	9% "	0.8	720	77	.006	.038
2	18% "	.02	1440	83	.004	.025
3	35% "	<.0	2800	91	.002	.014

Lignite: Raw untreated lignite ground to -14 mesh.

Leach Conditions: 200 ml leach solution per 50 g. lignite agitated for 16 hours at room temperature.

* 100 ml leach solution per 50 g. sample lignite.

Note:
1. Tests with Na_2CO_3 gave an unfilterable slurry.
2. Tests with $(NH_4)_2CO_3$ required 12-16 hours to filter.
3. All of the leaches filtered slowly with the exception of the 9% H_2SO_4 leach (L-1).

Table 2

COLUMN TESTS ON RAW LIGNITE

Test No.	Leach Agent	Solution Solid Ratio ml/g.	Final pH	Original H_2SO_4 lb./ton Raw Lignite	% Uranium Extracted	Tailing (% U) Raw Basis	Tailing (% U) Ash Basis
L-7	5 % NaCl	3.2	2.8		0	.022	.110
10	20 "	4.8	2.1		0	----	----
12	5 $NH_4H_2PO_4$	4.5	2.8		9	----	----
8	9 H_2SO_4	3.2	0.3	580	93	.002	.010
9	35 "	4.2	<.0	2900	86	.003	.015
28A	1.25 H_2SO_4	2.0	1.5	50	7	----	----
B	" "	2.0	1.35	50	14	----	----
C	" "	2.0	1.15	50	11	----	----
D	" "	2.0	.95	50	9	----	----
Total				200	41		

Lignite: Raw untreated lignite ground to -14 mesh.

Test Conditions: Leach solution was passed through a 1 1/2" column of lignite at the rate of 3.5 to 4.0 ml/min.

Note: Test 28 - 100 g. of raw lignite was treated with 800 ml. of H_2SO_4 (200 lb./ton) in 200 ml increments.

Table 3

DIRECT LEACHING OF RAW LIGNITE

Test No.	Pulp Density %	Leach Temp. °C	Orig. H_2SO_4 in Leach Lbs./ton Dry Lignite	Orig. H_2SO_4 in Leach Lbs./ton Ash	Filtrate pH	% Uranium Extracted	Tailing (% U) (Ash)*	Acid Consumed Lbs./ton Dry Lignite	Acid Consumed Lbs./ton Ash
L-30	50	80	100	333	2.1	27	.110	88	292
31	40	80	150	500	1.6	48	.071	106	353
32	33	80	200	666	1.4	59	.061	124	413
33	29	80	250	833	1.4	70	.050	137	456
34	25	80	300	1000	1.3	71	.050	144	480
35	33	30	200	666	1.6	48	.080	125	416
36	29	30	250	833	1.5	52	.070	145	483

Lignite: Dried 16 hours at 110°C and ground to -20 mesh.

Leach Conditions: Lignite agitated with 5% H_2SO_4 for 6 hours.

*Tailing Analysis: The raw tailing was ignited and uranium analysis made on the ash. The dry lignite contained 30% ash.

Acid Consumption: Obtained by free acid titration.

Filtration Rate: Filtration rate was good with the exception of test L-30.

filtration was quite rapid. It is possible that with insufficient acid the extracted metals reprecipitated as gelatinous hydroxides, whereas, at high acid condentrations, the organic matter in the lignite was partially decomposed.

Leaching with Base

Over two-thirds of the uranium was extracted from the raw lignite by a 5% solution of ammonium carbonate, but the resulting slurry was exceedingly difficult to filter. In tests with sodium carbonate solutions, the slurries were not filterable and extraction data were not obtained.

Leaching with Salts

If the uranium were held by the lignite in a chemi-adsorbed condition, it should be possible to cause elution by treating with salt solutions which contain enough acid to prevent hydrolytic precipitation. Results from preliminary batch and column tests (Tables 1 and 2) would indicate that the uranium, if adsorbed at all, is quite tightly held.

Water Leaching of Roasted Lignite

Only two additional low temperature roast, water leach tests have been made (see first two tests in Table 6). The results confirm earlier work[1] in that 70-80% of the uranium was removed from the 500°C ash by simply treating with water. The roasting time, as previously indicated, controls the extraction to some extent, e.g., about 70% of the uranium was extracted after a 1-hour roast and about 80% after 16 hours. The extraction of molybdenum was, of course, negligible.

Acid Leaching of Roasted Lignite

Upon increasing the lignite roasting temperature from 500° to 800°C, the acidic constituents are decomposed and the ash becomes basic[1]. Using lignite sample ND-1, however, about 75% of the uranium can be extracted from the 800°C ash into dilute sulfuric acid with only moderate amounts of acid being consumed.

In Table 4 are shown the quantities of basic constituents dissolved when 800°C ash is treated with acid at 80°C in large excess (5% H_2SO_4) at 10% pulp density. The sums of the calculated amounts of acid required for the dissolution of each constituent show total calculated consumptions of about

Table 4

IMPURITIES DISSOLVED BY DIRECT LEACHING OF LIGNITE ASH

Test No.	Roast Time (hrs)	Roast Temp. (°C)	Leach Agent	Impurities Dissolved and Acid Consumed** Fe 1	Fe 2	Al 1	Al 2	Ca 1	Ca 2	Mg 1	Mg 2	Na 1	Na 2	K 1	K 2	Total Acid Consumed Lbs/ton Ash
LA-21	4	800	5% H_2SO_4	9.4		19.0		28.0		2.8		40.0		16.0		
20	4	800	H_2O	0.0		0.0		15.0		1.8		27.8		11.0		
			*	9.4	26	19.0	102	13.0	32	1.0	4	12.2	26	5.0	6	196
23	6	800	5% H_2SO_4	2.0		20.0		27.0		2.2		19.8		4.6		
22	6	800	H_2O	0.0		0.0		12.4		1.4		10.8		2.0		
			*	2.0	6	20.0	108	14.6	36	0.8	4	9.0	20	2.6	4	178
17	2	1000	5% H_2SO_4	220		22.6		19.2		4.6		13.0		2.6		
16	2	1000	H_2O	0		0.0		15.8		0.0		6.0		1.2		
			*	220	588	22.6	122	3.4	8	4.6	18	7.0	14	1.4	2	752
19	4	1000	5% H_2SO_4	2.8		22.6		40.0		0		7.2		0		
18	4	1000	H_2O	0.0		0.0		22.2		0		1.0		0		
			*	2.8	8	22.6	122	17.8	44	0	0	6.2	14	0	0	188

Ash: Raw lignite roasted and the ash ground to -20 mesh.

Acid Leach: 10 ml of 5% H_2SO_4 per gram ash stirred for 1 hour at 80°C. (1000 lb. H_2SO_4/ton ash).

H_2O Leach: 10 ml of H_2O per gram ash stirred for 1 hour at room temperature.

** 1. Impurities dissolved in lbs. per ton ash.
2. Acid consumed in lbs. H_2SO_4/ton ash (calculated).

* Total impurities dissolved by acid leaching less those dissolved by a water leach.

200 lbs. H_2SO_4/ton of ash. Using smaller quantities of acid at lower temperatures, 75% extraction of the uranium can be maintained with smaller consumptions of acid (see data in Table 5).

The results from tests with 1000°C ash were erratic. Using identical leach conditions, the calculated acid consumption for one sample (Table 4) was about 200 lbs./ton and 750 lbs./ton for another. Due to unexplained reasons, large quantities of iron were extracted from the second ash sample. As reported previously, uranium extractions were low in both cases.

Leaching of Ash with Ammonium Carbonate

Investigation of leaching the lignite ash with ammonium carbonate, described previously in ORNL-1384, has been continued.

Roast Conditions

A roasting temperature above 850°C diminishes the availability of uranium to an ammonium carbonate leach (see Table 6). When the lignite was treated at 1000°C for various lengths of time, the uranium extractions were entirely erratic. This may be due to the partial formation of uranium silicates, ferrites, or other compounds. Another possibility is the retention of uranium by physical locking, although most of the ashes below 1150°C were not appreciably sintered.

A prolonged roasting time did not increase the availability of the uranium.

A roasting temperature above 500°C was favorable for the extraction of molybdenum. At 800°C, and above, 55% of the molybdenum could be solubilized.

It was furthermore found that at 800°C and higher the extractions of the molybdenum and the sulfate were fairly parallel. An extraction of 90% or better of the SO_4 was accompanied by an extraction of the molybdenum of 50% or better. The uranium extractions from high temperature (1000°C) ash, however, seemed to be greatest when the extractions of molybdenum and sulfate were low. This point will receive further checking.

Leach Conditions

The effects of the leaching conditions are shown in Tables 7 and 8. Although a fairly good extraction can be

Table 5

ACID LEACHING OF LIGNITE ASH

Test No. LA-	Roast Time (hrs)	Leach Time (hrs)	Leach Temp. (°C)	Leach Pulp Density (%)	Original H_2SO_4 in Leach Lbs./ton Dry Lignite	Original H_2SO_4 in Leach Lbs./ton Ash	Filtrate pH	% Uranium Extracted	Ash Tailing (% U)	Acid Consumed Lbs./ton Dry Lignite	Acid Consumed Lbs./ton Ash
104	2	3	80	40	45	150	3.2	83	.031	45	150
109	2	3	80	33	60	200	2.4	76	.038	60	200
106	2	3	80	25	90	300	1.5	83	.029	63	210
103	2	3	30	33	60	200	1.3	81	.034	32	106
110	2	3	30	25	90	300	1.3	76	.038	41	136
21	4	1	80	9	300	1000	.5	82	.026	60*	196*
23	6	1	80	9	300	1000	.4	76	.026	53*	178*
107	4	1	80	9	300	1000	1.0	83	.030	62	208
108	6	1	80	9	300	1000	1.0	85	.033	62	208

Ash: Raw lignite roasted at 800°C.

Leach Conditions: Ash agitated with 5% H_2SO_4.

Acid Consumption: Obtained by free acid titration.

* Calculated from the acid soluble impurities found in the pregnant leach solution (table 4).

Table 6

EFFECT OF ROAST CONDITIONS

Test No.	Roast Time (hrs.)	Roast Temp. (°C)	Leach Time (hrs.)	Leach Temp. (°C)	pH		% U Extracted	Tailing (% U)	Extractions % Mo	Extractions % SO_4
LA-39	1	500	2	30	3.0	*	68	.040	2	35
49	16	500	3	30	2.6	*	85	.025	6	45
36	16	500	2	80	8.3		84	.031	45	98
34	16	500	2	110	8.0		75	.038	38	97
37	16	500	2	110	8.8	**	75	.040	47	98
52	2	800	2	60	8.4		72	.042	54	97
47	2	800	2	80	8.5		75	.039	57	95
59	2	800	2	110	---		77	.038	55	97
35	2	800	2	110	8.4		79	.034	55	96
55	1	900	2	60	8.2		57	.062	6	83
53	1	900	2	80	8.4		69	.044	16	83
46	1	900	2	110	8.9	**	65	.059	50	90
40	1/4	1000	2	110	8.8	**	35	.105	58	97
41	3/4	1000	2	110	8.7	**	59	.052	9	60
43	1 3/4	1000	2	110	9.3	**	17	.118	54	91
50	2	1000	2	80	8.8		58	.063	6	22
45	1	1100	2	110	8.9	**	11	.116	48	98

Ash: -100 mesh.

*H_2O Leach Conditions: 10 ml H_2O per g. ash.

Leach Conditions: 45 g. $(NH_4)_2CO_3$ per 100 ml H_2O (or 80 ml H_2O - 20 ml NH_4OH)** were used to leach 50 g. ash. The Tests were carried out in an autoclave under pressure.

* Ash given H_2O leach only.
** 80 ml H_2O, 20 ml NH_4OH (28% NH_3) added.

Table 7

$(NH_4)_2CO_3$ LEACH CONDITIONS

Test No.	$(NH_4)_2CO_3$ Conc. g/ 100ml H_2O	Leach Time (hrs.)	Leach Temp. °C	Leach ~Pressure psi.	% U Extracted	Tailing (% U)	Extractions % Mo	Extractions % SO_4
LA-70	18	5	30	Atm.*	69	.050	57	96
65	18	2	45	5	69	.048	60	97
66	18	2	60	15	70	.050	51	96
61	18	2	80	20	67	.050	56	97
72	30	5	30	Atm.*	74	.039	56	98
64	30	2	80	40	71	.040	55	97
54	45	16	30	0	71	.042	42	98
52	45	2	60	25	72	.042	54	97
56	45	2	60	20	79	.036	51	97
47	45	2	80	55	75	.039	57	95
59	45	2	110	125	77	.038	55	97
35	45	2	110	130	79	.034	55	96
76	45	2	130	200	61	.054	58	96
77	45	2	150	250	69	.052	56	96
63	45	1/2	80	45	72	.050	48	96
60	45	1	80	55	70	.045	50	96
48	45	4	80	50	73	.046	53	96

Ash: Raw lignite roasted for 2 hours at 800°C and the resulting ash ground to -100 mesh.

Leach Conditions: 50 g. samples of ash per 100 ml H_2O plus $(NH_4)_2CO_3$ agitated in an autoclave.

* Leached in an open beaker.

Table 8

EFFECT OF $(NH_4)_2CO_3$ CONCENTRATION IN ATMOSPHERIC AND AUTOCLAVE LEACHING

Test No.	$(NH_4)_2CO_3$ Conc. g/ 100ml H_2O	Pressure psi.	pH	Temp. °C	% U Extracted	Tailing (% U)	Extractions % Mo	Extractions % SO_4
LA-68	15	40	7.7	80	65	.049	51	96
75	15*	10	9.1	80	70	.048	53	98
61	18	20	8.3	80	67	.050	56	97
62	24	25	8.2	80	74	.042	65	96
64	30	40	8.2	80	71	.040	55	97
47	45	55	8.5	80	75	.039	57	95
67	12	Atm.	---	30	65	.054	40	85
70	18	"	8.5	30	69	.050	57	96
71	24	"	8.6	30	66	.052	49	96
72	30	"	8.6	30	74	.039	56	98

Ash: Raw lignite roasted for 2 hours at 800°C and the resulting ash ground to -100 mesh.

Atmospheric Leach: 50 g. samples of ash per 100 ml H_2O plus $(NH_4)_2CO_3$ were agitated for 5 hours at room temperature.

Pressure Leach: 50 g. samples of ash per 100 ml H_2O plus $(NH_4)_2CO_3$ were agitated in an autoclave for 2 hours at 80°C.

* 20 ml NH_4OH added (28% NH_3).

achieved at 30°C and atmospheric pressure, the overall values obtained indicate the optimum temperature range lies between 60° and 110°C. At higher temperatures, the uranium extractions appear to decrease.

Within one hour all soluble constituents of the ash could be extracted. Prolonging the extraction time did not increase the availability of uranium, molybdenum or sulfate.

Apparently about 3/4 of the uranium is present in an easily reactive form, while the remaining fourth cannot be brought into solution, either by changing roasting time or temperature, or by changing the leaching conditions with respect to time, temperature, ammonium carbonate concentration or pH of the leach liquor.

The pH of leach liquor usually ranges between 8.2 and 8.8. An increase to over 9 by adding ammonium hydroxide did not result in an improved extraction.

The minimum concentration of ammonium carbonate in the leach solution must be in excess of that which will react with the $CaSO_4$ in the ash. Requirements for this reagent cannot be accurately determined until the average concentration of $CaSO_4$ can be predicted.

Treatment of High Temperature Ash

Various ways are being explored to solubilize the last quarter of the uranium from lower temperature ash and to extract uranium from a high temperature (1000°C and over) ash. As shown in Table 9, quenching of the ash has not produced encouraging results.

In order to find out whether part of the uranium was present in the tetravalent state and, therefore, insoluble in the reagents employed, some leachings were made with ammonium carbonate solutions containing potassium permanganate and potassium persulfate. No improvement could be found.

Other more promising ways are now under investigation.

Treatment of Chars

A small (300 ml) retort has been constructed according to the design of F. Fischer and H. Schrader.[3] Residues from distillation of the tars are being treated with various reagents to determine the availability of the uranium. The compositions of the off-gases from the retorting operations

Table 9

EFFECT OF QUENCHING

Test No.	Roast Temp. (°C)	Cooling Treatment	$(NH_4)_2CO_3$ gms. per 100ml H_2O	% U Extracted	Tailing (% U)	Extractions % Mo	Extractions % SO_4
LA-74	800	*	45	76	.038	62	97
82	"	Quenched	30	74	.040	63	95
83	"	Quenched	45	58	.060	49	89
53	900	*	45	69	.044	16	83
84	"	Quenched	45	71	.045	60	81
43	1000	*	45	17	.118	54	91
86	"	Quenched	45	7	.099	29	90

* Raw lignite was roasted for 1-2 hours and the ash allowed to cool slowly in air. The ash was ground to -100 mesh.

Quenching: Raw lignite was dried at 110°C for 16 hours, ground to -20 mesh and roasted for 2 hours. The hot ash was dumped on an open tray and then into water (approximate time from furnace to water was 45 seconds). $(NH_4)_2CO_3$ was then added.

Leaching: 50 gms. Ash per 100 ml H_2O (+$(NH_4)_2CO_3$) was stirred for 2 hours at 80°C in an autoclave. The pressure developed was ~45 psi.

are also being determined. Chars from lignite gasification will be examined. Preliminary tests include leaching with acids and with $(NH_4)_2CO_3$. Sufficient NH_3 and CO_2 might be available from the off-gases for an ammonium carbonate treatment.

COMPOSITION AND PROPERTIES OF LIGNITE SAMPLES

Uniformity of Sampling

A second drum of lignite from sample ND-1 has been opened and prepared for laboratory studies according to the procedure described in ORNL-1308. The composition of this material has been determined by wet chemical and spectrographic methods and a comparison of the analysis of lignite from the two drums opened thus far is shown in Tables 10 and 11. Both the chemical and spectrographic analysis of the two samples are very similar.

Uranium Content of Mineral Fractions

As mentioned last quarter, fourteen samples of organic-rich material were hand-picked from a large batch of dried lignite. Each sample was ashed and submitted for a wet chemical uranium analysis as well as spectrographic analysis for the trace metal constituents. Previous work has shown that the uranium was not associated with any of the major mineral constituents of the lignite sample, but that it definitely concentrates with the organic-rich fraction.[1] The purpose of these tests was to determine whether the uranium in the organic fraction is associated with the organic matter itself or with some other trace metallic constituent which has concentrated with the organic material. Results are shown in Tables 12 and 13 for the fourteen samples so treated.

Since the ash content of the hand-picked samples was about 15% (dry basis) compared to 30% for the normal lignite, all elements associated with the organic material should be present in concentrations about 2.5 times those normally obtained. In the case of uranium such a change in concentration is observed (see Tables 12 and 13) and the association of the uranium with the organic matter is again confirmed. Similar changes in the concentration of other trace constituents were not obtained. (Table 13.) Minor differences did occur between some of the samples in barium, calcium and potassium concentrations, but none of these appear to vary in any systematic manner with changes in the uranium concentration. Molybdenum was of special interest since there has been some indication of correlation between molybdenum and uranium contents of different lignites.[4] Such a correlation would not be indicated, however, by the data in Table 13.

The interpretation of the data is limited, unfortunately, because insufficient quantities of material was submitted for precise spectrographic analyses. This type of study will be repeated using three or four larger samples of hand-picked lignite.

Table 10

WET CHEMICAL ANALYSES OF LIGNITE SAMPLE ND-1

FROM DIFFERENT CONTAINERS

	Drum No. 2			Drum No. 1		
	Anal. As Submitted	Calcul. to Dry Basis	Calcul. to "As-Rec'd." Cond.	Anal. As Submitted	Calcul. to Dry Basis	Calcul. to "As-Rec'd." Cond.
Loss at 110°C, (H_2O)	5.19	0.00	39.4	5.6	0.0	42.6
Total Carbon	35.4	37.3	22.6	33.4	35.4	20.3
Nitrogen	0.59	0.62	0.38	0.46	0.49	0.28
Sulfate Sulfur	11.02	11.52	7.00	10.8	11.4	6.54
Total Sulfur (SO_4)	12.63	13.35	8.10	12.8	13.6	7.81
Carbonates	0.07	.074	.047	0.08	0.085	0.049
Ash	32.3	34.1	20.6	28.8	30.5	17.5
Uranium	0.0322	0.034	0.0206	0.044	0.047	0.027
Silicon	3.61	3.81	2.31	3.40	3.60	2.07
Potassium	0.275	0.29	0.176	0.17	0.18	0.10
Sodium	0.763	0.805	0.488	0.74	0.78	0.45
Calcium	2.88	3.04	1.84	2.82	2.99	1.72
Magnesium	0.133	0.14	0.085	0.30	0.32	0.18
Phosphorus	0.062	0.065	0.039	----	----	----
Iron	5.41	5.71	3.46	5.98	6.33	3.63
Titanium	0.104	0.11	0.067	----	----	----
Aluminum	1.62	1.71	1.04	1.69	1.79	1.03
Molybdenum	0.091	0.096	0.058	0.080	0.085	0.049

Table 11

SPECTROGRAPHIC ANALYSES* OF LIGNITE

SAMPLE ND-1 FROM DIFFERENT CONTAINERS

Element	Drum No. 2 %	Drum No. 1 %	Element	Drum No. 2 %	Drum No. 1 %
Ag	<.04	<.04	Mo	0.1	0.15
B	0.008	0.02	Ni	<.08	<.08
Ba	0.1	0.08	Pb	<.04	<.04
Be	<.001	<.001	Sn	<.02	<.02
Cd	<.04	<.04	Sr	<.1	<.1
Co	<.04	<.04	Ta	<1	<1
Cr	<.04	<.04	V	<.04	<.04
Cu	<.04	<0.04	W	<1	<1
Li	0.02	0.01	Zn	<.3	<.3
Mn	0.08	0.01	Zr	<.08	<.08

*The spectrographic test results reported herein 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.

Table 12

ASH AND URANIUM CONTENTS OF HAND-PICKED AIR-DRIED LIGNITE SAMPLES

Sample	% Ash	% U in Ash
Unsorted Lignite (Dry)	30.5	0.13
BN-1	15	0.45
BN-2	18	0.29
BN-3	15.1	0.39
BN-4	15.5	0.34
BN-5	14.6	0.42
BN-6	13.2	0.46
BN-7	15.9	0.36
BN-8	15	0.41
BN-9	14	0.45
BN-10	13.5	0.42
BN-11	14.4	0.39
BN-12	14.1	0.41
BN-13	14.4	0.37
BN-14	14.4	0.40

Table 13

SEMI-QUANTITATIVE SPECTROGRAPHIC DATA ON ASHED SAMPLES OF HAND-PICKED LIGNITE*

Element	BN-1	BN-2	BN-4	BN-6	BN-7	BN-8	BN-11	BN-12	Normal Ash
U	0.45	0.29	0.34	0.46	0.36	0.41	0.39	0.41	0.13
Ag	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04
B	.03	.04	.03	.03	.03	.03	.03	.03	.06
Ba	.2	.08	.08	.08	.08	.2	.04	.04	.08
Be	.001	.001	.001	.001	.001	.001	.001	.001	.001
Ca	.6	.3	.2	.3	.3	.3	.3	.3	<5
Cd	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04
Co	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04
Cr	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04T
Cu	.08	.08	.08	.04	.04	.04	.08	.08	<.04
K	.6	1	.3	.3	.3	.3	.3	.2	---
Li	.02	.02	.02	.02	.02	.02	.02	.02	---
Mg	.6	.6	.6	.6	.6	.6	.6	.6	1
Mn	.04	.04	.04	.04	.04	.04	.04	.04	.08
Mo	.3	.3	.3	.3	.3	.3	.3	.3	.3
Na	2	2	2	2	2	2	2	2	---
Ni	<.08	<.08	<.08	<.08	<.08	<.08T	<.08	<.08	<.08T
Pb	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04
Sn	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02
Sr	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1T
Ta	<1	<1	<1	<1	<1	<1	1	<1	<1
Ti	.15	.15	.15	.15	.15	.15	.15	.15	.2
V	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04	<.04
W	<1	<1	<1	<1	<1	<1	<1	<1	<1
Y	<.15T	<.15T	<.15T	<.15T	<.15T	<.15T	<.15T	<.15T	---
Zn	<.3T	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3
Zr	<.08	<.08	<.08	<.08	<.08	<.08	<.08	<.08	<.08

* Because of space limitations, data are presented for only eight of the fourteen samples.

Physical Separations

Air Classification of Raw Lignite

A sample of raw, dried lignite was submitted to the Metallurgy Division of ORNL for air classification tests in a Roller Particle Size Analyzer (American Instrument Company). Before submission, the sample was dried for 18 hours at 100°C and stage ground to minus 100 mesh. The specific gravity of the material was measured at about 1.5 and this value was used in establishing the instrument settings.

Four products were collected during the test - the residue and the material from the three classification chambers. All of these were submitted for particle size determination, chemical analysis, spectrographic analysis and a cursory mineralogical examination.

The following observations can be made from the data as summarized in Table 14.

1) No important separation of uranium and/or carbon from other constituents was obtained.

2) The concentrations of uranium, silica and carbon decreased somewhat as the particle size of the various fractions decreased.

3) The concentration of sulfate and the total ash content was considerably greater in the fine fractions.

4) Spectrographic analysis and microscopic studies (not reported) show that the greater sulfate concentration in the fine fractions is due to increased concentration of both gypsum and jarosite.

Additional air classification tests are being made using different test conditions.

Air Classification of Lignite Ash

Three samples of lignite ash obtained by burning the lignite at temperatures of 500°C, 800°C and 1000°C were also submitted to the ORNL Metallurgy Division for air classification in the particle size analyzer. In these tests, the instrument settings were based on data supplied with the instrument for the air classification of fly ash. Chemical analysis and microscopic studies of the various sized products are described in Table 15.

Table 14

DATA FROM AIR CLASSIFICATION OF RAW LIGNITE

	Residue	1 1/8" Chamber	2 1/4" Chamber	9" Chamber
% of Total Wt.	48	14.0	20.0	18.0
Particle Size (μ)	200(Max.) 90(Av.)	60(Max.) 34(Av.)	29(Max.) 15(Av.)	19(Max.) <5(Av.)
U (%)	0.053	0.043	0.042	0.039
Si (%)	4.6	3.8	2.9	2.6
Total C (%)	38.9	36.6	31.2	26.7
SO_4 (%)	5.9	8.2	14.9	19.1
Ash (%)	22.5	25.6	30.7	35.9
Loss at 110°C (%)	9.9	9.8	8.3	7.7

Table 15

DATA FROM AIR CLASSIFICATION OF LIGNITE ASH

	500°C Ash			
	Residue	1 1/8" Chamber	2 1/4" Chamber	9" Chamber
% of Total Wt.	9.7	9.7	25.8	54.8
Particle Size (μ)*	200-50	110-25	50-10	<5
U (%)	.001	.001	0.02	0.2
SiO_2 (%)	20.1	18.3	12.0	5.7
Fe (%)	6.1	5.7	8.2	25.0
SO_4 (%)	25.9	28.1	35.9	23.4
	800°C Ash**			
Particle Size (μ)*	180-35	90-25	45-10	<10
U (%)	0.03	0.08	0.12	0.22
SO_4 (%)	16	15	27	11
	1000°C Ash**			
Particle Size (μ)*	180-45	110-30	40-10	<10
U (%)	0.08	0.14	0.15	0.21
SO_4 (%)	12	15	28	14

* Measurement of 50 grains of each fraction at random.

**The fractions of 800° and 1000°C ash were not weighed. Visual observation would indicate about the same weight distribution as for the 500°C ash.

In the case of the 500°C ash, the following observations may be made:

1) Over fifty percent of the particles are below 5 microns in size.

2) The uranium is almost entirely concentrated in the finest fraction with the coarsest fraction being almost barren.

3) Iron is also concentrated in the fines whereas the opposite is true for silica.

4) Sulfate is fairly random in distribution, with a somewhat greater concentration in the 10-50 micron range.

5) Spectrographic results (not reported here) show increased concentrations of molybdenum, magnesium and manganese in the fines.

With ash formed at higher temperatures (800° and 1000°C), the results are as follows:

1) The uranium concentration is greatest in the finest fraction, but, unlike the 500°C ash, appreciable concentrations are also found in the coarse fractions.

2) Appreciable amounts of sulfate are found in all size fractions with the greatest quantity in the 10-50 micron material.

3) Spectrographic results (not reported here) show increasing concentration of iron, magnesium and manganese with decreasing particle size. The molybdenum concentration appeared fairly constant in all fractions.

Sink-Float Tests

Three sink-float tests were made previously using -8 to +20 mesh, -20 to +60 mesh, and -100 to +325 mesh lignite. Other tests have now been run using dried unsized lignite which had been totally stage ground to pass 100 mesh. Experimental procedures were the same as previously described.

The results from these tests, as reported in Table 16, differ from those obtained in earlier experiments. Although, float products were obtained which contained greater concentrations of uranium and carbon, and lower concentrations of non-volatiles than did the head, the total recoveries of uranium and carbon into these fractions were not more than 50%, as compared to 80% in previous work. This difference

Table 16

SINK-FLOAT TESTS

Sample	Chemical Analysis (As submitted) % H_2O	% Tot.C.	% Ash	% U	Test Results (Dry) Wt. % Ret.	Cum.Wt. % Ret.	% Distribution (Dry) Tot. C.	Ash	U
Test No. 4 (Material all -100 mesh by stage grinding.)									
Head Samp.	10.4	33.7	29.7	0.036	-----	-----	-----	-----	-----
Sink 1.70	3.5	23.5	49.2	0.027	66.0	66.0	52.3	81.1	53.6
Float 1.70	6.5	40.4	21.7	0.044	34.0	100.0	47.8	18.9	46.4
Totals	----	----	----	-----	100.0	100.0	100.0	100.0	100.0
Test No. 5 (Material all -100 mesh by stage grinding.)									
Sink 1.70	4.6	22.9	43.2	0.032	62.1	62.1	46.8	76.5	52.8
Float 1.70	9.4	40.4	20.7	0.045	37.8	100.0	53.2	33.5	47.2
Totals	----	----	----	-----	100.0	100.0	100.0	100.0	100.0

is probably due to the fact that appreciable quantities of very fine lignite were present in the unscreened samples used for the recent tests and these fines prevented a sharp separation of the products. Centrifuging will be tried in future separations.

Flotation Tests

Negative results were obtained from six flotation tests in which attempts were made to float the carbonaceous matter from the gangue using No. 2 fuel oil and/or kerosene as the collecting agents and pine oil as the frother.

Encouraging results were obtained from one test in which the gangue constituents were floated from the carbonaceous matter. Experimental conditions included a natural circuit pH of 3.5 - 4.0, a pulp density of 15-16% (with a preliminary conditioning period at 30% solids), and water at a temperature of 50°C. Reagents used were quebracho and R653 as depressants for the carbonaceous matter, lead nitrate as a quartz activator, armac TD as the promoter, and pine oil as the frother. A mixture of No. 2 fuel oil and kerosene was also added as a gangue promoter assisting agent.

Results are shown in the following table. The major portion of the inorganic material in the concentrate is jarosite, a mineral which was not expected to float in this scheme.

FLOTATION TEST NO. 3B*

	Analysis of Submitted Sample				Test Results (Dry Basis)	% Distribution (Dry)		
Product	% H_2O	% Tot.C.	% Ash	% U	Wt. %	Tot.C.	Ash	U
Conc.	9.83	42.9	18.25	.044	63.7	73.5	47.8	71.4
Tails	6.90	28.3	35.9	.032	36.3	26.5	52.2	28.6
Calc.Heads Totals	41.33	26.85	0.0433		100.0	100.0	100.0	100.0

*Feed was raw, dried lignite, -48 +325 mesh.

FUTURE WORK

Additional samples of uraniferous lignite which are more representative of the usual run of material in uranium content and, perhaps, the contents of other constituents must be studied as soon as possible. The only lignite sample currently available is relatively high in uranium concentration. Although extractions of 75% of the uranium are rather easily obtained, the actual concentrations remaining in the tailings are quite large. If the same extraction procedures were employed on lignite samples of lower original uranium concentration, the extraction results would be difficult to predict from current data. Other information as to the average composition of uraniferous lignites from a particular district would also be important to processing studies, e.g., concentrations of pyrites, gypsum, bases and carbonaceous material.

Process exploration work will be devoted to examination of methods for extracting uranium from -

1) Raw lignites.

2) Lignites that have been ashed at intermediate temperatures.

3) High temperature lignite ash.

4) Lignite chars as obtained from gasification, retorting, etc.

Methods for physical concentration of the uranium will also be examined.

[redacted]

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