RECOVERY OF URANIUM FROM LIGNITES*

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In 1934, Irvin Lavine,¹ University of North Dakota, stated that the low-rank coals (i.e., lignite and subbituminous) of this country represent a vast tonnage of fuel of commercial value and predicted that some day they will play an important role in our economic welfare. Lavine also pointed out that one of the major problems with efficient utilization of the low-rank coals is their high moisture content. Following the discovery of uranium-bearing lignite in the Williston basin of North and South Dakota in 1948 by D. G. Wyant and E. P. Beroni, detailed investigations were conducted (primarily during 1950 to 1954) by members of the U. S. Geological Survey (USGS) to evaluate the geologic factors and economic possibilities of the radioactive lignites as a source of uranium. The information gained in this study and summarized in several papers indicated that a large potential reserve of uranium is contained in the subbituminous coal and lignite deposits of the Dakotas and Wyoming.²⁻⁴ Most investigators concluded that an epigenetic emplacement of uranium in the coal by means of circulating groundwater and the more extensive concentrations of uranium in coal are apparently related to the permeability of the rocks enclosing the coal beds. Breger⁵ and others have shown that uranium is readily absorbed by coal and is held irreversibly as a disseminated adsorbed constituent.

Briefly, lignite beds containing 0.1 to 10% uranium have been discovered in the Dakotas and Wyoming. The distribution of uranium was found to

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be erratic and was usually concentrated in thin layers, which were characteristically 10 to 14 in. thick and occasionally 30 to 36 in. thick. Lignite beds more than 3 ft thick generally contain more uranium at the top of the bed than at the bottom. Special strip mining techniques are required to mine these thin uraniferous layers.

Paralleling these investigations by the USGS, there was a concentrated effort by Battelle Memorial Institute,⁶ National Lead Companies Winchester Laboratory,⁷ and Oak Ridge National Laboratory (ORNL)⁸ to characterize selected lignite samples and test their amenability to various recovery procedures. Unfortunately, this work was halted before recovery processes were completely developed and reported because of the discovery of large amounts of relatively low-cost uranium in western U.S. sandstone deposits.

During 1963 to 1967, several companies,^{9,11,12} including Kermac, Union Carbide, Susquehanna Western, and Mines Development, Inc., recovered about 1 million pounds of U_3O_8 from uraniferous lignite in the Williston Basin. Production ceased because of limited uranium resources, and technical and environmental problems.

In 1969, M. Steinberg,¹⁰ Brookhaven National Laboratory, estimated that about 240,000 tons of uranium, at an average concentration of 20 ppm, is contained in 11,970 million tons of western subbituminous coal and lignite that will be consumed by the year 2000. He further estimated that a total of 21 million tons of U_3O_8 is contained in these deposits. Steinberg suggested that earlier explorations were made with the view of obtaining rich uranium ore; the extraction of power from coal was a secondary consideration. He recommended that a thorough survey and more extensive exploration be made of the coal geology in the western areas to confirm the resource information available for uranium and coal.

In a recent report by the Electric Power Research Institute (EPRI) on nonsandstone uranium deposits, one chapter is devoted to uraniferous coal resources.¹¹ They concluded that by-product production of uranium from the burning or gasification of coal and lignite is economically borderline; recovery is technically problematic and the extent of the resource is relatively insignificant. Most known uranium-coal deposits are low in either uranium or heating value and are isolated from production centers. They show an updated version of major uraniferous coal deposits which includes locations, tonnage, percent of U_3O_8 in the coal, and pounds of U_3O_8 in the ash. The data indicate that about 95,000 tons of U_3O_8 is contained in 3730 million tons of coal.

Additional updated information on uranium in coal deposits lists numerous samples from the USGS national coal resources data system and includes a large bibliography.¹² They conclude that only 1 to 3 % of the domestic uranium requirement can be met by processing coal ash, provided processing technology can be developed for uranium recovery at acceptable costs.

There is a renewed interest in lignites and possibly uranium as a source of fuel.^{11,13} This paper summarizes the experimental work carried out at ORNL during 1952 to 1954 that deals with the sulfuric acid leaching of lignite ash. A section on the possible utilization of sulfur dioxides in flue gases should be of value to those companies planning to process lignites.

Lignite

Description of Samples

Our investigations were done on selected samples obtained in 1951 to 1952 by USGS personnel from the Sentinel Butte region of North Dakota, the Slim Buttes region of South Dakota in Harding County, and the Red

Desert area of Wyoming in Sweetwater County, North of Wamsutter. The samples were taken at least 3 ft from any exposed edge or outcropping that would have been subject to weathering or leaching by wind and rain. Because the highest concentration of uranium was in the top portion of the bed, only the top portion of the seams were included in the bulk samples after first removing the final overburden by hand. Thus it was fairly certain that the samples contained no extraneous mineral matter and that the complete upper portion of the top seam was included.

The bulk samples were crushed to -4 mesh, quartered, riffled, and submitted for analysis. Portions were air dried and ground to -20 mesh for leaching and roasting studies.

Proximate and ultimate analyses were made to characterize the lignite samples as to their rank (Tables 1 and 2). Compared to a typical lignite, the moisture and ash contents were somewhat high and the fixed carbon and volatile matter were low. Also, the samples were low in carbon and hydrogen and high in oxygen. According to Table 3, the tar yield and heating value of the samples were on the low side.

The uranium content (dry basis) varied from 0.047% for the North Dakota sample to 0.007% for the subbituminous Wyoming sample. The group of east-side South Dakota samples was generally lower in uranium content than those from the west side -- 0.007 to 0.013% as compared with 0.010 to 0.032%.

The noncarboniferous material was mainly composed of analcite, jarosite, gypsum, clay minerals, and quartz. The major inorganic constituents in the samples are discussed later in the section pertaining to the ash.

Distribution of Uranium

Numerous tests were made to determine whether the uranium was associated with the organic matter or with any of the mineral constituents in the lignite.

The most graphic test (Table 4) shows very clearly that the uranium is not associated with any of the major mineral constituents but definitely concentrates in the organic-rich fraction. To make these tests, a petrographer* handpicked small amounts of the major minerals from a large batch of air-dried lignite and analyzed them for uranium.

It was later established that 93% of the uranium in a typical lignite taken from the Mendenhall strip mine, Harding County, South Dakota, was present in the form of organouranium complexes or ionic organouranium compounds that are soluble at a pH <2.18.¹⁴ Only about 1% of the uranium was held by ion exchange, and over 98% of the uranium was soluble in hot 6 N HCl.

Beneficiation

Several techniques — screen analysis, sink-float, air classification, and flotation — were tested in an attempt to concentrate the uranium or remove part of the reagent consuming materials. None of these methods showed any promise.

Direct Treatment of Raw Lignite

About 75% of the uranium could be extracted from raw (-14 mesh) lignite at ambient temperatures with mineral acids. At 80°C, recoveries were 10 to 15% higher. Fig. 1 shows the data for sulfuric acid, which was slightly better than nitric, hydrochloric, or phosphoric acids. In these single-batch tests, large quantities of acid were required for maximum solubility (~1000 lb H₂SO₄ per ton of lignite). This consumption could be reduced considerably by using a cyclic leach process, but acid requirements based

* Dr. T. N. McVay, Bureau of Mines, Tuscaloosa, Ala.

on uranium recovered were still excessive for most of the samples tested (Table 5). For example, 2000 to 2700 lb H_2SO_4 was consumed per pound of uranium dissolved from the Slim Buttes-East and Wyoming samples.¹⁵ These data, plotted in Fig. 2, show the effect of lignite grade on acid consumption. As the concentration of uranium in the lignite decreases below 0.15 lb/ton (0.0075% uranium) the acid requirement increases dramatically.

Thickening and filtration of raw-lignite leach slurries was difficult. When the acid supply was either insufficient or excessive, filtration was very slow. With intermediate quantities, filtration was quite rapid. With insufficient acid the extracted metals reprecipitated as gelatinous hydroxides, whereas at high concentrations of acid the organic matter was partially decomposed. The leach solutions were, in all cases, discolored by organic matter and, unless this material is removed by activated carbon, it would cause serious problems during recovery.

Treatment of Char

The dissolution of uranium from samples of char, prepared by retorting lignite under reducing conditions at 500 to 800°C with mineral acids was only 5 to 10% (Table 6). Recoveries were not improved by the addition of oxidants during leaching. However, if the char was given an oxidizing roast at 500°C prior to leaching, a carbon-free ash was produced from which 80 to 85% of the uranium was extracted by leaching with water.

Although uranium in raw lignite is almost completely soluble in both dilute acid and carbonate solutions (data not included), almost complete removal of carbon is required for optimum leaching efficiency of burned lignite. This is also true for the extraction of uranium from carbonaceous material associated with sandstone ores.^{16,17}

Preparation and Leaching of Ash

Major emphasis was placed on developing methods to recover uranium from lignite ash rather than raw lignite. Roasting concentrates the uranium significantly, thereby reducing the size of the leaching facility for an equivalent uranium throughput, and reduces the acid requirement. Removal of organic matter also greatly simplifies recovery of uranium from the leach liquors.

A standard roasting or burning procedure was adopted that gave definite and reproducible material in our laboratory tests. However, a relationship to a given fire-box temperature in a large furnace was never established.

In our tests, the ash samples were usually prepared by spreading raw lignite in a thin (0.25 to 0.5 in.) bed on a tray in a muffle furnace with the controls set at the desired ashing temperature. Measurements with an imbedded thermocouple during burning indicated that combustion caused the temperature of the burning lignite to exceed that of the furnace. For example, as shown in Table 7, at a furnace setting of 400°C, measured bed temperatures approached a maximum of 565°C; some particles may have reached higher temperatures as evidenced by a bright red glow, which indicated temperatures of ~700°C. Unless otherwise noted, the temperatures in this paper are furnace settings. A burning or roasting time of 1.5 to 2 h in air was required to burn off the carbon at 400 to 800°C. Longer times were required with deeper beds.

In screen analysis and air-classification studies of lignite ash produced under oxidizing conditions at temperatures of 500, 800, and 1000°C, the uranium (and molybdenum) tended to concentrate in the fine sizes of the 500°C ash. As the temperature was raised to 800°C, increasing percentages of both elements appeared in the coarser sizes. At 1000°C, the ash had

aggregated to a large extent. The data suggest that the uranium originally held in the lignite by organic matter, upon burning, becomes an inherent part of the rather uniform fine ash fraction. As the burning temperature is increased, the uranium becomes refractory by 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 heating time increase.

Most of the lignites tested formed an acidic ash when roasted at a low temperature (400 to 500°C), and ~75% of the uranium in this ash was water soluble (Table 8). Sulfur oxides, which are formed from the oxidation of sulfides in the raw lignite, may react to form sulfate salts such as ferric sulfate. A water leach will dissolve these salts and become acidic due to hydrolysis of the metal ion. In fact, dilute solutions of ferric sulfate have been successfully used for leaching constituents from ores in several hydrometallurgical processes.^{18,19}

As the temperature was increased to ~800°C, the acid-forming sulfate salts decomposed and the ash became basic, but the uranium was still readily soluble in dilute acid (Table 8). At 1000°C, the ash became more basic, the uranium became more refractory due to the formation of stable silicates, and recoveries dropped to ~50% with dilute acid. These refractory silicates are not attacked by the common leaching agents and, once formed, only complete destruction (e.g., with fluoride compounds) will open up the mineral and allow recovery of the uranium.

As the lignite is burned, sulfate is lost from the material through both decomposition and reduction, as shown in Table 9. The reactions that occur during roasting of lignite are similar to those which occur during the roasting of oil shale.²⁰ A very important difference, however, in a

low-temperature roast (400 to 500°C) of shales and lignites is that the length of the roast time required in the lignite treatment to form an acidic ash in which the uranium can be extracted into water is only 1.5 to 2 h as compared to 10 to 15 h for shales. This is encouraging from a process standpoint and offers an attractive processing route for recovery of uranium from uraniferous lignites that should be explored further.

When the lignite roasting temperature was increased to 800°C, the acidic constituents were decomposed and the ash became basic. However, 70 to 80% of the uranium could still be extracted into dilute sulfuric acid from any of the lignites even though large quantities of acid were consumed in some cases. The approximate quantities of acid consumed by each sample under conditions selected for nearly maximum uranium recovery are shown in Table 10. As with the raw lignites, the greatest acid consumers were the Slim Buttes-East and the Wyoming samples. These data are plotted in Fig. 3 to show the effect of ore grade on acid consumption. As the concentration of uranium in the lignite decreased below about 0.6 lb per ton of ash, the acid requirement increased dramatically.

Table 11 shows the important inorganic constituents in the 800°C ash samples in which the uranium has been concentrated by a factor of about 4 from 0.06 to 0.6 lb/ton in the air-dried raw lignite to 0.24 to 2.7 lb/ton in the ash. Also, significant concentrations of molybdenum and aluminum are present that may be recovered as by-products, thereby improving the economics of uranium recovery.

The metal cations contributing to the consumption of acid were determined for most of the samples. The quantities of these elements dissolved and their equivalent quantities of sulfuric acid are shown in Table 12 for representative samples from each location. The calculated consumptions

of acid are in good agreement with titration measurements considering that no allowance was made for consumption by calcium minerals which reacted but remained in the residue as calcium sulfate.¹⁵

Aluminum compounds were by far the largest consumers of acid. In the examples shown, 57 to 86% of the consumed acid can be accounted for by the reaction with aluminum. A significant amount of the aluminum present in the ash was dissolved and could be recovered as a by-product. For example, 50 and 84% of the aluminum were dissolved from ash samples Wyo-2 and -92 respectively. This aspect is discussed in more detail the section on by-product recovery.

If uraniferous lignite were to be used as a power plant fuel, the burning temperature would obviously be maintained at the highest acceptable level, possibly in the range of 1200 to 1400°C. Thus, a few scouting tests were made for short periods at temperatures as high as 1400°C. The results described in Table 13 show that 70 to 80% of the uranium can be extracted with dilute sulfuric acid from ash subjected to temperatures as high as 1400°C if the exposure time was only 15 to 60 s. Samples heated for 5 min at 1200°C were sintered and the uranium become more refractory (~60% recovery). When the temperature was raised to 1300°C the sample became molten after a few minutes. These results were very encouraging, because they indicated the possibility of flash burning of the lignite at a high temperature (such as that reached by a power plant fuel) without causing the uranium to become refractory. To test this theory a small, gas-fired burner was designed and built.

Raw, oven-dried (110°C) -100 and -200 mesh lignite was fed to the burner at approximately 400 g/h by a screw feeder into the top of a 5-in. porcelain tube that was 3-ft long. The tube, surrounded by fire brick, was heated with one to three gas burners (No. 4A tip for National 3A blow pipe). The

resulting ash was sucked through a water-cooled, stainless steel cooling chamber into a vacuum cleaner from which it could easily be removed for chemical analysis and testing. Three thermocouples inside the tube (top, middle, and bottom) and three in the air space between the tube and the fire brick were used to measure the burning temperature and to aid in controlling the burning. Temperatures were recorded on a 12-point Brown potentiometer.

Air, or air and oxygen mixtures were fed with the lignite through the screw feeder. In addition to aiding the ignition, the air stream was important in feeding or dispersing the lignite in the tube. A mirror at the bottom of the cooling chamber was used to observe the burning of the lignite. The majority of the lignite appeared to burn in a jet 4 to 8 in. long as it entered the tube, and secondary burning occurred spasmodically in a swirling motion throughout the upper half of the tube. A certain amount of the ash stuck to the tube walls, and over a period of several runs it built up as a slag that dripped from time to time into the Buchner funnel.

The tube was usually preheated to $\sim 200^{\circ}\text{C}$ less than that desired, because the introduction of the lignite caused an immediate increase in temperature, which made up the deficit. Burning temperatures to 1000 to 1400°C were easily attained and controlled.

Representative samples of the lignites were burned in the furnace at 1000° to 1400°C in air and at 1300°C in a 50% air--50% oxygen stream. In general, 70 to 80% of the uranium from all the ash samples was readily soluble in dilute sulfuric acid (Table 14). The acid requirements were quite high, mainly due to the loss of sulfur during burning and partly to the formation of soluble iron and aluminum compounds. As described below, this may be

overcome to a large degree by recovery and recycle of the sulfur compounds from the off- or flue gases.

Combustion was essentially complete at 1000 to 1400°C. The lower limit of burning is probably 1000°C as shown by a higher percentage of carbon (~1 to 3%) in the ash and as evidenced by visual observation of the burning. At 1400°C, ~15% of the recovered ash was slag. This slagging was thought to be caused by an accumulation of dust on the burner walls, which became molten and dripped from the burner, rather than by actual fusing of the free falling particles. The upper limit for burning, 1300°C, is apparently optimum.

The amount of oxygen present during burning is very important, not only to the rate and degree of combustion, but to the formation of acid consumers in the ash. For example, as the temperature was raised from 1000 to 1400°C (in air), the percentage of sulfate in sample-109 ash dropped from 17 to 5, and the acid consumed during the subsequent leach increased from 614 to 830 lb H_2SO_4 /ton. When the sample was burned under more-oxidizing conditions (50% O_2 --50% air) the sulfate was more stable and most of it remained in the ash (17%, compared to 11% in air at 1300°C). In this case acid consumption was only 400 lb/ton.

Molybdenum extraction values are also included in Table 14. Higher recoveries were obtained at the higher burning temperatures and from the most completely oxidized ash. The data also suggest that molybdenum requires more free acid for dissolution than does the uranium.

Under the same conditions, some of the lignite samples did not burn as completely as others. The temperature and degree of oxidation need to be adjusted for the type of lignite being burned to optimize recoveries of uranium and potential by-products (molybdenum, aluminum). A major

problem for a large commercial roaster or burner is control of the combustion temperature and rapid dissipation of the heat to minimize sintering and slagging.

Utilization of Sulfur Dioxide from Flue Gas

Flue gases from the burning lignite normally contain significant quantities of sulfur dioxide. In the samples tested, the amount of SO_2 released during burning was, on the average, equivalent to ~ 300 lb H_2SO_4 per ton of ash. It was known that SO_2 in aqueous solution may be oxidized to sulfate by air in the presence of metal ions.^{19,20} Thus we made a few scouting tests in which synthetic flue gas, prepared by mixing air- N_2 - SO_2 - CO_2 in the proportions usually found in typical flue gases, was bubbled through a slurry of ash and water for various times and temperatures. These preliminary tests showed that SO_2 was readily oxidized and converted to sulfuric acid on contact with the slurry (Table 15).

A 1-h addition of synthetic flue gas containing SO_2 equivalent to 1000 lb H_2SO_4 per ton of ash to a leach slurry consisting of 1150°C Wyo-1 ash and water at room temperature produced a filtrate pH of 2.5 and a solubilization of 25% of the uranium. The sulfate content of the filtrate was 7.5 g/L or ~ 300 lb H_2SO_4 per ton of ash. Prolonging the leaching time from 1 to 5 h resulted in only a slight increase in uranium solubilization to 35%, whereas raising the temperature to 95°C produced a sizeable increase in sulfuric acid (~ 400 lb/ton) and uranium dissolution (54%). A 3-h leach at 95°C resulted in 65% dissolution of the uranium, which is equivalent to that obtained by leaching the sample with sulfuric acid (Table 10). Additional 6-h, 85°C tests confirmed that air (or oxygen) is necessary to convert the SO_2 to acid. In these tests only 30 to 40% of the SO_2 was converted

to sulfuric acid, and the control and measurement of the SO_2 flow was not as good as desired.

We made a few additional tests using very accurate measuring methods for the flow, particularly that of the SO_2 which was measured with a calibrated, pressure-differential device. Sodium hydroxide scrubbers containing hydrogen peroxide were used to measure any SO_2 that escaped the leach vessels so that we could obtain a material balance over the system.

These data (Table 16) show that about 40% of the SO_2 was absorbed in a single leach when the quantity of SO_2 (7 cc/min x 60 min) evolved during the burning of Wyo-1 at 1150°C was passed through the leach slurry. In this test, ~14% of the uranium was solubilized and an equivalent of 135 lb H_2SO_4 per ton of ash was analyzed in the filtrate. An additional leach of the ash with 300 lb H_2SO_4 /ton increased the recovery to 53%.

Increasing the SO_2 flow by 50% while maintaining a constant air flow rate at 450 cc/min did not result in an improvement in SO_2 conversion or in uranium extraction. However, when the amount of air was increased and the leaching time extended to allow more time for oxidation, 58% of the SO_2 was absorbed and over 40% of the uranium was solubilized. It is rather apparent that these tests were limited by inadequate oxidizing conditions. Also, SO_2 absorption tends to decrease as the pH decreases.

So that process efficiency could be improved, a series of tests was made in which the flue gas was cycled through five consecutive leach slurries. In these tests, 96% of the SO_2 was absorbed and ~50% of the uranium was solubilized without additional acid.

These tests, although limited in scope, were very encouraging and indicate that a large part of the acid requirement for uranium recovery may be obtained

from the lignite itself. To determine whether these reactions can be utilized on a practical operating basis with actual flue gases will require much additional work. Such a process would also help relieve the environmental disposal of sulfur dioxides in the plant.

Product Recovery and By-product Possibilities

Recovery is not complete until the uranium is recovered from the leach solutions and converted to a relatively pure U_3O_8 product that is acceptable to uranium refineries that produce UF_6 . Our work on lignites was halted before we had an opportunity to study this part of the problem. However, it was studied at several other laboratories^{6,7} and during the intervening years a very large amount of information has been accumulated on the recovery of uranium and other metal values from similar solutions using solvent extraction and ion exchange techniques. The front end, which includes mining, ore preparation, burning, leaching, thickening and/or filtration of the leach slurry is considered to be the most cost-intensive part of a process scheme. Recovery of uranium from clean liquors should be relatively simple and inexpensive.

The quantities and composition of coal and lignite residues or ash make this material a potentially valuable resource for numerous important metals in addition to uranium. These include molybdenum, aluminum, and iron plus a number of other metals that are present in trace quantities. Several investigators²¹⁻²⁵ are currently evaluating various methods for recovering these products from commercial coal wastes, and a similar program has begun on Chattanooga oil shale leach solutions.²⁶ The major goal of these studies is to determine the economics of by-product metal recovery. Based on the cost of energy generation from lignite at $\$0.30/10^6$ Btu and

current spot prices for uranium, molybdenum, aluminum, and iron, the value of 1 ton of ash is \$119 (Table 17) or ~\$12 per ton of raw lignite "as-received." This does not include any value for trace elements or sulfur that may be recovered during burning and used for leaching the metal values. Although total recovery, as shown in Table 17, cannot be achieved, such an analysis indicates some of the advantages of co-recovery of thermal energy and metal values.

Summary and Conclusions

Our studies showed that uranium in raw lignite is associated with the organic matter and is readily soluble in acid (and carbonate) solutions. However, treatment of raw lignite did not, and does not now, appear to be attractive because reagent consumptions are high, liquid-solid separations are difficult, and the liquor is fouled by organic matter. Beneficiation techniques were not successful for concentrating the uranium or removing part of the reagent-consuming materials.

Once the lignite was heated by roasting, retorting, or charring, the uranium became much less soluble in both acid (and carbonate) solutions, and essentially complete removal of carbon was required to convert it back to a soluble form. Proper burning (with respect to time, temperature, and oxidizing conditions) tends to improve acid-leaching efficiency; that is, it reduces the reagent consumption and concentrates the uranium, thereby reducing plant size for comparable uranium throughput, and it eliminates organic fouling of leach liquors. Restrictions are necessary during burning to prevent the uranium from becoming refractory. In general, although a prolonged roasting time has a beneficial effect on the uranium extractability of a low-temperature (500°C) ash and no appreciable effect on a

medium-temperature (800°C)* ash, it has a definite detrimental effect on a high-temperature (>1000°C) ash. When the lignite was roasted or burned at 1000 to 1100°C for 0.5 to 1.5 h, the uranium extractions were erratic. The general effect of increased temperatures (for rather long periods of time) was to decrease the availability of the uranium.

The most encouraging results were obtained by flash-burning lignite at 1200 to 1300°C and utilizing sulfur dioxide released during burning to supplement the acid requirement.

The major acid consumers were aluminum and iron. At the time this study was made, these constituents were considered waste products; today, because of changing economics, such material is a potential resource, and co-recovery could result in significant cost savings.

It should be emphasized that the material tested in this study may not be completely representative of the average mineable material desired for power production. Ash can vary within rather wide limits, not only in its composition but also in its chemical behavior, depending on its history, the type of lignite, roasting time and temperature, previous dressing operations, etc. Before successful production of power can be coupled with the economical recovery of uranium and other potential by-products, additional information is needed concerning the properties of ash produced in commercial lignite-fueled power, gasification, and liquefaction plants. Ideally, a balance in operating conditions is needed to obtain maximum heating values, or gaseous or liquid products without causing excessive uranium refractory.

*These results do not agree with current information, which states that uranium recoveries are impaired at temperatures of 600°C.¹¹

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List of Figures

- Fig. 1. Direct leaching of air-dried (5% H₂O) raw-lignite 109 at 20% pulp density.
- Fig. 2. The effect of uranium concentration on acid consumption from raw lignite (conditions in Table 5).
- Fig. 3. The effect of uranium concentration on acid consumption from ash (conditions in Table 10).

ORNL-DWG 80-1240

Table 1. Proximate Analyses of Lignite Samples^a

Lignite No.	Percent			
	Moisture	Ash	Fixed Carbon	Volatile Matter
<u>Sentinel Butte</u>				
ND-1	42.5	17.5	22.0	18.0
<u>Slim Buttes -- East</u>				
86	40.0	27.2	17.6	15.2
92	48.8	12.3	14.8	24.1
121	46.5	16.8	16.7	20.0
141	41.3	11.8	23.2	23.7
<u>Slim Buttes -- West</u>				
95	40.0	20.0	21.7	18.3
97	44.0	13.5	22.6	19.9
101	46.7	11.0	19.9	22.4
103	41.3	14.2	23.7	20.8
109	38.6	18.3	23.1	20.0
<u>Wyoming</u>				
Wyo-1	28.1	12.4	24.1	35.5
Wyo-2	28.8	20.0	19.8	31.4
<u>Typical Lignite^b</u>				
	36.0	7.0	30.0	27.0

^a As-received basis^b See ref. 1.

Table 2. Ultimate Analysis of Lignite Samples^a

Lignite No.	Percent				
	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur
<u>Sentinel Butte</u>					
ND-1	51.0	5.0	42.3	0.7	1.0
<u>Slim Buttes - East</u>					
86	60.6	3.9	31.9	2.2	0.6
92	59.2	3.1	35.6	1.6	0.5
121	66.5	3.9	27.3	1.6	0.7
141	59.2	2.9	35.7	1.7	0.5
<u>Slim Buttes - West</u>					
95	60.7	3.5	33.5	1.2	1.1
97	59.8	7.8	33.0	1.7	1.7
101	63.9	3.7	30.1	1.5	0.8
103	52.5	3.3	42.2	1.3	0.7
109	57.2	2.6	35.2	1.2	3.8
<u>Wyoming</u>					
Wyo-1	59.7	3.3	33.5	2.0	1.5
Wyo-2	59.7	3.3	33.0	2.1	1.9
<u>Typical Lignite</u> ^b					
	68.0	5.5	24.5	1.0	1.0

^aMoisture and ash-free basis.^bSee ref. 1.

Table 3. Potential Fuel Values of the Lignites^a

Lignite No.	Uranium (%)	Sulfur (%)	Heating Value (btu/lb)	Tar (gal/ton)
<u>Sentinel Butte</u>				
ND-1	0.047	0.7	5400	7.0
<u>Slim Buttes - East</u>				
86	0.0075	0.3	4835	2.7
92	0.012	0.4		6.3
121	0.013	0.5	7085	5.4
141	0.008	0.4	6645	8.2
<u>Slim Buttes -- West</u>				
95	0.032	0.7	5935	2.0
97	0.010	1.3	6640	5.9
101	0.015	0.6	6998	2.5
103	0.019	0.5		
109	0.021	2.6	5695	2.5
<u>Wyoming</u>				
Wyo-1	0.0075	1.4	8750	7.6
Wyo-2	0.0079	1.5	7550	6.0

^aDry-basis

Table 4. Uranium Content of Mineral Fractions

Constituent ^a	Percent
Jarosite	0.002
Coarse-grained clay	0.003
Fine-grained clay	0.003
Gypsum, "satin-spar"	0.002
Gypsum, dehydrated ^b	0.002
Lignite, carbonaceous	0.055
Head sample, approximate	0.044

^aNone of the samples was completely free from carbonaceous matter.

^bThe ash content was not measured. Similar samples have shown about 15% ash whereas the head material is about 30%.

Table 5. Uranium Extraction from Raw Lignite with Sulfuric Acid

Lignite No.	Uranium (%)	lb/ton	H ₂ SO ₄ Consumed	
			lb/ton ash	lb/lb uranium
<u>Sentinel Butte</u>				
ND-1	71	0.60	140	235
<u>Slim Buttes-East</u>				
86	67	0.07	190	2715
92	69	0.11	280	2545
121	70	0.13	250	1925
141	69	0.12	230	1915
<u>Slim Buttes-West</u>				
95	83	0.43	140	325
97	69	0.09	120	1335
101	84	0.25	150	600
103	87	0.22	160	725
109	86	0.33	210	635
<u>Wyoming</u>				
Wyo-1	42	0.06	136	2265
Wyo-2	51	0.07	144	2055

Leach conditions: -14 mesh partly air-dried (20% moisture) lignite leached at 20% pulp density for 4 h at 80°C with 12.5% H₂SO₄ (1000 lb H₂SO₄ per ton of lignite)

Table 6. Uranium Extraction from Lignite Char

Retorting Temp (°C)	Leach Agent	Uranium Extracted (%)
500	H ₂ SO ₄	8
500	H ₂ SO ₄ + KMnO ₄ ^a	10
Char Roasted Under Oxidizing Conditions at 500°C		
500	H ₂ O	86
600	H ₂ O	81
700	H ₂ O	82
800	H ₂ O	84
Retorting conditions: -14 mesh lignite (ND-1) heated for 2 h under reducing conditions in a 300-ml Fischer retort.		
Leaching conditions: -100 mesh retorted lignite or roasted char leached at 10% pulp density for 4 h at 80°C with H ₂ O or 5% H ₂ SO ₄ .		
^a 1 g KMnO ₄ /10 g char.		

Table 7. Furnace vs Bed Temperatures
of Burning Lignite

Furnace (°C)	Bed (°C)
400	565
500	625
600	745
700	796
800	900

Table 8. Effect of Roast Time and Temperature
on Extraction of Uranium from Lignite

Roast Conditions		Leach Agent	Final pH	Uranium Extracted (%)
Time (h)	Temp (°C)			
3	400	H ₂ O	3.2	68
2	500	H ₂ O	3.0	68
5	500	H ₂ O	2.7	68
16	500	H ₂ O	2.7	76
4	800	H ₂ O	7.8	0
4	800	H ₂ SO ₄	0.5	82
6	800	H ₂ O	8.0	0
6	800	H ₂ SO ₄	0.4	76
2	1000	H ₂ O	11.0	0
2	1000	H ₂ SO ₄	1.4	45
4	1000	H ₂ O	12.0	0
4	1000	H ₂ SO ₄	0.4	55

Roast conditions: Raw lignite (ND-1) placed in a muffle furnace at 400°C and heated rapidly to the desired temperature.

Leach conditions: -20 mesh ash leached at a pulp density of 10% for 1 h at 80°C with H₂O or 5% H₂SO₄.

Table 9. Loss of Sulfate During Roasting

Furnace temp (°C)	time (h)	SO ₄ in ash (%)
		37 ^a
500 ^b	16	30
800	2	22
900	1	20
1000	0.75	18
1000	1.75	14
1100	1	11

^aCalculated from head analysis.

^bPlaced in furnace at 500°C; others were placed in furnace at 400°C and the temperature was raised to that indicated.

Table 10. Uranium Extraction from Lignite Ash
Formed at 800°C

Lignite No.	Extraction		H ₂ SO ₄ Consumed	
	Uranium (%)	lb/ton	lb/ton ash	lb/lb uranium
<u>Sentinel Butte</u>				
ND-1	80	2.7	200	74
<u>Slim Buttes - East</u>				
86	71	0.24	510	2125
92	80	0.77	1000	1300
121	80	0.68	1000	1480
141	66	0.50	760	1520
<u>Slim Buttes - West</u>				
95	79	1.40	210	150
97	77	0.67	400	600
101	80	1.28	410	320
103	80	0.98	290	295
109	80	1.09	300	275
<u>Wyoming</u>				
Wyo-1	71	0.43	928	2180
Wyo-2	65	0.26	887	3410

Roast conditions: Ash samples were prepared by placing a thin $\frac{1}{4}$ to $\frac{1}{2}$ inch bed of raw lignite on a tray in a muffle furnace for 2 h at 800°C in an air stream.

Leach conditions: -20 mesh ash leached at a pulp density of 10% for 1 h at 80°C with 5% H₂SO₄ (1000 lb H₂SO₄ per ton of ash).

Table 11. Chemical Analyses of Lignite Ash Samples

Lignite No.	Chemical Analysis (%)								
	U	Mo	Fe	Al	Ca	Mg	Na	K	SO ₄
<u>Sentinel Butte</u>									
ND-1	0.17	0.29	17.1	4.6	7.4	0.7	1.8	0.5	25.7
<u>Slim Buttes - East</u>									
86	0.017	0.12	10.5	8.6	2.8	1.0	2.4	1.1	6.5
92	0.048	0.14	11.5	7.8	7.2	1.2	1.6	0.4	4.6
121	0.042	0.14	10.5	8.4	7.4	1.4	1.8	0.9	5.8
141	0.038	0.17	10.7	4.8	8.1	0.9	4.7	0.5	18.2
<u>Slim Buttes - West</u>									
95	0.090	0.17	13.9	9.3	7.6	0.8	1.8	0.9	18.0
97	0.043	0.07	7.5	6.6	6.3	1.8	3.9	1.0	18.4
101	0.080	0.27	9.7	4.6	9.3	2.4	5.0	0.7	26.8
103	0.062	0.17	12.9	4.6	10.8	1.0	1.6	0.6	25.7
109	0.069	0.31	12.3	6.0	9.8	1.2	1.8	0.6	23.4
<u>Wyoming</u>									
Wyo-1	0.030		6.0	14.1	6.4	1.5	0.3	0.3	12.1
Wyo-2	0.020		6.5	14.7	4.9	1.1	0.3	0.5	8.2

Roast Conditions: 15 g of 3/8-in. air-dried lignite in a quartz tray (bed depth, 1/4 in. to 1/2 in.; surface area, 65) was inserted in a muffle furnace at 400°C. The temperature was rapidly increased to 800°C until ignition was complete (~1.5 h).

Table 12. Impurities Dissolved and Acid Consumed by a
Sulfuric Acid Leach of Lignite Ash^a

Impurities Dissolved	ND-1		92		109		Wyoming-2	
	1b H ₂ SO ₄		1b H ₂ SO ₄		1b H ₂ SO ₄		1b H ₂ SO ₄	
	lb/ton	(ton)	lb/ton	(ton)	lb/ton	(ton)	lb/ton	(ton)
Al	19	102	131	715	30	163	140	762
Fe	9	26	17	45	10	26	25	66
Ca	13	32	20	50	12	29	19	47
Mg	1	4	6	25	3	12	6	24
Na	12	26	23	50	28	60	<1	<1
K	5	6	4	5	5	6	4	5
Total		196		890		296		904
Acid Consumption by Titration		200		1000		285		887

^aSee Table 10 for roast and leach conditions.

Table 13. Uranium Extraction from Lignite Ash
Formed at High Temperatures

Burning		Uranium Extracted (%)	H ₂ SO ₄ Consumed	
Temperature (°C)	Time (s)		lb/ton ash	lb/lb uranium
<u>Slim Buttes - East, No. 86</u>				
1200	15	75	480	2000
	30	82	430	1650
	60	71	330	1370
	300	58	235	1100
1300	15	81	475	1800
	30	75	420	1500
	60	69	315	1400
	300	Sample Molten		
1400	15	78	480	2000
	30	77	370	1400
	60	69	280	1275
<u>Slim Buttes - West, No. 109</u>				
1200	15	84	300	320
	30	77	220	260
	60	76	175	225
	300	74	340	320
1300	15	84	320	300
	30	85	275	270
	60	78	240	245
1400	15	81	320	280
	30	82	270	220
	60	81	260	210

Leach conditions: ash leached at 10% pulp density for 3 h
at 80°C with 5% H₂SO₄.

Table 14. Uranium Extraction from Flash-Burned Lignite Ash

Lignite No.	Burning Temp (°C)	Ash (% SO ₄)	Extraction		H ₂ SO ₄ Consumed
			Uranium (%)	Molybdenum (%)	lb/ton ash
<u>Slim Buttes - East</u>					
86	1100	3	81	59	632
	1300	2	62	75	448
	1380	1	84	7	1000
92	(double leach)		89	78	1500
<u>Slim Buttes - West</u>					
97	1100	12	74	39	756
	1300	8	76	39	846
	1300 ^a	12	72	59	686
101	1100	10	77	11	1022
	1300	8	74	1	922
	1300 ^a	19	84	81	790
109	1000	17	80	51	614
	1100	17	80	56	572
	1200	14	81	59	600
	1300	11	82	66	615
	1300 ^a	17	84	69	400
	1400	5	76	65	830
<u>Wyoming</u>					
Wyo-1	1150	4	68		690
Wyo-2	1150	3	56		640

Leach conditions: -100 mesh ash leached at 10% pulp density for 4 h
at 80°C with 5% H₂SO₄ (~1000 lb H₂SO₄ per ton of ash).

^a50% air -- 50% O₂ during burning; others burned in 20% excess air.

Table 15. Extraction of Uranium from Flash-Burned
Lignite Ash Using Synthetic Flue Gas

Air	Gas (%)			Leach		pH	Filtrate		Uranium Extracted (%)
	N ₂	CO ₂	SO ₂	Time (h)	Temp (°C)		SO ₄ (g/L)	lb H ₂ SO ₄ ton of ash	
83	0	17	0.25	1	30	2.5	7.5	300	25
				5	30	2.2			35
				1	95	1.3	10.5	420	54
				2	95	0.73	22.0	880	54
				3	95	0.85	22.0	880	65
				5	95	0.60	44.5	1780	63
				6	95	0.50	38.0	1520	60
100	0	0	0.25	6	95	0.46			56
83	0	17	0	6	95	7.5			7
0	83	17	0.25	6	95	4.0			10
10	73	17	0.25	6	95	1.15			52

Ash: -100 mesh Wyo-1 ash burned at 1150°C in flash burner.

Leach conditions: Synthetic flue gas (as shown) was bubbled at a total flow rate of ~4.9 liters per min. through a slurry consisting of 200 ml of H₂O and 10 g of ash.

Table 16. Absorption of Sulfur Dioxide in a Leach Slurry

Gas Flow (cc/min)		Filtrate			SO ₂ Absorbed (%)	Uranium Extracted (%)	
Air	SO ₂	pH	SO ₄ (g/L)	lb H ₂ SO ₄ Ton ash		1	2 ^c
450	5.0 ^b	3.3	2.9	118	48	12	49
450	7.0 ^b	3.0	3.3	135	39	14	53
450	10.5	3.1	3.3	135	27	11	52
4050	16.5	1.9	9.3	380	48	42	56
4050	16.5 ^a	2.2	11.4	466	58	44	

Ash: -100 mesh Wyo-1 burned at 1150°C in flash burner.

Leach Conditions: Synthetic flue gas containing air-N₂-CO₂-SO₂ was bubbled through a slurry consisting of 200 ml H₂O and 10 g of ash for 1 h at 85°C.
Total gas flow was 4.9 l./min.
CO₂ flow was 850 cc/min.
N₂ flow may be obtained by difference.

^a The tailing from the flue gas treatment was given an additional 4 h leach at 80°C with 5% H₂SO₄ (300 lb H₂SO₄/ton ash).

^b Represents the quantity of SO₂ evolved during burning.

^c Ash leached 2 h after gas flow was stopped.

Table 17. Products in Lignite

Product	Content ^a	Ash (\$/ton)
Heating value, Btu/lb	6550 ^b	24.00 ^c
Uranium, lb/ton	1.4	45.00
Molybdenum, lb/ton	3.5	32.00
Aluminum, lb/ton	150	8.00
Iron	215	10.00
Total		119.00

^aAs oxide except for heating value; based on average values from Tables 1, 3, and 11.

^bDry basis.

^cBased on an average ash content of 16.3%.