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OXIDATION OF A LOW-TEMPERATURE LIGNITE TAR PITCH

John S. Berber and Richard L. Rice

U. S. Department of the Interior, Bureau of Mines
Morgantown Coal Research Center, Morgantown, W. Va.

INTRODUCTION

As part of a broad program of coal research, Bureau of Mines scientists are conducting research on the characterization and upgrading of low-temperature tar. An important part of this work is the study of pitch from low-temperature lignite tar.

In the processing of tar obtained by low-temperature carbonization of coal, a residue or pitch is obtained that distills above 350° C and has physical characteristics intermediate between those of coke oven (high-temperature) tar pitch and those of petroleum bitumens. Low-temperature pitches are complex resinous masses of polymerized and polycondensed compounds. They are amorphous, solid or semisolid plastic materials, and consist predominantly of carbon with several percent by weight of hydrogen, somewhat less oxygen, nitrogen, and sulfur, and small amounts of inorganic materials. They are chemically similar to the tars from which they are prepared, being mainly mixtures of the higher homologs of the compounds contained in the distillable fractions of the tar. The pitch fraction from low-temperature tar usually is 30 percent by weight or more of the tar, depending upon the source of the tar and processing conditions. There has been little demand for the material because it is hard and brittle. The Bureau of Mines is attempting to modify this pitch to convert it into a more marketable product.

One method that has worked with high-temperature pitches is to blow air through the pitch mass while the mass is being heated. Other methods include solvent refining, the use of additives, the use of catalysts, and thermal treatment in an inert atmosphere. This paper discusses the results of air-blowing tests designed to convert pitch into a material useful as electrode binder.

ELECTRODE BINDER PITCH

Pitch is used as a binder in the manufacture of four major classifications of electrodes: baked-in-place (cathodes), Soderberg, preformed baked, and graphitized high density. To make each of these types, the aggregate is mixed with the solid or melted pitch in a special mixer until the aggregate is completely coated. The mixture is then rammed in place, extruded or molded into the desired shape, then baked (2).*

* Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Soderberg electrodes are produced by mixing pitch binder with a graded aggregate of calcined petroleum coke, pitch coke, anthracite coal, bituminous coal coke, or mixtures of these. In the aluminum industry, only calcined petroleum or pitch coke is used to make electrodes to keep the impurities at a minimum.

So little is known about the structure or exact chemical composition of pitches that it is not possible to establish specifications other than by reference to arbitrary tests. Generally, the main properties involved in specifications for electrode binder, besides the softening point and carbon-to-hydrogen ratio, include specific gravity, coking value, ash content, distillation test, the amounts insoluble in benzene and soluble in quinoline, and the concentration of iron, silica, sulfur, and boron.

Softening point is particularly important in the production of electrode binder because the binder must be soft enough to properly mix with the electrode carbon and still contain enough resins to impart the desired compressive strength to the finished electrode. For electrode binder, the softening point should be about 95° to 110° C for Soderberg electrodes and 105° to 115° C for prebaked electrodes.

Electrode binder pitch must contain at least 20 percent of so-called "beta-resin," which is that portion soluble in quinoline, but insoluble in benzene (3). Concentrations of tar acids, tar bases, paraffins, saturated cyclic compounds, olefins, and alkyl groups attached to aromatic nuclei must be minimal because an excess of these adversely affect the properties of the pitch (1).

Carbon-hydrogen ratio is another property that pitch users consider of importance as it is an indication of plasticity, ductility, and elasticity of the binder. Most high-temperature pitches have a carbon-hydrogen ratio of about 1.8. The low-temperature pitch from lignite used in the tests in this report, however, had a carbon-hydrogen ratio of only about 0.84, and a low-temperature pitch from a bituminous coal had a C-H ratio of about 1.0. It can be readily seen that the C-H ratio of the low-temperature tar pitch must be increased if the material is to more nearly resemble commercial pitches.

The pitch used in these tests was obtained by batch distillation, under vacuum, of a low-temperature tar produced by the Texas Power and Light Company from Sandow lignite. Properties of the pitch are given in Table 1.

AIR-BLOWING OF PITCH

Since the binder characteristics of low-temperature tar pitch differ from those of high-temperature tar pitches, the pitch must be modified or upgraded if it is to be used for that purpose. As indicated, blowing with air (or oxygen) has been used to convert certain high-temperature bituminous pitches into material meeting specifications. It is a means of increasing the binder resin content of the pitch. The oxygen in the air acts as a condensation and dehydrogenating agent. The formation of water indicates that dehydrogenation has taken place, and the presence of carbon monoxide and carbon dioxide in the exit gases shows carbon has been lost. Little combined oxygen is found in the oxidized pitch.

As mentioned previously, a high carbon-to-hydrogen ratio appears a requisite for an acceptable electrode binder. Softening point and carbon-to-hydrogen ratio were taken as criteria of the effectiveness of the air-blowing treatment of these experiments to produce an electrode binder.

RESULTS

In the tests, the pitch was placed in a reactor (Figure 1), heated to the desired temperature, air or oxygen admitted at 2 to 4 scfh per pound, and agitation started at about 925 rpm. Runs ranged from 1 to 5 hours in length. Results are tabulated in Table 2.

It was found that the softening point generally increased in proportion to the length of time the air was blown through the pitch. The data plotted in Figure 2 illustrate the trend for air rates of 2.7 to 3 scfh per pound. Figure 2 also shows that for fixed run lengths, the softening point went up with increase in temperature of the heated mass.

Figure 3, a plot of reaction temperature versus softening point, better illustrates the effect of temperature. Blowing with oxygen raised the softening point temperature more than blowing with air.

Air rate also affected the softening point (Figure 4). It is apparent that air-blowing gave a very wide range of softening points, depending upon the reaction conditions. These conditions must be controlled very closely to give reproducible results.

A limited number of tests were made to determine the effect of sulfur addition on the softening point. Table 3 gives these results. In general, no definite pattern is apparent to indicate a material advantage for this treatment.

Blending was investigated to a limited extent. Industrial pitches are produced by distillation from high-temperature coke oven tars selected and blended to give the properties desired in the finished product, which vary in the different uses (4). It appeared that blending of different pitches, as shown in Table 4, would give a product having predictable characteristics. These blends, evaluated by the United States Steel Corporation electrode binder testing laboratory, indicate that the blends do not compare favorably with the pitch from coke oven tar in such properties as apparent density, crushing strength, electrical resistivity, and CO₂ reactivity. Table 5 gives the properties of the test electrodes.

CONCLUSIONS

This study on the air-blowing of pitch from low-temperature lignite tar was undertaken to prepare an effective electrode binder possessing properties of a bituminous pitch. Except for softening temperature, none of these properties were attained. The carbon-hydrogen ratio was increased slightly, but not significantly, and was below that of the blends made with high-temperature bituminous coal pitch which did not produce acceptable electrodes. Addition of sulfur does not significantly increase the carbon-hydrogen ratio. Either the blowing procedure was inadequate or air oxidation is not an effective means of upgrading low-temperature lignite tar pitch.

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TABLE 1. - Typical composition and properties of pitch before air-blowing compared with the desired properties

Properties	Typical	Desired
Softening point, °C	90 ¹	95-110
Analysis, weight-percent		
Moisture	0.00	0.00
Carbon	83.78	92-93
Hydrogen	8.27	4-4.5
Sulfur	1.04	< 1.00
Nitrogen	1.06	1.00
Oxygen ²	5.71	1-2
Ash	0.14	< 0.3
C-H ratio, atomic	0.84	1.8
Solubility, weight-percent		
Benzene	87.1	60
Petroleum ether	31.9	10

¹ Ring-and-ball softening point.

² Oxygen obtained by difference.

TABLE 2. - Air-blowing of pitch from low-temperature lignite tar

Run no.	Length of run, hours	Temp., ° F	Air rate, scfh/lb	Softening point at start, ° C	Softening point at end, ° C	Carbon, wt-pct	Hydrogen, wt-pct	C-H atomic ratio
110	3	300	2	92	111	83.50	7.59	0.92
14	2	428	2	--	121	84.08	7.67	0.91
15	2.5	428	2	--	123	83.10	7.68	0.90
16	3	428	2	--	132	83.54	7.71	0.90
27	3.5	482	2	--	207	84.15	7.30	0.96
115	1	300	2.7	90	93	85.42	7.47	0.95
116	2	300	2.7	90	96	85.23	7.61	0.93
114	1	350	2.7	90	94	85.30	7.58	0.94
112	2	350	2.7	90	109	84.92	7.64	0.93
113	2	350	2.7	90	109	84.48	7.65	0.92
117	3	350	2.7	90	118	85.16	7.73	0.92
118	3.5	350	2.7	90	119	85.08	7.77	0.91
18	4	428	2.7	--	150	83.85	7.59	0.92
19	2	455	2.7	--	146	83.94	7.44	0.94
23	4	455	2.7	--	168	83.41	7.33	0.95
24	2	482	2.7	--	154	84.55	7.55	0.93
107	2.5	300	3	92	101	84.00	7.68	0.91
109	3	300	3	92	111	83.90	7.45	0.94
78	5	334	3	--	159	83.80	7.47	0.93
7	1	400	3	--	108	83.72	7.97	0.88
6	1	455	3	--	129	83.00	7.90	0.88
26	3	482	3	--	185	84.04	7.22	0.97
2	1	500	3	--	166	83.59	7.68	0.91
1	2	500	3	--	202	84.58	7.54	0.93
95	1	300	4	76	95	84.00	7.43	0.94
46	2	482	4	--	175	84.00	7.29	0.96

TABLE 3. - Pitch blown with oxygen, nitrogen, and air, with sulfur added

Run no.	Length of run, hours	Temp., °F	Rate, scfh/lb	Carbon, wt-pct	Hydrogen, wt-pct	C-H atomic ratio	Softening point, °C	Softening point before treating, °C	Sulfur, pct
----- Oxygen -----									
41	2	428	0.3	83.25	7.61	0.91	123		
42	3.5	527	0.4	86.79	6.74	1.07	>250		
44	4	500	0.3	83.20	7.20	0.96	>250		
49	3	482	0.27	85.49	7.13	0.99	>250		
121	1	275	0.57	84.98	7.68	0.92	108	105	
122	1	275	0.57	85.19	7.74	0.92	117	105	
123	2	300	0.57	85.35	7.68	0.93	121	105	
124	1	275	0.57	84.69	7.78	0.91	113	105	
54	5	400	0.27	84.17	7.33	0.96	>250		5
57	2	400	0.27	83.28	7.76	0.89	130		3
58	2	428	0.27	83.30	7.78	0.89	141		3
59	2	455	0.27	84.10	7.48	0.94	172		3
----- Nitrogen -----									
60	2	400	2.7	83.47	7.85	0.89	136		3
61	4	400	2.7	83.44	7.75	0.90	123		3
62	4	455	2.7	83.50	7.65	0.91	121		3
63	4	500	2.7	83.72	7.68	0.91	129		3
66	2	482	2.7	83.78	7.76	0.90	118		3
67	2	482	2.7	83.76	7.80	0.89	121		3
68	4	482	2.7	83.58	7.70	0.90	121		3
69	23.65	482	2.5	84.09	7.17	0.98	178		3
71	31.25	482	2.7	84.15	7.18	0.98	>250		5
----- Air -----									
55	5	400	2.7	83.39	7.21	0.96	>250		5
56	3	400	2.7	83.40	7.44	0.93	177		3
132	1	282	2.7	81.60	7.57	0.90	105	90	5
135	1	240	3	84.76	7.55	0.94	111	93	5
136	1	350	3	84.79	7.52	0.94	112	93	5
137	1	420	3	84.86	7.56	0.94	124	93	5
138	1	470	3	85.30	7.44	0.96	132	93	5
139	1	440	3	85.18	7.47	0.95	128	93	5
140	1	410	3	85.00	7.52	0.94	116	93	2.5

TABLE 4. - Data on samples evaluated by
U.S. Steel for electrode binders

Properties	Pitch blends	
	No. 1 ¹	No. 2 ²
Carbon	86.05	85.73
Hydrogen	6.40	6.39
C-H ratio	1.12	1.12
Softening point, °C	106	105
Penetration	0	0
Benzene insolubles	30	24

¹ 60 Percent low-temperature tar with softening point of 110° to 112° C and 40 percent high-temperature tar with softening point of 104° to 108° C.

² 60 Percent low-temperature tar with softening point of 97° to 101° C and 40 percent high-temperature tar with softening point of 110° to 121° C.

TABLE 5. - Properties of electrodes prepared
with Bureau of Mines binders

Properties	Bureau of Mines pitch blends		U. S. Steel coke oven pitch
	No. 1	No. 2	
Optimum binder content, wt-pct ¹	34	31	34
Apparent density, g/cm ³	1.32	1.38	1.46
Electrical resistivity, ohm-cm x 10 ⁻⁴	79.3	72.0	59.2
Crushing strength, kg/cm ²	302	388	642
CO ₂ reactivity, mg/g/hr	79.5	74.5	74.3
Dust, wt-pct	10.4	6.4	3.1

¹ Standard commercial aggregate, mix temperature 155° C.

CONTINUOUS DETERMINATION OF MOISTURE IN COAL BY NEUTRON THERMALIZATION

Robert F. Stewart and Arthur W. Hall

U. S. Department of the Interior, Morgantown Coal Research Center
Bureau of Mines, Morgantown, W. Va.

An automatic and continuous method of measuring the moisture content of coal is needed by the coal industry. Automatic control of the coal quality would reduce the cost of coal preparation, improve the product and thus indirectly increase the use of coal.

Moisture in coal can be determined by several methods, but the time required to obtain samples and analyze them by existing methods make it difficult, if not impossible, to control the quality of the product. Both producers and consumers need a method for continuous and instantaneous measurement of moisture content without sampling in order to regulate process equipment and keep the moisture content of coal within specifications.

At the Morgantown (W. Va.) Coal Research Center we are developing a nuclear method for continuous measurement of moisture in coal. This method is based on the thermalization of fast neutrons by hydrogen in the water and organic matter of coal. Neutrons from a small radioisotope source penetrate the coal, are scattered by hydrogen and measured by a thermal neutron detector. The number of thermal neutrons counted can be directly correlated with the moisture content of coal. Design of a moisture meter based on neutron thermalization depends on many variables, any or all of which can affect the sensitivity of the meter. These factors include those related to the nuclear aspect--type and size of neutron flux and source, type of detecting device, and background count--and those related to the coal being tested--rank, particle size, and ash content. A survey was initiated to eliminate the relatively insignificant factors and to ascertain the magnitude of the major effects. Such information was necessary to fully evaluate the technique and to establish design criteria.

Coal contains a relatively large amount of hydrogen in the organic coal substance and the water of hydration of the shaly material as well as in the moisture.

To apply this concept of moisture measurement to coal requires that the organic substance in coal from any one seam of a particular mine be uniform in hydrogen content. The difference in total hydrogen content of wet and dry coal is relatively small, so that a moisture measurement based on this concept requires a measurement between two large numbers to a high degree of precision. Thus, it was necessary to develop a highly precise instrumentation system for continuous measurement and to obtain a physical arrangement permitting measurement of moving coal with a minimum effect from density variations.

Experiments with Trays of Coal. Tests were conducted with metal trays containing 50 to 100 pounds of coal to develop an instrument system of high precision. A scaling system with a maximum instrument error of 0.2 percent was used to test different types of thermal neutron detectors. The most stable type of detector was a boron-10-lined proportional counter tube. While this type of detector showed satisfactory stability, extensive testing disclosed a long-term count reduction probably due to some type of deterioration in the detector. However, development of an electronic system using dual detectors eliminated this deterioration as a serious problem.

Table 1 shows typical results with a one curie plutonium-beryllium neutron source and a thermal neutron detector beneath a tray of coal and illustrates the

TABLE 1. Repetitive measurements of moisture in trays of coal

Consecutive tests, counts/10 min.	Tests on same tray at 1-day intervals		Different trays of same coal, counts/10 min.	% H ₂ O, calculated.
	counts/10 min.	% H ₂ O, calculated		
322406	525229	1.299	525490	1.300
320855	525376	1.299	513720	1.270
322452	525677	1.300	513240	1.269
321174	527906	1.305	514080	1.271
321348	524378	1.297	514360	1.272
320757	528416	1.307		
320381	524832	1.298		
320954	524362	1.296		
320226				
321099	516850*	1.300		
320073	514260*	1.297		
320062	517890*	1.300		
	522530*	1.312		
avg 320980				
% s.d.=0.25				

*Various parts of same tray, same day.

TABLE 2. Moisture measurements of hvab Pittsburgh-seam coals
of different moisture contents

% H ₂ O, ASTM analysis	Lump Coal			
	B-10 detector		BF ₃ detector	
	counts/10 min.	% H ₂ O	counts/10 min.	% H ₂ O
2.6	575176	2.61	1036164	2.60
	574084	2.61	1038184	2.60
	571850	2.60	1042280	2.60
1.9	533320	1.7	967950	1.9
1.8	541500	1.8	-	-
.3-1.3*	525770	.2	-	-
.3	526810	.2	724550	.4
0	520230	.1	646090	0
	<u>Pulverized coal, variable density</u>			
1.2 dried	581420	1.1	839460	1.16
	528690	-	697160	-
.78 dried	568810	.8	753760	.6
	522620	-	658120	-

*Variable due to loss of moisture during storage.

precision of measurement. Consecutive measurements of thermal neutrons at various times and positions beneath the same or different trays show a precision equivalent to $\pm 0.1\%$ H₂O. With the successful development of a precise measuring system, several nuclear problems could be investigated. Figure 1 shows a typical distribution of thermal neutrons in a tray of bituminous coal obtained with a small thermal neutron detector buried in the coal. The contour lines indicate the relative flux distribution expressed as counts per minute per unit volume of detector (about two cubic inches). It can be seen that the count rate decreased with distance from the source, about 7 inches of coal being required to decrease the count rate to half that measured at a two inch distance. The contours are peaked in the forward direction, indicating the initial preferential scatter at small angles.

The thermal neutron count decreased when the detector was moved away from the source (points A, B, C) and the effective volume of coal measured was altered. A different calibration curve relating count rate and percent moisture, obtained from each of the locations A, B, and C, was found to vary in shape from concave through linear to convex with increase in distance between source and detector. At a certain distance between source and detector, a point was found at which density changes in the coal had practically no effect on the count rate. At this point the volume of coal measured by the detector compensates for changes in density of the coal. This effect may be pictured as a reduction in source size (the volume of measured coal) with increasing density that compensates for the shorter distance of measurement with increasing density. The net effect of this arrangement is that to a large extent the moisture content can be measured independent of fairly large changes in density or particle size of the coal.

Sensitivity of Measurement. Several tests were made with different coals using experimentally determined calibration curves. The coals were air and oven dried to constant moisture content and carefully mixed. Typical results, shown in table 2, illustrates the sensitivity of the method with coals having small differences in moisture content. Neutron measurements of lump coal agreed with analysis by ASTM methods within 0.2 percent moisture. The neutron measurements of pulverized coal were consistent, but the results cannot be compared directly with results from the lump coal because a physical arrangement compensating for density was not used in these tests. The results indicate that the nuclear measurement of moisture content can be empirically related with actual moisture content as determined by standard methods of sampling and analysis within an accuracy of 0.2 percent moisture. For a more detailed investigation of variations in the effects of particle size ash content, rank of coal, etc., improved methods of blending, mixing and sampling were necessary. Automatic mixing and sampling could best be done in a dynamic system of moisture measurement using pilot-plant scale equipment.

Pilot-Plant Testing. A pilot-scale system was designed and installed to test the operation of a neutron moisture meter in a system of moving coal. Figures 2 and 3 show the equipment used.

In this system, coal is recycled by a Zipper-type conveyor through an automatic sampler and blending duct into the moisture meter test section. This moisture test section holds 600 to 1,000 pounds of coal in a 30-inch square duct. Centered in this 4-foot depth of coal is a 6-inch port containing the neutron source and thermal neutron detector. Moisture content of a spherical volume of coal is measured as the coal moving through the duct passes the measuring port. Because of the shielding effect of coal, radiation levels outside the 30-inch duct are near background levels. The thermal neutron detector is connected by co-axial cables to a separate instrument system which records the increase in count rate of wet coal above a preset value for dry coal.

Pilot-Plant Results. In tests to determine the accuracy of the nuclear method, the pilot-scale unit operated satisfactorily in runs lasting up to 50 hours. Coal samples were collected periodically with the automatic sampler for moisture a-

analysis and compared with the experimental values. In one test, the system was filled with 859 pounds of 3/4-inch by 3/8-inch hvab Pittsburgh seam coal of 1.6% H₂O. The neutron moisture meter recorded a value of 1.5% moisture for several hours dropping slowly as the coal lost moisture during recycling, finally becoming constant at 1.3%. At this constant moisture value, the meter recorded an average value of 1.3% for the next 24 hours, varying only 0.3%. At irregular intervals, usually about 8 hours, the meter had to be reset because of instrument drift. Except for this instrument drift, the results from the meter were within 0.5% of the chemical analysis at settings giving rapid response, and within 0.3% H₂O for slow-response settings.

Response time and precision of measurement were calculated by adding 100-pound lots of wet coal to the 800 pound charge of dry coal and recording the time between peaks as coal passed the measuring port. For example, when a lot of coal containing 4% H₂O was added, the moisture recorded increased from 1.2% to 3.5% the first cycle, then returned to 1.2 percent moisture. On the second pass of this lot of wet coal, the reading increased to 2.5% then returned to 1.2%. The third pass showed a slight increase, with a final reading leveling out at 1.5 percent moisture. Tests of this type were used to relate response time to precision of measurement.

Precision of Measurement. The precision of measuring moisture content is related to response time--the longer the response time the better the precision. A precision of ± 0.5 H₂O was obtained in a 20-second interval; $\pm 0.3\%$ H₂O with a 2-minute response time; and $\pm 0.2\%$ H₂O after 10 minutes of measurement. To increase the response time a neutron source considerably larger than 1 curie of plutonium-beryllium would be needed. A compromise between response time and precision of measurement depends on the specific application.

Discussion. The neutron meter for continuous moisture measurement in coal recorded the moisture content of coal moving at 1 to 20 tons per hour within 1/2 percent. We expect to increase the precision of the method by improving the electronic system. There are several ways this system might be used in industrial applications. For example, it could be used at the end of a conveyor to continuously measure moisture in coal moving at tonnage flow rates--50 to 100 tons per hour. It also could be applied in a by-pass system measuring coal at 10 tons per hour from an automatic sample cutter. We plan to obtain a more rugged electronic instrument system and test a prototype neutron moisture meter in a commercial plant. This should provide a sound evaluation of the practicability of the method for industrial use.

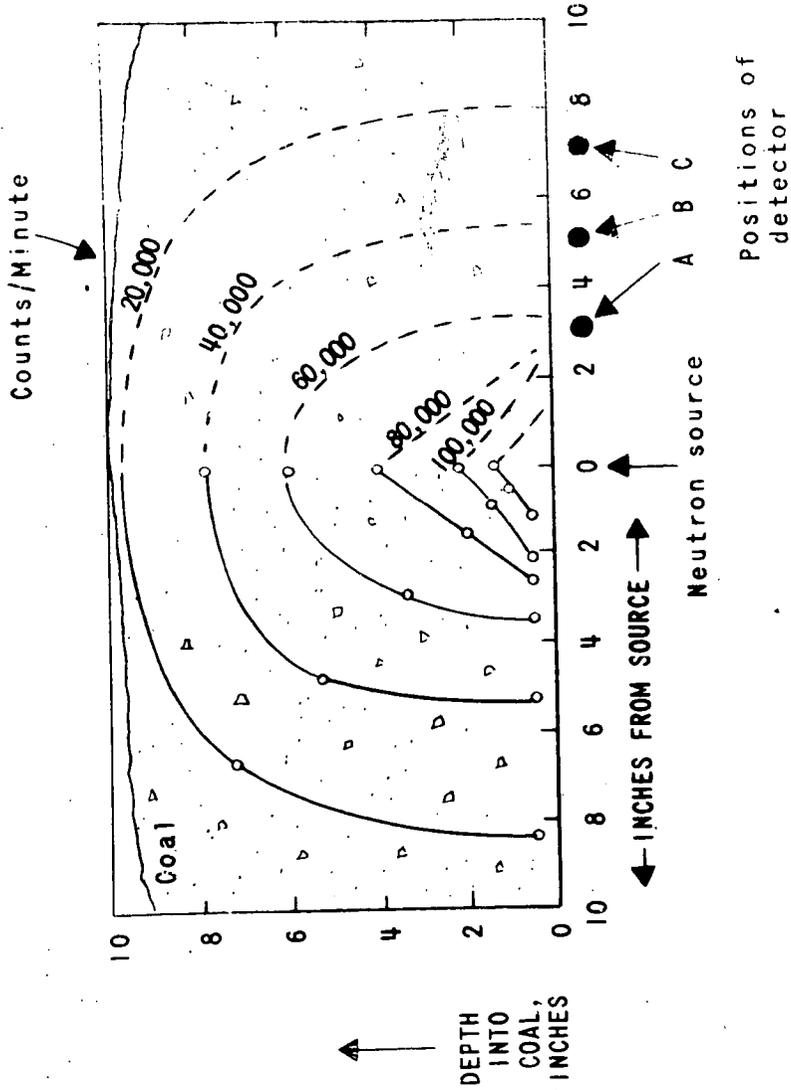


FIGURE 1 Cross Section of Tray of Coal Showing Distribution of Thermal Neutrons

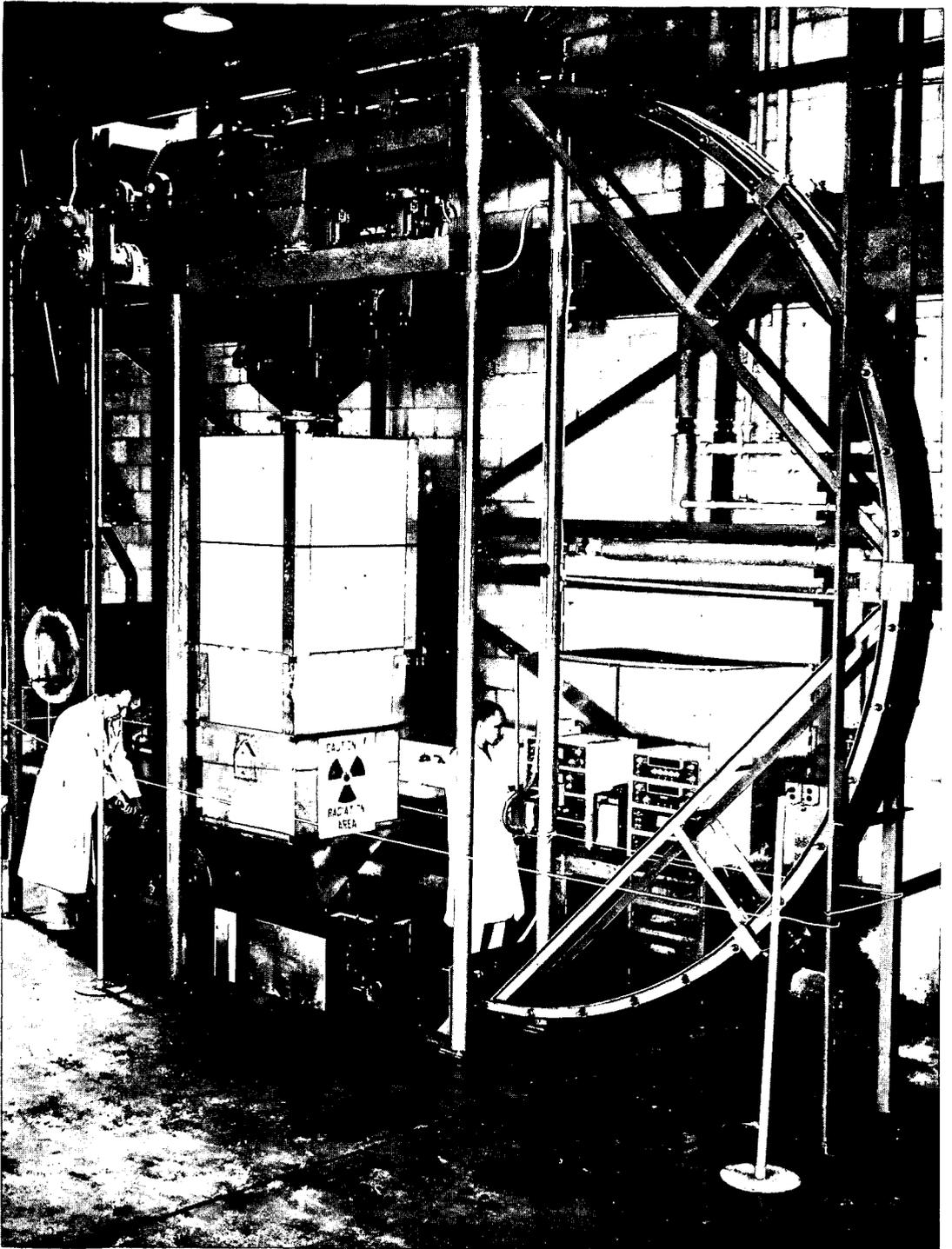


FIGURE 2-Pilot-Scale Equipment for Testing Continuous Moisture Meter for Coal

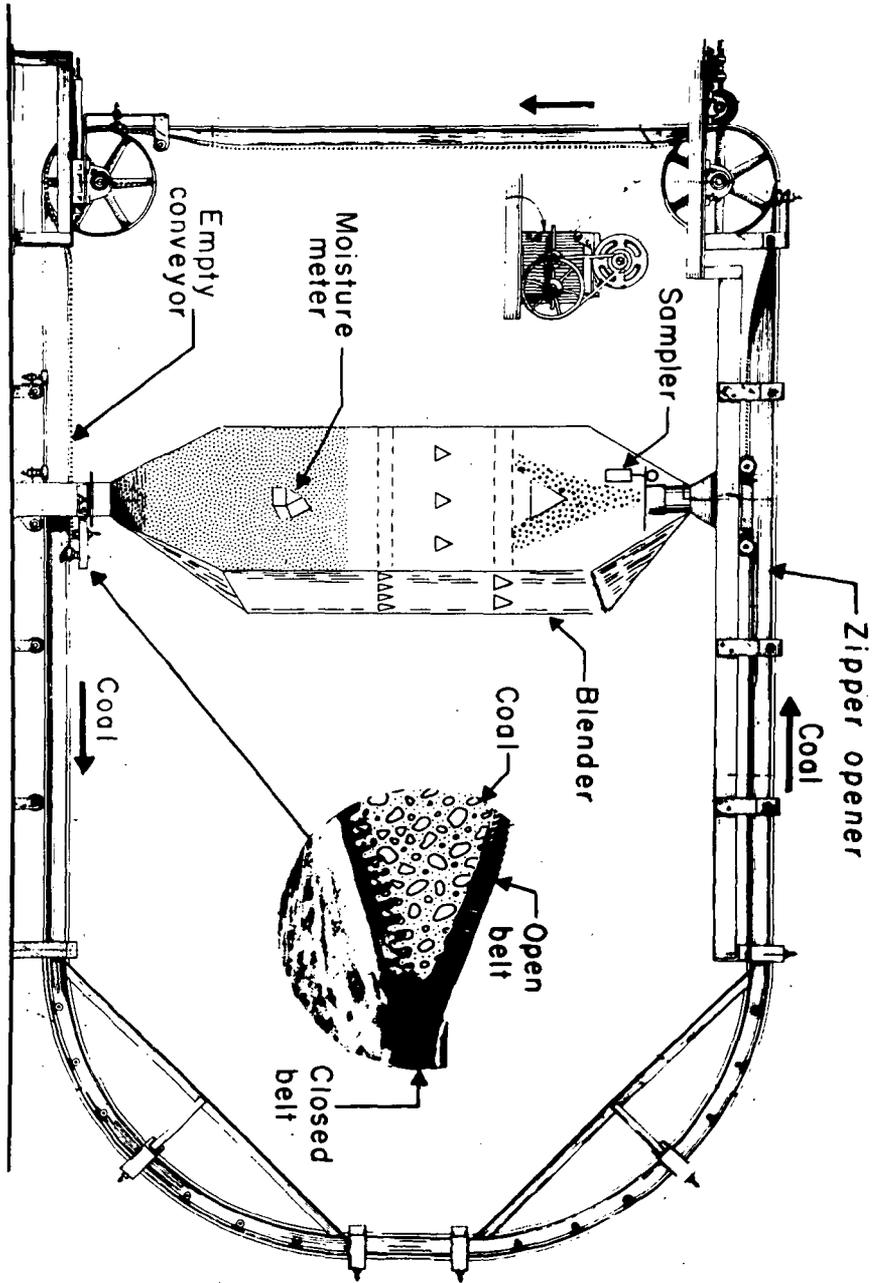


Fig. 3 - Zipper Conveyor - Elevator for Use With Moisture Meter