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CLAY MINERALOGY AND CERAMIC PROPERTIES OF LOWER CABANISS UNDERCLAYS IN WESTERN MISSOURI

BY ANTHONY C. TENNISSEN

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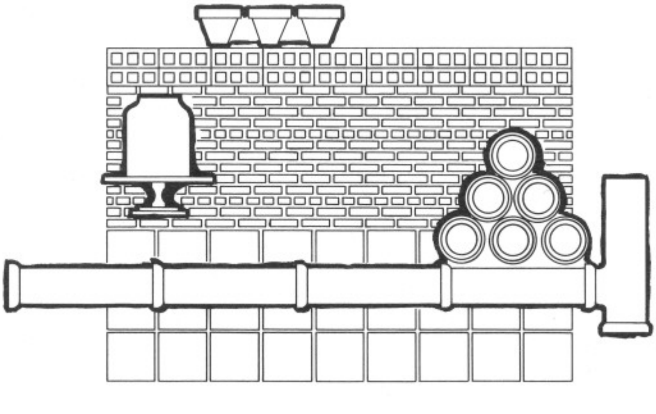
MISSOURI GEOLOGICAL SURVEY AND WATER RESOURCES
WILLIAM C. HAYES · STATE GEOLOGIST AND DIRECTOR



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CONTENTS

ILLUSTRATIONS

Page

Figure

Figure Page

TABLES

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by

Anthony C. Tennissen*

ABSTRACT

The mineral and chemical components, the petrography, and the ceramic properties of the Weir-Pittsburg, Tebo, and Mineral underclays in Barton, Vernon, St. Clair, and Henry Counties of western Missouri have been investigated by X-ray diffraction, differential thermal, spectrographic, microscopic, and certain ceramic testing techniques. The underclays are composed principally of illite, kaolinite, and mixed-layer illite-montmorillonite. Illite is the dominant mineral. The principal nonphyllosilicate minerals are quartz and pyrite.

The clays vary considerably in composition both laterally and vertically, but these variations are random rather than directional. The underclays cannot be distinguished from one another on the basis of either their mineral or chemical composition.

Ceramic tests show that the underclays are suitable only for low grade ceramic ware. Their P.C.E. values range from 6 to 16. Only very general correlations can be established between composition and ceramic properties.

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INTRODUCTION

Although the Pennsylvanian sediments of southwestern Missouri have been studied for many years by paleontologists and stratigraphers, very little attention has been given to the mineralogy, ceramic properties, and general usability of fairly extensive Cabaniss underclays. The purpose of this investigation was to determine the mineral composition and ceramic properties of the clays which underlie lower Cabaniss coals, specifically, the Weir-Pittsburg, the Tebo, and the Mineral.

Identification of the clay minerals in the underclays was based principally on X-ray diffraction, supplemented by microscopy, differential thermal, chemical, and spectrographic analyses. Microscopic techniques were used to study mineral relationships and to identify impurities. The properties of the raw clay and the firing characteristics of the clays were determined by the Department of Ceramics Engineering of the University of Missouri at Rolla.

Acknowledgements.--The writer wishes to thank those who assisted in the completion of this report. Dr. Thomas R. Beveridge, Chairman, Department of Geology, University of Missouri at Rolla, suggested the study as one which might be helpful to the clay industry in Missouri.

Dr. Walter V. Searight, former Principal Geologist of the Missouri Geological Survey, a specialist in the Pennsylvanian stratigraphy of Missouri, acquainted the writer with the stratigraphy of the section involved in this study and discussed various stratigraphic problems as they arose.

Miss Mabel E. Phillips, Chemist at the Survey, made the spectrographic analyses and many partial analyses.

Dr. T. J. Planje, Dean of the School of Mines and Metallurgy, University of Missouri at Rolla, supervised the testing of the green and fired properties of the clay samples and assisted in evaluating the economic potential of the clays.

Thanks also are extended to several coal companies for giving permission to collect samples from their properties in southwestern Missouri.

The late Dr. O. R. Grawe, Professor of Geology at the University of Missouri at Rolla at the time this study was in progress, critically reviewed the results of the mineralogical study.

PENNSYLVANIAN STRATIGRAPHY OF WESTERN MISSOURI

General Regional Stratigraphy

Pennsylvanian strata crop out in more than two-thirds of the counties of Missouri. Remnants of Pennsylvanian rocks are scattered throughout the Ozark region and indicate that rocks of this system formerly may have covered all of the state. In Missouri, the Pennsylvanian rocks are commonly clastic (sandstone, siltstone, and shale), but some non-clastic rocks (limestone and coal) also are present. The total thickness of the system in Missouri is about 2,000 feet (Searight, 1961, p. 78).

In Missouri the Pennsylvanian strata have been subdivided into series which, in ascending order, are: Morrowan, Atokan, Desmoinesian, Missourian, and Virgilian. Outcrops of the Morrowan and Atokan Series generally are restricted to the area southeast of the Desmoinesian outcrop belt on the Ozark uplift and Springfield plateau. The distribution of the Morrowan and Atokan Series is patchy in southwestern Missouri, but in the Forest City Basin of northwestern Missouri the Atokan is much better represented in the subsurface. Desmoinesian and Missourian strata crop out in a relatively broad belt across western and northern Missouri and underlie most of these portions of the state, but the Virgilian Series is exposed only in the northwestern part of the state.

The underclays of interest in the present investigation are members of the Desmoinesian Series which includes all strata younger than Atokan and older than Missourian. The major rock units in this series are the Cherokee and Marmaton Groups. The Cherokee, or lower group, has been divided into the Krebs (lower) and Cabaniss (upper) Subgroups. It consists mainly of sandstone and shale, and some limestone and coal. The subgroups have a thickness of 300 feet in western Missouri. The Marmaton Group, composed of the Fort Scott (lower) and Appanoose (upper) Subgroups, consists of more limestone, less coal, shale, and sandstone. The total thickness of this group is more than 250 feet.

Rocks extending upward from the top of the Atokan Series to the top of the Seville Formation are included in the Venteran Stage; those from the top of the Seville to the Holdenville Formation are in the Cygnian Stage. The rocks of the Venteran Stage constitute the Krebs Subgroup, and post-Venteran Cherokee beds make up the Cabaniss Subgroup. The Cabaniss Subgroup and the Marmaton Group together make up the Cygnian Stage.

The classification of Desmoinesian strata of western Missouri as set forth by the Missouri Geological Survey (Searight, 1961) is given in Table 1.

Stratigraphy of Lower Cabaniss Subgroup

The underclays discussed in this report are units in the Weir, Tebo, Scammon, and Mineral Formations of the Cabaniss Subgroup of Barton, Vernon, St. Clair, and Henry Counties of western Missouri (Fig. 1). The average thickness of the Cabaniss Subgroup in this area is about 200 feet. A comparable thickness is present in southeastern Kansas, but the thickness increases southward into Oklahoma. Most of the mineable coal beds in southeastern Kansas and southwestern Missouri are included in this subgroup. The classification for lower Cabaniss beds, adopted in 1953, is presented in Figure 2. The stratigraphy of the Cherokee Group, effectively summarized for southeastern Kansas by Howe (1956) is applicable to western and southwestern Missouri.

Weir Formation.--The Weir Formation includes all beds from the top of the Seville Formation to the top of the Weir-Pittsburg coal. Although the formation consists primarily of the coal and its underclay, two other thin and discontinuous coals below the main seam are included. The thickness of the Weir Formation varies from 10 feet to 35 feet in western Missouri.

The underclay is about 3 feet thick. It usually is dark to medium gray and is highly pyritic. Fossil root impressions and slickensides are common in this underclay. The overlying Weir-Pittsburg coal, with an average thickness of 2 feet, is the thickest coal mined in western Missouri. It is often high in sulfur in a form which is difficult to remove in preparation of the coal for market.

Tebo Formation.--The Tebo Formation includes all beds from the top of the Weir-Pittsburg coal to the top of the Tebo coal. The formation is well exposed in many strip mines in western Missouri, particularly in areas where the deeper Weir-Pittsburg coal is mined. The thickness of the Tebo Formation varies from a few feet in Henry County, near Windsor, to 26 feet near Mindenmines in Barton County.

In western Missouri, the lowermost unit of the Tebo Formation consists principally of reddish-brown to gray, silty shale a few inches to about 7 feet thick and containing clay-ironstone concretions. The lower part is often darker and less silty than the upper part. In Barton County this shale is overlain by an impure nodular limestone which generally is absent over much of the rest of western Missouri, but in Kansas it becomes a massive bed about 10 inches thick.

TABLE 1

CLASSIFICATION OF THE DESMOINESIAN SERIES IN MISSOURI

SERIES	GROUP	STAGE	SUBGROUP	FORMATION
Desmoinesian	Marmaton	Cygnian	Appanoose	Holdenville Lenapah Nowata Altamont Bandera Pawnee Labette
			Fort Scott	Higginsville Little Osage Blackjack Creek
	Cherokee		Cabaniss	Excello Mulky Lagonda Bevier Verdigris Croweburg Fleming Robinson Branch Mineral Scammon Tebo Weir
		Venteran	Krebs	Seville Bluejacket Drywood Rowe Warner Hartshorne
Atokan				Riverton Burgner McLouth Cheltenham
Morrowan				Hale

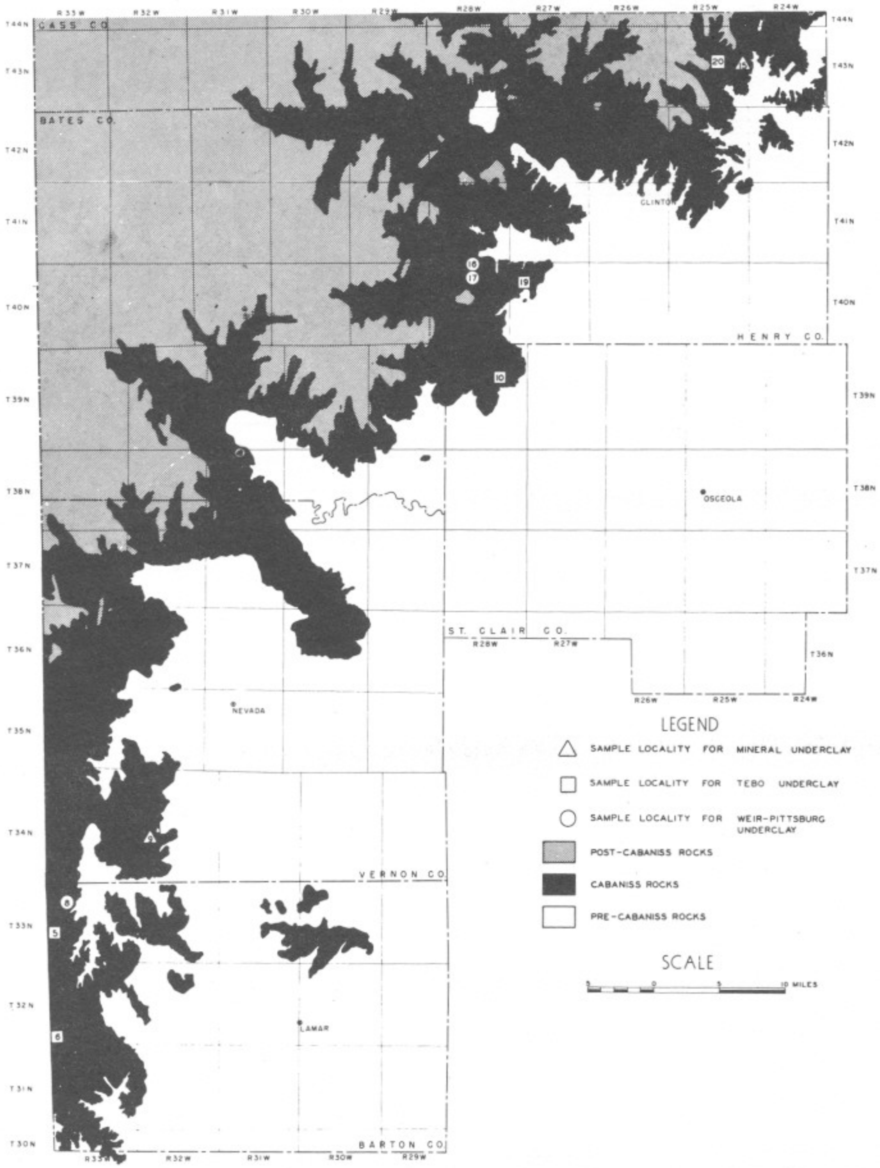
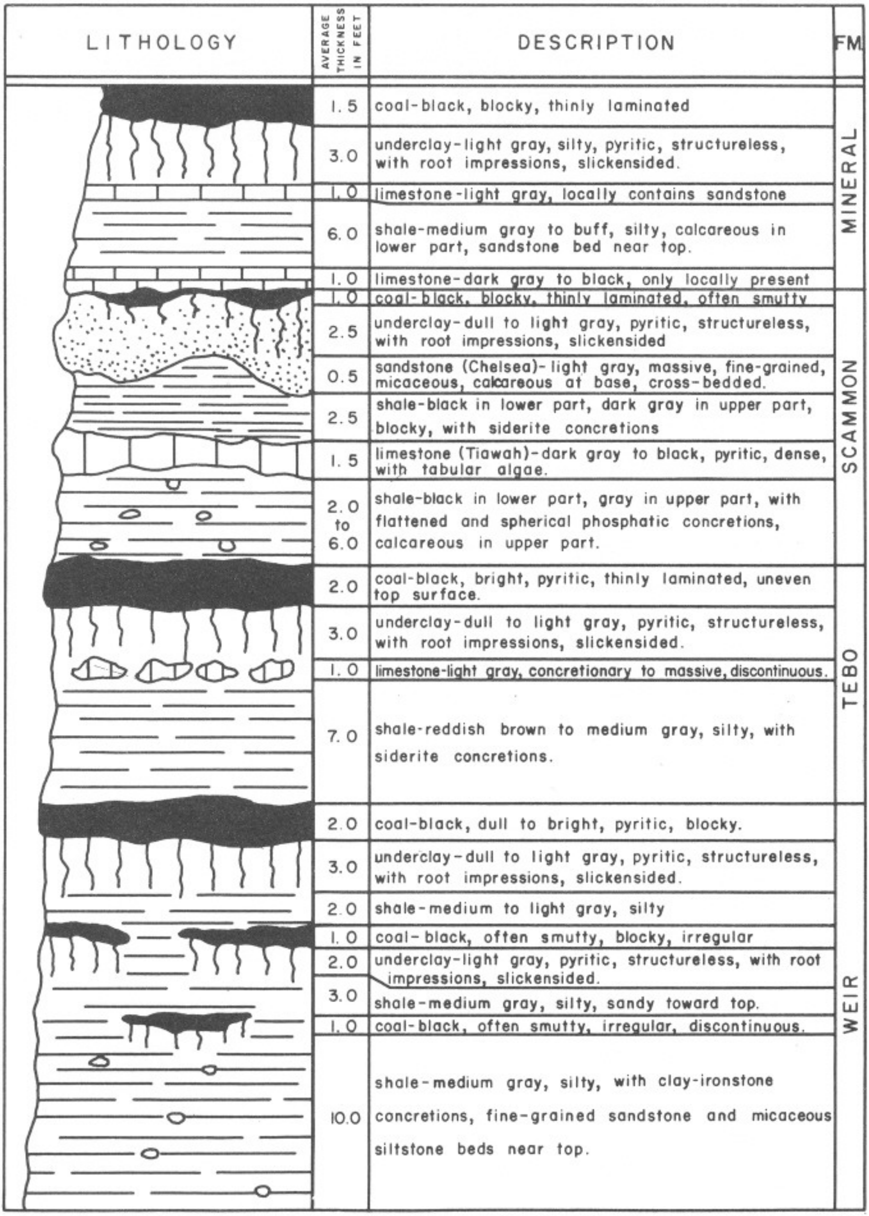


Figure 1. Distribution of Cabaniss beds in western Missouri.



LITHOLOGY	AVERAGE THICKNESS IN FEET	DESCRIPTION	FM
	1.5	coal-black, blocky, thinly laminated	MINERAL
	3.0	underclay-light gray, silty, pyritic, structureless, with root impressions, slickensided.	
	1.0	limestone-light gray, locally contains sandstone	
	6.0	shale-medium gray to buff, silty, calcareous in lower part, sandstone bed near top.	
	1.0	limestone-dark gray to black, only locally present	
	1.0	coal-black, blocky, thinly laminated, often smutty	SCAMMON
	2.5	underclay-dull to light gray, pyritic, structureless, with root impressions, slickensided	
	0.5	sandstone (Chelsea)-light gray, massive, fine-grained, micaceous, calcareous at base, cross-bedded.	
	2.5	shale-black in lower part, dark gray in upper part, blocky, with siderite concretions	
	1.5	limestone (Tiawah)-dark gray to black, pyritic, dense, with tabular algae.	
	2.0 to 6.0	shale-black in lower part, gray in upper part, with flattened and spherical phosphatic concretions, calcareous in upper part.	
	2.0	coal-black, bright, pyritic, thinly laminated, uneven top surface.	TEBO
	3.0	underclay-dull to light gray, pyritic, structureless, with root impressions, slickensided.	
	1.0	limestone-light gray, concretionary to massive, discontinuous.	
	7.0	shale-reddish brown to medium gray, silty, with siderite concretions.	
	2.0	coal-black, dull to bright, pyritic, blocky.	WEIR
	3.0	underclay-dull to light gray, pyritic, structureless, with root impressions, slickensided.	
	2.0	shale-medium to light gray, silty	
	1.0	coal-black, often smutty, blocky, irregular	
	2.0	underclay-light gray, pyritic, structureless, with root impressions, slickensided.	
	3.0	shale-medium gray, silty, sandy toward top.	
	1.0	coal-black, often smutty, irregular, discontinuous.	
	10.0	shale-medium gray, silty, with clay-ironstone concretions, fine-grained sandstone and micaceous siltstone beds near top.	

Figure 2. Lower Cabaniss beds in western Missouri.

Above the shale and limestone is the underclay of the Tebo coal. This clay is dark to medium gray, of variable silt content, and about 4 feet thick near Montrose in Henry County but only a few inches thick near Bowen. Root impressions and slickensides are quite common in this underclay. Overlying the clay is the top member of the formation, the Tebo coal. Its average thickness is 24 inches in many parts of western Missouri, but in Kansas it is too thin to mine economically. The Tebo coal thickens to about 6.5 feet in the Bowen trough. This thick body of coal is sinuate and has a somewhat south of east trend.

Scammon Formation.--The Scammon Formation includes all beds from the top of the Tebo coal to the top of the Scammon coal. It is not well exposed in Missouri. Its average thickness is about 15 feet.

The lowermost unit of the formation is a black, fissile shale containing phosphatic concretions. The shale unit is 2 to 6 feet thick. Above the shale is a dark gray, dense limestone, the Tiawah, characterized by an abundance of the tabular algae, Archeolithophyllum missouriense. This limestone usually is 8 to 16 inches thick and is very persistent in western Missouri. Above the Tiawah lies a black, tough, blocky shale containing siderite concretions. The shale is 2 to 3 feet thick, but it is somewhat erratic in its areal distribution. Above the siderite-bearing shale is a gray to brown fine-grained micaceous sandstone, the Chelsea, which locally cuts downward through the underlying beds. The thickness of the sandstone is quite variable, but it may reach a maximum of 25 to 30 feet in western Missouri.

Above the sandstone is the underclay of the Scammon coal. This underclay is usually light gray, iron-stained, and plastic. It is as much as 3 feet thick in Kansas where the Scammon coal is of commercial importance, but it is usually absent in western Missouri. The Scammon coal above the clay is too thin to mine in western Missouri.

Mineral Formation.--The Mineral Formation includes all beds from the Scammon coal to the top of the Mineral coal. Its average thickness is 20 feet. The lowermost member of the Mineral Formation is a dark gray to black limestone which, on the outcrop, often forms a fairly prominent ledge 2 to 14 inches thick. This limestone is known in only a few localities in western Missouri. It is succeeded upward by a dark gray, thinly laminated shale 6 to 8 feet thick, which is overlain by another limestone. This limestone is argillaceous and is interlaminated with iron-stained plastic clay. The unit is 1 to 2 feet thick and in some localities includes a thin sandstone bed. The underclay of the Mineral coal is dark to medium gray, about 3 feet thick, and contains root impressions throughout.

The mineral coal is about 20 inches thick in most of the localities where it is mined, but in some places it is only 14 to 16 inches thick. It usually occurs about 70 feet above the Weir-Pittsburg coal, but in southeastern Kansas the interval is considerably less.

CLAY MINERALOGY OF LOWER CABANISS UNDERCLAYS

Sampling Method

Samples of lower Cabaniss underclays were collected from active and abandoned coal strip pits in Barton, Vernon, St. Clair, and Henry Counties (Table 2). At each collecting site, separate 25-pound samples were taken from the upper, middle, and lower portions of each underclay for ceramic tests, and one-pound samples were taken from the same zones at regular intervals along the highwalls. The shales lying immediately below each underclay and immediately above each coal also were sampled.

Differential Thermal Analyses

Typical differential thermal curves obtained from the upper, middle, and lower portions of each of the clays which underlie the Mineral, Tebo and Weir-Pittsburg coals are shown in Figures 3 to 5. Each curve is characterized by: 1) a low temperature endothermic dip between 100° and 200°C caused by the loss of loosely held H_2O; 2) a moderate exothermic peak from 250° to 400°C caused by the oxidation of organic material; 3) a weak to strong exothermic peak between 400° and 470°C due to the oxidation of pyrite; 4) a prominent endothermic dip between 500° and 600°C caused by the destruction of the hydroxyl groups of illite, kaolinite, and mixed-layer clay; 5) an exothermic peak which begins at about 900°C and reaches a maximum at 950° to 980°C. Some curves exhibit a slight endothermic dip between 850° and 900°C which is rather characteristic of illite, but the dip at 600° to 700°C usually observed in montmorillonite was absent.

The intensity of the endothermic dip at 500° to 600°C generally is in accord with the total amount of illite and kaolinite present. The intimate mixture of kaolinite and illite and the presence of carbonaceous matter and pyrite limit the diagnostic usefulness of the differential thermal curves in a study of the underclays. Yet the curves do bring out the close similarity of the clays underlying the three coals and the lack of differentiation or zonation of the clay underlying any one coal.

TABLE 2

LOCALITIES OF UNDERCLAY SAMPLES

Loc. No.	County	Sec.	T.	R.
		MINERAL UNDERCLAY		
9	Vernon	SE¼ 18	34 N.	32 W.
15	Henry	NW¼ 23	43 N.	25 W.
		TEBO UNDERCLAY		
6	Barton	NW¼ 31	32 N.	33 W.
5	Barton	NW¼ 19	33 N.	33 W.
10	St. Clair	SE¼ 2	39 N.	26 W.
19	Henry	NE¼ 7	40 N.	27 W.
20	Henry	SW¼ 14	43 N.	25 W.
		WEIR-PITTSBURG UNDERCLAY		
8	Barton	SW¼ 7	33 N.	33 W.
16	Henry	NW¼ 2	40 N.	28 W.
17	Henry	NW¼ 2	40 N.	28 W.

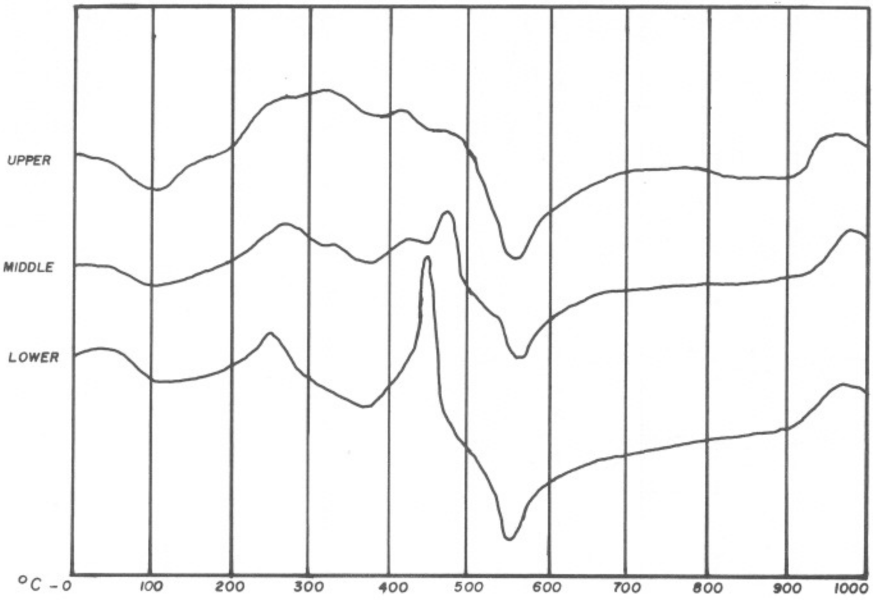


Figure 3. Differential thermal curves for upper, middle, and lower portions of Mineral underclay at Locality 15, NW¼, sec. 23, T. 43 N., R. 25 W., Henry County, Missouri.

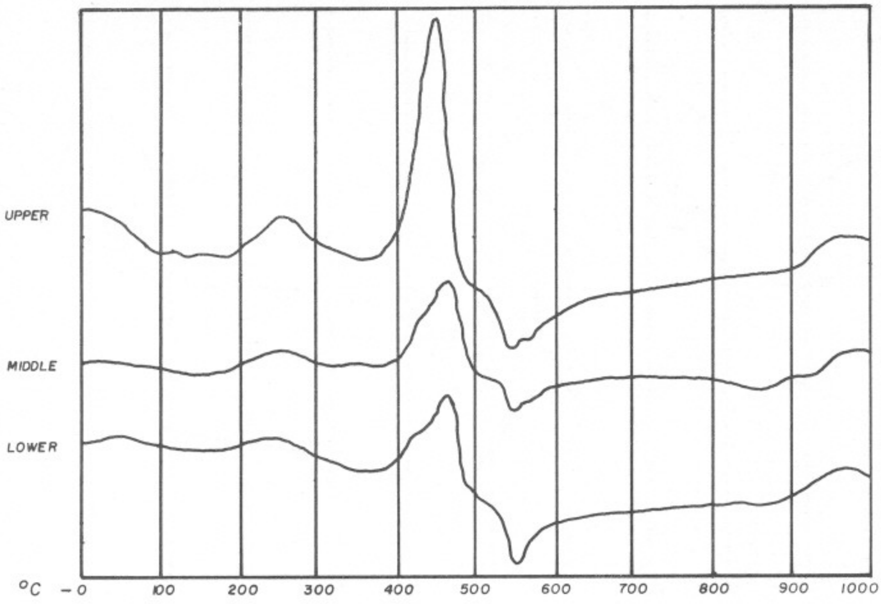


Figure 4. Differential thermal curves for upper, middle, and lower portions of Tebo underclay at Locality 10, SE¼, sec. 2, T. 39 N., R. 26 W., St. Clair County, Missouri.

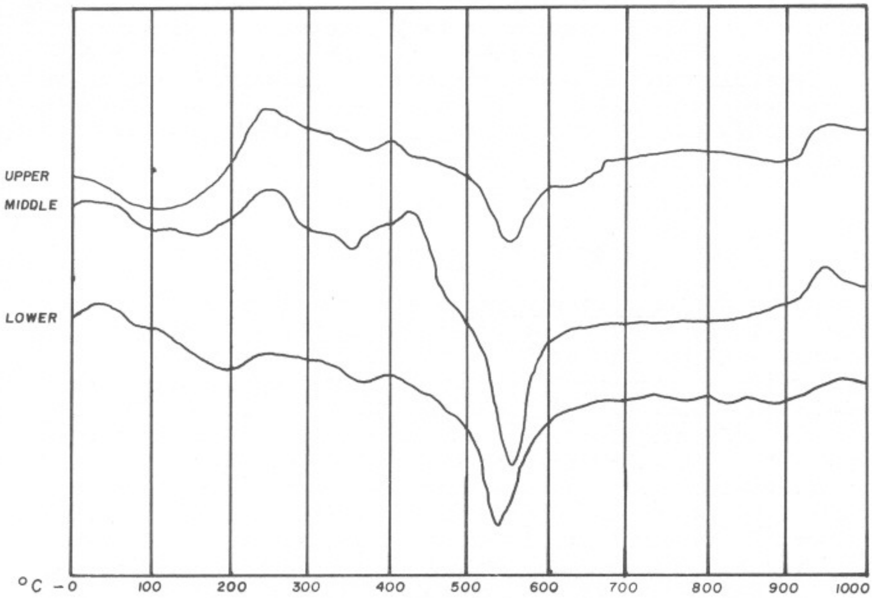


Figure 5. Differential thermal curves for upper, middle, and lower portions of Weir-Pittsburg underclay at Locality 17, NW¼, sec. 2, T. 40 N., R. 28 W., Henry County, Missouri.

Thermograms of the black shales above the coals are characterized by larger exothermic peaks in the 300° to 350°C region due to the oxidation of larger amounts of organic matter and pyrite. The shales below the underclays yield differential thermal curves which are more nearly like those for the underclays, but small endothermic dips characteristic of the dissociation of siderite, calcite, and gypsum were noted.

Fine Fraction Analyses

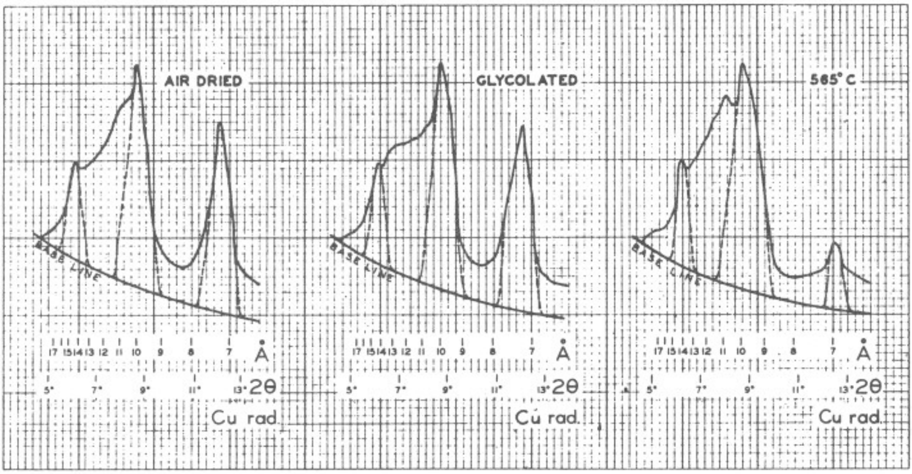
X-ray diffraction analysis.--Oriented slides of the minus 2-micron fraction of the clay samples were prepared by allowing a suspension of the fine fraction to settle on a glass slide as the water evaporated. The samples were analyzed with a Norelco X-ray diffractometer, using nickel-filtered CuK radiation and a scanning rate of 2 degrees (2θ) per minute. As many as three X-ray diffractometer traces of the oriented sections of the minus 2-micron fraction of each sample were run: one on the original air-dried material; another on the same section after it was sprayed until damp with ethylene glycol; and, when a 14 Å spacing was detected, the clay was heated to 550° to 565°C for one hour and a third diffractometer trace was made to determine if the mineral which yielded the 14 Å basal spacing was destroyed by the heat.

Qualitative analysis.--The principal clay minerals in lower Cabaniss underclays are illite, kaolinite, and mixed-layer illite-montmorillonite. A mineral yielding a basal spacing of 14 Å is present. It is principally chlorite but is in part vermiculite. The 14 Å spacing was detected in 42 percent of the underclay samples analyzed. In 19 percent of those containing a 14 Å component, vermiculite was detected. The 17 Å basal plane diffraction, characteristic of montmorillonite, does not appear on the diffractograms of glycolated samples. Illite occurs both alone and interlayered with montmorillonite. Diffractograms of many glycolated samples show an asymmetry of the 10 Å peak toward higher values. Kaolinite occurs alone and is characterized by strong, sharp diffractions at 7.14 Å and 3.57 Å.

The 14 Å diffraction peak was attributed to chlorite or to vermiculite, depending on the diffraction pattern obtained after heating the clay to 500° to 565°C for one hour. If the 14 Å peak persisted after heating, the mineral was identified as chlorite. If it disappeared and the 10 Å peak was enhanced, the mineral was considered to be vermiculite.

The distinction between chlorite and kaolinite is somewhat more difficult to make when the chlorite does not yield

SMOOTHED DIFFRACTOMETER TRACES



CALCULATIONS

$$\frac{K}{C+X+I+K} = \frac{59}{28+125+94+59} \times 100 = 13.9\%$$

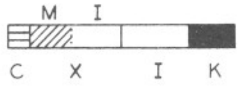
C, X, and I calculated similarly

M (in X) $= 40.9 \times 38.5 = 15.7\%$ of total

I (in X) $= 40.9 - 15.7 = 25.2\%$ of total

Total illite $= 30.6 + 25.2 = 55.8\%$

PERCENTAGE BAR



K - kaolinite
I - illite
X - mixed layer
M - montmorillonite
C - chlorite

Figure 6. Calculation of clay mineral percentages from diffractometer traces.

a strong first order (basal plane) peak at 14 Å, because the second order basal reflection of chlorite is nearly identical in position with the first order basal reflection of kaolinite, i.e., 7.0 Å. When the sample is heated to 550° to 565°C for one hour, the kaolinite structure collapses, and its effect on the 7 Å peak disappears, while the chlorite structure persists; therefore, any peak at 7 Å observed after this heat treatment was considered to be due to chlorite.

When the 14 Å material was determined to be vermiculite, no consideration was given to the possible effect of its (002) reflection on the intensity of the 7 Å kaolinite peak in determining the percentage of kaolinite, because the intensity of the low second order diffraction from (001) of vermiculite becomes negligible at the low concentration of this mineral in the underclays.

Quartz is present in almost all underclays, and many of the diffractograms showed a strong peak at 26.6° corresponding to the 3.34 Å interplanar spacing characteristic of quartz.

Quantitative analysis.--The amount of each clay component in a sample was calculated in accordance with a method outlined by Schultz (1955, p. 421). Figure 6 is presented to illustrate the procedure. The areas enclosed by the diffractometer peaks due to first order diffractions from the basal planes of the clay minerals were measured with the polar planimeter. First order peaks of equal area were considered to be due to the same amounts of the clay minerals causing them.

The true shapes of the 10 Å illite and the 7 Å kaolinite peaks were determined by comparing them with the peaks obtained from purified materials. The low angle asymmetry of the 10 Å peak was assumed to be due to the interlayering of montmorillonite (more rarely chlorite) with illite, because the mean position of this peak shifted to lower 2θ values (higher interplanar spacing values) when the clay was glycolated, thereby increasing the interplanar spacing of the montmorillonite component. The proportion of montmorillonite to illite in the mixed-layer material was determined from the mean position of the low angle peak after glycolation, assuming that this mean position is proportional to the relative amounts of montmorillonite and illite in the mixed-layer component. For example, in Figure 6 the mean position of the peak for the mixed-layer clay is at a 2θ angle of 8.74 degrees, corresponding to an interplanar spacing of 12.7 Å, which is 2.7/7.0, or 38.5 percent of the mixed-layer clay mineral and illite makes up the remaining 61.5 percent. A small amount of chlorite was detectable in the mixed-layer component of a few samples by the failure of the mixed-layer component to collapse completely to 10 Å when heat treated.

Total illite in the sample was calculated by adding the percentage of illite indicated by the 10 Å peak to the percentages of illite in the mixed-layer component. For example, in Figure 6, the percentage of discrete illite is 30.6; the percentage of illite in the mixed-layer component (which makes up 40.9 percent of the entire sample) is 61.5. The total illite content, therefore, is 30.6 + 40.9 x 61.5, or 55.8 percent.

The relative amounts of the various silicate clay minerals are presented by a bar diagram (Fig. 7) which permits rapid visual comparison of the composition of the clay samples. Kaolinite is shown in solid black at the right-hand side of the bar. Discrete illite is shown as a white area just to the left of the kaolinite area and is separated from the mixed-layer area by a solid vertical line. The mixed-layer component is represented by two areas separated by a dotted vertical line, the white representing the illite portion and the oblique-lined area representing the montmorillonite portion of the mixed-layer component. In this way, the total percentage of illite in the sample is readily observed. The amount of chlorite-vermiculite is shown as the horizontally lined portion of the bar. It is separated by a solid vertical line from that part of the bar representing the amount of mixed-layer clay.

The results of the analyses of the minus 2-micron fractions of all the clay and shale samples analyzed are presented graphically in Figures 8 to 17. In these figures, the bars are arranged to show the relative positions of samples along the highwalls of the various strip pits in the area studied. Bars in the same column represent analyses of samples at a single sample location. They are presented in their relative stratigraphic positions. Bars in the same row represent analyses of clay or shale from the same horizon along the highwall or some other exposure at a single pit. Abbreviations to the left of the bars designate rock types.

Relative Abundance of Clay Minerals

Underclay samples from the top, the middle, and the bottom of each underclay at 45 localities were analyzed mineralogically in order to determine the vertical variation in the clay mineral content. The mineralogical analyses indicate that chlorite-vermiculite is present in 43 percent of the underclay samples and in 59 percent of the shale samples. Its percentage ranges from 0 to 13 in the underclays and from 0 to 12 in the shales. The remaining three clay components, mixed-layer illite-montmorillonite, illite, and kaolinite, are present in variable amounts in all underclay and shale samples studied. Montmorillonite never occurs as discrete grains, but always interlayered with illite. It comprises from 5 to 30 percent of the underclays and from 5 to 25 percent of the associated shales. Mixed-layer illite-montmorillonite ranges from 15 to 65 percent in the underclays and from 18 to 65 percent in the associated shales. Illite, occurring both as discrete grains and as mixed-layers with montmorillonite, varies from 9 to 65 percent in the underclays and from 19 to 68 percent in the shales. In the majority of samples, illite is the major clay constituent. Kaolinite is quite variable, ranging from 5 to 65 percent in the underclays and from 7 to 39 percent in the associated shales.

Other Minerals

Several other minerals were identified in the underclays and shales by microscopic techniques. The following minerals are present in quantities generally less than one percent: feldspar, pyrite, limonite, rutile, muscovite, biotite, tourmaline, zircon, calcite, siderite, gypsum, pyroxene, garnet, amphibole, and epidote.

SPECTROGRAPHIC ANALYSES

Fifty-three samples of underclay and three samples of shale associated with lower Cabaniss coals were analyzed for chemical elements by the rapid and relatively inexpensive semiquantitative spectrographic method. Well homogenized samples of the same volume were vaporized in a d-c arc operated at 10.5 to 11.5 amperes and 35 to 45 volts, and the spectrum was photographed on Spectrum Analysis No. 1 emulsion on 4- x 10-inch plates in a Baird Associates 3-meter spectrograph carrying a mounted grating ruled with 15,000 lines per inch. The plates were analyzed by Miss Mabel E. Phillips of the Missouri Geological Survey on a Jarrell and Ash type comparator-densitometer. Four exposures were made for each sample: 0.5 minute, 1.0 minute, 2 minutes, and again 2 minutes.

The lines used for comparison are given in Table 3. In Tables 4, 5, and 6, the analyses are given. In these tables, the analyses are grouped according to the material analyzed and in geographical sequence according to the localities from which the samples were obtained, from southwestern Barton County to northeastern Henry County.

The analyses show that the major constituents of the clays and shales detected by the spectrograph are: silicon, aluminum, titanium, magnesium, and iron. Manganese, calcium, chromium, vanadium, zirconium, copper, nickel, cobalt, boron,

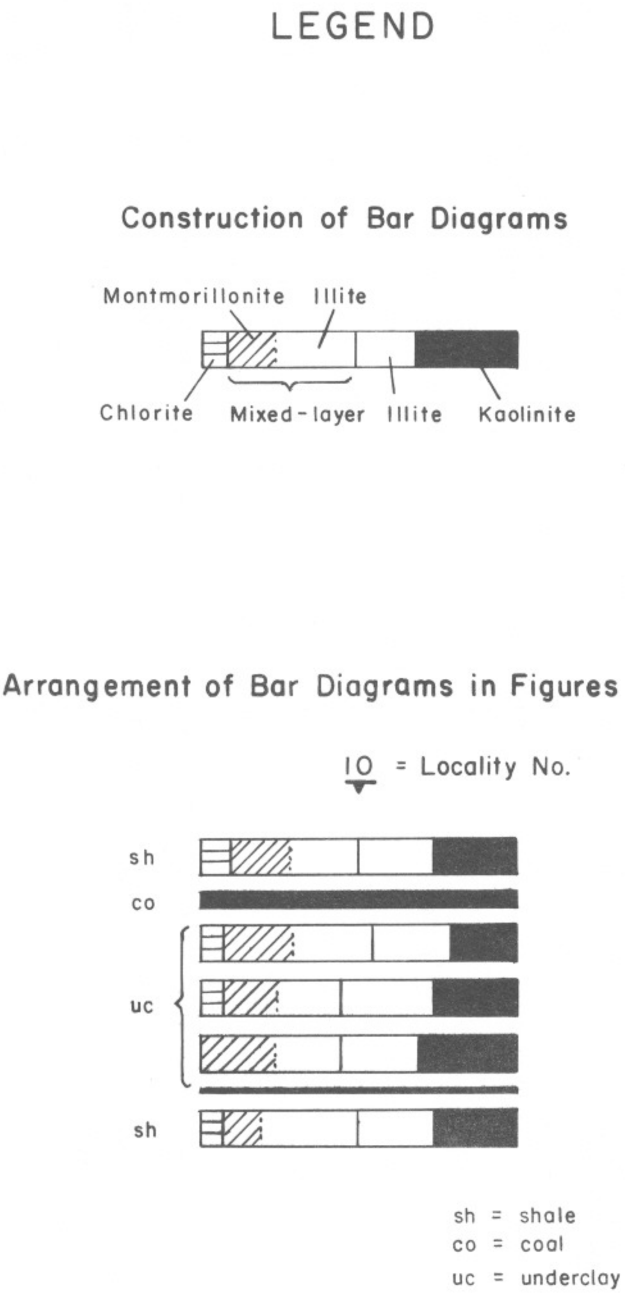


Figure 7. Legend for Figures 8 to 17.

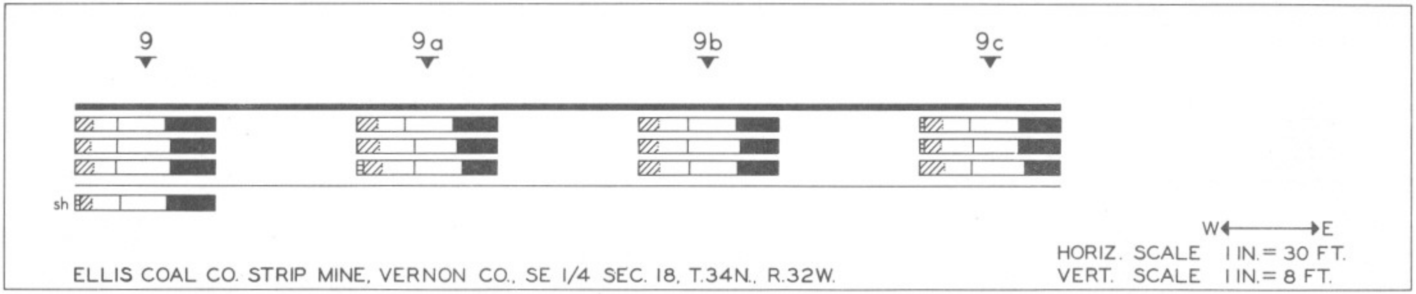


Figure 8. Clay mineral analyses: Mineral underclay: Locality 9.

Figure 9. Clay mineral analyses: Mineral underclay: Locality 15.

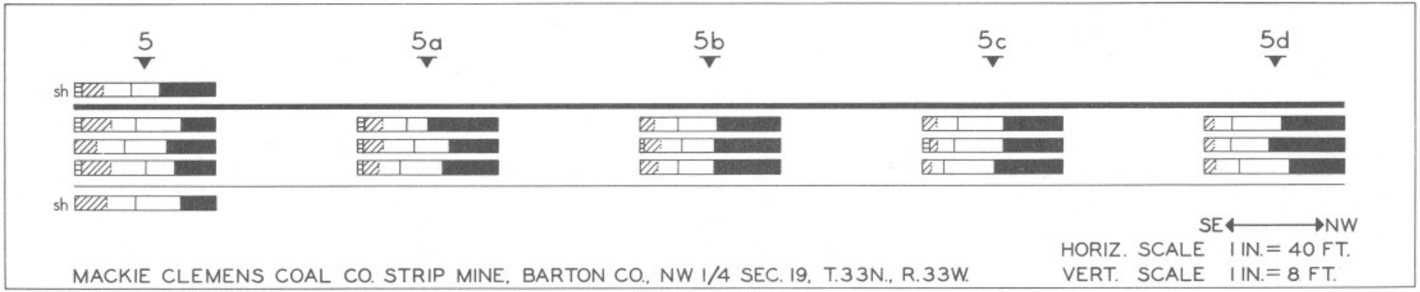


Figure 10. Clay mineral analyses: Tebo underclay: Locality 5.

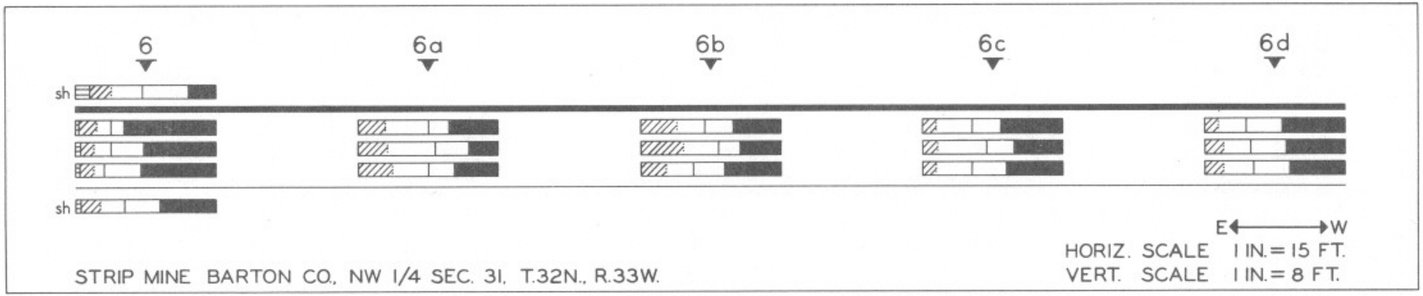


Figure 11. Clay mineral analyses: Tebo underclay: Locality 6.

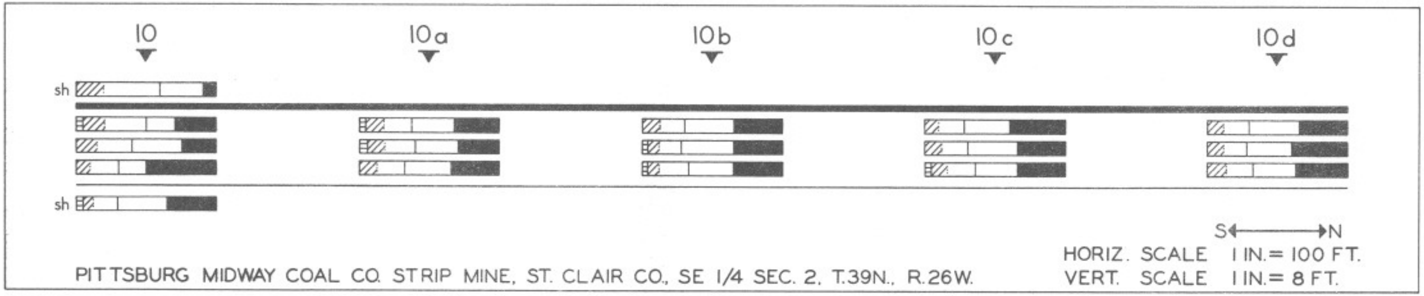


Figure 12. Clay mineral analyses: Tebo underclay: Locality 10.

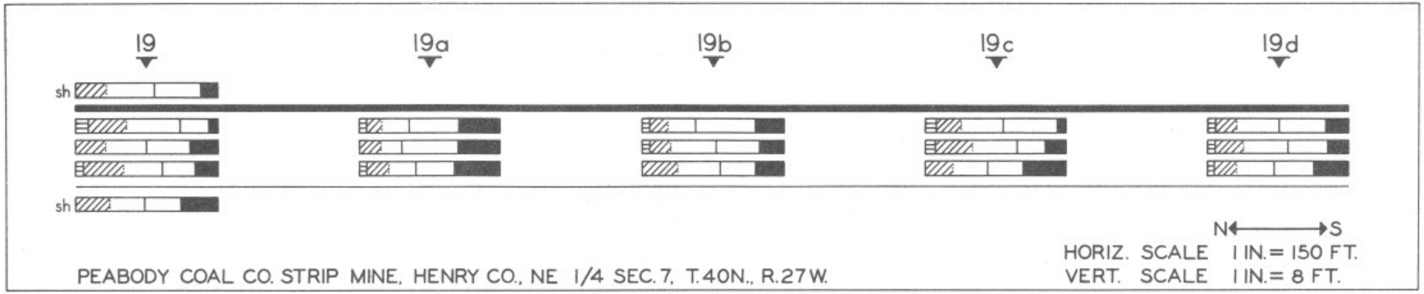


Figure 13. Clay mineral analyses: Tebo underclay: Locality 19.

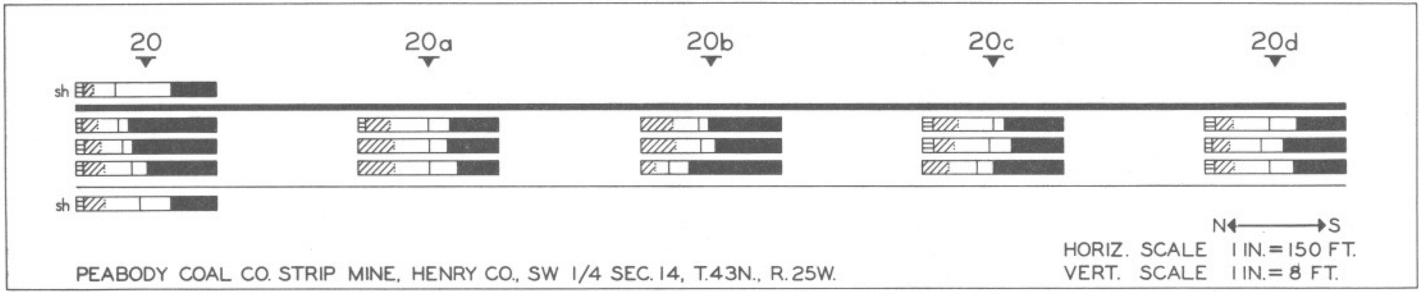


Figure 14. Clay mineral analyses: Tebo underclay: Locality 20.

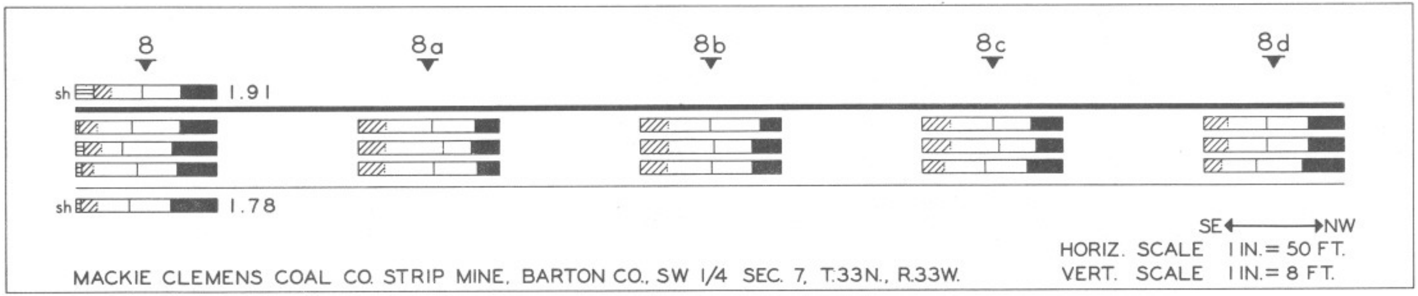


Figure 15. Clay mineral analyses: Weir-Pittsburg underclay: Locality 8.

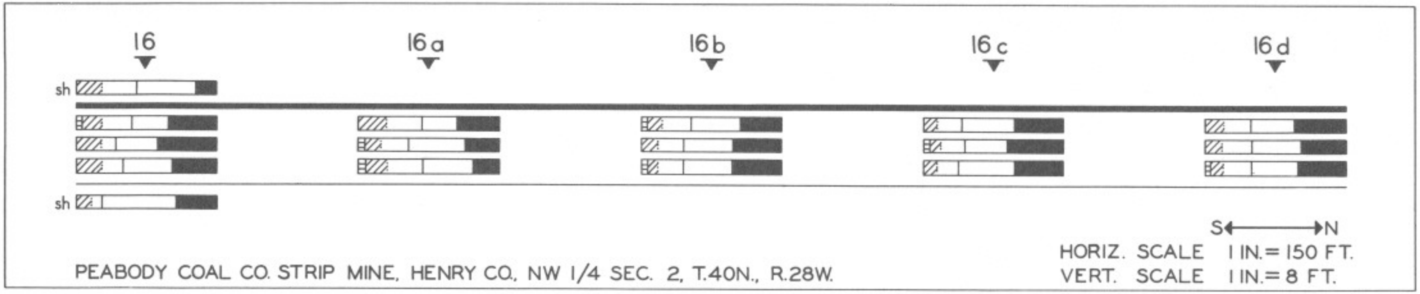


Figure 16. Clay mineral analyses: Weir-Pittsburg underclay: Locality 16.

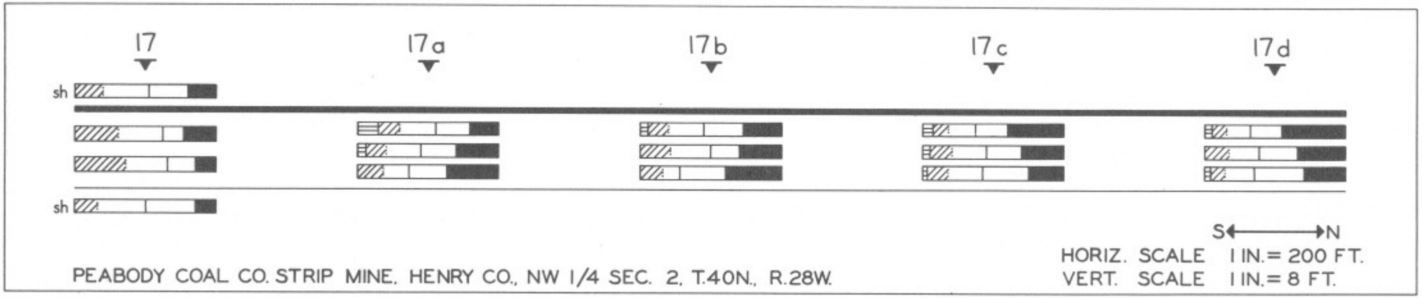


Figure 17. Clay mineral analyses: Weir-Pittsburg underclay: Locality 17.

TABLE 3

EMISSION LINES USED IN SPECTROGRAPHIC ANALYSES

Element	Symbol	Wave Length in A. U.
Aluminum	Al	3082.155 and 3092.713
Antimony	Sb	2877.915 and 2598.062
Arsenic	As	2456.53
Barium	Ba	3071.591
Beryllium	Be	3321.343, 3321.031, and 3321.086
Bismuth	Bi	3067.716 and 2897.975
Boron	B	2496.778 and 2497.733
Cadmium	Cd	3403.653, 3466.201, and 3467.656
Calcium	Ca	3158.869 and 3179.332
Chromium	Cr	3593.488
Cobalt	Co	3453.505 and 3465.800
Columbium	Cb	3094.183 and 3225.479
Copper	Cu	3247.540 and 3273.962
Germanium	Ge	3039.064
Iron	Fe	3020.640 and 3021.073
Lead	Pb	2833.069
Lithium	Li	3232.61
Magnesium	Mg	2852.129
Manganese	Mn	2794.812, 2798.271, and 2801.064
Mercury	Hg	2536.519
Molybdenum	Mo	3132.594, 3170.347, and 3193.973
Nickel	Ni	3414.765 and 3492.956
Phosphorus	P	2534.01
Silicon	Si	2881.578
Silver	Ag	3280.683 and 3382.891
Strontium	Sr	3380.711 and 3464.457
Tantalum	Ta	3311.162
Thallium	Tl	2767.87 and 3229.75
Tin	Sn	2839.989
Titanium	Ti	3088.025
Tungsten	W	3300.820, 3311.382, and 3326.190
Vanadium	V	3183.406, 3183.982, and 3185.396
Zinc	Zn	3345.020 and 3302.588
Zirconium	Zr	3391.975 and 3438.230

TABLE 4

SPECTROGRAPHIC ANALYSES OF MINERAL UNDERCLAY

Sample Description			Elements																					
No.	Loc.	Zone	Si	Al	Ti	Fe	Mg	Ca	Sr	Ba	Zr	Cr	V	Mo	Mn	Co	Ni	Cu	Ag	Zn	B	Sn	Pb	P
15 MI 3	15	MIDDLE 1'	M	M	m	m+	m	T+	T	O	F	T	T	T	T+	T	T	T	F	O	T	O	T	O
15 MI 4		LOWER 1'	M	M	m	m+	m	T	O	O	O	T	T	T	m	T	T+	T	O	F	T	O	F	O
15a MI 1	15a	UPPER 1'	M	M	m	m+	m	T	O	O	O	T	T-	F	m	T	T+	T	F	O	T	O	T	O
15b MI 1	15b	UPPER 1'	M	M	m	m+	m	T	O	O	O	T	T	F	T+	T	T	T	O	F	T	O	T	O
15b MI 2		MIDDLE 1'	M	M	m	m+	m	T	O	O	O	T	T	F	T+	T	T	T	F	O	T	O	T	O
15b MI 3		LOWER 1'	M	M	m	m	m	T	O	O	O	T	T	F	T	T	T	T	F	F	T	O	T	O
15d MI 1	15d	UPPER 1'	M	M	m	m	m	T	O	O	T	T	T	F	T	F	T	T-	F	O	T	F	F	O
15d MI 2		MIDDLE 1'	M	M	m	m	m	T	O	O	T	T	T	O	T	T	T	T-	O	O	T	O	F	O
15d MI 3		LOWER 1'	M	M	m	m	m	T	F	O	T	T	T	O	T	T	T	T-	O	O	T	O	F	O

As Be	Sb Ge	Bi Tl	Cd Ta	Hg Cb	Li W

LOOKED FOR IN ALL SAMPLES BUT NOT DETECTED

KEY

M	MAJOR COMPONENT
I	INTERMEDIATE COMPONENT
m	MINOR COMPONENT
T	TRACE AMOUNT
F	FAINT TRACE AMOUNT
O	NOT DETECTED
N	NOT DETERMINED

TABLE 5

SPECTROGRAPHIC ANALYSES OF TEBO UNDERCLAY

SW

Sample Description			Elements																										
No.	Loc.	Zone	Si	Al	Ti	Fe	Mg	Ca	Sr	Ba	Zr	Cr	V	Mo	Mn	Co	Ni	Cu	Ag	Zn	B	Sn	Pb	P	As Be	Sb Ge	Bi Tl	Cd Ta	Hg Cb	Li W
6 TE 1	6	SHALE ABOVE	M	M	m	m	m	T	O	O	O	T	T	O	T+	F	T	T	O	O	T	O	F	O						
6 TE 2		UPPER 1'	M	M	m	m	m	N	O	O	N	T	T	F	T-	N	T	T	O	O	T	O	F	O						
6 TE 3		MIDDLE 1'	M	M	m	m	m	N	O	O	N	T	T	F	T-	T	T	T	F	O	T	O	F	O						
6 TE 4		LOWER 1'	M	M	m	m	m	N	O	O	N	T	T	F	T	T	T	T	F	O	T	F	F	O						
5 TE 2	5	UPPER 1'	M	M	m	m	T	F	O	O	O	T	T	O	T	F	T	T	O	O	T	O	F	O						
5 TE 3		MIDDLE 1'	M	M	m	m	T	O	O	O	O	T	T	O	T	F	T	T	O	O	T	O	F	O						
5 TE 4		LOWER 1'	M	M	m	m	T	T	O	O	F	T	T	O	T	F	T	F	O	O	T	O	F	O						
5 TE 5		SHALE BELOW	M	M	m	m	T	O	O	O	F	T	T	O	T	F	T	F	O	O	T	O	O	O						
5a TE 1	5a	UPPER 1'	M	M	m	m	m	O	O	O	F	T	F	O	T	F	T	T	O	F	T	O	F	O						
5a TE 2		MIDDLE 1'	M	M	m	m	m	T	O	O	F	T	T	O	T	F	T	T	O	O	T	O	F	O						
5a TE 3		LOWER 1'	M	M	m	m	m	T	O	O	F	T	T	O	T	F	T	T	O	O	T	O	F	O						
5b TE 1	5b	UPPER 1'	M	M	m	m	m	F	O	O	O	T	T	F	T+	F	T	T	O	O	T	O	F	O						
5b TE 2		MIDDLE 1'	M	M	m	m	m	T	O	O	F	T	T	O	T+	F	T	T	O	O	T	O	F	O						
5b TE 3		LOWER 1'	M	M	m	m	m	F	O	O	F	T	T	F	T+	F	T	T	O	O	T	O	F	O						

LOOKED FOR IN ALL SAMPLES BUT NOT DETECTED

NE

Continued next page

TABLE 5 (CONTINUED)

SW ↑

Sample Description			Elements																									
No.	Loc	Zone	Si	Al	Ti	Fe	Mg	Ca	Sr	Ba	Zr	Cr	V	Mo	Mn	Co	Ni	Cu	Ag	Zn	B	Sn	Pb	P	As Be	Sb Ge	Bi Tl	Cd Te	Hg Cb	Li W_
10 TE 2	10	UPPER 1'	M	M	m	m	m	T	O	O	N	T	T	F	T	T	T	T	T	O	T	F	F	O						
10 TE 3		MIDDLE 1'	M	M	m	m	m	T	O	O	N	T	T	F	T	T	T	T	F	O	T	O	F	O						
10 TE 4		LOWER 1'	M	M	m	m	m	T	O	O	N	T	T	T	T	T	T	T	T	O	T	O	F	O						
19 TE 2	19	UPPER 1'	M	M	m	m	T	F	O	O	O	T	T	F	T	T	T	T	O	O	F	O	F	O						
19 TE 3		MIDDLE 1'	M	M	m	m	T	F	O	O	O	T	T	T	T	T	T	T	O	O	T	O	F	O						
19 TE 4		LOWER 1'	M	M	m	m	T	T	O	O	O	T	T	T	T	T	T	T	O	O	T	O	F	O						
19a TE 1	19a	UPPER 1'	M	M	m	m	m	T+	O	O	N	T	T	T	T+	T	T	T	T	O	T	O	F	O						
19a TE 2		MIDDLE 1'	M	M	m	m	m	T+	O	O	N	T	T	T	T+	T	T	T	T	O	T	O	F	O						
19a TE 3		LOWER 1'	M	M	m	m	m	T+	O	O	F	T	T	T	T+	T	T	T	T	O	T	O	F	O						
19b TE 1	19b	UPPER 1'	M	M	m	m	m	T+	N	O	N	T	T	F	T+	T	T	T	T	O	T	O	F	O						
19b TE 2		MIDDLE 1'	M	M	m	m	m	T+	T	O	F	T	T	F	T+	T	T	T	T	O	T	O	F	O						
19b TE 3		LOWER 1'	M	M	m	m	m	T+	T	O	F	T	T	F	T+	T	T	T	T	O	T	O	F	O						
19c TE 1	19c	UPPER 1'	M	M	m	m	m	m	O	O	O	T	T	T	T	T	T	T	F	F	T	O	F	F						
19c TE 2		MIDDLE 1'	M	M	m	m	m	m	F	F	F	T	T	T	T	T+	T+	T	T	F	T	F	F	T						
19c TE 3		LOWER 1'	M	M	m	m	m	T	O	O	O	T	T	T	T	T+	T+	T	T	T+	T	F	F	T						
20 TE 2	20	UPPER 1'	M	M	m	m	m	T	O	O	O	T	T	T	T	T	T	T	T	T	T	F	F	O						
20 TE 3		MIDDLE 1'	M	M	m	m	m	T	O	O	O	T	T	T	T	T	T	T	T	T	T	O	F	O						
20 TE 4		LOWER 1'	M	M	m	m	m	T	O	O	O	T	T	T	T	T	T	T	T	F	T	O	F	O						
20b TE 1	20b	UPPER 1'	M	M	m	m+	m-	T-	O	O	O	F	F	T	T+	T	T	T	T	T	T	O	F	O						
20b TE 2		MIDDLE 1'	M	M	m	m+	m-	T-	O	O	O	F	T	T	T+	T	T	T	T	T	T	O	F	O						
20b TE 3		LOWER 1'	M	M	m	m+	m-	T-	O	O	O	F	T	T	T+	T	T	T	F	T	F	O	F	O						

↓ NE

KEY

M	MAJOR COMPONENT
I	INTERMEDIATE COMPONENT
m	MINOR COMPONENT
T	TRACE AMOUNT
F	FAINT TRACE AMOUNT
0	NOT DETECTED
N	NOT DETERMINED

TABLE 6

SPECTROGRAPHIC ANALYSES OF WEIR-PITTSBURG UNDERCLAY

SW ↑

Sample Description			Elements																				
No.	Loc.	Zone	Si	Al	Ti	Fe	Mg	Ca	Sr	Ba	Zr	Cr	V	Mo	Mn	Co	Ni	Cu	Ag	Zn	B	Sn	Pb	P
8 WP 1	8	SHALE ABOVE	M	M	m	m+	m	T	O	O	F	T	T	F	T	T	T	T	O	F	T	F	T	O
8 WP 2		UPPER 1'	M	M	m	m+	m	T+	O	O	F	T	T	F	T	T	T+	T	F	F	T	F	T	T
8 WP 3		MIDDLE 1'	M	M	m	m	m	T	O	O	F	T	T	F	T	T	T+	T	F	F	T	F	T	O
8 WP 4		LOWER 1'	M	M	m	m	m	m	O	O	O	T	T	F	T	T	T	T	F	F	T	O	T	T
16 WP 2	16	UPPER 1'	M	M	m	m+	m	T	F	O	T	T	T	F	T	T	T	T	F	O	T	F	T	O
16 WP 3		MIDDLE 1'	M	M	m	m+	m	T	F	O	T	T	T	F	T	F	T	T	F	O	T	O	F	O
16 WP 4		LOWER 1'	M	M	m	m+	m	T	F	O	F	T	T	F	T	F	T	T	O	F	T	O	F	O
17 WP 2	17	UPPER 1'	M	M	m	m+	m	T	O	O	F	T	T	F	T	T	T	T	F	F	T	O	F	O
17 WP 3		LOWER 1'	M	M	m	m+	m	T	O	O	F	T	T	F	T	T	T	T	F	O	T	O	F	O
17b WP 1	17b	UPPER 1'	M	M	m	m+	m	T	O	O	F	T	T	T	T	F	T	T	F	O	T	O	T	O
17b WP 2		MIDDLE 1'	M	M	m	m+	m	T	O	O	F	T	T	F	T	F	T	T	F	O	T	O	T	O
17b WP 3		LOWER 1'	M	M	m	m+	m	T	T	O	F	T	T	O	T+	O	T-	T	O	O	T	O	T	O

↓ NE

As Sb Bi Cd Hg Li
Be Ge Tl Ta Cb W

LOOKED FOR IN ALL SAMPLES BUT NOT DETECTED

KEY

M MAJOR COMPONENT
I INTERMEDIATE COMPONENT
m MINOR COMPONENT
T TRACE AMOUNT
F FAINT TRACE AMOUNT
O NOT DETECTED
N NOT DETERMINED

and lead are always present in small but variable amounts. Silver, molybdenum, tin, barium, strontium, and phosphorus were detected in some samples and traces of gallium and lithium were detected in only three samples. Arsenic, antimony, bismuth, cadmium, mercury, beryllium, germanium, thallium, tantalum, columbium, and tungsten were sought but not detected.

Because the photographic film used is insensitive to the strongest lines of sodium and potassium, these elements were determined with a flame photometer and the results are presented in Table 7.

TABLE 7

COMPARISON OF SODA AND POTASH CONTENT OF TEBO AND WEIR-PITTSBURG UNDERCLAYS WITH THEIR ILLITE CONTENT

Loc. No.	Underclay	Zone	Na_2O	K_2O	% Illite
20	Tebo	upper	0.19	1.51	22
		middle	0.12	1.49	23
		lower	0.08	1.53	30
20b	Tebo	upper	0.08	1.22	24
		middle	0.15	1.06	27
		lower	0.12	0.96	22
8	Weir-Pittsburg	upper	0.19	3.92	57
		middle	0.11	2.50	48
		lower	0.15	3.56	58
17	Weir-Pittsburg	upper	0.10	2.80	44
		lower	0.09	2.74	48
17b	Weir-Pittsburg	upper	0.16	3.27	52
		middle	0.08	3.31	48
		lower	0.10	2.89	43

The most abundant elements of clay minerals are oxygen, hydrogen, silicon, and aluminum. Titanium is a minor constituent of many clays and shales, and its presence in the analyzed samples was known because microscopic examination had revealed the presence of approximately one percent of the titanium dioxide mineral, rutile.

The presence of magnesium in the underclays of western Missouri was expected because magnesium-bearing illite, chlorite, and mixed-layer clay minerals had been found by an X-ray diffraction technique.

Iron in the form of limonite and pyrite had been identified microscopically. It may also be present in some of the clay minerals, and it certainly is present in some of the detrital minerals. The high iron content of the Tebo (Loc.20) and Weir-Pittsburg (Loc. 16, 17, 17b) underclays in Henry County is due to a local increase in pyrite.

Traces of calcium were detected in most, but not all, of the samples of underclay. Manganese was observed to vary from "faint trace" to "minor component".

CERAMIC PROPERTIES AND USES

Ceramic tests were conducted on samples of the lower Cabaniss underclays to determine the economic potential of these deposits. The green and fired properties and the firing characteristics of the clays were determined in accordance with testing procedures specified by the American Society for Testing and Material Committee (1943) and by the American Ceramic Society (1928).

The ceramic properties of clays are dependent upon several factors: 1) clay mineral composition; 2) nonclay mineral composition; 3) textural characteristics, such as particle size, packing, and orientation of both clay and nonclay components; 4) amount and kind of exchangeable bases and soluble salts; and 5) amount and kind of organic matter (Grim, 1950, p. 465). The most important factor controlling the properties of clay usually is the clay mineral composition, but sometimes other factors, such as the presence of fluxing agents, furnace environment, conditions of firing, and rate of firing, are influential.

Clays essentially are aggregates of very minute crystalline particles of members of one or more groups of minerals known as the clay minerals, the most important of which are kaolinites, illites, and montmorillonites. These clay minerals, are hydrous aluminum silicates, in which aluminum frequently is replaced by iron and magnesium, and by small amounts of alkali and alkaline-earth elements. Variable amounts of other materials, such as quartz, feldspar, pyrite, and organic matter may be present as minor or major constituents.

Variations in the properties of clays are exceedingly difficult to predict on the basis of mineralogy and chemical analyses alone. Actual firing tests are required to determine and evaluate their commercial potential, but a degree of correlation between properties and mineral composition may be expected. Such correlations as have been detected in lower Cabaniss underclays are presented briefly herein in graphs and tables.

Selection and Preparation of Samples for Ceramic Tests

The large clay samples for ceramic tests were collected from the highwalls of the same mines where the samples for mineralogical studies were obtained. A 25-pound sample was collected from each of the upper, middle, and lower portions of the underclay at each locality. The three 25-pound samples then were thoroughly mixed to yield a representative sample of a workable thickness of underclay.

Each composite sample was crushed to minus 6-mesh by passing it through rolls. This was the material used in subsequent tests. The powdered clay was then used to prepare test bars. The clay was moistened with water and handworked to a uniform stiff mud. This tempered stiff clay was fed into an extrusion press equipped with a die having a circular opening one inch in diameter. The extruded clay was cut into lengths suitable for subsequent tests.

The test pieces were dried carefully at room temperature for several hours and then were dried to constant weight at 110°C in an electric drier.

Unfired Properties of Raw Underclay

Water of plasticity.--The amount of water that must be added to a dry clay in order to bring it to a good working consistency is known as the water of plasticity. In general, the water of plasticity is relatively high for plastic, fine-grained clays and low for sandy, nonplastic clays. The phenomenon of plasticity results from the interplay of the attractive forces tending to hold the clay mineral flakes together, the thickness of the water film keeping the flakes apart, and the lubricating properties of the water film. Variations in particle size and the character of exchangeable bases determine the range of plasticity in clays.

Good working properties generally are imparted to clays composed of illite and kaolinite by small amounts of water, whereas clays rich in montmorillonite and in mixed-layer material usually take up large quantities of water and develop a very plastic state. The presence of nonclay minerals often provides improved workability. Other constituents often exert a strong influence on the properties of a clay. Small amounts of organic matter generally enhance the plasticity of clays, but this influence is not always predictable. The presence of exchangeable bases often changes the plasticity of clays, and angular grains of quartz and feldspar would disrupt the makeup of a clay leading to plasticity. In order to determine the water of plasticity, test pieces of the lower Cabaniss underclays were weighed in the plastic state and again at the end of the drying period. The water of plasticity was calculated according to the equation:

$$\text{Water of plasticity (\%)} = \frac{\text{Weight in plastic state - dry weight}}{\text{dry weight}} \times 100$$

Linear drying shrinkage.--When the water held at the surface of clay particles is driven off, the clay particles are drawn closer together and the mass shrinks. Excessive shrinkage causes cracking, warping, and distortion, thereby rendering the clay unfit for use. Clays differ considerably in their amounts of shrinkage on drying. Those which require large amounts of water to develop full plasticity have high shrinkage. This is well illustrated in the scatter diagram of Figure 18. High shrinkage and the attendant tendency to crack may be reduced by the addition of substances unaffected by water, such as sand, flint, or grog.

Clays consisting of illite and kaolinite tend to have moderate shrinkage on drying, unless the grains are exceedingly small, but the presence of even moderate amounts of mixed-layer illite-montmorillonite greatly increases drying shrinkage.

The linear drying shrinkage of the lower Cabaniss underclays was determined by measuring the overall length of a clay bar first in the plastic state and then after drying at 110°C. The amount of linear drying shrinkage was calculated as follows:

$$\text{Linear drying shrinkage (\%)} = \frac{\text{plastic length - dry length}}{\text{dry length}} \times 100$$

The results of the determinations of the water of plasticity and the drying shrinkage of the underclays are presented in Table 8. The plasticity values vary from 14.8 to 24.3 percent. The drying shrinkage varies from 2.78 to 6.68 percent. The drying shrinkage seems to have little relation to the abundance of mixed-layer clay, contrary to expectation (Fig. 19). From this one may conclude that physical characteristics of the lower Cabaniss underclays are more important than mineral composition in governing shrinkage.

TABLE 8

COMPARISON OF PERCENT WATER OF PLASTICITY AND PERCENT DRYING SHRINKAGE WITH PERCENT MIXED-LAYER CLAY

Loc. No.	Water of Plasticity	Percent Drying Shrinkage	Mixed-layer Clay
MI 9	24.3	6.68	29
MI 15	19.8	6.20	46
TE 5	16.2	5.06	39
TE 6	17.5	4.86	20
TE 10	22.0	5.92	38
TE 19	20.6	6.05	56
TE 20	15.8	5.55	29
WP 8	23.5	4.31	34
WP 16	20.1	5.27	32
WP 17	14.8	2.78	62

Drying scum characteristics.--Clays which contain soluble salts yield a scumlike surface on drying. This scum is caused by the presence of soluble salts in the clay mass which are brought to the surface of the body by capillary creep and are deposited there as the water evaporates (Grim, 1962, p. 86). The most common scum-forming salts are sulphates of calcium, magnesium, iron, sodium, and potassium. An excessive amount of scum produces unattractive colors. Scums caused by sulphates may be counteracted with barium salts. The amount and kind of soluble salts present are indicated by the extent and color of the scum deposited on test pieces after drying. These characteristics were determined visually and are presented in Table 9. Most of the underclay samples exhibited drying scum to a marked degree. These scums were determined to be chiefly alkali and alkaline-earth sulphates and very minor amounts of vanadates and ferrites.

Firing Characteristics

Mode of testing.--When clays are heated from about 100° to 3000°F., progressive changes in porosity, volume, color, hardness, mechanical strength, and specific gravity accompany such processes as dehydration, volatilization, oxidation, and chemical interaction of the minerals present in the raw clay. These changes largely determine the value and utility of the clay and indicate the heat treatment it should receive in the manufacture of particular wares.

TABLE 9

DRYING SCUM CHARACTERISTICS OF LOWER CABANISS UNDERCLAYS

Sample No.	Drying Scum Characteristics
MI 9	slight gray
MI 15	extensive white
TE 5	moderate white
TE 6	slight brown
TE 10	slight white
TE 19	none
TE 20	extensive grayish green
WP 8	slight gray
WP 16	none
WP 17	slight brown

Pyrometric cone equivalent.--In ceramic engineering, the fusion or softening point of a clay is expressed as its Pyrometric Cone Equivalent (P.C.E.). This is determined by molding a clay into a cone of standard shape and size and heating it on a plaque with standard cones used as temperature indicators. The number of the standard cone which behaves most nearly like the specimen cone in firing is taken as the P.C.E. of the clay.

The P.C.E. and other characteristics obtained on firing the lower Cabaniss underclays are presented in Table 10. The P.C.E. values are low, varying from 6 to 16. These low values are due to several factors, the most important of which is the high illite and mixed-layer clay content. Minerals of the illite and montmorillonite groups contain alkalies and alkaline-earths which act as fluxes in lowering the fusion temperatures. Also, the presence of pyrite in the underclays exerts a strong influence. In general, as the flux content increases, the P.C.E. of a clay decreases, but the exact nature of this relationship is not known. The low P.C.E. values are not wholly accounted for by characteristics determined in this study.

High alumina kaolin clays tend to have high P.C.E. values, but fluxes exert a controlling influence on the fusion temperatures. In figure 20, a scatter diagram showing the relation of the kaolinite content to the P.C.E. values of the under-

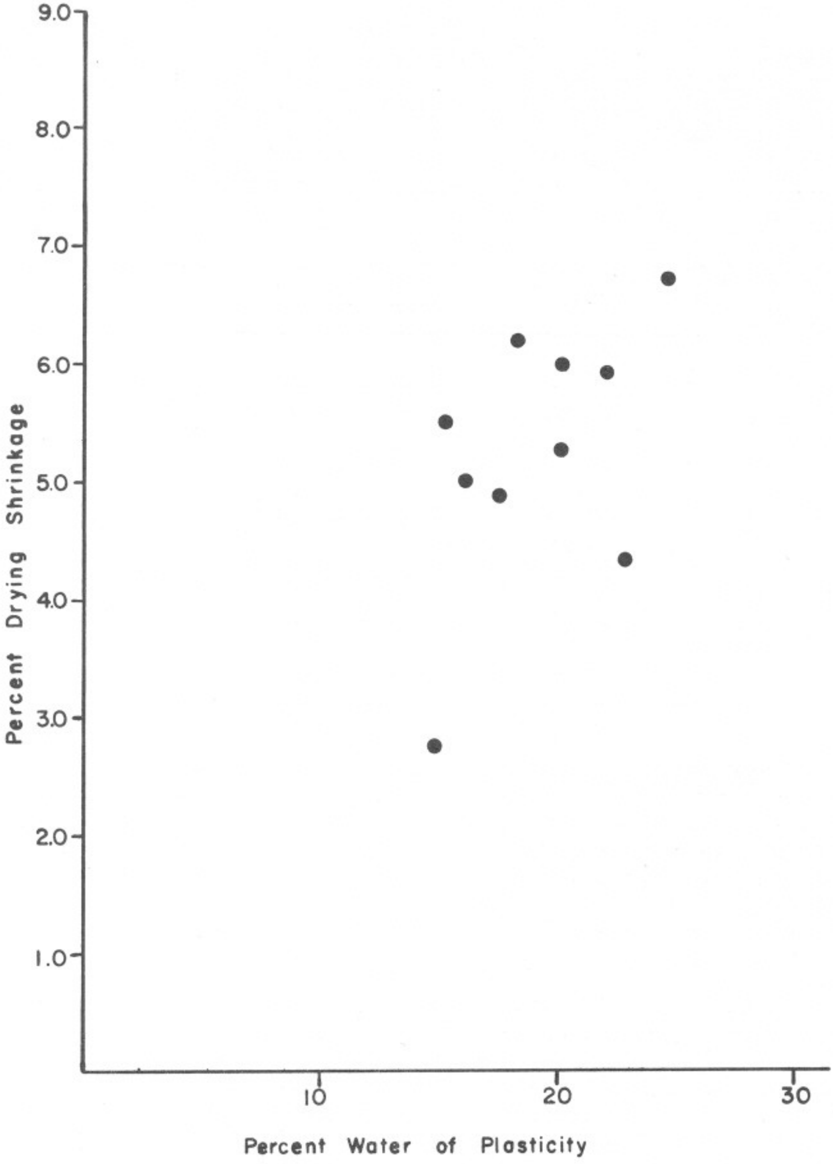


Figure 18. Relation of drying shrinkage to water of plasticity in lower Cabaniss underclays.

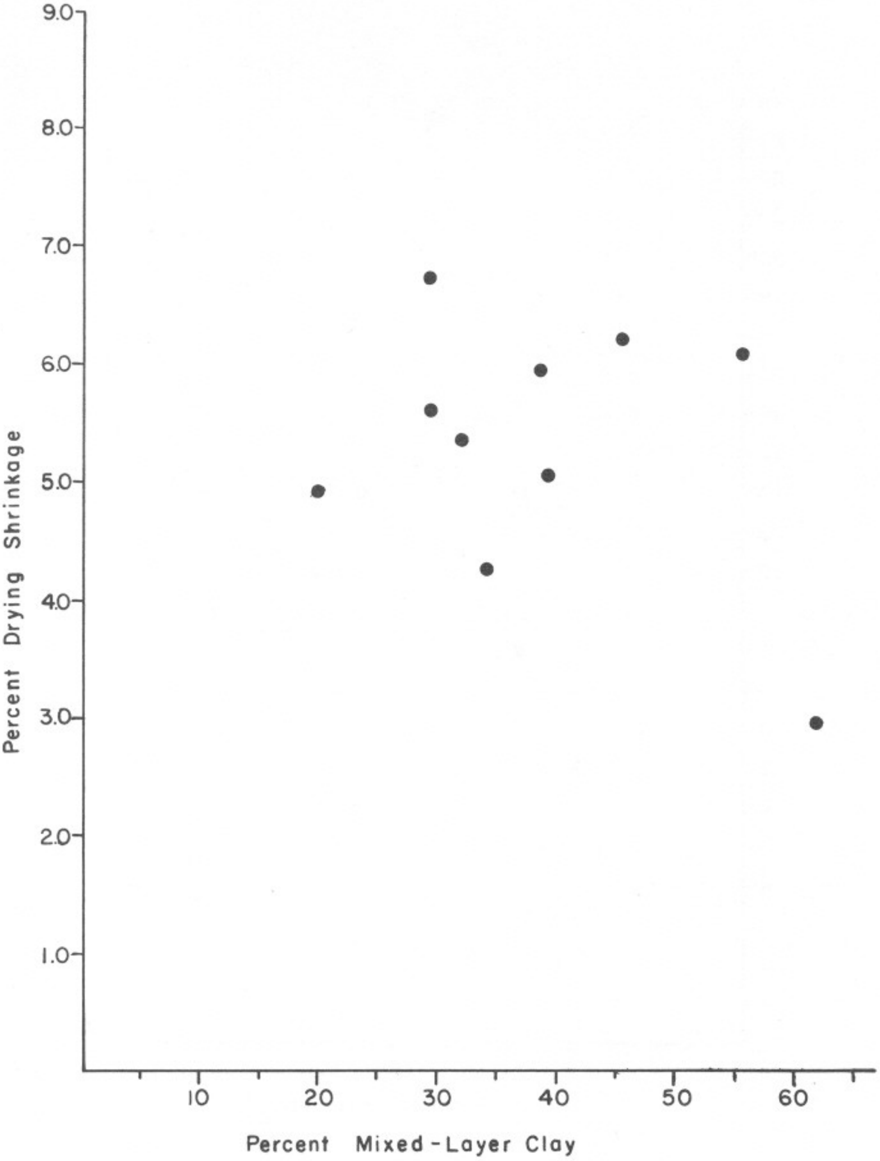


Figure 19. Relation of drying shrinkage to amount of mixed-layer clay in lower Cabaniss underclays.

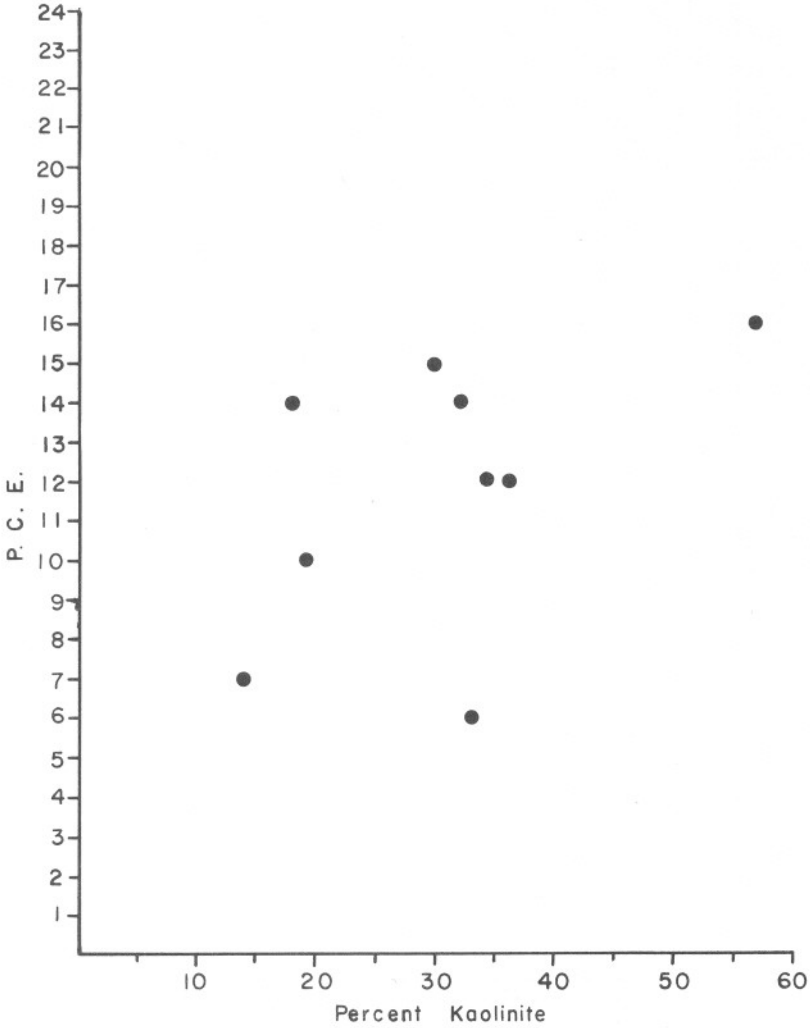


Figure 20. Relation of P.C.E. to amount of kaolinite in lower Cabaniss underclays.

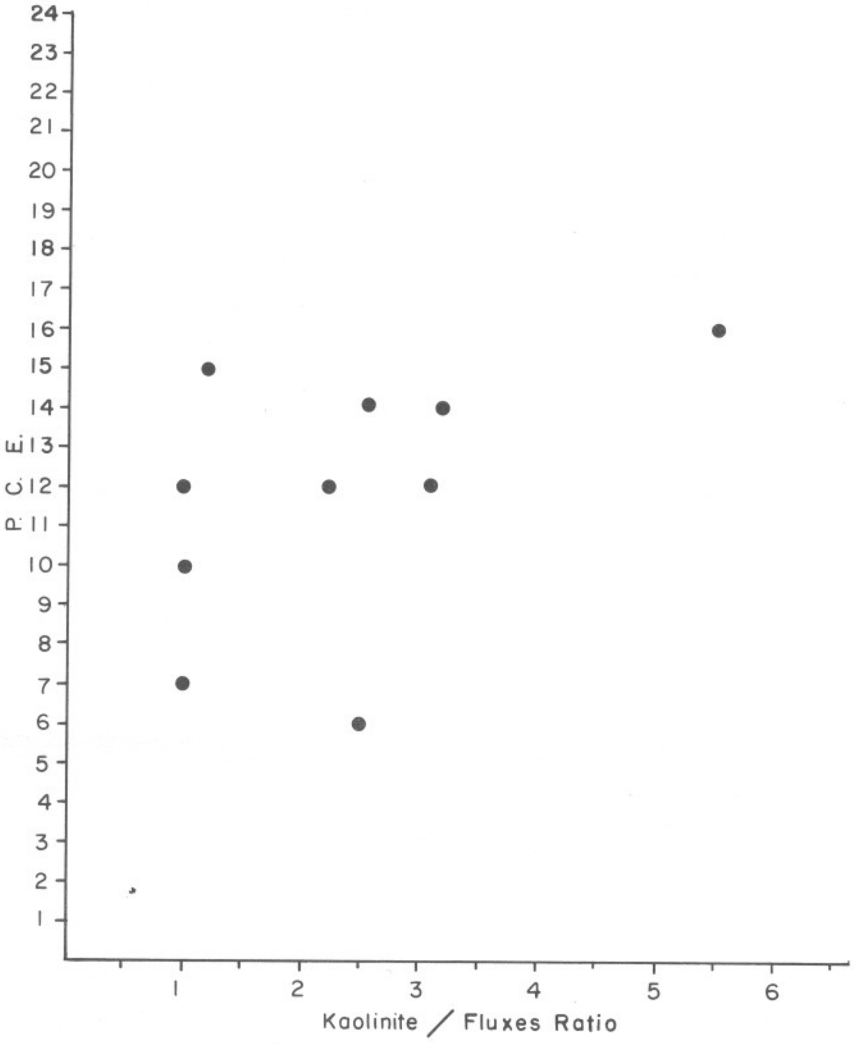


Figure 21. Relation of P.C.E. to kaolinite/fluxes ratio in lower Cabaniss underclays.

clays is presented. From this diagram, one may conclude that the fusion temperatures are influenced more by the presence of fluxes, such as FeO, CaO, MgO, Na_2O, K_2O, TiO_2, MnO_2, P_2O_5, and SO_4, than by the amount of kaolinite. When kaolinite/flux ratios are plotted against P.C.E. values (Fig. 21), some positive correlation may be noted.

Fired colors.--The colors developed on firing of the underclays were observed in the test pieces drawn from the kiln at various temperatures. They are white, pink, red, buff, and brown (Table 10). For the most part, these colors are due to the presence of iron in the illite, montmorillonite, and pyrite. Iron in the ferric form is a powerful coloring agent (Grim, 1962, p. 122).

Kaolinite clays tend to be light-burning; but when the quantities of illite and montmorillonite are appreciable, the fired colors darken to reds and browns, for in these minerals iron replaces aluminum and gives rise to red and and yellow colors in the fired clays.

Pyrite, under the influence of heat, is first decomposed to ferrous sulphide (FeS) and sulphur. These oxidize to FeO, Fe_3O_4, Fe_2O_3 and SO_2 and SO_3, depending upon the furnace conditions. These iron oxides yield red, brown, or black colors. The presence of titanium oxide in clay bodies yields a bluish-gray color under reducing conditions and a yellowish color under oxidizing conditions (Stout, 1923, p. 501). Calcium oxide (CaO) and magnesium oxide (MgO) may alter or neutralize colors produced by iron-oxide, by combining with it to form ferrites. Manganese oxide (MnO_2) is a strong coloring agent. It decomposes when heated and imparts gray or mottled shades, dark browns and brownish blacks to ceramic ware.

Efflorescence.--The powdery crust formed on a fired clay due to the deposition of salts on its surface is known as an efflorescence. The formation of an efflorescence is detected in a drying room where test specimens of fired clay are immersed in one inch of water and after seven days are inspected for efflorescence.

Efflorescences on the lower Cabaniss underclays range from none to extreme (Table 10). The variation is caused by the presence of variable amounts of sulphur in the form of pyrite and sulphates in the clays. Sulphur forms soluble salts which are effective in scumming of products. In burning, the scum develops a dirty white unattractive appearance.

Scum and efflorescence generally are due to nonclay mineral constituents, but clay minerals, other than kaolinite, which have alkalies or alkaline earths in their structure, also may cause scumming and efflorescence. In sulphate form, magnesium is influential in producing scum on wares, and once formed these scums are hard to remove.

Black coring.--Several of the test pieces exhibited a black core (Table 10), when specimens were broken in the modulus of rupture test. This black core usually is caused by the presence of unoxidized iron and carbon compounds, but in some cases sulphur compounds play a significant role. As vitrification proceeds, ferrous silicates are formed which dissolve and move through the clay. Unoxidized organic matter also may be deposited in the fired ware. Sulphur liberated from sulphides during firing may react with aluminum and iron released by the partial breakdown of lattice structures of some clay minerals and may form sulphates which are resistant to decomposition.

Black cores occur when the exteriors of clay pieces vitrify early and prevent oxygen penetrating to the interiors. Ample circulation of air through the bodies will effectively prevent black coring.

Other characteristics.--The fired test specimens were examined for other defects: ironspots, cracks, blisters, stains, and streaks. These observations are presented in Table 10.

Fired Properties

Firing Shrinkage.--The shrinkage of a dried clay on firing is due to the loss of chemically combined water and other volatile substances, to vitrification, and to recrystallization. Firing shrinkage may vary between wide limits, and, if excessive, it will cause distortion and cracking of the ware into which the clay is made. Linear firing shrinkage is determined by measuring the length of a dried clay bar before and after firing and computing the shrinkage according to the equation:

$$\text{Linear firing shrinkage (\%)} = \frac{\text{dry length} - \text{fired length}}{\text{dry length}} \times 100$$

Firing shrinkages, developed on the underclays, range from 0.43 to 6.61 percent at the 2100°F temperature, as shown in Table 11. In general, the firing shrinkages are low. A few above 5.0 percent may be considered moderate. Firing shrinkage is controlled by the composition of the clay minerals present, the size-grade distribution of the clay particles, the amount of organic material present, the firing temperature,

TABLE 10

FIRING CHARACTERISTICS OF LOWER CABANISS UNDERCLAYS

Sample No.	P.C.E.	Firing Temp. °F.	Color Appraisal	Efflorescence	Other Characteristics
MI 9	12	1700	dark red	moderate white	iron spots
		1900	dark brown	none	pink spots; bloated; black core
		2100	brown	--------------	badly bloated
MI 15	14	1700	light red	moderate white	iron spots; cracks
		1900	reddish brown	some brown	------------------
		2100	reddish brown	none	bloated
TE 5	15	1700	light pink	moderate white	red stains
		1900	pink to buff	slight white	------------------
		2100	tan to pink	slight white	------------------
TE 6	16	1700	white to pink	moderate white	red stains
		1900	light tan	slight tan	------------------
		2100	light tan	none	------------------
TE 10	6	1700	pink	extensive yellow	iron spots
		1900	tan to brown	none	spotted; bloated; black core
		2100	light brown	none	iron spots; bloated; black core
TE 19	7	1700	light red	moderate white	iron spots
		1900	brown	none	iron spots; black core
		2100	dirty brown	none	bloated
TE 20	12	1700	light red	extensive yellow	iron spots
		1900	reddish brown	moderate brown	iron spots; black core
		2100	deep red	moderate red	iron spots
WP 8	14	1700	pink	moderate white	red streaks
		1900	orangish brown	none	iron spots; cracks
		2100	orangish brown	none	iron spots; cracks
WP 16	12	1700	white to pink	extensive white'	iron spots
		1900	tan to buff	none	white and brown spots
		2100	light brown	none	white spots; bloated
WP 17	10	1700	pink	extensive white	iron spots; red stain
		1900	light to pink	none	iron spots; slight black core
		2100	tan to brown	none	slight bloating

TABLE 11

FIRING PROPERTIES OF LOWER CABANISS UNDERCLAYS

Sample No.	Firing Temp. °F.	Firing Shrinkage Percent	Porosity Percent	Absorption Percent	Bulk Density	Ignition Loss Percent	Modulus of Rupture lbs./sq. in.
MI 9	1700	1.77	27.5	11.4	2.41	8.3	315
	1900	4.58	7.4	3.2	2.40	8.8	3042
	2100	----	----	----	----	---	----
MI 15	1700	0.01	29.8	12.6	2.36	10.3	572
	1900	2.68	18.8	7.1	2.64	10.8	2066
	2100	----	----	----	----	----	----
TE 5	1700	-0.68	28.3	11.9	2.35	6.3	420
	1900	0.60	27.4	11.4	2.43	6.9	1731
	2100	2.29	19.8	7.9	2.56	6.9	1581
TE 6	1700	-0.46	31.0	13.4	2.30	5.9	614
	1900	0.89	29.1	12.2	2.38	6.3	2767
	2100	2.26	21.2	8.3	2.55	6.3	1726
TE 10	1700	1.99	23.8	9.4	2.54	8.4	1383
	1900	4.33	3.8	1.5	2.51	9.1	1294
	2100	-0.43	8.8	5.3	1.67	9.3	2461
TE 19	1700	1.51	24.5	10.1	2.44	9.4	281
	1900	4.89	7.1	2.7	2.69	10.5	1174
	2100	1.62	13.8	9.0	1.54	10.5	1910
TE 20	1700	1.88	35.6	15.1	2.36	19.6	850
	1900	4.01	26.9	10.4	2.61	19.7	688
	2100	6.24	13.5	4.9	2.77	19.8	144
WP 8	1700	-0.81	40.0	20.1	2.00	7.9	636
	1900	2.35	31.2	13.3	2.35	8.3	1946
	2100	6.61	11.1	3.9	2.83	8.4	1023
WP 16	1700	-0.89	31.6	13.7	2.30	7.9	351
	1900	0.89	27.8	11.3	2.46	8.9	1593
	2100	4.42	9.6	9.6	2.83	9.1	1618
WP 17	1700	-0.23	30.3	13.2	2.29	8.2	756
	1900	1.21	27.9	11.5	2.41	8.8	1745
	2100	4.71	9.9	3.6	2.78	9.0	2266

and the presence of nonclay components in the clay material.

In general, plastic clays have higher firing shrinkage than nonplastic clays, and the presence of organic material usually causes higher shrinkage. Shrinkage of clays generally increases as the temperature increases, but shrinkage is difficult to predict without tests. Clays composed of a mixture of clay minerals are likely to have lower firing shrinkages than clays consisting of a single mineral.

The presence of quartz particles in clays generally decreases the firing shrinkage, but the influence of such material depends upon the kind of product and use. The presence of sulphur compounds and carbon may cause some bloating of clays during firing.

A few of the test specimens bloated during firing (Table 11). Bloating is caused by the development of a liquid glassy phase during firing and the entrapment of gases produced by decomposition of the contained constituents (Harold, et al., 1958, p. 20).

Apparent porosity.--Hardening and vitrification in a clay during firing is accompanied by a decrease in porosity. The apparent porosity of a fired clay is defined as the percent of the volume occupied by the open pores of the material. It is determined by saturating a fired test piece with water, determining the increase in weight, and utilizing the following equation:

$$\text{Apparent porosity (\%)} = \frac{\text{saturated fired weight - fired weight}}{\text{fired volume}} \times 100$$

Absorption.--Absorption is dependent upon the porosity of a fired body. It is defined as follows:

$$\text{Absorption (\%)} = \frac{\text{saturated fired weight - fired weight}}{\text{fired weight}} \times 100$$

Bulk density.--Bulk density is the weight in grams of a cubic centimeter of the fired test piece. It is calculated by the formula:

$$\text{Bulk density} = \frac{\text{dry weight in grams}}{\text{volume in cubic centimeters}}$$

In ceramic wares, these three terms are somewhat interrelated. They are important in evaluating certain uses of heat-treated products. The crux of these determinations hinges on measuring the pore space.

The results of these determinations at three firing temperatures are given in Table 11. The porosity values of 4 to 21 percent and absorption values of 1 to 10 percent for the underclays are considered low, but the bulk densities of 2.5 to 2.7 are moderate to high.

Fired strength and modulus of rupture.--The most commonly used measures of the strength of a clay are compressive strength and transverse breaking strength. Round bars of clay are formed and dried carefully to avoid warping or cracking, and fired. The bars are broken in a crossbreaking machine, and the modulus of rupture is determined. The modulus of rupture or transverse breaking strength generally is used to express the mechanical strength of a clay. This property influences the mode of manufacture and usefulness of the product. The modulus of rupture is calculated as follows:

$$\text{Modulus of rupture in pounds per square inch} = \frac{8\ PL}{d^3}$$

where, P = breaking load in pounds

L = distance between knife edges in inches

d = diameter of bar in inches

Owing to the variability always found in clay specimens, a wide range of values of modulus of rupture may be obtained on different specimens. The moduli of rupture of specimens of lower Cabaniss underclays are reported in Table 11. The modulus of rupture was found to be greater than 600 pounds per square inch for most specimens and is sufficient for use of the clay in low grade ceramic ware.

Possible Uses

The P.C.E. values, together with colors developed on firing and other properties, show that the clays are suitable only for lower grade ceramic ware. Among the uses to which these clays may be put are: common brick, tile, sewer pipe, terra cotta, stoneware, ladle brick, and bloating clay.

Brick.--The underclays are suitable for the manufacture of common brick. The pink to buff to red colors, developed at 1800° to 2000°F., are attractive and commonly useful. The clays have proper plasticity for molding, possess low to medium drying shrinkages, and possess good strength, having moduli of rupture of greater than 600 pounds per square inch after firing. Clays with low to medium drying shrinkage are desirable for common brick, but clays of high shrinkage may be used when mixed with grog or sandy clay. The percentages of absorption (less than 10 percent at 1900° and 2100°F.) shown by these underclays, should be desirable for such products.

The underclays also are suitable for the manufacture of face brick. Again, the red, buff, and white colors developed on burning are desired for this type of product. In addition, good workability and minimum warping and cracking in drying and firing make the underclays suitable. Occasionally iron-spots developed on firing, but these are not necessarily a condemning factor, if they are correctly distributed. When properly distributed, they yield a pleasing appearance and the bricks are called "iron-spot" brick. The moduli of rupture, low absorption percentages, and low to medium drying and firing shrinkages, also are important factors for this type of brick. The low soluble salt content of the underclays permits scumming to be held at a minimum, and the brick can be glazed if desired.

Hollow tile and conduit.--Hollow tiles and conduit are made from clays having much the same properties as those used for face brick. Because of their shapes, hollow tiles must be made from clays having good drying and firing properties with low shrinkage to eliminate serious warping (McNamara, 1945, p. 418). They must burn to a relatively dense hard body. The clay must be plastic enough to be formed by the stiff-mud process. The low shrinkage, high bulk density, and good plasticity of lower Cabaniss underclays make them suitable for the manufacture of hollow tile. Hollow tiles are not required to be vitreous and are fired at lower temperatures than face brick. Color is of little importance because the tile usually is covered or painted.

Conduit is made in much the same way as hollow tile, but conduit must be impervious to moisture and so must be well vitrified and glazed.

Sewer Pipe.--The red color developed on firing of the underclays is an important property in the manufacture of sewer pipe. In addition, the plasticity of the underclays is sufficient to permit the clay to be extruded readily from a stiff-mud machine. The good strength, minimum warping and cracking, and low absorption of the underclays also are suitable properties for the manufacture of sewer pipe. The low soluble salt content will permit the bodies to be salt-glazed.

Terra cotta.--Terra cotta bodies usually are compounded of mixtures of clays and grog. Both red burning and buff burning clays are used. The clays must have sufficient plasticity to give good workability for hand molding or for the stiff-mud process. When properly fired, terra cotta should have a modulus of rupture of about 1,500 pounds per square inch. Low shrinkage, low porosity, dense texture, and low soluble salt content are other important properties for the production of terra cotta. The fired properties and characteristics of lower Cabaniss underclays make clays suitable for terra cotta. One unfavorable property for this use is the development of spotting during firing.

In the production of terra cotta, a single firing is employed, and the terra cotta bodies seldom are fired to any great degree of vitrification. Terra cotta bodies usually are glazed.

Stoneware.--Stoneware clays usually are low-grade refractory or semi-refractory clays. Sometimes a mixture of clays is used to impart desired properties. Stoneware clays must possess sufficient plasticity so they may be turned on a potter's wheel. In addition, they should burn to a dense body without excessive shrinkage at relatively low temperatures. The characteristic property of all stoneware is its impervious structure. Porosity is usually less than 1 percent. Also, the clays should develop good strength and possess a long firing range. Stoneware is usually glazed with a prepared glaze or with a clay slip, and it is desirable that the body burn to a white, cream, or buff color.

Lower Cabaniss underclays are suitable for stoneware. The good plasticity, low shrinkage, low porosity, good strength, and low soluble content of the underclays are the properties desirable in the manufacture of stoneware.

Ladle brick.--Brick used to line ladles in open-hearth and electric steel plants generally are a special kind of fireclay brick which has the property of expanding considerably when heated to operating temperatures. The expansion helps to make tight linings (Searle, 1950, p. 781). Such brick must stand up under sudden changes of temperature without spalling. The density, refractoriness (cone 16), porosity (about 16 percent), and expansion characteristics of some of the lower Cabaniss underclays presented in Table 10 and 11 are properties which are suitable for ladle brick manufacture.

Bloated clay products.--Although specific tests to determine the bloating characteristics of the underclays were not made, some of the fired samples bloated to some degree.

Bloating tests to determine if clays are suitable for the manufacture of lightweight aggregate usually are conducted under faster heating rates than those employed during this study. Temperatures up to a maximum of about 2200°F. are employed. If a clay is to bloat on heat treatment, an adequate glassy phase must be developed to trap gas produced by the decomposition of certain components. Reaction which evolve gas during the firing of clay are the oxidation of organic carbon, the oxidation of pyrite producing SO_2 and SO_3, and the decomposition of calcium and magnesium carbonates.

The lower Cabaniss underclays may be suitable for the manufacture of lightweight aggregate, if proper firing conditions are employed.

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