GEOLOGIC AND MINERALOGIC FACTORS CONTROLLING THE PROPERTIES AND OCCURRENCE OF LADLE BRICK CLAYS

by

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ABSTRACT

Bloating refractory bricks are particularly useful for lining the ladles which transport molten steel. In use they expand irreversibly sealing any cracks in the ladle lining. The ASTM requires that they have a P.C.E. of 16 (M.P. = 1470°C) or greater and a linear reheat expansion of 15% or more.

Bloating is caused by the trapping of a gas phase within the brick. Over 97% of the gas evolved is oxygen. The two possible reactions which could produce the gas at these temperatures (1100°C - 1350°C) are the reduction of hematite:

$$\text{Fe}_2\text{O}_3 \xrightarrow{1350^\circ\text{C}} \text{log} p \text{O}_2 = 10^{-2} \rightarrow 2\text{FeO} + 1/2\text{O}_2$$

and/or the dissociation of mica anhydride.

A correlation matrix showed a significant inverse relationship (R = -0.73) between porosity of the brick before bloating and reheat expansion. If the bricks are porous at reheating temperature, evolved gasses can escape. However, if porosity is low, gas is trapped causing bloating. Percent (mica + vermiculite) was positively correlated (R = 0.68) with porosity. The amount of mica is critical because it forms the glassy phase that fills open pores,
thus decreasing porosity. Bricks which exceeded 15% linear reheat expansion could be separated from those which failed to meet specifications with 85% reliability using 37% mica as a discriminant.

The mineralogy of the lower Kittanning underclay was mapped for the area of western Pennsylvania. These maps were used in conjunction with defined mineralogic criteria (>35% mica, >35% kaolinite and <30% quartz) to outline areas with a generally favorable mineralogy for ladle bricks. The genesis of the underclay was interpreted and used to predict favorable locations. These concepts were also used to provide guidance in local prospecting and mining of deposits.
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CHAPTER I GEOLOGIC BACKGROUND AND SCIENTIFIC PROCEDURES

Introduction

Underclays of Pennsylvanian cyclothems have been used extensively in making bricks, ranging in quality from ordinary face bricks to super duty fire bricks capable of withstanding high temperatures. Western Pennsylvania is one of the largest producers of fire brick made from underclays. Predicting the occurrence and properties of refractory clays is of great importance to the refractory brick industry, not only in discovering new sources, but also in developing new products. The refractory clays of western Pennsylvania have been studied by Weitz (1954), Weitz and Bolger (1951), Erickson (1963), Williams et. al. (1968), and Bragonier (1970).

In addition to high duty refractories, western Pennsylvania also supplies clay for making expanding ladle bricks, which not only must withstand high temperatures (1470°C and higher) but must also exhibit at least 15% linear expansion. Underclays suitable as raw material for such bricks have been produced principally from one stratigraphic position (below the lower Kittanning coal).
This study results from a cooperative program between business and The Pennsylvania State University through Small Industries Research. Resco Products Inc., a ladle brick company, needed to find new reserves of raw materials for their product. In order to accomplish this, a research proposal was submitted by E. G. Williams of the Geology Department through James Lundy of Small Industries Research to Robert Enoch of Resco Products Inc. The project was approved and cooperatively funded by Resco Products and Small Industries Research for two years. Both writers are very grateful for all the help contributed during this time.

This paper is principally composed of the first, second, and last chapters of the younger writer's Ph.D. dissertation on the same subject. In places these Chapters have been modified to provide continuity to the paper. Chapters III through VI of the dissertation were eliminated from this paper because their interest is principally scientific. Only the relevant conclusions from these Chapters were retained and are presented in this paper. The interested reader may refer to the dissertation if he wishes the full details of the scientific arguments. The following paragraph shows the structure of the reasoning pattern.

The exploration philosophy employed in the dissertation is illustrated in Figure 1. In essence, the prediction of the occurrence and properties of ladle brick
clays requires an integration of the ceramic properties of the clays with the sedimentary and structural history of the depositional basin. If one can demonstrate such relationships, predictions can then be made.

The plan begins and ends with the desired ceramic properties of ladle bricks. They are a linear reheat expansion in excess of 15% and a pyrometric cone equivalence greater than 16. This is shown in the upper left hand block of the schemata. In order to geologically predict this, these critical properties must be related to geologic parameters. In Chapter II the desired ceramic properties are related to mineralogic, chemical and physical properties of the raw materials. Chapter III is devoted to the characterization of all of the major minerals found in the underclays of western Pennsylvania. This characterization allows conclusions as to the genesis of the minerals and to their usefulness as raw materials.

The distribution of these minerals perpendicular to bedding is presented in Chapter IV. This mineralogic distribution is related to the megascopic properties observed in underclays. These two lines of evidence are used to classify and interpret underclay types. Mineralogic maps of the lower Kittanning underclay are presented in Chapter V. These maps are compared to maps of the underlying and overlying strata. The detailed mineralogy from Chapter III and the genesis of underclay
Figure 1: Schemata to show the overall plan for predicting the occurrence of underclay deposits suitable for the manufacture of ladle bricks. Thesis chapters are related to steps in the process and relationships where the output of one chapter are used as partial input to another are drawn as arrows.
profiles from Chapter IV provide limiting conditions to the interpretation of mineralogic maps. The genesis of the lower Kittanning underclay is interpreted through a synthesis of all the preceding information.

Chapter VI is devoted to the interpretation of the genesis of cyclothem maps, within which underclays occur. A general chemical system including underclays, coals, and shales is outlined based upon the gleying process in underclays. The age of underclays is used as critical evidence to determine whether or not sea level was changing during the Pennsylvanian. The presence or absence of sea level changes would effect the distribution pattern of underclays useful for the manufacture of ladle bricks.

In Chapter VII, the information as to the probable pattern of the deposits are combined with the mineralogic maps from Chapter V to predict the occurrence of underclays useful for ladle bricks. The same maps are also used to predict the locations of underclays useful for super duty refractory bricks, face bricks and sewer tile. This completes the cycle used for the geologic prediction of ceramic properties. Knowledge thus arranged is more than the solution to several technical problems. The solution of each technical problem is used to illuminate other problems. This results in an even greater expansion of knowledge than the sum of the smaller problems solved.
Scope

Over a period of three years 78 lower Kittanning underclay sites and about 30 sites from other stratigraphic levels were visited. These covered the entire western Pennsylvanian plateau as well as a few sites in West Virginia and Ohio. Although over half of the area had been previously mapped, about an hour was spent at each site sketching the outcrop, measuring the section and looking for fossils and nodules. After this, one to two hours were spent sampling the overlying shale and the underclay.

Each of the over 500 samples were fine ground and analyzed using X-ray diffraction techniques. Seventy-five of these samples were chosen for chemical analyses, and a more detailed mineralogic analysis was performed on over 50 samples for special purposes. This portion of the work involved over 500 man hours of work in preparation and analysis.

The analysis of the data, study of the relevant literature, and preparation of the dissertation probably also involves over 500 man hours of work.

Although the lower Kittanning coal is extensively strip mined in western Pennsylvania, the underlying underclay is not well exposed. Therefore, considerable effort was expended in locating complete exposures of the clay as well as suitable sites for hand augering. The best outcrops occurred in the high wall of Vanport limestone quarries.
Most of the augered sections were obtained in strip mines where the lower Kittanning coal was exposed in the floor. **Definition**

Underclays are so named because of their common occurrence below coals. They are usually composed of medium to light gray clay-rich sediments. Typically they contain fossil roots (*Stigmaria*) and lack normal sedimentary bedding. They also often contain slickensides which most geologists interpret to be caused by some early, non-tectonic, mass movement within the clay. Some workers prefer to define an underclay on the basis of the above described internal characteristics without any particular reference to an overlying coal.

The term "seatearth" is used synonymously with underclay. It is meant to encompass those materials upon which the peat forming plants took root and grew. This term is often meant to imply that this material is principally a sedimentary deposit as distinguished from a soil.

The working definition for an underclay used in this study is, "that material which underlies the lower Kittanning coal." It is a stratigraphic definition and makes no reference to color, structure, or composition. The variability which occurs in this stratigraphic position should illuminate the events prior to, and during the accumulation of the lower Kittanning coal.
Geologic Background

The properties of the lower Kittanning underclay are a result of the properties of the source area, and subsequent modifying processes. In continental environments, the relevant processes are weathering, erosion, transportation, sedimentary fractionation and deposition. A given particle may go through several cycles of these processes before final deposition and burial. In marine environments, or concentrated brine lakes, differential flocculation and authigenesis (the formation of new minerals from solution) are also operative.

All of these processes are affected by paleotopography. Differential flocculation and marine authigenesis occur only in the marine basins. The rates of erosion and transportation are largely a function of the slope of the land. The rate of weathering is a function of the drainage of a soil. Because higher locations generally experience better drainage, weathering rates are generally faster on paleotopographic highs.

Other factors also influence the character of the above mentioned processes. These factors, such as climate, vegetation, concentration of solutions, and permeability are either difficult or impossible to determine from the rock record. These factors are not entirely independent of paleotopography and inferences with respect to them can also be made. Therefore, a knowledge of the paleo-
topography is extremely helpful in the interpretation of past processes.

Williams (1972, in press) outlined four orders of paleotopographic control. They are, 1. the shape of the basin, 2. major folds, 3. minor folds and faults, and 4. local paleotopography resulting from erosion and sedimentation. Gwinn (1964) outlined the major structural features in the basin. Figure 2 is a map of western Pennsylvania showing the major anticlines and lineaments. Folds with over 800 feet of structural relief are outlined and stippled. Folds with 300 to 800 feet of structural relief are marked by showing the anticlinal axes. The plunge of these anticlines is denoted by arrows at the end of anticlinal axes. Structural lineaments are marked with broken lines. Apparently the crust has moved differentially along the lineaments as demonstrated by higher amplitude folds on one side of a lineament. Williams (1972, in press) has demonstrated that the folds were probably actively growing during Pennsylvanian sedimentation.

Meckel (1967) reconstructed the sedimentologic pattern for the Pottsville formation in western Pennsylvania. Figure 3 shows his reconstruction. This same general paleocurrent pattern persisted through lower Allegheny time. Sediments were shed from a tectonic highland to the southeast and a cratonic highland to the north. There were periodic marine invasions into the Appalachian basin from the southwest.
Figure 2. Tectonic map of western Pennsylvania. Adapted from Gwinn (1964).
Figure 3. Sedimentologic pattern in the lower Pennsylvanian Pottsville Formation. Taken from Meckel (1967).
The cross hatched area, which marks the approximate maximum extent of these marine invasions, also approximates the shape of the basin.

Underclays occur just below coals in repetitive sequences called cyclothems as described by Weller (1930), Wanless (1936). Many different types of cyclothems are recognized. In the Allegheny basin, the lower Kittanning is largely a transgressive coal, overlain by a brackish or marine shale over most of the basin area. Above this shale, the sediments usually show a gradual coarsening upwards. The stratigraphic column, shown in Figure 4, illustrates some of the variability in cyclothems.

The Pennsylvanian system of western Pennsylvania is divided into four stratigraphic units. From oldest to youngest, they are the Pottsville, Allegheny, Conemaugh, and Monogahela groups. Figure 4 is a generalized Pennsylvanian stratigraphic column from the Clearfield County area which was taken from Williams et. al. (1968). The lower coals are overlain by brackish and marine shales. The upper coals are overlain only by fresh water shales. This stratigraphic column partially demonstrates that during successive transgression, the sea generally covered less and less of the area of the basin.

Edmunds (1968) interpreted that cyclothems are caused by sea level changes and constructed the following genetic cycle. The sedimentary rocks of a cycle are
Figure 4. Stratigraphic column of the Pottsville and Allegheny series in Clearfield County. Taken from Williams et. al. (1968).
divided into five genetic groups. They are as follows:

5. Continental (fluvial-deltaic sediments).
4. Regressive swamp sediments.
3. Open water sediments.
2. Transgressive swamp sediments.

The numeric sequence represents their depositional order. The relationship of these genetic groups in cross section are shown in Figure 5.

In stage 1 of this figure, the backswamp sediments (Unit 1) are gleyed only under continental conditions. As sea level rises, Unit 1 is transgressed by a peat swamp which produces the overlying coal (Unit 2). Stage 2 shows that as sea level rises further, the coal is transgressed by open water sediments (Unit 3) which would usually be either brackish or marine muds.

Then as sea level begins to fall, as shown in stage 3 of Figure 5, regressive sediments, either coals or swamps sediments, are deposited over Unit 3. With further regression as shown in stage four, base level is considerably lowered and deep erosion and weathering is possible. Then, as sea level again rises, fluvial-deltaic (Unit 5) and backswamp (Unit 1) sediments are deposited as a consequence of the rising base level.

The results of the changing sea level model are shown in stage 5 of Figure 5. The model allows for a
Figure 5. Generalized simple transgression and regression of the sea and resulting sediment types. Taken from Edmunds (1968).
variety of relationships between the peat and the underlying sediments. Coals generally overlie the backswamp gleyed deposits called underclays (Unit 1). They can also overlie fluvial or deltaic sands (Unit 5). Although the sequence is orderly in Figure 5, it is also possible for the coal to overlie Unit 3. This could occur either through erosion or non-deposition of Units 4, 5 and 1 before the accumulation of swamp sediments.

Figures 6, 7, and 8 are genetic maps of a given area at various times through a cycle. Figure 6 shows the areal relationships of underclay (Unit 1), coal (Unit 2), and brackish or marine shale (Unit 3) during a transgressive phase. After a complete transgression of this area, sea level drops and Units 4 and 5 come to overlie Unit 3, as shown in Figure 7. The area is being eroded in the fluvial environments and the interfluvial environments are being eroded and weathered. Later in the cycle, with further regression, the area is composed entirely of fluvial and interfluvial environments, as shown in Figure 8.

Edmunds (1968) model calls for the deposition of backswamp deposits (Unit 1) before the next transgression. It is interpreted that in many cases the sea transgressed over Units 3, 4, or 5 in places where Unit 1 was not deposited. These sediments would possess the same megascopic appearance because they are subjected to the same soil process, gleying, in the backswamp environment.
Figure 6. Generalized map of environments of deposition during transgressive phase. Taken from Edmunds (1968).

Figure 7. Generalized map of environments of deposition during early regressive phase. Taken from Edmunds (1968).
Figure 8. Generalized map of environments during late regressive phase. Taken from Edmunds (1968).
History of Underclay Study

During the middle of the 19th century, two hypotheses were proposed to account for the origin of underclay, each consequent on hypotheses regarding the origin of coal (McMillan, 1956). The autochthonous (or in place) hypothesis of coal formation, which was first offered, holds that underclay is the fossil soil upon which the peat forming plants grew (Logan, 1942). The second, or allochthonous hypothesis, holds that an underclay is part of a normal sedimentary sequence, wherein the overlying coal, was rafted to its present location in the form of vegetable debris (Gresley, 1887).

Logan (1842) observed that Stigmaria, the roots of the extinct tree Lepidodendron, was present in the sediments underlying every coal seam that he observed. He considered this to be strong evidence for autochthonous hypothesis. Gresley (1887) was an early opponent of the fossil soil theory of underclay. The alternative, that at least some of the plant material was rafted in, is always possible. However, he could not present positive evidence for this and instead pointed out some of the weaknesses in the autochthonous hypothesis. He noted that there are Stigmarian clays without coal and noted that he never observed a Stigmaria to pass into a coal bed.
Neither of Gresley's arguments are convincing. It is certainly possible to oxidize the stem and leaves of plants without destroying the roots. This would produce a Stigmaria clay without an overlying coal. With regard to Gresley's second point, it is pointed out that coals are frequent glide planes in the folding and faulting of rocks. If a coal is displaced even slightly from its original position, possible connections between the Stigmaria and the coal would be broken. Moore (1940) observed upright tree trunks in coal beds which were rooted in the underclay. Based upon this and other relationships, he concluded that the autochthonous hypothesis was much more plausible.

Allen (1932) performed a petrologic and mineralogic study of some Pennsylvanian age underclays in Illinois. He found them to be mainly potash beidellite (illite) which he interpreted to have been purified before deposition. He found feldspars, muscovite, quartz and other minerals mixed with the clay, presumably during deposition in water. There was evidence of the removal of carbonates from the upper horizons through soil processes. The weathering profiles developed on the underclays resemble those on the Wisconsin till.

Grim and Allen (1938) did a further study of Pennsylvanian underclays in Illinois. They noted that the stratigraphically lower underclays contained no carbonates whereas the higher ones did. The same relationship
occurs in western Pennsylvania. They found no appreciable vertical variation in the six completely non-calcareous underclay profiles studied. They concluded that underclays had been subjected to little, if any, weathering.

Schultz (1958) studied the aerial and stratigraphic variability of Pennsylvanian underclays in the eastern United States. He noted that in several locations there was an apparent time gap between underclay formation and coal formation. Therefore, he concluded that underclays were not soils upon which the peat forming plants grew.

The writer takes issue with Schultz at this point. Just because some of the properties of underclays were acquired before peat accumulation, does not mean that they were not the soil upon which the peat forming plants grew. Schultz (1958) found that underclays from the central parts of geosynclinal basins differed from those of the shelf in that the former contain less kaolinite and more 14Å clay.

He also noticed that lower Pennsylvanian underclays were generally more kaolinitic than upper Pennsylvanian underclays.

McMillan (1956) was the first to clearly state that the process of underclay formation is analogous to the process which forms modern gleys. Briefly, the process involves the dissolution of iron in a sediment through the action of microorganisms. The process works best in soils that are generally wet but periodically aerated (Laughery, 1956). The removal of iron oxides produces the
gray color, iron mottles, and lack of bedding which is characteristic of both gleys and underclays.

Keller (1968) defined flint clay as a dominantly kaolinitic underclay which breaks with a conchoidal fracture and resists slaking in water. Flint clay is invariably associated with coal bearing measures. He interpreted that the gradual lateral variation in underclays from diaspore and flint clay to an illitic shale was caused by in place degradation of an original illitic parent material. He believed that the illitic parent material was de-potassified and recrystallized into kaolinite in low lying fresh water swamps. He inferred that the illite alteration process was accomplished by dialysis.

Williams et al. (1968) detected no significant weathering profiles in ten lower Pennsylvanian underclays of western Pennsylvania. They concluded that high alumina underclays are located predominantly in swampy areas on abandoned clastic wedges fringed by shallow seas. Like Keller (1968), they concluded that both stratigraphic and geographic variations in the clay mineral composition of underclays are largely controlled by the chemistry of the depositional environment. They felt that the variations in clay mineralogy in lower Allegheny underclays were caused by selective colloidal precipitation of clays and syngenetic removal of soluble bases and silica. Because no weathering profiles were detected, a mechanisms similar to Keller's (1968) dialysis is implied.
Method of Sampling and Analysis

The lower Kittanning underclay was sampled at 78 locations in western Pennsylvania and parts of Ohio and West Virginia. Figure 9 is a map showing these sample locations and the approximate outcrop limit of the lower Kittanning coal.

Each available foot of rock below the coal or coals was sampled, composing 471 lower Kittanning sub-samples. In addition to these, 30 Clarion, 26 middle Kittanning, and 19 Freeport sub-samples were collected. These were not mapped but were used to evaluate stratigraphic variability. Two different sizes of sub-samples were taken at each location. A one to eight pound sample was obtained uniformly from each foot to be made into test bricks. In addition to this, an approximately 30 gram sample was taken from each foot of outcrop below the coal by obtaining 12, approximately 2 1/2 gram pieces of rock from each foot. One piece was taken from each inch of that foot. If the clay did not outcrop it was sampled using a five-foot hand augur. The augur was raised after each foot, attempting to clean the hole as much as possible. If the sample was wet and stuck to the augur, a pinch of sample was obtained from each coil of the augur for the 30 gram sample. If the sample was dry, it was spread out and random pinches taken from the pile to make the 30 gram sample. The remainder of the sample was then bagged to be the test
Figure 9. Map showing lower Kittanning underclay sample locations.
brick sample. This procedure eliminates the need for later sample splitting.

Each 30 gram sample was then dried in a drying oven at 105°C for over four hours and ground to less than 50 microns by grinding for 60 seconds in a tungsten carbide "Bleuler" rotary mill. Samples were prepared for X-ray diffraction analysis by pressing the rock flour against a smooth surface and X-raying the smooth surface with a Norelco diffractometer. All samples were run on the same machine using CuKα radiation at machine settings of 40 kilovolts exciting potential and 16 milliamps current.

Of the 471 lower Kittanning sub samples, 172 were mounted using hand pressure of about 100 psi, and the remaining 299 were mounted by pressing with a hydraulic press, at 15,000 psi, a procedure first described by Hidalgo and Renton (1970). This procedure enhanced the 001 reflections by about three or four times over the lower pressure mounting method. The enhancement was accomplished by both increasing the density of the sample analyzed and by increasing the number of clay particles oriented parallel to the plane surface. The increase in preferred orientation was over 250 percent greater than the hand pressed pellets as measured by a comparison of the 001/020 ratios of kaolinite for the two methods used. Lithgow (1972) believed that the high pressure mounting method lowered the detection limit for 14Å minerals, which are often present in low abundance.
Quartz Estimation

Pressed powder mounting methods were chosen for this mineral because it has been shown that wet oriented mounting techniques usually greatly underestimate quartz due to differential settling (Gibbs, 1965, 1968). Gordon and Harris (1955) have shown that quartz gives a maximum diffraction intensity when the average particle size is between 2 and 30 microns. The standard grinding procedure, grinding 60 seconds in a "Bleuler" rotary mill, brings the mean particle size of quartz within this range.

A standard curve was constructed by mixing 5, 10, 15, 25, 50, 75% and 100% fine ground (2-5μ) quartz with a standard underclay. Four replicate mixtures were made for each percentage of quartz and their average was plotted on the curve. The points plotted very close to a straight line between the origin and the value for 100% quartz. After this, no further standard curves were constructed and it was assumed that the quantity of quartz in underclay samples is directly proportional to the area under the 4.27Å quartz peak using the formula:

\[
\% \text{ Quartz} = \frac{\text{Area under } 4.27\text{Å peak.}}{\text{Average area under } 4.27\text{Å peak for } 100\% \text{ quartz standard.}}
\]

This procedure is workable for lower Kittanning underclays because most underclays have generally low iron
contents, usually less than 4% Fe₂O₃. Iron's X-ray absorption edge in near the CuKα wavelength and when iron is present in greater amounts if significantly attenuates the peak intensities. The other major oxides present, Al₂O₃, K₂O, and MgO have mass absorption coefficients either identical with or very close to quartz and so have little effect on the analysis.

**Clay Mineral Identification**

The various types of clay minerals were identified by scanning the first order basal diffraction maxima from 0° to 14° 2θ. Of the 471 samples analyzed, 308 contained only 7 Å and 10 Å diffraction maxima. When this was the case, kaolinite and mica were identified and no additional treatment was performed. A possible error in identification might arise from the presence of a collapsed smectite or small amounts of random mixed layers giving a 10 Å diffraction maximum. Wyert (1968) in his studies of smectite found that the 10 Å basal spacing was only obtained when samples were equilibrated at relative humidities less than 10%. Above this humidity, a 12 Å or 14 Å maxima was present. All the samples for this study were equilibrated to a 65% relative humidity in an air conditioned room for several hours before X-ray analysis. It is doubtful that smectite could remain collapsed under these conditions.

If a 12 Å and/or a 14 Å maxima was present, the samples were saturated with ethylene glycol and the area between
$0^\circ$ and $7^\circ$ 2θ was scanned to determine whether or not the mineral expanded, and if so, to what extent. Then the samples were heated to 300°C for several hours and placed in a dessicator while awaiting X-ray analysis. Smectite was identified when the basal spacing expanded to $17\text{Å}$ upon glycolation and contracted to $10\text{Å}$ upon heating (Brindley, 1966). Vermiculite was identified when the basal spacing would either expand only slightly or not at all upon glycolation and only partially contract upon heating (Brown, 1953), (Hathaway, 1955). Chlorite was identified when a $14\text{Å}$ basal spacing neither expanded upon glycolation nor contracted upon heating (Brown, 1953), (Martin, 1955). Chlorite almost invariably showed a sharp diffraction maximum whereas montmorillonite and vermiculite invariably had broader peaks, which is partially a function of their smaller particle size.

No regular interstratified minerals were detected on any of the scans and of the few attempts made to determine the presence of random interstratified minerals by the presence of non-integral basal spacings, most were negative. For those samples with highly assymetrical peaks, the maximum was still at $10\text{Å}$. Several of these samples were glycolated, but no change in the shape of the peak was noticed. Therefore if random mixed (10Å + 14Å) layers are present, the mixed layers in these cases were not the common expanding variety.
Quantitative Clay Mineralogic Estimation

The relative concentration of clay minerals are proportional to the intensity of their X-ray diffraction maxima. For the minerals kaolinite, mica, vermiculite, and smectite, percentage abundance was found to be directly proportional to the 001 peak height for the respective minerals. Because the 002 maxima for smectite and vermiculite is very weak or absent, no correction was needed for the correct estimation of percent kaolinite. When chlorite was present, its abundance was found to be proportional to 1.70 times the 001 chlorite peak. The large 002 peak of chlorite coincides with the kaolinite 001 peak which necessitates a correction. Therefore, 1.70 times the chlorite 001 peak was subtracted from the intensity of the 7Å peak in order to estimate percent kaolinite.

When chlorite is absent, the calculation procedure is relatively simple. The data and steps in a calculation are shown below:

Data

Peak Heights

\[ {\text{14Å = 0.0 cm.}} \]

\[ {\text{10Å = 11.4 cm.}} \quad \text{percent quartz} = -26\% \]

\[ {\text{7Å = 5.2 cm.}} \quad \text{percent clay} = 74\% \]
Steps

1. Subtract the estimated percent quartz from 100% to obtain the total percent clay.
   \[ \text{percent quartz} = 100\% \]
   \[ \text{percent clay} = 26\% \]

2. Add the measured peak heights for kaolinite and mica.
   \[ \text{mica} = 11.4 \text{ cm.} \]
   \[ \text{kaolinite} = 5.2 \text{ cm.} \]
   \[ \text{total ht.} = 16.6 \text{ cm.} \]

3. Determine the factor of proportionality.
   \[ \frac{74\%}{16.6 \text{ cm.}} = 4.45\%/\text{cm.} \]

4. Multiply measured peak heights by the factor of proportionality to get percent clay minerals.
   \[ 11.4 \text{ cm.} \times 4.45\%/\text{cm.} = 50.7\% \]
   \[ 5.2 \text{ cm.} \times 4.45\%/\text{cm.} = 23.3\% \]

If vermiculite or smectite is present, their intensity is added in step 2. Their abundance is estimated by multiplying their peak height times the same proportionality factor used for kaolinite and mica.

If chlorite is present, a different calculation procedure is used. The data and steps of this procedure are shown below:
Data

Peak Heights

14Å = 4.1 cm.
10Å = 11.0 cm.
7Å = 9.8 cm.

percent quartz 100%
percent clay 74%

Steps

1. Multiply the 14Å peak by 1.70.
   4.1 cm. x 1.70 = 7.0 cm.

2. Subtract that height from the height of the 7Å peak
   9.8 cm. - 7.0 cm. = 2.8 cm.
   to obtain the kaolinite intensity.

3. Add the kaolinite, mica and chlorite peak heights.
   2.8 + 11.0 + 7.0 = 20.8

4. Determine factor of proportionality.
   \[ \frac{74\%}{20.8 \text{ cm.}} = 3.56 \]

5. Multiply peak heights by factor to get percent clay minerals.
   mica
   11.0 x 3.56 = 39.1%

   kaolinite
   2.8 x 3.56 = 10.0%

   chlorite
   7.0 x 3.56 = 24.9%
CHAPTER II  CORRELATION OF CERAMIC TO MINERALOGIC PROPERTIES
OF THE CLAYS, DISCUSSION AND INTERPRETATION.

Introduction

In order to predict the occurrence of underclays suitable for the manufacture of ladle bricks, one must first determine what properties of the raw material are critical to the performance of the bricks. These properties were heretofore largely unknown, and this knowledge is one of the principal goals of the research. At the outset, the only information available relating performance to raw materials in ladle bricks was that, when sulfur was added to the raw clay materials, a 2-3% increase in reheat expansion usually resulted. This, however, only occurs for bricks having more than 10% reheat expansion, and the larger problem still remains. What is the origin of reheat expansion?

Internal Structural Analysis

A microscopic analysis of thin sections cut from bricks burned for 80 hours at 1100°C, and similar bricks reheated to 1350°C for two hours revealed that the reheat expansion at 1350°C is accompanied by the presence of many trapped bubbles within the brick (Plate 1). It was believed that this phenomenon might be analogous to the bloating of lightweight aggregate which is partially
Plate 1. Photomicrograph showing the structure of a brick after being reheated to 1350°C for two hours. It showed a 15% lineal reheat expansion. The photomicrograph was taken using plain light and represents about 1.4 millimeters of width. Bricks which show a 15% reheat expansion commonly show this structure throughout.
controlled by chemistry, (Riley, 1951), and mineralogy (Lithgow, 1972). All of the possible gas sources mentioned for lightweight aggregate however, except the dissociation of Fe₂O₃, would have completely surrendered their gas below 1100°C. The slow rate of firing and long burning time for ladle bricks (80 hours) probably precludes any non-equilibrium trapping of gases evolved at lower temperatures. Although the two types of bloating are megascopically similar, the mechanisms for the formation and trapping of gas are probably different.

The burned bricks are chiefly composed of isotropic glass, quartz and mullite needles which are too small to be identified optically but were identified using X-ray diffraction. Hematite grains, probably formed by oxidation of pyrite found in the clay, are often found surrounded by air pockets in the reheated bricks. Therefore, the reduction of hematite probably accounts for some portion of the gases trapped.

Individual particles of crushed clay, from 2-5 millimeters in size, can still be discerned in the burned brick. They have a distinct preferred orientation, tending to parallel the pressing die used to fabricate the dry (about 5% water) clay into a brick. Bricks that met the 15% linear reheat expansion required by the industry had diffuse boundaries between particles which were filled with glass, as shown in Plate 2. In bricks that failed
Plate 2. Photomicrograph showing the structure of a brick which later showed a 15% reheat expansion. This brick was fired for 80 hours at 1100°C. The photomicrograph was taken using plain light and the width of the photomicrograph is about 1.4 millimeters. This brick has very few open pores.
to meet industrial specifications, the particles were bounded by long cracks which paralleled the surface of the particle as shown in Plate 3. These long cracks probably have a profound effect on the ability of the brick to trap gas. When present, they provide easy avenues of escape for any gas that might be generated.

Hutchison (1964) in a study of the effects of compaction pressure and water content on the bulk density and apparent porosity of bricks formed from a lower Kittanning underclay, concluded that most of the structure present in the burned test bricks was inherited from the raw clay particles. He concluded that his subsequent short firings (less than 8 hours) had little effect upon the original structure. Diamond (1971), also noted that clays compacted on the dry side of optimum moisture content (usually 14-30% H₂O), exhibited a domain structure with adjacent domains largely separated by micrometer-size interdomain voids; clays compacted at or above the optimum moisture content for a particular clay showed a more nearly massive structure. The more massive structures with lower apparent porosities are probably better for the trapping of gas in ladle bricks. Diamond (1970), also found that different clays consistently yielded different apparent porosities when compacted under similar conditions. Of the clays tested, Fithian illite, an Illinois underclay, yielded the lowest apparent porosity and Macon kaolinite,
Plate 3. Photomicrograph showing the structure of a brick burned at 1100°C for 80 hours which had less than a 15% lineal expansion upon reheating. The photomicrograph was taken using plain light and represents about 1.4 millimeters width. The grains are generally distinct from each other and long pores are preferentially located at these grain boundaries.
the highest. Therefore, the clay mineralogy of an underclay is probably one important variable controlling the apparent porosity of a ladle brick, both before and after it is burned for 80 hours.

The plasticity of a clay mixture is the likely avenue through which the clay mineralogy controls the porosity of clays compacted under similar conditions. Dumbleton and West (1966) have studied some of the factors affecting the relation between clay minerals and their plasticity. They found that kaolinite (Supreme Kaolin), has a plasticity less than half that of montmorillonite (Surrey finest). When quartz was added to clay mixtures, the decrease in plasticity was directly proportional to the percent quartz present. They concluded that quartz lowers plasticity by simply acting as a diluting agent in the plastic clay mixtures. They also found that silt-size mica reduced the plasticity of clay mixtures to a greater amount than quartz. Because high quartz content and coarser mica particle size commonly occur together, their separate, deleterious effects are generally combined in nature.

Dumbleton and West (1966) stated that the mineralogy and particle size of clay-quartz mixtures usually exert the controlling influence over plasticity. Sometimes, however, their influence is overridden by the presence of natural cements. This effect is also observed by brick manufacturers who find that hard clays and shales,
although sometimes mineralogically similar to soft clays, will not bond to form bricks.

The length of time and temperature at which a brick is fired are also important variables. Plate 4 shows a thin section of a test brick fired for 2 hours which does not bloat upon reheating to 1350°C. Notice the long cracks present at the grain boundaries. But this same brick changes its texture to one like that shown in Plate 2 after 80 hours firing at 1100°C, and is then a successful bloater.

During the time between 2 and 80 hours, the pore present in the short fired specimens are apparently gradually closed by a slight creep in the glass phase which is probably highly viscous at these temperatures (W. Wehl, personal communication, 1972). This is probably accompanied by an interdiffusion of ions across the old grain boundary. The viscous creep and ionic diffusion bond the grains to each other and thus reduce the apparent porosity. If firing procedures are kept somewhat constant, as has been done in the past, the changes that occur during this firing should again be primarily a function of the mineralogy of the clay.

Correlation of Mineralogic and Ceramic Properties

Table I is a correlation matrix containing the measured mineralogy of the raw materials used to make test bricks and the resulting ceramic properties. The matrix provides a good summary of the strong and weak
Plate 4. Photomicrograph showing the structure of a brick fired at 1100°C for 1 hour. When temperature was raised to 1350°C it showed a negligible reheat expansion. This brick also has many distinct grains and pores preferentially located on grain boundaries. However, when bricks made from this same clay were fired for 80 hours at 1100°C, they developed a structure similar to Plate 1 and showed a 15% lineal reheat expansion when reheated. This change in reheat expansion is largely attributed to the change in structure.

This photomicrograph was taken using plain light and represents about 1.4 millimeters width.
Table I: Correlation matrix between mineralogy of underclays and the ceramic properties of bricks formed from these underclays.

<table>
<thead>
<tr>
<th></th>
<th>MICA</th>
<th>KAOL</th>
<th>QUARTZ</th>
<th>%SHR</th>
<th>L.O.I.</th>
<th>POROS</th>
<th>DENS</th>
<th>LINREH</th>
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inter-relations among the variables. The second strongest correlation in the matrix is percent kaolinite (KAOL) to the logarithm of the loss on ignition (L.O.I.). Ideal kaolinite would have a 14.0% loss on ignition, mica 4.5%, and quartz 0% on ignition. Figure 10 shows a plot of percent kaolinite vs. log loss on ignition. They are proportional according to the equation:

\[ \log \text{L.O.I.} = 0.487 + (0.892 \times \% \text{KAOLINITE}) \]

with a regression coefficient of 0.88. This line extrapolates to 24.4% loss on ignition for pure kaolinite and 3.7% loss on ignition for 100% mica + quartz.

The measured loss on ignition for mica + quartz agrees with the theoretical loss of 4.5%, when one allows for the quartz impurities. But, the loss on ignition associated with these poorly crystallized kaolinites is 24.4% vs. 14.0% for ideal kaolinite. This extra 10.4 wt. percent loss is probably water partially bound between the layers. The other common possibilities for excess losses on ignition such as sulfides, sulfates, carbonates, and organic carbon, are present in only minor amounts. Thus, it would be possible for a company to roughly estimate percent kaolinite from the loss on ignition.

As shown in Table I, linear reheat expansion (LINREH) is negatively correlated to apparent porosity (POROS), with
Figure 10. Scatterplot of percent kaolinite vs. log loss on ignition.
a coefficient of -0.7275. Linear reheat expansion is positively correlated to bulk density of the burned bricks (DENS), with a correlation coefficient of 0.6597. Apparently, bricks with higher density have lower porosity and a greater reheat expansion. Figure 11 shows the quantitative relationship between linear reheat expansion and apparent porosity. The negative correlation is significant at the 99% Snedecor's F confidence interval. All samples which met industrial specifications had less than 10% porosity. Apparent porosity was measured by weighing the amount of water which can penetrate into a burned brick. Thus, apparent porosity is a direct measure of the number of open passageways through which gas might escape.

Also shown in Table 1, percent mica + vermiculite, labeled (MICA), is positively correlated to density (DENS) and linear reheat expansion (LINREH) and negatively correlated to porosity (POROS). Greater quantities of mica are probably helpful in forming more dense and less porous bricks. Therefore, bricks made from clays with higher mica content generally give a greater expansion upon reheating. A high pyrometric cone equivalence (P.C.E.) is important to the industry because more refractory bricks tend to last longer in use. Percent kaolinite (KAOL) has the highest positive correlation with (P.C.E.). It is probably advantageous to have as high a kaolinite content
Figure 11. Scatterplot of percent linear reheat expansion vs. percent apparent porosity.
as possible in a brick that still meets the reheat expansion requirements.

Brindley and Udagawa (1961), have measured the porosity of burned bricks made from mixtures of fine powdered kaolinite, mica, and quartz. These three minerals usually compose over 90% of the minerals present in lower Kittanning underclays. Their findings should closely approximate the ceramic behavior of a wide range of underclays. Figure 12 shows the relationship between the clay minerals and porosity of brick fired for 2 hours at 1100°C and 1200°C. This figure shows the same relationship as observed in the correlation matrix, (i.e.), low porosities are associated with high mica content. The samples with less than 10% porosity should have the highest probability of meeting the industrial, 15% linear reheat expansion requirements. The 10% porosity contour, for 1100°C, roughly coincides with mixtures containing over 30% mica and under 30% quartz.

Similar results were obtained using the 34 natural underclays as shown in Figure 13. Those burned bricks with less than 10% porosity could be separated from those with greater porosity by a line drawn at 37% mica content with 85% of the samples correctly classified. All of these low porosity samples had less than 31% quartz. Thus, there is substantial agreement between the findings of the two studies.
Figure 12. Apparent porosity of bricks fired for two hours at 1100°C plotted on the three phase diagram kaolinite-mica-quartz. Adapted from Brindley and Udagawa (1961).
Figure 13. Apparent porosity of bricks fired for 80 hours at 1100°C plotted on the lower half of the 3 phase diagram kaolinite-(mica + vermiculite)-quartz.
The samples that were incorrectly classified on Figure 13 are circled. They were investigated to determine what other factors might affect their ceramic behavior. Dumbleton and West (1966), noted that coarser particle size in mica caused unusually low plasticity. One of the two mis-classified, high mica clays had an unusually high apparent mica thickness. Perhaps this caused a higher porosity in the burned brick.

Two of the mis-classified, low mica clays had an unusually low apparent mica thickness. This probably caused them to have a higher than normal plasticity, partially because of the smaller particle size. Another contributing factor would be that any random mixed layers would also tend to increase plasticity.

Two of the five mis-classified samples cannot be explained by their apparent mica thickness. Undoubtedly there are other factors which affect apparent porosity and these remain for future study. The small number of mis-classified samples, however, makes it difficult to determine these factors.

Mica particle size is of secondary importance to its quantity in the manufacture of low porosity bricks, but, it could be important in certain cases. If given a choice of raw materials for ladle bricks, the finer particle size micas would be preferred. It might be possible to get slightly better refractory properties in bricks by
selecting higher kaolinite clays associated with finer particle size of micas or illites.

The same 37% mica discriminant line can separate with 85% reliability clays which meet industrial linear reheat expansion specifications from those that do not. As shown in Figure 14, three of the 5 mis-classified samples are the same ones that occurred in Figure 11. Therefore, the porosity of a burned brick is a slightly better predictor of reheat expansion then the mineralogy. On this diagram, most of the mis-classifications involve predicted bloaters that failed to bloat. The diagram is more reliable at predicting clays that will not bloat satisfactorily than it is at predicting those that will bloat well.

Although these relationships are not perfect, they are adequate to define a preferred mineralogy for ladle bricks which has a high probability of meeting industrial specifications. Figure 15 defines two areas on the three phase diagram, both of which must have over 37% mica. Ideal clays have less than 15% quartz, which has the deleterious effects of increasing porosity and also acts as an inert diluting agent decreasing the amounts of mica and kaolinite. More than 40% kaolinite is desirable in order to maintain refractory properties. Several Freeport underclays with less than 40% kaolinite bloated very well but failed to meet P.C.E. requirements. The second area of useable clays has higher allowable quartz contents and
Figure 14. Percent linear reheat expansion at 1350°C plotted on the lower half of the three phase diagram kaolinite-(mica + vermiculite)-quartz.
Figure 15. Diagram defining mineralogic areas on the three phase diagram kaolinite-mica-quartz which would produce satisfactory and optimum ladle bricks.
slightly lower allowable kaolinite contents. Both the ideal and useable clays have kaolinite (mica + vermiculite) ratios of about 1.0. These desirable clays could be prospected for by mapping the kaolinite/(mica + vermiculite) ratios and percent quartz of the underclays sampled.

Analysis of the Causes of Bloating

In order for bloating to occur, a gas phase must either be already present and trapped in the closed pores of the burned brick, or evolved by some chemical reaction near the time when the brick is at the proper viscosity. It is desirable that this proper viscosity be achieved as close as possible to 1350°C, the necessary reheating temperature. If bricks are too refractory and not viscous at that temperature, no bloating is possible. If the proper viscosity is reached well below 1350°C, the chances of meeting the P.C.E. requirement are decreased. The temperature interval between achieving the proper viscosity for bloating, and melting is relatively constant. W. O. Williamson (personal communication, 1972) surmised that the trapping of bubbles might temporarily increase viscosity, somewhat analogous to the viscosity change when one whips cream or egg whites. But, he would not speculate on the extent of this increase. If one only considers successful bricks, however, this factor should also be relatively constant.
Consider the first possibility, the expansion of already trapped gas. Gases trapped in a burned brick at 1100°C are probably at or near atmospheric pressure because any overpressure gas could probably escape this non-viscous brick. An ideal gas expands 1/273 for every degree centigrade increase if the pressure remains constant. Using the temperature difference of \((1350°C - 1100°C = 250°C)\), one could then write the equation:

\[
\text{volume of pores in burned brick} \times \frac{250°C}{273°C} = \text{volume of pores in reheated bricks.}
\]

The porosity of the brick shown in Plate 1 was measured by point counting, using 24 traverses of 79 points each. The measured porosity was 2.1%. If all of these pores were closed, the expansion of the trapped gasses could account for a 1.9% volumetric expansion. Any linear reheat expansion as a result of this volumetric expansion would probably be less than 1.5%. Obviously, the thermal expansion of previously trapped gases is inadequate to cause a 15% linear reheat expansion.

As shown in Figure 16, the unconfined volumetric reheat expansion of ladle bricks is related to the linear reheat expansion according to the formula:

\[
\log(\text{Volumetric Reheat Expansion}) = (0.0270 \times \text{Linear Reheat expansion}) + 1.375.
\]

for values between 7 and 22% linear reheat expansion.
Figure 16. Scatterplot of the log of percent volumetric reheat expansion vs. linear reheat expansion.
Below 7% the curve slopes down more steeply. Its intersection with either axis is uncertain because some non bloating bricks contract upon reheating. A 15% linear reheat expansion would imply a 337.5% volumetric reheat expansion if the expansion was isotropic. A 15% linear reheat expansion is correlated to a 154% volumetric reheat expansion. Apparently, the bricks expand preferentially parallel to the pressing dies according to the previous equation.

Microscopic observation of reheated bricks shows hundreds of times more pores than occur in burned bricks. Therefore, it seems likely that some reaction is taking place within the brick between 1100°C and 1350°C, which liberates tremendous volumes of gas.

Table II shows a gas analysis of a sample brick reheated at 1350°C in a carbon crucible under a high vacuum. A note was attached to the bottom of the analysis stating that any oxygen evolved from the brick would react with the crucible to form CO and CO₂. No carbon is detected in burned bricks so the gas phase is oxygen. Assuming a brick density of 2.00 grams/cc., this volume of gas is over 100 times the volume of the brick from which it came. Because the gas is oxygen, only oxygen releasing reactions need be considered.

Of the oxides present in the bricks, Fe₂O₃ is the only one which evolves a gas phase at these temperatures.
Table II: Vacuum fusion gas analysis for burned brick sample DH 15.

<table>
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<tr>
<th>Gas</th>
<th>c.c. of gas/gram of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>1.3</td>
</tr>
<tr>
<td>O</td>
<td>none</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.22</td>
</tr>
<tr>
<td>CO</td>
<td>50</td>
</tr>
<tr>
<td>H</td>
<td>none</td>
</tr>
<tr>
<td>SO₂</td>
<td>none</td>
</tr>
<tr>
<td>Methane</td>
<td>0.019</td>
</tr>
<tr>
<td>C₂–C₄</td>
<td>0.017</td>
</tr>
</tbody>
</table>
The gas evolving reaction, according to Muan and Osborne (1955), is:

\[
\text{Fe}_2\text{O}_3 \quad \xrightarrow{1350^\circ C} \quad \log pO_2=10^{-2} \quad \xrightarrow{} \quad 2\text{FeO} + \frac{1}{2}O_2
\]

The test sample analyzed contained 3.48% Fe$_2$O$_3$. According to the above reaction, this amount of Fe$_2$O$_3$ could produce about 140X the volume of the brick from which it came at 1350°C.

This reaction is an easily reversible one controlled by the equilibrium between Fe$_2$O$_3$ and the oxygen pressure at a given temperature. In test bricks, the reaction of Fe$_2$O$_3$ would tend to be buffered by the oxygen trapped around the mineral. In a ladle, or a carbon crucible, the log \( pO_2 \) is as low as \( 10^{-20} \). Under these low oxygen pressures, Fe$_2$O$_3$ would tend to be reduced to Fe° liberating much larger quantities of gas.

Hematite and silica glass are immiscible as long as the hematite is not reduced (Maun and Osborn, 1955). The color change, from buff to light gray, that accompanies the reheat expansion of ladle bricks, could be interpreted as the result of the reduction of hematite within the brick followed by the dissolution of the then colorless ferrous iron into the glass.
Another possible source for the oxygen generated is from within the major minerals. The $\text{Si}^{4+}$ ions in quartz is 4 coordinated to oxygen, both below and above 1350°C and is therefore an unlikely gas source. Kaolinite loses its hydroxyl water at about 600°C and shows an exothermic D.T.A. peak at 950°C, which is attributed to a change in the oxygen packing. Above 1000°C, more profound changes in oxygen packing can occur and mullite is formed (Grim, 1968, p.304). As previously mentioned, significant amounts of mullite are detected in the burned brick, and this mineral is stable to well above 1350°C. Kaolinite does not seem to be a promising prospect as a gas source.

Muscovite dehydrates in less than an hour at 1050°C, (Grim, 1968, p.304). Sudius and Bystrom (1953), studied the decomposition products of mica and found the muscovite-anhydride structure stable at temperatures between 1000°C and 1250°C. If some portion of the muscovite-anhydride structure survives the 80 hours at 1100°C, it could be a potential gas source. Aluminum is probably coordinated to 6 oxygen ions in the muscovite anhydride structure and is believed to be 4 coordinated in minerals and glasses stable at high temperature. This type of coordination change reaction would produce one mole of oxygen for every mole of Al that undergoes this transformation. A 100X sample volume of gas could be produced if 1.25 wt. percent
of Al in the bulk sample undergoes this change in Al-O coordination. Although no muscovite-anhydride was detected in the burned bricks, it could be present in small percentages or exist as small domains (<50Å) of 6 coordinated Al in the glass. This gas producing reaction would not be a direct function of the \(pO_2\).

The relationship of bloating to \(pO_2\), therefore, could provide a test to distinguish which of the two gas producing reactions predominates. If bloating is strongly \(pO_2\) dependent, \(Fe_2O_3\) reduction is the predominant reaction. If bloating is independent of \(pO_2\), changes in Al-O packing is the predominant reaction.

Brick manufacturers have observed that slightly greater reheat expansions occur when bricks are fired in reducing atmospheres, so that probably a significant portion of the gas results from hematite reduction. Although hematite grains in the bricks are surrounded by bubbles, there is no apparent correlation between percent \(Fe_2O_3\) and reheat expansion. This could be because 3.5% \(Fe_2O_3\) can produce 100 X the volume of the brick in gas. A brick need only trap 1.5% of this available gas to give a 15% reheat expansion. Therefore, the porosity of the brick is probably tens of times more important than the volume of gas available.

By comparison of these raw materials with other raw materials which also produce bloating ladle bricks, one
can elucidate the common factors and determine which are most important. The Japanese manufacture a bloating ladle brick using pyrophyllite. Like muscovite, its anhydride phase is stable to around 1000°C, and also like muscovite, it produces a highly viscous glass upon melting. This is partially because these two minerals are rich in silica and alumina, both of which have a high field strength. Both minerals have a low concentration (4%) of hydroxyl water in their lattice. When this water is lost upon heating, the mineral is not terribly out of charge balance and can survive as an anhydride to higher temperature. Kaolinite, although also composed of silica and alumina, has 14% hydroxyl water in its lattice. When this is lost upon heating, the ions must reorganize themselves quickly, in order to maintain close packing and charge balance.

Any trioctahedral clay mineral with large amounts of Fe²⁺, Mg²⁺, or other low field strength ions, would decompose at lower temperatures and produce a low viscosity glass upon melting. These would almost certainly not be useful for ladle bricks.

**Summary**

Figure 17 is a graphical summary of the interrelations that affect the properties of ladle bricks. Relationships controlled by the prior state of the material are drawn as solid black arrows, and relationships that can be controlled by man with dashed arrows. Independent
Figure 17: Schemata describing the inter-relations which control the achievement of industrially required properties for bloating ladle bricks.

KEY

Independent Variable =
Dependent Variable =
Relationship Controllable by man --- ➔
Relationship controlled by prior state of the material ➔
variables are underlined, and dependent variables are enclosed in boxes. The mineralogy of the raw materials and the presence or absence of cement are the two relevant variables describing the properties of the raw materials. Water content (added prior to pressing), pressure of pressing, and firing procedures can be modified by man. As shown by Hutchison (1964), and Diamond (1970, 1971), the water content and pressure of manufacture affect the porosity of manufacturer compacts. If one restricts himself to dry pressing techniques, which have proven to be most acceptable to the consumers, he has a very small degree of freedom within which to operate. The firing procedures must be tailored to develop a low porosity without destroying the gas producing phase; hence the ceramically unusual procedure of firing bricks for a long time (80 hours) at 1100°C. It is believed that if higher temperatures were used to get the low porosity more quickly, the gas producing reaction would occur prematurely and remove the possibility of a later reheat expansion.

The pyrometric cone equivalence can also be slightly affected by firing procedures, indicating that these probably affect the internal structure of the glass, which is presently not observable by any of our instruments. The mineralogy, however, exerts a much larger control over
P.C.E. The P.C.E. must be low enough to develop viscosity at 1350°C, but high enough not to melt before 1470°C.

If all of these variables are controlled in the appropriate way, a successful ladle brick will result. The variables which can be controlled by man should be directed toward achieving low porosity in the burned bricks. The variables which are a function of the raw materials, namely, mineralogy, particle size and natural cement, should be carefully monitored. These properties can vary considerably in alluvial deposits within tens of feet and, at present the only accurate monitoring tool is the X-ray diffractometer.

It is only through a detailed knowledge of the raw materials and a good theoretical knowledge of reheat expansion that one could make rational choices on how to modify pressing and firing procedures. The relationships presented in this chapter should give manufacturers a good start in this direction.
CHAPTER III  THE PREDICTION OF THE GEOGRAPHIC LOCATION OF LOWER KITTANNING UNDERCLAYS WHICH WOULD BE USEFUL FOR THE MANUFACTURE OF LADLE BRICKS.

Introduction

The purpose of this work is to geologically predict the occurrence of underclays which will exhibit a particular ceramic behavior. In Chapter I, the scheme for predicting the location of clays useful for ladle bricks was outlined. It was a circuitous path which involved the understanding of many aspects relevant to the problem. In this Chapter the relevant conclusions from the previous chapters will be summarized and synthesized into a rational predictive theory.

The first step was to determine what mineralogical or chemical factors influence the unusual ceramic behavior of ladle bricks. Manufactured bricks with low apparent porosities were much more successful at meeting the reheat expansion requirements. It was determined that bloating ladle bricks. Manufactured bricks with low apparent porosities were much more successful at meeting the reheat expansion requirements. It was determined that bloating ladle bricks which met the A.S.T.M. requirements usually contained over 37% mica + vermiculite. Quartz was
detrimental to the performance of ladle brick because it increased porosity. Over 35% kaolinite was required to meet the P.C.E. requirements. Decreasing quartz content and decreasing clay mineral particle size tends to increase the plasticity of the clay. Higher plasticity makes it easier to achieve low porosities.

The following conclusions were reached in the chapters of the dissertation. In Chapter III it was determined that the lower Kittanning micas had a similar chemical composition and mineralogy throughout the basin. Therefore, the above generalizations can be applied to any lower Kittanning underclay in the Appalachian basin. Nearly all of the mica in the basin is the 2M₁, high temperature polymorph. Normal geothermal gradients and the low rank coals present indicate a low temperature history for these sedimentary rocks. Therefore, all of the 2M₁ mica must have formed outside the basin. Areal variability cannot be explained by any mechanism which forms mica within the basin.

The vertical variability in underclays was examined and interpreted in Chapter IV. The underclay profiles are a mixture of continental alluvial deposits, and brackish or marine deposits. Over a third of these deposits have pronounced weathering profiles superimposed upon them. Previous workers detected no significant weathering profiles in the few underclays which they sampled.
Their theories as to underclaygenesis do not include any normal weathering mechanism. This work is a break from previous concepts with respect to weathering in underclays.

The areal variability of the lower Kittanning underclay was examined in Chapter V. The shape of the lower Kittanning basin was determined by Williams (1960) through a study of the fossils contained in the shale overlying the lower Kittanning coal. The shape of the kaolinite/mica contours in the lower Kittanning underclay conform closely to the shape of the basin. Higher average kaolinite contents were associated with documented paleotopographic highs. The more pronounced weathering profiles were also associated with these highs. Therefore, differential weathering was interpreted as the principal cause of areal variability.

In Chapter VI the inter-relationships between underclays and the rest of a sedimentary cycle were explored. The shape and distribution of favorable deposits is naturally a function of how they were deposited. The changing sea level model for the origin of cyclothem was a much stronger model. Therefore, prospecting should be better guided by this model, which was outlined by Edmunds (1968).

Each step in this procedure was taken to improve the quality of the prediction. Certain steps like the ceramic-mineralogic correlations, and the construction of
mineralogic maps were absolutely necessary. The other steps were taken to establish the most likely explanations of the causes of this variability. These are helpful at all levels of exploration from the contouring of a state map, the the mining of a deposit.

**Prediction of Favorable Ladle Brick Locations**

In order to geologically predict the location of underclays which would be favorable for the manufacture of ladle bricks, clay and quartz mineralogic maps must be integrated with the diagram defining the optimum mineralogy (Figure 15). Mineralogic maps and figures are plotted in slightly different terms, so the following discussion is presented to demonstrate how they can be integrated.

Figure 15 shows the three phase kaolinite- (mica + vermiculite) - quartz diagram which outlined the optimum and useful mineralogies for the manufacture of bloating ladle bricks. Any point on this three phase diagram can be uniquely described with two parameters. The two that can be most rationally mapped are the kaolinite/(mica + vermiculite) ratio and the percent quartz.

Figure 18 reveals the relevant topologic rules of a 3 phase diagram and how they can be used to outline favorable areas on a map. First, any straight line from the quartz apex to the opposite base line is a line which has a constant kaolinite/(mica + vermiculite) ratio. The three relevant kaolinite/(mica + vermiculite) contour lines
Figure 18. The kaolinite-quartz-(mica + vermiculite) three phase diagram showing the favorable mineralogic areas and topologic rules used for geologic prediction.
which are drawn on the map are $k/(m+v) = 0.88$, 1.00, and 1.50. Their relationship to the defined mineralogic areas are shown on the three phase diagram. An underclay with a kaolinite/(mica + vermiculite) ratio of 1.00 has a usable mineralogy if it contains less than 26% quartz. An underclay with a kaolinite/(mica + vermiculite) ratio of 1.50 has the proper mineralogy if it contains less than 7% quartz. No underclays had an average quartz content as low as 7%, so a kaolinite/(mica + vermiculite) ratio of 1.50 would generally be too high in kaolinite for ladle bricks. Therefore, the area near the kaolinite/(mica + vermiculite) ratio of 1.50 would generally be too high in kaolinite for ladle bricks. Therefore, the area near the 1.00 kaolinite/(mica + vermiculite) ratio lines on the mineralogic map are probably most favorable for future prospecting. Any deposit with a kaolinite/(mica + vermiculite) ratio less than 0.88 would fall outside the useable clay areas on the 3 phase diagram.

The horizontal line on Figure 18 is the 30% quartz line. Any samples with over 30% quartz would plot above this line and be undesirable for the manufacture of ladle bricks. The 30% quartz contour line on the prospecting map would have the same significance. Areas with an average quartz content over 30% would be generally unfavorable.
Figure 19 is a map of the lower Kittanning underclay showing the average kaolinite/(mica + vermiculite) contour lines and the 30% average quartz contour line. Areas where chlorite is found in the underclay are marked with "C"s. The areas which contain chlorite would be unacceptable for ladle bricks due to their high iron content. The areas which are considered to be favorable for ladle brick clay prospecting are marked with cross hatching on the map. The three locations which have produced usable ladle brick clay for Resco Products, Inc. are marked on the map with "X"s. These are contained within the favorable clay area. Areas where the specific samples taken met all of the mineralogic criteria for usable and optimum ladle brick clays are classified as highly favorable. These are marked with double cross hatching.

Because the average mineralogy of underclays is influenced by paleotopography, this can be used as a guide to prospecting where mineralogic analyses are absent. The first order of paleotopographic control, as defined by Williams (1972, in press), is the shape of the basin. The cross-hatched area conforms to the shape of the basin. In the western half, favorable areas are 10 to 20 miles from the basin margin. In the eastern half the favorable area extends to the basin margin in some places.

The second order of paleotopographic controls, defined by Williams (1972, in press), are the major folds and
Figure 19. Map of the kaolinite/mica ratio, and percent quartz in the lower Kittanning underclay which outlines the areas favorable for ladle brick prospecting.
lineaments. In the eastern portion of the basin, paleotopography is largely controlled by the existing folds. Areas where the folds have over 800 feet of structural relief are shown with inverted "V"s on Figure 2. Gwinn's (1964) map, shown as Figure 2 (Chapter I), or Williams' maps (1972, in press) would be helpful in the analysis of this paleotopography.

The growing anticlines were probably slight paleotopographic highs during lower Kittanning times. Their relative relief was probably on the order of 50 feet or less. The lineaments on Gwinn's map, (Figure 2), are interpreted as faults along which occurred differential movement of the crust. These probably also had some topographic expression during lower Kittanning time.

These second order, structurally controlled paleotopographic highs probably experienced better drainage than the surrounding lows. Consequently weathering rates were faster and kaolinite was enriched to a greater degree. The highest average kaolinite contents occur in the Allegheny mountain section. This is an area southwest of Altoona where the folds have over 800 feet of structural relief.

The third order of paleotopographic controls are the minor folds and faults. Laurel Hill anticline has from 300-800 feet of structural relief in Clearfield and Cambria counties. The position of this anticline is shown
on Figure 2. There is evidence for kaolinite enrichment at many locations on Laurel Hill anticline. Williams (1972, in press) has shown that portions of this anticline were probably paleotopographic highs during lower Kittanning time. However, there are several areas where samples overlying the anticline had low kaolinite contents.

The fourth order of paleotopographic controls are differential erosion and sedimentation. Under certain circumstances the effect of these controls can override the effects of the previously mentioned controls. Laurel Hill anticline was probably breached in several places by streams. These water gaps would be paleotopographic lows which overlie anticlines. The low kaolinite samples, which overlie Laurel Hill, are interpreted to be water gap deposits.

There is little structural relief in the western half of the Allegheny Plateau. In this region, the lower Kittanning topography was chiefly a result of prior sedimentation and compaction. The topographic expression of the Clarion age deltas was evident during the sedimentation of the Vanport limestone as shown by Ferm and Williams (1964). The lower Kittanning underclays which overlie these deltas contain well-developed weathering profiles. The 1.50 contour line on Figure 19 outlines these Clarion deltas in the western half of the basin. The map demonstrates the paleotopographic control over
weathering by the major features in the basin. This map can guide prospectors to favorable areas for ladle brick clays. The positions of anticlines, synclines, and major underlying sand bodies can usually be obtained from the geologic literature for a given area.

There is considerable mineralogic variability within the favorable area illustrated on Figure 19. Undoubtedly, there are many alluvial sand bodies which were not detected by the necessarily large sampling interval. Their high sand content would be unfavorable for the manufacture of ladle bricks. Several chloritic areas were found near favorable underclays on Figure 19. There may also be chloritic underclays within the favorable area which were not detected. One would also expect some mineralogic variability due to differential weathering within the favorable area. Therefore, one should not expect all of the samples within the favorable area to produce successful ladle bricks. The favorable area, however, has the highest probability of containing useable ladle brick clay.

The prospecting and development of ladle brick clays should be guided by precise mineralogic analyses and ceramic testing. It is not possible to make recommendations as to specific deposits without a much closer (approximately 100 foot) sampling interval. Any particular deposit should be sampled at such an interval before actual mining operations begin.
The mineralogic and ceramic properties of underclays on the small scale are also controlled by geologic factors. Several geologic rules are here presented in order to assist anyone constructing geologic maps of underclays on this scale. Because of the detrimental effect of quartz on ladle brick clays, it is important to know where quartz-rich (sandy) underclays occur. If a sandy underclay is found on a given property, its actual extent should be determined before mining operations begin. The first, and most important rule, is that a stream and its resulting sandy deposit is continuous from its source to its mouth. Therefore, if one sandy underclay is found on a property, it probably is continuous. These sandy deposits are termed "shoe-string sands" by the oil industry because of their linear winding geometry.

It was concluded that the mineralogy and other properties of underclays were developed principally during a regressive stage. The shore line, at this time, may have been in the area of West Virginia. The entire favorable mineralogic area was a continental area at this time. Edmunds' (1968) diagram, (Figure 8), shows the general paleotopography of the favorable area during a regressive phase. The sinuous streams shown in this diagram would produce sandy deposits. The general direction of these sandy deposits would be from the basin margin to its center. This direction would be approximately north-south along the northern margin of the
basin and southeast-northwest along the eastern margin of the basin.

Underclays deposited in the fluvial environment on Figure 8 should not possess weathering profiles. Underclay from the interfluvial environment probably contains weathering profiles and might contain a bulk mineralogy different from the fluvial environment. Clay mineralogic profiles must be obtained and mapped for a given property in order to delineate these environments. They should bear the same relationship to sandy deposits as is shown in Figure 8. The use of geologic rules should greatly facilitate the construction of geologic-mineralogic maps.

The second rule is that local paleotopographic highs are better drained than the nearby lows. In this sense, a small scale map should be similar to the map of Pennsylvania. Paleotopographic highs usually have higher kaolinite contents than the surrounding lows. The third and fourth order controls over paleotopography predominate on the local scale. These controls are minor structural features, such as folds and faults, and paleotopography resulting from differential erosion and sedimentation.

The structurally controlled paleotopography can be determined from the geologic maps for a particular area. Anticlines would probably be paleotopographic highs and synclines would be paleotopographic lows. Faults which were active during sedimentation would also affect paleotopography. On geologic maps, the sense of movement
is usually recorded on each fault. If a "U" is found along a fault trace, it indicates the side of the fault which moved up, relative to the other side. Each fault would have to be examined to determine whether or not it was active during sedimentation. If the coal thickness is the same on both sides of the fault, the fault probably occurred after sedimentation and thus would not affect paleotopography. However, if the coal thickness changes across the fault, it is probable that the upthrown side was a paleotopographic high during sedimentation.

Paleotopography resulting from differential sedimentation and compaction can usually be observed in the field. Where one can observe highs and lows in a coal bed, the present topography is usually similar to the paleotopography. Often the coals thin or disappear toward the highs and thicken in the lows. This is a manifestation of differing drainage conditions resulting from paleotopography. One would expect higher kaolinite contents to be associated with locally thinner coals. The properties of both coal and clay are controlled by paleotopography.

The above rules are intended only to assist the person constructing geologic-mineralogic maps. The rules do not specify what bulk mineralogy will be found in a given place. As in the case of the mineralogic map of the state of Pennsylvania, if a geologic-mineralogic
relationship is established, it can be used to improve the contouring on a mineralogic map.

The current industrial practice is to construct maps of ceramic properties for a particular deposit. These maps are useful, but are no substitute for geologic-mineralogic maps. The best properties to contour for prediction, are those which are directly controlled by the processes which caused them. The ceramic properties of percent reheat expansion, P.C.E., percent shrinkage, etc. result from the combined influence of mineralogy, iron content, and manufacturing procedures. These properties have little predictive power, particularly if the person interpreting them is unaware of any possible genetic connections.

Areas containing chlorite have been excluded from the favorable area for ladle brick clay prospecting. The presence of chlorite drastically lowers the P.C.E. of a deposit and the high iron content causes an unacceptable reddish color in the bricks. On the state map (Figure 19), chloritic underclays appear to occur in groups. If a chloritic underclay is discovered on a particular property, its extent should be determined and outlined. This clay would not be useable for ladle bricks.

Mining Recommendations

The geologic-mineralogic maps should be used to guide mining procedures. Their use could insure better quality control over the raw materials entering a plant. Presently
clay and coal are mined in the same way. The assumption is that both coal and clay are uniform laterally. Therefore, mining methods are directed solely toward convenience in the handling of overburden.

In addition to this, mining methods should be directed toward providing uniform raw materials to the consumer. If there is a lower Kittanning paleostream deposit nearby, cuts should be planned to avoid these sandy areas. Cuts taken parallel to a paleostream deposit should provide more uniform material than those taken perpendicular to it. If a chloritic underclay area has been outlined, cuts taken parallel to this boundary would also tend to provide more uniform raw materials. If the person producing a particular deposit is aware of the variability in an underclay, he can design a mutually satisfactory mining method. He could probably satisfy the consumer's need for uniform raw materials as well as his own need to efficiently handle overburden.

**Other Potential Uses of Mineralogic Maps**

The map, shown as Figure 19, could also be used to prospect for other industrial raw materials. All the flint clays sampled were associated with known paleo-topographic highs. It was interpreted that flint clay formed from the diagenetic re-silication of gibbsite. The gibbsite is concentrated through in place weathering mechanisms. Thus, residual flint clays would form preferentially in well drained sites. Paleotopographic
highs around the basin margin have the highest probability of containing flint clay.

The manufacturers of face brick and sewer pipe could also use the map shown as Figure 19. The manufacturers of face bricks are interested in lower P.C.E raw materials which will produce bricks of a uniform color. The color of the burned bricks is principally a function of the total iron content. Thus, the face brick manufacturer is interested in the drainage of the underclays. He is searching for a weathered, high-mica underclay which is free from chlorite. Several of these areas were outlined on Figure 19.

The high-mica underclays are usually no more than slightly weathered. Most of these were probably poorly drained and thus may contain abundant iron. The lower part of high-mica profiles are occasionally reddish in color. The person producing underclay for face bricks should avoid taking any reddish colored underclay. Reddish underclay would probably produce reddish bricks, that would probably not match the color of other bricks. Sometimes, high-mica profiles have high iron content in their lower parts with no reddish color present. A conservative way of mining such a deposit would be to mine only the upper 3 or 4 feet. This procedure would probably save the manufacturer the cost of many discolored bricks.
The manufacturers of sewer pipe commonly use a mixture of underclay and shale as raw materials. The underclay is needed as a bonding material to hold shale particles together. Most underclays have sufficient plasticity to bond these particles. However, if the manufacturers are interested in high plasticity, the high-mica clays should be most useful for this purpose. For maximum plasticity, small "apparent mica thickness" and low quartz content should be sought out. The sewer pipe manufacturers are not concerned with the burned color of the underclay because the iron in the shale already imparts a reddish color to this ware.

The cat clay deposits, with yellow mottles and basic ferrous sulfate streaks, had the highest apparent plasticity observed in the field. These underclays would probably be best for any industrial process requiring high plasticity, if the color of the finished ware is unimportant. The Freeport underclays have, on the average, high mica contents and high plasticity. However, care must be taken to avoid mining the iron nodules often found in Freeport underclays. One possible method of avoiding these nodules would be to mine these underclays on the local paleotopographic highs where drainage was slightly better than in the adjacent lows.
Conclusions

The important conclusions or contributions of this work occur in the area of geology, ceramic technology, and the prospecting and development of underclays.

1. It was concluded that over a third of the underclay profiles sampled had been significantly weathered. This finding is in contrast to the conclusions of all previous underclay workers who found no evidence for kaolinite enrichment.

2. The average age of the 20 weathered profiles was estimated using Hensel and White's (1963) weathering rate. They found that 0.1% $K_2O$ was lost from the top 6" of gumbotil soils per 1000 years. The average estimated age of the lower Kittanning underclay weathering profiles was 20,400 years. The greatest estimated age was 35,900 years.

3. The clay mineralogic pattern of the lower Kittanning underclay is similar to the pattern revealed by the fauna in the overlying shale. Both patterns indicate the shape of the basin during this time. High kaolinite contents are closely associated with documented paleotopographic highs. The most pronounced weathering profiles are also associated with paleotopographic highs. It was concluded that the areal variability in the lower Kittanning underclay was caused by differential weathering, which was controlled by paleotopography. This conclusion
contrasts with those of previous underclay workers who used differential flocculation, changing source areas, authigenesis, dialysis, and the chemical properties of the depositional environments to explain areal variability.

4. The evidence as to sea level changes during the Pennsylvanian has been largely interpretive. Therefore, the origin of cyclothems is still controversial. The currently popular, constant sea level model allows an underclay to be weathered during the interval between deltaic deposition and subsidence below sea level. This interval is typically several hundred to a few thousand years. The lower Kittanning weathering profiles suggest that these underclays were weathered for a much longer time interval. This evidence weighs in favor of a changing sea level model for the origin of cyclothems.

5. The phenomenon of reheat expansion is caused by the trapping of gaseous oxygen bubbles in ladle bricks. The required volume of gas could only be released through a chemical reaction which occurs between 1100°C and 1350°C. The dissociation of Fe₂O₃, and the mica-anhydride→mullite reaction are the only oxygen releasing reactions known at these temperatures.

The ability of a brick to trap gas is inversely proportional to its porosity. Only bricks with less than 10% porosity met the 15% linear reheat expansion requirements. Underclays with over 37% (mica +
vermiculite), less than 30% quartz, and over 35% kaolinite produced bricks which usually met industrial requirements. The 37% mica criteria was 85% reliable in separating bricks with over 15% linear reheat expansion from those which failed to meet industrial specifications. This mineralogic control over ceramic properties allows a mineralogic-geologic prospecting technique.

6. The mineralogy of an underclay is chiefly controlled by geologic events during the regressive phase of a cycle. Favorable areas for ladle brick clay prospecting were outlined on a lower Kittanning mineralogic map. Geologic interpretations of the variability within favorable areas were presented to be of further assistance to the underclay prospector. The geologically observable parameters were presented in terms of their inferred ceramic consequences. These should benefit all underclay consumers from the manufacturers of super duty refractories to those manufacturing sewer tile. The application of this knowledge should improve the efficiency of any manufacturing process involving underclays and thus be an economic benefit to the manufacturer. This should ultimately result in greater economic and social benefits for the state and country.
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