NORTH DAKOTA GEOLOGICAL SURVEY

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INVESTIGATION OF SOME NORTH DAKOTA CLAYS AND SHALES

by

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ABSTRACT

In recent years there has been very little research done to promote the use of clays and shales of North Dakota in additional ceramic industries. A long range program has now been started and the results of a preliminary investigation have been included in this report. It will serve as a general survey of the unfired and fired properties of clays and shales from various outsrops and commercial deposits in North Dakota. The data collected during this investigation will form the basis for more thorough investigatigation of the most promising samples from the viewpoint of production of ceramic products which at present are not manufactured in the state.

The twenty samples tested were gathered from various outcrops and from some commercial deposits in North Dakota. The tests performed were as follows: screen analyses with microscopic examination of the screen fractions by the use of a petrographic microscope; determination of linear drying shrinkage and water of plasticity from hand-made specimens; slaking test of dried specimens; and determination of fired linear shrinkage as well as apparent porosity and water absorption of specimens fired at Cones 015,01,3,7,8 (salt glaze) and 12 in various commercial kilns.

Since proper equipment for high temperatures was not available at the university at the time of this investigation, some of the trial specimens were sent to commercial ceramic plants in Canada. At the Medicine Hat Potteries in Medicine Hat, Alberta, samples were fired to cones 3 and 7 in a natural gas-fired, circular tunnel kiln; at the National procelain plant in Medicine Hat, samples were fired to cone 12 in a gas fired, rectangular kiln; and at the Alberta Clay Products plant in Medicine Hat, samples were fired to cone 8 in a round, down-draft, gas fired, sewer pipe kiln.

Samples were fired to cones 015 and 01 in the low temperature kilns of the ceramic department at the University of North Dakota. These are fired with a mixture of kerosene and distillate.

INTRODUCTION

"A clay (3) is an earthy material resulting from the decomposition of rocks, chiefly feldspar rocks, and containing hydrated alumina silicates. It usually becomes plastic when wet and will form a hard, rock-like mass when heated to a high temperature. Since it is the decomposition product of a rock, it contains a mixture of the residual minerals formed during decomposition. Most clays contain a rather large percentage of particles small enough to have colloidal properties. A clay does not have a definite chemical composition but it is a very fine grained mixture of mineral fragments. All clays contain hydrated alumina silicates and in most clays, the mineral kaolinite has been identified."

Granite is a common type of rock composed of quartz and feldspar. Mica and other minerals may be found in granite as minor constituents called accessory minerals. The chemical formulas for quartz, feldspar and mica will be considered as follows for this report: Quartz- SiO_2; Feldspare - $K_2O.Al_2O_3.6SiO_2$; Mica (Muscovite) - $K_2O.3Al_2O_3.6SiO_2.2H_2O$.

Quartz is highly resistant to any alteration by mechanical or chemical means and the mica usually remains unaltered. Feldspar, however, after the granite has been weathered by the action of water, wind or ice, is easily attacked and altered to kaolin (clay substance) as shown by the following molecular equation as given by Worcester (4): $K_2O.Al_2O_3.6SiO_2$ (feldspar) plus weathering plus H_2O (water) plus carbon dioxide (CO_2) equals $Al_2O_3.2SiO_2.2H_2O$ (kaolinite) plus $4SiO_2$ (silica) plus K_2CO_3 (potassium carbonate).

In most instances the kaolin is colored by the presence of some impurity in the original clay forming rock such as titanium and iron compounds. The resulting fired color causing by impurities often determines the use for which a clay is suitable.

If the kaolin remains in place associated with the parent rock and with quartz, mica and other impurities, it is classified as a residual or primary clay or kaolin. The action of rivers and other moving bodies of water has in most cases carried away those materials which are of small enough particle size to keep in suspension. Changes in velosity of the water have resulted in formation of beds or layers consisting of different sized particles. The finest particles have been deposited in the quiet waters of lakes and oceans and are classified as lake and marine deposits.

The secondary clays resulting from transportation of the residual clays are not only sorted into different particle sizes but undergo other changes. There has been reduction in particle size by abrasion, addition or removal of impurities, oxidation, hydration, and physical changes resulting from intermixing or removal of sands, rock dust or organic material. Eventually most of these secondary or sedimentary clays were consolidated into laminated beds called shale by the pressure of subsequent deposits. These shales are usually quite hard but when crushed and mixed with water they become workable and form the raw material for a great variety of ceramic products.

The action of retreating glaciers has produced surface deposits of clay containing large amounts of pulverized rock flour and often many pebbles and stones. These are the poorest types of clays and are used chiefly in the manufacture of common brick.

Beds of wind blown clay, known as loess, are used to a small extent in the manufacture of common brick and other red-burning ware.

Most clays - whether primary or secondary - contain the admixtures quartz, mica, feldspar and other impurities, so in general when speaking of clay, we refer to a mixture of clay with other materials.

GEOLOGICAL OCCURENCE OF NORTH DAKOTA CLAYS AND SHALES

The clays of North Dakota occur in the Pleistocene, Tertiary, and Cretaceous formations. Baboock and Clapp (1) state that there is a transition period between the Tertiary and Cretaceous called the Laramie, but these beds are now (5) referred to the Fort Union (Tongue River) of the Tertiary period and to the Hell Creek of the Cretaceous period.

In former years, some of the best clays utilized were those deposited in old glacial lakes similar to Lake Agassiz. Good common brick clays are found as the alluvium of the flood plains and terraces of some of the rivers. Underlying the east central part of the state in a north-south belt are Cretaceous clays of the Benton, Niobrara and Pierrie beds. They are covered with a deep layer of drift but the Benton and Niobrara are exposed in the valleys of rivers in the Pembina Mountrains and the Pierre which lies above the Benton and Niobrara is exposed in the cut banks of the Pembina, Sheyenne and James Rivers.

The western half of the state is directly underlain by coal bearing beds. (1) These are referred largely to the Fort Union group and consist chiefly of sands and clay. They are also covered by drift, except in the south-western quarter of the state. However, there are numerous outcrops exposed in valleys and buttes.

Babcock and Clapp (2) state that the Benton, Niobrara and Pierre beds are marine shale and that the clays in the western half of the state, occurring with lignite, are lake deposits. They also claim that there are no residual clays as well as no loess deposits in the state.

LOCATION OF VARIOUS OUTCROPS AND DEPOSITS OF CLAY AND SHALE

SAMPLE NO.	LOCATION
52-1	T.148 N.,R.99 W., Section 27. Outcrop of Blue shale in North Roosevelt Park, 0.7 miles north of the entrance, adjacent to Highway #85 and on the east side of the road. There is 20 feet of the blue shale exposed, with 5 feet of carbonaceous shale above.
52-2 & 52-3	T. 138 N., R 98 W., Section 23. A small outcrop in the Little Bad Lands near Dickinson. The outcrop is 15 feet high with 12 feet of gray,

52-11 T. 140 N., R. 96 W., Section 25. An exposure of gray plastic clay on the west side of Davis Butte, 3 miles north and 3 miles east of Dickinson.

52-12 & 52-13 T. 140 N., R. 90 W., Section 11. Hebron Brick Plant deposits. Samples 52-12 and 52-13 are from a new pit situated 7 miles north and 1 mile east of Hebron. No. 52-12 is from a 5 ft. seam of dark gray clay with 10 ft. of hard, dark gray clay and 10 feet of overburden above. No. 52-13 is from a grayish white seam below the dark gray seam from which 52-12 was taken.

52-14 & 52-15 Samples 52-14 and 52-15 are from the older workings 1 mile S. E. of the new pit. No. 52-14 is exposed in numerous places and is very similar to sample No. 52-10. No. 52-15 is exposed in one place on the west side of the pit in a 3 foot seam of light gray clay.

52-16 T. 139 N., R. 81 W., Section 32. A 5 feet. seam of gray stoneware clay situated 6 miles west of Mandan and ¼ mile north of No. 10 Highway. It is exposed on the west side of a hill.

52-17 & 52-18 T. 139 N., R. 81 W., Section 32. Cannonball Marine shale exposed in a cut west of Mandan and south of the No. 10 Highway and the railroad. Sample 52-17 is from a seam of 10 feet of dark green the surface. A typical whiteware porcelain mixture is as follows:

Kaolin	40%
Ball Clay	10%
Flint	20%
Feldspar	30%

A whiteware clay must burn white or nearly so. The whitest burning clays are the kaolins associated with quartz and mica impurities which are often removed by washing to obtain a pure china-clay. The plasticity of kaolins varies from the slightly-plastic, residual kaolins to the quite plastic, finer-grained secondary kaolins. The dry transverse strength varies as the plasticity. Kaolins are essentially pure kaolinite and are the most refractory of all clays. Whiteware mixes are compounded with a kaolin base to give the desired whiteness. The vitrification range of kaolin is very gradual so feldspar is added to the whiteware mix to produce a dense, translucent piece at lower temperatures.

However, this produces a very fluid mixture at the maturing temperature, so quartz in the form of flint is added to increase the viscosity and thus prevent sagging or warping. Since feldspar and quartz are non-plastic and most kaolins only slightly plastic, ball clays are added to give a workable mix.

In contrast with kaolins, ball clays are very sticky, plastic, fine-grained, and have high dry and bonding strengths. They usually contain more impurities and often fire to a light-cream color. The vitrification range for ball clays is very long and the fired porosity quite low.

2. Refractory Clays. Any test cone made of a refractory clay must not soften or deform at a temperature lower than cone 19, Although ball clays and kaolins can be properly classified as refractory clays, they have been classified separately because of their fired color. The remaining clays

belonging to the refractory group are fire clays, refractory bond clays, and sagger clays.

Fire clays range in plasticity from the clightly plastic, flintlike clays to the very plastic, high strength clays. The service conditions for fire brick and other psecial shapes made from fire clays will in some instances require high temperature resistant materials while in other cases a material of considerable mechanical strength is required. The highest grade fire clays do not deform below a temperature of cone 31. Some of the fire clays with low deformation temperatures are often used in the manufacture of face brick, stoneware and sewer tile.

Refractory bond clays are highly plastic, with exceptional bonding power which is manifested by the coating of the non-plastic materials like flint, grog and graphite which are used in refractory mixes. These clays find application in the manufacturing of glass melting pots, clay crucibles, zinc retorts, etc. and consequently must be highly refractory.

Some refractory clays are used to make saggers to protect ceramic ware from flame, smoke and fly-ash in a kiln. Saggers are open type boxes, which are filled with ware and then stacked one above each other in the kiln. In general, a sagger clay is quite plastic and a good bonding clay but the main requirement is a minimum of deformation under load and temperature, with low coefficient of expansion.

3. Pottery Clays. A pottery clay refers to any clay used in the manufacture of stoneware, some earthenware, art ware, garden pottery and flower pots. In contrast with whiteware bodies, these products have a dark cream, gray or red fired color and in most cases only clay is used with no addition of non-plastics like flint and feldspar.

Clays suitable for stoneware, earthenware and art ware should be highly plastic and have high dry strength. A total shrinkage of 12% at cone 8 is permissible but it is more important that there be a minimum of warping and twisting while being fired. The fired color varies from light cream to buff when soft burned to light gray when well vitrified. To produce the desired color they should be as free from iron as possible as well as lime and other salts.

Red burning clays used for garden pottery and flower pots should have good plasticity and fairly low shrinkage and warpage.

4. Sewer-Pipe Clay. Clays used for sewer pipe, paving brick and roofing tile are similar to the pottery clays. Clays or shale used for sewer pipe should be quite plastic, very tough and have high dry strength, with low drying shrinkage. Iron in finely divided state is desirable to produce a deep mahogany colored salt glaze. The glaze is usually obtained by the addition of common salt, which is introduced into the kiln with the fuel. It vaporizes and reacts with the clay to form the glaze.

Recently, several plants have begun to spray compounded glazes on the pipe prior to firing and in time will probably replace salt glazing. It is essential that there be no scum forming salts present in the clay to interfere with the formation of salt glaze or the application of compounded glazes. There should be sufficient fluxes present to produce a dense body of low porosity and of high fired strength. Low grade fire clays, stoneware clays and shales are used alone or as mixtures to obtain the desired properties for good sewer pipe.

Paving brick clays are similar to sewer pipe clays and must fire to a dense, tough body. Most paving brick clays are red firing but some buff firing clays are used. The fired color of roofing tile clays or shale is of the greatest importance. They must be plastic and tough when wet and hard and strong when dry.

5. Brick Clays. A modern classification of brick clays should distinquish between common brick and face brick clays.

Any clay or shale which is plastic enough to be shaped and will burn hard and strong at low temperatures is suitable for common brick. They are usually high in iron or lime content but this is only of secondary importance since the vitrification range and color may vary considerably. Surface clays or soft shales are commonly used for common brick to be used for backing up face brick, stone or plaster.

A clay or shale suitable for face brick must produce a hard, pleasing surface which is durable under all conditions of atmosphere and climate. Red burning surface clays and some red burning shales are suitable for face brick as well as semi-refractory buff or almost white burning clays. Face brick must have low drying and firing shrinkage and a minimum of warpage and must fire to a hard, strong, dense body.

Drain tile clays and shales are similar to common brick clays.

EXPERIMENTAL PROCEDURE

Field Methods

The sampling of the various outcrops and commercial deposits was done during the latter part of November, 1952. Four days were spent in the field while sampling the nineteen clays and shales included in this report. Sample 52-20 was obtained from the assistant Geologist of the Great Northern Railroad. Samples averaging twenty-five pounds each were taken and numbered with the refix 52 to denote the year and with numbers 1 to 19 for the individual samples.

Laboratory Methods

It is necessary to perform several tests on both unfired and fired samples to enable one to determine how useful the clays and shales will be as ceramic raw materials.

The samples, as received from the field, should be visually inspected and a record made of the color, structure, hardness, texture and any visible impurities. A screen analysis is very helpful and a dried portion of the sample is allowed to slacken in water for several days if necessary, prior to running the screen analyisi. Usually, screens with less than 200 meshes per square inch are used and the fractions caught on the various screens are dried, weighed and examined with a petrographic microscope.

To determine numerous other unfired properties and some fired properties, it is necessary to mold small trial pieces. Before these are made, the samples should be crushed if necessary and then ground to finer than 20 mesh sizing. Sufficient water is mixed with a portion of the ground material to produce the best working consistency and after aging and thorough wedging, the trial pieces are molded. It is possible to determine water of plasticity, linear drying and firing shrinkage, slaking characteristics, fired color, fired apparent porosity and water absorption, using only a few trial pieces of suitable dimensions. An apparatus for determining the transverse strength of dried trial pieces is necessary for any large scale clay research program.

Since the fired properties are of utmost importance, it is necessary to fire trial pieces at intervals of 2 cones from the start of insipient vitrification to overfiring, or if the clay is too refractory, to at least cone 14. When dealing with refractory clays, it is necessary to determine the pyrometric cone equivalent of test cones so as to properly classify the clay.

Although the tests which have been briefly outlined here would be sufficient for determining the ceramic value of clays, a more conclusive evaluation would be possible if chemical analyses, differential thermal analyses, and determinations of particles finer than 200 mesh, were performed.

The investigation of the 20 clays and shales included in this report was done in the shortest time possible and with the use of limited facilities, so as to obtain a general picture of the clays and shales of North Dakota.

Of the following pages is an outline of the laboratory procedure followed while testing the clays and shales included in this report.

1. The clay and shale samples were crushed in a Sturtevant fine crusher and then ground to finer than 20 mesh material in a Denver Fire Clay disc pulverizer. During the crushing operation, samples of the uncrushed material were taken for visual inspection and for the screen analyses.

2. Dried 25 gram samples of the uncrushed material were allowed to slacken in water for at least 24 hours prior to running the screen analyses. After thorough washing of the finer than 200 mesh material through a series of screens (Tyler Standard Screens Nos. 35, 65, 100, 150 and 200) the various screen fractions were dried, weighed and examined with a petrographic microscope.

3. In preparation for the making of trial pieces, ten pound samples were mixed with sufficient water to give the best working consistency. After 24 hours aging in a damp box, the batches were wedged by hand in a manner similar to kneading the bread dough to remove most of the air pockets and to have the material thoroughly mixed with the water.

4. Twelve trail pieces for each sample, with original dimensions of 4 5/8" x2"x5/8", were made in a steel mold. Blanks cut from the wedged material were forced into the mold by hand pressure, the excess cut off with a wire and the surface slicked off with a spatula. A manually operated plunger permitted easy removal of the trial pieces from the mold. Shrinkage marks 10

centimeters apart were placed on eack trial piece and the weights of three trial pieces for each sample were recorded.

5. After drying at room temperature, the trial pieces were dried in a thermostatically controlled electric drier at 210° to 230° F. The dried trial pieces were measured for linear shrinkage and the weights recorded.

6. For the slaking test, standard Tyler screens of 8" diameter and with .72 inch openings were inverted and placed in water contained in large pans so that the screen surfaces were one inch below the water level. Two trial pieces were laid flat on each screen surface and the time required for the trial pieces to slake and fall through the screen was recorded.

7. Since a proper furnace was not available at the University of North Dakota for firing samples at intervals of two cones to a maximum of cone 12 or 14, it was necessary to fire some of the trial pieces in large commercial kilns. The kilns at the University of North Dakota were suitable for the lower temperatures, but since most of the samples included in this report are quite refractory, trial pieces were only fired to cones 015 and 01 at the University. Other trial pieces were sent to plants at Medicine Hat, Alberta, Canada.

At the Medicine Hat Potteries, a tunnel kiln for firing whiteware was available for firing to cones 3 and 7; at the Alberta Clay Products. Co. Ltd. plant trial pieces were fired to cone 8 in a sewer pipe kiln with salt glazing; at the National Porcelain plant a temperature of cone 12 was reached in an electrical porcelain kiln.

7. After firing, a record was made of the fired shrinkage, color, and other visible characteristics. The dried fired weights were determined and after immersion of the trial pieces in boiling water for two hours, they were weighed suspended in water and then wiped lightly with a damp paper towel

and weighed in air. The apparent porosity and water absorption values were calculated and a graph appearing in Figure 2, page 18A was plotted, showing porosity and fired shrinkage values against cone temperautres.

FORMULAS FOR CALCULATIONS

1. The linear drying shrinkage is expressed as a percentage of original length of the freshly molded trial pieces by subtracting the length in millimeters of the distance between the shrinkage marks on the dried trial pieces from the original distance of 100 millimeters.

2. The percentage water of plasticity is calculated from the formula

$$\frac{\text{Wt. of freshly molded trial piece -- wt. of fried trial piece}}{\text{Wt. of dried trial piece}} \times 100$$

3. The percentage linear fired shrinkage is determined by subtracting the length in millimeters of the distance between the shrinkage marks on the fired trial pieces from the length in millimeters of the distance on the dried trial pieces.

4. The apparent porosity is calculated from the formula

$$\text{Percentage apparent porosity} = \frac{W-D}{V} \times 100$$

where

W is saturated wt. in grams of the fired trial piece

D is the dried fired wt. of the trial piece

V is the volume of the trial piece in cubic centimeters

The volume is calculated from $V = W - S$, where W is the saturated wt. and S is the suspended wt.

5. The water absorption values are calculated from $\frac{W-D}{D} \times 100$

OBSERVATIONS AND DISCUSSION

Fortunately, the samples of clay and shale can be grouped into four main divisions with the members of each respective group having quite similar unfired and fired characteristics. These groups will be discussed in detail on the following pages.

General Discussion

The clays and shales included in this report produced a minimum of warping and twisting while being fired, except where overfiring occured. There was no scumming on the dried trial pieces but a few of the trial pieces fired to cone 01 produced a yellow or yellowish green efflorescence. This became noticeable while the trial pieces were drying after they had been placed in boiling water. All the trial pieces fired to cone 015 have expanded, based on the dimensions of the dried trial pieces. The conversion of quartz to tridymite at this temperature produces an expansion. Limonite is present as an impurity in all the samples.

Group 1

Samples:. 52-4, 52-11, 52-12, 52-15, 52-19, 52-20

The field samples of group 1 have the following characteristics:

1. Light gray to brown in color.
2. Slightly to very soapy to the touch.
3. Occurring in consolidated limps.
4. Easily scratched with a finger nail.

All members of group 1 are fine grained with over 92% passing through a 200 mesh screen. Five of the samples have the following impurities present, in order of decreasing amounts; quartz, limonite, gypsum, pyrite, and muscovite. (sample 52-20 contains limonite nodules as the main impurity).

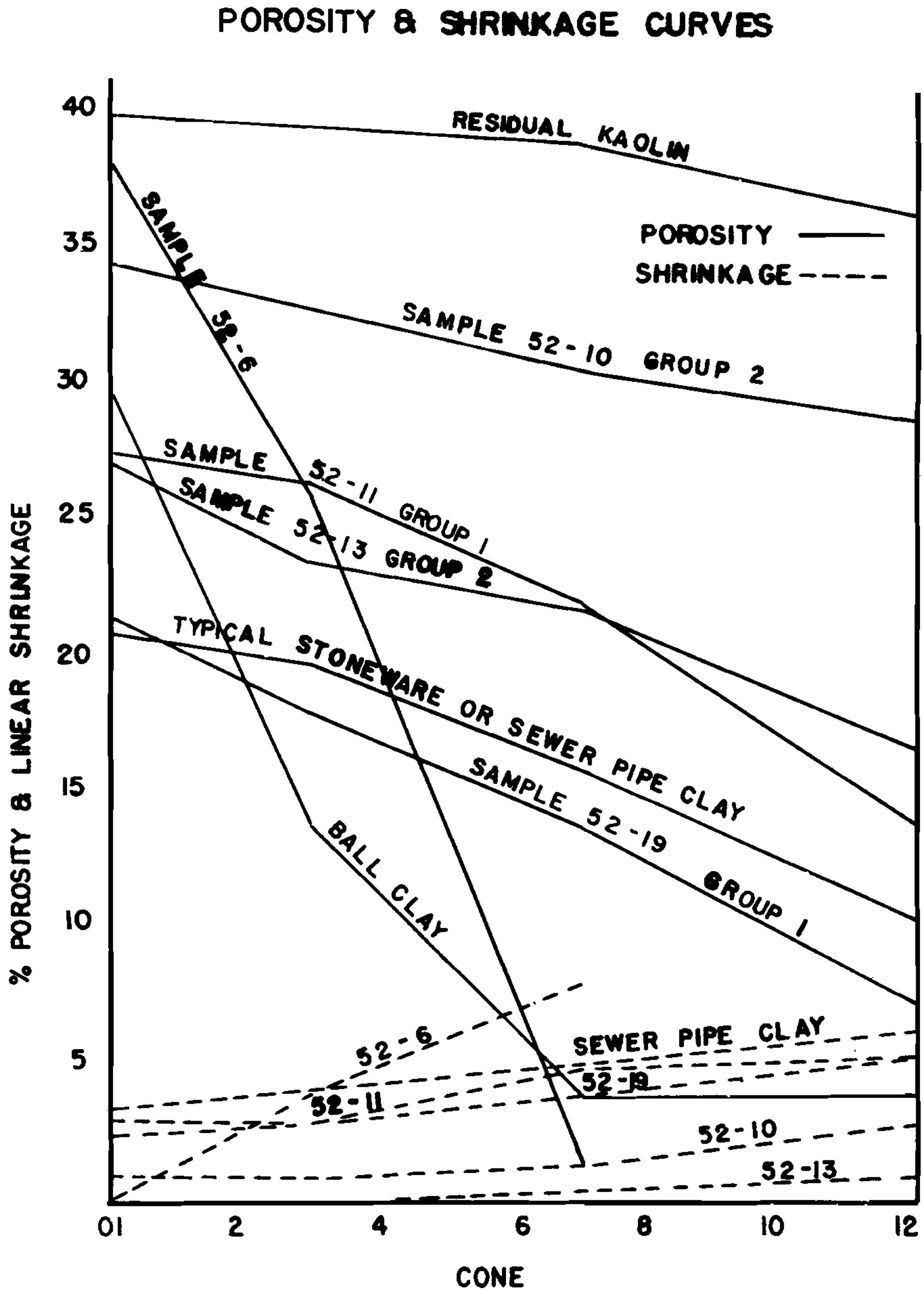
POROSITY & SHRINKAGE CURVES
40
35
30
25
20
15
10
5
% POROSITY & LINEAR SHRINKAGE
RESIDUAL KAOLIN
POROSITY
SHRINKAGE
SAMPLE 52-6
SAMPLE 52-10 GROUP 2
SAMPLE 52-11 GROUP I
SAMPLE 52-13 GROUP 2
TYPICAL STONEWARE OR SEWER PIPE CLAY
SAMPLE 52-19 GROUP I
BALL CLAY
52-6
SEWER PIPE CLAY
52-19
52-11
52-10
52-13
01
2
4
6
8
10
12
CONE

FIGURE 2

Table 1

Water of Plasticity, Dry and Fired Linear Shrinkage,

Apparent Porosity and Absorption Values

Group 1

	52-4	52-11	52-12	52-15	52-19	52-20
Water of Plasticity (%)	31.2	32.5	25.1	29.6	31.1	31.3
Dry Linear Shrinkage (%)	7.7	8.0	7.4	8.0	9.0	8.1
Fired Linear Shrinkage(%)						
Cone 015	-	-1.0	-0.9	-0.5	-1.0	-1.6
01	2.3	2.5	1.6	3.0	3.0	1.9
3	2.8	3.0	1.6	3.0	3.0	2.4
7	4.8	5.0	3.1	4.0	4.0	3.4
8	5.3	5.0	2.6	4.0	4.5	4.9
12	5.8	5.5	3.6	5.0	5.5	5.9
Porosity (%)						
Cone 015	-	31.0	24.7	27.9	26.6	28.5
01	25.8	27.7	21.3	25.3	21.6	24.2
3	23.4	26.5	18.2	20.9	18.0	21.5
7	18.6	22.2	15.5	16.7	13.8	16.8
8						
12	10.9	14.0	9.8	11.2	7.3	7.8
Absorption (%)						
Cone 015	-	18.4	13.2	16.0	14.6	16.1
01	13.8	15.3	10.7	13.6	11.1	12.7
3	11.7	13.5	8.8	10.5	8.9	10.9
7	9.2	11.2	7.4	8.1	6.5	8.2
8						
12	5.1	6.8	4.6	5.1	3.2	3.4

When making trial pieces, samples 52-11 and 52-19 were observed to be very plastic and quite tough so that the trial pieces were not easily deformed by handling. The other samples were very soft and the trial pieces easily deformed.

Surfaces of the dried trial pieces vary from quite soapy to very soapy to the touch. Judging by the pressure required to break the trial pieces by hand, sample 52-12 has the highest transverse strength, whereas sample 52-20 has the lowest, and the others have intermediate values.

For all the samples, slaking proceeded very rapidly at the beginning and within 30 minutes, five of the trial pieces had completely slaked (the trial pieces from sample 52-12 required 75 minutes).

There is no correlation between the plasticity, comparative strength, the degree of soapiness and toughness of the samples. Sample 52-12 has the lowest value for water of plasticity, has the highest transverse strength and the longest slaking time.

As previously mentioned, the trial pieces fired to cone 015 show an expansion. The cone 01 trial pieces are all quite soapy to the touch and vary in color from light to dark cream. There is a slight conctration of yellow efflorescence on trial pieces of four of the samples (the trial piece from sample 52-11 has a very heavy concentration of yellow efflorescence and 52-20 has a slight concentration of yellow green efflorescence). The efflorescence on the trial piece from sample 52-11 was analysed as a chromium salt by Prof. N.N. Kohanowski at the University of North Dakota.

The trial pieces fired to cones 3 and 7 show no signs of efflorescence but have the same soapiness and shade of cream color as those fired to cone 01.

Those trial pieces fired to cone 8 in the sewer pipe kiln produce some good examples of salt glazing. The trial piece from sample 52-15, although gray in color instead of the desired mahogany, has a very uniform and smooth glaze with no pitting or crazing. The trial piece from sample 52-20 has the desired uniform, uncrazed mahogany colored glaze, but there is pitting caused by the limonite nodules. Sample 52-19 produced a gray, uncrazed glaze interspersed with greenish brown badly crazed, thickly glazed spots. For firing, the trial pieces were set with one of the originally 4 5/8"x5/8" faces resting on a support in the kiln. The trial pieces from samples 52-4 and 52-11 have a good application of mahogany colored glaze on the face opposite to that which rested on the kiln support, and which extends down the large faces, giving way to a brown, practically unglazed semi-circle with diameter on the bottom face. The trial piece from sample 52-12 has the same brown semi-circle but the glaze on top is gray instead of mahogany.

Those trial pieces fired to cones 01, 3 and 7 show no signs of iron specking, but at cone 12 this condition is evident. The cream color of those trial pieces fired to cone 12 is slightly lighter than that produced at lower temperatures, and on the trial pieces from samples 52-19 and 52-20 it is partly obsured by bluestoning. There is more pronounced warping of the trial pieces fired to cone 12 than at lower temperatures and the surfaces of the trial pieces are slightly harder than quartz. The surfaces of those fired to lower temperatures (01, 3, and 7) are not quite so hard as quartz. The surfaces of the trial pieces fired to cone 12 appear more glassy than those fired to lower temperatures, as evidenced by low porosity values.

Referring to Fig. 1, page 6A, it is observed that the porosity and fired shrinkage curves for samples 52-11 and 52-19 show a gradual decrease and increase respectively, over the temperature range from cone 01 to 12. Similar curves for the other members of group 1 lie between those for 52-11 and 52-19. The curve shown for a typical sewer pipe or stoneware clay corresponds very closely to those for 52-11 and 52-19. However, some of the samples of group 1 which have higher porosity values at the various temperatures, are slightly more refractory than the typical sewer pipe or stoneware clay. Water of placticity and linear drying shrinkage values are shown in Table 1, page 19.

Group 2

Samples: 52-5, 52-10, 52-13, 52-14, 52-16

The characteristics of the field samples for this group are as follows:

1. All gray in color except sample 52-5 which is brown.

2. All quite sandy with rough texture.

3. Occurring in loosely concolidated lumps which are easily crumbled by rubbing bdtween the fingers.

The impurities present in this group are quartz, limonite, and muscovite. Samples 52-13 and 52-16 correspond to those in group 1 by having over 91% finer than 200 mech whereas sample 52-10 has only 67% finer than 200 mesh. The samples Nos. 52-5 and 52-14 have approximately 80% finer than 200 mesh. With the exception of sample 52-5, there was no difficulty experienced while performing the screen analyses.

The water of plasticity and linear drying shrinkage values for all the samples, except 52-16, are lower than those for group 1. See Table 2, page 23.

Group 2 samples are only slightly plastic and therefore rather difficult to wedge. Although the trial pieces from sample 52-16 were not easily deformed, the other trials were easily deformed by handling.

Table 2
Water of Plasticity, Dry and Fired Linear Shrinkage,

Apparent Porosity and Absorption Values

Group 2

	52-5	52-10	52-13	52-14	52-16
Water of Plasticity (%)	24.5	22.6	21.0	21.1	31.0
Dry Linear Shrinkage (%)	6.5	5.0	6.0	5.4	9.0
Fired Linear Shrinkage (%)					
Cone 015	0.0	-0.5	-1.5	-0.9	-0.6
01	0.5	-1.0	0.0	0.1	1.4
3	0.5		0.0	0.1	1.9
7	0.5	1.0	0.5	0.6	1.9
8	3.5	1.5	1.5	1.1	2.9
12	4.5	3.0	1.0	0.6	3.4
Porosity (%)					
Cone 015	29.3	31.5	24.6	27.0	28.1
01	29.8	34.6	27.3	29.5	28.0
3	27.1		23.6	26.8	24.1
7	26.1	30.7	21.8	24.2	22.4
8					
12	13.2	28.9	16.7	20.6	13.3
Absorption (%)					
Cone 015	16.4	17.8	13.2	14.6	15.6
01	16.3	19.6	14.6	16.1	15.2
3	14.2		12.3	14.2	12.7
7	13.2	17.0	11.4	12.8	11.7
8					
12	6.3	15.6	8.4	10.7	6.4

Transverse strengths vary considerably from the coarse grained trials of samples 52-10 with low strength to the higher strength finer grained trials of samples 52-13 and 52-16. The slaking times for samples 52-10 and 52-13 are 10 and 15 minutes respectively, whereas, for samples 52-5, 52-14, and 52-16, they vary from 45 to 60 minutes.

Trial pieces fired to cone 015 show an expansion and are easily scratched with a steel knife. Those fired to cone 01 are light cream color and on the surface of the trial pieces from samples 52-2 and 52-10, there is a slight concentration of yellow offlorescence. The trial pieces fired to cones 3 and 7 have almost the same shade of cream as those fired to cone 01.

There was quite a variation of glaze application on the trial pieces fired in the sewer pipe kiln. The trials from samples 52-13 and 52-14 are gray colored but with almost no glaze present. Sample 52-10 produced surfaces which are badly pitted and appear like dark gun metal. A slightly crazed, fair application of gray colored red glaze appears on the top of the trial piece from sample 52-5 and gives way to a brown, semi-circle at the bottom. The trial from sample 52-16 has a glaze application very similar to that of 52-19 in group 1.

The trial pieces fired to cone 12 have larger iron specks as well as a higher concentration than those of group 1. As in group 1, there is more pronounced warping and lighter cream color than those trials fired at lower temperatures. The trials from samples 52-5 and 52-16 are slightly bluestoned.

The surfaces of those trial pieces fired to cones 01, 3 and 7 are not quite so hard as quartz and those fired to cone 12 are slightly harder than quartz.

As for group 1, the porosity and shrinkage curves as shown in Fig. 1, page 6A, correspond to those for the typical sewer pipe or stoneware clay, but some of the group 2 clays are much more refractory.

Group 3

Samples: 52-6, 52-7

The field sample of 52-6 is yellow brown and rather silty; that of 52-7 is gray and quite sandy. The clays of this group are poorer grade than preceeding groups and have the following impurities: quartz, limonite, lignite, gypsum, pyrite and lime. More than 94% of sample 52-6 if finer than 200 mesh, whereas, sample 52-7 has 76% finer than 200 mesh and 98% finer than 150 mesh.

When making the trial pieces, it was observed that both samples were only slightly plastic and the trial pieces easily deformed by handling. Trial pieces from sample 52-7 have somewhat higher transverse strength than those of 52-6. Water of plasticity and linear drying shrinkage values are shown in Table 3, page 26.

The trial pieces fired to cone 015 show an expansion and are easily scratched with a steel knife. Those trial pieces fired to cone 01 are cream with iron specking, and from a distance of 6 feet, the trial pieces from sample 52-6 appear as having a solid medium brown color whereas, the 52-7 trial piece appears as a darker brown. The surfaces of the cone 3 trial pieces produced larger and darker iron specks, and are slightly softer than quartz.

At cone 7, both samples overfired and bloated slightly. The trial piece from sample 52-6 is dark greenish brown and that from sample 52-7 is dark brown with cream colored specks. They are both harder than quartz.

Trial pieces from both samples fused at cone 8 in the sewer pipe kiln. The curve in Fig. 1 for sample 52-6 shows the short vitrification range of these two clays in contrast to the gradual range of those of group 1 and 2.

Table 3

Water of Plasticity, Dry and Fired Linear Shrinkage,

Apparent Porosity and Absorption Values

Group 3

	52-6	52-7
Water of Plasticity (%)	27.3	32.3
Dry Linear Shrinkage (%)	6.0	8.0
Fired Linear Shrinkage (%)		
Cone 015	-1.5	-1.0
01	0.0	0.0
3	4.0	2.0
7	8.0	2.0
Porosity (%)		
Cone 015	33.0	36.2
01	38.5	36.2
3	26.3	27.0
7	1.7	9.0
Absorption (%)		
Cone 015	18.7	19.7
01	23.4	21.5
3	13.8	15.0
7	0.8	4.5

Group 4

Samples: 52-1, 52-8, 52-17, 52-18

Sample 52-1, as received from the field, is a grayish blue shale which is readily broken down by pressure from the fingers; sample 52-8 is very hard, brown shale with high dry strenght; sample 52-17 is olive drab colored, silty shale; sample 52-18 is greenish black, loosely stratified shale.

The samples of 52-8 and 52-18 did not slake well enough to run a screen analysis. Sample 52-1 was readily screened but sample 52-17 gave some difficulty. Of sample 52-1, 93% is finer than 200 mesh and of 52-17, almost 100% is finer than 200 mesh. Limonite is present in both and in addition, sample 52-1 contains lignite and gypsum impurities. The fired trial pieces of samples 52-8 and 52-18 contain a few white particles resulting from decomposition of gypsum.

The samples in Group 4, when wet, are all quite sticky and tough so that wedging is rather difficult. However, the molded specimens were handled easily without deformation. The water of plasticity and linear shrinkage values are quite high and account for slow drying, warping, and in the case of trial pieces made from sample 52-1 there was some checking or cracking of the trial pieces, See Table 4, page 29.

All the dried trial pieces of group 4 are quite soapy to the touch, are very hard and have high dry strength. Slaking time varies from 20 minutes for sample 52-1 to 50 minutes for sample 52-8.

The trial pieces of group 4 were overfired at cone 01 and as a result, no trial pieces were fired at higher temperatures. At cone 015 the trial pieces are light to medium orange and show expansion.

At cone 01, the trial pieces are dark red to red brown. The trial piece from sample 52-1 has a good brick red, but is slightly overfired and bloated; that from sample 52-8 is dark red brown with a few white specks and is badly bloated;

that from 52-17 has a good brick red and is quite badly warped; the trial piece from sample 52-18 is dark brick red with white specks and is warped more than 52-17. All the samples fired to cone 01 are slightly harder than quartz.

Porosity and shrinkage values were obtained only for trial pieces fired to cones 015 and 01 so no curves were drawn for group 4 shales. See Table 4, page 29.

Miscellaneous Samples

Samples: 52-2; 52-3, and 52-9

Sample 52-2 is a light cream colored, sandy clay; sample 52-3 is light brown with yellow staining and is badly slaked; sample 52-9 is light green and very brittle.

Samples 52-2 and 52-9 were rather sticky for good screening, and sample 52-3 required considerable amounts of water because of the bentonitic nature of the sample. The samples contain quartz, limonite and gypsum as impurities. For each particular sample there were almost equal fractions on each screen, with the finer than 200 mesh as follows: 52-2 25.4%; 52-3 8.4%, 52-9 12.4%.

Sample 52-2 was so sticky that wedging was impossible. Sample 52-3 could not be formed into a solid mass by wedging because of the bentonitic nature. However, trial pieces were made with difficulty, only to have them check within 1½ hours. Sample 52-9 was very sticky and quite tough, and the dried trial pieces were very hard and badly checked.

Since the samples in this group were almost unworkable, no trial pieces were obtained suitable for firing.

Table 4

Water of Plasticity, Dry and Fired Linear Shrinkage,

Apparent Porosity and Absorption Values

Group 4

	52-1	52-8	52-17	52-18
Water of Plasticity (%)	50.0	42.6	45.1	53.0
Dry Linear Shrinkage (%)	12.0	9.2	11.3	13.2
Fired Linear Shrinkage (%)				
Cone 015	-1.0	-0.7	-0.3	0.3
01	-4.5	3.8	6.7	6.8
Porosity (%)				
Cone 015	31.4	34.3	47.8	32.2
01	3.7	7.7	10.4	2.9
Absorption (%)				
Cone 015	18.1	21.1	27.5	19.3
01	2.6	4.5	4.7	1.5

CONCLUSIONS

1. Judging from the results of this investigation, there are wide spread deposits of high grade clay in the state.

2. The samples of group 1, although they are from different localities have similar properties well suited to the manufacture of stoneware and sewer pipe, as well as semi-refractory products. Referring to Figure 1 on page 6A, the similarity of porosity and shrinkage curves of group 1 and of a typical stoneware or sewer pipe clay, is noted.

With reference to pages 11 and 12 of this report, the following characteristics of group 1 clays are ideal for stoneware and sewer pipe:

1. Relative freedom from sulphate and carbonate impurities.
2. Good plasticity.
3. Minimum of firing warping and twisting.
4. Long vitrification range.

Those particular characteristics suitable for stoneware are:

1. Uniform cream color from cone 01 to cone 7, with no specks.
2. Relative freedom from iron impurities.

For sewer pipe, the deep mahogany color of some of the trial pieces is ideal.

Some of the properties of these clays which are undesirable for good stoneware or sewer pipe are:

1. Low dry strenght and lack of toughness.
2. The clays are a little too refractory.
3. The presence of limonite nodules, causing specking in stoneware and pitting in sewer pipe.
4. The lack of finely divided iron compounds in some of the samples, resulting in a gray glaze instead of the desired mahogany.

The semi-refractory nature of the clays of group 1 would make them suitable for low-heat refractory mixes.

3. The clays of group 2 are more refractory than those of group 1 because of higher silica content, resulting in higher porosity values and lower firing shrinkages. The free silica causes lack of plasticity, low drying shrinkage and lack of firing warping or twisting. The refractory nature of these group 2 clays, as well as the lack of plasticity are undesirable properties for stoneware or sewer pipe. They could most likely be used in fire clay mixes with plastic, tough clays. No such clays have yet been sampled for this investigation.

4. The desirable features of group 3 clays are the low shrinkage and very slight warping. However, they are not plastic, have poor dry strength and low vitrification range. If used alone they are unsuitable for common or building brick and because of the iron content are undesirable for high grade products. The blending of group 4 shales with group 3 will increase the plasticity and the dry strength of group 3 clays.

5. The shales in group 4 produced some very pleasing red brick samples. However, they are too sticky if used alone and have excessive drying shrinkage, warping and checking. It appears that the red burning shales in the state are all sticky, so the addition of any other clay would be at the expense of the red color. Both the fired color and hardness of the trial pieces fired to cone 01 are desirable features for red face brick.

6. Sample 52-3 may have value as bentonite. Bentonites are used in very small amounts to increase plasticity of whiteware bodies, to prevent settling of glazes and as suspending agents for enamels. Samples 52-2 and 52-9 have no ceramic value.

SUGGESTIONS

1. Since the clays of group 1 have low dry strengths, the addition of organic binders would greatly increase the strength. Also, the addition of tougher, higher strength clays should produce mixes more suitable to sewer pipe manufacturing.

2. Because of the refractory nature of the clays of both groups 1 and 2, considerable experimenting could be done with additions of tougher, more refractory clays as well as calcined clay or grog additions, with the object in mind of making fire brick or other refractory mixes.

3. Further work on clays similar to those of groups 1 and 2 should include:

1. Chemical analyses.
2. Differential thermal analyses.
3. Determination of transverse strength.
4. Particle size determination of particles finer than 200 mesh.

4. The clays of group 3 may be useful for common brick or face bridk if mixed with light burning, more plastic clay with longer vitrification range or possibly, the addition of red burning shale would be helpful. The final results could well be a plain, mottled or speckled brick.

5. The shales of group 4 were overfired at cone 01, and because of the wide temperature range between cone 01 and the next lowest temperature to which they were fired, namely cone 015, it would be advisable to fire more of the trial pieces of these samples at closer intervals between these two temperatures.

Since the red burning shales of group 4 are too sticky, it is suggested that some of the shale be calcined and then added to the raw material to minimize the stickiness and excessive shrinkage. The addition of calcined shale will also retain the desired red color of the fired ware.

6. It is further suggested that all deposits be well sampled so as to be certain of uniformity and that they be surveyed to give an estimate of reserves.

GLOSSARY OF CERAMIC TERMS USED IN THIS REPORT

Bentonite: A clay-like mineral, derived from volcanic ash with the clay mineral, montmorillonite ($Al_2O_3.4SIO_2.9H_2O$) as the chief constituent. There are two types: 1. Those that swell enormously when wetted, and 2. those that swell no more than other plastic clays.

Pyrite; Referred to as iron pyrites or fool's gold, it is a sulfide of iron (FeS_2). It often occurs in clay as cubical crystals, but usually is oxidized and hydrated to limonite.

Pyremetric Cones: Small, slender three sided pyramid made of ceramic or refractory material for use in determining the time- temperature effect of heating. They are numbered from 022 to 01 and from 1 to 42. If fired at a definite rate they will soften or deform at certain temperatures; at a slower rate they will soften at a lower temperature and at a faster rate they will soften at a higher temperature. Regardless of the firing schedule, the softening of a certain cone in different kilns will indicate equivalent heat treatment.

The temperatures will be given for the cones used in this report, corresponding to a heating rate of 20°C per hour.

Cone 015	1418°F (770°C)	Cone 7	2210°F (1210°C)
Cone 01	2030°F (1110°C)	Cone 8	2237°F (1225°C)
Cone 3	2093°F (1145°C)	Cone 12	2390°F (1310°C)

Pyrometric cone equivalent: Samples of clay and other refractory materials are made into cones similar to the standard pyrometric cones and are fired in the same furnace so as to compare the softening point of the clay with a standard cone.

Quartz: The only form of silica that occurs naturally in sufficient quantity to be commercially important.

Refractoriness: The property of being resistant to softening or deformation at high temperatures.

Scumming: Soluble salts present in raw clay will often be deposited on the surface of bricks and other objects, during the drying operation.

Silica: One of the common minerals, with the formula SiO_2.

Slaking: When clay or shale is placed in water, the water usually penetrates the material, causing swelling and finally disintegration of the clay or shale.

Vitrification: As a clay is being fired, the most fusible constituents melt and take unfused material into solution. The liquid formed flows into the pores causing shrinkage and when there is no more appreciable decrease in shrinkage or porosity, it is called incipient vitrification. When all the pores are filled with liquid, a dense body with practically zero porosity results, and a state of complete vitrification has been obtained. Not all clays can be fired to complete vitrification, because the liquid is often too fluid and the ware will deform under its own weight. Whem some clays are fired, gases resulting from the decomposition of carbonates, sulphates, and other compounds do not escape before the surface has been sealed by fusion, and in order to escape, these gases cause expansion or bloating, and overfiring results.

Water Absorption: The percentage of water absorbed by piece of ware, expressed as percentage of the dry weight of the material.

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