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THE BLOATING OF MISSOURI'S SHALES

BY

PETER KURTZ, JR.

————

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN CERAMIC ENGINEERING

Rolla, Missouri

1953

Approved by: _____
Chairman, Department of Ceramic Engineering

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INTRODUCTION

The first objective of this investigation was to determine which deposits of clays, shales, and loesses in Missouri are suitable for use in the production of lightweight aggregate by virtue of their expanding characteristics upon heating. The second objective was to determine, if possible, commercially feasible additions that will produce the bloating property in shales that do not naturally bloat.

There are two conditions which must be met in firing in order to bloat a clay or shale. First, a gas must be formed and evolved during firing. Second, enough glass of the proper viscosity must be formed to trap the gas and permit expansion.

There has been a good deal of research conducted in an effort to determine the bloating agents. The only conclusion one can draw in general from this work is that the bloating agents vary and it is difficult to tie down specifically the agents and reactions involved, and in this regard each clay and shale is a separate problem. It is a matter of record, however, that the majority of shales show some bloating, this was also found true of Missouri shales. In this work, no direct attempt was made to determine gas producing agents since in the majority of cases these agents occurred naturally in the shales. Therefore, the second part of this work was concerned with finding a suitable additive which would promote the formation of glass of the proper viscosity at the right temperatures.

This problem is of considerable economic importance since there is an acute demand for lightweight concrete aggregate. Lightweight concrete aggregate is very popular for use in the production of concrete

blocks because of its lightweight, insulating and acoustic properties. In large concrete structures the use of lightweight aggregate can effect a very worth while saving in structural steel and thus justify its slighly higher cost.

Previous to this work very little had been known as to the bloating characteristics of the clays and shales in Missouri.

In the process of this investigation, firing behaviors have been run on all the samples collected and these data might in the future be valuable to the structural clay products industry.

REVIEW OF PREVIOUS WORK

In 1903 T. E. Jackson[1] theorized that the bloating of clays was caused by the evolution of oxygen liberated by the dissociation of ferric oxide. He did not present any experimental evidence, however, to support this theory.

Orton and Staley[2] did not believe ferric oxide was the cause of bloating since all clays would then bloat at the same temperature and their experiments showed that clays bloated at temperatures ranging from 1100° to 1700°C., and also many clays that contain iron do not bloat. They believed that the oxidation of various forms of carbon could cause bloating. They also suggested that iron sulfide was not dissociated in firing but was dissolved in the melt and as more silica was dissolved the melt became acid causing the sulfur to come out of solution as sulfur dioxide which could cause bloating.

Wilson[3] believed that bloating resulted in the decomposition of compounds such as $CaSO_4$. He listed two causes of bloating: 1. incomplete oxidation during firing below the vitrification temperature, and

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[1]Jackson, T. E., p. 43, discussion of the paper "Changes in Color of Clays on Ignition in Clayware Kilns," by Arthur Hopwood, Trans. Ceram. Soc. (Engl.), 1903, pp. 37-43.

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[2]Orton, E., and Staley, H. F., Status of C, Fe, and S in Clays During Various Stages of Burning; 3 rd. report, National Brick Manufacturers' Association, Indianapolis, Indiana, 1908.

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[3]Wilson, Hewitt, Ceramics - Clay Technology. McGraw-Hill Book Co., Inc., New York, 1927, 296 pp.

2. evolution of gases during and above the vitrification range.

Bleininger and Montgomery[4] recognized that physical conditions such as rate of heating and kiln atmosphere affected bloating.

F. G. Jackson[5] attempted to determine what compounds were formed with sulfur, iron, and silica before, during, and after the liberation of gases such as SO_2, SO_3, and CO_2. He mixed various impurities with pure kaolinite and fired to 750°C. He found that not all sulfur was evolved at low temperatures. Bloating, he believes, is due to that sulfur retained at high temperatures in complex compounds with iron and silica.

Austin, Nunes, and Sullivan[6] quantitatively determined the gases evolved during bloating by heating various bloating clays in a tube furnace. They studied the effects of heating rates, air flow and different atmospheres on bloating. The gases evolved were CO_2, SO_3, and H_2O. They believed that the CO_2 was formed from the oxidation of elemental carbon by the reduction of ferric oxide, since good bloating was attained in a nitrogen atmosphere. They suggested that the SO_3 resulted from the decomposition of sulfates originally present in clay or formed during the firing. The water was not believed to come from a clay mineral.

[4] Bleininger, A. V., and Montgomery, E. T., "Effect of Overfiring Upon the Structure of Clays," Trans. Am. Ceram. Soc., 15, 71-85 (1913).

[5] Jackson, F. G., "Oxidation of Ceramic Ware During Firing: 2, Decomposition of Various Compounds of Iron with Sulfur Under Simulated Kiln Conditions," J. Am. Ceramic Soc., 7 (4) 223-37 (1924).

[6] Austin, C. R., Nunes, J. L., and Sullivan, J. D., "Basic Factors Involved in the Bloating of Clays," Am. Inst. Mining & Met. Engrs., Tech. Pub. No. 1486; Mining Technol., 6 (4) 11 pp. (1942).

Conley, Wilson and Klinefelter[7] studied the engineering aspects of bloating clays for concrete aggregate. They also did research on the cause of bloating. They tried to find a correlation between chemical components and bloating by making numerous chemical analyses of bloating and non-bloating clays. They added many substances to non-bloating clays. They got good results with sulfates, carbonates, flowers of sulfur, red phosphorus and others with different clays. They concluded that many non-bloating clays could be made to bloat by proper admixtures and that poor bloating clays could be improved, but that each clay was an individual problem.

Riley[8] by utilizing a large number of chemical analyses of bloating and non-bloating clays defined the limits of bloating on the composition diagram Al_2O_3 - SiO_2 - Flux. The "area of bloating" on this diagram showed the desirable composition of clays which satisfy the condition that a bloating clay must form enough glassy phase of high enough viscosity to trap a gas at bloating temperatures. He tested this area by adding alumina and silica to non-bloating clays. These mixtures bloated. He also found that many igneous rocks whose compositions fall within this area bloated when ground and cast into briquettes and fired. Riley believed that bloating is caused by the reduction of Hematite and the formation of SO_2 from pyrite.

[7]Conley, J. E., Wilson, Hewitt, Klinefelter, T. A., "Production of Lightweight Concrete Aggregates from Clays, Shales, Slates, and Other Materials," U. S. Bur. Mines Repts. Invest., No. 4401, 121pp (1948).

[8]Riley, C. M., "Relation of Chemical Properties to the Bloating of Clays," J. Am. Ceram. Soc., 34 (4) 121-28 (1951).

Larson[9] fired twelve shale and clay samples from different locations in Missouri. He fired 1" x 3/4" s 3/4" blocks in a gas fired muffle furnace until they bloated or melted down. Of the twelve samples fired he reported seven as good bloating. Five of these seven good bloating samples were retested in this work, three of which were considered to be good bloating.

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[9] Larson, L. N., "Ceramic Possibilities of Some Missouri Clays and Shales," Thesis 753, Missouri School of Mines and Metallurgy, Rolla, Missouri

SAMPLING AND PREPARATION FOR TESTING

The locations from which the samples were taken were chosen by Dr. E. L. Clark. All the samples were collected by Mr. W. R. Higgs. Appendix A contains the exact locations of the samples and the geologic descriptions of the outcrops as written by Mr. Higgs.

Many of the locations contained three or four geologic formations of interest, each of which was sampled and tested separately.

The majority of the samples were collected from natural outcrops. A few were taken from open pit excavations at coal and brick plants. The samples were collected by channeling so as to eliminate weathered material.

The formations sampled ranged from twelve feet to fifty-three feet and approximately one hundred pounds were taken for each sample.

A total of fifty-five individual samples were obtained from forty-two locations in twenty-five counties.

Each sample was air dried and put first through a jaw type crusher and then a hammer mill. Each sample was piled and quartered until a twenty pound fraction remained. This fraction was again piled and quartered until a five pound portion remained. The five pounds were passed through a 20 mesh sieve (U. S. Standard) and enough water was added to make it workable. One inch cubes were then molded from the clay and marked. After drying at 110°C these cubes were used in the firing tests.

For running chemical analysis and differential thermal analysis a representative 100 grams were removed and ground to pass a 100 mesh sieve.

FIRING TESTS FOR BLOATING

It has long been recognized that there are two conditions that must be met by a sample in firing in order to produce a good bloat. First, the sample must contain compounds which dissociate or react with other compounds upon heating to form a gas. Second, the sample must have formed enough glass of the proper viscosity to trap the gas and permit expansion. It can readily be seen that the viscosity and amount of the glass formed is fairly critical. If the glass is too fluid, the gas will bubble out leaving rather large connected pores in the mass and little expansion will take place, if too little glass is formed the gas will not be trapped in the mass. In view of this, two firing tests were run on every sample. The first firing test was a ceramic firing behavior which is characterized by a slow rate of heating. The second firing test was a very rapid heating intended to show whether the rate of heating had anything to do with whether a sample would bloat or not. It was thought that if gas evolution started before there was sufficient vitrification a slow heating rate might complete gas evolution without bloating the sample, therefore a rapid fire would be necessary.

Besides the rate of heating, there was another difference between the two firing tests which proved to be far more significant. This significant difference was in the furnace atmosphere. The firing behaviors were conducted in an electrically heated air furnace and the atmosphere would be oxidizing while the rapid firing was conducted in a gas fired furnace which tended to be reducing since the air-gas mixture was kept rich in gas as shown by yellow flames shooting out the top and door of the furnace.

For running the firing behavior eighteen one inch cubes of each sample were made. These cubes were marked with the sample number and the pyrometric cone at which they were to be fired. Two cubes were fired to each cone. Samples were withdrawn from the furnace at cones 06, 04, 02, 1, 3, 5, 7, 9, and 11, these correspond approximately to temperatures of 1005, 1050, 1125, 1145, 1180, 1210, 1250, and 1285°C, respectively. Pyrometric cones were used instead of arbitrarily chosen withdrawal temperatures for two reasons: 1. the thermo couple could not be easily shifted around in the furnace and the use of pyrometric cones eliminated the necessity of determining the temperature gradient in the furnace and the effect of withdrawing samples, and 2. pyrometric cones are a measure of heat treatment or time as well as temperature.

After the cubes had been made, marked, and dried, their weights and volumes were taken and recorded. After running the firing behavior, the weights and volumes were again taken and recorded. These measurements permitted a calculation of fired density and per cent shrinkage or expansion. Weights were taken to one tenth of a gram. Volumes were taken with a mercury volumeter and read to one hundredth of a cubic centimeter. These data, although valuable to one interested in making brick or pottery, only tell one of two things of interest concerning their value as lightweight aggregate. The pore structure of the bloated piece is just as important as the amount of expansion. The data on density and expansion *are* not included in this work but will be reported in another thesis. The result reported in this work is simply whether a bloated piece floated on water or not. This was the criterion used to determine if the expansion was sufficient for use as lightweight aggregate.

The furnace used for the firing behaviors was an upright muffle furnace. The heating elements were six "Globars." The rate of heating was controlled by a Micromax temperature indicating program controller. The rate of heating was 60°C. per hour to 1050°C. and then 20°C. per hour.

The size of the furnace permitted six firing behaviors to be run at once.

The samples to be withdrawn at one cone were placed on a $\frac{1}{2}$" x $4\frac{1}{2}$" x 9" "Mullfrax" split along with the proper pyrometric cone. A peep hole was left in the furnace door and when a cone went down the door was opened and one entire split was removed and placed in a pan of fire clay grog, grog was also poured on top of the split and samples to prevent shattering from thermal shock.

The rapid firings were run in a gas fired semi-muffle furnace. One cube of each sample was fired and two samples were fired at once. The dried cubes were placed on a "Mullfrax" split which had been dusted with silica sand. The samples were fired until they either bloated or melted down. If one bloated and the other one did not bloat or melt down, the latter was repeated later. The atmosphere in the furnace was kept reducing by keeping the air-gas mixture such that yellow flames issued from the top and around the door of the furnace. The rate of heating was approximately 600°C. per hour. The temperature was read with an optical pyrometer.

After running both firing tests on all of the samples, those that bloated had to meet two arbitrarily chosen tests in order to be considered good. First, the sample must float on water or almost float once the nonporous "skin" which always formed was broken off. Second, the pores formed must be small and not interconnected. The first test

measured in a small way the extent to which the pores were interconnected but the second test was necessary since in some samples the pores were large, not well disseminated, and only separated by a thin glassy, very brittle wall. This, of course, made the bloated piece very weak and unsuitable for this reason. At first, it was thought that a separate estimation of the strength would be desirable but it was found that if the pore structure was considered good the strength was also good.

Table I contains the results of both firing tests; it includes a separate comment on the bloating, if any, during both firings, whether the sample floated on water, a comment on the pore structure, and the best bloating temperature.

The bloating samples fell into two groups: those that bloated during both firing tests, and those that bloated only upon quick firing in a reducing atmosphere. Samples 3A, 7, 10B, 20B and C, 23, 27, 33, 36, 37, and 38 bloated during both firings. Samples 1, 2, 3B, 4, 5, 6, 8A, 15B, 24, 26, and 29 bloated during the quick firing.

A comparison of the samples that bloated well in both firing tests indicates that the rate of firing does not seem to be very important for these size samples. The slower firing rate of the firing behavior did improve the pore structure a little since the pores were smaller with very few connected. This difference in pore structure would be expected to become greater as the size of the sample increased, but no investigation was conducted on this point.

Two facts can be concluded about the samples that bloated during both firings. One, the rate of heating is not important for small samples, and two, the furnace atmosphere does not effect the bloating of these samples.

The fact that some of the samples only bloat in the reducing atmosphere of the rapid firing test merely tells us that bloating is promoted either by rapid firing or a reducing atmosphere. Although no direct tests were conducted to determine which of these two factors promoted the bloating, the work on additives influences the writer to believe that it is the furnace atmosphere rather than the rate of firing.

In general, it was noticed that the best of the good bloating samples were the ones that bloated during both firing tests.

Plates 1, 2, and 3 are actual size pictures of nine of the good bloating samples. Each of these samples floated on water and it is readily seen that the pores are small, separated, and uniformly spaced.

TABLE I

Sample # 1

Excellent bloating in the reducing atmosphere of the quick firing test, pore structure excellent, specific gravity less than one, best bloating temperature 1250° ± 20°C.

Very slight bloating at cone 9 in the oxidizing atmosphere of the firing behavior test. Sample melted at cone 11.

Sample # 2

Excellent bloating in the reducing atmosphere of the quick firing test, specific gravity less than one, pore structure excellent, best bloating temperature 1150° ± 50°C.

Slight bloating from cones 7 to 11 in the oxidizing atmosphere of the firing behavior.

Sample # 3A

Good bloating during the firing behavior at cones 7 and 9, oxidizing atmosphere, specific gravity less than one, pore structure good, bloating temperature 1250° ± 20° C.

Good bloating at same temperature during the quick fire.

Sample # 3B

Good bloating under the reducing conditions of the quick firing, specific gravity about one, pore structure fair, bloating temperature 1200° ± 50°C.

Slight bloating during the firing behavior at cones 7 and 9 under oxidizing conditions, melted at core 11.

TABLE I (Cont'd.)

Sample # 3C

Good bloating under the reducing conditions of the quick firing, pore structure very bad with large connected pores, bloated at 1250°C.

Very slight bloating during the firing behavior, melted at cone 11.

Sample # 3D

Very slight bloating during both firings. It didn't melt at cone 11 but was very well vitrified.

Sample # 4

Good bloating during the quick firing, reducing conditions, specific gravity less than one, good pore structure, bloating temperature 1300° ± 20°C.

Very slight bloating under the oxidizing conditions of the firing behavior, did not melt at cone 11 but was well vitrified.

Sample # 5

Good bloating during the quick firing, reducing conditions, specific gravity less than one, poor pore structure, bloating temperature 1250° ± 30°C.

Very slight bloating under the oxidizing conditions of the firing behavior, did not melt at cone 11 but was very well vitrified.

Sample # 6

Good bloating under reducing conditions of the quick firing, pore structure fair, specific gravity about 1, bloating temperature 1300° ± 30°C.

TABLE I (Cont'd.)

Slight bloating during the firing behavior, did not melt at cone 11.

Sample # 7

Excellent bloating during both firings, oxidizing or reducing conditions, specific gravity less than one, excellent pore structure, bloating temperatures 1200° ± 50°C.

Sample # 8A

Good bloating during the quick fire, reducing conditions, specific gravity about 1, good pore structure, bloating temperatures 1250° ± 50°C.

Fair bloating under the oxidizing conditions of the firing behavior, pore structure not well developed, specific gravity greater than one, melted at cone 11.

Sample # 8B

Poor bloating during both firings, oxidizing or reducing conditions, pore structure not well developed, specific gravity greater than one, did not melt down at cone 11 but very well vitrified.

Sample # 8C

No bloating in either firing. Sample was well vitrified at cone 11.

Sample # 9A

Slight bloating during the firing behavior, oxidizing conditions, pore structure not well developed, specific gravity greater than one, melted at cone 11.

No bloating when quick fired to 1260°C in a reducing atmosphere.

TABLE I (Cont'd.)

Sample # 9B

No bloating under reducing conditions of quick firing to 1300°C.

No bloating during firing behavior, did not melt at cone 11 but was well vitrified.

Sample # 9C

Poor bloating during the firing behavior at cones 9 and 11, pore structure not well developed, specific gravity greater than one.

No bloating under the reducing conditions of quick firing to 1270°C.

Sample # 10A

Poor bloating under the oxidizing conditions of the firing behavior at cones 9 and 11, pore structure not well developed, very well vitrified at cone 11.

No bloating under the reducing conditions of quick firing to 1260°C.

Sample # 10B

Fair bloating under the oxidizing conditions of the firing behavior at cones 9 and 11, pore structure good, specific gravity less than one, bloating temperature 1300 ± 20°C.

Fair bloating under the reducing conditions of quick firing to 1300°C.

Sample # 11

Poor bloating under the oxidizing conditions of the firing behavior at cone 11.

No bloating under reducing conditions of quick firing to 1270°C.

Sample # 12

Very poor bloating in the oxidizing atmosphere of the firing

TABLE I (Cont'd.)

behavior at cones 9 and 11.

No bloating in the reducing atmosphere of quick firing to 1270°C.

Sample # 13

Very poor bloating in the oxidizing atmosphere of the firing behavior at cones 7, 9 and 11, very well vitrified at cone 11.

No bloating in the reducing atmosphere of quick firing to 1275°C.

Sample # 14

Very slight bloating in both firing tests at 1300°C, but very well vitrified at this temperature.

Sample # 15A

Very slight bloating in the oxidizing atmosphere of the firing behavior at cone 7. At cone 9 the bloating was good but the pore structure was bad (large, open and interconnected pores), sample melted down at cone 11.

Very slight bloating in the reducing atmosphere of quick firing to 1270°C.

Sample # 15B

Good bloating in the reducing atmosphere of quick firing to 1330°C., pore structure good, specific gravity less than one.

Slight bloating in the oxidizing atmosphere of the firing behavior at cones 5 and 7, sample melted at cone 9.

Sample # 16A

Poor bloating in the oxidizing atmosphere of the firing behavior

TABLE I (Cont'd.)

at cone 11.

Poor bloating in the reducing atmosphere of quick firing to 1275°C., sample was well vitrified at this temperature.

Sample # 16B

Poor bloating in the oxidizing atmosphere of the firing behavior at cones 7, 9 and 11, practically melted down at cone 11.

No bloating when quick fired to 1275°C. in a reducing atmosphere.

Sample # 17

Slight bloating at cones 9 and 11 in the oxidizing atmosphere of the firing behavior. Sample was well vitrified at cone 11.

Very slight bloating when quick fired to 1275°C. in a reducing atmosphere.

Sample # 18

Very slight bloating at cones 7, 9 and 11 in the oxidizing atmosphere of the firing behavior. Sample was well vitrified at cone 11.

No bloating when quick fired to 1270°C. in a reducing atmosphere.

Sample # 19

No bloating in either firing test. Sample was well vitrified at cone 11 and also when quick fired to 1355°C.

Sample # 20A

No bloating in either firing test. Sample melted completely at cone 9.

Sample was quick fired to 1270°C. and melted completely without any bloating.

TABLE I (Cont'd.)

Sample 20B

Excellent bloating in both firing tests, oxidizing or reducing
atmosphere, excellent pore structure, specific gravity less than one,
best bloating temperature 1250° ± 20°C.

Sample # 20C

Excellent bloating in both firing tests, oxidizing or reducing
atmosphere, excellent pore structure, specific gravity less than one,
best bloating temperature 1250°C. ± 20°C.

Sample # 21

No bloating in either firing test. Sample was well vitrified at
cone 11 and when quick fired to 1250°C.

Sample # 22

No bloating in either firing test. Sample was well vitrified at
cone 11 and also when quick fired to 1300°C.

Sample # 23

Excellent bloating in both firing tests, oxidizing or reducing
atmosphere, excellent pore structure, specific gravity less than one,
best bloating temperature 1200° ± 50°C., this sample showed the longest
bloating range, the bloating was excellent from cone 1 through cone 9.

Sample # 24

Fair bloating when quick fired in a reducing atmosphere to 1200°C.,
pore structure fair, specific gravity less than one.

TABLE I (Cont'd.)

Slight bloating at cone 5 in the oxidizing atmosphere of the firing behavior. Sample melted down at cone 7.

Sample # 25

Slight bloating at cones 9 and 11 in the oxidizing atmosphere of the firing behavior. Sample well vitrified at cone 11.

Very slight bloating when quick fired to 1225°C. in a reducing atmosphere.

Sample # 26

Good bloating at cones 9 and 11 in the oxidizing atmosphere of the firing behavior test, good pore structure, specific gravity less than one.

Fair bloating when quick fired to 1270°C. in a reducing atmosphere, good pore structure, specific gravity greater than one.

Sample # 27

Excellent bloating in both firing tests, oxidizing or reducing conditions, excellent pore structure, specific gravity less than one, best bloating temperature 1225 ± 25°C.

Sample # 28

Poor bloating at cones 9 and 11 in the oxidizing atmosphere of the firing behavior test, pore structure fair, specific gravity greater than one. Sample very well vitrified at cone 11.

No bloating when quick fired to 1210°C. in a reducing atmosphere.

TABLE I (Cont'd.)

Sample # 29

Good bloating when quick fired to 1210°C. in a reducing atmosphere, fair pore structure, specific gravity less than one.

Slight bloating at cones 5 and 7 in the oxidizing atmosphere of the firing behavior test. Sample was pretty well melted down at cone 9 with large interconnected pores.

Sample # 30

Very slight bloating in both firing tests. Sample was very well vitrified at cone 11 and when quick fired to 1275°C.

Sample # 31

Very slight bloating at cone 11 in the oxidizing atmosphere of the firing behavior test, sample was well vitrified at cone 11.

No bloating when quick fired to 1245°C. in a reducing atmosphere.

Sample # 32

Slight bloating at cones 5 and 7 in the oxidizing atmosphere of the firing behavior test. Sample was almost completely melted down at cone 7.

Over bloated and melted down when quick fired to 1210°C. in a reducing atmosphere, the pores were large and interconnected.

Sample # 33

Fair bloating at cone 5 in the oxidizing atmosphere of the firing behavior test, fair pore structure, specific gravity about 1, sample melted down at cone 7.

TABLE I (Cont'd.)

Fair bloating at 1190°C. when quick fired in a reducing atmosphere, poor pore structure, specific gravity greater than one.

Sample # 34

Slight bloating at cones 7 and 9 in the oxidizing atmosphere of the firing behavior test, sample was well vitrified at cone 11.

No bloating when quick fired to 1250°C. in a reducing atmosphere.

Sample # 35

No bloating in either firing test. Sample was well vitrified at cone 11 and when quick fired to 1355°C.

Sample # 36

Good bloating at cones 7 and 9 in the oxidizing atmosphere of the firing behavior test, excellent pore structure, specific gravity less than one, sample melted down at cone 11.

Good bloating when quick fired to 1275°C. in a reducing atmosphere, poor pore structure because of over-firing.

Sample # 37

Good bloating at cone 7 in the oxidizing atmosphere of the firing behavior test, fair pore structure, specific gravity less than one, sample melted at cone 9.

Slight bloating at 1190°C. when quick fired in a reducing atmosphere, pore structure not well developed but uniform and well disseminated.

TABLE I (Cont'd.)

Sample # 38

Fair bloating at cone 7 in the oxidizing atmosphere of the firing behavior test, poor pore structure, specific gravity greater than one, almost melted down at cone 7 and completely melted at cone 9.

Over bloated and melted down when quick fired to 1245°C. in a reducing atmosphere.

Sample # 39

No bloating in either firing test. Fairly well vitrified at cone 11 and very well vitrified when quick fired to 1355°C.

Sample # 40

Very slight bloating in both firing tests. Sample well vitrified at cone 11 and when quick fired to 1250°C.

Sample # 41

No bloating in either firing test. Sample well vitrified at cone 11 and when quick fired to 1250°C.

Sample # 42

No bloating in either firing test. Sample fairly well vitrified at cone 11 and very well vitrified when quick fired to 1355°C.

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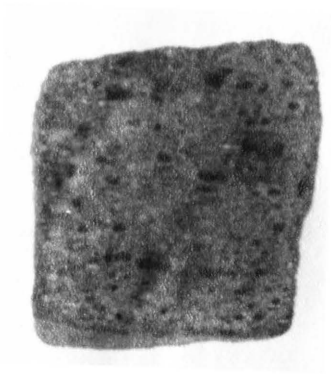
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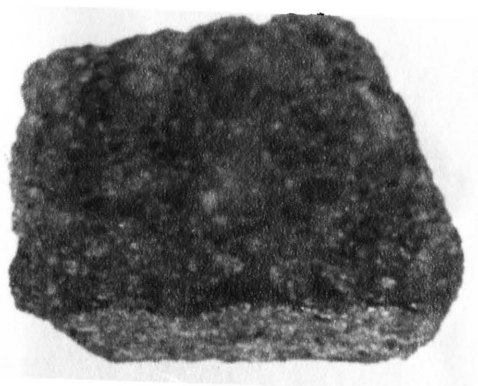
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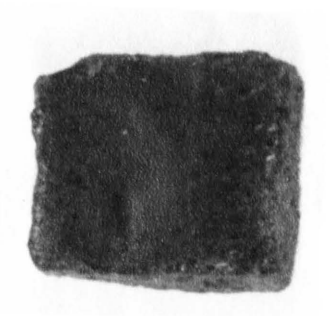
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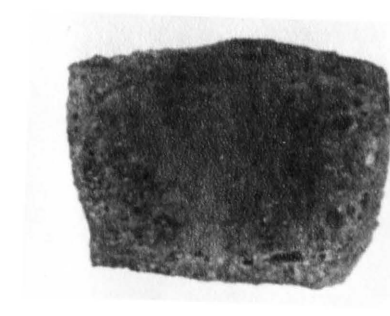
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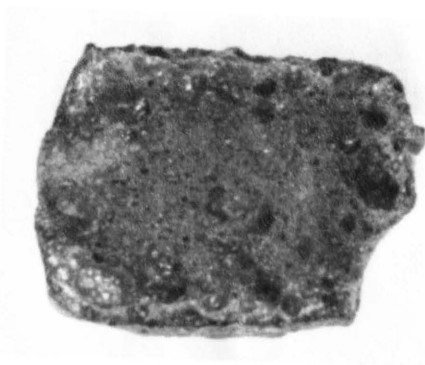
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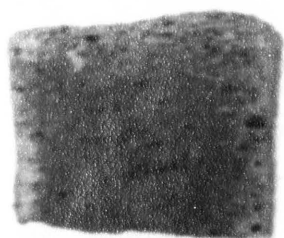
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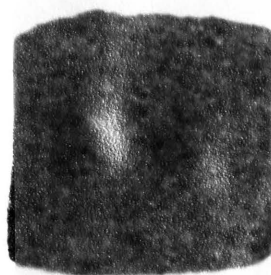
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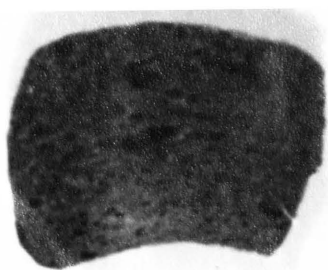
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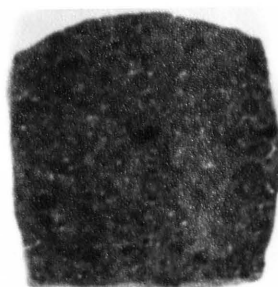
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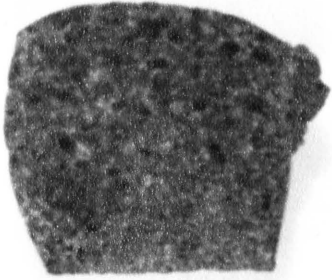
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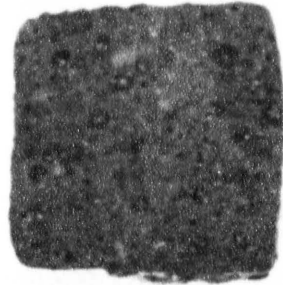
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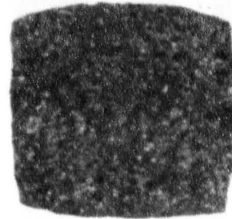
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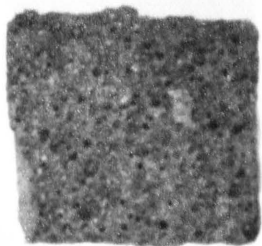
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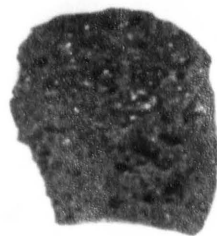
37

CHEMICAL ANALYSIS

Complete chemical analyses were run, by the writer, on eight of
the good bloating samples. The complete analysis consisted of deter-
mining SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O, K_2O, and loss on
ignition. A short chemical analysis was run on six of the good bloating
samples. The short analysis consisted of determining SiO_2, Al_2O_3,
Fe_2O_3, TiO_2, and loss on ignition (L.O.I.). The procedure followed in
the chemical analysis was the one recommended by the A.S.T.M. for fire
clays, designation C 18-45. The results are shown in Table II.

Riley[8] formed a triaxial diagram with Al_2O_3, SiO_2, and fluxes
at the apexes of the diagram. Using the chemical analyses of his bloat-
ing samples and some 81 analyses reported by Conley, Wilson and Kline-
felter[7] he defined a "bloating area" within the diagram. The plotting
of the analyses was done on a loss on ignition basis. Riley's[8] con-
tention was that if the analysis of a clay or shale fell within this
area it met one of the requirements for bloating, i.e. the sample will
form sufficient glass of proper viscosity at bloating temperatures.
Figure 1 is the triaxial with the "bloating area" outlined on it, with
a dotted line. The writer has plotted his analyses on this diagram.
Only three of these samples are definitely outside the "bloating area"
and these are very close considering that the area is only approximate
to begin with. The writer considered this result as enough of a
substantiation of Riley's[8] hypothesis to use it in the work on

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[8] Riley, op. cit., p. 5.

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[7] Conley, Wilson, Klinefelter, op. cit., p. 5

additives.

The accuracy of the bloating area is surprising considering the vast difference in the fluxing properties of the various oxides that are bunched at one apex of the triaxial. Riley[8] was even successful in bloating some igneous rocks whose analyses placed them in the "area." Although no extensive work was done with pure oxides, to see if the "area" applied, the writer did make one firing using alumina, silica and hematite plus carbon with no success.

Conley, Wilson, and Klinefelter[7] reported the chemical analyses of 81 clays and shales, 39 were considered good bloaters. They could find no definite correlation between chemical analysis and bloating. The writer was not successful, either, in locating any consistency in his analyses.

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[8]Riley, op. cit., p. 5.

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[7]Conley, Wilson, Klinefelter, op. cit., p. 5.

TABLE II
Chemical Analysis of Good Bloating Samples

	1	2	3A	4	6	7	8A	23	27	29	33	36	37	38
SiO_2	60.4	61.4	55.5	59.1	67.7	62.6	61.4	59.4	60.0	52.7	55.9	74.0	59.4	53.2
Al_2O_3	21.2	20.2	21.4	19.4	17.8	18.8	17.4	14.3	12.7	21.3	12.1	10.3	20.0	13.5
Fe_2O_3	1.1	1.9	0.7	2.8	3.2	2.2	3.0	3.5	5.1	7.6	1.7	1.6	3.2	3.6
TiO_2	0.7	1.1	0.4	1.0	0.8	1.0	1.7	1.0	0.7	1.1	0.8	1.1	1.1	0.9
CaO	1.6	2.7	1.6	2.1		1.1		4.9	3.9					6.2
MgO	1.8	2.9	2.1	2.6		1.6		2.1	2.5					2.0
Na_2O	1.0	1.2	0.4	0.1		0.5		0.7	0.3					1.5
K_2O	2.2	1.8	1.5	0.8		4.5		3.5	3.3					2.7
LOI	8.1	7.2	15.7	10.8	8.3	6.5	11.5	7.9	11.6	9.3	15.1	8.7	12.5	13.1
Total	98.1	100.4	99.3	98.7	97.8	98.8	95.0	97.3	100.1	92.0	85.6	95.7	96.2	97.2

FIGURE I

100% SI O$_2$

36

6

37

I

3A

4

7

2

8A

29

27

23

33

38

60% AL$_2$O$_3$

60% FLUX
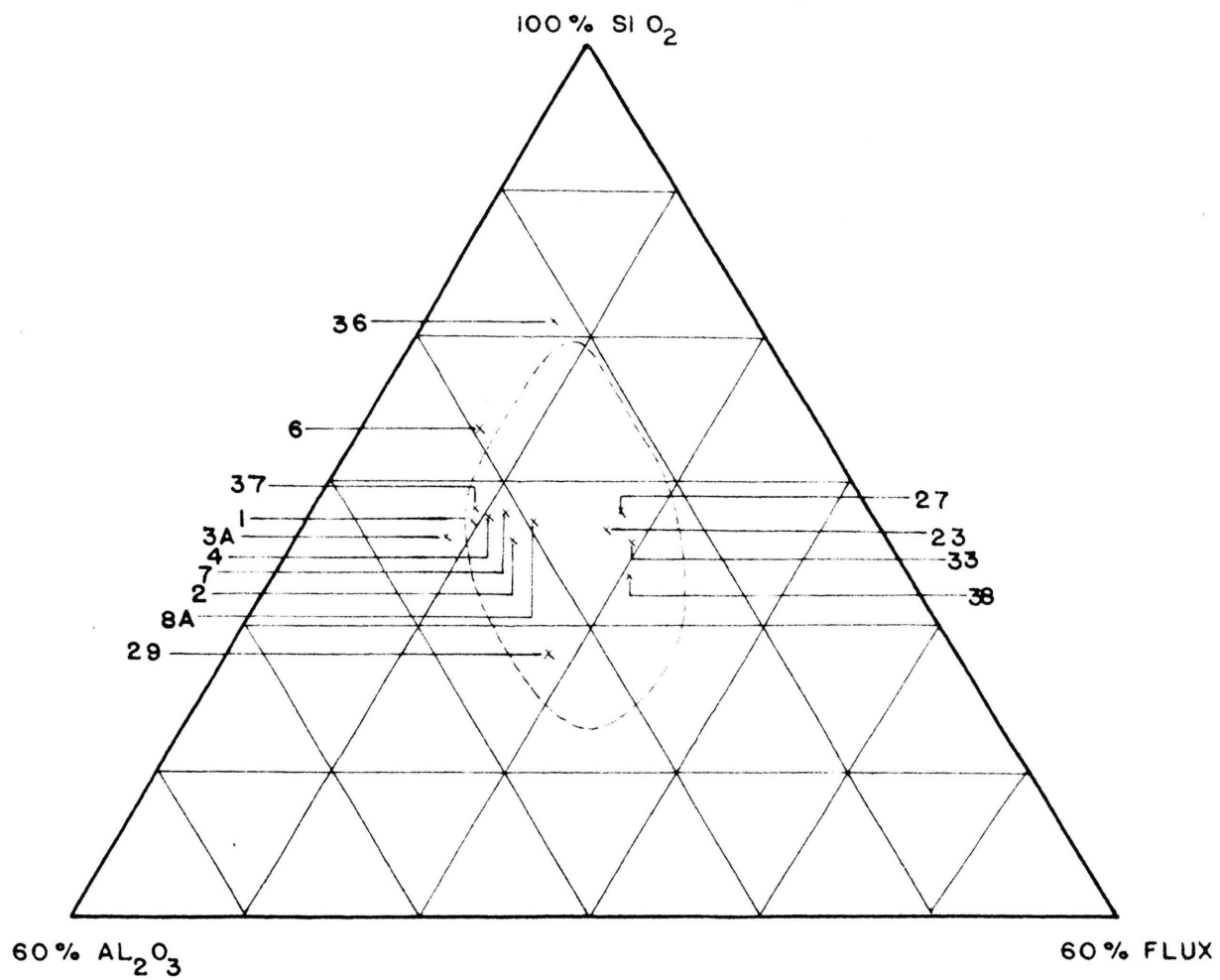
DIFFERENTIAL THERMAL ANALYSIS

Differential thermal curves were run on eight of the naturally bloating shales; these were samples 1, 2, 3A, 4, 7, 23, 27, and 38. The curves appear in Figure 2.

The differential thermal apparatus used continually records an amplified magnitude of the emf. generated in the differential thermocouple versus time. The furnace was raised at a uniform rate of 10°C. per min. to 1000°C.

Although one of the objects of this work was not to find out what caused bloating, it was hoped that these curves might give some insight into this problem and thus simplify the problem of finding successful additives. The work on additives will show that the interpretation of these curves helped in the selection of an additive that proved very successful in all of the samples investigated.

Everhart and Van Der Beck[10] ran differential thermal curves on many structural clay bodies. Along with the curves they made weight loss determination and chemical analyses of the gases evolved during firing. From these data they were able to identify the thermal reactions. The principal reactions they identified were the exothermic burning out of organic carbon above 100°C., the sharp exothermic peak occurring at about 500°C. caused by the primary oxidation of pyrite and marcasite, and the slight endothermic peak occurring between 750°C. and 850°C. caused by the decomposition of calcium and magnesium carbonates. These reactions are the first ones one would think of when

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[10] Everhart, J. O., and Van Der Beck, R. R., Jr., "Differential Thermal Analyses as a Means of Predicting Firing Behavior of Structural Clay Materials," Am. Ceram. Soc. Bull., 32 (7), pp. 239-41, (1953).

considering the bloating of shales. Since the structural clay bodies they used consisted of shales or shales mechanically mixed with clays, the interpretation of their differential thermal curves may be applied directly to the curves obtained in this work.

When one is looking for a reason for bloating, it would naturally be hoped that all the bloating is due to one cause. Since all of the curves, Figure 1, are of good bloating shales, they were examined for some similarity. The only similarity evident is the long smooth exothermic curve due to the oxidation of organic carbon. The oxidation of the iron sulfides are plainly evident on the curves for samples 1, 3A and 4 but are only slightly observed if at all on the other curves. It will be remembered from the section on firing that 1 and 4 bloated only in the reducing atmosphere of quick firing while sample 3A bloated during both firing tests.

The endothermic peaks due to the decomposition of the carbonates only appear in curves 3A and 4 and these peaks are probably emphasized by the endothermic reaction due to the evolution of the water of crystallization.

The significance of these curves was considered to be the continued oxidation of organic carbon even at 1000°C., and also that there was no evidence that this oxidation was anywhere near completed at this temperature. In fact, the curves indicate that the maximum oxidation has not yet been reached at 1000°C. in most cases. This evidence coupled with the fact that the best bloating occurred from 1100°C. to 1300°C. leads the writer to attribute bloating to the oxidation of organic carbon. It must be remembered, however, that bloating cannot take place unless glass of the right fluidity is formed before all the carbon is burned out. Fortunately, glass formation and its fluidity can

be adjusted by additives and the rate of carbon oxidation can be partially controlled by keeping a reducing atmosphere in the furnace. A reducing atmosphere would tend to greatly deter the oxidation of carbon unless there was also a compound in the sample that was unstable at high temperatures and in the process of changing forms liberated oxygen that could combine with the carbon. This reasoning was put to use in the work on additives. The work on additives substantiates, in the writer's opinion, the indications, shown by the differential thermal curves, that the cause of bloating in these shales is the oxidation of organic carbon.

Some researchers into the problem of the bloating of shales have maintained that the oxidation of carbon cannot cause bloating because many high carbon shales do not bloat, while some low carbon shales do. But this argument is not a good one unless the amount and fluidity of the glass formed at bloating temperatures is considered. There is also another consideration that must be taken into account and that is the furnace atmosphere. In the work on additives, it will be shown that the furnace atmosphere is of prime importance, since in at least 6 cases, all those tried, very little bloating occurred in an oxidizing atmosphere while an excellent bloat resulted from firing in a reducing atmosphere. Also, if one calculates the theoretical amount of carbon necessary to bloat a sample 100%, the percentage is remarkably small. The dry volume of the samples was approximately one cubic inch or about 16 cc. Under standard conditions one mole of gas will occupy 22.4 liters. Therefore, at standard conditions 16/22400 or 0.000714 of one mole of gas will expand a 16cc. sample 100%. Of course, the fraction of a mole would even be less at bloating temperatures if the

pressure inside a sample could be neglected, but since the calculation is just an illustration, standard conditions will be assumed. To continue; 0.000714 times the molecular weight of carbon gives about 0.0086 grs. of carbon. The dry weight of the samples averaged about 25grs., therefore, 0.034% of carbon would bloat a 25 grs. sample 100%. Bloating a sample 100% would make the bulk density 0.834 grs/cc. which is less than water and, therefore, would satisfy the criterion used for suitable expansion.

FIGURE 2
DIFFERENTIAL THERMAL CURVES
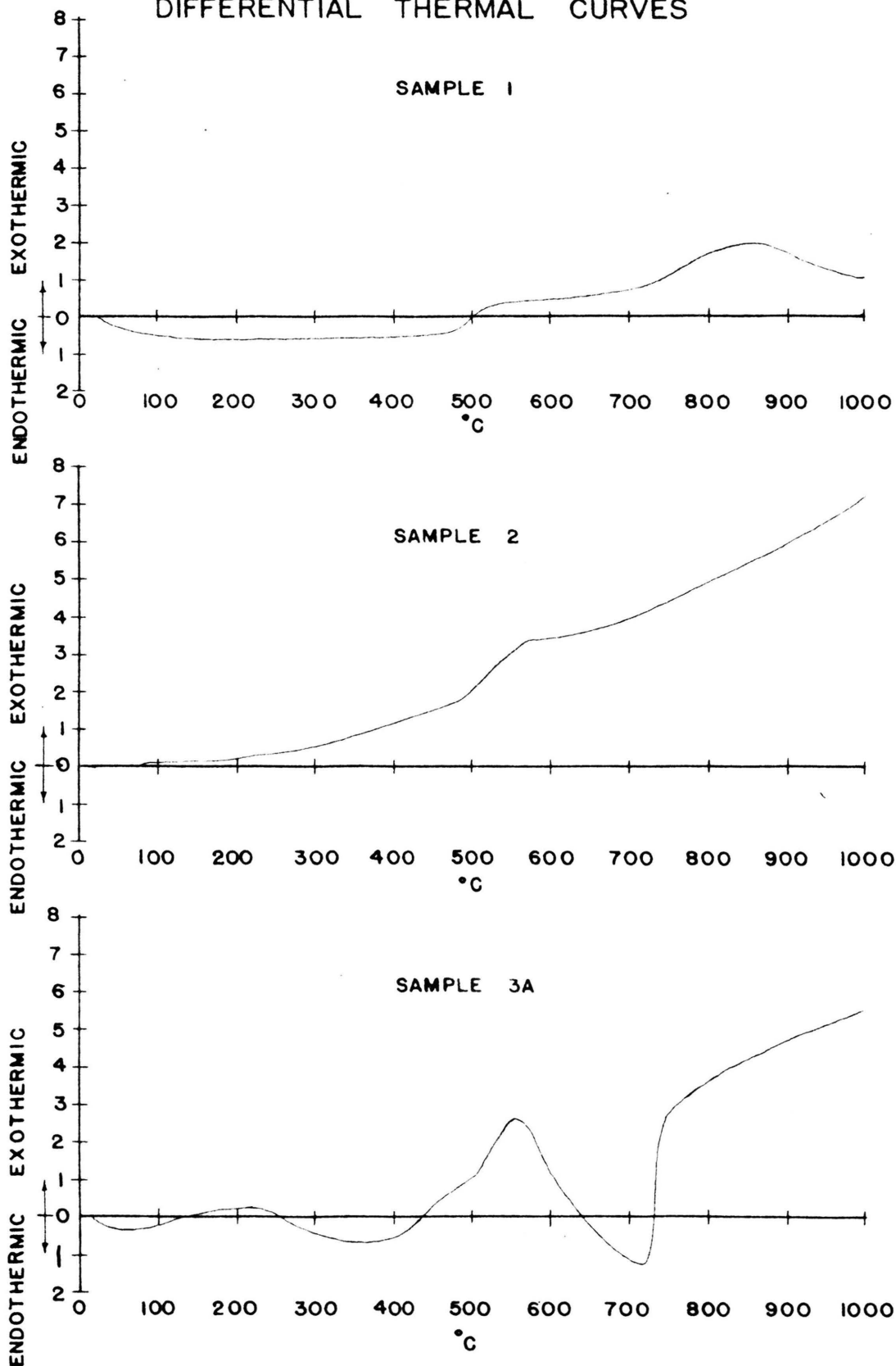
FIGURE 3
DIFFERENTIAL THERMAL CURVES
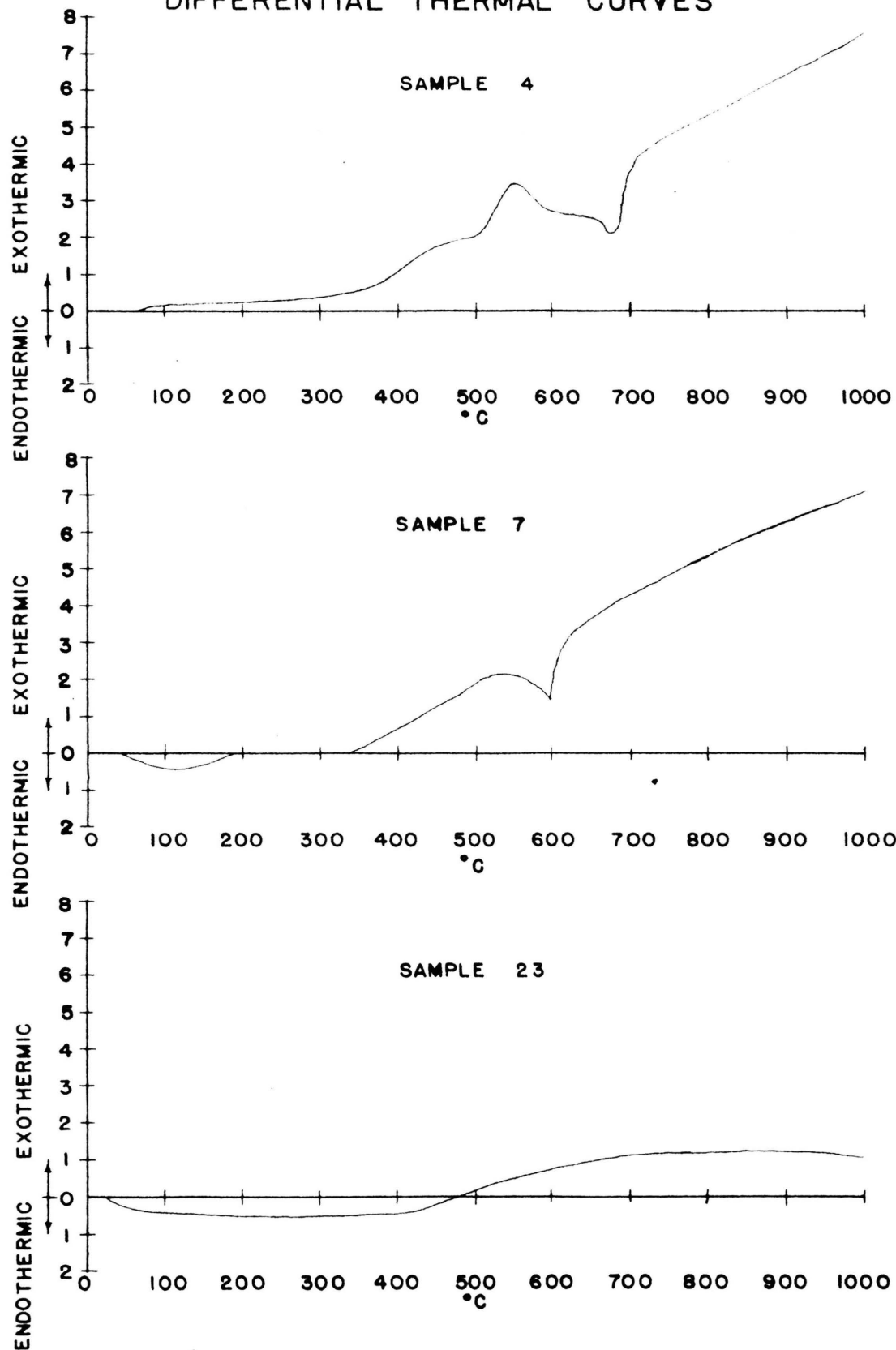
FIGURE 4
DIFFERENTIAL THERMAL CURVES
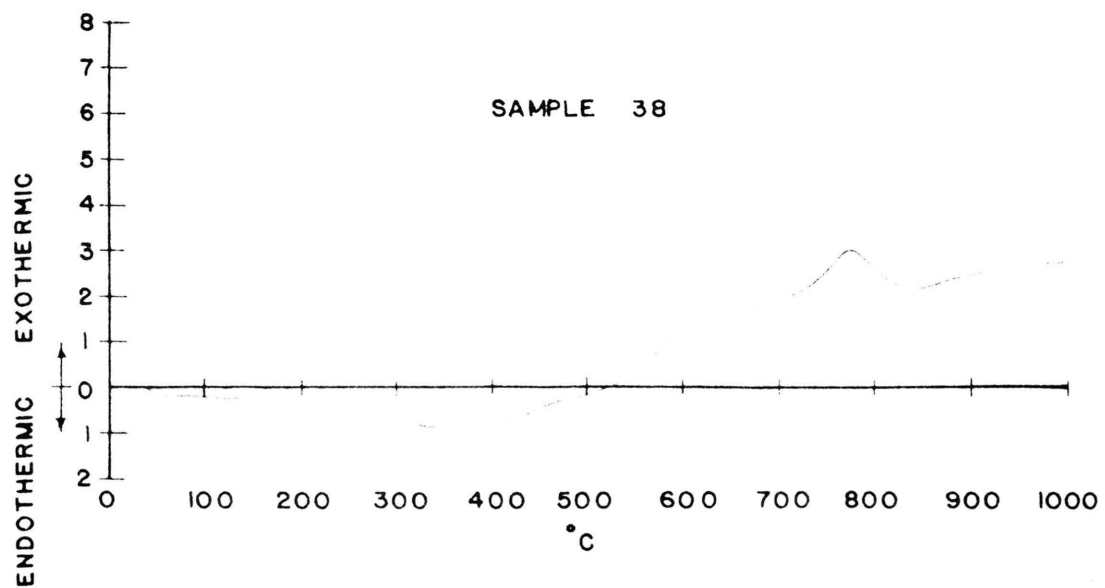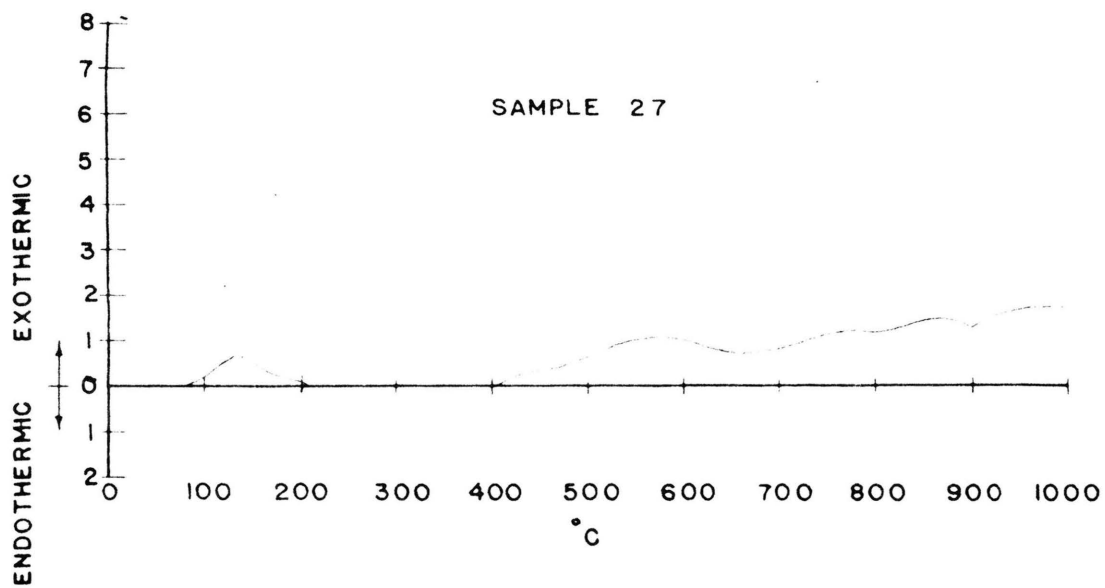
SAMPLE 27

SAMPLE 38

ADMIXES

The first admixes tried were $CaSO_4$ and $CaCO_3$ because these would be the most convenient if they proved successful. The theoretical percentages of CO_2 and SO_3 it would take to bloat a sample 100% were calculated and added to samples 10A and 41. These amounts were 9.7% $CaSO_4$ and about 7.2% $CaCO_3$. The samples were fired in both oxidizing and reducing atmospheres in a gas fired furnace. The atmosphere was controlled by the air-gas mixture, excess air gave an oxidizing atmosphere and excess gas gave a reducing atmosphere. In all cases, the rate of heating was approximately 600C°/hr. The results were just about what would be expected by anyone familiar with the fluxing properties of most calcium compounds. The samples melted down completely and rapidly at about 1100°C., no bloating was apparent. Samples 10A and 41 were chosen, more or less arbitrarily, for these first tests. Sample 10A was chosen because it showed some inclination to bloat with no admixes and 41 was chosen because it showed no bloating at all in either of the previous firing tests.

There has been a good deal of work on admixes to produce bloating. The most extensive, as already mentioned, was by Conley, Wilson, and Klinefelter[7]. The only method of choosing additives has been to make an intelligent guess and see what happened. In all cases, the guess was an effort to add a gas producing agent.

The writer noted that of the 55 samples fired, only 10 showed no bloating at all in either firing test, this suggested that the gas

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[7]Conley, Wilson, Klinefelter, op.cit., p. 5.

producing agents were present in most cases. If this was indeed the case, then the logical approach to admixtures was selecting ones that properly adjusted the amount and viscosity of the glass formed at bloating temperatures. In this light the triaxial and "bloating area" defined by Riley[8] could perhaps be used. With this in mind the writer ran seven short chemical analyses on samples that show slight bloating. The samples were chosen from different parts of the state and were 10A, 11, 12, 16B, 17, 25, and 34. Table 3 gives their analyses. After recalculating these analyses to a L. O. I. basis, they were plotted on the Al_2O_3-SiO_2-Flux composition diagram. Figure 5 shows this triaxial with the seven points plotted. The "bloating area" is also outlined by a dotted line in Figure 5. As can be seen, most of these slight bloating samples fell within the bloating area, therefore they supposedly met the second requirement for good bloating samples, i.e., enough glass of the proper viscosity is formed at bloating temperatures. Therefore, either the writer's assumption , that the gas producing agents are present, was wrong, or else the "bloating area" hypothesis is not entirely correct. It was decided that the "bloating area" contention was weak because of the nature of the triaxial in which it was plotted. In this triaxial all fluxes are bunched at one apex regardless of their fluxing properties. Therefore, iron compounds which are in general poor fluxes are given the same importance as calcium compounds which are very active fluxes. With this in mind, the writer decided to add a "weak" flux so that appreciable amounts could be added, thus assuring a good density of glass formed at bloating

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[8] Riley, op. cit. p. 5

TABLE III

	10A	11	12	16B	17	25	34
SiO_2	61.4	61.8	64.5	54.7	59.5	71.3	74.6
Al_2O_3	16.5	17.6	20.4	20.1	16.1	11.7	8.5
Fe_2O_3	4.1	7.9	3.8	3.2	6.8	5.4	2.8
TiO_2	1.9	1.1	0.9	0.8	1.9	1.0	1.0
L.O.I.	12.4	7.1	7.4	10.5	12.3	5.4	10.9
Total	96.3	95.5	97.0	89.3	96.6	94.8	97.8

FIGURE 5

100 % SI O_2

34

25

12 ————————————10A

17

POTASSIUM
FELDSPAR

11

16B

NEPHELITE

60 % AL$_2$O$_3$ 60 % FLUX
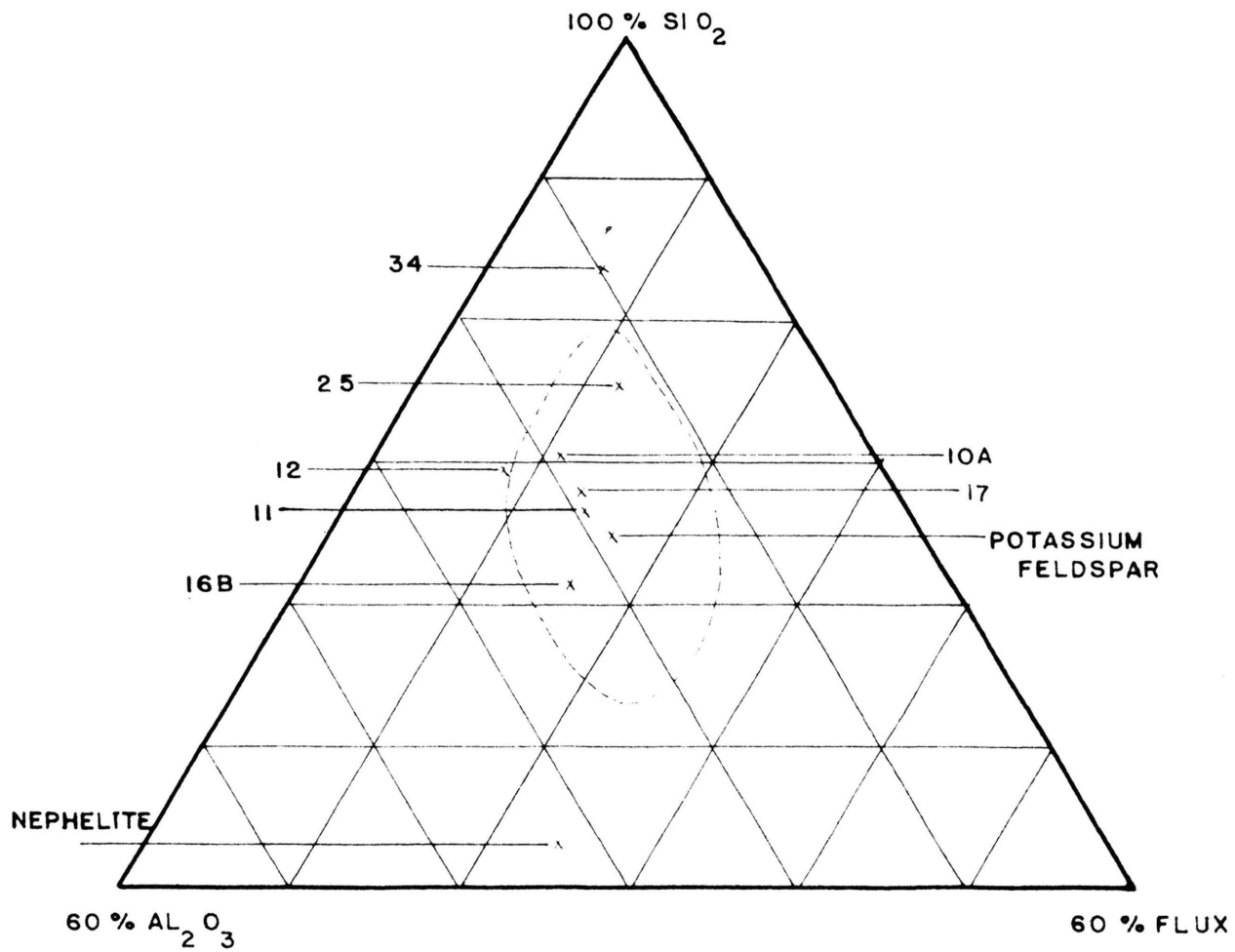
temperatures. Also, the flux added must not form a very fluid glass. These conditions eliminated calcium compounds since not only are they very active fluxes but calcium glasses are very fluid. The writer decided upon Fe_2O_3. The reasons for choosing Fe_2O_3 were threefold: 1. it met the above conditions arbitrarily imposed on the additive by the writer; 2. Fe_2O_3 is reduced to FeO liberating oxygen at about 1000°C. according to Hostetter and Roberts[11] and, therefore, would make available the oxidizing conditions inside the sample necessary for the oxidation of organic carbon; and, 3. it is readily available as hematite.

Referring to Figure 5, it was possible to add percentages of ferric oxide so as to keep six of the seven samples within the bloating area. These six were 10A, 11, 12, 16B, 17, and 25.

Fe_2O_3 was added to 10A, 12, 16B and 17. Table 4 gives the percentages added and the new position of the mixtures in the triaxial as percentages of SiO_2, Al_2O_3, and Flux; it also contains all additive firing results. The samples plus the Fe_2O_3 were placed in ball mills and mixed in this way for about an hour. They were then mixed with water and made into one inch cubes for firing. After drying at 110°C. they were fired rapidly in a gas fired furnace. The atmosphere was kept oxidizing by adjusting the air-gas mixture. The results of this firing were very significant. In all cases the samples did not bloat but when broken open showed that a bloated structure had formed in the center. This meant that the furnace atmosphere had prevented bloating to the depth that it was effective. The pieces were then fired in a reducing atmosphere in the same furnace. Each of these four samples bloated

[11]Hostetter, J. C., and Roberts, H. S., "Notes on the Dissociation in Glass and Its Relation to the Color of Iron-Bearing Glasses," J. Am. Ceram. Soc., 4 (11) 927-38 (1921).

excellently. They had excellent pore structure and floated on water.

The result of adding Fe_2O_3 and producing an excellent bloat only in a reducing atmosphere coupled with the indications, from the study of the differential thermal curves, of the good bloating samples, that the oxidation of organic carbon was the bloating agent leads the writer to believe the cause of bloating in these samples is solved. In a reducing atmosphere, organic carbon would not be burned out, therefore, at a high temperature when Fe_2O_3 is reduced to FeO liberating oxygen, the carbon is still there to be oxidized forming CO and CO_2 which bloats the sample. To test this hypothesis Fe_2O_3 was added to samples 6 and 8A, which were good bloating samples during the quick firing test with no additives. Eleven per cent Fe_2O_3 was added to sample 6 and 5.9% was added to sample 8A. Eleven per cent Fe_2O_3 placed sample 6 within the "bloating area" since it was not before, and 5.9% Fe_2O_3 kept 8A within the area. Samples 6 and 8A were then quick fired in an oxidizing atmosphere and neither sample bloated but formed small bloated cores as did the slight bloating samples. When fired in a reducing atmosphere, however, both bloated excellently, in fact, much better than they had with no additive. Plate 4 contains actual size pictures of sample 6, bloated with no additive and when bloated containing 11% Fe_2O_3.

To further test this hypothesis, two bodies were made up using non-bloating, naturally occurring minerals. Figure 5 shows the theoretical position of Nepheline Syenite, $2(Na_2O, K_2O) \times 4Al_2O_3 \times 9SiO_2$, in the triaxial. To Nepheline Syenite enough silica was added to place the mixture in the "bloating area" and to this mixture Fe_2O_3 and lamp black were added. Table 4 gives the percentages and the mixture's position in the triaxial. The other body contained just potassium feldspar, Fe_2O_3,

and lamp black since feldspar falls within the "bloating area". Table 4 gives the percentages of each.

Each of these mixtures were ground and mixed in ball mills for 2 to 3 hours. After forming them into one inch cubes and drying, they were fired rapidly in a reducing atmosphere, both bloated. The feldspar sample bloated enough to be considered good. Plate 6 contains actual size photographs of both these bloated samples.

The remaining slight bloating samples to which only Fe_2O_3 was added, 11 and 25, were fired in a reducing atmosphere. They both bloated well. The results are included in Table 4. Sample 11 was particularly interesting. Since it fell in the middle of the bloating area, see Figure 5, at first 2% Fe_2O_3 was added and the resulting bloating was poor. Upon adding 5% Fe_2O_3, however, an excellent bloat resulted. If the theoretical percentage of Fe_2O_3 needed to bloat a sample 100% is calculated assuming the Fe_2O_3 is reduced to FeO the percentage is 11.4%. Referring to Table 3, sample 11 has a calculated Fe_2O_3 percentage of 7.9, when this is added to the 5% Fe_2O_3 which produced the excellent bloat the total percentage is 11.9 which is only 0.5% higher than the theoretical percentage.

Sample 34 could not be brought into the bloating area by the addition of flux alone. Nepheline Syenite whose theoretical analysis is 42.8% SiO_2, 32.4% Al_2O_3, and 24.8% Flux, was added to sample 34 alone with Fe_2O_3. Table 4 gives the percentages used. This mixture fell within the bloating area. Upon firing this mixture to 1135°C. only poor bloating resulted but the sample looked as if it would bloat at a higher temperature. This was not tried, however.

Hematite was also added to samples 33 and 36. These samples bloated with no admix during both the original firing tests, oxidizing as well as reducing atmospheres. Therefore, it was of interest to see whether Fe_2O_3 when added would affect the bloating. Table 4 contains the percentages of Fe_2O_3 added and the mixture's new position on the triaxial. Both samples bloated much better than they did with nothing added and at a lower temperature.

Plates 4 and 5 are actual size photographs of some of the bloated samples before and after adding the Hematite.

TABLE IV

Sample # 6 + 11% Fe_2O_3

Makes the fired analysis 65% SiO_2, 17% Al_2O_3, 18% Flux.

Excellent bloating when fired in a reducing atmosphere to 1135°C. in 2 hours. This sample bloated well upon quick firing with no additive, see Table I.

Sample # 8A + 5.9% Fe_2O_3

Makes the fired analysis 65% SiO_2, 18% Al_2O_3 and 17% Flux.

Excellent bloating when fired in a reducing atmosphere to 1175°C. in 3 hours. This sample bloated well upon quick firing with no additive, see Table I.

Sample # 10A + 5.9% Fe_2O_3

Makes the fired analysis 65% SiO_2, 18% Al_2O_3, and 17% Flux.

Excellent bloating when fired in a reducing atmosphere to 1175°C. in 3 hours.

Sample # 11 + 5% Fe_2O_3

Makes the fired analysis 58.7% SiO_2, 16.7% Al_2O_3, and 24.6% Flux.

Excellent bloating when fired in a reducing atmosphere to 1120°C. in 3 hours.

Sample # 12 + 11.4% Fe_2O_3

Makes the fired analysis 61% SiO_2, 19.5% Al_2O_3 and 19.5% Flux.

Excellent bloating when fired in a reducing atmosphere to 1135°C. in 2 hours.

TABLE IV (Cont'd.)

Sample # 16B + 4.1% Fe_2O_3

Makes the fired analysis 59% SiO_2, 20.5% Al_2O_3, and 20.5% Flux.

Excellent bloating when fired in a reducing atmosphere to 1115°C. in 2 hours.

Sample # 17 + 7.8% Fe_2O_3

Makes the fired analysis 65% SiO_2, 18% Al_2O_3 and 17% Flux.

Excellent bloating when fired in a reducing atmosphere to 1115°C. in 2 hours.

Sample # 25 + 6.7% Fe_2O_3

Makes the fired analysis 70% SiO_2, 11.5% Al_2O_3 and 18.5% Flux.

Good bloating when fired in a reducing atmosphere to 1130°C. in $3\frac{1}{2}$ hours, specific gravity about 1.

Sample # 34 + 31.4% Nepheline Syenite + 5.7% Fe_2O_3

Makes the fired analysis 60.9% SiO_2, 16.0% Al_2O_3, and 23.1% Flux.

Poor bloating when fired in a reducing atmosphere to 1135°C. in 3 hours. Should be fired to a higher temperature but was not in this work.

Sample # 33 + 3.4% Fe_2O_3

Makes the fired analysis 63% SiO_2, 14% Al_2O_3 and 23% Flux.

Excellent bloating when fired in a reducing atmosphere to 1130°C. in $3\frac{1}{2}$ hours. This sample bloated with nothing added, see Table I.

TABLE IV (Cont'd.)

Sample # 36 + 6.7% Fe_2O_3

Makes the fired analysis 75% SiO_2, 10.5% Al_2O_3, and 14.5% Flux.

Good bloating when fired in a reducing atmosphere to 1175°C. in 3 hours. This sample bloated with nothing added, see Table I.

Nepheline Syenite   49.8%

SiO_2 43.1%

Fe_2O_3 7.1%

Lamp black   4% added

Makes the fired analysis 65% SiO_2, 16.5% Al_2O_3, and 18.5% Flux.

Fair bloating when fired in a reducing atmosphere to 1135°C. in 3 hours, would not float but was exceptionally hard.

Feldspar   96.7%

Fe_2O_3 3.5%

Lamp black   3% added

Makes the fired analysis 62.5% SiO_2, 17.5% Al_2O_3, and 20% Flux.

Good bloating when fired in a reducing atmosphere to 1115°C. in 3 hours, specific gravity less than 1, pore structure very uniform and well separated.

PLATE 4
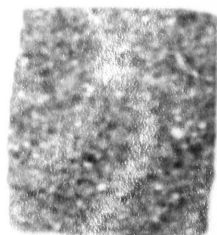
6
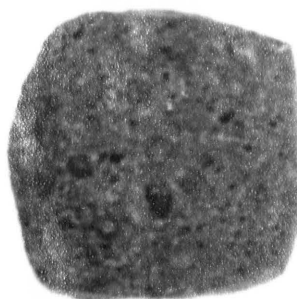
6 + 11% Fe$_2$O$_3$
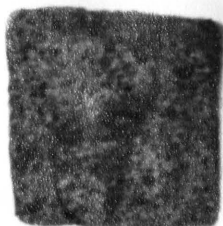
10A
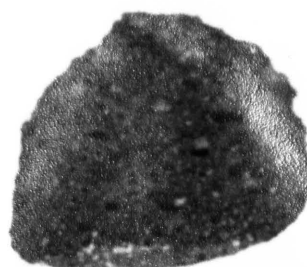
6 + 5.9% Fe$_2$O$_3$
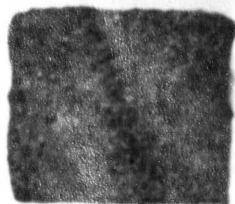
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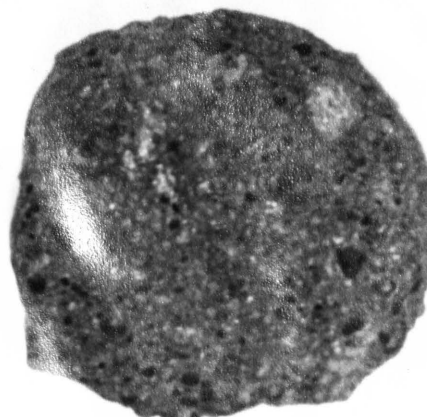
11 + 5% Fe$_2$O$_3$

PLATE 5
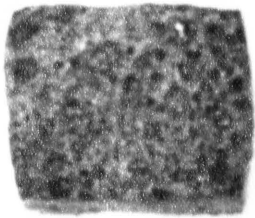
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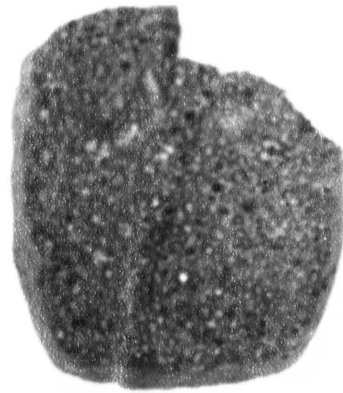
12 + 11.4% Fe$_2$O$_3$
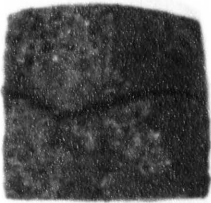
16B

16B + 4.1% Fe$_2$O$_3$
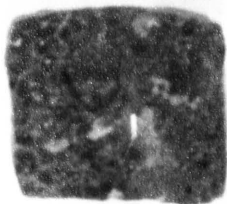
17
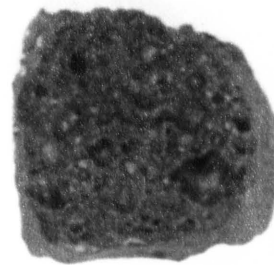
17B + 7.8% Fe$_2$O$_3$

PLATE 6
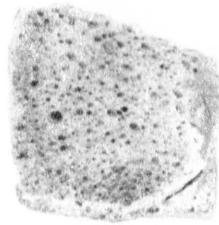
93.6% Potassium feldspar

3.4% Fe_2O_3

3.0% Lamp black
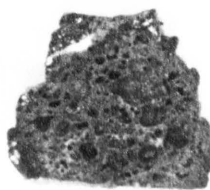
41.5% SiO_2

47.9% Nepheline syenite

6.8% Fe_2O_3

3.8% Lamp black

ROTARY BATCH TYPE KILN

During the summer of 1953, the writer designed and built with the help of W. T. Harper a batch type rotary kiln. This kiln is to be used in further work on this project.

The kiln is 54 inches long with an outside diameter of 36 inches. The firing chamber is 36 inches long and 18 inches in diameter.

It is friction driven by 4 rollers 6" long and 6" in diameter. Power is supplied by a 1/3 hp. ratio motor. The drive is transmitted from the ratio motor by chains and sprockets through a jack shaft.

The kiln can be made to rotate at different speeds by changing the sprocket on the jack shaft.

The kiln is fired by an air-gas premixer burner and can easily reach 1200°C. in 4 hours.

The kiln can be charged with approximately 100 pounds of raw clay. Unfortunately, however, time did not permit the firing of any of the samples.

CONCLUSIONS AND SUMMARY

There are many excellent bloating shales occurring naturally in Missouri. Of the 55 samples tested, eleven bloated sufficiently to be used to produce lightweight aggregate practically regardless of firing time and regardless of the kiln atmosphere. These samples were 3A, 7, 10B, 20B and C, 23, 27, 33, 36, 37 and 38A, see Appendix A for their locations. For the best bloating all of these samples should be fired above 1200°C.

The remaining eleven of the naturally occurring good bloating samples must be fired in a reducing atmosphere to produce a suitable bloat. These samples were 1, which is now being used commercially in the production of "Haydite," 2, 3B, 4, 5, 6, 8A, 15B, 24, 26 and 29, see Appendix A for their locations. For the best bloating all but sample 2 should be fired above 1200°C. for best results. Sample 2 bloats best at about 1150°C. and is the only one of the 22 good bloating samples that should be fired below 1200°C. Table I gives specific firing temperatures and conditions for each of these samples.

The differential thermal analyses of some of these naturally good bloating samples indicates that the oxidation of organic carbon is the prime reason for bloating.

The addition of Hematite, in amounts over 5%, produced good bloating in all of the poor bloating samples to which it was added, provided the Al_2O_3 - SiO_2 - Flux percentages in the mixture placed it in or near the "bloating area" defined by Riley[8], see Figure 1 or 5. The addition of

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[8]Riley, op. cit., p. 5.

Hematite also improved the bloating of samples that bloated sufficiently without an additive. The firing of a sample in which Hematite has been added must take place in a reducing atmosphere. The temperatures to which these mixtures must be fired is about 100°C. lower than the naturally bloating samples, or in the 1100° to 1200°C. range. Poor bloating samples 10A, 11, 12, 16B, 17 and 25, produced excellent bloats when hematite was added. Table 4 gives the percentages used and specific firing data.

Synthetic bloating bodies were made up using Nepheline syenite, silica, hematite and lamp black and potassium feldspar, hematite and lamp black. The percentages used and the firing data appears in Table 4.

This work indicates that bloating is caused in these samples by reduction of Fe_2O_3 to FeO releasing oxygen that combines with organic carbon forming CO and CO_2 which is the bloating gas.

APPENDIX A

Sample # 1

Section in clay pit at Carter-Waters Corporation, Haydite plant; NW¼ SE¼ NW¼ sec. 14, T. 54 N., R. 35 W., Platte County, six-tenths mile south of New Market on east side of U. S. Highway 71.

| | Thickness | |
| | Feet | Inches |

Pennsylvanian System

  Missourian Series

    Peedee group

      Iatan formation

        2. Limestone, blue-gray - - - - - - -   8

      Weston formation

(Spl. # 1) 1. Shale, medium gray, weathers to

          light gray, hard where fresh;

          contains scattered fragments of

          clam shells, forms steep slope - - 30

  Note: Description according to Greene and Howe.

Sample # 2

Section in clay pit at United Brick and Tile Company plant,
SE¼ sec. 5, T. 44 N., R. 31 W., Cass County, about one mile southwest
from Harrisonville.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Missourian Series

    Pleasanton group

      Exline limestone

        6. Limestone, and calcareous shale;
limestone earthy, slabby; bed
contains Euphenrites, Trepospira,
Crurithyris, Marginifera splendens - 0   4-10

  Unnamed coal

        5. Coal, streak - - - - - - - - - - -

  Unnamed clay

        4. Clay (underclay) - - - - - - - - - - 1-3

  Hepler sandstone

        3. Sandstone, impure and calcareous,
and impure nodular limestone;
limestone is marine and forms
ledge; limestone locally conglom-
eratic, containing fragments of
coal and silicified wood - - - - - - 0-3

        2. Sandstone, shaly - - - - - - - - - - 5-6

Desmoinesian Series

   Marmaton group

    Holderville formation

(Spl. # 2)   1. Shale, sandy and silty; sand

occurs as varve-like stringers in

upper part; entire unit used in

manufacture of building brick - - - - 35^{+}_{-}

Note: Description of section according to Howe, W. B.

Sample # 3A, 3B, 3C, 3D, 3E

Section in pit of Crowe Coal Company, center of North line NW¼ sec. 12, T. 42 N., R. 27 W., Henry County, about six miles northwest of Clinton.

	Thickness	
	Feet	Inches

Pleistocene System

        Loess

(Spl. # 3E) 12. Clay, sandy in basal 4 feet;

        mottled brown and gray - - - - - - $14^{\pm}$

Pennsylvanian System

  Desmoinesian Series

    Cherokee group

    Unnamed shale

(Spl. # 3D) 11. Shale, drab or buff "soapstone,"

        contains clay-ironstone and

        secondary joint deposits of

        lime - - - - - - - - - - - - - - - $8^{\pm}$

    Unnamed beds

        10. Limestone - - - - - - - - - - - - - 0   0-10

         9. Coal - - - - - - - - - - - - - - - 0   4-10

         8. Shale and underclay, limey

        at base; $2\frac{1}{2}$-3 feet true under-

        clay - - - - - - - - - - - - - - - $4^{\pm}$

(Spl. # 3C) 8. Shale, light gray "soapstone,"

        subconcoidal fracture; weathered

	contains clay-ironstone concretions, also secondary gypsum - -	3	
(Spl. # 3B)	6. Shale, "slate," dark, phosphatic and clay-ironstone concretions and streaks, possibly limey, marine fossils at base; pyrite masses in lower part - - - - - -	3-4	
	5. Coal, blocky, bright - - - - - -	0	0-1½
(Spl. # 3A)	4. Shale, "slate," black, slickensided in upper part, no concretions - - - - - - - -- - - - - -	1-3	
	3. Limestone, hard, gray (Tebo cap rock) - - - - - - - - - - - -	1	2
	2. Shale, "slate," black, limey, somewhat fissile, with phosphatic concretions - - - - - - - - -	4	
	1. Coal, (Tebo) - - - - - - - - -	2	6

Note: Description according to Searight and Howe.

Sample # 4

Section in pit of Johnson Coal Company, NW¼ sec. 7, T. 40N., R. 26W., Henry County, about four miles west and north from Deepwater.

| | Thickness | |
| | Feet | Inches |

Pleistocene System (?)

      3. Clay - - - - - - - - - - - - - - $6^{\pm}$

Pennsylvanian System

  Desmoinesian Series

    Cherokee group

    Unnamed shale

(Spl. # 4)   2. Shale, dark gray; thin clay-iron-

             stone bands and nodules scattered

             throughout; upper 10 feet sandy - - $22^{\pm}$

        1. Coal (Jordan) - - - - - - - - - - - 0   30 (Av.)

Sample # 5

Section in pit of Mackie-Clemens Coal Company, on west line and 2500 feet north of south line of sec. 19, T. 33 N., R. 33 W., Barton County, Missouri, about three miles north of Mulberry, Kansas.

	Thickness	
	Feet	Inches

Pleistocene System (?)

      7. Clay, yellow — — — — — — — — — 3-4 (Av.)

Pennsylvanian System

  Desmoinesian Series

   Cherokee group

    Unnamed shale

      6. Shale, light gray to black waxy — $3^{\pm}$

      5. Coal (Pilot Coal — — — — — — — —   0   8

      4. Clay, underclay, blocky, gray

         to gray-green   — — — — — — — — 3-4

(Spl. # 5)   3. Shale (?) very dense, greenish-

         gray — — — — — — — — — — — — — 1-3

      2. Shale, medium gray, silty — — — — $11^{\pm}$

      1. Coal (Weir-Pittsburg) — — — — — — 2   6

Sample # 6

Section in bluff face on west side of Little North Fork Creek, SW corner sec. 12, T. 30 N., R. 33 W., Barton County, about thirteen miles west of Jasper. (Section taken in part from Searight).

		Thickness	
		Feet	Inches
7.	Soil cover containing fragmental sandstone, cobble to boulder size - - - - - - - - - -	6^+_-	

Pennsylvanian System

Desmoinesian Series

Cherokee group

6.	Coal (smut) - - - - - - - - - -	0	3
5.	Shale, black to dark gray, with siderite bands, poorly exposed -	16	
4.	Limestone, dark, many fragmented fossils; hard, gray dense masses in upper part, to 2 feet in diameter with cone-in-cone - - - -	1	6
3.	Coal (Rowe) hard, blocky - - - -	0	10
2.	Clay, underclay, light gray, buff mottled, hard silty, some stigmaria - - - - - - - - - - - - - - -	3	
1.	Shale, lower 4 feet black, hard, medium to dark gray above - - - -	15	

(Spl. # 6)

Sample # 7

Section in bluff on east side of Mikes Creek, SW¼ SE¼ NE¼ sec. 12, T. 22 N., R. 30 W., McDonald County, about four miles northeast from Powell, top of grade north from Sugarcamp Hollow.

	Thickness	
	Feet	Inches

Mississippian System

  Kinderhookian Series

    St. Joe group

      Compton formation

          2. Limestone, gray, crinoidal, forms high vertical bluff - - -   20±

      Chattanooga formation

(Spl. # 7)   1. Shale, light gray at top, grading downward through greenish gray to black; hard, blocky - - - - - - - - - - - -   6

Sample # 8A, 8B, 8C

Section in clay pit of Hydraulic Pressed Brick Company, center of NE¼ SE¼ sec. 10, T. 45 N., R. 5 E., St. Louis County, about one and three-quarter miles west of U. S. Highway 66, on south side of Ladue Road.

| | Thickness | |
	Feet	Inches

Pleistocene System

(Spl. # 8C) 5. Loess, tan color - - - - - - - - - 20 (Est.)

Pennsylvanian System

  Desmoinesian Series

    Cherokee group

        4. Sandstone, tan - - - - - - - - - 1   6 (Est.)

(Spl. # 8B) 3. Clay, upper 1 foot, gray, lower 4

        feet reddish-purple to maroon - - - 5

    Squirrel sandstone

        2. Sandstone, tan - - - - - - - - - 3-5

    Lagonda shale

(Spl. # 8A) 1. Shale, maroon in upper part, gray

        in lowermost 2-3 feet - - - - - - 30$^{\pm}$

Sample # 9A, 9B, 9C

Section in clay pit at Alton Brick Company plant, center NE¼ NE¼ sec. 26, T. 46 N., R. 5 E., St. Louis County, one-quarter mile northwest from U. S. Highway 66, on Dorsett Road.

		Thickness	
		Feet	Inches
Pleistocene System			
(Spl. # 9C)	8. Loess, tan color - - - - - - - - -	30 (Est.)	
Pennsylvanian System			
Desmoinesian Series			
Marmaton group			
	7. Limestone, gray - - - - - - - - -	2 (Est.)	
	6. Coal, smut - - - - - - - - - - - -	0	1
	5. Clay, gray, blocky, hard - - - - -	6	
	4. Limestone, greenish-gray, hard -	1	
Cherokee group			
(Spl. 9B)	3. Clay, reddish-purple to maroon - -	4	
Squirrel sandstone			
	2. Sandstone, tan - - - - - - - - - -	1	
Lagonda shale			
(Spl. # 9A)	1. Shale, maroon, somewhat silty; gray in lowermost 4 feet - - - - -	34	

Sample # 10A, 10B

Section in clay pit at Missouri Portland Cement Company plant, center west line SW¼ SE¼ sec. 10, T. 46 N., R. 7 E., St. Louis County, about three miles south of Chain of Rocks Bridge and on the west side of U. S. Highway 66 (City Route).

	Thickness	
	Feet	Inches

Pleistocene System

(Spl. # 10B) 5. Loess, tan – – – – – – – – – – – 20-30

(Sample 10B collected from 20')

Pennsylvanian System

Desmoinesian Series

4. Sandstone (?) – – – – – – – – – 2 (Est.)

Cherokee formation

3. Clay, upper 3-4 feet gray, lower,

maroon – – – – – – – – – – – – – – 12-15

Squirrel sandstone

2. Sandstone, tan – – – – – – – – 2 (Est.)

Lagonda shale

(Spl. # 10A) 1. Shale, maroon, somewhat silty – 54

Sample # 11

Section in clay pit at Midland Brick and Tile Company plant, NW$\frac{1}{4}$ SE$\frac{1}{4}$ sec. 18, T. 57 N., R. 24 W., Livingston County, about one-quarter mile northwest of Utica, and five miles west of Chillicothe, Missouri.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Missourian Series

    Pleasanton group

      Knobtown sandstone

          3. Sandstone, tan color, weathered - 15-20 (Est.)

      Unnamed shale

(Spl. # 11)   2. Shale, gray, somewhat silty

             in upper part, topmost 6-10

             feet highly sandy; two clay-

             iron stone bands in the bottom

             2 feet of section, 2 feet apart,

             upper band 2 inches thick - - - -   60

      Exline limestone

          1. Limestone, impure, wavy bed-

             ding; massive; forms floor of

             quarry; distinctive polygonal

             jointing; abundant horn corals,

             crinoid fragments, etc. - - - -   0   8-10

Sample # 12

Section in clay pit at Columbia Brick and Tile Company plant, center of E½ NE¼ SW¼ sec. 8, T. 48 N., R. 12 W., Boone County, one mile east of Columbia city limits (U. S. Highway 63).

	Thickness	
	Feet	Inches

Pennsylvanian System

  Desmoinesian Series

   Marmaton group

    Fort Scott formation

	Feet	Inches
9. Soil cover and green-gray clay- -	5±	

   Houx limestone member

	Feet	Inches
8. Limestone, light gray, abundant crinoid stems - - - - -	2±	

   Unnamed clay

	Feet	Inches
7. Clay, light olive-green, at top grades down to black-waxy above smut - - - - - - - - - - - - - - -	1	9
6. Smut - - - - - - - - - - - - - - -		6

   Unnamed clay

	Feet	Inches
5. Clay, light olive-green, grades down to green-brown - - - - - - -	6	

   Unnamed limestone

	Feet	Inches
4. Limestone, nodular - - - - - - -	1	9

  Cherokee group

   Squirrel sandstone

3. Shaly sandstone, light gray,
   fine grained, weathers with wide
   yellow brown streaks; finely
   micaceous, grades down into 20
   inch bed highly sandy shales
   that weathers rusty-brown - - - - $9\pm$

Lagonda shale

2. Shale, light gray, highly silty
   in upper 10 feet, lowermost
   2-3 feet dark gray to gray-
   black - - - - - - - - - - - - - - $17\pm$

1. Bevier coal (not measured)   - - -   1 (Est.)

Sample # 13

Section in bank on property of R. C. Renner, center NW$\frac{1}{4}$ SW$\frac{1}{4}$ sec. 4, T. 50 N. R. 33 W., Platte County, north side of Missouri Highway 45, at west apex of triangular intersection of U. S. Highways 69, 71, 169, and Missouri Highway 45, and two-tenths mile east of entrance to Fairfax bridge.

| | Thickness | |
| | Feet | Inches |

Pennsylvanian System

  Missourian Series

    Kansas City group

      Cherryvale formation

         3. Undifferentiated alternating layers of limestone beds 1 foot thick and tan silty shale beds 3-7 feet thick (possibly slump material) - - - - - - - - - - - 12

      Westerville limestone member

         2. Limestone, light gray - - - - - - 3-5

      Wea shale member

(Spl. # 13)   1. Shale, blackish gray where fresh- 15

Sample # 14

Section in stone quarry of Midwest PreCote Company, center of
North line SE¼ sec. 25, T. 51 N., R. 34 W., Platte County, west side
of gravel road about one and one-half miles north of intersection with
Missouri Highway 45 at U. S. Air Force Bulk Storage Plant.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Missourian Series

    Stanton formation

      Eudora shale member

        4. Shale, poorly exposed mostly
soil covered - - - - - - - - - - 5-10 (Est.)

        3. Captain Creek limestone,
light gray member - - - - - - - 3 (Est.)

    Vilas shale formation

(Spl. # 14)   2. Shale, light gray, somewhat
weathered - - - - - - - - - - - 3

    Plattsburg formation

        1. Spring Hill limestone member,
light gray, jointed, with orange-
brown residual material in
joints and horizontal partings -   5

Sample # 15A, 15B

Section in high bank on east side of Main Street cut, about 0.3 mile south of Union Depot, Kansas City; center of East line SE$\frac{1}{4}$ SW$\frac{1}{4}$ sec. 8, T. 49 N., R. 33 W., Jackson County.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Missourian Series

    Kansas City Group

      Zarah subgroup

        Wyandotte formation

          Argentine limestone member

            9. Limestone, gray - - - - - - - -   6-8

          Quindaro shale member

            8. Shale, black — - - - - - - - -   1$\pm$

          Frisbie limestone member

            7. Limestone, gray - - - - - - - -   1$\pm$

        Lane Formation

(Spl. # 15A)   6. Shale, blackish-gray, weathers
               light gray, contains scattered
               small clay-ironstone concretions;
               three light gray concretionary
               limestone layers 1 to 2 inches
               thick are found at 5, 13, and 17
               feet from bottom of section - -   27$\pm$

        Iola formation

          Raytown limestone member

      5. Limestone, gray 6- - - - - - - - -   7

Muncie Creek shale member

      4. Shale, black, thin, platy,

        hard - - - - - - - - - - - - - - $1^{\pm}$

Paola limestone member

      3. Limestone, gray - - - - - - - - $1^{\pm}$

Chanute formation

(Spl. # 15B)   2. Shale, blackish gray at top,

        grading downward to greenish

        gray at bottom; clay-iron-

        stone concretions scattered

        throughout section; three

        concretionary, light gray

        limestone layers in lowermost

        5 feet; the bottom layer

        averages 3 inches in thickness

        and is about 2 feet above base of

        section; the middle layer

        averages $2\frac{1}{2}$ inches in thickness

        and is about $1\frac{1}{2}$ feet above

        bottom layer; the topmost layer

        averages 2 inches in thickness

        and is about $1\frac{1}{2}$ feet above

        middle layer - - - - - - - - - - $21^{\pm}$

Linn subgroup

Drum formation

Cement City limestone member

    1. Limestone, gray (exposed) - - - $8^{\pm}$

Sample # 16A, 16B

Section in road cut, center of SE¼ SE¼ SE¼ sec. 22, T. 53 N.,
R. 33 W., east side of U. S. Highway 169 at southwest edge of Smith-
ville, Clay County. Section is composite of two sample locations
about 100 feet apart, one a crest of hill and other on north facing
slope of same hill.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Missourian Series

    Lansing group

      Plattsburg formation

        5. Limestone, light-brownish-

          gray (exposed) - - - - - - - - -   3-4

    Kansas City group

    Zarah subgroup

      Bonner Springs shale formation

(Spl. # 16B) 4. Shale, upper 20 feet somewhat

          weathered, dark brown color;

          color grades downward to dark

          gray in lower 30 feet; a few thin

          clay-ironstone layers in

          upper 20 feet - - - - - - - -   53

     Wyandotte formation

      Farley limestone member

        3. Limestone, light-brownish-

          gray, fossiliferous - - - - - -   6 (Av.)

(Spl. # 16A)   2. Shale, medium gray with occasional

clay-ironstone nodules - - - - -   17

1. Limestone, light-brownish-gray

(exposed) - - - - - - - - - -   3

Sample # 17

Section in bank at King Hill, center East line SW¼ NW¼ sec. 29, T. 57 N., R. 35 W., St. Joseph, Buchanan County, on east side U. S. Highway 59 in south part of city.

	Thickness	
	Feet	Inches

Pleistocene System

    3. Loess, tan - - - - - - - - - - -   20 (Est.)

Pennsylvanian System

  Virgilian Series

   Douglas group

    Lawrence formation

     Amazonia limestone member

      2. Limestone, gray, crinoid stems

        observed in lower one foot - - -   7

     Unnamed shale member

(Spl. # 17)   1. Shale, medium gray; weathers

        light gray, uppermost 2 feet

        medium brown and silty; occa-

        sional clay-ironstone concre-

        tions found throughout section -   21

Note: McQueen and Greene (Missouri Geol. Survey and Water Resources Vol. XXV) assign an average thickness of 56 feet to bed No. 1 in northwestern Missouri.

Sample # 18

Section in bluff, center NE¼ NE¼ NE¼ sec. 1, T. 58 N., R. 36 W., about three-quarter mile south of Amazonia, Andrew County, on east side of County Road K.

| | Thickness | |
| | Feet | Inches |

Pennsylvanian System

  Virgilian Series

    Douglas group

      Lawrence formation

        Amazonia limestone member

          2. Limestone, gray, caps bluff — —   2

        Unnamed shale member

(Spl. # 18)   1. Shale, medium gray, upper 10 feet silty, weathered to dark brown; color grades downward to dark gray. Occasional clay ironstone concretions found in section — — — — — — — — — — — 42

  Note: McQueen and Greene (Missouri Geol. Survey and Water Resources Vol. XXV) assign an average thickness of 56 feet to bed No. 1 in northwestern Missouri.

Sample # 19

Section at Lover's Leap, N½ SE¼ sec. 28, T. 57 N., R. 4 W., east edge of Hannibal, Marion County.

	Thickness	
	Feet	Inches

Mississippian System

  Osagean Series

    Burlington formation

      9. Gray to cream-colored coarsely crystalline limestone, beds 3-4 feet thick, containing beds and concretions of chert, some beds of brown sandy limestone, one 18 inch bed of brown sandstone near the top. Exposed as vertical cliffs and not accessible for detailed description - - - - - - - - - - - - - - -   80-90 (Est.)

      8. Highly crinoidal, coarsely crystalline, brown limestone; typical brown Burlington limestone - - - - - - - - - - - - - -   10-12

      7. Brown limestone in one bed - - -   1

      6. Finely crystalline, highly crinoidal brown limestone - - -   6-8

        Partial thickness of Burlington limestone - - - - - -   111

Kinderhookian Series

Chouteau group

Hannibal formation

(Spl. # 19)   5. Greenish-brown to greenish-gray
sandy shale, with beds of very
argillaceous greenish-brown
sandstone. One of these sand-
stone beds is about 5 feet
above the base of the forma-
tion - - - - - - - - - - - - - - 70

Louisiana formation

     4. Brown argillaceous dolomite - -   1   8-12

     3. Thin lenslike beds of brown
dolomite and drab dolomitic
limestone; dolomitic beds pre-
dominating and more contin-
uous - - - - - - - - - - - - - - 8-10

     2. Brown dolomite in thick beds,
with some few thin beds - - - -   15

     1. Alternating beds of dense gray
to drab dolomitic limestone and
brown argillaceous dolomite; beds
4-8 inches thick - - - - - -   5

     Partial thickness of Louisiana
limestone   30-32

Note: Description of J. S. Williams, U. S. Geol. Survey, Prof.
Paper 203, p. 23.

Sample # 20A, 20B, 20C

Section along Ilasco Creek, N½ SW¼ sec. 19, T. 56 N., R. 3 W., Ralls County, in bank, south side of creek, south of road, about 1½ miles southwest from Saverton, Missouri.

	Thickness	
	Feet	Inches

Mississippian System

  Kinderhookian Series

    Chouteau group

      Louisiana formation

		Feet	Inches
	5. Limestone, partial section, exposed in bank; dense; buff colored, beds 6-8 inches thick separated by yellow sandy clay partings about 1 inch thick - -	9-18	

      Saverton formation

			Feet	Inches
(Spl. # 20A)	4.	Silty blue-gray mudstone- - - -	2	6
(Spl. # 20B)	3.	Blue-gray to brown silty shale, grades into mudstone above and into black fissile shale below -	11	

      Grassy Creek formation

			Feet
	2.	Very thin bedded black fissile shale (platy), weathers brown- -	6
(Spl. # 20C)	1.	Blackish-gray shale, fissile, to creek bottom - - - - - - - -	3

Sample # 21

Section at Ardeola Hill, SE corner NW¼ NW¼ sec. 10, T. 27 N., R. 11 E., Ardeola, Stoddard County, Missouri, in bank on north side of road.

	Thickness	
	Feet	Inches

Pleistocene System

      9. Loess, tan - - - - - - - - - - -   6

Tertiary System

  Pliocene (?) Series

    "Lafayette" formation

      8. Gravel, rounded, brown to

         red brown with light to dark

         brown sand - - - - - - - - - - -   4-5

  Paleocene Series

    Midway group

      Porters Creek formation

         7. Clay, dark gray-green on fresh

            exposure, weathers to light

            gray, with infrequent, thin

            layers of clay iron-stone - - -   45

      Clayton formation

         6. Clay, green, glauconitic,

            coarse sand in lower part - - -   5

Cretaceous System

  Gulfian Series

    Owl Creek formation

(Spl. # 21) 5. Clay, yellow-brown, very sandy -- 5

Clay, laminated, white and

yellow sand with brown clay

weathering to light gray-brown

with yellow-brown stains, fossil-

iferous - - - - - - - - - - - - 6

Clay, brown, with muscovite a-

long parting planes, inter-

bedded sand, white to yellow-

brown, varying from less than

0.1 inch to about 0.2 inch;

fossiliferous - - - - - - - - - 11

McNairy (Ripley) formation

4. Sand, white to yellow-brown cross-

bedded, slightly lignitic, local

limonite bands - - - - - - - - 11

3. Clay, brown, light to blackish

gray, interbedded sand, limonite

and muscovite along bedding

planes - - - - - - - - - - - - - 27

2. Lignite, sandy - - - - - - - - - 1

1. Sand, white with iron oxide

stains only two feet exposed - - 2

Note: Section taken mostly from Farrar (Missouri Geol. Survey and

Water Resources, The Geology and Bleaching Clays of South-

eastern Missouri, App. 1, Bienn. Rept. 58, 1935).

Sample # 22

Section in road cut, center North line NE¼ NW¼ sec. 28, T. 27 N.,
R. 11 E., one-half mile northwest of Zeta, Stoddard County, Missouri,
on southside of County Road Y, east face of hill overlooking lowlands.

	Thickness	
	Feet	Inches

Pleistocene System

      3. Loess, tan - - - - - - - - - - - 5-20

Tertiary System

  Pliocene Series

    "Lafayette" formation

      2. Gravel, yellow-brown, rounded,

        with light brown sand - - - - - 1-3

  Paleocene Series

   Midway group

   Porters Creek formation

(Spl. # 22) 1. Clay, dark greenish-gray,

      weathers light gray, with in-

      frequent clay ironstone nodules,

      some partings contain very thin

      silty, micaceous bands. Only

      upper 20 feet of section suit-

      able for sampling - - - - - - - 20

Sample # 23

Section in bluff NW¼ SW¼ SE¼ sec. 32, T. 30 N., R. 14 E., Cape Girardeau, Cape Girardeau County, Missouri, west side of Main Street, 100 yards north from intersection with Broadway.

	Thickness	
	Feet	Inches

Pleistocene System

      5. Loess, tan - - - - - - - - - - -   5$\pm$

Ordovician System

  Upper Series

    Maquoketa-Thebes formations

      4. Thebes sandstone, light brown,

        fine grained - - - - - - - - - -   5-6

(Spl. # 23) 3. Maquoketa shale, reddish-brown

        weathers light gray, poorly

        exposed - - - - - - - - - - - -   8-12

    Fernvale formation

      2. Limestone - - - - - - - - - - -   8

  Middle Series

    Kimmswick formation (Undifferentiated)

      1. Limestone, gray,

        fossiliferous - - - - - - - - -   15$\pm$

Sample #24

Section along West Fork, Cape La Croix Creek, SE¼ SW¼ SW¼ sec. 2, T. 31 N., R. 13 E., Cape Girardeau County, about one-half mile northwest of Randol School, and 5 miles directly east of Jackson, Missouri.

	Thickness	
	Feet	Inches

Ordovician System

  Upper Series

    Maquoketa-Thebes formations
    (Orchard Creek Shale)

(Spl. # 24)   1. Shale, fissile, yellow-green to brown at top grading downward to dark greenish-gray in lower half of section, weathers light gray to buff, clay-ironstone bands 3/8 inch to 3/4 inch thick about 9 inches to 12 inches apart found locally. Soil cover contains chert fragments and scattered boulders of lithographic limestone with chert concretions - - - - - - - - - - 18±

Sample # 25

Section in clay pit of Kasten Brothers Brick Company, Jackson, Missouri, E½ SE¼ NW¼ sec. 12, T. 13 N., R. 12 E., Cape Girardeau County, Brick Plant is just southwest of intersection, U. S. Highway 61 and Missouri Highway 25.

	Thickness	
	Feet	Inches

Pleistocene System

(Spl. # 25) 1. Loess, tan clay - - - - - - -   35±

Sample # 26

Section in bed and bank of East Fork, Cape La Croix Creek, at common intersecting corner for secs. 13, 14, 23, 24, T. 31 N., R. 13 E., Cape Girardeau County, about seven-tenths of a mile northeast from junction with the West Fork.

| | | Thickness | |
| | | Feet | Inches |

Ordovician System

  Upper Series

   Maquoketa-Thebes formations

			Thickness	
			Feet	Inches
	2.	Thebes sandstone, light to dark brown, fine grained - - - - -	$5\pm$	
(Spl. # 26)	1.	Maquoketa shale, light brown to blackish-brown, silty, fossiliferous, weathers light brown and light green - - - - -	$4\pm$	

Sample # 27

Section in bank of Missouri Highway 25, about 75 feet inside city limits, north edge of St. Marys, Ste. Genevieve County.

		Thickness	
		Feet	Inches

Mississippian System

  Chesterian Series

    Renault formation

       2. Sandstone, light brownish-gray - - - - - - - - - - - - $3^{\pm}$

(Spl. # 27) 1. Shale, thinly fissile, slaty, purple, with alternating light gray-green bands, 3 to 4 inches thick (exposed) - - - - - - - $5^{\pm}$

Sample # 28

Section in low-angle bank, cut into hillside at abandoned oil test well site, on Carl Hunter farm, center N$\frac{1}{2}$ NE$\frac{1}{4}$ NE$\frac{1}{4}$ sec. 16, T. 64 N., R. 41 W., Atchison County, about 3 miles south of Rockport; east side of Missouri Highway 111, 0.3 mile south of junction of County Road E with Missouri Highway 111.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Virgilian Series

    Wabaunsee group

      Richardson subgroup

        French Creek formation

		Feet	Inches
5.	Shale, gray, undulating boundary with black soil cover - - - - - - - - - - - -	3±	

        Jim Creek formation

		Feet	Inches
4.	Limestone, impure, brown fossiliferous, weathered - -	1±	6

        Dry-Friedrich formation

			Feet	Inches
(Spl. # 28)	3.	Shale, upper 5 feet rusty brown, sandy, not sampled; lower part light olive green grading downward to very dark gray in the lowermost 2 feet; plant imprints throughout, fine mica particles in parting planes - - - - - - - - - - -	19	6

Dover formation

    2. Limestone, brown, impure,

       fossiliferous, weathered --   0   6±

Langdon formation

    1. Shale, gray-brown (exposed) -   1±

Sample # 29

Section in ditch, north side of section line road, 3 miles south
of Fairfax, center south line sec. 3, T. 63 N., R. 40 W., Atchison
County; 1½ miles west of U. S. Highway 275 and 59, on west facing slope
of hill, 300 feet east of driveway to house north of road.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Virgilian Series

    Wabaunsee group

      Nemaha subgroup

        Elmont formation

		Feet	Inches
	3. Limestone, blue-gray to brown-ish-gray, fossiliferous - - -	$2^{\pm}$	

        Harveyville formation

| (Spl. # 29) | 2. Shale, dark gray with undu-lating varve-like layers of light olive green color; finely micaceous, clay-iron-stone concretions concen-trated in band about 1 foot thick in center of section - | 13 | 6 |

        Reading formation

| | 1. Limestone, blue-gray, fos-siliferous (exposed) - - - - | $2^{\pm}$ | |

Sample # 30

Section in high bank, east side of road along foot of bluffs, center of south line SE¼ NW¼ sec. 12, T. 63 N., R. 41 W., Atchison County, 1-3/4 miles east-southeast from Nishnabotna, about 150 feet north of farmhouse, and about 0.3 mile north along road from quarry in hillside.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Virgilian Series

    Wabaunsee group

      Nemaha subgroup

      Willard formation

(Spl. # 30)   1. Shale, hard, dense, blocky, gray olive-green to dark brown, weathers light greenish-tan to light gray, silty, finely micaceous, scattered clay-ironstone concretions and plant imprints. (exposed) - - - - - - - - - - 10$\pm$

Note: Hand levels run from quarry to shale outcrop indicate sample taken between 30 and 40 feet below base of Tarkio limestone.

Sample # 31

Section in road cut along east side of Missouri Highway 13, NE¼ NW¼ NW¼ sec. 10, T. 54 N., R. 28 W., Ray County; about 2.6 miles south of railroad viaduct at Polo Gravel road east, 0.15 mile south of section.

			Thickness	
			Feet	Inches

Pleistocene System

(Spl. # 31)   1. Gumbotil, light gray with rusty brown spots and mottling in upper 7 feet; mostly light gray in lower 3 feet; gummy and silty throughout, weathers very light gray with polygonal-like system of cracks (exposed) — — — — — — — — — — —   10±

Sample # 32

Section is composite of two sample locations: the first, at southwest corner of intersection of gravelled east-west section-line road with Missouri Highway 13, the second, in gulley feeding a north-flowing tributary of Long Creek. Road intersection is common corner for sections 3 and 4, T. 55 N., R. 28 W., and sections 33 and 34, T. 56 N., R. 28 W.; and gulley and its junction with tributary is at center SW¼ NW¼ sec. 3, T. 55 N., R. 28 W., four miles north of Polo, Caldwell County.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Missourian Series

    Kansas City group

      Linn subgroup

        Cherryvale formation

          Block member

		Feet	Inches
5.	Limestone, dark gray, fossiliferous, two beds; upper 9 inches thick, massive, jointed; lower 12 inches thick, slabby, layers ½ inch to 2 inches thick, fusulines common - - -	1	9

       Fontana member

(Spl. # 32)

		Feet	Inches
4.	Shale, fissile blackish-gray, grades downward to dark gray - - - - - - - - - - - -		17

3. Limestone, impure, brown
color, slabby, layers sep-
arated by rusty-brown silty
clay - - - - - - - - - - - -   1

2. Clay, dark gray, coal-like in
upper 1 foot, dark gray in
lowermost part; irregular
4 inches of concretionary,
nodular limestone in center
of section - - - - - - - - -   2   6

Bronson subgroup

Dennis formation

Winterset member

1. Limestone, light buff-gray,
brachiopods and crinoid
stems common; outcrop shows
partings up to 1 inch filled
with brown silty clay, lime-
stone layers, 2 to 8 inches
thick (exposed)- - - - - - -   14

Sample # 33

Section in west bank of north-flowing tributary to Long Creek,
near center of SW¼ SW¼ SW¼ sec. 21, T. 55 N., R. 28 W., just north of
Missouri Highway 116, about 0.9 mile west of Polo, Caldwell County.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Missourian Series

    Kansas City group

      Linn subgroup

        Iola formation

          Raytown member

5. Limestone, gray; brown silty
   clay partings (exposed) - - -   3±

          Muncie Creek member

4. Shale, black, thin, platy,
   hard - - - - - - - - - - - - -   1   4

          Paola member

3. Limestone, gray - - - - - - -   0   5±

        Chanute formation

(Spl. # 33)   2. Shale; blackish-gray in upper
   9 feet, light olive-green in
   lower 4 feet. Base of upper
   part contains a one foot
   thickness of dark gray, gritty
   limey, shale, overlain by a

bed of coal $\frac{1}{2}$ to 1 inch thick.
Lowermost 2 feet of entire sec-
tion, immediately above under-
lying limestone, silty and
blocky. Plant impressions found
throughout section - - - - - - -   13$\pm$

Drum formation

Cement City member

    1. Limestone, gray, fossiliferous
      (exposed)- - - - - - - - - - - -   2$\pm$

Sample # 34

Section in north bank of road cut, center SW¼ NE¼ NW¼ sec. 31, T. 51 N., R. 9 W., Audrain County, about 3.4 miles west of cemetery at west edge of Mexico City limits; on east facing hill slope, 150 feet east of driveway to house of H. C. Hublitz north of road.

| | Thickness | |
| | Feet | Inches |

Pleistocene System

(Spl. # 34)　1.　Gumbotil, light gray with rusty-
brown spots; weathers light
gray. (Soil cover about 7±
feet) - - - - - - - - - - - -　22±

Sample # 35

Section in bank, east side of intermittent creek, $W\frac{1}{2}$ $NE\frac{1}{4}$ $NE\frac{1}{4}$ $SE\frac{1}{4}$
sec. 26, T. 29 N., R. 14 E., Scott County, about 200 feet north of
County Road N. from a point about 350 feet east of A. J. Miller home.
West edge of Commerce about 1 mile east.

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                                           Thickness
                                         Feet    Inches
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Cretaceous System

  Gulfian Series

    McNairy (Ripley formation

      "Leaf member"

(Spl. # 35)   3. Clay, brownish-maroon, weathers
                    light chocolate brown, highly
                    silty, finely micaceous, leaf
                    impressions common; interbed-
                    ded orange-brown sand lenses
                    $2^{\pm}$ inches thick, of varying
                    lateral extent occur at in-
                    frequent intervals in vertical
                    face of bank; total thickness
                    of entire section variable
                    owing to undulating contact
                    with underlying beds, and the
                    depth land surface has been
                    eroded into the formation - - - 22-27

2. Sand, bright rusty-brown layers
about $\frac{1}{2}$ inch to $1\frac{1}{2}$ inches thick,
cemented with limonite locally,
separated by bands of white
sand 2 to 3 inches thick. Thick-
ness of entire bed varies greatly
over short lateral extent -- -- -- 1-3

"Zodoc member"

1. Clay, 2 to 3 feet thick, black-
ish brown, finely micaceous,
with interbedded white sand
layers about 1 foot thick,
streaked with 1/8 to $\frac{1}{2}$ inch
sandy-clay bands, brown to
black (lignitic); exposed in
creek bed about 100 feet up-
stream is a bed of lignite,
apparently underlying the clay.
This member shows evidence of
much disturbance and exact thick-
ness impossible to measure.
Total thickness exposed varies
between 3 to 5 feet -- -- -- -- -- 3-5

Sample # 36

Section in bank on south side of Grassy Creek, E$\frac{1}{2}$ SW$\frac{1}{4}$ NW$\frac{1}{4}$ SE$\frac{1}{4}$ sec. 19, T. 54 N., R. 2 W., Pike County, on property of Mr. Arch Hufford, about six miles west of Louisiana.

		Thickness	
		Feet	Inches

Ordovician System

  Upper Series

   Maquoketa formation

		Feet	Inches
(Spl. # 36)	3. Shale, dark brown, overlain by soil with Louisiana lime-stone float, contains graph-tolite impressions and Linguella fragments - - - - - -	12	
	2. Shale; hard, sandy, nodular, dark to medium gray - - - - - -	0	6-8
	1. Shale, black to dark gray, with four hard sandy shale layers each about 4 inches thick, and approximately 2$\frac{1}{2}$ feet apart in lowermost part of section just above creek bed (exposed) - - -	26±	

Sample # 37

Section in ditch on north side of county-line road, south side SW¼ SW¼ SW¼ sec. 33, T. 55 N., R. 29 W., Caldwell County, on east facing hill slope leading down to Brushy Creek, about 4.2 miles east of U. S. Highway 69, and about 7 miles west and south of Polo.

		Thickness	
		Feet	Inches
Pennsylvanian System			
Missourian Series			
Kansas City group			
Zarah subgroup			
Wyandotte formation			
Frisbie member			
11. Limestone, medium gray, fossiliferous - - - - - - - - -		5±	
Lane formation			
10. Shale, light gray, silty finely micaceous - - - - - -		8	
(Spl. # 37) 9. Shale, medium gray - - - - - -		2	6
8. Coal, and smut - - - - - - -		0	3
7. Shale, medium gray - - - - - -		6±	
Linn subgroup			
Iola formation			
Raytown member			
6. Limestone, medium gray, fossiliferous - - - - - - - -		5	6

Muncie Creek member

    5. Shale, black, platy, fissile,
with upper 11 inches olive
green and soft, probably
weathered - - - - - - - - - -   2   4

Paola member

    4. Limestone, gray - - - - - - - -   0   4

Chanute formation

    3. Shale, gray - - - - - - - - - -   5   6

    2. Shale, hard, silty, finely
micaceous - - - - - - - - - - -   0   7±

    1. Shale, gray, weathered (ex-
posed) - - - - - - - - - - - -   3±

Sample # 38

Section in west bank of north flowing creek, tributary to Long Creek, center SW¼ SE¼ SW¼ sec. 29, T. 55 N., R. 28 W., Caldwell County, 400 feet north of an east-west road from a point about 750 feet west of railroad crossing, and about 1.8 miles southwest of Polo.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Missourian Series

    Kansas City group

      Zarah subgroup

        Land formation

		Feet	Inches
	4. Shale, silty, blue-gray, with rusty-brown stains - - - - - - -	2	6
(Spl. # 38)	3. Coal, thin banded with smut- - -	0	6
	2. Shale, blackish-gray, fissile- -	10±	

      Linn subgroup

        Iola formation

          Raytown member

            1. Limestone, dark gray, in bed of creek - - - - - - - - - - -

Sample # 39

Section in road cut, U. S. Highway 54 on west facing slope of
hill top, south side SE¼ SW¼ NE¼, and north side NE¼ NW¼ SE¼ sec.
30, T. 36 N., R. 28 W., Cedar County, about 1-3/4 miles west of
junction of Missouri Highway 82 with U. S. Highway 54 at south edge
of El Dorado Springs.

<div align="right">
Thickness
Feet   Inches
</div>

Pennsylvanian System

  Desmoinesian Series

    Cherokee group

      Dederick formation

        Unnamed sandstone

           2. Sandstone, thin bedded almost
platy; buff and brown bandings,
finely micaceous, weathers light
brown to gray — — — — — — — —   11±

        Unnamed shale

(Spl. # 39)   1. Shale, black, platy, fissile,
weathers dark to light brown,
(exposed) — — — — — — — — — —   11±

Sample # 40

Section in bank at east side of road-cut, Missouri Highway 39, on south facing hill slope, center of west side SW¼ SW¼ NW¼ sec. 7, T. 35 N., R. 26 W., Cedar County, about 2-3/4 miles northwest of Caplinger Mills.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Desmoinesian Series

    Cherokee group

      Dederick formation

        Unnamed sandstone

2. Sandstone, thin bedded, almost platy, buff, brown, and rusty brown banding, partings contain brown clay, finely micaceous — — — — — — — $4^{\pm}$

        Unnamed shale

(Spl. # 40)   1. Shale, black, fissile, platy, color grades downward in lower-most 17 feet from black to dark gray and brown, also becoming less platy and fissile (exposed) — — — — — — — — — — — —   27   6

Sample # 41

Section in north bank of pit of A. P. Green Fire Brick Company
E$\frac{1}{2}$ SE$\frac{1}{4}$ SW$\frac{1}{4}$ sec. 31, T. 51 N., R. 8 W., Audrain County, about 1-$\frac{1}{2}$
miles southeast of main office building at brick plant.

	Thickness	
	Feet	Inches

Pennsylvanian System

  Desmoinesian Series

    Cherokee group

    Cheltenham clay

(Spl. # 41)   1. Clay, waxy, black to dark olive

                green; bloaky - - - - - - - - -   2   6

    Note: This sample taken from an irregular band that appears at
           varying elevations from bottom of pit. It is most prom-
           inently exposed in the north bank.

Sample # 42

Section in pit of Plumb Mining Company NW¼ sec. 17, T. 34 N., R. 13 W., Cole County, about 3½ miles southeast of Russelville, north bluffs of South Moreau Creek.

<div style="text-align: right;">Thickness
Feet   Inches</div>

Pennsylvanian System

(Spl. # 42)   1. Shale, dark to blackish brown, light weight; (sinkhole deposit) - - - - - - - - - - - - (unknown)

Note: Sample collected by Carl Plumb of Plumb Mining Company.

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VITA

Peter Kurtz, Jr. was born May 25, 1927 in Chicago, Illinois to Mr. and Mrs. Peter Kurtz. His father was general manager of meat markets for a Chicago chain.

At the age of 6 years, he moved to Webster Groves, Missouri with his mother when his mother and father were divorced. He attended Lockwood grade school in Webster Groves and completed Junior high there. He played C-team football during the 10th grade at Webster.

In 1943 his mother took a high school teaching position in Hesperia, Michigan. In Hesperia he completed the 11th grade. He finished high school at Ferris Institute at Big Rapids, Michigan during the summer of 1944.

In May of 1945 he joined the Navy as an enlisted man and spent the next fourteen months in that capacity. The majority of that time he spent aboard the U. S. Shelikof, a small sea plane tender.

He was honorably discharged July 15, 1946.

He attended Washington University night school during the fall semester of 1946 at St. Louis, Missouri. In January of 1947, he transferred to Westminister College, Fulton, Missouri where he pursued a pre-medical curriculum. He completed one year and a half at Westminister and then transferred to Washington University in the fall semester 1948. He completed 3 semesters at Washington in the Liberal Arts School.

In January 1950 he married Opal Lucille Wallace of Fulton, Missouri and transferred to Missouri School of Mines and Metallurgy, Rolla, Missouri. He enrolled for the Ceramic Engineering Curriculum. While at M. S. M. he joined the American Ceramic Society, and the honorary

societies of Keramos, Tau Beta Pi, Phi Kappa Phi, and Sigma Pi Sigma. He served as secretary of Keramos during his senior year.

In May of 1952 he received a B. S. in Ceramic Engineering at M.S.M., graduating with first honors.

During the school year 1952-1953 and during the summers of 1952 and 1953, he has been doing graduate work at M.S.M. as partial requirement for a Master's Degree in Ceramic Engineering.