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OXIDATION AND LOSS OF WEIGHT OF CLAY BODIES DURING FIRING

A REPORT OF AN INVESTIGATION CONDUCTED BY

THE ENGINEERING EXPERIMENT STATION UNIVERSITY OF ILLINOIS

IN COOPERATION WITH

THE CLAY PRODUCTS ASSOCIATION

BY

WILLIAM R. MORGAN

BULLETIN No. 284
ENGINEERING EXPERIMENT STATION
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UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS
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WILLIAM R. MORGAN
INSTRUCTOR IN CERAMIC ENGINEERING

UNIVERSITY OF ILLINOIS
ENGINEERING EXPERIMENT STATION

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OXIDATION AND LOSS OF WEIGHT OF CLAY BODIES
DURING FIRING

I. INTRODUCTION

1. Purpose of Study.—The progress of the oxidation of various types of clay during firing has been studied by the observation of the color of specimens withdrawn at different stages, by the chemical analyses of the clay with respect to carbon, sulphur, and the state of oxidation of iron compounds after various heat treatments, and by the selective absorption of the gases evolved from clay upon heating; while in one instance quite general observations concerning the ease of oxidation of clays were made incidentally in connection with a study of dehydration by the loss of weight method.* A preliminary study of oxidation by the loss of weight method,† to which the present study is a sequel, served to develop the method into a satisfactory laboratory test.

The purpose of the present study was to determine the temperature intervals in which loss of weight occurred most rapidly and to correlate loss of weight, loss of water, carbon, and sulphur with the oxidation properties of a large number of commercial bodies used in the manufacture of heavy clay products, in ascertaining the most advantageous temperature range for proper oxidation.

2. Scope of Work.—Forty-one commercial clay bodies, used in the manufacture of heavy clay products, were tested in the temperature range from 75 to 1800 deg. F. according to the procedure for determining the loss of weight during firing adopted as a result of a series of preliminary tests. Tennessee Ball Clay No. 5 and H & G A-1 English China Clay were tested also, for comparison with the commercial bodies. A statistical analysis of the results was made.

Absorption train tests were made in which the losses of water, carbon and sulphur were determined, in the temperature range specified, for six of the commercial bodies which were considered to be representative.

In addition, determinations of the effects of neutral (nitrogen) atmosphere, volume of air circulated, cross-sectional area of specimens, and heating rate on the loss of weight of individual bodies were made.

3. Materials.—The commercial bodies consisted of shales and fire-clays and various mixtures of the two types of clay, with, in some cases, admixtures of surface clay, sand rock, and calcined clay. The unburned clays varied in color from light gray to brown, and the burned bodies from light buff to red. With the exceptions of bodies 14F, 18F, 20F, and 33F, which were coarse grained, and 6F, which was of intermediate coarseness, all of the bodies slaked when wet, and were essentially fine grained. The materials were obtained from twenty-two companies located in the following eleven states: Alabama, Colorado, Georgia, Illinois, Indiana, Iowa, Kansas, Kentucky, Minnesota, Missouri and Texas.

4. Acknowledgment.—The data presented in this bulletin were obtained from 1929 to 1931 in an investigation which was conducted by the Engineering Experiment Station of the University of Illinois, of which M. S. Ketchum, then Dean of the College of Engineering, was director, in cooperation with the Clay Products Association. The studies were carried out in the Department of Ceramic Engineering, of which C. W. Parmelee, Professor of Ceramic Engineering, is the head.

Acknowledgment is made to Prof. Parmelee for his cooperation and helpful suggestions at the instigation and during the progress of the work; to Prof. R. K. Hursh and to Mr. George H. Duncombe, Jr., for helpful discussion and constructive criticism; and to Eugene C. Clemens, Lane Mitchell, and Carl H. Rapp for their careful and conscientious work, both in the development of the experimental technique and in the subsequent tests.

II. REVIEW OF LITERATURE

5. Water in Clay.—After a clay has been dried at 230 deg. F., water which can be removed only at higher temperatures still remains. Hygroscopic moisture which is strongly adsorbed on the surfaces of the clay grains is removed in the approximate temperature range of from 250 to 400 deg. F. Chemically combined water, according to Rieke,* begins to be given off between 750 and 930 deg. F.; Bauer† gives 930 to 1110 deg. F. as the range; Searle‡ gives 750 to 1110 deg. F.; and Brown and Montgomery¶ state that the bulk of the water is given off at 842 deg. F., that evolution becomes rapid at

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*Rieke, R., Sprech. 44, 637 u. 653, 1911.
†Bauer, E. P., Keramik, p. 24.
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930 deg. F., and is complete at 1470 deg. F. Ries,* after a digest of the more important data, concludes that the range in which dehydration occurs is between 930 and 1110 deg. F.

6. Carbon in Clay.—Carbonaceous matter, which is present in greater or lesser amounts in practically all clays, may occur in several forms, ranging from wood, peat, lignite, bituminous and asphaltic materials, to those of the nature of anthracite coal and graphite, in which the total carbon in the carbonaceous matter varies approximately from 50 per cent for wood to 93 per cent for anthracite coal;† graphite being practically pure carbon. In general, as the total carbon increases, the percentage of “fixed carbon” also increases, and the percentage of volatile matter decreases. Thus anthracite coal has higher “fixed carbon” and lower volatile content than bituminous coal.

Shales usually contain the greatest proportion of carbon,‡ varying from 0 to 10 per cent, which frequently is in the form of the troublesome bituminous or asphaltic material. Fireclays contain less carbon, the content varying from 0 to 2 or 3 per cent, while clays of glacial and alluvial origin contain the least carbonaceous matter, the content varying from 0 to 1 per cent.

Wood and peat normally may be burned out of clay readily at comparatively low temperatures, and, if present in relatively small amounts, cause no trouble in the firing of clay products.

Lignitic, bituminous, and asphaltic materials ignite at dull red heat, and are subject to destructive distillation, during which highly combustible gases are evolved so that, if these materials are present in considerable amounts, sufficient heat may be produced to raise the temperature rapidly to a point at which the surface of the clay may be sealed, and then the expansion of the entrapped gases will cause swelling.

Carbonaceous matter of the nature of anthracite and graphite ignite at higher temperatures and burn slowly without flame, causing little difficulty, but requiring considerable time for complete oxidation.

After the volatile constituents of the carbonaceous material in clay have been removed by heating,¶ a residue of fixed carbon of

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the nature of coke or charcoal, which can be removed only by oxidation, remains. Such carbon residues can be removed usually in a properly oxidizing atmosphere if sufficient time is allowed, unless the removal is unduly retarded by the structure of the clay, or by excessive temperatures, which tend to seal the surface of the clay and prevent further oxidation. Carbon may also be removed by contact with reducible materials such as Fe₂O₃, MnO₂, and SO₃ at approximately 1830 deg. F.

7. Temperature at Which Carbon Is Removed.—Gases and volatilized liquid products* are given off when coal is heated to about 570 deg. F. without access to air, such primary decomposition being complete between 930 and 1020 deg. F. The gases are given off in quite small quantities and the liquids in large quantities at the lower temperatures, while the gases given off increase and liquids given off decrease with increasing temperature. The dark viscous liquids constitute the crude tar of commerce, a higher yield being obtained at low temperatures of from 750 to 1200 deg. F. When the process is carried out below 1200 deg. F., it is called "low-temperature carbonization," while above that temperature, the process is called "high-temperature coking." Schreiber‡ and Baer‡ found that severe cracking of distillation products greatly decreased the combustibility of the resulting coke in oxygen and air, which agrees with the results obtained by Fischer,¶ who found that low-temperature coke, free from carbon deposited by the cracking of primary tars, reacted more rapidly with CO₂ than high-temperature coke. This greater combustibility was not due to the higher volatile matter content of low-temperature coke, since low-temperature cokes which had been treated in a neutral atmosphere at 2010 deg. F. showed the same combustibility as before heating.

Undoubtedly these properties of coal play an important part in the oxidation of carbonaceous material contained in clay and determine, partly at least, the best temperature for the oxidation process. Orton, Griffin, and Staley§ state that removal of carbon begins at comparatively low temperatures, and that the safe maximum temperature is about 1650 deg. F.; above this temperature the surface of the clay may become sealed, and oxidation be stopped.

Riddle and McDanel,** in their study of porcelain bodies, recommend

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§ See footnotes MI p. 9.
maintenance of oxidizing conditions up to about 1750 deg. F., and Wilson* includes the range from 660 to 1760 deg. F. All of these investigators agree that oxidation begins at comparatively low temperatures, but progresses more rapidly at higher temperatures, the safe maximum temperature ranging from 1650 to 1750 deg. F.

Oxidation at lower temperatures has been advocated by Jackson,† who removed carbon completely from fireclay at 860 deg. F., with an increase in the rate of oxidation at higher temperature; by Kraner and Fritz,‡ who, in their studies of porcelain bodies and ball clay, found that carbon dioxide began to be given off at temperatures as low as 390 deg. F., and concluded that, in general, oxidation could be accomplished by maintaining thoroughly oxidizing conditions up to 1200 deg. F. without providing an "oxidation period," and that even close-grained ball clays could be completely oxidized at from 1300 to 1475 deg. F.; and by Arnold and Duncombe,¶ who concluded that difficulty with "black-coring" was most easily eliminated by slow heating between 500 and 1000 deg. F.

Maintenance of proper oxidizing conditions is, of course, of great importance in all instances, and has a marked influence on the rate of oxidation, as shown§ by the fact that the time required for oxidation in one instance when specimens were heated in a muffle in contact only with air was only 34 per cent of the time required when the specimens were heated in contact with the combustion gases from fuel burned with 160 per cent excess air.

8. Carbon in the Form of Carbonates.—Carbon occurs in small quantities in clays in the form of carbonates of iron, calcium, and magnesium, which, according to Orton,** decomposed slowly at 800 deg. F., between 1110 and 1650 deg. F., depending on the nature of the kiln gases, and at about 750 deg. F., respectively.

9. Sulphur in Clay.—Sulphur occurs commonly in clay as sulphides of iron and as sulphates of iron, calcium, and magnesium.

Iron sulphide (FeS₂), more familiarly known as pyrite, "fools gold," or "shiners," loses half of its sulphur by distillation at about∗∗††
750 deg. F. when heated slowly out of contact with air. In contact with air the sulphur burns immediately to sulphur dioxide and trioxide. The reactions start slowly at about 650 deg. F. and go to completion at 800 deg. F. if the temperature is held. Orton* believes that the first half of the sulphur is removed between 750 and 1110 deg. F., while Bole and Jackson† state that it is completely removed below 930 deg. F. The last half of the sulphur, according to Orton,‡ is removed below 1650 deg. F., although Mellor§ found that pyrite was not completely decomposed at that temperature when heated alone in a gentle current of air. It seems probable that Mellor did not heat his samples for a sufficient length of time, for Bole and Jackson¶ also found that decomposition was complete at about 1700 deg. F. after prolonged heating, particularly if the circulation of the oxidizing gases was good.** Carbon was found to retard the oxidation of pyrite.††‡‡

According to Orton,¶¶ however, in commercial practice, proper conditions are seldom maintained for a sufficient length of time, so that complete removal is not effected before the beginning of vitrification, and becomes increasingly difficult as vitrification progresses. In addition, ferrous sulphide (FeS), which melts at about 2175 deg. F., may soften and react in contact with impure clays to form silicates at temperatures as low as 1800 to 2000 deg. F., thus preventing the removal of the last traces of sulphur. Jackson§§ also has noted the difficulty of removing the last part of the sulphur remaining in clay during firing, and has suggested the possible formation of a "ferrous sulfo-silicate."

10. Absorption of Sulphur Gases.—During firing, sulphur gases which are given off in warmer parts of the kiln may be condensed or absorbed by ware in cooler parts of the kiln. Seger*** has discussed the absorption of sulphur gases by clay when introduced into the combustion gases under experimental conditions, particularly with reference to the effect on the color of the fired bodies. Jackson†††
found that sulphurous acid so formed was decomposed at low temperatures, but that sulphuric acid formed by sulphur trioxide may attack the mineral constituents in the clay until the acid is decomposed at about 500 deg. F. The sulphates formed in this manner usually are decomposed at higher temperatures. In addition, sulphur may be held in the clay in the form of an insoluble “ferrous sulpho-silicate” up to about 1300 deg. F., at which temperature it begins to decompose. According to Bole* and others, the character of the kiln atmosphere, whether oxidizing or reducing, influences the temperature and rate at which the absorption and evolution of sulphur occurs, which is in agreement with the earlier opinions of Seger† and Jackson.§§ The latter also found§ that less sulphur was absorbed than was expected, in that only a small part of the bases reacted, and that the reactions were more a function of temperature than of any other factor, maximum absorption occurring at about 840 to 925 deg. F. The effect of the concentration of sulphur in the combustion gases was small.

11. Formation and Decomposition of Ferric and Ferrous Sulphates.—Ferric sulphate is the product normally formed during the weathering of iron-sulphur compounds in clay, and also may be formed during the decomposition of iron sulphide, or by the absorption of sulphur from the kiln gases during firing. The absorption of sulphur by iron compounds is greatest** at about 840 deg. F., and Jackson†† states that ferric sulphate may be formed up to a temperature of about 1100 deg. F. There is a marked evolution of sulphur from ferric sulphate‡‡ at about 930 deg. F., although decomposition may be said to occur chiefly¶¶ in the temperature range from 1040 to 1430 deg. F., without being complete, however, at the latter temperature.§§ The decomposition takes place more readily under reducing than under oxidizing conditions.***

Ferrous sulphate which is formed during the decomposition of iron sulphide in firing, according to Orton,††† decomposes directly under oxidizing conditions at dull red heat, about 1000 to 1200 deg. F., and

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†See footnote ** p. 12.
‡See footnote §§ p. 12.
††See footnote ‡‡ p. 12.
‡‡See footnote §§ p. 12.
¶¶See footnote ¶¶ p. 12.
§§See footnote §§ p. 12.
***See footnote §§ p. 12.
by reaction with carbon under reducing conditions. Jackson,* however, obtained only partial decomposition of ferrous sulphate, the maximum rate occurring about 930 deg. F., and suggested the formation of a "ferrous sulpho-silicate" as a possible explanation of failure to remove all of the sulphur. The decomposition was accelerated and more complete under reducing conditions.

12. Calcium Sulphate.—Jackson† found that the maximum amount of calcium sulphate was present in the clay tested between 750 and 950 deg. F.; above this range the amount steadily decreased, decomposition being practically complete at 1600 deg. F. Calcium sulphate, under oxidizing conditions, decomposes slowly at 2200 deg. F. and rapidly at 2415 deg. F.;‡ both of these temperatures are above the normal maturing temperatures for most of the bodies studied. Under various reducing conditions calcium sulphate has been decomposed between 930 and 1560 deg. F. by Williams,¶ by Powell,§ and by Jackson.** The decomposition of calcium sulphate is influenced by contact with other materials, since silica lowers its dissociation temperature to 1830 deg. F. and ferric oxide lowers the dissociation temperature to 2010 deg. F.†† Marchal‡‡ found that pure calcium sulphate had a dissociation pressure of 8 mm. at 1830 deg. F. The dissociation pressure was increased by the presence of ferric oxide, silica, alumina, and kaolin, the latter increasing it to 1070 mm. at 2140 deg. F.

13. Iron Compounds.—Iron is commonly present in clay in the form of oxides, sulphides, sulphates, and carbonates.

Ferric oxide alone is likely to give uniform color. In hydrated forms ferric oxide varies from light yellow to deep brown, and in the dehydrated forms it can be found in all shades of red through brown to black. The yellow color of certain bricks has been thought to be due to a colloidal yellow modification of anhydrous ferric oxide made stable by alumina.¶¶ Seger§§ demonstrated that both alumina and lime had a marked effect on the fired color of iron-bearing clays.

On the other hand, the degree of agglomeration is probably an important factor,*** because fine grinding of the darker varieties always gives a powder of lighter color.

*See footnote §§ p. 12.
†See footnote ¶ p. 13.
‡See footnote † p. 13.
**See footnote ¶ p. 13.
"Yoe* has studied the subject extensively and states that the true color of masses of fine particles of ferric oxide is yellow and the usual red appearance is due to agglomeration, which can be prevented by stabilizing agents. Alumina, when present to the extent of 10 per cent or more, functions as a stabilizing agent, as does barium sulphate, although 84 per cent of the latter is necessary."

Iron oxide itself, not in contact with clay, is reduced by carbon monoxide† at temperatures above about 570 deg. F., the major portion of the ferric oxide in the first stage of reduction changing to magnetite, which is black in color. When magnetite is in contact with air, active oxidation does not begin until a temperature of about 750 deg. F. is reached, and then the oxidized iron formed seems to act as a protective skin and retards the reaction. Tests have shown such reoxidation to be only 95 per cent complete after 100 hours at 1830 deg. F., although at higher temperatures the rate of oxidation increases.

Under reducing conditions iron oxide (Fe₂O₃) in clay is changed to ferrous oxide (FeO).

In contrast to the difficult reoxidation of magnetic iron oxide when heated alone, ferrous oxide in porous non-vitrified clay bodies is reoxidized quite readily after "flashing," probably because of its highly dispersed state and comparatively low concentration, which would tend to prevent the formation of protective surface layers. The formation of such surface layers would retard the reoxidation process of the greater part of a concentrated mass of iron oxide. The presence of the clay also contributes some catalytic action.

Heated with sulphur vapor, ferric oxide (Fe₂O₃) yields ferrous sulphide, and sulphur dioxide. With sulphur dioxide at 1290 to 1470 deg. F., it forms magnetic oxide (Fe₃O₄) and sulphur trioxide (SO₃).‡

Actually in clays both red ferric oxide (Fe₂O₃) and black ferrous oxide (FeO) are nearly always present, a small amount of the black oxide being present in a red body, and a small amount of the red oxide being present in a black body.

Iron sulphide (FeS₂) always occurs in granular form, never small enough to produce red color, and appears in the fired clay as black specks or slagged spots. Its decomposition has been discussed under sulphur compounds.

Ferric and ferrous sulphates both have been discussed under sulphur compounds.

Ferrous carbonate exists both in concretionary and in disseminated form and may give rise to black specks in a red burning matrix. Orton* states that ferrous carbonate (FeCO₃) in clay begins to decompose slowly as low as 800 deg. F.

14. Relation Between Carbon, Sulphur, Iron, and Colored "Cores."—Orton and Staley† have stated that the size of "black-core" is not an accurate measure of the amount of carbon remaining in the discolored clay body. They demonstrated by chemical analyses that the carbon in the black-core may decrease and even completely disappear without a corresponding decrease in the area of the core. No carbon was found in the black-core of vitrified bodies, or in the darkened surface of heavily-reduced or flashed bodies. It seems probable, then, that carbon is the cause of dark cores in clay only at comparatively low temperatures in the early stages of firing, and that the presence of carbon is seldom if ever the cause of dark cores in poorly-oxidized clays fired to maturing temperatures.

When carbon is removed at relatively high temperatures and at a correspondingly rapid rate, some carbon monoxide is quite likely to be formed temporarily in the clay and will, no doubt, reduce some of the iron oxide, producing a black discoloration or core of different character from that of the initial carbon core, even though carbon itself is effectively removed. Since the reoxidation of magnetite progresses very slowly, it seems probable that such cores, once formed, will be removed with great difficulty, unless the body remains porous.

Orton‡ states that black cores are caused by ferrous oxide or by ferrous silicates. Orton and Staley¶ in their studies of oxidation and black-coring made chemical analyses of the material in the oxidized and black-cored areas to determine the relative rate of removal of carbon and sulphur and the state of oxidation of the iron. They found that the sulphur was removed much more slowly from the carbon-impregnated or black area than from the red oxidized area from which carbon had been completely removed.

They also found that, in the red exterior area, the iron oxidized readily, the percentage of ferric oxide rapidly increased, while the percentage of ferrous oxide rapidly decreased. Just the opposite occurred, however, in the black interior area, in which the ferrous oxide increased and the ferric oxide decreased steadily from their initial quantities until, at the finish of the burn, only a small fraction of

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*See footnote ¶ p. 9, p. 96.  
†See footnote ¶ p. 9, pp. 56, 57.  
‡See footnote ** p. II.  
¶See footnote ¶ p. 9.
one per cent of red ferric oxide remained in the black core. It is evident that a steady reduction of the iron took place in the presence of carbon and sulphur, rather than oxidation.

Analyses of material from the black-cored areas at the finish of a burn failed in every case to show the presence of carbon, but sulphur and reduced iron were always present.

Some clays, under certain conditions, form red cores, the effect being more striking in clays which have a relatively low iron content and normally have a buff color when fired. Seger studied the phenomenon and found that red cores in this type of clay are formed when sulphur gases are absorbed under reducing conditions, the first change to a gray or pale yellow color being followed by the development of a red color when the clay is reoxidized. The stability and intensity of the color increases with increasing temperature of formation. The color does not burn out, but darkens and gradually turns brown, as would be expected of colors produced with iron, with further increase in firing temperature. Orton also has discussed the formation of such colors, and attributes them to the reoxidation of iron compounds reduced previously by carbonaceous matter present in the clay.

III. Loss of Weight Determinations

15. Description of Apparatus and Test Pieces.—The apparatus consisted essentially of a balance from which a sample could be suspended in an electric furnace below, the temperature of the latter being controlled by a rheostat and wattmeter. The volume of air flowing through the furnace was regulated by a flowmeter, and the furnace temperature was measured with a potentiometer and two base metal couples, one at the top and one at the bottom of the sample. The general arrangement is shown in Fig. 1.

An ordinary two-kilogram-capacity balance with the arm graduated from one to ten grams in 0.1 gram divisions, sensitive to less than 0.05 gram, was used. The arm and rider were calibrated against standard calibrated weights. The weighings were accurate to the first decimal, the second decimal being estimated.

All the test pieces were ground to the same green dimensions, \( \frac{3}{4} \) in. \( \times \frac{3}{4} \) in. \( \times \) 5 in., which gave a convenient sample of 90 to 100 grams weight, eliminated variations in sample sizes where bars cut from commercial products were used, and eliminated the effect of surface skin due to the manufacturing process.

*See footnote *** p. 12.
†See footnote ** p. 11.
The test piece was suspended by drilling a small hole about a half inch from one end, at right angles to either pair of parallel faces, through which a short piece of 22 ga. chromel wire was passed, extending on each side through the eye of a miniature clevis or bucket bail, also of chromel wire. A connecting link of chromel wire of proper length to lower the test piece into the furnace was hooked through the bail on the sample and the loop on the pan support of the balance, the balance being mounted above the furnace in such a position that the center of the right-hand pan was directly over the vertical axis of the furnace.

16. Operation.—After drying for five hours at 230 deg. F. and cooling in a dessicator, the test piece was weighed as rapidly as possible and suspended in the furnace, the weights used in weighing being transferred from the first balance to the left-hand pan of the second balance from the right-hand pan of which the test piece was suspended. In this manner any gain in weight between the original weighing and the beginning of the test was not recorded as a loss of weight during the test.

Air was passed through the furnace at a rate of 500 cc. per minute, which was approximately eleven times the volume of the test piece.

The average furnace temperature was raised at a rate of 500 deg. F. per hour, and after a little experience could be held to schedule generally within ± 15 deg. F.
The sample was weighed at the end of each fifteen minute period, corresponding to a temperature rise of 125 deg. F. Since the sample was suspended from the right-hand pan with the rider at the left in zero position, the loss of weight could be read directly simply by balancing the system with the rider as the sample decreased in weight, reading the loss on the beam. The readings thus taken were the cumulative losses in grams at the temperatures at which the readings were taken.

The current was turned off when an average furnace temperature of 1800 deg. F. was reached, and the furnace and sample permitted to cool.

The weight of the sample, when cool, was checked against the weight at the end of the test, before removing from the furnace. After removal, the sample was weighed again, and the difference between initial and final weight checked against the loss as weighed directly during the test.

17. Accuracy of Measurements.—The results of five tests on five different samples of the same fireclay body are given in Table I as an indication of the accuracy with which such tests could be duplicated. The results are also shown in Fig. 2, the heavy curve representing the mean value for the five samples, and the light curves above and below, the mean plus or minus the probable error.

18. Effect of Heating Rate.—The general effect of the heating rate
was determined by heating specimens to constant weight at a series of temperatures from atmospheric temperature to 1800 deg. F., this treatment being equivalent to an infinitely slow heating rate, since equilibrium was attained at each temperature.

The procedure for the loss of weight test remained the same in every respect except the heating rate. Starting at room temperature (approximately 75 deg. F.) the furnace temperature was raised 125 deg. F. in fifteen minutes to 200 deg. F. (at a rate of 500 deg. F. per hour) where it was held until the loss of weight of the sample in a fifteen minute period did not exceed 0.05 gram. The temperature was then raised 125 deg. F. to 325 deg. F., where again it was held until the loss did not exceed 0.05 gram in a fifteen minute period. This procedure was repeated at 125 deg. F. intervals up to 1800 deg. F. The results then obtained indicated the total loss at equilibrium at each temperature.

Laboratory samples of bodies Nos. 6, 18, 27, 35, 41 and 42 and Tennessee Ball Clay No. 5 were tested in this manner.

The results are shown in Fig. 3, the original results on the same
FIG. 3. DISTRIBUTION OF WEIGHT LOSSES IN TEMPERATURE RANGE 75 TO 1800 DEG. F. AND EFFECT OF HEATING RATE ON TEMPERATURES AT WHICH LOSSES OCCUR.
materials using a heating rate of 500 deg. F. per hour also being given for comparison.

The curves representing losses when the specimens were heated to constant weight at the various temperature intervals are essentially equilibrium curves, and are independent of the size of the specimen, while the curves representing losses when the furnace temperature was increased at the rate of 500 deg. F. per hour are dependent on time as well as on temperature, and apply only to the size of specimen used in the tests.

When the furnace temperature was increased at the rate of 500 deg. F. per hour, the maximum loss occurred in each case in the interval from 1075 to 1200 deg. F., while under equilibrium conditions the maximum loss occurred in the interval from 825 to 950 deg. F., except for body 6F, for which the maximum loss occurred in the interval from 700 to 825 deg. F., probably because of its high carbon content.

The effect of increased heating rates was to cause the maximum rate of loss to occur at a higher furnace temperature. This is the same effect as was produced by increased size of specimens, which would be expected, because of overlapping of the various weight loss periods when losses occur over a temperature range rather than instantaneously at a given temperature, and also because of the temperature lag in the specimens. Either an increased rate of rise of furnace temperature for a given size of specimen, or an increase in size of specimen with a fixed rate of furnace temperature rise would tend to increase the temperature lag in the specimen and thus cause the maximum loss to occur at a higher furnace temperature. In addition, in the case of increased size of specimens, resistance to diffusion of gases evolved would be increased and tend to cause the loss of weight to occur more slowly.

19. Effect of Volume of Air Passing Through Furnace.—Standard size samples, $\frac{3}{4}$ in. x $\frac{3}{4}$ in. x 5 in. of Tennessee Ball Clay No. 5, were used to determine the effect of the volume of air on the rate of loss of weight.

A heating rate of 500 deg. F. per hour was used in all tests, and duplicate tests were made with the following amounts of air per minute flowing through the furnace—0.0 cc., 20 cc., 100 cc., and 500 cc.

The greatest difference appeared between 0.0 cc. and 20 cc. of air per minute, between the temperatures of 1075 and 1325 deg. F. With 20 cc. of air the greatest loss occurred between 1075 and 1200 deg. F. With no airflow the greatest loss occurred between 1200 and 1325 deg. F.
LOSS OF WEIGHT OF CLAY BODIES DURING FIRING

The results are shown graphically in Fig. 4a.

While the difference in effect of a given volume of air and the next higher volume was not significant statistically, the differences produced by the maximum difference in air flow were significant and it,
therefore, seems probable that the indicated effect of air flow, while small, did exist.

20. Effect of Cross-sectional Area of Specimens.—Samples of Tennessee Ball Clay No. 5, square in cross-section, were ground to the following dimensions:

\[
\begin{align*}
\frac{1}{4} \text{ in.} \times \frac{1}{4} \text{ in.}, & \quad \frac{1}{2} \text{ in.} \times \frac{3}{2} \text{ in.}, \quad \frac{3}{4} \text{ in.} \times \frac{3}{4} \text{ in.}, \quad \text{and} \quad 1 \text{ in.} \times 1 \text{ in.}
\end{align*}
\]

All samples were 5 in. long.

A heating rate of 500 deg. F. per hour, and a volume of 500 cc. of air per minute were used for all tests.

In general, the percentage of the total weight lost at any given temperature below 1150 deg. F. decreased with increase in the cross-sectional area of the sample, the loss being approximately inversely proportional to the least dimension of the specimen for the shape of specimen used.

The maximum rate of loss occurred at progressively higher furnace temperatures as the cross-sectional area of the sample increased. Both the tendency to produce a temperature lag in the specimen because of the rapid heating rate, and the resistance to diffusion of the gases evolved would be increased by increased dimensions of the specimens, and would tend to produce the effect observed. The results are shown graphically in Fig. 4b.

21. Relation Between Loss of Weight and Color and Size of Core Under Oxidizing Conditions.—Individual samples \(\frac{15}{16} \text{ in.} \times \frac{15}{16} \text{ in.}\) in cross-section were heated at a rate of 500 deg. F. per hour in the loss-of-weight furnace through which air was passed at the rate of 500 cc. per minute.

The first sample was heated to 825 deg. F., was immediately removed from the furnace, and cooled in a desiccator. The second sample was also heated to 825 deg. F., but was held at that temperature for a few hours before removing and cooling in a desiccator. This process was repeated at the same temperature, each successive sample being held for a greater length of time, until a sample was obtained from which all visible evidence of black-core had disappeared. The loss of weight also was checked. This process was repeated at 1075 deg. F., 1325 deg. F., and 1800 deg. F.

Thus data were obtained showing the relation between the time required to remove black-core, the temperature at which it was removed, and the corresponding loss of weight.
For the material and size of sample used, 24 hours total elapsed time, including heating up period, was required to remove black-core at 825 deg. F., 8 hours at 1075 deg. F., 5½ hours at 1325 deg. F. and 4 hours at 1800 deg. F.; at those times and temperatures the samples had come to practically constant weight.

At 825 deg. F. the core was only slightly darker than the gray color of the clay, and blended gradually into the clay at the boundary between the clear and cored areas.

At 1075 deg. F. the clay had acquired a faint “pink” color and the “black-core,” only slightly darker gray than the green clay, still blended into the clear area at the boundary.

At 1325 deg. F. the core was distinctly black, the clear area “pink,” and the boundary between the two was sharp and well defined.

At 1800 deg. F. the core was light gray surrounded by a thin ring of pale gray which, in turn, was surrounded by a ring approximately ½ in. wide of clear oxidized body.

All of the samples burned clear when held for the length of time recorded, except that at 1800 deg. F. the gray cored area became pale buff in color.

The results, which are shown graphically in Fig. 5, indicate that the initial dark core due to carbon can be removed completely at a temperature as low as 825 deg. F. and that the rate of removal increases with increased temperature, i.e., less time is required at the higher temperatures.

Under strongly oxidizing conditions, the complete removal of discoloration corresponded closely with the arrival of the sample at constant weight at each temperature. Under reducing conditions, it probably would be impossible to correlate removal of the visible carbon core with loss of weight because the carbon core would be replaced by a dark core colored by iron compounds, and under this condition change in color would be difficult to detect.

Hence the absence of black discoloration might be a good indication of the absence of carbon, but the presence of black discoloration could indicate the presence of carbon, the presence of carbon and reduced iron compounds, or the presence of reduced iron compounds only.

22. Effect of Neutral Conditions (Nitrogen Atmosphere).—One specimen of the same material was heated to 1800 deg. F. at a rate of 500 deg. F. per hour in an atmosphere of nitrogen obtained by passing
500 cc. per minute of the gas through the tube furnace. This was done to determine whether or not the relation between black-core and loss of weight existed under neutral conditions.

The sample heated in nitrogen lost 8.2 per cent in weight as compared with a loss of about 8.05 per cent when heated in air, but, except for about 1/62 in. of clear body at the surface, the entire sample was very dark gray in color.
A second test of the same material was made in a gas-tight tube furnace, through which nitrogen gas was passed as before, without weighing the specimen except at the beginning and at the end of the test. The appearance of the specimen was the same as in the first test, and the loss of weight was 8.14 per cent. Thus the average loss of 8.17 per cent in an atmosphere of nitrogen was slightly higher than the loss of 8.05 per cent in air. If the oxidation of carbon in the clay is accomplished by reduction of iron compounds, it would be expected that losses in nitrogen would be higher than those in air because of the loss of oxygen from the iron compounds.

23. Statistical Study of Loss of Weight.—The forty-one bodies which were tested were divided into two groups, one containing thirty-six bodies, each experiencing a loss of weight of less than 8.0 per cent and the second containing five bodies, each experiencing a loss of weight of more than 8.0 per cent at 1800 deg. F. Four of the latter group had pyrometric cone equivalents of 28 or above, while two in the first group had ones of 23 and 26, the remainder having ones of 19 or less.

In addition, specimens of Tennessee Ball Clay No. 5 and H & G A-1 English China Clay were tested for comparison with the commercial bodies.

Two loss of weight tests were made on each body.

Results of Tests.—

First Group

The total loss at 1800 deg. F. varied from 4.28 to 8.00 per cent, with a mean of 6.53 per cent, and a probable error of 0.12 per cent, indicating that the chances are even that arithmetic means, obtained from samples of 36 specimens similar to those tested, may be expected to fall within 0.12 per cent of the true mean or within the range $6.53 \pm 0.12$ per cent. The mean curve is shown in Fig. 6a.

The data have been recalculated on the basis of weight lost in percentage of the total loss at 1800 deg. F., the values being shown graphically in Fig. 6b. The maximum loss of $28.28 \pm 0.46$ per cent of the total occurred between 1075 and 1200 deg. F.; at the latter temperature 77.4 per cent of the total loss had occurred.

Second Group

The total loss of weight at 1800 deg. F. varied from 8.79 to 10.84 per cent, with a mean of 9.85 per cent, and a probable error of 0.28 per cent, indicating that the chances are even that arithmetic means
for similar groups of bodies might be expected to lie within the range of $9.85 \pm 0.28$ per cent. The data are shown graphically in Fig. 6a.

The data have been recalculated on the basis of weight lost in percentage of the total loss at 1800 deg. F., the values being shown graphically in Fig. 6b. The maximum loss of $34.57 \pm 1.76$ per cent
occurred between 1075 and 1200 deg. F.; at the latter temperature 72.63 per cent of the total loss had occurred.

**Tennessee Ball Clay No. 5**

The total loss at 1800 deg. F. was 11.30 per cent, and the maximum loss of 31.14 per cent of the total loss occurred between 1075 and 1200 deg. F. The data are shown graphically in Figs. 6a and 6b.

**H & G A-1 English China Clay**

The total loss at 1800 deg. F. was 12.54 per cent, and the maximum loss of 29.32 per cent of the total loss occurred between 1200 and 1325 deg. F. The data are shown graphically in Figs. 6a and 6b.

**IV. Absorption Train Studies**

In addition to the determination of the total loss of weight of clay specimens at various temperatures by direct weighing of the sample while suspended in a furnace, further tests were carried out in which the quantities of carbon dioxide, sulphur dioxide, and water composing the total loss were determined by absorption by suitable reagents. For this purpose an absorption train was connected to the furnace.

24. *Description of Apparatus.*—The absorption train as finally assembled consisted of a preliminary train for treatment of the air before it passed over the sample, and a final absorption train for the determination of the products evolved by the clay during heating, as shown in Fig. 7.

The air passed first through a flowmeter which measured the approximate volume of air and served to make possible the duplication of test conditions. From the flowmeter the air passed through a preliminary calcium-chloride drying tube into two large U-tubes arranged in series, the first containing ascarite and anhydrone, and the second anhydrone only. Ascarite was used to remove any carbon dioxide from the air, since the normally low carbon dioxide content might have been materially increased by a nearby power plant and locomotive testing laboratory. The series of drying tubes reduced the moisture in the air to a negligible amount, the quantity collected in a weighing tube after preliminary drying amounting to approximately 0.002 grams per half hour with air flowing at the rate of 250 cc. per minute.

From the last preliminary drying tube the treated air passed
directly through the tube furnace in which the sample was heated, and out through a two-way stop-cock used for changing from one train to another.

The air and combustion products passed first through two weighing tubes, in series, packed with anhydrone, which removed the moisture. The second tube rarely recorded an appreciable gain in weight, but was used as a precautionary measure.

From the anhydrone tubes, the gas bubbled through an iodine-starch solution, which absorbed the sulphur dioxide. A negligible quantity of iodine was volatilized by the gases passing through the solution.

From the iodine-starch solution the gases passed through an anhydrone tube, which removed the moisture taken up from the iodine solution, and into the ascarite weighing tube, which removed the carbon dioxide. Since the ascarite, although in granular form, might have given up some moisture to the gases passing through, a small anhydrone tube was made an integral part of the ascarite tube to collect such moisture as might be given off.

The remaining gases were exhausted through the pressure-equalizing chamber and aspirator, by means of which the gases were drawn through the train.

The moisture was determined by direct weighing of the anhydrone tubes, the sulphur dioxide by back titration with sodium thiosulphate solution, and the carbon dioxide by direct weighing of the ascarite tube.

The 1/2 in. x 1/2 in. x 5 in. sample was heated in a furnace, the temperature of which was raised at a rate of approximately 500 deg. F. per hour from atmospheric temperature to the final temperature of 1800 deg. F., and air was passed through the furnace at a rate of approximately 260 cc. per minute.
Loss of Weight of Clay Bodies During Firing

Weighings were made at four different temperatures, a different train being used for each interval.

Duplicate determinations were made, the weighings being made at different intervals in each test. Since the final temperature for each test was 1800 deg. F., the duplicate tests gave determinations at seven different temperatures and a check on the total loss for each sample.

In addition, the total loss as determined by the absorption train was checked against the actual loss of weight of the sample.

25. Accuracy of Measurements.—Determinations were made on five different samples of the same fireclay body to check the accuracy of the test.

Since the exact form in which the sulphur and carbon occurred in the clay body was more or less problematical, the sulphur was assumed arbitrarily to be in the form of iron pyrites, and the carbon to be in the form of lignite.

For the purpose of comparison with the loss of weight as determined by actually weighing the sample, the sulphur dioxide was calculated back to an equivalent weight of sulphur, and the carbon dioxide to an equivalent weight of carbon. The total water given off when the clay was heated included not only the hygroscopic and chemically-combined water in the clay but also the water formed by the combustion of hydrogen in the carbonaceous impurities. Since lignite contains approximately five parts of hydrogen to seventy parts of carbon, only the hydrogen and not the water formed from the combustion of the hydrogen could be considered as loss of weight of the sample. For this reason the difference between the weight of the water, formed by the combustion of the hydrogen, and the weight of the hydrogen was subtracted from the total weight of water absorbed by the anhydrone tube.

The sum of the net weight of water, sulphur, and carbon was then compared with the loss of weight as determined by weighing the sample before and after the test.

The results of the five tests are given in Table 2, and are shown graphically in Fig. 8a.

The results of the five tests on the same body indicated that water, which was present in relatively large amounts, could be determined with a probable error of 1.41 per cent, which was quite satisfactory. The determinations of carbon dioxide were somewhat erratic, as indicated by the high probable error of 7.75 per cent. The sulphur dioxide evolved, while quite low, was determined with a satis-
TABLE 2
CALCULATED AND DETERMINED LOSS OF WEIGHT FOR BODY NO. 27

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Percentage Loss as Calculated</th>
<th>Total Percentage Loss as Determined by Weighing</th>
<th>Percentage Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>CO₂</td>
<td>SO₂</td>
</tr>
<tr>
<td>11</td>
<td>6.15</td>
<td>1.73</td>
<td>0.043</td>
</tr>
<tr>
<td>12</td>
<td>6.60</td>
<td>2.20</td>
<td>0.034</td>
</tr>
<tr>
<td>13</td>
<td>6.39</td>
<td>2.36</td>
<td>0.040</td>
</tr>
<tr>
<td>15</td>
<td>6.80</td>
<td>3.03</td>
<td>0.046</td>
</tr>
<tr>
<td>16</td>
<td>6.19</td>
<td>2.36</td>
<td>0.040</td>
</tr>
<tr>
<td>Mean</td>
<td>6.43</td>
<td>2.23</td>
<td>0.042</td>
</tr>
<tr>
<td>Probable Error</td>
<td>±0.091</td>
<td>±0.173</td>
<td>±0.0015</td>
</tr>
<tr>
<td>Percentage Probable Error</td>
<td>±1.41</td>
<td>±7.75</td>
<td>±3.57</td>
</tr>
</tbody>
</table>

*The percentage difference is calculated on the basis of actual weights rather than percentages. The figure is obtained by dividing the difference between the actual and calculated loss of weight in grams by the actual loss in grams.

factory probable error of 3.57 per cent. The total loss was determined with a probable error of considerably less than 2.0 per cent, the accuracy being influenced by the accuracy of the water determinations.

26. Evolution of Water, Carbon Dioxide, and Sulphur Dioxide.—The results of absorption train tests for all six bodies are shown graphically in Figs. 8a to 8f, inclusive.

The first weighings were made at about 425 deg. F. at which temperature losses of the order of 0.3 per cent water, 0.1 per cent carbon dioxide, and 0.02 per cent, or less, sulphur dioxide were obtained.

Water was given off most rapidly between 825 and 1200 deg. F., evolution being practically complete at 1400 deg. F., although a small amount continued to be given off up to the finishing temperature of 1800 deg. F.

Carbon dioxide was given off most rapidly between 700 and 950 deg. F., evolution being practically complete at 1400 deg. F., although, in this case also, a small amount continued to be given off up to the finishing temperature of 1800 deg. F.

Sulphur dioxide, when evolved in small amounts, was given off at a fairly uniform rate up to 1400 deg. F., but above that temperature the rate of evolution increased quite rapidly up to the finishing temperature of 1800 deg. F. In the case of bodies containing relatively large amounts of sulphur, however, sulphur dioxide was evolved at a maximum rate between approximately 825 and 1075 deg. F. The
Fig. 8. Relation between temperature and cumulative losses of water, carbon dioxide, and sulphur dioxide for six clays.
rate of evolution decreased from 1075 deg. F. to about 1300 deg. F., and then remained constant up to the finishing temperature of 1800 deg. F.

The percentage of the total loss which was produced at 825 deg. F. at equilibrium was roughly proportional to the total carbon removed from the body. That is, the higher the carbon content, the greater the percentage of the total weight which was removed up to 825 deg. F.

The percentage of the total loss which was produced at 950 deg. F. at equilibrium was, roughly, inversely proportional to the sulphur content of the body, for sulphur tends to retard the normal reactions. The higher the sulphur content, the lower the percentage of the total weight which was removed up to 950 deg. F.

The samples high in sulphur lost weight (total of water, carbon dioxide, and sulphur dioxide) more slowly than did those low in sulphur. This is shown clearly in Table 3, which gives the percentage of total weight lost up to 1800 deg. F. for each body, when held at the indicated temperature until practically constant weight had been attained.

Even though the total losses approached completion between 1400 and 1450 deg. F., the individual curves for sulphur alone indicated that it continued to be given off up to the finishing temperature of 1800 deg. F.

V. SUMMARY OF RESULTS

27. Discussion of Results.—The factors which influence the loss of weight of a given clay body during firing under strongly oxidizing conditions, exclusive of the nature and amount of oxidizable and volatile constituents, are the heating rate and the size of the specimen.
It has been shown that when a clay is heated to equilibrium, a given loss may occur at a temperature as much as 350 deg. F. lower than that corresponding to the same loss when the furnace temperature is increased at a rate of 500 deg. F. per hour. It has been shown further that the loss of weight below 1150 deg. F. for a temperature rise of 500 deg. F. per hour is approximately inversely proportional to the least dimension of the specimen, for the shape of specimen used.

Obviously therefore, measurements of loss of weight either by direct weighing of the specimen, or by absorption of and weighing of the gases evolved, can have no particular significance unless both the heating rate and the size of the sample are specified.

In the absorption train tests water was given off rapidly between 825 and 1200 deg. F., the maximum rate occurring at about 1050 deg. F. In the tests in which the specimens were heated to constant weight the maximum loss occurred at 950 deg. F., while in the tests in which the temperature was increased at a rate of 500 deg. F. per hour the greatest loss occurred between 1075 and 1200 deg. F., with the maximum rate at about 1125 deg. F. The lower temperature in the absorption train tests is explained by the fact that the specimens were \( \frac{1}{2} \) in. \( \times \frac{1}{2} \) in. in cross-section as compared with the \( \frac{3}{4} \) in. \( \times \frac{3}{4} \) in. cross-section used in all other tests. Since water constitutes the greater part of the loss of weight of clays, it may be safely assumed that the large losses weighed directly are due to loss of water, and it seems probable, therefore, that under equilibrium conditions water is lost rapidly between 825 and 950 deg. F., the maximum rate being nearer 950 than 825 deg. F., while under conditions of rapid heating previously specified the loss of water would occur rapidly in the range from 1075 to 1200 deg. F. with the maximum rate at about 1125 deg. F. for the \( \frac{3}{4} \) in. \( \times \frac{3}{4} \) in. \( \times 5 \) in. specimen used. The results of the tests under equilibrium conditions are, in general, in accord with the results obtained by Brown and Montgomery,* who found that the bulk of the water was given off at 842 deg. F. The temperature range of 930 to 1110 deg. F. given by Ries† seems too high for equilibrium conditions, and may be the result of the heating rate (not specified), since Kraner and Fritz‡ found water to be given off most rapidly in the same range when a heating rate of 45 deg. F. was used. It seems probable then that the true maximum rate of evolution of water occurs in the range from 825 to 950 deg. F., but that the apparent temperature at which maximum evolution occurs

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*See footnote ¶ p. 8.
†See footnote * p. 9.
‡See footnote † p. 11.
may be raised to as high as 1200 deg. F. by increased heating rates and by increased size of specimens.

Carbon dioxide began to be evolved at temperatures as low as 425 deg. F., which is in agreement with the 410 deg. F. determined by Bole and Jackson,* and with the 390 deg. F. determined by Krauer and Fritz.† In the absorption train tests carbon was removed rapidly in the range from 700 to 950 deg. F., the maximum rate occurring at about 825 deg. F., and the removal being practically complete at 1400 deg. F. Under equilibrium conditions constant weight was attained and black-core removed at a temperature as low as 825 deg. F., which is in agreement with the results obtained by Bole and Jackson,‡ who completely removed carbon at 860 deg. F. This conclusion cannot be made general, however, for it is known that in some clays, such as ball clays, only part of the carbon can be removed at low temperatures, and it has been shown by Krauer and Fritz¶ that the temperature at which the maximum rate of evolution occurs differs quite widely for different ball clays. Carbon was removed more rapidly at higher temperatures, which is in general agreement with the results reported in the literature.

Sulphur dioxide began to be given off at temperatures as low as 425 deg. F. and continued to be given off up to 1800 deg. F. in all tests, which agrees with the results obtained by Bole and Jackson.§ In the absorption train tests sulphur dioxide was evolved rapidly between 825 and 1075 deg. F., the maximum rate occurring at about 950 deg. F. While a direct comparison is not possible, it may be said that this result agrees in general with the work of Bole and Jackson,** who completely removed the first half of the sulphur from pyrite at 930 deg. F. and completely decomposed pyrite by prolonged heating at about 1700 deg. F. In contrast to the bodies just described, which contained relatively large amounts of sulphur, those bodies which contained small amounts of sulphur evolved sulphur dioxide at a uniform rate up to about 1400 deg. F.; above this temperature the rate increased.

In general, a slight loss of hygroscopic moisture should occur between 250 and 400 deg. F. which for pure clays would be followed by a large rapid loss of chemically-combined water between 1075 and 1200 deg. F. If the pure clay is diluted with anhydrous and non-

*See footnote † p. 11.
† See footnote ‡ p. 11.
‡ See footnote ¶ p. 11.
¶ See footnote § p. 11.
§ See footnote † p. 11.
** See footnote † p. 11.
volatile impurities such as uncombined quartz, the losses of water and the total loss at 1800 deg. F. will be reduced in proportion.

However, if the clay contains carbon, additional losses will occur from 400 deg. F. up to about 1400 deg. F., with a maximum rate of evolution at about 825 deg. F., thus bridging the gap between 400 and 1075 deg. F., increasing the loss in that range, and eliminating the more or less abrupt change in slope of the loss curve for pure clay at the point at which chemically-combined water is given off.

If sulphur is present without carbon half of it will be removed between approximately 750 and 950 deg. F., and the remainder will be given off slowly above that temperature.

If both carbon and sulphur are present in large quantities losses between 400 and 1075 deg. F. should occur because of carbon (and sulphur also if the carbon is satisfactorily removed), and losses should continue at a greater than normal rate above about 1075 deg. F. because of remaining sulphur.

The decomposition of carbonates and sulphates would be contributing factors.

28. Refinement of Test.—Further refinement of the test might be obtained by the establishment of a series of standard curves showing the quantitative effects of increasing amounts of carbon and sulphur on the loss-of-weight characteristics of clays. Such information could be obtained in either of two ways. Either a series of natural clays could be selected at the mines, including clays which would be discarded ordinarily as unsatisfactory for commercial use because of high carbon and sulphur; or a series of synthetic mixtures could be prepared using a pure clay and suitable forms of carbon and sulphur. In either case a series of standard curves could be prepared showing the effect of carbon and sulphur on the loss-of-weight characteristics of clays.

29. Loss of Weight Test as a Standard Laboratory Test.—Since it has been shown that the relation between loss of weight and temperature is greatly influenced by the heating rate and the size of the specimen, these must be definitely specified before loss-of-weight data can have any significance.

The use of strongly oxidizing conditions associated with the flow of a large volume of air through the furnace is a necessary part of the test, since, when heated rapidly under weakly oxidizing or neutral conditions, almost all clays will form a black core. The formation
of black-core in all cases would make it impossible to distinguish between those clays which could and those which could not be properly oxidized.

The loss of weight test, which requires about three hours, effects a considerable saving in time since from one to several days may be required for the present draw trial tests or semi-commercial or commercial tests.

The data on loss of weight are for commercial bodies which presumably can be oxidized properly under commercial conditions. Since only three bodies out of a total of forty-one showed evidence of black-core, it seems probable that a body which could be oxidized under the conditions specified for the loss of weight test could be oxidized under commercial conditions.

The test offers a method of classification of clays on the basis of the total weight lost at 1800 deg. F., since the loss of weight increases with the increasing purity of the clay, because of the water content of the clay minerals which are present in greater amounts in the purer clays.

The test also offers a method for the determination of the general oxidation characteristics of clays from the shapes of their loss of weight curves by comparison with average curves such as are given in this bulletin.

30. Safe Temperatures for Oxidation.—The maximum safe temperature for the oxidation of clays will depend chiefly upon the nature and relative amounts, and upon the dissociation temperatures, of the carbon and sulphur compounds present, but also, to a lesser extent, upon the vitrification characteristics of the clay.

Shrinkage and a decrease in the size and volume of the pores in clay, which reduce the permeability, will retard and may stop oxidation if the surface of the clay becomes sealed over by partial fusion. In general, clays increase in porosity with increased firing temperature, reaching a maximum in the range from about 800 to 1200 deg. F. for plastic fireclays, and in the range from about 1200 to 1600 deg. F. for shales; following this the porosity decreases with further increase in firing temperature. The consideration of the porosity and permeability of clay bodies alone would indicate that these temperature ranges would be best for oxidation, but, while these physical properties influence the time required for oxidation, the factors which determine the best temperature for oxidation are the nature, the relative amounts, and the dissociation temperatures of the carbon and sulphur compounds present.
It must be remembered that carbon seldom, if ever, is found in black-cored areas, while sulphur is nearly always present; that the presence of carbon retards the oxidation of sulphur; and that excessively rapid rates of oxidation of either carbon or sulphur tend to cause reduction of iron compounds present in the clay. Furthermore, since the carbonization of coal below 1200 deg. F. results in a more combustible coke than when severe cracking of the distillation products is caused by carbonization at higher temperatures, carbonization of the carbonaceous matter in clay should be completed below about 1200 deg. F., irrespective of whether the resulting residue is oxidized above or below that temperature. Safe oxidation, then, involves the removal of carbon at temperatures at which it is most combustible, at a rate sufficiently slow to prevent the formation of appreciable amounts of carbon monoxide which would tend to reduce the iron compounds in clay, and at temperatures below which iron-sulphur compounds dissociate rapidly and are readily reduced.

Pyrite loses half of its sulphur below 930 deg. F., the reaction starting slowly at temperatures as low as 650 deg. F. The remaining half of the sulphur is completely oxidized between 1600 and 1700 deg. F. Ferric sulphate, which may be formed either by weathering of iron-sulphur compounds, by the decomposition of iron sulphide during firing, or by the absorption of sulphur from the kiln gases, begins to dissociate at as low as 930 deg. F., but decomposes chiefly in the range from 1040 to 1430 deg. F. Ferrous sulphate, which is formed during the decomposition of iron sulphide in firing, decomposes between 1000 and 1200 deg. F. In the presence of relatively large amounts of pyrite, carbon should be oxidized below 900 deg. F., and preferably at the lowest temperature at which it can be completely removed, or about 800 deg. F. If the clay has been weathered so that the pyrite originally present has been converted into ferric sulphate, the carbon may be removed safely below about 900 deg. F. Following the oxidation of carbon and half of the sulphur in pyrite at low temperature, the sulphates of iron will be decomposed in the range from about 1000 to 1400 deg. F., although the last traces of sulphur probably will not be removed until temperatures of from 1600 to 1700 deg. F. are reached. In this latter range, the decomposition of calcium sulphate also will be accomplished. The removal of all sulphur is quite difficult, and it is probable that in commercial practice the last traces will not be completely removed.

The amounts and relative proportions of carbon and sulphur in clay will vary over a wide range. If the carbon content is low, it is
possible that the oxidation of carbon will be completed by the time that temperatures of 800 to 900 deg. F. are reached, so that no special precautions will be necessary. If the sulphur content is quite low, the carbon residue formed below 1200 deg. F. may be oxidized above that temperature, because such oxidation will be safe in the absence of sulphates. In some cases, as in ball clays, in which the carbon residue is difficult to oxidize, temperatures above 1200 deg. F. may be required to remove the last part of the carbon core.

In general, it may be said that carbonaceous matter should be carbonized below 1200 deg. F.; that, when sulphur is present in relatively large amounts, carbon should be completely removed between 800 and 900 deg. F.; that sulphates should be decomposed as completely as possible between 1000 and 1400 deg. F.; and that the last traces of sulphur, or the last traces of carbon in a low-sulphur body, should be removed at temperatures not exceeding the upper limit of the range in which the porosity of the body is at a maximum.
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