IMPROVEMENT OF SOME KANSAS CLAYS THROUGH THE CONTROL OF pH AND OF SOLUBLE SULFATES

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ABSTRACT

For a number of years brick manufacturers have found that the control of pH through the addition of an alkaline salt, usually sodium carbonate, to some types of clays and shales results in an improvement of extrusion characteristics, dry strength, fired strength, and color, and lowers the absorption of the fired brick. Dakota formation fire clays used in the manufacture of face brick were investigated to determine the optimum amount of sodium carbonate required to produce the desired results. Inasmuch as the presence of sulfates in the clay or tempering water reduces the effectiveness of the sodium carbonate additions, tests were also conducted to determine the amount of barium carbonate required to convert all the sulfate to insoluble barium sulfate. Brick made in a laboratory extrusion machine were used to determine the improvement of the green and fired characteristics of the brick by the additions. Results were also checked by plant production of brick containing the same additions. In one case the use of barium carbonate alone proved sufficient.

INTRODUCTION

Investigations of the improvement of stiff-mud extruded brick by the control of pH through the addition of small amounts of sodium carbonate (soda ash) to the clays and shales were started in 1930 at the University of Wisconsin. The results of these investigations were first published in the Journal of the American Ceramic Society by Barker and Truog (1938). Additional articles by the same authors appeared in the Journal in 1939 and 1941. Since 1938 the methods recommended by Barker and Truog have been used rather extensively. In some cases the addition of the correct amount of soda ash to the clay or shale has resulted in marked improvements both in ease of manufacture and quality of finished brick.

The green working characteristics and the fired properties of clays are determined by the particle size and types of clay minerals present, by the particle size and chemical characteristics of the nonclay fraction, by the proportion of clay to nonclay constituents, and by the ion-exchange characteristics of the clayey mass. Kaolinitic clays have low ion-exchange capacity, illitic clays occupy an intermediate position, and montmorillonoids have high ion-exchange capacity. In clay materials the commonest exchangeable cations are Ca^{++}, Mg^{++}, H^{+}, K^{+}, NH_4^{+}, and Na^{+}, frequently in about that order of relative abundance. The common anions in clay materials are SO_4^{--}, Cl^{-}, PO_4^{---}, and NO_3^{-}. The relative abundance of the anions is not yet known (Grim, 1953).

Throughout this report the term "ion exchange" is used in preference to the more common but less accurate "base exchange." This usage, as well as the general information given on ion exchange, is taken from Grim (1953, pp. 126-160).

If the clay mass contains available ions in the form of compounds such as calcium carbonate, sulfuric acid, or alkaline feldspars, the base exchange positions will be taken up by the available ions, and calcium, hydrogen, or sodium clays will result. Hydrogen and sodium clays deflocculate easily, whereas calcium clays tend to flocculate. In the case of soils, improvements result from the addition of calcium carbonate in the form of pulverized limestone to acid or sodium soils by the resulting flocculation which confers a granular or porous structure. The opposite effect is usually desired in clays used for manufacturing brick or other ceramic articles. The deflocculated clay contains a minimum of water and dries to a dense and hard mass. Sodium compounds such as sodium hydroxide, sodium carbonate (soda ash), and sodium silicate are commonly used to produce deflocculation in clays used for ceramics. In the heavy clay products industries soda ash is the cheapest and most effective.

In a sense the title of this report is misleading. The control of pH does not in fact produce the improvements in clays. The improvements are caused by the deflocculation of the clays through the addition of reagents such as sodium carbonate. The determinations of the pH of clays to which varying amounts of the reagent have been added is the method used for the determination of the optimum amount of the reagent (in this case, sodium carbonate) to be used for deflocculation. Empirical tests indicate that optimum additions of the reagent can be revealed by plotting the pH determinations on a graph. A leveling off, or a bench on the curve, occurs with the optimum additions of the reagent.

The dominant clay mineral present in clays of the Dakota formation in Kansas is kaolinite, although minor amounts of illite, montmorillonite, and mixed-layer minerals may be present. Theoretically these clays should be hydrogen clays with a pH on the acid side. Actually almost all fresh clays from this source give a basic reaction ranging from 7.1 to 10.0 pH when tested with the glass electrode meter. After aging the pH of the clays becomes acid, pH readings ranging from 6.9 down to 3.5, possibly due to both complete drying and to slow disintegration of small

amounts of iron sulfide. Calcium is usually present in these clays in small amounts as shown by a total CaO content of less than 1 percent. Alkalies are present in somewhat larger quantities, but sodium oxide and potassium oxide usually do not exceed a total of 3 percent. The alkalies are brought into the clay by illite and montmorillonite clay minerals, feldspar, and muscovite. Magnesium is usually more abundant than calcium in the Dakota formation clays, but total MgO, as determined by chemical analysis, seldom exceeds 2 percent. Sulfur trioxide ranges from a slight trace to 0.1 percent. Chemical analyses of the three clays discussed in this paper are given in Table 1.

It will be noted that the constituents normally expected to affect ion-exchange positions and the deflocculation of clays are present in these three clays in amounts much less than the maximums given above. If, however, even a small proportion of the calcium, sodium, and magnesium is available to fill exchange positions the pH and deflocculation characteristics of the clays would be definitely affected. Calcium hydroxide added in amounts as small as 0.035 percent produce easily detected changes in a clay.

The very light-buff or nearly white bricks produced from siliceous fire clays in the Dakota formation of Kansas must be fired to relatively high temperatures ranging from cone 5 (approximately 2160° F.) to cone 10 (approximately 2300° F.). In some cases the high percentage of quartz in the clays results in excessive power consumption in extruding the stiff mud. It was concluded that alterations of the pH of the clays through the correct additions of soda ash should decrease power consumption, produce a tougher dry brick, and decrease firing temperatures.

At the request of two brick plants, such tests were conducted on specific clay blends. Samples for the tests were furnished by the companies, and the results of plant tests were also reported to us by them.

TESTING

METHODS USED IN TESTING

The method outlined by Barker and Truog (1938, 1939, 1941) for the determination of the optimum pH of a clay was used by us in this investigation, but with slight modifications.

Samples consisting of 100 grams of clay were put in beakers and 250 cc distilled water added to each. Varying amounts of sodium carbonate ranging from 0.1 to 1.0 percent of the dry weight of the clay were added. The clay suspensions were stirred for 15 minutes, then the pH of each determined by the glass electrode method. Additional pH determinations were made after periods ranging up to 24 hours, or until the pH had reached a stable level. The pH values resulting from these tests were plotted on graph paper on the vertical axis (as ordinates) and the percentages of sodium carbonate added on the horizontal axis (as abscissas). Barker and Truog (1941) classified the curves obtained with various clays into three general types (Fig. 1).

The type-A curve has a definite single break in the slope. Experiments have proved that the optimum percentage of sodium carbonate is indicated by the break in the curve, just after it flattens out. The type-B curve has two or more breaks in the curve. In this case the optimum percentage of sodium carbonate required is not so clearly indicated. In general, if the first break in the curve occurs at a pH below 7.0 the next higher break represents
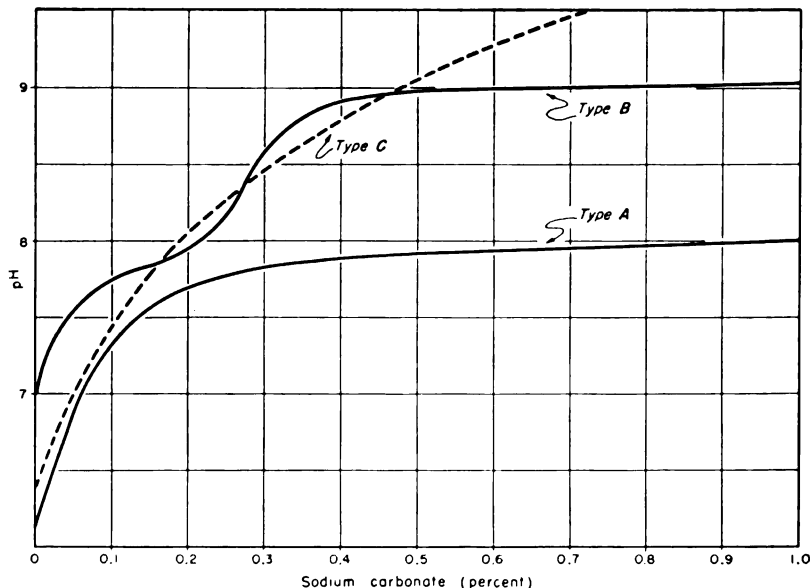

Fig. 1.—Graph showing three generalized types of pH versus sodium carbonate curves.

the optimum percentage. If the first break occurs at a pH above 7.0 it is possible that the percentage of sodium carbonate indicated at that break will be sufficient.

The type-C curve has no definite break in the slope and therefore no definite percentage of sodium carbonate is indicated for the optimum. The presence of relatively large percentages of exchangeable magnesium may produce this type of curve in a clay. Since illitic clays contain exchangeable magnesium they are likely to produce a type-C curve. The addition of a very small amount of calcium hydroxide to the clay suspension changes the characteristics of the clay so that in some cases a type-A or type-B curve is produced.

Because the C-54-A clay produced a type-B curve with an indeterminate break-off point to indicate the optimum addition of sodium carbonate, additional tests were run with a small percentage of calcium hydroxide added in equal amounts to each of the beakers containing the varying amounts of sodium carbonate. To test the effect of calcium hydroxide without the influence of the sodium carbonate addition varying amounts of calcium hydroxide were added to the clay by the same method employed for the sodium carbonate additions. In all cases the necessary amount of barium carbonate was included in the test batches (Figs. 3 and 4).

In addition to the pH determinations specified by Barker and Truog we determined the relative amount of deflocculation with varying additions of the sodium or calcium salts by measuring the height of sediment remaining in the beakers after standing from 18 to 72 hours. In suspensions that were insufficiently deflocculated the sediment had settled to a relatively low level with a large amount of clear water at the top. The deflocculated suspensions had almost no clear water at the top and the sediment level was correspondingly high (Figs. 5 and 7).

In addition to the pH determinations with a series of increasing percentages of sodium carbonate additions, we also determined the minimum barium carbonate required to eliminate sulfate scum on the fired clays. Inasmuch as barium carbonate is used by both brick plants for this purpose it was necessary to include the effects of barium carbonate in the sodium carbonate addition tests. Furthermore, barium carbonate has a definitely beneficial effect on the deflocculation characteristics of the clay

because it converts the detrimental soluble sulfates to insoluble barium sulfate.

The method used to determine the amount of barium carbonate required to convert the soluble sulfates in a clay is the one commonly employed by the heavy clay industries for this purpose. A series of 100-gram samples of the clay are weighed into beakers. Increasing amounts of barium chloride are added to each in the series, beginning with 0.05 percent and increasing to 1.00 percent. Distilled water in amounts sufficient to produce a thin slip is added to each of these and the mixture stirred thoroughly. After standing for 12 hours or more the clay settles out leaving clear liquid at the top. This solution contains the excess barium chloride, if present. A small amount of sulfuric acid is added to each of the beakers. In the beakers containing more barium chloride than necessary to neutralize the soluble sulfates the barium chloride is converted to barium sulfate by the acid and the clear solution becomes cloudy. The liquid in beakers containing insufficient additions of barium chloride remains clear. The correct addition of barium chloride is indicated by the beaker containing a cloudy solution and the smallest percentage of the barium salt. An equivalent addition of barium by the use of barium carbonate is calculated from the percentage of barium chloride required. In the tests we ran the water used at the brick plants was added to the distilled water in the amount used to temper the stiff mud used for extrusion. This procedure was necessary because the tempering water contains more soluble sulfates than the clay.

CHEMICAL, MINERALOGICAL, AND PHYSICAL PROPERTIES

The two light buff- to white-firing clays tested in this investigation are typical of those found in the upper (Janssen) member of the Dakota formation in central and north-central Kansas (Plummer and Romary, 1947). In both cases slightly less than 20 feet of clay is mined from the Janssen member, and the clays are very much alike in general appearance. The uppermost part of the beds is dark gray to nearly black, and the lower part ranges from gray to very light gray. The clays are overlain by sand or silt within which is the contact between the upper Dakota formation and the lower part of the Graneros shale formation. The red-

firing clay from Barton County (BT-3-R) occurs in the upper part of the Terra Cotta member of the Dakota formation, and immediately underlies the light-firing clay of the Janssen member described above. Almost 20 feet of buff-firing clay underlies the light-firing clay from Cloud County (C-54-A and C-54-P). This clay also occurs in the Janssen member. Red-firing clay of the Terra Cotta member underlies a total of nearly 40 feet of buff-firing clays of the Janssen member.

Cloud County clay.—The light-buff to nearly white-firing clay blends, C-54-A and C-54-P, are mined in the SE¼ sec. 32, T. 7 S., R. 2 W., Cloud County. These two clay blends are mined from the same deposit and differ only in that C-54-P contains a slightly greater proportion of plastic clay. The upper part of the bed consists of a slightly silty, almost black clay containing lignite associated with pyrite. The lower and greater proportion of the deposit mined consists of very light-gray silty clay containing very little lignite. Pyrite is present in this clay in the form of rounded pellets. Most of these pellets are coarse enough to be retained on a 100-mesh sieve (Bowdish, 1953).

Differential thermal analysis of the combined clays from this bed (C-54-A) indicates that the dominant clay mineral present is kaolinite (Fig. 2). The major endothermic peak below 600° C. and the exothermic peak at about 960° C. are typical for kaolinite. Minor endothermic deflections at 200°, 700°, and 900° C. indicate small percentages of illite and montmorillonite. The lignite and other organic matter and the pyrite produce the large exothermic deflection at 400° C. The C-54-P blend included in the series of tests is taken from the same deposit as C-54-A, and differs from it only in that a greater proportion of more plastic clay is included.

Chemical analysis (Table 1) of this clay indicates that illite and montmorillonite are present in relatively small amounts (the percentages of magnesium oxide and the alkalies are quite low). Allowing for the small amount of muscovite known to occur in this clay and the probability of some feldspar, the proportion of illite or montmorillonite to kaolinite is even lower than if all the potassium were ascribed to the clay minerals. If all the alumina present in this clay is calculated as present in kaolinite the total clay content is less than 35 percent. The remaining 65 percent is largely made up of finely divided quartz.
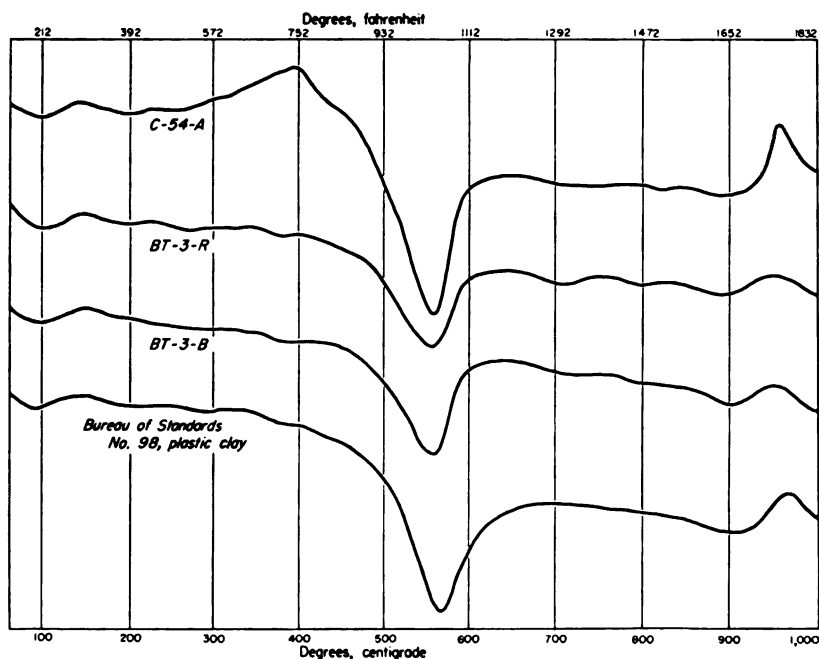
FIG. 2.—Differential thermal analysis curves of three test clays and Bureau of Standards plastic clay standard 98.

Despite the low percentage of clay minerals and the relatively high quartz content this clay is fairly plastic and works unusually well in stiff mud extrusion. As might be expected with a clay of this type no unusual drying problems are encountered.

Considered as a mixture of kaolinite and quartz this is an unusually pure material containing very few fluxes in the form of calcium, magnesium, sodium, or potassium oxides. As a result this clay is quite refractory and requires high-temperature firing to produce a sound brick. Laboratory tests (Table 3) indicate that at cone 8 (about 2240°F.) the C-54-A clay is slightly under-fired. The primary purpose in investigating this clay was to find a means of decreasing the absorption and increasing the compressive strength of the brick. Although the chief method used to achieve this purpose was through pH and sulfate control, firing schedules based on reactions revealed by differential thermal analysis (Fig. 2) were recommended, as well as changes in drying methods.

TABLE 1.—*Chemical analyses of the three clays investigated and Bureau of Standards plastic clay standard sample 98*

Constituent	C-54-A	BT-3-B	BT-3-R	Bureau of Standards no. 98
SiO_2	76.05	78.75	73.18	59.11
Al_2O_3	13.77	12.43	12.14	25.54
Fe_2O_3	1.21	1.21	5.84	2.05
TiO_2	1.35	1.20	1.16	1.43
CaO	0.25	0.26	0.53	0.21
MgO	0.39	0.35	1.10	0.72
P_2O_5	nil	trace	0.10	0.08
SO_3	trace	nil	trace	0.07
K_2O	0.48	1.02	1.38	3.17
Na_2O	0.08	0.21	0.21	0.28
Ignition loss	5.85	4.17	4.65	7.23
Total	99.43	99.63	100.34	99.94*

*ZrO_2, V_2O_5, Cr_2O_3, MnO, and CuO, totaling 0.10 percent, raises the grand total to 100.04 percent.

Barton County clay.—The Barton County clays included in this investigation (BT-3-B and BT-3-R) are mined in the SW¼ sec. 21, T. 18 S., R. 13 W., and are used in the manufacture of light-buff to red face brick. The materials are mined in benches and combined at the plant. The upper and lower benches of the buff-firing material consist of plastic gray clay with a small amount of black clay at the top of the upper bench. The middle bench is a slightly clayey, fine-grained, light-gray silt. The red-firing clay underlies the buff-firing material.

Differential thermal analysis of the mixture (BT-3-B) used in the manufacture of light-buff face brick (Fig. 2) shows that kaolinite is the dominant clay mineral. Small inflections at 700° and 900° C. indicate illite and montmorillonite in amounts slightly greater than found in the C-54-A clay. Chemical analysis (Table 1) confirms this conclusion in that the potassium oxide content is also slightly higher. The slightly lower firing temperature of this clay as compared to C-54-A or C-54-P also indicates the presence of the alkaline fluxes in greater amounts. In either case, however, the flux content is fairly low. The total clay mineral content of the two clays is approximately the same, and the dominant mineral present is finely divided quartz. Pyrite is present in very small amounts. The red-firing clay (BT-3-R) mined be-

low the buff-firing section is similar to the upper section with the exception of a higher iron oxide content (Table 1). To judge from the yellow color of the clay the iron is present in the form of limonite and the differential thermal analysis shows minor endothermic inflections between 250° and 400° C., which is within the correct range for the thermal reactions of limonite.

These clays (BT-3-B and BT-3-R) are fairly plastic despite the high quartz content, but require a rather high consumption of power on extrusion, especially the buff-firing clay. Reduction of power consumption was the primary objective of the pH and sulfate ion control tests on these clays. Other and rather unexpected benefits were realized, however.

DATA ON pH AND SULFATE ION CONTROL TESTS

Cloud County clay.—Seven series of pH determinations were run on the C-54-A clay with varying additions of deflocculating agents. Series 1 consisted of increasing additions of sodium carbonate ($NaCO_3$) to the dilute clay-distilled water suspensions. Inasmuch as the clay itself has a pH of 7.41, the plotted pH-soda ash (sodium carbonate) curve is all in the alkaline pH range. This curve is an indeterminate type-B with no positive indication of optimum pH (curve 1, Fig. 3). A slight bench occurs in the curve at a pH of 8.45 at the 0.3 percent addition of sodium carbonate, a second at 8.87 at the 0.5 percent addition of sodium carbonate, and a broad bench extending somewhat below 9.18 pH and above 9.21 with an indicated optimum of about 0.75 percent sodium carbonate. The pH curve takes another upward slope, however, from 9.25 pH at the addition of 0.9 percent sodium carbonate. It was judged that the amounts indicated were much too high from the point of view of economy unless the slightly indicated 0.3 percent addition was correct.

Inasmuch as barium carbonate is used at the brick plant and would necessarily influence the addition of any deflocculating material added we decided to use barium carbonate in all subsequent tests. The optimum percentage addition of barium carbonate required to make the soluble sulfates insoluble was determined by the method previously described. This optimum percentage is between 0.25 and 0.30 percent barium carbonate.

Labels within the graph:
- With 0.3 % BaCO₃
- With 0.3 % BaCO₃ + 0.1 % Na₂CO₃
- 100 % plant water used in all tests except No. 1
- With 0.3 % BaCO₃ + 0.15 % Ca(OH)₂
- Without BaCO₃; with distilled water
- With 0.3 % BaCO₃

x-axis: Sodium carbonate (percent); curves 1, 2, and 3 / Calcium hydroxide (percent); curves 4 and 5

y-axis: pH

FIG. 3.—Graph showing changes of pH of clay C-54-A with increasing additions of sodium carbonate (series 1, 2, and 3) and with increasing additions of calcium hydroxide (series 4 and 5).

Series 2 was the same as series 1 with the exception that 0.3 percent barium carbonate was added to each of the tests in the series. The general shape of the plotted curve (curve 2, Fig. 3) was similar to that for series 1. Slight benches occurred in the curve at a pH of 8.03 (0.2 percent Na_2CO_3), at a pH of 8.58 (0.5 percent Na_2CO_3), and near the end of the curve at a pH of 9.04 (0.8 percent Na_2CO_3). On the whole this series of tests gave no positive indication of an optimum sodium carbonate addition.

According to Barker and Truog (1941, pp. 320-321) the addition of calcium hydroxide ($Ca(OH)_2$) will in some cases greatly favor the adsorption of sodium by the exchange material, especially with clays giving the C-type curve. Inasmuch as the curves for series 1 and 2 were somewhat like a C-type curve we considered it advisable to add equal amounts of calcium hydroxide to a series of samples containing varying amounts of sodium carbonate. In series 3 we added 0.15 percent calcium hydroxide (hydrated lime) to each of the beakers in series 2. An anomalous curve trending generally downward was obtained by plotting the pH determinations made on series 3 (curve 3, Fig. 3). Obviously the addition of 0.15 percent calcium hydroxide complicates rather than solves the problem.

The next step in the investigation was to add varying amounts of calcium hydroxide to a series of tests. Barium carbonate was added in equal amounts to each as discussed above. It was hoped that this test would give an indication of the optimum amount of calcium hydroxide to use. A smooth A-type curve was obtained from the plotted pH determinations on series 4 (curve 4H, Fig. 3) with approximately 0.8 percent calcium hydroxide at a pH of 12.00 as the indicated optimum. In series 5, 0.1 percent sodium carbonate was added in equal amounts to series 4 (curve 5, Fig. 3). The shape of the plotted curve was again a smooth A-type, but the general level of the pH determinations was lower. About 0.8 percent calcium hydroxide was also indicated as the optimum, but the pH at this addition was lowered to 11.70. At one point on the curve (when 0.05 percent calcium hydroxide was added), however, the 0.1 percent addition of sodium carbonate raised the pH from 8.17 to 8.41.

For series 1, distilled water was used in the suspension. In series 2, 3, 4, and 5, water from the brick plant well was used. At this point in the tests we decided that the use of 250 cc brick plant water to 100 grams of clay was introducing an error in that less than 20 percent brick plant water (water used in tempering amounts to 20 percent of the dry weight of the clay) is used in tempering water for the extruded brick. In the remaining series of tests only 20 cc brick plant water was used. To this 180 cc distilled water was added to correct the ratio of water to clay.

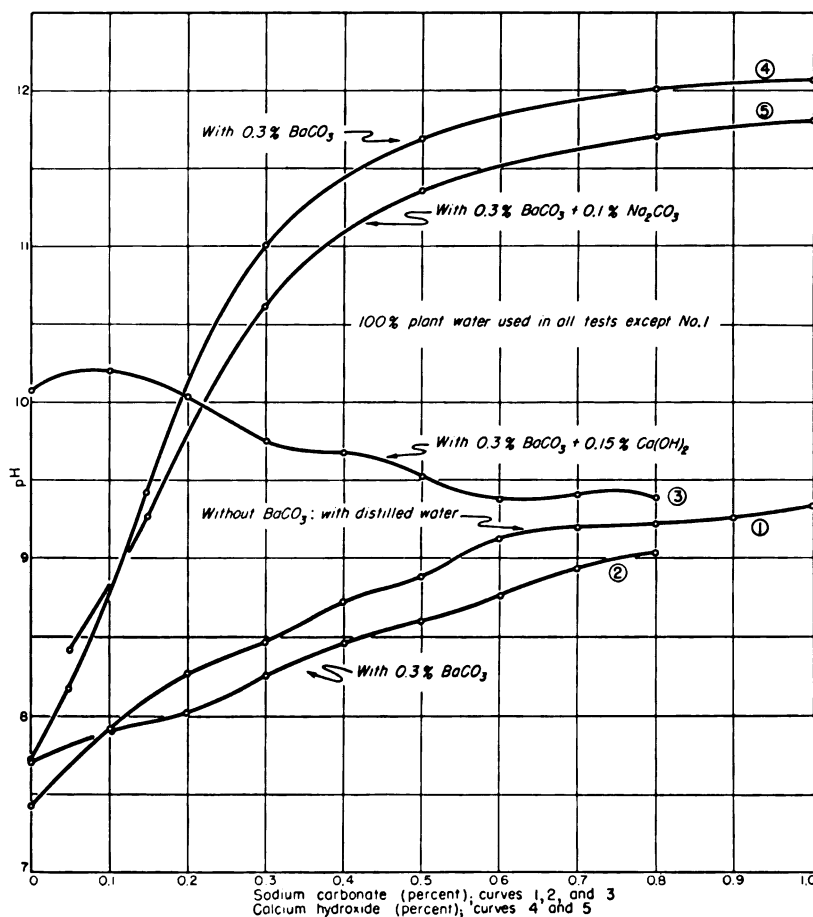In series 6 the beakers contained 20 percent plant water, 180 percent distilled water, 0.27 percent barium carbonate, and vary-
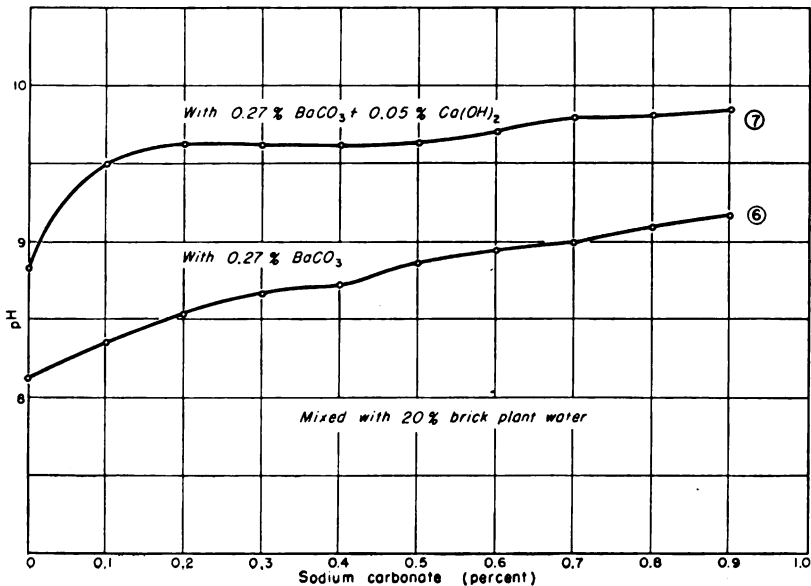
FIG. 4.—Graph showing change of pH of clay C-54-A with increasing additions of sodium carbonate (series 6 and 7).

ing amounts of sodium carbonate. The substitution of some brick plant well water for distilled water raised the pH of the beaker containing barium carbonate but no sodium carbonate from 7.70 to 8.12.

The curve plotted from series 6 (curve 6, Fig. 4) was essentially the same as that for series 2, although at a higher pH level, and the benches occurred at pH 8.66 to 8.72 (0.35 sodium carbonate added) and between pH 8.94 to 9.00 (0.65 percent sodium carbonate).

Series 7 differed from series 6 only in that 0.05 percent $Ca(OH)_2$ (calcium hydroxide) was added to each of the beakers in the series. The curve (curve 7, Fig. 4) plotted from the pH determinations in this series was a definite type-B, closely approaching a type-A. A broad bench was apparent at the points on the curve where 0.2, 0.3, and 0.4 percent was added. In each case the pH was 9.12. There was a slight rise in pH above this with 0.5, 0.6, and 0.7 percent additions of sodium carbonate, but the curve tends to level off again on the 0.8 and 0.9 percent additions, reaching a maximum pH of 9.35 when 0.9 percent sodium carbonate was added. With no sodium carbonate added, but with

0.05 percent calcium hydroxide and 0.27 percent barium carbonate, the pH was 8.82. The increase from a pH of 8.12 in series 6 to 8.82 in series 7 was due entirely to the 0.05 percent calcium hydroxide added.

Inasmuch as the curve plotted from series 7 gave a positive indication of an optimum addition of sodium carbonate plus calcium hydroxide and barium carbonate we considered the pH determination tests completed. The optimum amount of sodium carbonate addition was judged to be 0.25 percent because this position on the curve is just above the break. With this amount of sodium carbonate plus 0.05 percent $Ca(OH)_2$ and 0.27 $BaCO_3$ the pH of the suspension was 9.12.

After the beakers containing the clay suspensions with varying amounts of reagents had stood in the laboratory for several hours we found a regular variation in the height of sediment in the bottom of the beakers and the amount of clear water remaining at the top. In poorly deflocculated suspensions we found a minimum height of sediment in the bottom and a maximum amount of clear water at the top of the beakers. The more complete the deflocculation the greater was the height of the sediment, and the clear water on top decreased to almost zero, and was cloudy with colloidal suspensions.

It occurred to us that the height of the sediment in the beakers was a rough but definite measure of the degree of deflocculation. The height of sediment in each beaker was carefully measured and plotted on graphs similar to those used to plot the pH-soda ash curves (Fig. 5).

Plotted height-of-sediment or deflocculation curves are given for four of the series of tests. For series 2 containing 0.3 percent barium carbonate and varying amounts of sodium carbonate the deflocculation curve is a definite type-A with a maximum deflocculation attained with the addition of slightly more than 0.5 percent sodium carbonate (curve 2H, Fig. 5). The deflocculation curve for series 7 (curve 7H, Fig. 5) which was judged to indicate the correct percentage additions is a definite B-type curve with a clearly defined bench produced with additions of 0.1 and 0.2 percent sodium carbonate and a definite maximum deflocculation with the addition of 0.6 percent sodium carbonate. If the lower bench is considered indicative the 0.25 percent addition of sodium carbonate is more than sufficient.
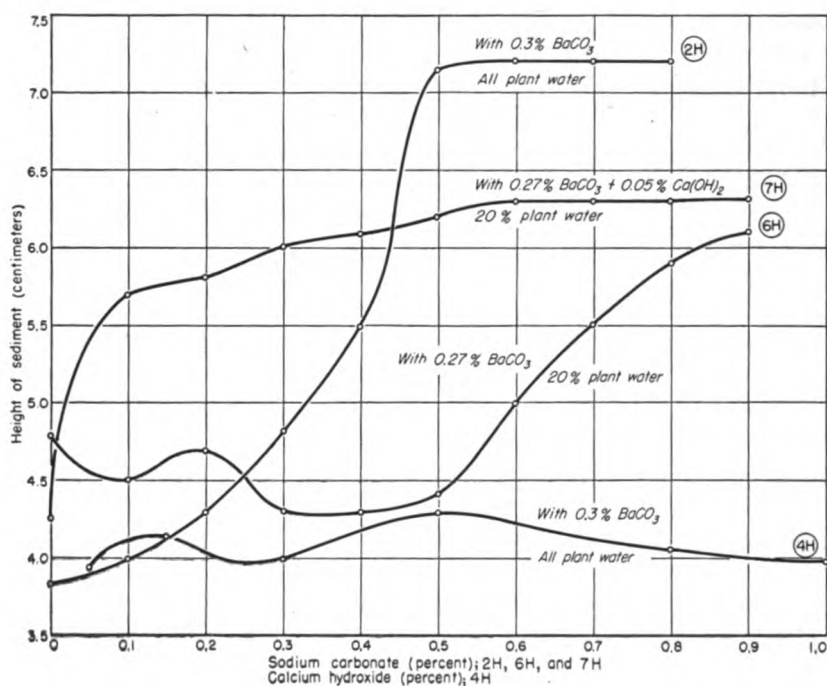
Fig. 5.—Graph showing change in height of sediment of C-54-A clay with increasing additions of sodium carbonate for series 2, 6, and 7, and with increasing additions of calcium hydroxide for series 4. Height of sediment indicates degree of deflocculation.

The deflocculation curve for series 6 (curve 6H, Fig. 5) is irregular, with two downward inflections at 0.1 percent addition of sodium carbonate (Na_2CO_3) and again at 0.3, 0.4, and 0.5 percent additions. The curve rises sharply at additions of more than 0.5 percent sodium carbonate, but does not flatten out at the end. It seems that the excess of plant water used in series 2 was definitely beneficial to deflocculation (curve 2H, Fig. 5), although the bench above 0.5 percent addition of sodium carbonate indicates an amount in excess of that desired from the point of view of cost.

The deflocculation curve for series 4 in which calcium hydroxide was used instead of sodium carbonate (curve 4H, Fig. 5) differs markedly from the pH curve for the same series (curve 4, Fig. 3). Although the increasing additions of calcium hydroxide produced a smooth A-type curve for the pH determinations, the

deflocculation curve reveals that calcium hydroxide does not deflocculate. The deflocculation is irregular and has a downward trend above 0.5 percent addition of calcium hydroxide. The upward inflections probably indicate buffering of the suspension.

A second series of tests was run on the more plastic clay blend C-54-P. Inasmuch as this blend differs so little from C-54-A blend it was possible to take some short cuts in the testing procedure. For example, additions of sodium carbonate did not exceed 0.55 percent.

A series of test suspensions containing varying amounts of barium chloride indicated that 0.25 percent barium carbonate is sufficient to neutralize the soluble sulfates in the C-54-P clay. This is slightly below the 0.27 percent indicated for the C-54-A blend. In the subsequent tests with varying additions of sodium carbonate and calcium hydroxide 0.25 percent was added to the clay. As in the previous tests with C-54-A, 20 percent water from the brick plant well plus 180 percent distilled water was used in the preparation of the suspensions.

In series 8 all the suspensions contained 0.25 percent barium carbonate, but increasing amounts of sodium carbonate. The curve showing increase of pH with increasing additions of sodium carbonate (curve 8, Fig. 6) is about half way between an A-type and a C-type curve except that the lower slope of the curve up to 0.25 percent addition of sodium carbonate has a slight downward inflection. It is possible that additions of more than 0.55 percent sodium carbonate would have revealed a flattening out to an A-type curve, but the amount of sodium carbonate would have been excessive as far as cost is concerned.

In an attempt to modify this curve, 0.035 percent calcium hydroxide $(Ca(OH)_2)$ was added to each of the suspensions in series 9. The curve resulting from these additions (curve 9, Fig. 6) is a definite B-type with a definite plateau between 0.05 and 0.10 percent additions of sodium carbonate (pH 8.19) and another from 0.35 percent addition of sodium carbonate (pH 8.73) and the end of the curve at 0.55 percent sodium carbonate (pH 8.77).

Series 10 was identical to series 9 except that 0.05 percent calcium hydroxide instead of 0.035 percent was added to each of the test suspensions. The resulting plotted curve (curve 10, Fig. 6) was generally modified downward as compared to series 9, but the plateau between 0.05 (pH 8.15) and 0.10 percent (pH
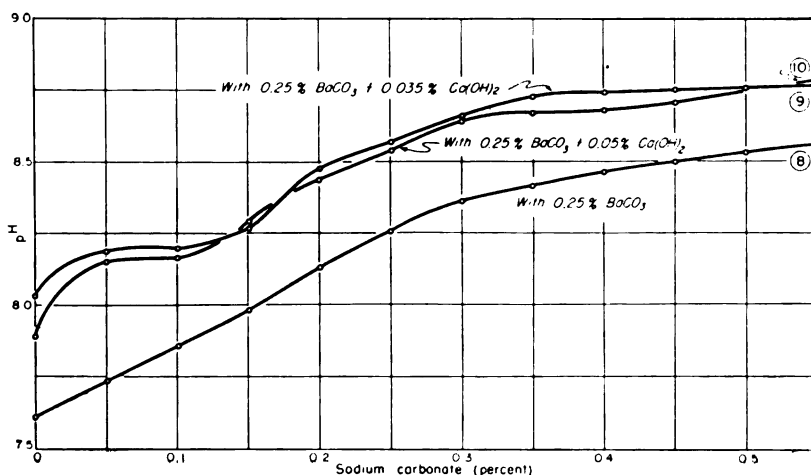
FIG. 6.—Graph showing change of pH of C-54-P clay with increasing additions of sodium carbonate for series 8, 9, and 10.

8.16) additions of sodium carbonate remained, and the higher plateau showed a more definite flattening between 0.3 (pH 8.66) and 0.4 percent (pH 8.70) additions of sodium carbonate. Above this point the curve turned upward slightly and reached a maximum of pH 8.78 with the addition of 0.55 percent sodium carbonate.

The height of sediment accumulated in the beakers after 24 hours settling was plotted against percentage sodium carbonate to obtain a deflocculation curve similar to that obtained for previous tests. In series 8, containing only barium carbonate and varying amounts of sodium carbonate, the plotted curve (8H, Fig. 7) showed three very definite plateaus. The first occurs between additions of 0.15 and 0.30 percent sodium carbonate, the second between 0.35 and 0.40 percent additions, and the third from 0.50 to 0.55 percent additions of sodium carbonate. The upper break or plateau apparently represents complete deflocculation because all the sediment remained in suspension with no clear water at the top.

The deflocculation curve for series 9 (curve 9H, Fig. 7) showed an upward bend at 0.10 percent addition of sodium carbonate, slight break in the curve beginning at 0.20 percent and ending at 0.30 percent additions of sodium carbonate, and a plateau from 0.50 to 0.55 percent additions of sodium carbonate. The plateau
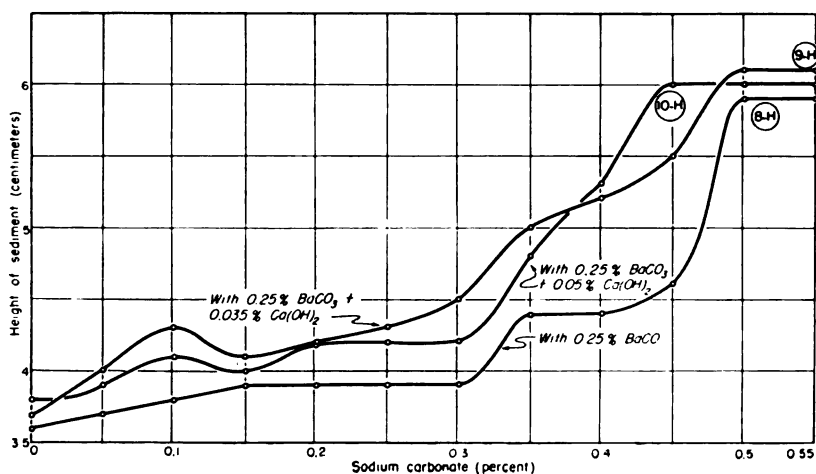
Fɪɢ. 7.—Graph showing change in height of sediment of C-54-P clay with increasing additions of sodium carbonate for series 8, 9, and 10.

for curve 9H occurred within the same range as the third for curve 8H. This series contained uniform additions of 0.035 percent calcium hydroxide and varying amounts of sodium carbonate.

Series 9 contained uniform addition of 0.50 percent calcium hydroxide and varying amounts of sodium carbonate. The deflocculation curve for this series (curve 10H, Fig. 7) was similar to curve 9H. The upward bend occurred at the same point, but instead of an intermediate break in the curve as in 9H a plateau occurred between 0.20 and 0.30 percent additions of sodium carbonate. The upper plateau for curve 10H extended from 0.45 percent to 0.55 percent additions of sodium carbonate, instead of from 0.50 to 0.55 as in curve 9H. In both series 9 and 10 complete deflocculation was achieved by the additions of sodium carbonate as indicated by the upper plateau.

On consideration of both the pH versus sodium carbonate and the height-of-sediment versus sodium carbonate curves we concluded that series 10 gave the most definite indications for optimum additions of sodium carbonate and calcium hydroxide.

Barton County clay.—Only two series of pH determinations were run on the BT-3-B clay from Barton County (Fig. 8). Series 11 was run without barium carbonate and the suspensions were prepared with distilled water. The curve plotted (curve 11, Fig. 8) from series 11 was a distinct B-type with a well-defined
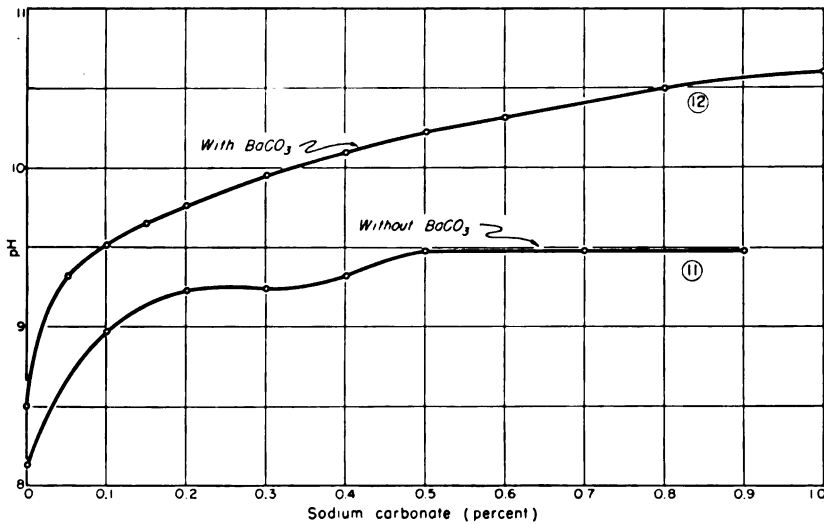
FIG. 8.—Graph showing change of pH of BT-3-B clay with increasing additions of sodium carbonate for series 11 and 12.

bench at a pH of 9.23 and with additions of 0.2 to 0.3 percent soda ash. Above a pH of 9.47 the curve was flat to the end. This curve definitely indicates that 0.2 to 0.25 percent soda ash is sufficient for this clay.

Inasmuch as barium carbonate was to be used in the clay mix for the purpose of correcting sulfate scum, a series of tests was run to determine the optimum addition of barium carbonate. The clay itself contains almost no soluble sulfates, as shown by both chemical analysis and the usual brick-plant testing technique. Tests run on the plant water, however, indicated that 0.08 to 0.10 percent barium carbonate was required to produce insoluble sulfates from the soluble ones present in the clay and the water.

In series 12, therefore, 0.08 percent barium carbonate was added to all the tests in the series containing increasing percentages of soda ash. The pH determinations were plotted (curve 12, Fig. 8) and produced a distinct type-A curve. The break in the curve occurred at a pH of 9.50, indicating that slightly more than 0.1 percent sodium carbonate would be required for deflocculation. Actually, 0.12 percent was chosen as representing an adequate amount.

Mixed with distilled water only the clay has a pH of 8.12. The clay from the Cloud County plant, under the same conditions, has

a pH of 7.41. After the addition of the required amount of barium carbonate (0.27 percent) the pH of C-54-A clay was increased to 8.12, whereas the addition of the required 0.08 percent barium carbonate to the BT-3-B clay increased the pH to 8.50.

After optimum additions of barium carbonate and sodium carbonate to the BT-3-B clay the pH increased to 9.56. The addition of optimum percentages of barium carbonate, sodium carbonate, and calcium hydroxide to the C-54-A clay increased the pH to 9.12.

Only a few pH determinations were run on the red-firing clay from Barton County (BT-3-R). These few determinations indicated that the characteristics of the clays were so similar that separate tests were not necessary.

LARORATORY TEST BRICK PRODUCTION

Test brick were produced with an International Clay Machinery Company de-airing extrusion machine identical in operating principle to the full-scale de-airing brick plant machines. A square die 1.125 by 1.125 inches was used, producing a brick this size in cross section and any length desired. For this series of tests the bricks were cut off by a wire in 7-inch lengths. Full vacuum was used on the de-airing. The water content of the clay was adjusted to produce an extruded column with nearly the same degree of softness, or apparent plasticity for all the tests. This was done in order to make the straight clay runs and those containing additives as nearly comparable as possible. After careful and complete drying to 110° C. the bricks were fired on a slow schedule to the temperatures used in the manufacture of brick from these clays.

On each set of test brick the absorption after 24 hours submersion in cold water, absorption after 5 hours submersion in boiling water, saturation coefficient, and modulus of rupture (transverse breaking strength) for both raw dry and fired bricks were determined according to A.S.T.M. standard method of sampling and testing brick (A.S.T.M., 1952, Designation C 67-50).

The water of plasticity, linear drying shrinkage, linear fired shrinkage, bulk specific gravity, and apparent specific gravity were determined by the American Ceramic Society's standard methods (Watts and others, 1928).

Cloud County.—Three batches of C-54-A clay were prepared for the extrusion tests. Water from the brick plant well was used for mixing all three batches. The batch compositions and assigned laboratory numbers are given in Table 2.

The percentage of water used, based on the dry weight of the ingredients, was determined by trial extrusions. The percentages given were determined from the loss of weight on drying, and are, in fact, the water of plasticity.

The C-54-A clay, without additions except barium carbonate, extrudes almost perfectly, forming a smooth, firm column. Test batch C-54-AB, containing 0.80 percent calcium hydroxide (slaked lime) was harsh and seemed to require more power for extrusion. The extruded column was firm but lacked the cohesiveness of the straight clay (C-54-A) batch. Test batch C-54-AC containing barium carbonate, soda ash, and calcium hydroxide was very similar to the C-54-A batch with the exception that the clay column seemed slicker.

After the bricks were completely dry part of each batch was broken on a transverse strength testing machine on 5-inch spans. The test brick were then fired slowly to cone 8 (approximately 2240° F.). Part of the fired brick were also tested in the transverse strength testing machine, also on a 5-inch span.

The data on the ceramic tests of these three test batches are given in Table 3.

Data on batch C-54-AC, containing 0.27 percent barium carbonate, 0.25 percent sodium carbonate, and 0.05 percent calcium hydroxide shows that these additions have definitely improved the quality of both the unfired and the fired brick over the C-54-A test batch containing only clay and barium carbonate. Because the clay is deflocculated in the C-54-AC test batch the water of plasticity is lower. Inasmuch as the dimensions of the freshly extruded bricks are the same, the deflocculated clay bricks contain more clay and are therefore more dense. This fact is re-

TABLE 2.—*Batch composition of C-54-A clay for extrusion tests*

Test batch number	C-54-A clay, percent	Water, percent	Sodium carbonate, percent	Barium carbonate, percent	Calcium hydroxide, percent
C-54-A	99.73	16.44	0	0.27	0
C-54-AB	98.93	20.24	0	0.27	0.80
C-54-AC	99.43	15.05	0.25	0.27	0.05

TABLE 3.—*Data on ceramic tests of C-54-A clay with various additions*

	C-54-A	C-54-AB	C-54-AC
PLASTIC AND DRY DATA			
Water of plasticity, percent	16.44	20.54	15.05
Linear shrinkage, percent	5.18	4.84	3.86
Modulus of rupture, psi	502	467	677
FIRED DATA (cone 8)			
Linear shrinkage, percent	1.16	1.65	1.26
Total linear shrinkage, percent	6.33	6.44	5.14
Cold water absorption, percent	9.88	12.25	8.71
Boiling water absorption, percent	12.31	14.64	11.27
Saturation coefficient	0.80	0.84	0.77
Apparent specific gravity	2.57	2.52	2.50
Bulk specific gravity	1.95	1.84	1.95
Modulus of rupture, psi	1915	1260	2004

flected in the lowered drying shrinkage, and in the higher dry transverse strength of the dried bricks. Both lowered shrinkage and higher transverse strength should decrease losses in handling, in setting the kiln, and in the kiln after setting. It was hoped that the increased dry strength, plus slightly lower temperature sintering, would reduce losses in the kiln due to the load borne in the lower part of the setting, particularly at the point in the firing when the bricks are the weakest. This point probably occurs just after the molecular water is driven off at about 1100° F. This point is indicated by the return of the endothermic peak to the base line in the differential thermal analysis (Fig. 2).

The fired C-54-AC treated test bricks have lower absorptions and a significantly lower saturation coefficient in comparison to the C-54-A control batch. The modulus of rupture (transverse strength) is 4.6 percent higher.

The C-54-AB test batch containing 0.8 percent calcium hydroxide in addition to the barium carbonate produced a poorer quality of brick in every respect. This indicates without doubt that the clay was flocculated and that a pH curve derived from increasing addition of calcium hydroxide ($Ca(OH)_2$) has no significance so far as diagnosis for improvement of clays is concerned.

For the ceramic tests on the C-54-P plastic clay blend three batches were prepared. The test batch compositions, with assigned laboratory numbers, are given in Table 4.

TABLE 4.—*Batch composition of C-54-P clay for extrusion tests*

Test batch number	C-54-P clay, percent	Water, percent	Sodium carbonate, percent	Barium carbonate, percent	Calcium hydroxide, percent
C-54-PA	99.75	17.37	0	0.25	0
C-54-PB	99.50	15.70	0.20	0.25	0.05
C-54-PC	99.25	14.82	0.45	0.25	0.05

The 0.20 percent addition of sodium carbonate is clearly indicated only on the deflocculation curve (10H, Fig. 7). The 0.45 percent addition of sodium carbonate is clearly indicated on the deflocculation curve but on the pH versus sodium carbonate curve (10, Fig. 6) this amount is slightly in excess of the indicated optimum.

No significant difference was noted in the extrusion characteristics of the three test batches. It will be noted that the percentage of water required to give comparable workability decreases with the addition of sodium carbonate, however.

Immediately after extrusion long bars of the wet clay were placed in a drier previously heated to 212° to 230°F. Neither the C-54-PA nor the C-54-PB batches showed any significant cracking. The brick made from the C-54-PC batch was cracked only slightly.

The ceramic tests for the C-54-P batches were exactly the same as those described for the C-54-A batches. The results of these tests are given in Table 5.

The data on the three test batches made from the C-54-P clay mix are very similar to those for the C-54-A mix. The only vari-

TABLE 5.—*Data on ceramic tests of C-54-P clay with various additions*

	C-54-PA	C-54-PB	C-54-PC
PLASTIC AND DRY DATA			
Water of plasticity, percent	17.37	15.70	14.82
Linear shrinkage, percent	5.09	4.60	4.33
Modulus of rupture, psi	521	776	838
FIRED DATA (cone 8)			
Linear shrinkage, percent	1.72	2.02	1.82
Total linear shrinkage, percent	6.81	6.62	6.15
Cold water absorption, percent	8.29	7.18	6.48
Boiling water absorption, percent	10.61	9.38	8.83
Saturation coefficient	0.78	0.76	0.73
Apparent specific gravity	2.54	2.52	2.50
Bulk specific gravity	2.00	2.04	2.05
Modulus of rupture, psi	2668	2800	2933

able in the C-54-P batches is the percentage of sodium carbonate. C-54-PA contains no sodium carbonate, C-54-PB contains 0.20 percent, and C-54-PC contains 0.45 percent. Increasing amounts of sodium carbonate decrease the water of plasticity and linear drying shrinkage and increase the modulus of rupture on the dry bricks to a remarkable extent. The dry transverse strength (modulus of rupture) of C-54-PB is 49 percent greater than C-54-PA and C-54-PC is 61 percent greater than C-54-PA.

The test batches fired to cone 8 show the differences that should be expected for all the data except the linear firing shrinkage. The linear shrinkage for C-54-PB is greater than that for either C-54-PA or C-54-PC. Absorptions, saturation coefficient, and bulk specific gravity indicate a definite improvement of the clay mix with the addition of 0.20 percent sodium carbonate, and a greater improvement with the 0.45 percent addition. This correlates with a 5.0 percent increase in the modulus of rupture with 0.20 percent addition of sodium carbonate (C-54-PB) and a 9.9 percent increase with the addition of 0.45 percent sodium carbonate (C-54-PC).

Inasmuch as the C-54-PC batch shows greater improvement in all dry and fired properties it is obvious that the addition of 0.45 percent sodium carbonate, plus 0.05 percent calcium hydroxide and 0.25 percent barium carbonate, is definitely indicated.

Barton County.—Three test batches were also prepared from the BT-3-B clay but with additions differing from those used for the C-54-A and C-54-P clay blends. The batch compositions and assigned laboratory numbers are given in Table 6.

Although a more accurate test would have been made with the use of brick plant water, distilled water was used in all the tests, 18 percent being added to each batch. Slight differences in moisture content of the clay resulted in the differences in tempering water shown in Table 6.

All three batches produced a clean column on extrusion, but the ones with sodium carbonate added (BT-3-BN) and with both

TABLE 6.—*Batch composition of BT-3-B clay for extrusion tests*

Test batch number	BT-3-B clay, percent	Water, percent	Sodium carbonate, percent	Barium carbonate, percent
BT-3-B	100	18.60	0	0
BT-3-BN	99.85	18.49	0.15	0
BT-3-BB	99.80	18.71	0.12	0.08

sodium carbonate and barium carbonate (BT-3-BB) produced a smoother column, especially BT-3-BB. Power consumption on extrusion was measured by means of an ammeter on the extrusion machine motor and indicated that the additions reduced power consumption. The reduction of power required for extrusion was the primary objective of the tests, yet other improvements resulted.

Subsequest tests were carried out as outlined for the C-54-A clay. The results of the tests are given in Table 7.

Although the test batches containing additions show definite improvement over the straight ·clay batch (BT-3-B), the one containing both barium carbonate and sodium carbonate (BT-3-BB) is superior to one containing only sodium carbonate (BT-3-BN). Surprisingly the batch containing only soda ash has a higher drying shrinkage than either of the others. This indicates that deflocculation was not complete. The modulus of rupture (transverse strength) of the BT-3-BN batch was also lower than the other two, despite the fact that an improvement in all other fired properties has resulted from the addition of 0.15 percent sodium carbonate. It is possible that incomplete deflocculation may have a detrimental effect on fired strength but there is no obvious explanation of the effect produced.

From the above data the BT-3-BB test batch additions were recommended for a full-scale production test. From the laboratory data we concluded that the desired reduction in power consumption for extrusion would be realized, and that drier and

TABLE 7.—*Data on ceramic tests of BT-3-B clay with and without additions*

	BT-3-B	BT-3-BN	BT-3-BB
PLASTIC AND DRY DATA			
Water of plasticity, percent	18.60	18.49	18.71
Linear shrinkage, percent	6.03	6.55	5.78
Modulus of rupture, psi	693	852	797
FIRED DATA (cone 5)			
Power required indicated by amperes	2.20	2.11	2.07
Linear shrinkage, percent	1.71	1.61	1.52
Total linear shrinkage, percent	7.74	8.16	7.50
Cold water absorption, percent	8.04	7.67	7.63
Boiling water absorption, percent	9.74	9.53	9.68
Saturation coefficient	0.83	0.80	0.79
Apparent specific gravity	2.53	2.52	2.54
Bulk specific gravity	2.03	2.03	2.04
Modulus of rupture, psi	2685	2667	2869

handling losses would be lower. We also concluded that losses in the kiln would be reduced, and that a stronger brick with lower absorption would result. The fact that the saturation coefficient was lowered from 0.83 to 0.79 is significant in that the producer of face brick having a saturation coefficient of 0.80 or lower can waive the A.S.T.M. requirements on absorption and compressive strength.

<div align="center">BRICK PLANT PRODUCTION TESTS</div>

Plant trials were run on the Barton County clays BT-3-B and BT-3-R with additions of barium carbonate and with additions of barium carbonate plus sodium carbonate (soda ash). The addition of the recommended amount of barium carbonate alone reduced power consumption somewhat, brightened the color of the fired brick, and lowered the temperature required to obtain the desired absorptions (produced a harder-fired brick at the same temperature). An unexplained benefit from the addition of barium carbonate was the reduction of burning time by a half-day, apparently because the heat traveled through the mass of ware more rapidly. The results from the addition of sodium carbonate were inconclusive.

Brick plant trials have not been run on the C-54-A clay blend, and one test run with the C-54-P mix containing 0.20 percent sodium carbonate (C-54-PB) did not furnish reliable data on the fired properties because of defects that occurred in drying due to the increased density of the treated clay. Conclusive results can be obtained only by modifying the drying techniques.

<div align="center">SUMMARY AND CONCLUSIONS</div>

The addition of small amounts of sodium carbonate (soda ash) to Dakota formation clays used in the production of face brick improved both the green and fired properties of test bricks produced in the laboratory. Less water was required for tempering the brick, resulting in a denser dried brick, decreased drying shrinkage, and a large increase in dried transverse strength. Due to increased density the treated brick must be dried more slowly. The fired brick to which sodium carbonate (and in some cases a very small amount of calcium hydroxide) had been added showed decreased absorption and saturation coefficient and increased transverse strength.

Although pH determinations were used to determine the amount of sodium carbonate needed for optimum deflocculation, the ratio of clear water to sediment in the beakers containing varying amounts of the reagent seemed to give a clearer indication of optimum deflocculation than the curves showing increase of pH with increasing additions of sodium carbonate.

Although plant tests have not been extensive enough to check the results of most of the laboratory tests, we have concluded the chief benefits will be realized in the decreased absorptions and increased strength of the fired brick. Improvement in the green, or unfired, properties of the Dakota clays is less significant because the untreated clays extrude easily and the dry strength is usually sufficient to permit handling without excessive breakage.

REFERENCES

AMERICAN SOCIETY FOR TESTING MATERIALS (1952) A.S.T.M. Standards, part 3, cement, concrete, ceramics, thermal insulation, road materials, waterproofing and soils: Baltimore, Md., pp. 1-634.

BARKER, G. J. AND TRUOG, EMIL (1938) Improvement of stiff-mud clays through pH control: Am. Ceramic Soc. Jour., vol. 21, pp. 324-329.

——— (1939) Factors involved in improvement of clays through pH control: Am. Ceramic Soc. Jour., vol. 22, pp. 308-312.

——— (1941) Further investigations in the improvement of clays through control of pH and character of base-exchange saturation: Am. Ceramic Soc. Jour., vol. 24, pp. 317-322.

BOWDISH, F. W. (1953) Experimental Separation of Iron-Bearing minerals from certain Kansas clays: Kansas Geol. Survey, Bull. 102, pt. 4, pp. 105-116.

GRIM, R. E. (1953) Clay Mineralogy: McGraw-Hill Book Co., New York, pp. 1-384.

PLUMMER, NORMAN, AND ROMARY, J. F. (1947) Kansas Clay, Dakota formation: Kansas Geol. Survey, Bull. 67, pp. 1-241.

WATTS, A. S., AND OTHERS (1928) Standard methods for sampling ceramic materials, preparation of clay trials, standard test methods, tentative test methods, and test apparatus: Am. Ceramic Soc. Jour., vol. 11, no. 6, pp. 442-467, 490-534.