

THE VARIATIONS OF WYOMING BENTONITE BEDS AS A FUNCTION OF THE OVERBURDEN

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ABSTRACT

The colloidal properties and base-exchange characteristics of five deposits in four different areas were determined. The variations of the clay were, in general, a function of the amount of overburden and have been related to that dimension.

From the standpoint of appearance, two types of clay were found in these areas. The highest grade clay has a yellow color whereas the other type, a blue clay, is customarily found to be of lower grade.

Differential thermal studies of the yellow and blue clay, when correlated with variations in colloidal properties, strongly suggest that the change from blue to yellow is due to oxidation of iron.

The primary cause for variation in properties is due to the Na/Ca ratio in the exchange positions regardless of whether the iron in the clay is in the ferrous or ferric state. Examination of purified clays indicates that the exchangeable base ratio of the field bentonites lies in a zone of instability. This zone occurs when the divalent ions amount to 40 to 60 percent of the base-exchange capacity.

INTRODUCTION

Previous Work

The Wyoming bentonites are very sensitive to small changes in their natural environment and yet they possess properties found in very few other bentonites. For this reason they have been the subject of investigation for many years, particularly in respect to colloidal properties and structure. Many of these data are reported in detail by Kelley (1948), Marshall (1949), Brindley (1951), and more recently in a symposium under the guidance of the AIME (1952).

The significance of many of these data, however, could not be assessed because often too little attention was given the previous history of the working sample or of the makeup of the exchangeable bases and excess soluble salts.

Accordingly, the purpose of this investigation was to increase our knowledge of the variations within bentonite deposits. Base exchange, electrolyte content, and structural relationships between purified bentonites and the natural clays were reported earlier by Williams, et al., (1953).

Because bentonite is one of the principal components of rotary-drilling fluids, the standard test procedures in use by that industry were followed.

Acknowledgment

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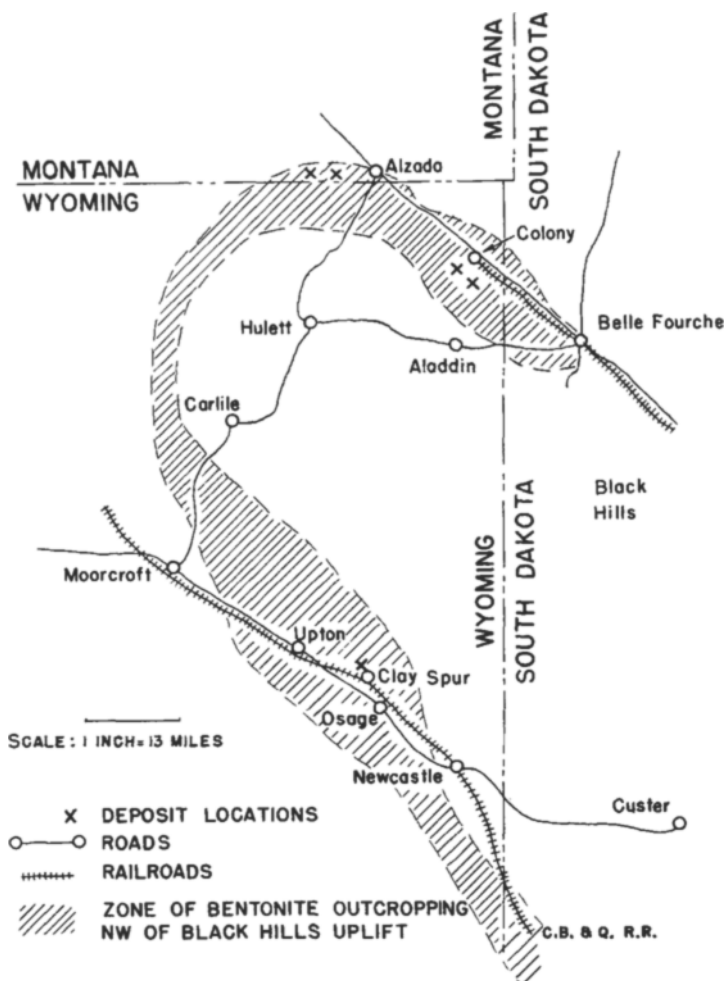


FIGURE 1.—General extent of the “clay spur or commercial bed” in the area studied.

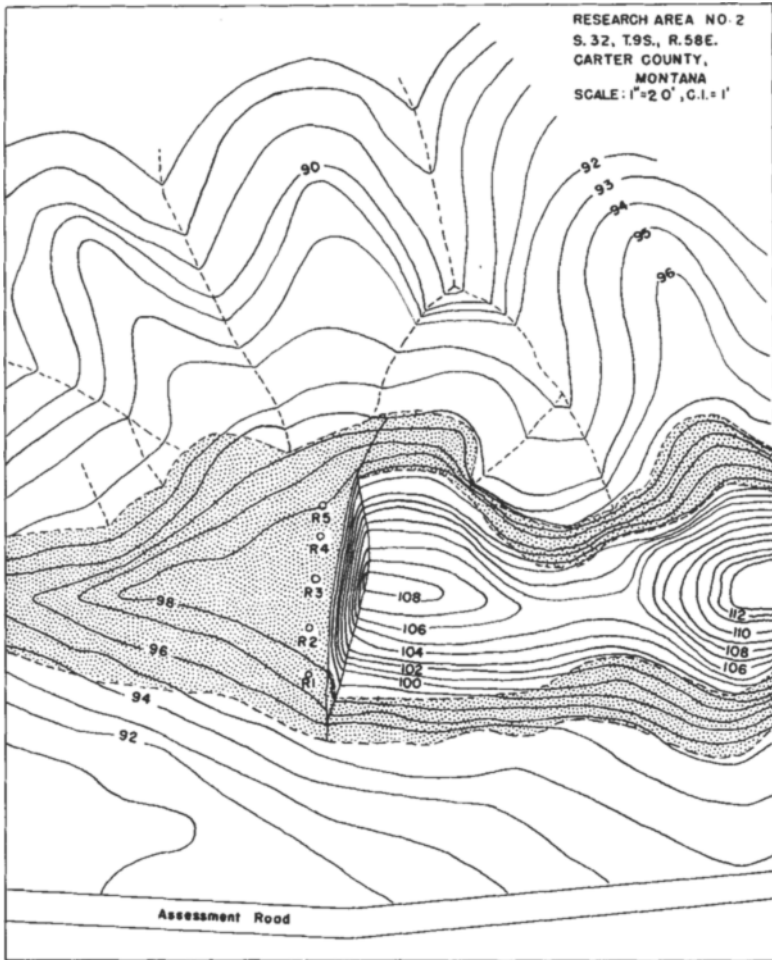


FIGURE 2.— Topographic map of a typical bentonite deposit.

MATERIALS AND EXPERIMENTAL METHODS

General Description

The bentonite samples used in this investigation were taken from the same stratigraphic horizon (locally known as the Clay Spur or Commercial Bed) near Clay Spur and Colony, Wyoming, Belle Fourche, South Dakota, and in Carter County, Montana.¹

¹ From the properties of the Baroid Sales Division, National Lead Company, Colony, Wyoming.

All samples may be described as Wyoming-type bentonites. Geographical location of the deposits is indicated by Figure 1.

To account for the variations within each deposit, most data have been correlated with the amount of overburden. A topographic map similar to that of Figure 2 was prepared for all deposits showing the attitude of the beds, drainage and other natural conditions.

Collection of field samples involved core-drilling transversely across five deposits in four different areas. Geologic features such as depth of overburden, thickness of deposit, mineralogy of the bentonite bed, and surrounding area were recorded.

Several samples representing major color variations as blue or yellow clay were preserved in their original condition for petrographic and differential thermal analyses.²

Evaluation was preceded by air-drying to 10 percent moisture followed by hammer-mill grinding to 80 percent minus 200 mesh. The more important rheological properties were based on measurement of viscosity, zero and 10 min. gel strength and filter loss.³ The methods used are in accordance with API Code 29 (1950). All sample calculations were corrected to the dry basis.

Specific conductivities were measured by means of a calibrated conductivity bridge and cell.

The base-exchange capacity was determined by the ammonium acetate method using the methods of Peech (1941). Exchangeable bases and soluble salts were determined on the leachates.

X-ray and differential thermal analysis (DTA) methods were in accordance with those in general use.

EXPERIMENTAL RESULTS AND DISCUSSION

Variation in Properties of a Vertical Section

Core drill samples taken through the thickness of the bentonite bed were segregated on the basis of the variations in color from one banded layer to the next. Figure 3 summarizes a few of the data obtained on one deposit. All five deposits were sufficiently similar so that only one needs to be discussed in detail.

Four distinct layers are apparent in this deposit. The bottom layer rests on a siliceous hardpan. The bentonite of this layer appears to be heavily contaminated with sand. Above this is a thick, massive, yellow-green clay which has much greater swelling power than any other layer of the bed.

² Courtesy of R. E. Grim, Illinois State Geological Survey, Urbana, Illinois.

³ Viscosity is determined at 600 rpm in a calibrated Stormer Viscosimeter with the center baffle removed. The gel strength is the weight in grams necessary barely to move the Stormer rotor. Yield is the number of 42 gallon bbl of 15 cp suspension obtainable from one ton of clay. Filter loss is the volume of filtrate in cc passing a 9 cm filter paper in 30 minutes under 100 psi.

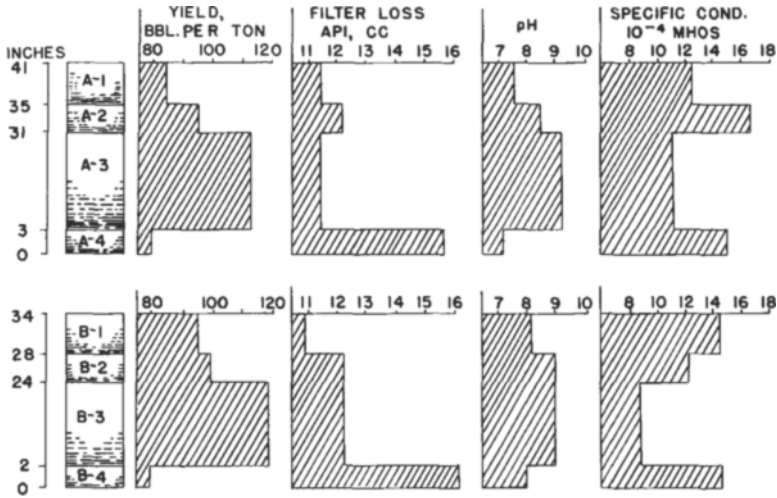


FIGURE 3.—Variation in properties through a vertical section of clay spur bed. Location B, 75 feet east of location A.

The third layer, designated as A-2 and B-2, is a yellow-green clay having a platy structure. Selenite crystals appear to be concentrated at the bottom of this stratum. The top 6-inch layer is a loose unconsolidated grayish material.

Both sections described here are in the outcrop area. Others taken toward the crown of the overburden progressively grade in color to a blue or dark gray.

In general, in a bentonite bed of which all portions have been subjected to about the same degree of weathering, a general trend in properties is evident vertically through the deposit: yield and pH rise to maximum and then decrease, with filter loss and specific conductance generally increasing with depth.

As a whole, the continuity of the layers as evidenced by the relative freedom from extraneous minerals indicates rather rapid deposition of the bed.

Variation in Properties of a Transverse Section

In the previous section distinct laminae through the thickness of the deposit were characterized. In order to unite the data in the form of a coherent picture which corresponds with the geological environment, five deposits were sampled transversely. The importance of these data resides in the fact that though the bentonitic lithofacies are still intact, diagenesis has caused significant variations in the composition and properties of the bed.

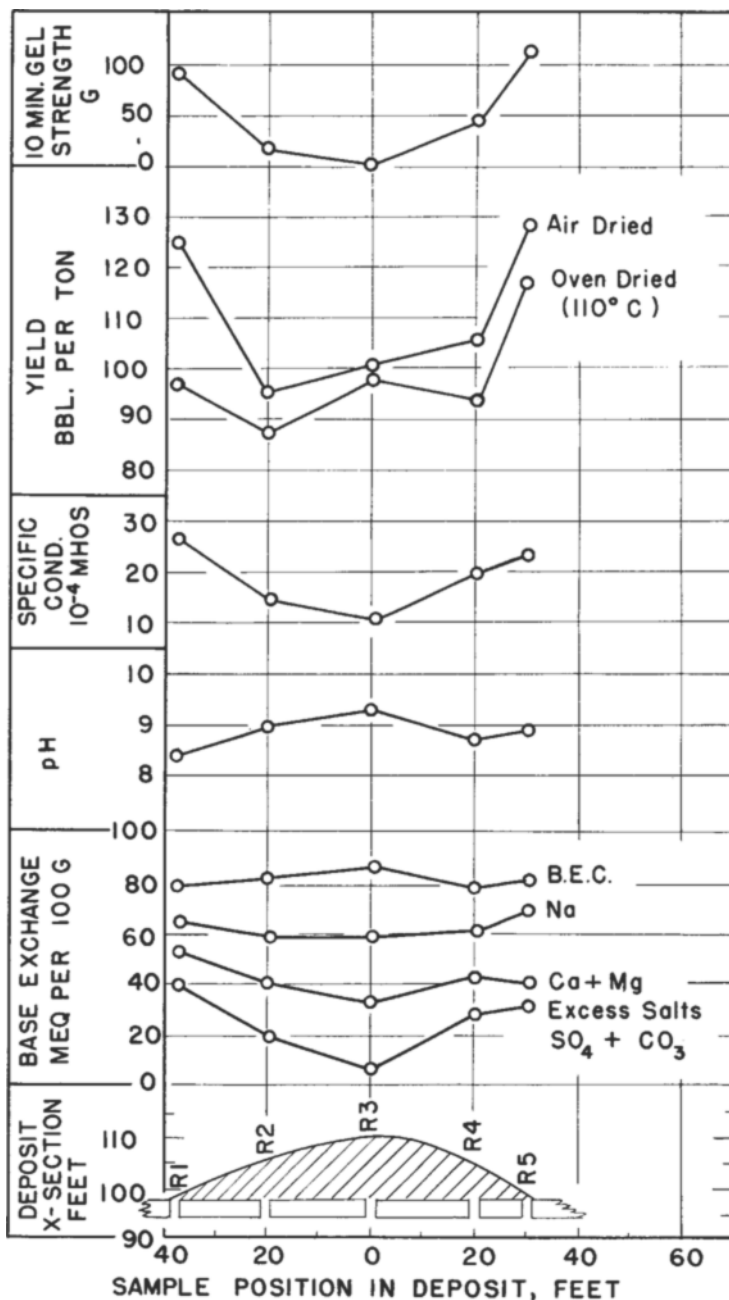


FIGURE 4. — Property correlations as a function of the overburden.

Figure 4 correlates the variations within a typical deposit with the overburden. The pH and base-exchange capacity vary directly with the overburden. The specific conductivity, yield, and gel strength vary inversely with the overburden. The exchangeable sodium, and calcium plus magnesium, and the excess salt as sulfate and carbonate vary in a similar inverse manner. The excess carbonate ion shows no correlation with the amount of overburden and ranges from 2 to 11 meq/100 g.

Though the clay is generally described as sodium bentonite, the exchangeable calcium plus magnesium ion constitutes 35 to 67 percent of the base-exchange capacity. From the standpoint of the rheology of the system this is in a zone of highest instability (Williams et al., 1953). For example, a small change in the Na/Ca ratio causes an enormous change in the viscosity of the system. This ratio therefore is ideal from the viewpoint of the commercial utility of the colloidal properties of the clay.

Geochemistry of the Wyoming Bentonite Deposits

Two types of clay, one yellow and the other blue, are found in this area. The higher-grade clay has a yellow color whereas blue clay is customarily found to be of lower grade when tested in terms of yield. Blue clay may occur as "blue eggs" within the yellow clay or as a distinct massive deposit grading into the yellow clay (Fig. 6).

DTA curves of the yellow and blue clays, when correlated with variations in colloidal properties, strongly suggest that the change from blue to yellow is due to oxidation of iron and that this oxidation is accompanied by an increase in yield. In Figure 5 it will be noted that the dual initial endothermic peak of the massive blue bentonite indicates the presence of an exchangeable cation other than sodium and probably divalent. This shoulder is absent in the DTA curves from the yellow clay and the transitional "blue egg." The generally lower viscosities of aqueous dispersions of the blue clay are suggestive of the presence of additional divalent cations over and above the determined calcium and magnesium, which could be accounted for on the basis of exchangeable ferrous ion. In the DTA curves of the two blue samples small exothermic peaks between 400° and 500°C are probably indicative of the oxidation of ferrous to ferric ion. Such oxidation would account for the change in color of the bentonite bed toward the outcrop. In the mildly alkaline environment of the clay hydrolysis would tend to convert ferric ion to hydrous ferric oxide with an attendant lowering of the pH of the system similar to that shown in Figure 4. This action, furthermore, is attested by the presence of orange deposits of hydrous ferric oxide throughout the beds of yellow clay and along the joint planes and by the complete absence of such in the blue clay. In the event that the ferrous ion originally existed as an exchangeable cation of the bentonite, then oxidation and subsequent hydrolysis would require an additional cation to take its place. Such vacancy could

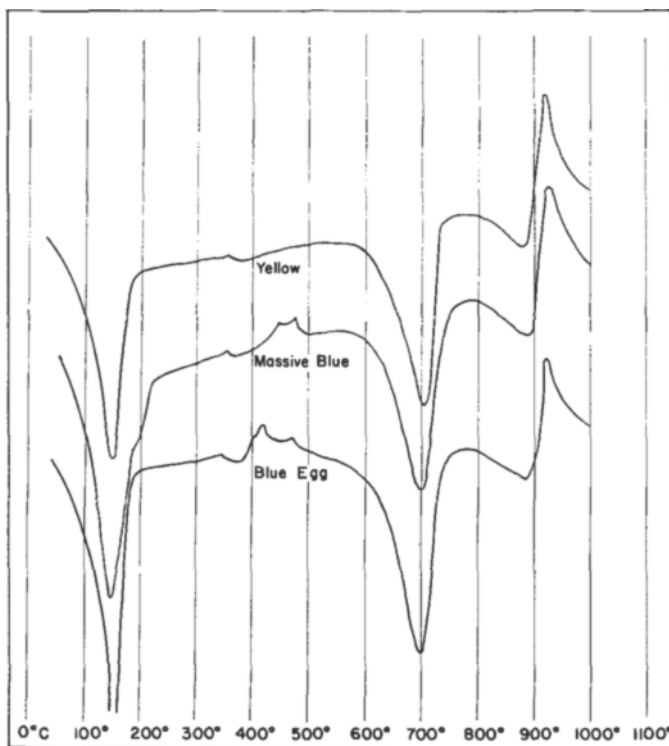


FIGURE 5.—DTA curves showing oxidation of ferrous iron in the blue bentonite.

be filled either by hydrogen ion arising during hydrolysis or by the cation of a soluble salt existing in the formation.

In considering the source of these additional cations it will be noted from the data of Figure 4 that the specific conductivity and excess salt increase toward the outcrops. This fact in conjunction with the presence of macroscopic crystals of gypsum in the yellow clay indicates that this mineral is of recent authigenic origin.

One possible reaction responsible for the formation of gypsum and the attendant increase of exchangeable sodium and calcium ions at the outcrops suggests that, concurrently with oxidation of the ferrous iron, solution of residual volcanic fragments such as feldspar releases active cations. Of these Lyon and Buckman (1947) state that the calcium ion is particularly active in the enzymic process involving bacterial oxidation of the sulfur occurring in many nitrogenous organic compounds. In the case of the Wyoming deposits the sulfur is probably derived from vegetation near the outcrop. As decay progresses the sulfur emerges as simple SO_4^{2-} ion in association with available bases, sodium and calcium.

Regardless of the processes involved, the sulfate content of the samples ranges from a minimum of 3 meq/100 g in the center of the deposit to a maximum of 36 meq/100 g at the outcrop. It was previously noted (Williams et al., 1953) that within this range the viscosity is at a minimum, i.e., more or less gypsum will cause an increase in viscosity.

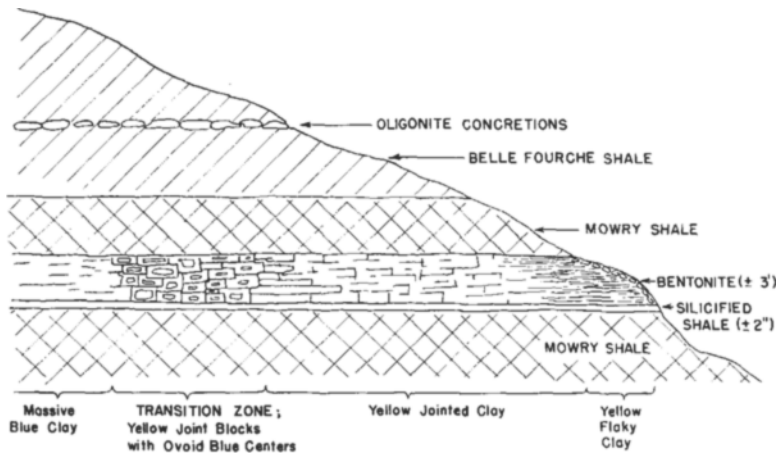


FIGURE 6.—Idealized cross-section of bentonite bed.

Figure 6 as a type section illustrates the logical progression of the reaction occurring as a result of normal weathering processes. It was noted that in the present-day transition zone the yellow jointed blocks of bentonite show iron-oxide stains at joints and fissures. Baver (1940) states that studies in the chemistry of ferric hydroxide have shown that this hydrated colloid becomes almost completely irreversible upon dehydration. Thus, considering the normal weathering process, the iron originally acting as a divalent flocculating or bonding agent for the clay mineral and subsequently being irreversibly removed from the system near the outcrop makes additional exchange positions available on the clay for calcium and sodium. Formation of sulfate ion in the weathered zone together with progressive dehydration toward the outcrop progressively removes calcium from the clay and puts more and more sodium in as counter ion. Near the outcrops the oxidized iron, now gelatinous in nature, may exert a blocking action on a portion of the exchange positions on the bentonite.

Essentially, this explanation conforms with the observed decrease in base-exchange capacity and the increase in yield observed near the outcrops. These quantitative figures, however, were based on air-dried samples. By a priori reasoning, oven-drying at 110°C should cause the formation of additional nondispersible aggregates or blocked exchange positions beyond the amount formed by air drying. The yield data of Figure 4 show that in

general, oven drying decreased the yield more in samples from the outcrop zone than in bentonite from the center of the deposit where ferric hydroxide is at a minimum.

Another factor known to affect the yield of the Wyoming bentonites is the content of nonclay minerals. These minerals include calcium sulfate as gypsum (selenite), biotite, feldspar, cristobalite, volcanic shards and quartz. Quartz is the primary nonclay diluent and ranges from 10 to 15 percent by weight. The particle size of the sharp, angular fragments of quartz ranges from 150 microns down to colloidal size.

While the dual effect of iron and exchangeable base composition has been shown to exert an influence on the clay in the field, the mechanism whereby the exchangeable calcium and sodium compete for the base-exchange sites has not been considered. As Kelly (1951) points out in his text, no satisfactory explanation of the varying effect of Na^+ ion on

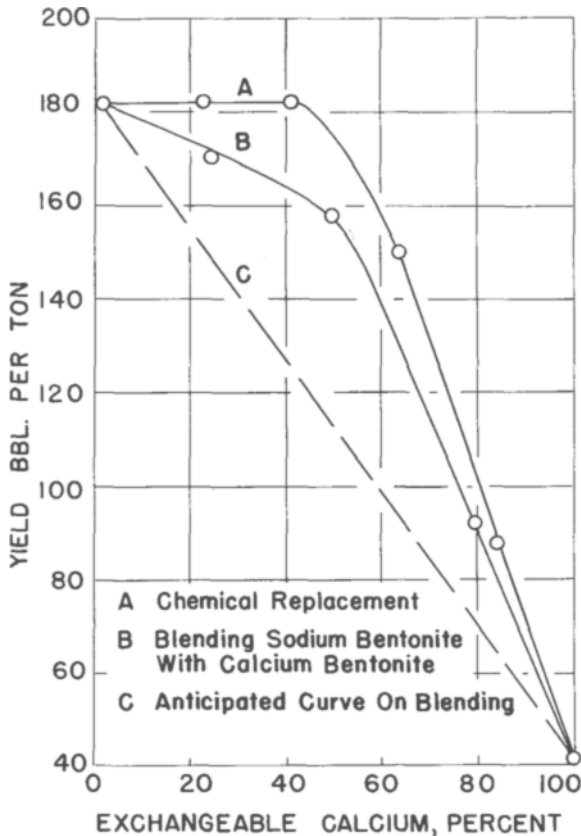


FIGURE 7.— The competitive effect of exchangeable Na and Ca on the yield of an aqueous bentonite suspension.

different deposits of montmorillonite is available. The data of Figure 7 have some relation to this problem by showing the effect of varying the Na/Ca ratio on a purified salt-free bentonite. Curve A indicates that the swelling power of a bentonite whose calcium has been added by chemical replacement is superior to the same clay with an identical Na/Ca ratio obtained through blending. Curve C is nonexperimental and shows the nonlinear relation of either method.

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