

# COMPARISON OF DRYING CORN USING SODIUM AND CALCIUM BENTONITE

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Bentonite is an abundant clay mineral that is suitable for adsorption drying of various grains. However, bentonite is not uniform in composition, being predominantly composed of montmorillonite along with a variety of other minerals. Also, different bentonites have different naturally occurring adsorbed ions which markedly affect the water adsorption characteristics. Corn drying experiments using two types of commercially available bentonite clay, calcium- and sodium-based, are reported. Moisture isotherms for the two clays are deduced from the experimental results and compared to other isotherm data. The experimental results showing the time history of the drying of the corn and wetting of the clay are predicted well using existing relationships. The more common calcium-based clay absorbs more moisture than sodium-based clay from corn at low-moisture contents in which the clay remains free flowing. Therefore, calcium bentonite is the preferred clay for drying corn on the basis of moisture capacity.

## INTRODUCTION

Desiccant drying of grain has been studied by several workers in the past due to its many advantages. Danziger et al. (1972) and Tomlinson and Miller (1981) have used expensive but effective silica gel to dry agricultural materials. Bern et al. (1981) used oven-dried corn as the desiccant. Sturton et al. (1981) and Graham et al. (1983) have investigated the use of bentonites in the drying of grain.

In all desiccant drying using clay, the wet grain and dry clay are intimately mixed in a sealed container at ambient temperature. The grain rapidly gives up its moisture to the surrounding clay with little or no temperature rise, as the heat of hydration is negligible. This process differs from batch-in-bin drying which causes overheating of some grain as the drying front moves upward from the hot air inlet. When using desiccants, the drying occurs uniformly throughout the bin; no regions in the grain remain wet for extended periods. The clay can be dried using low-cost solar energy during periods of sunshine in the spring and summer, thereby storing the energy in a readily accessible form for use when needed. Bentonites have one advantage not shared by the other desiccants: they have been shown by workers at the University of Guelph to reduce insect infestations in grain with which they are combined, probably because of the abrasive action of the clay on the insect as it moves through the mixture.

Bentonite clays are noted for their hygroscopic properties. However, the comparison and interpretation of adsorp-

tion results from different workers using different clays are complicated by several factors (Zettlemoyer et al. 1955). Bentonite clays have exchangeable ion sites and the number of the sites is not constant per unit mass of clay. The type and number of adsorbed ions alter the moisture adsorption and swelling properties of the clay. Different polar molecules in a swelling clay determine the amount of internal areas exposed. Also, there are variable amounts of impurities in each sample of clay. For low clay moisture contents, calcium clay adsorbs more moisture and accomplishes it faster than a sodium bentonite (Fig. 1).

Using corn with one type of sodium bentonite and one type of calcium bentonite this study will determine which type of bentonite is better suited to grain drying.

The purposes of this paper are to examine the theoretical base for moisture adsorption by the two types of bentonite clay; to report some experimental results of drying corn using both sodium- and calcium-based clays; to demonstrate that it is possible to predict the experimental results using existing relationships for corn drying; and to draw conclusions as to the best clay to use for drying grains.

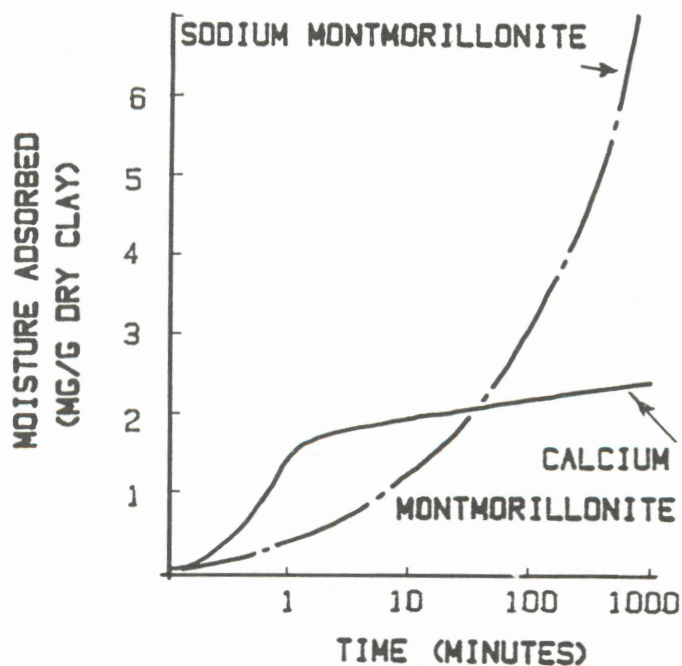


Figure 1. Temporal moisture adsorption curves for calcium and sodium bentonite.

## MOISTURE ADSORPTION BY BENTONITES

Bentonite clays are thought to be of volcanic origin (Grim 1968), although clays having a similar structure and properties have been found which were of a hydrothermal source. There is, therefore, a very large variation in composition. The basic composition of bentonite is about 55% silicon dioxide and 20% aluminum trioxide with smaller varying amounts of iron, magnesium, calcium, potassium, and sodium oxides. The dominant clay mineral material is smectite with varying amounts (sometimes up to 50%) of illite and kaolinite and sometimes cristobalite. Rarely is there less than 10% of non-clay minerals.

The hygroscopic characteristics of bentonites are due largely to the smectite component. However, the composition of smectite varies greatly in different bentonites, both in respect to the smectite lattice and the nature of the exchangeable cations. The most abundant exchangeable cation is  $\text{Ca}^{++}$  (Grim 1968), e.g. the Mississippi bentonite. Although few carry  $\text{Na}^+$  as the dominant ion, the Wyoming bentonite is a well-known example. These two bentonites vary both in the structure of the smectite lattice and adsorbed ions; hence their properties and end uses are considerably different.

Some workers (Keren and Shainberg 1979) have assumed that it is possible to change a sodium bentonite to a calcium bentonite and vice versa by saturating the clay with the appropriate ion. Grim (1968) indicates that such treatment does not bring a complete change in properties which suggests that the smectite lattice structure must be different.

The hydration of bentonite is a complex process. It appears that at very low moisture contents the water is adsorbed on the edge of the clay platelets and slowly moves between the platelets where the hydration of the interlayer cations takes place. The calcium ions tend to hydrate more readily forming a skeletal double water layer corresponding to the octahedral coordination of hydration water around the calcium ion. Two complete layers form for calcium clay for the relative humidity (RH) range of 30–80%. For sodium ions a first monolayer of water is formed in the RH range of 40–70%. The second water layer is complete at a RH of 90%. This process was observed in X-ray studies (Zettlemoyer et al. 1955) but is not always evident because adsorption of water on the outer surfaces and edges of the platelets mask water uptake between the platelets. It is because of the migration of

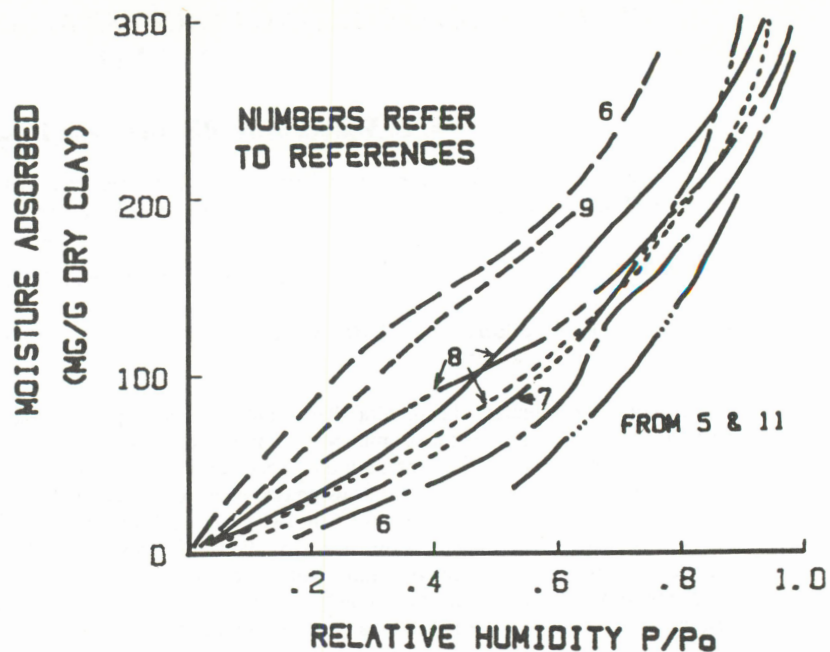


Figure 2. Variation of reported values of moisture adsorption isotherms for sodium bentonite.

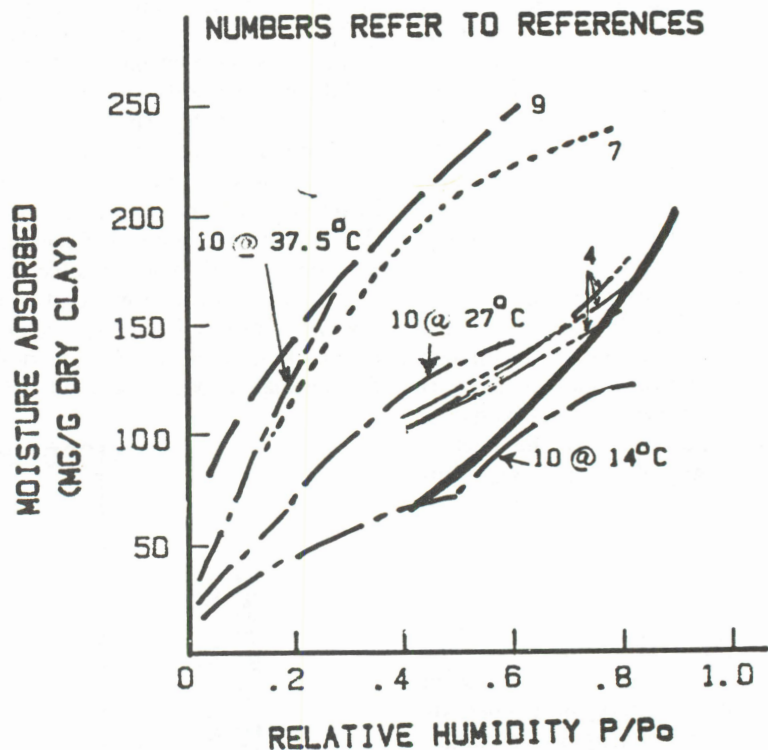


Figure 3. Variation of reported values of moisture adsorption isotherms for calcium bentonite. Number refer to references. Note the large temperature effect seen in reference 10.

TABLE I. CONSTANTS FOR POLYNOMIAL HYGROSCOPIC CURVES FOR DATA OF KEREN AND SHAINBERG (1979)

EFES	A	B	C	D
0	-0.41303	38.3196	-260.8395	689.4663
0.1	-0.30857	31.1142	-123.4283	231.4286
0.2	0.049111	27.6160	-634.817	241.0623
0.4	-0.044101	55.4839	-292.0185	515.8957
0.6	2.23965	40.9714	-295.3833	617.1455
0.1	11.12086	-83.7160	+351.4836	-564.1115

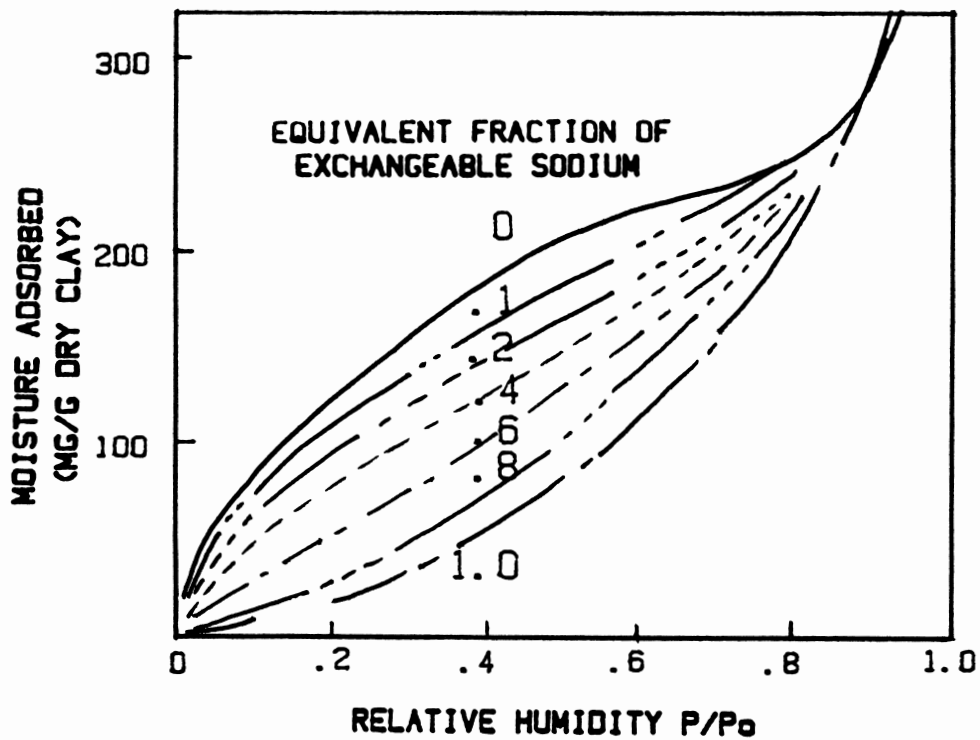


Figure 4. Moisture adsorption isotherms for monoionic clays (Keren 1979).

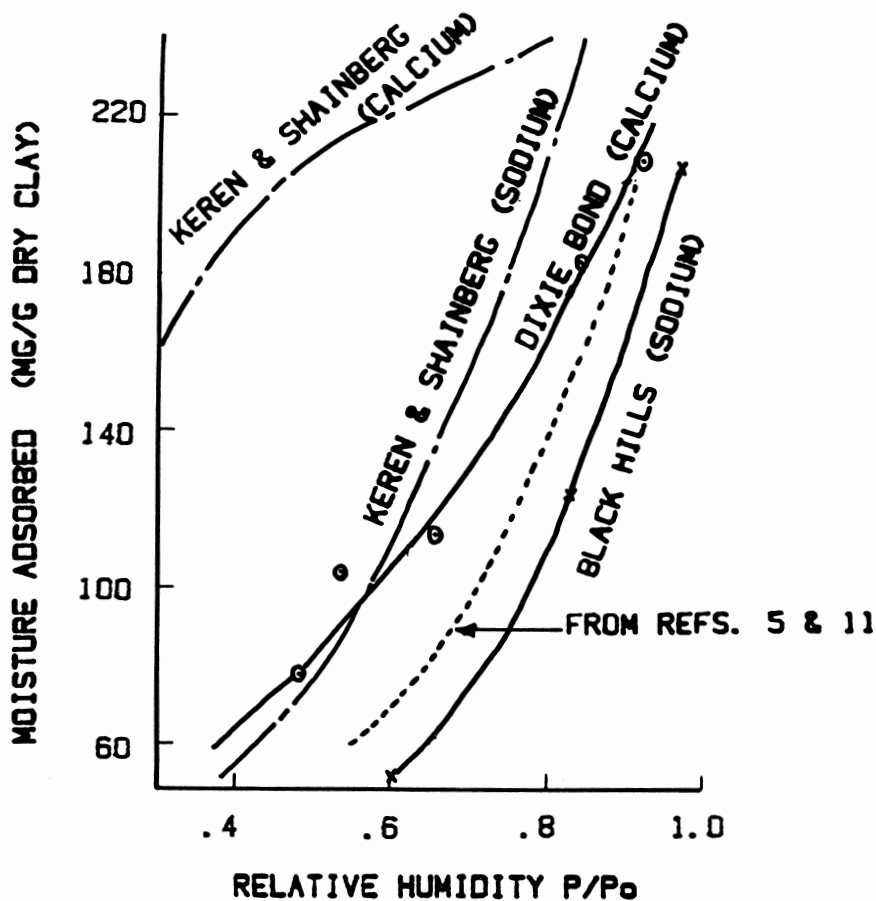


Figure 5. Moisture adsorption data for clays used in this study compared with several other workers.

# DRYING CORN WITH SODIUM BENTONITE

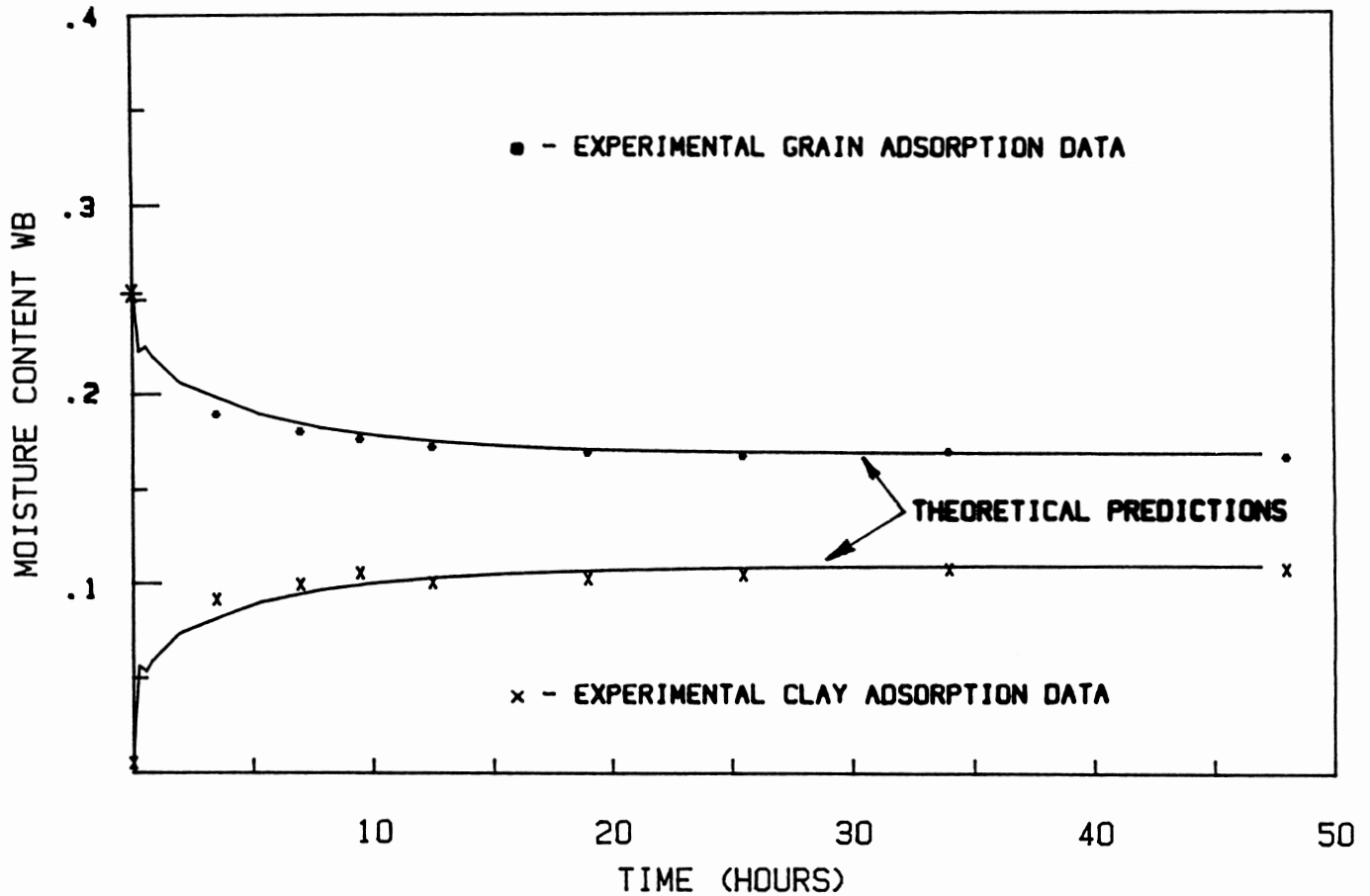


Figure 6. Corn drying with sodium bentonite. Lines are theoretical predictions.  $\cdot$  refers to the corn moisture content.  $x$  refers to the clay moisture content.

water between the platelets that equilibrium is not instantaneous and that the properties of the clay can change over the period of an hour or so. At higher relative humidities, moisture condenses on the external surfaces of the  $\text{Na}^+$  clay and osmotic swelling occurs.

The desorption isotherms for bentonites are quite reproducible while the adsorption isotherms are reproducible only after the first adsorption cycle and then only with difficulty (Grim 1968). This implies an apparent change in clay structure which is not returned to the original condition upon desorption. One can conclude from the foregoing that there will be a large variation in experimental data and difficulty in developing theoretical predictions.

## SUMMARY OF THE MATHEMATICAL MODEL

The mathematical model for sodium bentonite is being developed and is reported here in summary form and expanded to include calcium bentonite.

It is assumed throughout this paper that the clay and grain are intimately mixed and

that the drying process may be analyzed as a three-stage process with time as follows:

(1) moisture movement out of the grain into the air which is assumed to surround the grain;

(2) moisture adsorption by the clay from the air; and

(3) a change in relative humidity of the air due to the resultant moisture content of the clay and the grain.

The equilibrium relative humidities of the air corresponding to the initial moisture contents of the grain and clay differ widely; therefore, there is a rapid initial transfer of moisture from the grain to the air and into the clay. As the clay adsorbs more moisture, the equilibrium relative humidities converge with time.

Since the relative humidity of the air surrounding the grain changes with time, it is not possible to directly apply conventional drying equations which assume a drying medium with a constant relative humidity on entry. Hence, the process must be analyzed numerically with time.

The grain-moisture relationship specified for single kernel analysis of corn was (Brooker et al. 1974)

$$MR = \frac{6}{\pi^2} \left[ \exp(-Kt) + \frac{1}{4} \exp(-4Kt) \right] \quad (1)$$

where

$$MR = (M - M_{eq}) / (M_o - M_{eq}) \quad (2)$$

$$K_{\text{corn}} = 0.54 \exp\left(-\frac{5023}{\theta_{\text{abs}}}\right) \quad (3)$$

$M$  = average decimal moisture content (db)

$t$  = drying time (s)

$M_o$  = original moisture content

$M_{eq}$  = equilibrium moisture content

$\theta_{\text{abs}}$  = absolute temperature ( $^{\circ}\text{R}$ ) for the constants specified

The equilibrium moisture content of grain  $M_{eq}$  must be determined in order to use the above equation. However,  $M_{eq}$  is itself a function of the relative humidity of the air surrounding the grain which varies during the drying process. Hence  $M_{eq}$  for the corn must be continually evaluated during the process using the Chung equation (American Association of Agricultural Engineers 1982-1983).

$$M_{eq} = 0.33872 - 0.05897 \ln \left[ - (T + 30.205) \ln(\text{RH}) \right] \quad (4)$$

# DRYING CORN WITH CALCIUM BENTONITE

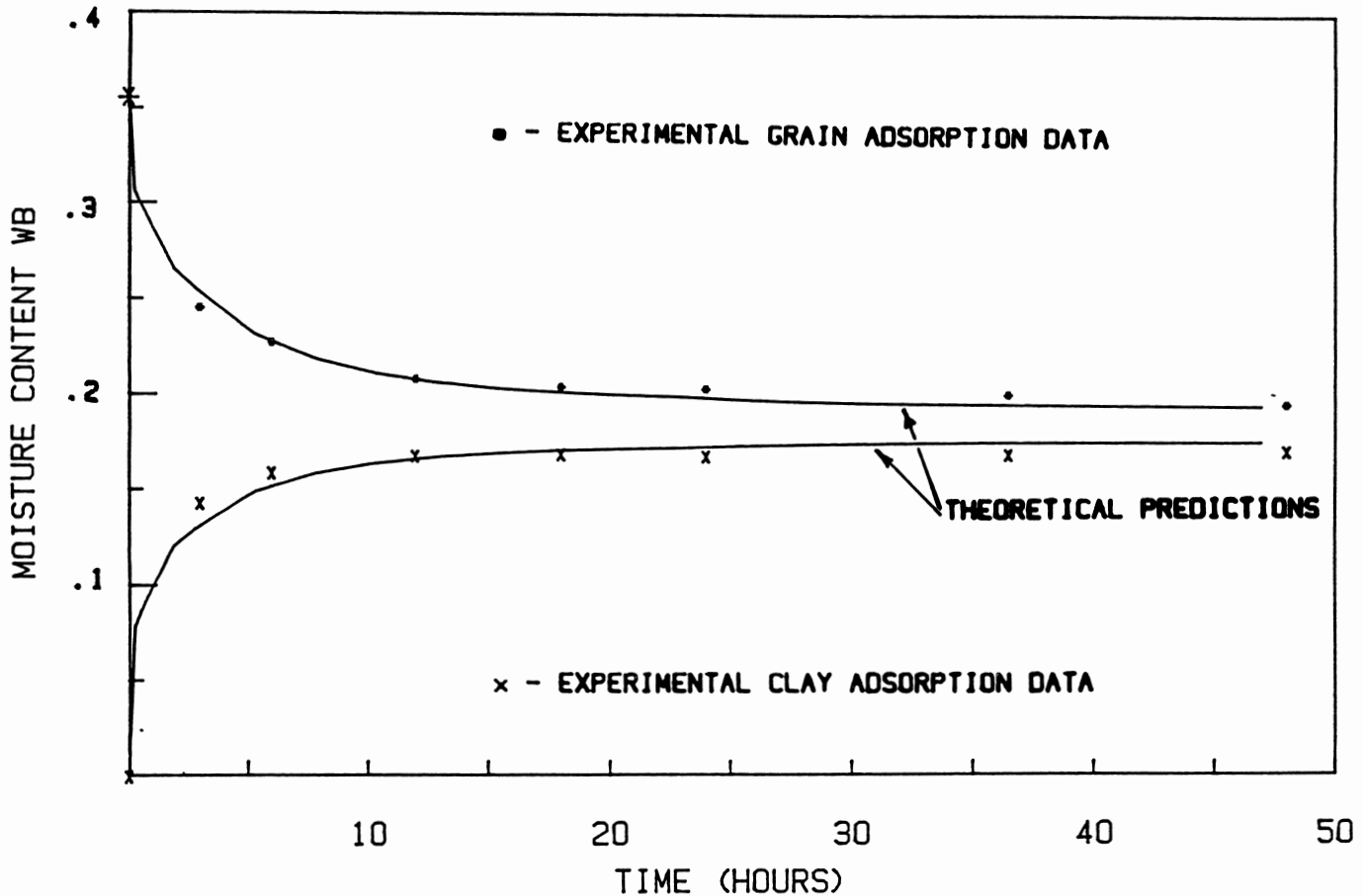


Figure 7. Corn drying with calcium bentonite. Lines are theoretical predictions.  $\bullet$  refers to the corn moisture content.  $\times$  refers to the clay moisture content.

where  
 $M_{eq}$  = equilibrium moisture, decimal (db)  
 $T$  = temperature ( $^{\circ}\text{C}$ )  
 $\text{RH}$  = relative humidity, decimal

The moisture adsorption properties of clays are complex functions of a number of variables as previously noted. This results in a wide scatter of results reported in the literature for predominantly sodium clays (Fig. 2) and predominantly calcium clays (Fig. 3). It is important to note the large variation in hygroscopic properties of bentonites since it dictates that the portion of interest of the moisture isotherm of each clay must be determined if accurate estimates of the drying capability of each clay are to be made. With such large variations in clay properties, prediction of grain drying using clay is somewhat involved. To simplify the problem and to obtain functional relationships for moisture isotherms for bentonites, one worker's results were chosen as a standard and all clays were related to that standard. The standard hygroscopicity curves needed must be a reasonable representation of most clays, have a wide range of types of clay, and

preferably be mathematically continuous over the range of relative humidities of interest. The work of Keren and Shainberg (1979) was most suitable (Fig. 4). Their data for low-moisture contents followed the BET theory which implies wetting of the first monolayer only. They also present data for the same bentonite clay saturated with varying amounts of calcium and sodium ions. Because Keren and Shainberg (1979) started with the same clay (Wyoming bentonite) as a base material and changed the exchangeable ions, the lattice structure differences between naturally occurring calcium and sodium bentonites are not incorporated. However, the continuous nature of the data is useful in obtaining mathematical expressions for the hygroscopicity curves. It was initially thought that the BET equation could be used to represent these curves, but above a relative humidity of 40% it is no longer valid. It was not possible to append another curve to the BET equation for higher relative humidities. Therefore continuous polynomial curves were derived for all of Keren and Shainberg's data having the form

$$\text{RH} = AX + BX^2 + CX^3 + DX^4 \quad (5)$$

where  
 $X$  = the amount of moisture adsorbed at pressure ( $P_o$ )  
 $\text{RH}$  = relative humidity ( $P/P_o$ )  
 $P_o$  = saturation vapor pressure  
 No constant is included in the equation because a clay of zero moisture content can only exist in an environment of zero relative humidity.

The values of the constants in Eq. 5 are given in Table I as a function of the equivalent fraction of exchangeable sodium (EFES), i.e. EFES = 0 means a clay which is totally saturated with calcium ions.

## EXPERIMENTAL STUDY

Commercially available sodium-based bentonite (Black Hills, Wyoming) and calcium-based bentonite (Dixie Bond, Mississippi) were used to compare the drying properties of clays with different exchangeable ions.

Nine experimental trials were conducted using intimate mixtures at 1:1 ratio by weight (wet basis) of corn and clay. A 1:1 ratio was used since no extra storage

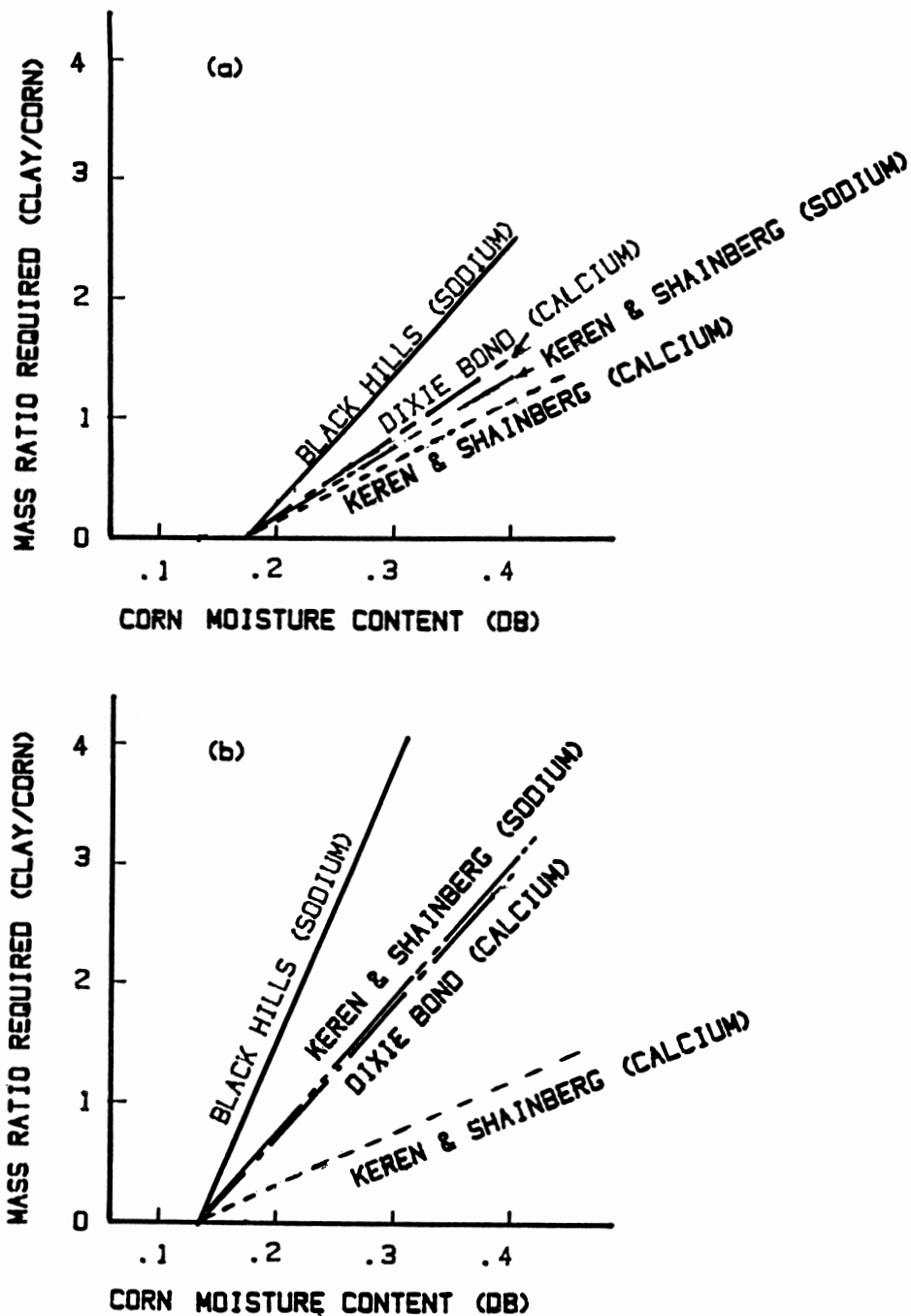


Figure 8. Mass ratio of clay to corn for four different clays for two different desired final moisture contents. (a) 0.13 db (b) 0.17 db

volume is required. Five experiments used calcium clay and four used sodium clay. Rewetted corn was cleaned and its moisture content was adjusted to various values between 16.6 and 40% wb and allowed to equilibrate for a minimum of 3 days. Three kilograms each of corn and clay were mixed together in air-tight containers at time zero. All tests were run at 25°C. At each sample time, as noted on the graphs, three 0.2-kg subsurface samples were removed from the mixture in each container and the clay was separated from the corn on a no. 4 sieve. All corn samples were dried at 105°C for a minimum of 48 h to obtain the final moisture content. The

remaining contents of the containers were remixed and the containers were resealed immediately after removing each sample. No corn fines were found in the clay samples and no clay was found on the corn kernels except when the initial corn moisture content was above 30% wb.

### RESULTS

The experimental data were validated by confirming that all the moisture removed from the grain entered the clay, i.e. the total moisture in a given bin must be constant for all times.

To estimate the hygroscopicity of the clays, one must assume that eventually the

relative humidity of the air surrounding the grain and the clay should be identical. If one also assumes that the hygroscopicity characteristics of the corn are well established and that the equilibrium moisture content of the corn determines the relative humidity of the voids, it is possible to obtain the hygroscopicity characteristics (moisture content vs. relative humidity) of the clay.

It was found that the commercially available calcium-based clay has better hygroscopicity characteristics (Fig. 5) than the commercially available sodium-based clay. It was also apparent that different batches of the same clay (Sturton et

al. (1981) and Graham et al. (1983) vs. present study) have different characteristics. This could be of some concern in specifying the characteristics of a given type of bentonite.

In order to predict the drying history of the intimate mixture of grain and clay it was necessary to have a functional form of the hygroscopicity characteristics of the clay. This was done by relating the experimentally determined hygroscopicity curves (Fig. 5) to Keren and Shainberg's values (Eq. 5) by means of a term called "Purity" which is defined as

$$\text{Purity (mc = constant)} = \frac{RH_{\text{Keren and Shainberg}}}{RH_{\text{clay}}} \quad (6)$$

The purity equations for the sodium-based and calcium-based clays are given as follows:

$$\text{Black Hills: Purity} = 0.31 + 1.03 RH - 0.48 RH^2 \quad (7)$$

(sodium-based)

$$\text{Dixie Bond: Purity} = 0.16 + 0.78 RH + 0.04 RH^2 \quad (8)$$

(calcium-based)

Numerically evaluating Eq. 1 at several time increments, and using Eqs. 2 – 8 as necessary, it is possible to obtain a time history of the drying of corn using Black Hills and Dixie Bond clays. Results for two experiments are shown in Figs. 6 and 7 in which the closeness of predicted and experimental values are noted.

One experimental condition was not modelled well in which experimental difficulties had also been noted. At very high corn moisture contents 30% wb the clay became sticky and it was not possible to separate the grain and the clay properly. Also at very high moisture contents the Chung equation (Eq. 4) is invalid, and prediction was not good.

The question as to which clay is best can be answered by considering the information in Fig. 8. To derive this graph it

was assumed that the initial clay moisture content was 0. Two desired final moisture contents were assumed, 12% wb (13.6% db) and 15% wb (17.7 percent db). The required mass ratio of clay to corn is then given for two types of sodium- and calcium-based clays for different initial grain moisture contents. It can be seen that a considerable saving in mass of clay can be obtained by using the calcium-based clay as compared to the sodium-based clay. It can also be noted that this advantage is a function of the final desired grain moisture content.

## CONCLUSIONS

(1) Calcium- and sodium-based bentonite clays commercially used in the steel industry can be employed in desiccant drying of grain.

(2) The desiccant properties of clays vary considerably from one source to another and even between shipments of clays from the same location.

(3) It is possible to predict the drying time history of both sodium- and calcium-based clays.

(4) The more common type of bentonite clay, the calcium-based clay, adsorbs more moisture than the sodium-based bentonite at low moisture contents and is preferable for grain drying applications.

## ACKNOWLEDGMENT

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