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Characterization of a Mexican halloysitic clay and behavior in dry pressing

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CHARACTERIZATION OF A MEXICAN HALLOYSITIC

CLAY AND BEHAVIOR IN DRY PRESSING

By

Jesus L. Derat, 1938-

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THESIS

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Approved by

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ABSTRACT

A Mexican clay, intended to be used as refractory raw material, was identified. Problems encountered in the characterization of halloysitic clays are discussed and emphasis is made on the use of the electron microscope (scanning or transmission type) as a definite evidence of the existence of halloysite due to its unique morphology within the kaolinite group of clay minerals.

Beneficiation of this particular clay was carried out on a small scale hydrocyclone equipment and the results are discussed.

In an attempt to increase the green density in dry pressing of this halloysitic clay, mixtures with grog were prepared using different additives, grinding and low temperature preheating treatment. The effect of these variables upon green density is given and discussed.

It is believed that an increase in the dry pressing density will be reflected in better after burning properties of bricks made out of clays.

Pressure levels in the dry pressing experiments were made in a range similar to an industrial power press production.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

Properties of clays depend on several factors. Origin, mineralogical composition, particle size distribution, morphology and the presence of impurities can be mentioned among the ones of most relevance.

The present work is devoted to a large extent to the characterization of a clay from southern Mexico intended to be used as refractory raw material. This particular clay, which in the course of the present study is called simply "The Clay," was found to contain appreciable amounts of halloysite.

The methods used to identify this mineral are given, and the distinctive properties of this halloysitic clay are explained on the basis of the above mentioned factors with emphasis on morphology.

Properties of a typical kaolinitic clay are also given as a comparison since both have the same basic structure.

Information regarding the behavior of the halloysitic clay in dry pressing, using pressures within the 10,000 psi range, is given.

Some variables were introduced into the clay-grog system in an attempt to increase green density, since the latter is believed to be highly influential in dry strength and behavior upon firing.

II. NATURE AND USES OF HALLOYSITE

Halloysitic clay minerals have been studied in considerable detail for a number of years and even as early as 1887 the name halloysite became widely known thanks to the publication of LeChatelier.[1] However, the name halloysite had been first used by Berthier[2] in 1826 as derived from that of Omalius d'Halloy, who found the mineral previously in the carboniferous limestone of Liége, Belgium, in a district of old zinc and iron mines.

As it is now generally accepted there are two types of halloysite, one with the formula $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$, known as the fully hydrated form, and the other with the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, called dehydrated halloysite. The former transforms at least partially but spontaneously into the latter even at temperatures as low as $60^{\circ}C$ in low humidity atmospheres, although temperatures as high as $400^{\circ}C$ are necessary to completely dehydrate the mineral.

There has been considerable confusion on the nomenclature of halloysites as it is shown by the following list of names that have been suggested over the years[3]:

Fully Hydrated Form
hydrated halloysite
halloysite
endellite

Dehydrated Form
dehydrated halloysite
metahalloysite
halloysite

The generic name halloysite will be used throughout this paper with the prefix hydrated, partially dehydrated

or fully dehydrated, if necessary to do so for the purpose
of clarity.

The very professional and excellent paper of Ross and
Kerr[4] (1934, p.136) distinguishes two types of halloysite
and they point out that generally "there are two types of
halloysite - one that is usually white or light-colored,
porous, friable, or almost cottony in texture; and another
that is dense, non porous, and porcelain like."

The currently accepted structure of halloysite is
basically that proposed by Hendricks[5] (1938) in which
$[(OH)_4 Si_2Al_2O_5]_n$ layers are intercalated with water molecules,
in other words, the same basic structure of kaolinite but
with additional water between the layers. In a later paper
Hendricks and Jefferson[6] (1938) even proposed that the water
molecules have a definite arrangement between the clay
mineral layers.

Alejander et al.[7] (1943, p.14) pointed out that x-ray
diffraction powder patterns of kaolinite and halloysite
"differ only in the character and strength of reflections...
always diffuse and weak in halloysite [and usually sharp in
kaolinite]."

The lattice constants for fully dehydrated halloysite,
as calculated by Brindley and Robinson[8] (1948) and in
accordance with other sources are a=5.14, b=8.90 and c=7.20 A°
versus 5.14, 8.93 and 7.132 A°, respectively for kaolinite.
The reported c value for fully hydrated halloysite is 10.1A°.

The similarity between the x-ray powder patterns of halloy-
site and kaolinite made these authors infer that both
minerals are built from the same type of atomic layers.

They also pointed out (p.399) that "the absence of
(hkl) reflections implies complete lack of order in the
stacking of the layers, or such a degree of disorder that
(hkl) reflections are of negligible intensity."

Brindley and Goodyear[9] (1948), working with a
halloysite from Eureka, Utah, found out by a direct weighing
method that at relative humidities of less than 15% the
magnitude of adsorbed and interlayer water is of the same
order, whereas at relative humidities above 15% the
interlayer water is greater than the adsorbed water. They
checked their data with x-ray work by measuring the relative
intensities of the peaks of 10.1 $\overset{o}{A}$ spacings for "fully"
hydrated and 7.4 $\overset{o}{A}$ for dehydrated halloysite.

It should be mentioned at this point that fully
hydrated halloysite probably has never been studied alone
due to the fact of its spontaneous dehydration at low
humidities. However, the most hydrated halloysites available
show reflections at both 10.1 and 7.4 $\overset{o}{A}$ spacings indicating
a certain distribution within the grains of fully hydrated
and dehydrated halloysite. After baking at 400°C complete
dehydration takes place and the (001) spacing approaches
almost that of kaolinite.

Generally, kaolinites observed under the electron

microscope show hexagonal platy particles whereas halloysites show tube-like particles partially split or unrolled. Bates et al.[10] (1950) making measurements on seven micrographs estimated the diameters and thicknesses of the tubes and tried to explain the morphology of halloysite on a "misfit" between the shorter gibbsite layer (5.06 x 8.62 A^O) and the larger silicon tetrahedra layer (5.14 x 8.93 A^O). According to them the OH-O bands are weakened in the presence of interlayer water molecules so that they cannot stretch themselves to overcome the "misfit" and "perfect pipes" are expected in fully hydrated halloysite. Upon exposure to vacuum as in the direct or replica method of the electron microscope halloysite dehydrates to a certain extent and tubes split or unroll giving the familiar pictures. They even went further as to calculate the expected diameters of the tubes from the difference in dimension between the gibbsite and silicon tetrahedra layers and came out with values of the same order of magnitude as the observed ones.

However, Pundsack[11] (1956), trying to determine the real shape of hydrated halloysite from Eureka, Utah, used a direct density method assuming that a massive structure composed of efficiently packed hollow tubes should contain a relatively large and measurable void volume. He stated that the measured void volume was around 10%, very far from the 30-40% calculated from the diameters reported in the work of Bates et al.[10], so that hydrated halloysite does not

exist as tubes but rather as laths that upon dehydration undergo considerable shrinkage and distortion - the known picture as observed under the microscope. Whether the voids between the tubes of hydrated halloysite - at the dimension level of microscopic sizes - are really "refill-able" with water, is left an open question at this stage.

Radoslovich[12] (1963) stated that in any case if the silicon-tetrahedra layers have to undergo contraction, this will be accomplished much easier by rotation of the tetrahedra and pointed out that Bates et al[10] (1950) explanation was not entirely satisfactory.

More recent works like the one from Chukhrov and Zvyagin[13] (1966) have shown that besides the elongated crystallites of halloysite, thicker ones are also observed suggesting that smaller ones emerge from the larger ones. These authors also report that tubular forms of some halloysites give sharp x-ray patterns and that some hexagonal platy kaolinites give electron diffraction patterns similar to the ones of disordered structures.

Minato and Utada[14] (1969) reported a rounded type of halloysite from the Iki island in Japan, that showed abnormally high weight loss (22%) at $500^{\circ}C$ probably due to the presence of alumina-rich amorphous material such as allophane.

It can be seen from the previous review that a great deal remains to be known about halloysite structure.

Although halloysitic clays are highly refractory their use has not spread because of problems encountered in firing. Expansion-contraction curves for halloysite differ from those of kaolinite especially around $1000^{\circ}C$ as reported by Hyslop and McMurdo[15] (1938). This fact is somehow related to the formation of high-temperature phases.

Grim[16] (1968, p.312) points out that "the tendency of halloysite to crack into pieces at high temperature makes it difficult to determine its vitrification range and fusion point... it seems that the mineral [halloysite] fuses at a slightly higher temperature than kaolinite and that the fusion point is preceded by a very short vitrification interval."

Hampel and Cutler[17] (1953) observed preferential orientation in the direction of extrusion of halloysitic mineral from Utah, with large differential shrinkages on firing. After a low temperature calcination process shrinkages were attributed to particle structure.

III. CHARACTERIZATION

In order to identify the main constituents of the clay several methods were used which will be briefly described in the following paragraphs.

A. Particle Size Distribution

The method used to obtain the particle size distribution of the clay was that based on sedimentation of particles in a liquid of known viscosity. The procedure used was as recommended by UNITED SIERRA, ref: B 3A. See Appendix A for the full description of this method.

This method is limited to sizes bigger than 1µ since below this value the process is very slow and inaccurate so that the aid of a centrifugal field of force is required.

The cumulative size distribution thus obtained is shown in Figure 1. Approximately 35% by weight of the clay has sizes below 2.5µ, and 12.5% above 37µ (400 mesh). However, the large sizes thus determined might not reflect the true size of the minerals due to the formation of aggregates.

As a comparison nacrite, dickite and kaolinite often exist as very small hexagonal crystals varying from less than 0.1µ to 2µ diameter. Ball clays, known for their high plasticity, normally have 70-80% by weight below 1µ.[18]

B. Chemical Analysis

Although chemical analyses alone do not suffice to

Figure 1: Cumulative size distribution of halloysitic
clay.

EQUIVALENT SPHERICAL DIAMETER IN MICRONS

Figure 1

10
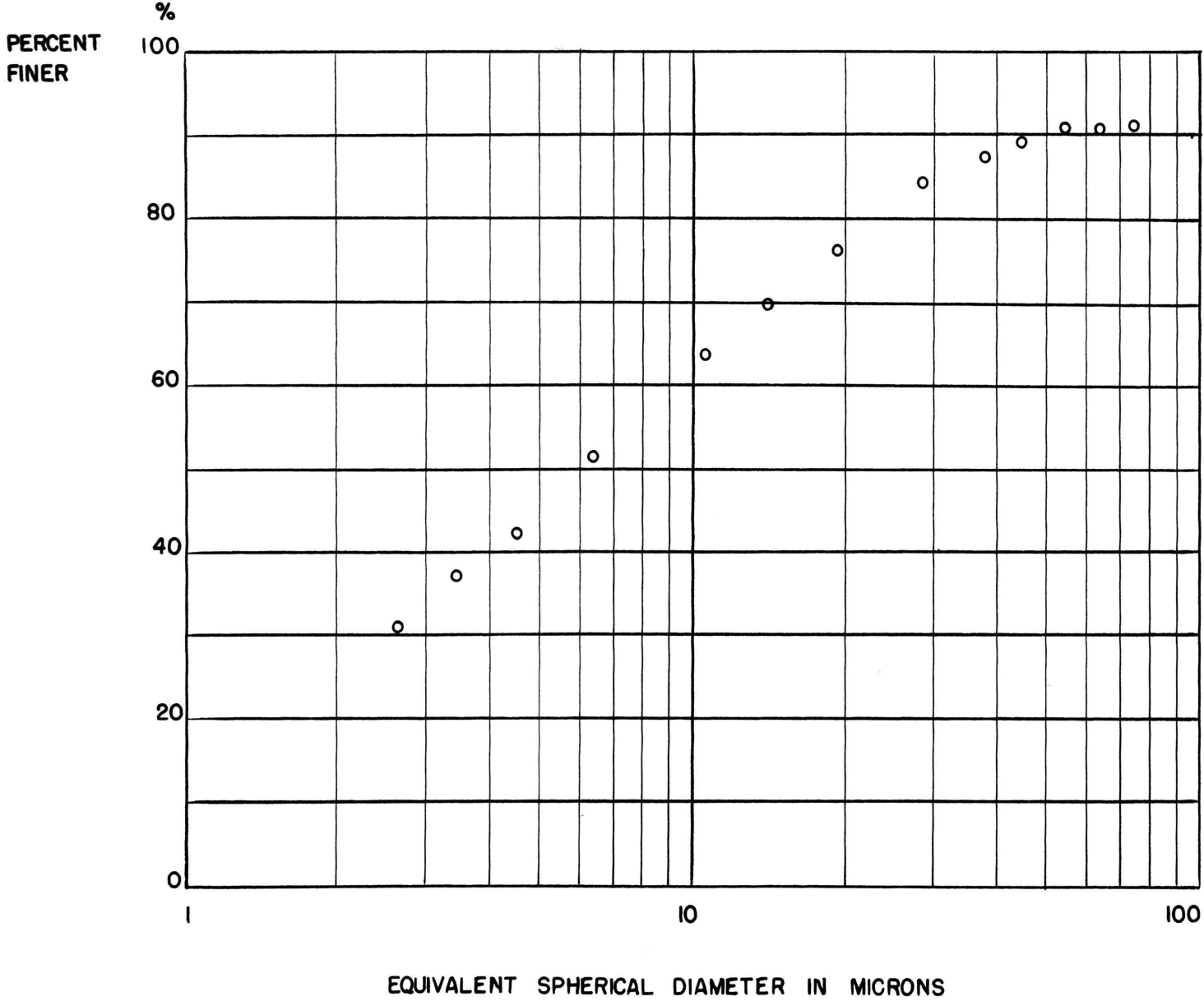
characterize the different minerals present in a clay, when
they are used in conjunction with data obtained from x-ray
diffraction a "rational" analysis can be estimated.

The chemical analysis of the clay carried out by
atomic absorption and wet methods is shown in Table I.
As shown later in this thesis, the clay was found to contain
appreciable amounts of the mineral, halloysite. However
time limitations did not permit the estimation of concentra-
tion, and therefore the claylike material is reported as
kaolinite in the rational analysis of Table II. All
alkalies were assumed to be present solely as micas.
Alumina was considered to be combined in three minerals,
kaolinite and soda and potash micas, so that by substracting
the amount of alumina present in the micas from the total,
the content of kaolinite was obtained. Finally, quartz
or free silica was calculated by substracting the silica
content in kaolinite and the micas from the total. The
organic matter content was found to be 0.5% by oxidation
with hydrogen poroxide.

It is estimated from information given later that only
30% of the free quartz in the original clay is coarser than
37μ (400 mesh) whereas 90% of the kaolinite material is
finer than 37μ.

C. X-Ray Diffraction

X-ray diffraction methods as a means of identifying

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TABLE I

Chemical Analysis of Halloysitic Clay

	CALCINED Basis %	DRY Basis %
SiO_2	60.8	54.4
Al_2O_3	34.5	30.8
Fe_2O_3	2.95	2.64
CaO, MgO, TiO_2	1.1	1.0
K_2O	0.58	0.52
Na_2O	0.07	0.06
IGNITION LOSS	----	10.60
TOTAL	100.00	100.02

TABLE II

"Rational Analysis"

(Dry Basis)

	%
Kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	73.00
Free Quartz SiO_2	18.10
K Mica $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	4.40
Na Mica $Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	0.70
CaO, MgO, TiO_2, Fe_2O_3	3.64
Organic Matter	0.50
TOTAL	100.34

clay minerals is an invaluable tool since it is based
on effects at the atomic structural level.

The majority of clay minerals are composed of gibbsite-
silica layers which extend indefinitely in the a and b
directions, and the basal reflections, often designated
(001), are directly related to the thickness of these
structural layers.

The unit cell of the structures may be composed of
more than one layer depending on the manner in which the
layers are stacked on each other.

The structure of halloysite as accepted at the present
time is shown in Figure 2.

The x-ray powder diffraction diagrams obtained with
copper K_α radiation and Ni filter are shown in Figure 3.

Figure 3A shows the diagram of "pure" kaolinite used
as reference material. The (001) and (002) basal reflections
are clearly visible corresponding to spacings of 7.15 and
3.57 $\overset{o}{A}$ respectively. These values are in close agreement
with those of Brindley and Robinson[19] (1946).

The (001) and (002) reflections for the untreated clay
are rather broad and weak and correspond to spacings of 7.21
and 3.58 $\overset{o}{A}$ respectively, (see Figure 3B). In addition a weak
and diffuse peak can be observed at approximately 10 $\overset{o}{A}$.

Figure 3C shows the x-ray diagram of the clay that was
heated to 200°C for four hours and cooled to room temperature.
Two important things that can be observed are: the 10 $\overset{o}{A}$

Figure 2:   Structure of hydrated halloysite showing a
            single layer of water molecules (after
            Hendricks and Jefferson[6], 1938).

SILICON
ALUMINUM
OXYGEN
HYDROGEN
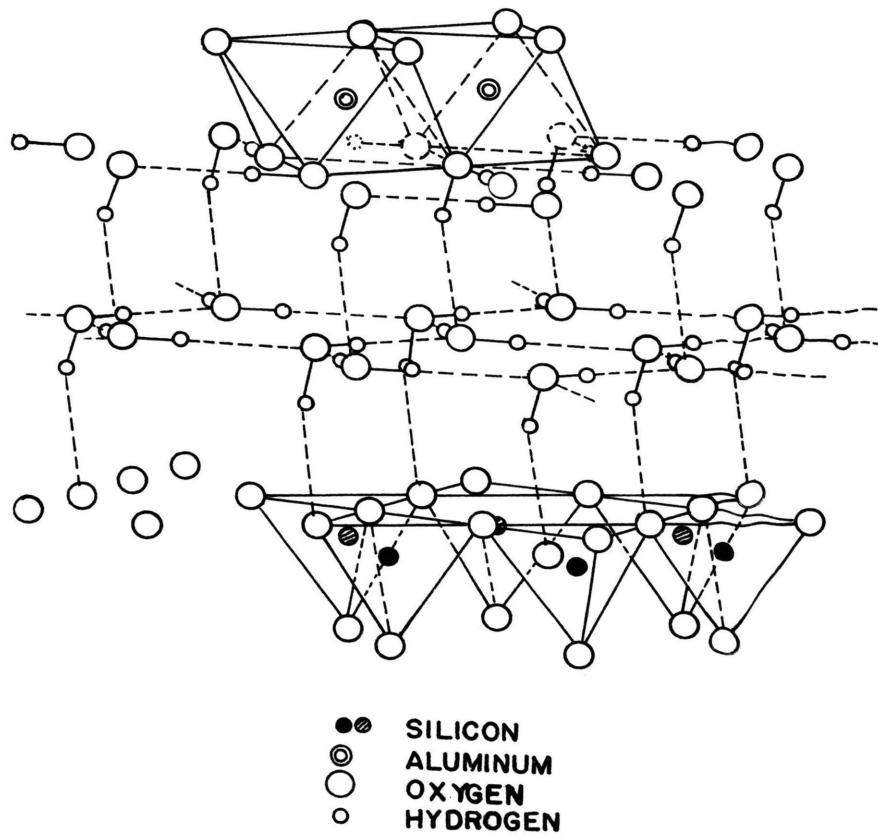
Figure 2

Figure 3: X-ray diffraction diagrams. (A) "pure"
kaolinite; (B) untreated halloysitic clay;
(C) halloysitic clay heated to 200°C for
4 hrs. and cooled to room temperature and
(D) -400 mesh portion of same clay heated
to 100°C overnight and cooled to room
temperature.

DEGREES 2θ Cu Kα

Figure 3

peak has almost disappeared or at least appears to be below the background and the basal reflections have become stronger and sharper. Essentially the same thing happened when the (-) 400 mesh portion of the clay was heated to 100°C overnight and cooled to room temperature.

From the above information there was strong evidence that halloysite or at least a mixture of kaolinite and halloysite was present in the clay, in agreement with Brown[20] (1961, p.69). The disappearance of the 10 $\overset{\circ}{A}$ reflection after the heating to 200°C suggests the expulsion of the interlayer water. Re-expanding of these layers was not achieved even after three days of exposure to a saturated atmosphere of ethylene glycol indicating that the structure has completely collapsed from 10 to 7.2 $\overset{\circ}{A}$; this is also in agreement with Brown[20] (p.76) who states the "if it [halloysite] is dehydrated almost completely, then little or no organic complex will form."

X-ray diagrams of the clay obtained by sedimentation onto a glass slide were of the same nature except for an increase in intensity of the (020) reflection. The quartz peaks also appeared to be less intense than in the previous diagrams. As a synthetic mixture of kaolinite and halloysite gives almost the same x-ray powder diagram of that of pure kaolinite (Brindley and Comer[21]), there was evidence at this stage which might suggest the presence of halloysite although

the possibility of a mixture of halloysite and poorly crystallized kaolinite could not be discarded.

D.   Electron Microscopy

The electron microscope can be used to determine the shape and size of the various clay minerals.

In electron transmission microscopy, a focused electron beam is directed onto the clay sample which scatters the electrons and they in turn hit a fluorescent screen producing the image of the clay particles. This is the fastest and easiest method for studying clays although samples can be altered by the vacuum of the microscope or heated by the absorption of energy from the electron beam. This is particularly true for halloysite materials which may be dehydrated during examination. Nevertheless, the transmission method was followed in this study by allowing small drops of clay suspension (dispersed with ammonia) to dry onto a carbon covered grid sample holder. The preparation of the samples is fully described in Appendix B, following the recommendation of De Souza Santos[22] (1957).

Time did not permit the use of the replica method, although the manner in which this technique is carried out at the present time still implies that the clay sample be exposed to vacuum during the coating or shadowing process, previous to removal of the clay[23] (1954).

The micrographs were taken with a HITACHI Electron

Microscope model HU 11A and most of them with 36,600 X magnification. Halloysite used as a reference material is shown in Figure 4 in which elongated, tube-like particles can be clearly seen. Figure 5 gives the appearance of the clay and the tubular form of the particles can be appreciated. Most of the tubular particles appear partially split or unrolled.

In comparison Figure 6 corresponds to a good refractory kaolinitic clay from Northern Missouri in which hexagonal platy particles can be observed.

The halloysitic clay is again seen in Figure 7 in which elongated particles appear to coalesce forming clusters.

Figure 8 shows a very coarse particle with a characteristic morphology probably corresponding to a material in the process of being altered to an argillic one.

Figure 9 shows an interesting aspect of the clay in which rounded grains can be observed in addition to the elongated particles.

Although the organic matter of this clay is estimated to be only 0.5%, a picture was obtained in which particles of clay are deposited on vegetation (see Figure 10). An enlargement of one area depicts book-like argillic particles adhered to organic matter.

Twenty samples were examined under the microscope

Figure 4:   Halloysite, Ward's.   Electron microscope,
            transmission.

Figure 5:   Halloysitic clay from Mexico.   Electron
            microscope, transmission.

Figure 4
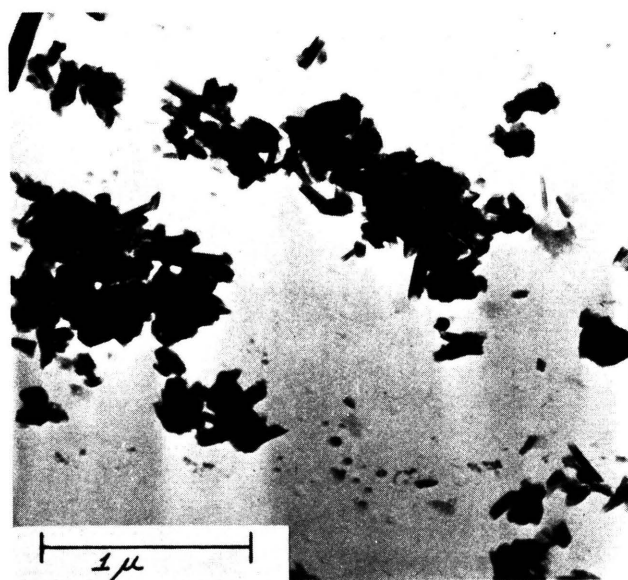
Figure 5

Figure 6: Refractory clay from Northern Missouri.
Electron microscope, transmission.

Figure 7: Halloysitic clay from Mexico. Electron
microscope, transmission.
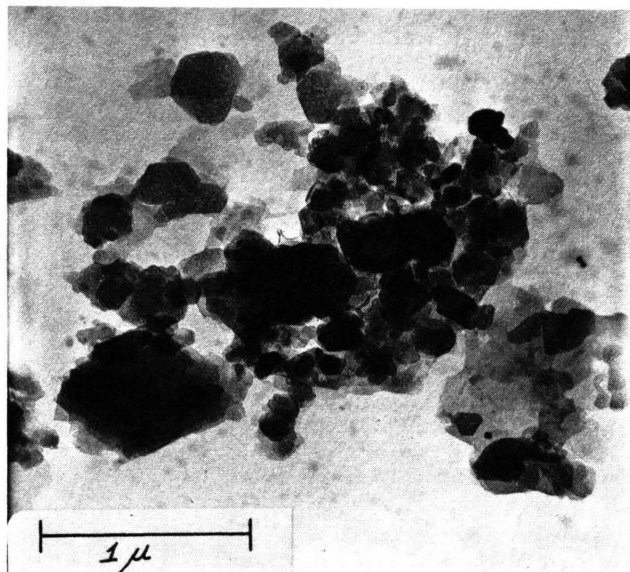
Figure 6
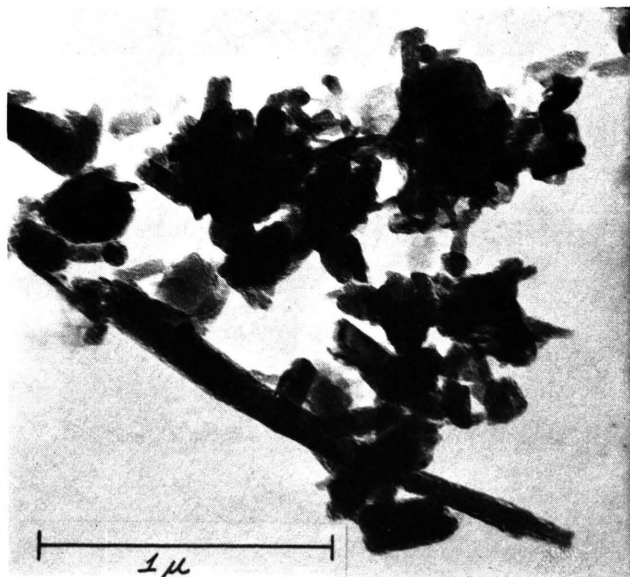
Figure 7

Figure 8: Halloysitic clay from Mexico (coarse parti-
           cle). Electron microscope, transmission.

Figure 9: Halloysitic clay from Mexico (rounded grains).
           Electron microscope, transmission.
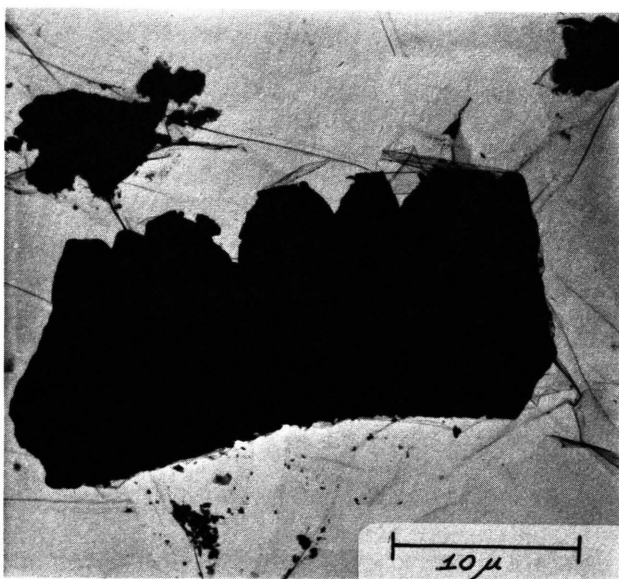
Figure 8
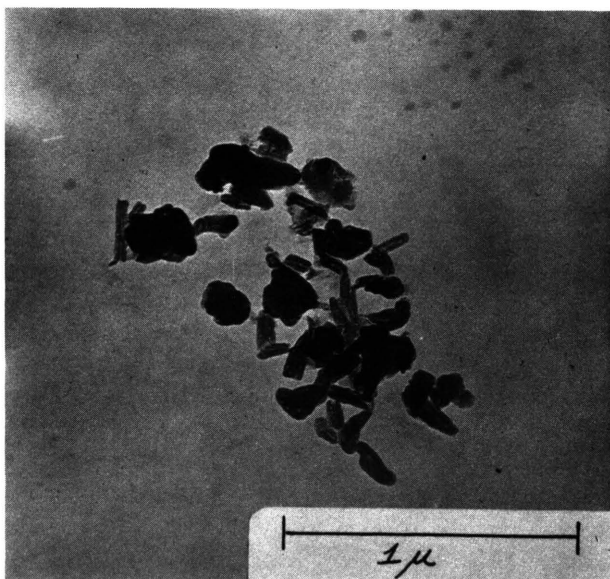
Figure 9

Figure 10: Halloysitic clay from Mexico. Argillic
particles adhered to organic matter. Electron
microscope, transmission.
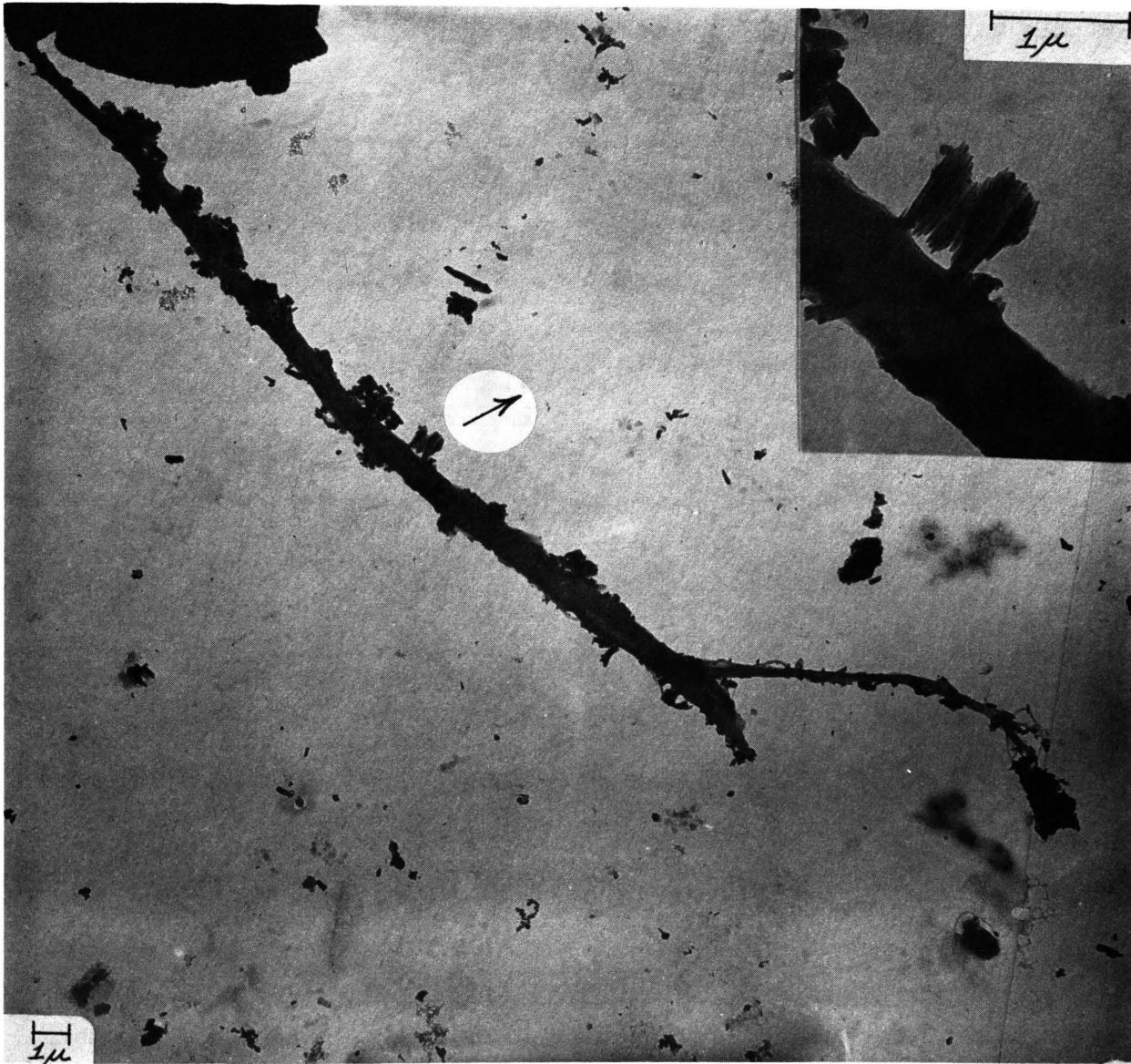
Figure 10

giving the same morphology of the micrographs previously described. All samples were obtained from the clay fine portion (-400 mesh) which constitutes 87.5% of the total.

From the above micrographs it was concluded that the clay was basically halloysitic in nature although no actual count was made to estimate the concentration of the halloysite clay minerals.

E. Differential Thermal and Thermogravimetric Analyses

Differential thermal analysis instruments record the temperature at which thermal reactions take place in a material while being heated at a predetermined rate. A thermocouple records the difference in temperature between the sample and an inert material like α-alumina, when both are heated at a uniform rate, this difference being proportional to the intensity of the thermal reaction.

The DTA diagrams were obtained with a STONE instrument model KAH at a heating rate of $10^{\circ}C$/min. Figure 11A is a thermogram of the untreated clay in which an abrupt endothermic peak can be observed around $100^{\circ}C$ attributable to the loss of adsorbed and interlayer water. The endothermic peak of the hydroxyl-water loss appears to be at a slightly lower temperature than for "pure" kaolinite which is shown in Figure 11B.

The thermogram of the clay, preheated to $130^{\circ}C$ and cooled to room temperature, is shown in Figure 11C in which

Figure 11:   DTA diagrams of (A) untreated halloysitic clay; (B) "pure" kaolinite and (C) halloysitic clay preheated to $130^{o}C$ and cooled to room temperature.
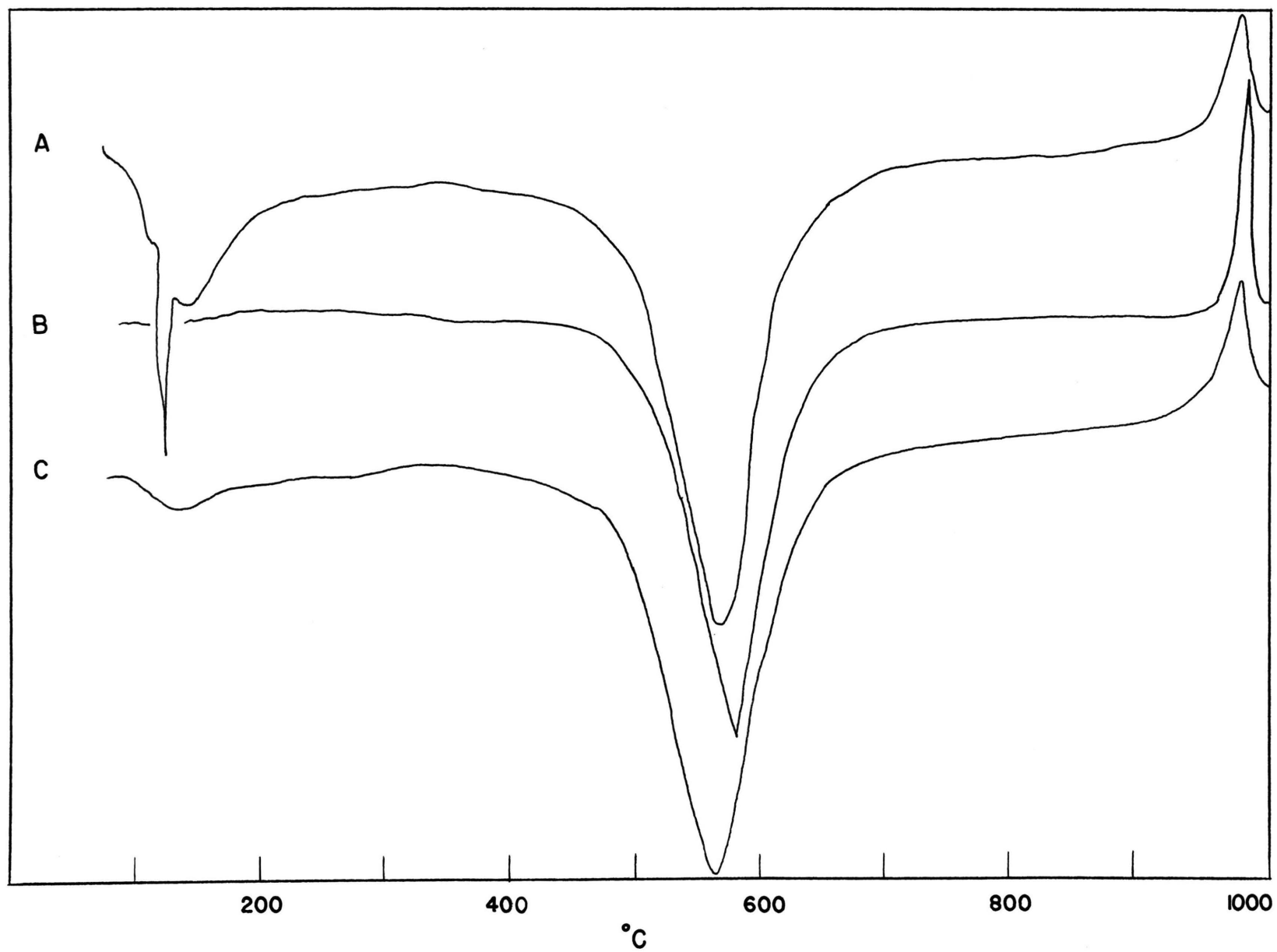
Figure 11

the dehydration peak is seen to be less intense than in the untreated clay.

Thermo-gravimetric analysis determines the weight loss as a sample is heated and this weight loss can be associated with energy changes of thermal reactions recorded by DTA.

TGA diagrams were obtained with a METTLER recording vacuum thermoanalyzer No. 44 in an atmosphere of air with a gas flow rate of 5.72 liters/hr. The diagrams converted to weight loss versus temperature are presented in Figure 12 for the untreated clay; the clay after being heated to $130^{O}C$ for 12 hours and cooled to room temperature; and for a good refractory kaolinite clay from Northern Missouri.

It can be seen that the weight loss in the $100^{O}-200^{O}C$ interval is much greater in the untreated clay than in the preheated clay, showing that in the latter the interlayer water has been driven off to a considerable extent.

As a comparison the kaolinitic clay shows a weight loss of only 2% at $200^{O}C$ as opposed to 4.5% for the untreated clay.

The presence of halloysite in this clay already established by electron microscope and x-ray diffraction methods was confirmed by DTA and DTG analyses.

Figure 12: TGA diagrams of (A) untreated halloysitic clay; (B) refractory kaolinitic clay from Northern Missouri and (C) halloysitic clay heated to 130°C for 12 hours and cooled to room temperature.
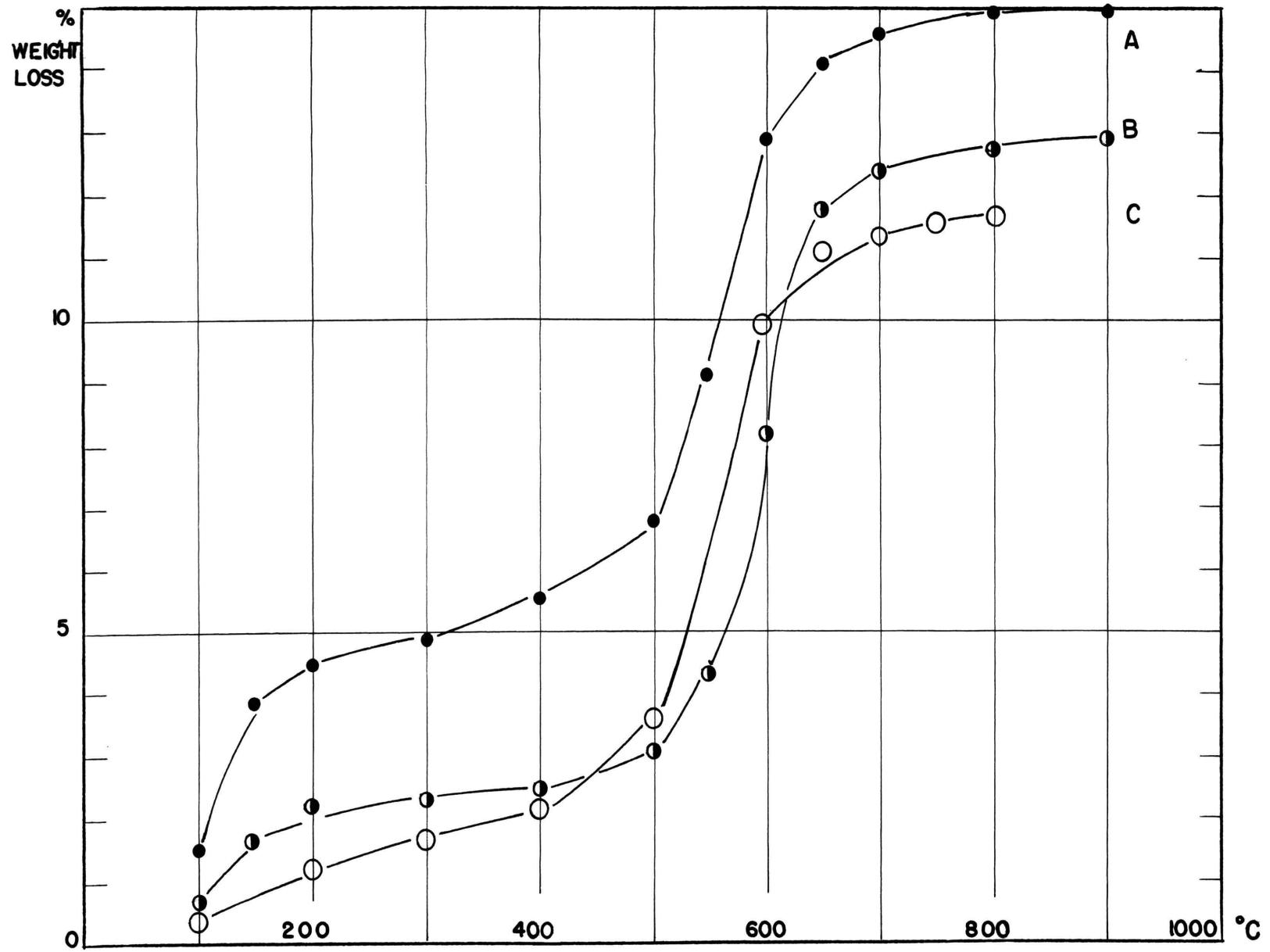
Figure 12

IV.   REMOVAL OF QUARTZ BY HYDROCYCLONE

Removal of quartz and other objectionable impurities has been carried out successfully by wet-cyclone methods. Calhoun and Powell[24] (1961) beneficiated some sandy flint and pyritic plastic clays increasing the alumina content by two to six percent; the PCE was raised one to three cones.

Beneficiation of the halloysitic clay was carried out on small scale hydrocyclone equipment. The details of the experiment are given in Appendix C. The Al_2O_3 content was raised only 1% while the PCE remained the same at 31 ($1685^{\circ}C$). The chemical analysis of the beneficiated clay is given in Table III and that of the (+) 400 mesh portion of the sand in Table IV.

Screen analysis showed that only 1% of the beneficiated clay was coarser than 37μ (400 mesh) vs. 12.5% for the raw clay. From the screen analysis of the sand it was estimated that only 30% of the free quartz in the original clay is coarser than 37μ.

Time did not permit full evaluation of the beneficiation method and further experiments may produce better results.

TABLE III

Chemical Analysis of Beneficiated
Halloysitic Clay (Dry Basis)

	%
SiO_2	59.20
Al_2O_3	35.70
Fe_2O_3	2.95
CaO, MgO, TiO_2	1.10
K_2O	1.00
Na_2O	0.08
	100.03

IGNITION LOSS: 11.00%

P.C.E.   31 (1685°C)

TABLE IV

Sand (+)   400 Mesh (Dry Basis)

	%
SiO_2	70.90
Al_2O_3	23.70
Fe_2O_3	3.20
CaO, MgO, TiO_2	1.60
K_2O	0.67
Na_2O	0.06
	100.13

V. DENSITY IN DRY PRESSING

The halloysitic clay under study has a porous and fluffy texture, similar to the one mentioned by Ross and Kerr[4] (1934, p.136). In comparison, this clay has a bulk density of only 0.96 gm/cm^3 vs. 1.36 gm/cm^3 for a refractory kaolinitic clay from northern Missouri, both ground so that 100% passes through 60 mesh.

In the manufacture of refractory brick halloysite presents several problems such as low green bulk density and the development of cracks during the burning process. The former is related to the structure of halloysite itself and the latter to the high temperature phase formations. Probably the expulsion of interlayer water also contributes to a certain extent to the mentioned problems when dealing with partially dehydrated halloysites.

This chapter will be devoted only to the study of variables that may affect green bulk density in dry pressing. High temperature phase formations have been the subject of several authors among whom Wahl and Grim[25] (1963) are worthy of mention.

A. Design of Experiments

In order to exaggerate the properties of the clay, a mixture of 40% grog - 60% clay (by weight) was chosen for the experiments. The grog consisted of ground, high duty, dry pressed brick with a size range from 0.35 to 1.68 mm

(12-45 mesh). The grinding level of the clay was such that 100% passed through 60 mesh (250μ). See Appendix D for full details of grain size distributions.

Four variables were chosen for evaluation: pressure, addition of binder, grinding and heat treatment, all of them at two levels each as illustrated in Figure 13.

A hydraulic laboratory press was used throughout the experimental work, pressing small discs 1 1/8" in diameter and with a height in the neighborhood of 3/4". The manometer of the press was held at the desired reading for 15 seconds before releasing the pressure. The bulk density was calculated by weighing the specimens on an analytical balance and by measuring the height with a micrometer; both operations being done within ten minutes after the pressing.

Preliminary experiments with binders[26,27] showed that with gum arabic and dextrine a slight increase in density was obtained and the appearance of the brick was definitely improved. The use of other binders while making the bricks appear stronger and with sharper corners actually decreased their bulk density. Dextrine was chosen for study because of its low price. Results on the binders considered are shown in Table V.

All mixing was done by hand until the mixture was thoroughly homogeneous; the water was added slowly while mixing so that a uniform distribution could be achieved. Sixteen experiments were carried out, each experiment

Figure 13: Factorial design of experiment with four variables each at two levels.

		A₁		A₂	
		B₁	B₂	B₁	B₂
C₁	D₁	a₁ 2.187	a₂ 2.135	a₃ 2.225	a₄ 2.202
	D₂	b₁ 2.213	b₂ 2.138	b₃ 2.230	b₄ 2.229
C₂	D₁	c₁ 2.174	c₂ 2.132	c₃ 2.223	c₄ 2.195
	D₂	d₁ 2.198	d₂ 2.151	d₃ 2.228	d₄ 2.196

A_1: CLAY HEATED TO 300°C B_1: CLAY-120 MESH
A_2: CLAY NOT HEATED B_2: CLAY- 60 MESH

C_1: 3% DEXTRINE D_1: 10 000 PSI
C_2: 5% DEXTRINE D_2: 15 000 PSI

Figure 13

TABLE V

Effect of Binders on the Bulk Density of a Mixture
of 40% Grog - 60% Halloysitic Clay at 10,000 psi. 10 Parts
of Water Per 100 Parts (By Weight) of Grog-Clay Mixture.

Type of Binder	Name	Bulk Density gm/cm^3*	Comments
	no binder	2.185	slight laminations perpendicular to direction of pressure
Protein	2% unflavored gelatin	2.130	very good brick
gums	2% gum Arabic**	2.200	very good brick material sticks to mold
	2% gum Ghatti**	2.150	very good brick material sticks to mold
	5% gum Tragacanth	2.076	excellent brick material sticks to mold
starch derivatives	2% Tapioca-Dextrine**	2.203	very good brick wet appearance
	2% Jaguar TP**	2.183	very good brick wet appearance
inorganic	5% Montmorillonite	2.196	slight luminations perpendicular to direction of pressure. Easy to press

*Average value of three specimens
**As supplied by Stein-Hall & Co., Inc., 605 Third Avenue, New York, N.Y. 10016

NOTE: The bulk density obtained with 40% grog-60% Missouri Kaolinitic clay was 2.303 gm/cm^3 without binder.

productive of three bricks whose average bulk density is shown within the squares of Figure 13.

B. Results

The results of the experiments obtained by the control chart method[28] (1958, p.97) are shown in Figure 14. For the calculation of limits for these charts, see Appendix E.

The best results were obtained with the clay that was ground to pass 120 mesh (125μ) while the lowest values corresponded to the clay that was heated to 300°C without further grinding. The 60 mesh clay and the clay heated to 300°C and ground to pass 120 mesh lie between the two extremes.

The effect of 3-5% binder is almost negligible and the same is true for the two levels of pressure.

Figure 14: Results of factorial design of experiments.
            Control chart method.
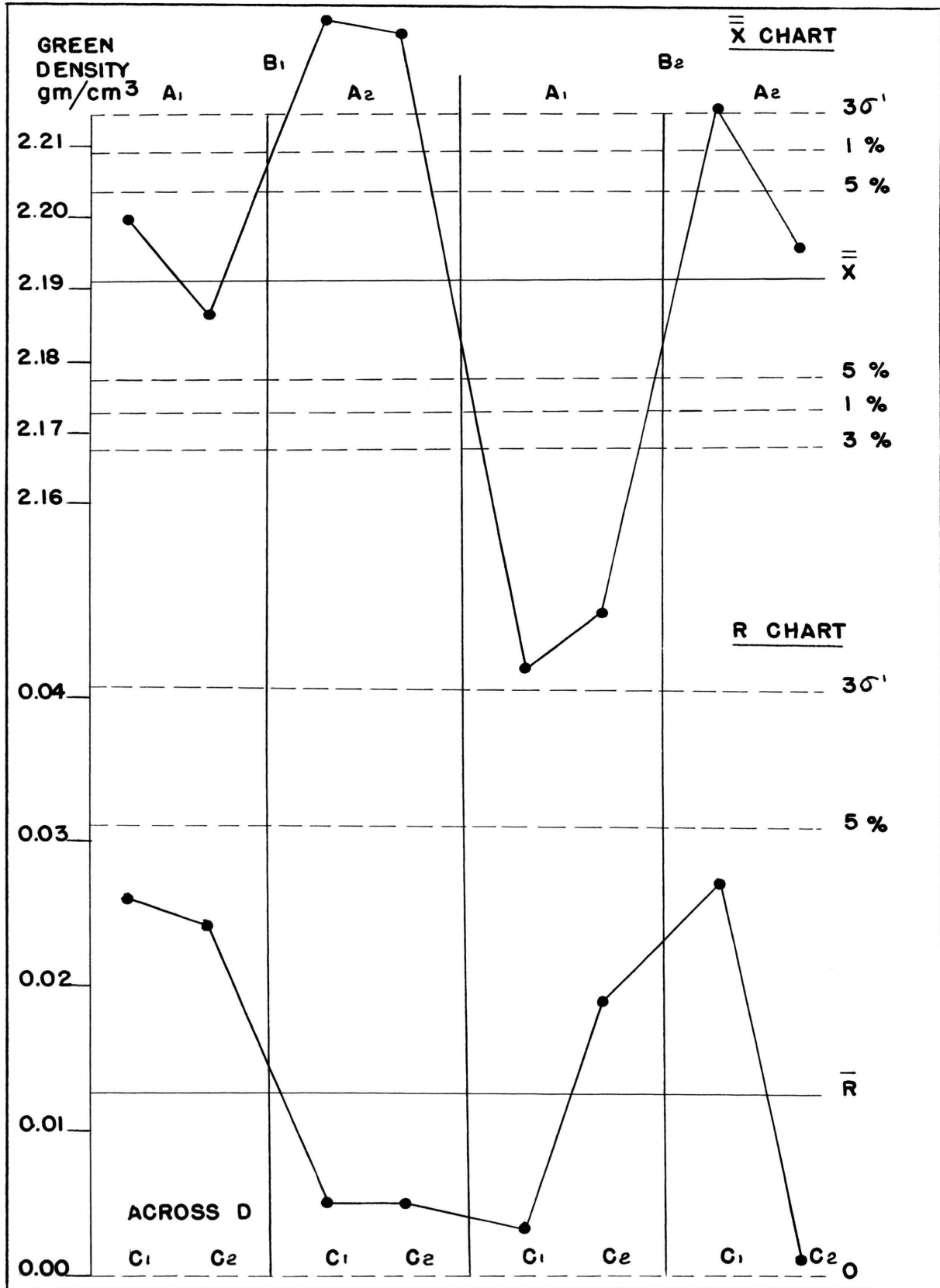
Figure 14

VI. DISCUSSION OF RESULTS

The addition of 3% dextrine to the grog-halloysitic clay mixture definitely improves the appearance of the brick and helps to avoid the formation of cracks in pressing. This amount of binder allows the bulk density to increase slightly while further additions beyond 3% have the opposite effect.

Increasing the pressure from 10,000 to 15,000 psi has almost a negligible effect upon density with the probable exception of the clay heated to 300°C without further grinding. In this case formation of cracks made it difficult to evaluate bulk density.

Grinding was established as the most important factor in increasing green bulk density.

VII. CONCLUSIONS & RECOMMENDATIONS

In order to improve the properties of refractory brick made out of halloysitic clay, several experiments were carried out to increase green bulk density. Grinding was definitely established as a method to achieve this goal, although the level of grinding that can be carried out economically to meet the desired density will depend on the specific costs and needs of a refractory manufacturer.

Several other factors should be taken into consideration such as addition of surfactants to refractory batches and the proper combination of different grog sizes to further improve the properties of brick.

Kukolev and Mikhailova[29] (1960), studied the use of surfactant materials like fatty acids (c_7 and c_9), kerosene and raw benzene as effective means of increasing bulk density and strength of refractory brick. According to these authors the addition of surface-active agents reduces the elastic after effects in pressing and also facilitates the grinding operation.

To obtain a brick of good density the proper grog size distribution should be used whether in combination with a halloysitic clay or any type of clay. Excellent papers have been written on the subject among which those of Westman and Hugill[30] (1930) and Norton and Gugel[31] (1962) are worthy to be mentioned. According to these authors at least two

different sizes of grog in the proportion 70% coarse - 30%
fines should be used to greatly reduce void space.
Refractory bodies have been prepared with no open pores
and no more than the conventional shrinkage and maximum
density in this manner.

All the bricks in the previously mentioned experiments
were burned in an electric furnace to cone 13-14 (1370°C)
for one hour, following a heating rate of 80°C/hr after they
were thoroughly dried. Most of the bricks developed surface
cracks probably due to shrinkage of the clay since a very
high clay-grog ratio was used.

Further experiments with different grog contents are
given in Appendix F.

From the behavior of the clay heated to 300°C, it
was inferred that although most of the interlayer water had
been driven off, some damage to the crystalline structure
of halloysite could have occurred. Further trials at
lower heating levels should be contemplated as promising.

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VITA

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He joined Harbison Walker Flir Refractories in Mexico City as an Engineer of the technical department in September 1959. In 1967 he was transferred to HW Flir's main office in Monterrey where he held the position of Head of the technical sales department until October 1970, at which time he moved again to Mexico City as manager of the technical sales department in that area.

Eight months after his marriage he enrolled as a graduate student in the Ceramic Engineering Department at the University of Missouri at Rolla in January 1972. He was granted a fellowship from HW Flir Refractories during his graduate appointment.

APPENDICES

APPENDIX A

PARTICLE SIZE DISTRIBUTION OF HALLOYSITIC CLAY

1. Sedimentation Test

The hydrometer method for sub-sieve size determination was carried out on the (-) 400 mesh portion of the clay following the procedure of United Sierra Division Cyprus Mines Corporation, Trenton, N.J., 08606. 1.2 gm of sodium hexametaphosphate (calgon) per every 50 gm of clay was found to be the correct amount for complete dispersion. The hydrometer* readings at different time intervals as well as values of P%, H_1, Hr, $A \times 10^3$, V and D in mm are given in the following table:

Temperature constant at 20°C

hydrometer reading of the "blank" constant at 1.001=r

Time	R	P%	H_1 cm	Hr cm	$A \times 10^3$	V	D_{mm}
2 min	1.031	96	0.35	8.33	11.2	0.070	0.028
5 min	1.028	87	1.40	9.38	11.2	0.032	0.019
10 min	1.026	80	2.15	10.13	11.2	0.017	0.014
20 min	1.0235	72	3.10	11.08	11.2	0.0095	0.0104
1 hr	1.019	58	4.75	12.73	11.2	0.0036	0.0063
2 hr	1.016	48	5.85	13.83	11.2	0.0018	0.0045
4 hr	1.014	42	6.65	14.63	11.2	0.00105	0.0034
7 hr	1.012	35	7.40	15.38	11.2	0.00062	0.0026

*Fisher Scientific Co., Cat. No. 14-331-5A
 Range 0.995 to 1.030

where:

R = hydrometer reading

P% = percentage solids corresponding to a hydrometer

reading

H_1 = depth of reading in cm (distance in centimeters)

from the top of the bulb to the reading of the

stem)

Hr = H_1 corrected for the volume of hydrometer bulb

$$Hr = H_1 + \frac{1}{2} (H - \frac{\text{volume of hydrometer bulb}}{\text{area of graduate}})$$

$$Hr = H_1 + \frac{1}{2} (18.4 - \frac{65}{26.5}) = H_1 + 7.98$$

H = length of the bulb in centimeters = 18.4 cm

volume of hydrometer bulb = 65 cm^3

area of graduate = 26.5 cm^2

P% is calculated from the formula

$$P\% = \frac{100}{S} (\frac{D}{D-L}) (R-d) \times 10^3$$

where:

S = grams of clay in 1000 ml of original suspension=50

D = specific gravity of clay = 2.65

L = specific gravity of suspending liquid (distilled

water) = 1.00

d = reading of "blank."

The particle size corresponding to a given hydrometer

reading may be readily calculated by finding the various

factors that are constant in the equation:

$$D_{mm} = \sqrt{A.V}$$

where:

A = 1800 η/c-ℓ and

η = viscosity of suspending liquid in poises

c = density of suspended particles

ℓ = density of suspending liquid

D_{mm} = diameter of particles in millimeters

and $\sqrt{V} = \sqrt{Hr/T}$

where:

Hr = effective or corrected depth of hydrometer
reading

T = time of sedimentation in seconds

2. Screen Analysis

The wet screen analysis* of the clay is as follows:

	%
on 200 mesh (74μ)	8.5
on 230 mesh (63μ)	0.9
on 270 mesh (53μ)	0.2
on 325 mesh (44μ)	1.4
on 400 mesh (37μ)	1.5
under 400 mesh	87.5
TOTAL	100.0

*dry basis

3. Cumulative Size Distribution

The cumulative size distribution was calculated from information given in parts 1 and 2. The results which are plotted in Figure 1 are as follows:

% less than given size	Size μ
91.5	74
90.6	63
90.4	53
89	44
87.5	37
84	28
76	19
70	14
63	10.4
51	6.3
42	4.5
37	3.4
31	2.6

APPENDIX B

SAMPLE PREPARATION FOR ELECTRON MICROSCOPY

1. Preparation of Clay Suspension

The clay as received from the mine* is washed with distilled water through a 400 mesh. The suspension is collected in a pan and then transferred to a beaker in which the amount of water is adjusted to obtain a concentration of 1 to 5%. A few drops of ammonia are added to completely disperse the clay. The suspension is stirred and samples are taken at different time intervals to cover the desired range of sizes.

2. Preparation of Samples

Copper grids (200 or 400 mesh) are covered with a film of carbon, on which a small drop of clay suspension is deposited. A hypodermal needle can be used for that purpose or an atomizer as suggested by De Souza Santos[21] (1957, p.133). The sample is dried under the heat of a lamp and mounted on a sample holder.

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*Care should be taken to avoid any damage to the clay particles such as grinding or any other mechanical treatment.

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APPENDIX C

BENEFICIATION BY HYDROCYCLONE

A batch of clay suspension in water (density 1.21 gm/cm^3) was placed in a conical vessel with an electric stirrer (500 rpm) to maintain the slurry in suspension. The slurry was then pumped into a cyclone with a tangential inlet, with a speed of 80 liters/minute. Some recirculation was done to control the flow into the cyclone.

The beneficiated clay or overflow was taken out of the top while the underflow or sand issued at the bottom of the cyclone; both products were filtered out and the cakes dried at 100°C.

The batch consisted of

    21 kgs of clay

    49 liters of water

    30 gm of calgon*

and the products

    overflow (beneficiated clay); 13.541 kgs.

    underflow (sand)   ;   4.311 kgs.

---
*Previous experiments showed that this was the amount of dispersing agent which would permit the lowest viscosity of the suspension.

APPENDIX D

GRAIN SIZE DISTRIBUTIONS OF CLAY AND GROG

1. Halloysitic Clay

The halloysitic clay was used in the experiments at two grinding levels designated 60 mesh and 120 mesh. The particle size distributions of both were as follows:

	60 mesh %	120 mesh %
on 60 mesh (250μ)	1	....
on 70 mesh (210μ)	4	....
on 80 mesh (177μ)	5	....
on 100 mesh (149μ)	6	....
on 120 mesh (125μ)	6	1
on 150 mesh (105μ)	6	5
on 170 mesh (88μ)	22	46
on 230 mesh (63μ)	34	30
on 270 mesh (53μ)	3	2
under 270 mesh	13	16
TOTAL	100	100

Note: Screen analysis made on the clay dried.

2. Grog

The screen analysis of the grog used was as follows:

	%
on 12 mesh (1680μ)	0.1
on 14 mesh (1410μ)	0
on 18 mesh (1000μ)	47.0
on 25 mesh (710μ)	30.0
on 45 mesh (350μ)	21.0
under 45 mesh	1.9
TOTAL	100.0

$$\bar{\bar{X}} = \frac{35.056}{16} = 2.191$$

Upper $3\sigma^1$: $\bar{\bar{X}} + 1.88 \times \bar{R} = 2.191 + 0.02332 = 2.21432$

Lower $3\sigma^1$: $= 2.191 - 0.02332 = 2.16768$

Upper 1% limit: $\bar{\bar{X}} + 1.46 \times \bar{R} = 2.191 + 0.0181 = 2.2091$

Lower 1% limit: $= 2.191 - 0.0181 = 2.1729$

Upper 5% limit: $\bar{\bar{X}} + 1.03 \times \bar{R} = 2.191 + 0.0127 = 2.2037$

Lower 5% limit: $= 2.191 - 0.0127 = 2.1783$

5. **Points on the Graph**

$A_1B_1C_1$
$$\begin{array}{r} 2.187 \\ +2.213 \\ \hline 4.400 \end{array}$$

$\bar{X} = 2.20$

$R = 0.026$

$A_1B_2C_1$
$$\begin{array}{r} 2.135 \\ +2.138 \\ \hline 4.273 \end{array}$$

$\bar{X} = 2.1365$

$R = 0.003$

$A_1B_1C_2$
$$\begin{array}{r} 2.174 \\ +2.198 \\ \hline 4.372 \end{array}$$

$\bar{X} = 2.186$

$R = 0.024$

$A_1B_2C_2$
$$\begin{array}{r} 2.132 \\ +2.151 \\ \hline 4.283 \end{array}$$

$\bar{X} = 2.1415$

$R = 0.019$

$A_2B_1C_1$
$$\begin{array}{r} 2.225 \\ +2.230 \\ \hline 4.455 \end{array}$$

$\bar{X} = 2.2275$

$R = 0.005$

$A_2B_2C_1$
$$\begin{array}{r} 2.202 \\ +2.229 \\ \hline 4.431 \end{array}$$

$\bar{X} = 2.2155$

$R = 0.027$

$A_2B_1C_2$ 2.223
              +2.228
              4.451

$\bar{X} = 2.2255$

$R = 0.005$

$A_2B_2C_2$ 2.195
              +2.196
              4.391

$\bar{X} = 2.1955$

$R = 0.001$

APPENDIX E

FURTHER EXPERIMENTS WITH DIFFERENT GROG CONTENTS

Several experiments with different grog contents were carried out in order to find the correct grog-clay ratio to avoid shrinkage cracks. The results showed that shrinkage becomes excessive as it leads to cracking with 50% clay or more with this particular system of grog and clay.

The results obtained were as follows:

BULK DENSITIES OF SPECIMENS PRESSED AT

10,000 psi AND FIRED AT 1370°C

Composition	Linear Shrinkage %	Bulk Density gm/cm^3* Green	Fired	Comments
50% grog-50% clay	8.7	2.184	1.994	very slight cracking
60% grog-40% clay	8.0	2.158	1.986	good brick
70% grog-30% clay	6.6	2.089	1.951	good brick
80% grog-20% clay	3.8	1.965	1.891	good brick

*average of two specimens.

Note: The 60 mesh clay was used in these experiments.