ALLOPHANES FROM LAWRENCE COUNTY, INDIANA

W. Arthur White*

Abstract

The properties of allophane from the South Gardner Mine, Lawrence County, Indiana, are presented. The optical properties indicate that the indices of refraction are a function of the adsorbed water. The differential thermal analyses suggest that the water above 100° C. is structurally held. The *x*-ray data indicate that allophane has a more ordered structure than glass. The base exchange is high and it is assumed that the base exchange capacity is due to unsatisfied bonds. Its bonding strength is low. Its soil mechanic properties would probably be similar to those of halloysite and its ceramic properties are light burning, high shrinkage, high P.C.E. value, and low plasticity.

Introduction

This report is concerned with the data obtained in analytical experiments with nearly pure allophane from the abandoned South Gardner Mine in sec. 28, T. 4 N., R. 2 W., Lawrence County, Indiana. The samples were collected in 1947 by the writer in the company of Dr. Eugene Callaghan, then of the Indiana Geological Survey, now Director of the New Mexico Bureau of Mines, and Dr. R. E. Grim and Dr. W. F. Bradley of the Illinois Geological Survey.

Allophane is the name applied to any amorphous substance which may be present in clay materials as extremely fine material and which has an indefinite composition. Since the allophanes vary in composition their characteristics may be expected to vary from sample to sample. Allophane has attracted little attention from clay students, probably because it is rarely found in the pure state and because its presence in soils and sediments is difficult to determine. Since there are so few data on allophanes available in the literature, it seems desirable to record information for these samples. Data for additional samples are needed before ranges of composition and properties of allophane are known. It must be remembered that the data which are derived from these samples may or may not be indicative of all other allophanes.

The allophanes in South Gardner mine are of two types: one is brittle, glassy, transparent, and blue; the other is granular and pink. As soon as the samples were collected, they were put into glass jars and sealed to prevent escape of moisture, and when brought to the laboratory a little distilled water was added to prevent any loss of water.

Optical Properties

The indices of refraction of the allophane samples were determined by the oil immersion method in oils which had been checked immediately

* Associate Geologist, Division of Clay Resources and Clay Mineral Technology, Illinois State Geological Survey.

preceding the analysis with a refractometer. Samples were used: (1) as they came from the mine, (2) after drying for two days in air, (3) after being heated at 100° C. and 140° C. over night, and (4) after being heated to 500° C. The indices were also determined on a sample of glassy allophane which had dried in air for a year.

The index of some of the particles of pink allophane (as taken from the mine) was first lower than that of the oil but when determined soon again was found to be above that of the oil. This is due either to the dehydration of the mineral and the adsorption of the moisture by the oil to lower the index of the oil or to the adsorption of the oil by the mineral.

TABLE 1. OPTICAL PROPERTIES OF THE ALLOPHANES FROM LAWRENCE COUNTY, INDIANA

Treatment	H_2O*	Indices of refraction *n*
Pink allophane		
As from mine	34.69	1.398–1.423
Dried in air 48 hrs.	23.47	1.450–1.472
Heated at 100° C. over night	10.58	1.473–1.480
Heated at 140° C. over night	—	1.470–1.485
Heated up to 500° C. in 1 hr.	—	1.465–1.474
Glassy allophane		
As from mine	30.13	1.440–1.460
Dried in air 52 hrs.	25.68	1.461–1.474
Dried in air 1 yr.	20.11	1.480–1.486
Heated at 100° C. over night	11.82	1.487–1.494
Heated at 140° C. over night	—	1.484–1.494
Heated up to 500° C. in 1 hr.	—	1.465–1.482

* Water lost on drying to 140° C.

The indices of refraction of the allophane increased with the loss of water, as shown in Table 1. The material as taken from the mine had indices of refraction which varied widely ($N=1.398$ to 1.460). After the allophane dried for 2 days the indices ranged from 1.450 to 1.474. The glassy allophane which had been dried for a year had an index range of 1.480 to 1.486, which was near the average value of 1.485 given by Ross and Kerr.[1] When samples were heated to 100° C. the indices ranged from 1.473 to 1.494; when heated to 140° C. the indices ranged from 1.470 to 1.494. After samples had been heated up to 500° C. the indices ranged

[1] Ross, C. S., and Kerr, P. F., Halloysite and allophane: *U. S. Geol. Survey Prof. Paper* **185G,** 135–148 (1934).

from 1.465 to 1.482. The data in Table 1 indicate that the water driven off below 100° C. is an important factor in determining the index of refraction, but that driven off above 100° C. has little effect on the index.

Chemical Data

The chemical analyses are given in Table 2.

Table 2. Chemical Analysis of Allophanes

	1	2
SiO_2	30.23	26.68
Al_2O_3	41.81	44.95
Fe_2O_3	0.31	0.12
MgO	0.04	none
CaO	2.86	2.37
P_2O_5	9.51	10.57
SO_3	0.44	0.22
Ign.	15.56	16.21
Total	100.81	101.30
H_2O-	34.69	30.13
H_2O+	15.61	16.39
$SiO_2:Al_2O_3$	1.23	1.01

1. Pink allophane, Lawrence County, Ind., analyzed by L. D. McVicker.
2. Glassy allophane, Lawrence County, Ind., analyzed by L. D. McVicker.

Differential Thermal Analysis

Thermal analyses were run by the method and with the equipment used by Grim and Rowland.[2] A sample of each allophane as it came from the mine was heated to 1000° C. in the differential thermal furnace (Fig. 1*B* shows curves). Since there is a large amount of adsorbed water, the first endothermic reaction, which ranged from about 60° C. to 350° C., was large compared with that of other clays. Then fresh samples were heated over night in an oven to 110° C. and after cooling they were heated to 1100° C. in the differential thermal furnace (Fig. 1*A* shows curves). More energy was required to drive off the water from the preheated samples than from the unheated samples, as is shown by the fact that a temperature of from 475° to 500° C. was required to finish driving off all the water from the preheated sample. The endothermic reaction beginning about 500° C. is probably due to a trace of alunite, halloysite, or pseudowavellite. The exothermic reaction (between 1015 and 1085° C.) involves the formation of a new compound (mullite).

[2] Grim, R. E., and Rowland, R. A., Differential thermal analysis of clays and shales, a control and prospecting method: *Jour. Am. Ceram. Soc.*, **27**, 65–76 (1944), or *Illinois State Geol. Survey R. I.* **96** (1944).

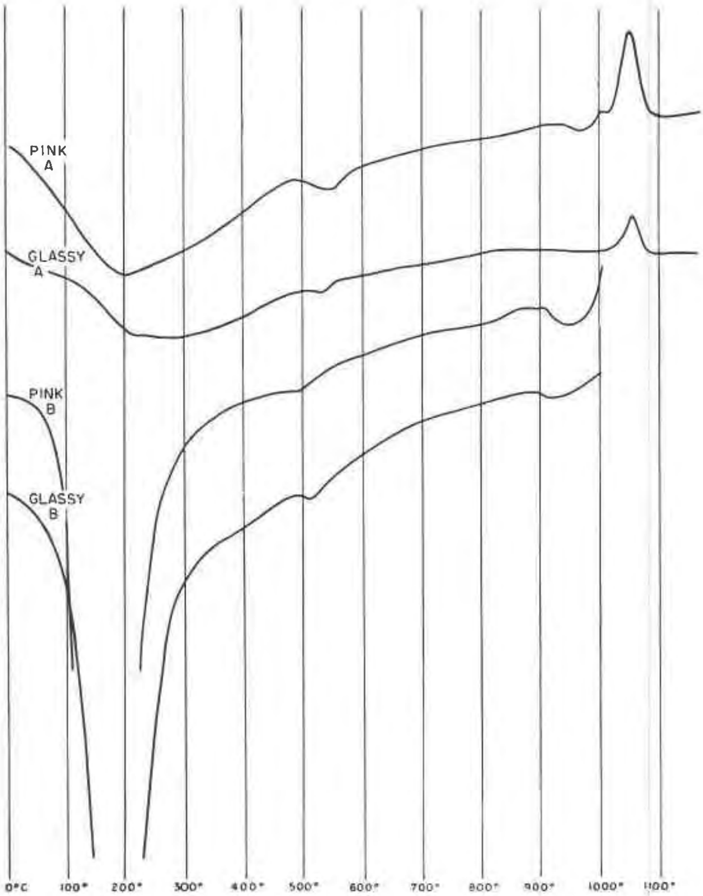
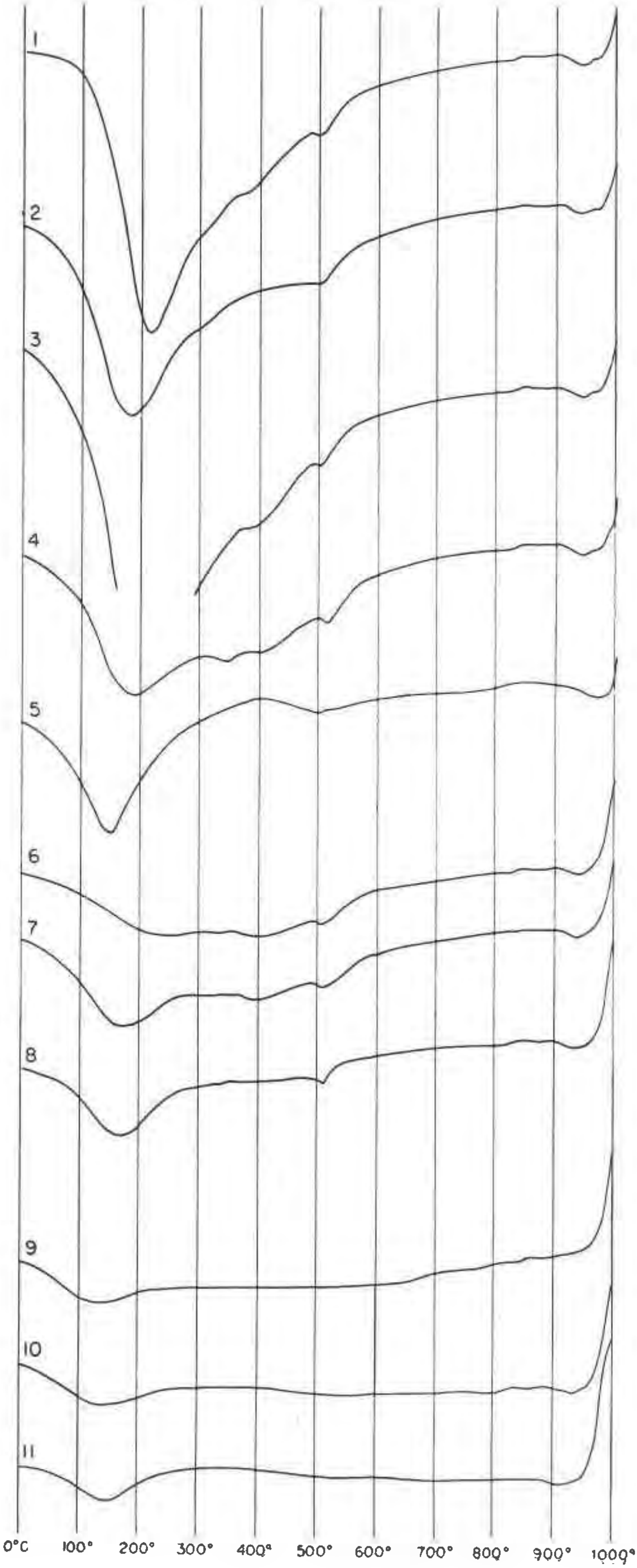


FIG. 1. Differential Thermalgram of Allophane. *A*. The allophanes were preheated at 140° C. over night before being heated in differential thermal furnace to 1100° C. *B*. The allophanes were heated in the differential thermal furnace as they came from the mine showing the large amount of adsorbed water.

DEHYDRATION AND REHYDRATION DATA

When allophane is heated to 100° C. most of the adsorbed water is driven off, but upon cooling, the water is readsorbed rapidly, as shown by the thermalgrams in Fig. 2. As allophane is heated to higher and higher temperatures, above 100° C., less and less water is readsorbed upon cooling, as shown by the thermalgrams in Fig. 2. This may indicate that allophane has some sort of open structure that can adsorb large quantities of water, but that, upon heating above 100° C., this porous network begins to collapse, owing to the fact that chemically



1
2
3
4
5
6
7
8
9
10
11
0°C
100°
200°
300°
400°
500°
600°
700°
800°
900°
1000°

combined water is being driven off. Upon cooling, probably very little, if any, water would be recombined chemically in the structure, and the amount of water that could be readsorbed by the collapsed structure would thus be reduced.

The thermalgrams suggest that almost all, if not all, the chemically combined water has been driven off below 500° C., and the water that is readsorbed is physically adsorbed for the most part.

X-Ray Data[3]

The *x*-ray powder diffraction pattern for the glassy and pink allophanes showed four diffuse very broad bands, with traces of others, and faint diffraction lines which indicate a mineral with the alunite crystallization probably pseudowavellite. Ross and Kerr[1] reported one diffuse band and traces of others. As nearly as the four bands could be measured, the first ranged from 3.5 to 3.0 Å; the second, from 2.26 to 2.08 Å; the third from 1.45 to 1.27 Å; and the fourth, from 1.22 to 1.12 Å. This would indicate that allophane has a more ordered structure than glass.

The samples of allophane were heated to 750° and 1100° C., and *x*-ray patterns were taken. The diffraction pattern of the glassy allophane having been previously heated to 750° C. showed a few faint diffraction

[3] I am indebted to W. F. Bradley of the Illinois State Geological Survey for the analysis and interpretation of the *x*-ray patterns.

←

Fig. 2. Differential Thermal Analyses of Allophanes being Preheated at Various Temperatures.

1. Glassy allophane was run immediately after being heated to 100° C. over night.
2. Pink allophane was run after sitting in air 24 hours after being heated to 100° C. over night.
3. Glassy allophane was run after standing in air 60 hours after being heated to 100° C. over night.
4. Pink allophane was run after standing 12 hours in air after being heated to 200° C. over night.
5. Glassy allophane was run after standing 4 days in air after being heated to 200° C. over night.
6. Glassy allophane was run after standing 12 hours after being heated to 300° C. for 1 hour.
7. Glassy allophane was run after standing 4 days after being heated to 300° C. for 1 hour.
8. Glassy allophane was run after standing in air 80 days after being heated to 300° C. for 1 hour.
9. Glassy allophane was run after standing 24 hours after being heated to 500° C. for 1 hour.
10. Glassy allophane was run after standing in air 6 days after being heated to 500° C. for 1 hour.
11. Glassy allophane was run after standing 84 days in air after being heated to 500° C. for 1 hour.

lines in the position and characteristic of the stronger lines of a mullite diffraction diagram indicating that mullite probably had started to form, but the diffraction pattern of the pink allophane heated to the same temperature did not show any diffraction lines indicating that no new phases had started to form. Both allophanes showed complete conversion to mullite at 1100° C. (Fig. 3).[4]

Base Exchange Capacity

The base exchange capacity of allophane was determined by the ammonium acetate method used by Bray.[5] The base exchange capacity of the glassy and pink allophanes is 69.0 and 73.5 m.e. per 100 gm. respectively, which is high for clay minerals. This high exchange capacity is probably due to unsatisfied bonds, since the crystal structure is so poorly organized. In the crystalline clay minerals (Table 3) having a high exchange capacity, the capacity is due chiefly to substitutions in the lattice; whereas in the crystalline clay minerals having a low exchange capacity, the capacity is due chiefly to unsatisfied bonds on the edges of the lattice.

Table 3. Base Exchange Capacity for Clay Minerals

Clay Minerals	me/100 gm.	Nature of Exchange Bases
Montmorillonite[6]	60–100	Substitutions in lattice chiefly.
Allophane	69–73.5	Unsatisfied bonds.
Illite[6]	20–40	Substitution in lattice and unsatisfied bonds on edges of lattice.
Attapulgite[6]	20–30	Unsatisfied bonds on edges of lattice.
Kaolinite[6]	5–15	Unsatisfied bonds on edges of lattice.
Halloysite[6]	6–15	Unsatisfied bonds on edges of lattice.

[6] Grim, R. E., Modern concepts of clay materials: *Jour. Geol.*, 50, 225–275 (1942).

Since allophane and halloysite frequently occur together, this may explain the high base exchange capacities obtained by some students of clay mineralogy for halloysite.

Bonding Strength

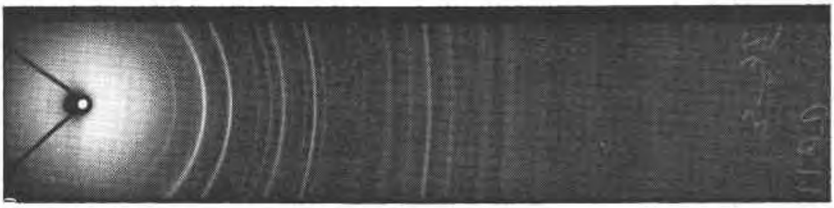
Clay-sand bonding strength tests for the pink and glassy allophanes were made by the standard procedure set up by the American Foundry-

[4] Used with permission of W. F. Bradley.

[5] Bray, R. H., Base exchange procedure: *Dept. of Agron., Ag. Exper. Station, U. of Ill. Coll. of Ag.*, Urbana, Ill., Jan. 1942 (5 pp.).

[6] Footnote in Table 3.

A



B

FIG. 3. *X*-ray Diffraction Patterns of Allophane heated to 1100° C.
A. Glassy allophane. *B*. Pink allophane.

men's Association.[7] The bonding strength for the allophanes was low compared with that of the crystalline clay minerals, as illustrated in Table 4.

TABLE 4. BONDING STRENGTH FOR CLAY MINERALS

	Clay per cent	Max. G.C.S.*
Kaolinite[8]	8	14.6
Illite[8]	8	12.7
Montmorillonite[8]		
Belle Fourche	8	24.1
Mississippian	8	30.5
Halloysite[8]	8	21.3
Attapulgite	8	7.4
Allophane	8	3.0

* Green Compression Strength.

[8] Grim, R. E., and Cuthbert, F. L., The bonding action of clays, Part I—Clays in green molding sands: *Illinois State Geol. Sur., R. I.* 102, 55 pp. (1945).

OTHER PROPERTIES

By the standard method of Atterberg for determining plasticity, the Lawrence County, Indiana, allophanes are not plastic as they will not roll into a thread $\frac{1}{8}$ inch in diameter at any water content. The soil

[7] Foundry Sand Testing Handbook, 1944 ed. Am. Foundrymen's Assoc., Chicago, Ill.

[8] Footenote in Table 4.

mechanic properties of these allophanes would in all probability be similar to those of halloysite.

The shrinkage was high. When fired to 1000° C. in the differential thermal furnace, the total shrinkage was estimated to be about 50 per cent volume shrinkage.

The burning color was white.

Although the inability of the cone to stand the blast from the P.C.E. furnace prevented determination of the fusion point, the facts that the allophanes showed very little vitrification at 1200° C. and that they have a high alumina ratio suggest that the fusion point is probably high.

The specific gravity as given by Ford[9] for allophane is 1.85–1.89.

Manuscript received Aug. 22, 1952.

[9] Ford, W. E., Dana's Textbook of Mineralogy, 3rd Ed., John Wiley and Sons, Inc., New York (1922), p. 580.