

PRETREATMENT OF SOILS AND CLAYS FOR MEASUREMENT OF EXTERNAL SURFACE AREA BY GLYCEROL RETENTION

by

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ABSTRACT

Heat treatment at 600°C has been the usual procedure for irreversible collapse of expanding clay minerals prior to determination of the external surface area of clays and soils by glycerol retention. Evidence is presented showing that this treatment is unsuitable since it greatly reduces the external surface area of certain minerals and increases that of others. Saturation with the triethylammonium cation avoids these difficulties and produces an effect analogous to the collapse of expanding minerals by stabilizing their basal spacing at 13.3 Å. This prevents the entrance of glycerol between the unit layers and confines the sorption to the external surfaces of the particles.

INTRODUCTION

In two previous reports (Kinter and Diamond, 1958; Diamond and Kinter, 1958) a method was presented for determining the surface area of clays and soils from the weight of sorbed glycerol retained by specimens after extended heating at 110°C in the presence of free glycerol vapor. For particles of clay minerals such as kaolinite, only external surfaces are available for sorption, but for expanding minerals such as montmorillonite, the glycerol is also retained on internal surfaces between the unit layers of the crystallites.

This internally sorbed glycerol forms what has been called a "mono-interlayer" complex, that is a monomolecular layer or film between two planar clay surfaces. Each molecule of glycerol in such a complex "covers" twice as much clay surface as does a molecule sorbed on external surfaces. The factor for conversion of a given weight of the internal film to values of surface area is therefore twice as large as for an equal weight of a similar film on external surfaces. For general use of the glycerol retention method with soils and clays, it is thus necessary to evaluate separately the glycerol retained on the two types of surface, unless it is known that even trace quantities of the expanding minerals are not present.

The procedure employed for this purpose was adapted from that used by Dyal and Hendricks (1950) in connection with the sorption of ethylene glycol by clays. As applied to the sorption of glycerol, this procedure consisted of determining separately the glycerol retained by an untreated sample and by a sample of the same material previously heated to 600°C. It was assumed that the heat treatment would irreversibly collapse expanding mineral lattices

so as to seal the internal surfaces against subsequent penetration by glycerol and permit sorption on only the *external* surfaces; and since the untreated material would retain glycerol on both types of surface, the difference in retention between the two samples was accordingly attributed to *internal* surfaces.

For this procedure to result in a realistic measure of the surface area of a given sample, it is obvious that the heat treatment must collapse completely and irreversibly any expanding layers present, but must not, at the same time, appreciably alter the original external surfaces of constituent particles. However, depending on the composition of the sample to be studied, one or both of these conditions may not be fulfilled. For example, in Kinter and Diamond (1958) the writers showed that with certain montmorillonites the 600°C heat treatment is not sufficient for irreversible collapse. These montmorillonites would, therefore, still sorb glycerol internally to some extent, and thus the amount attributed to external surfaces would be too high. On the other hand, temperatures above 600°C cannot be used to ensure irreversible collapse because evidence exists that this treatment sometimes would severely reduce external surface areas (Lopez-Gonzalez and Deitz, 1952).

Heat treatment at 600°C may also affect minerals other than montmorillonite. Nitrogen adsorption measurements (Gregg and Stephens, 1953) have shown that the surface area of kaolinite was reduced by about 20 percent on heating to this temperature. The present writers (unpublished data) had noted that a substantial reduction in glycerol retention is also produced with illite, but with this mineral the reduction was ascribed to irreversible collapse of expanding layers contained within the illite particles. The external surface of vermiculite, on the other hand, has been shown (Gregg and Packer, 1954) to *increase* threefold on heating to 600°C.

It is also to be expected that heating would result in pronounced increases in surface area with certain of the common accessory "nonclay" minerals of soils and clays. For example, Russell and Cochran (1950) observed that the surface area of an aluminum trihydrate closely similar to natural gibbsite *increased* from about 10 to 425 square meters per gram (m^2/g) on heating to 400°C; and a subsequent *decrease* to about 280 m^2/g occurred on heating to 600°C. Similar increases should be anticipated for the crystallized hydrous iron oxides, goethite and lepidocrocite, although conversely, heating an amorphous ferric oxide gel to 600°C has been shown (Gregg and Hill, 1953) to *reduce* the specific surface area from about 250 to 50 m^2/g .

In general, then, the value of the 600°C heating is doubtful at best for materials of such varied composition as soils and clays. In the search for a suitable substitute, it was thought that a chemical pretreatment might be found by which the entrance of glycerol molecules into the interlayer spaces of expanding minerals could be prevented, without either interfering with normal adsorption on external surfaces or reducing or increasing the external surface area of any of the minerals present.

Since exchangeable cations are known to be distributed between the unit layers of montmorillonite, attention was first given to cation exchange treat-

ments. None was found suitable, however, until, as suggested by the work of Greene-Kelly (1956), the triethylammonium cation (TEA) was tried. Greene-Kelly had reported that a montmorillonite saturated with TEA exhibited a consistent basal spacing of approximately 13.3 Å, regardless of whether the sample was air-dried, immersed in water or immersed in glycerol. In trials with several other montmorillonites, the present writers confirmed these observations and also noted that the 13.3 Å spacing was not altered when specimens were dried at 110°C or washed with water or acetone.

This apparently very stable spacing indicates a distance of about 3.8 Å between the montmorillonite layers, which would naturally exclude glycerol molecules since they are about 4.5 Å in diameter. Preliminary trials with montmorillonites indicated that saturation with TEA definitely blocked the penetration of glycerol into the interlayer spaces, and apparently did not interfere with normal adsorption on external surfaces.

The ensuing investigation of the use of TEA saturation as a replacement for the 600°C heat treatment forms the basis of the present report.

MATERIALS

The clays and soils used in the study are listed and described in Table I. They were selected to provide representatives of the principal silicate clay minerals and also one of the common hydrous oxides.

A normal solution of triethylammonium chloride used for saturating the soils and clays was prepared by neutralizing triethylamine (Eastman) with hydrochloric acid to pH 7.0 and diluting with distilled water.

EXPERIMENTAL

The retention of glycerol by the experimental materials was determined essentially as described previously (Kinter and Diamond, 1958). Briefly, the procedure as used here involved preparing duplicate 1–3 g specimens of material passing the no. 40 sieve; drying at 110°C in aluminum foil dishes and weighing to 0.2 mg; adding 10 ml of a 2 percent aqueous solution of glycerol and heating to constant weight at 110°C in a mechanical convection oven containing a constant supply of glycerol vapor at a partial pressure just below saturation. The gain in weight represents the glycerol retained and is expressed as a percentage of the 110°C oven-dry weight.

Three determinations of retention were made for each material: (a) untreated; (b) previously heated to 600°C for 4 hr; and (c) previously saturated with TEA. Saturation was accomplished by treating 10 g of material with an amount of the triethylamine chloride solution sufficient to exceed the cation exchange capacity fivefold. The material and solution were mixed thoroughly, centrifuged and the supernatant liquid decanted. This treatment produced strong flocculation with all the materials studied and gave very clear supernatant liquids with a minimum of centrifugation. After three such treatments, the material was thoroughly washed in the same manner with acetone, dried over a steam bath, and lightly pulverized.

TABLE I.—EFFECT OF PRETREATMENTS ON EXTERNAL SURFACE AREA

Sample No.	Material	Clay Mineral Type	Source	Glycerol Retention ⁶ (%)			External Surface Area (m ² /g)		
				110°C Dried	600°C Heated	TEA Saturated	Calculated from Glycerol Retention after		From Nitrogen Adsorption, BET Method
							600°C Heating	TEA Saturation	
R-145	Southern bentonite ¹	Montmorillonite	Parther Creek, Miss.	20.7	4.55	4.61	80.3	81.4	83.8 ¹
R-51	"Volclay" Wyoming bentonite	Montmorillonite	American Colloid Co.	19.0	2.56 ²	2.85	45.2 ²	50.3	—
R-164	Edgar plastic kaolin (EPK) ³	Kaolinite	Edgar Clay Co.	2.49	1.70	2.20	30.0	38.8	35.6 ³
R-165	Lustra kaolin ³	Kaolinite	Southern Clay Co.	0.81	0.72	0.85	12.7	15.0	—
R-152	Fithian illite	Illite	Fithian, Ill.	6.1	3.5	4.5	62	79	—
R-170	"Mountain Leather" ⁴	Palygorskite	Metalline Falls, Wash.	9.5	19.0	9.3	335	165	—
S-61	Ando soil ⁵	Allophane	Japan	16.2	8.3	16.2	146	293	—
PC-1110	Grizzly soil	Allophane, montmorillonite	B horizon; Crook Co., Oregon	13.0	4.4	7.0	78	124	—
PC-246	Linker soil	Gibbsite, kaolinite, soil chlorite	B horizon; DeKalb Co., Alabama	1.75	2.2	1.4	37	25	—

¹ Sample and nitrogen surface area value supplied through courtesy of V. R. Deitz, National Bureau of Standards.

² Sample heated to 700°C, since this temperature was required to secure irreversible lattice collapse.

³ Sample and nitrogen surface area supplied through courtesy of W. C. Ormsby, National Bureau of Standards.

⁴ Sample supplied through courtesy of E. B. Henderson, U.S. National Museum.

⁵ Sample supplied through courtesy of L. D. Whiteig, formerly of the U.S. Department of Agriculture.

⁶ Each glycerol retention percentage is an average of values from duplicate specimens.

Apparent values of external surface were calculated from the glycerol retained after either pretreatment by multiplying the percentage retained by the factor 17.65 ; the apparent internal surface in either case was computed by the formula :

internal surface area

$$= \left(\frac{\% \text{ glycerol retained by untreated sample}}{\% \text{ glycerol retained by treated sample}} \right) \times 35.3$$

(Diamond and Kinter, 1958). Since all calculations were made on the basis of the 110°C dry weight, specimen weights of the 600°C heated material were corrected for the loss in weight between 110°C and 600°C. A similar correction of the TEA-saturated material to the same basis would involve adjustment for the increase in weight due to the excess weight of the triethylammonium cation over that of the cation it replaced. This correction was applied only to the montmorillonite samples, since it was considered negligible for the others owing to their considerably lower cation exchange capacities.

RESULTS

Data for a comparison of the effects of the two pretreatments are given in Table 1, including experimental values of glycerol retention and the corresponding calculated values of external surface area. For two of the clays, surface area values obtained by the Brunauer–Emmett–Teller (BET) method using nitrogen sorption are also included. In the following discussion, the experimental materials are grouped according to mineral composition.

Montmorillonite

The external surface area obtained for Southern bentonite after 600°C heating agrees quite closely with that after TEA saturation. This agreement implies that with this montmorillonite, neither pretreatment significantly alters the mineral surfaces or interferes with normal adsorption, and that both effectively prevent the entrance of glycerol molecules into interlayer spaces. These implications are substantiated by the good agreement between the results for the glycerol sorption and the BET methods. The area indicated for the latter method was determined by Lopez-Gonzalez and Deitz (1952) on another specimen of the sample used in the present work.

With the Wyoming bentonite, on the other hand, it was necessary to heat to 700°C to collapse the lattice irreversibly, and the external surface area found after heating to this temperature is about 5 m²/g lower than that after TEA saturation. If this is a significant difference, it is probably due to a slight sintering effect of the heat treatment at the higher temperature.

Kaolinite

Table 1 includes data for two kaolins. With the Edgar plastic kaolin (EPK), TEA saturation resulted in a glycerol retention slightly lower than

that of the untreated material. The reduction is thought to be due to a small quantity of montmorillonite, amounting to about 1 percent. This mineral could not be identified in an x-ray diffraction examination of the whole material but was definitely detected in a very fine fraction separated by centrifugation. On the other hand, a further and substantial reduction in glycerol retention is indicated for the 600°C heat treatment. This is thought to be the result of a lowering of the surface area by the heat treatment itself, in accord with the experience of Gregg and Stephens (1953). It is also noteworthy that surface area values obtained from the glycerol retention are in good agreement with those given by the BET method for a sample from the same stock.

With the Lustra kaolin, TEA saturation did not result in a reduction in glycerol retention, indicating that this material is virtually free of montmorillonite. The 600°C pretreatment, however, produced a modest decrease in retention and surface area, again in agreement with the findings of Gregg and Stephens.

Illite

Saturation of Fithian illite with TEA reduced glycerol retention from 6.1 percent to 4.5 percent, which is interpreted as due to a collapse of expandable layers equivalent to a content of about 7 percent of interlayered montmorillonite. The indicated value of external surface area, 79 m²/g, is in good agreement with values quoted by Brooks (1955).

On the other hand, when the 600°C heat treatment was used, retention was 3.5 percent, which corresponds to an external surface of 62 m²/g. This effect closely parallels the findings of Orchiston (1954), who noted a reduction from 78 to 57 m²/g on heating Fithian illite to this same temperature.

Palygorskite

The sample of "mountain leather" consists chiefly of palygorskite, along with a small content of quartz. No montmorillonite could be identified by x-ray diffraction, in contrast to the more familiar "Georgia attapulgite" which the writers have found to contain a considerable amount. The absence of montmorillonite from the present sample is further attested by the fact that there is essentially no difference between the glycerol retention values of the untreated and the TEA-saturated materials.

In contrast to the negligible effect of the TEA saturation, the glycerol retention after 600°C heating was more than double that of the untreated material. This indicates that the heat treatment produces a large amount of new surface area, and apparently contradicts the results obtained by McCarter, Krieger and Heinemann (1950) with nitrogen adsorption measurements, which indicated no change in the surface area of the attapulgite form of the mineral on heating to this temperature. However, the results for the two adsorbates can be reconciled if the difference in molecular size is taken into account. The authors cited state that the dimensions of the structural

channels that run parallel to the long axis of the fibrous particles are such that the inner surfaces are already accessible to the nitrogen molecules in the unheated material. Therefore, the heating could not expose any additional surface of this type to nitrogen adsorption. On the other hand, it is thought that glycerol molecules are too large to enter the channels of the palygorskite before it is heated, but that the large increase in retention after heating suggests that they can then do so.

The external surface area calculated from the glycerol retention of the TEA-saturated palygorskite corresponds approximately to what would be expected from the dimensions of the individual fibers of attapulgite reported in the literature. The value of $165 \text{ m}^2/\text{g}$ given in Table 1 corresponds to an average fiber diameter of about 200 \AA ; examination of attapulgite in the electron microscope (Grim, 1953, p. 122) has indicated that the fibers are from 50 to 100 \AA thick and from 100 to 300 \AA wide.

Allophane

An Ando soil from Japan was selected for studying the surface area of allophane. This soil was shown by x-ray diffraction to consist of non-crystalline material, except for a small content of quartz and feldspar. Its DTA curve was identical to that of "allophane A" as described by Fieldes (1955, p. 341). The glycerol retention of the untreated material is almost as high as that of montmorillonites. Nevertheless, the fact that the retention is unchanged by TEA saturation is considered as further evidence that montmorillonite is not present, and that all the surface area is external.

In direct contrast, the 600°C pretreatment resulted in a reduction of retention to approximately half that of untreated or TEA-saturated specimens. This drastic effect is thought to be due to sintering, but regardless of its cause it clearly indicates that for soils and clays containing allophane, pretreatment at 600°C would lead to very large errors in surface area.

Allophane-Montmorillonite

The Grizzly soil was selected for study because x-ray diffraction indicated that it contains a large amount of amorphous material, along with an appreciable admixture of montmorillonite. Since this soil is the weathering product of materials of volcanic origin, the amorphous constituent is assumed to be allophane. Differential thermal analysis supported this interpretation and gave no indication of the presence of free hydrous oxides of iron or aluminum.

The glycerol retention data given in Table 1 are such as would be expected for a material containing montmorillonite and allophane. The retention value of the untreated material is reduced from 13.0 percent to 7.0 percent by the effect of the TEA saturation on montmorillonite; however, with heat treatment alone a retention of 4.4 percent was obtained, indicating some destruction of the surface area of the allophane constituent as a result of heating. Accordingly, in estimating the external surface area of this soil, a seemingly very low value of $78 \text{ m}^2/\text{g}$ is obtained after the heat treatment, whereas a more realistic value of $124 \text{ m}^2/\text{g}$ is given by TEA saturation.

The difference in retention of the untreated and the TEA-saturated soil indicates a montmorillonite content of about 25 percent. This is in substantial accord with the x-ray evidence.

Hydrous Oxides in Soils

The clay fraction of Linker soil, which was included to represent materials containing hydrous oxides, was shown by x-ray diffraction and DTA to consist largely of gibbsite, along with kaolinite and a soil chlorite as accessory minerals. A small reduction in the glycerol retention is noted for TEA saturation. If this is interpreted as due to internal surface, it corresponds to a little more than 1 percent of expandable layers, presumably contained as mixed layers in the soil chlorite.

In contrast to most of the other materials studied, the Linker soil was found to *increase* in retention as a result of the 600°C treatment. This can be attributed to an increase in surface area from the decomposition of the gibbsite, in accord with the work of Russell and Cochran (1950).

An analogous effect was noted for a relatively pure mineralogical sample of lepidocrocite, which showed an increase in retention from 0.3 percent, for the untreated material, to 3.0 percent for specimens previously heated to 450°C. Insufficient lepidocrocite was available for a thorough study, but the data for both of these materials indicate that the 600°C heat treatment is clearly unsuitable for soils and clays containing the crystalline hydrous oxides of iron or aluminum.

Effect of Pretreatment on Estimation of Internal and Total Surface Areas

In addition to the effects of the 600°C heat treatment on *external* surface areas, as discussed above, there are corresponding errors in the calculations of *internal* and *total* surface areas. Values of internal and total surface areas for both the 600°C heating and the TEA saturation treatments were calculated from the data in Table 1 and are presented in Table 2. Internal surface areas were calculated by the formula given earlier; the total area is, of course, the sum of the internal and external areas.

From the data given in Table 2, it is seen that for those samples having internal surface, the internal surface areas for the 600°C treatment differ quite widely from those for TEA saturation, except for the montmorillonite samples. In estimating the total surface area, on the other hand, the method of calculation itself provides a compensating mechanism, so that, except for the materials containing palygorskite or allophane, differences for the two pretreatments are not large.

CONCLUSIONS

The evidence presented indicates that when soils and clays are heated at 600°C as a pretreatment for the collapse of montmorillonite in determination of external surface area by glycerol retention, the external surface area of

TABLE 2.—EFFECT OF PRETREATMENTS ON INTERNAL AND TOTAL SURFACE AREAS CALCULATED FROM GLYCEROL RETENTION

Sample No.	Material	Clay Mineral Type	Internal Surface Area (m ² /g) Calculated from Retention, Using:		Total Surface Area (m ² /g) Calculated from Retention, Using:	
			600°C Heating	TEA Saturation	600°C Heating	TEA Saturation
R-145	Southern bentonite	Montmorillonite	570	568	650	649
R-51	Wyoming bentonite	Montmorillonite	580	570	625	620
R-164	Edgar plastic kaolin	Kaolinite	28	10.2	58	49
R-165	Lustra kaolin	Kaolinite	3.2	0	15.9	15.0
R-152	Ft.ian illite	Illite	92	56	154	135
R-170	"Mountain Leather"	Palygorskite	0	0	335	165
S-61	Ando soil	Allophane	278	0	424	293
PC-1110	Grizzly soil	Allophane, montmorillonite	304	212	382	336
PC-246	Linker soil	Gibbsite, kaolinite, soil chlorite	0	12.3	37	37

several other associated minerals is seriously affected and a complete collapse of montmorillonite is not necessarily obtained. This pretreatment accordingly may introduce large errors in surface area measurements, and it therefore is unsuitable.

On the other hand, the data show that pretreatment by saturation with triethylammonium cation effectively prevents adsorption of glycerol on the internal surfaces of expanding clay minerals, but does not alter external surfaces nor otherwise interfere with their normal adsorption of glycerol. Triethylammonium saturation thus permits accurate measurements of surface area, and it therefore is suitable for general use with soils and clays.

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