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SURFACE AREA MEASUREMENTS OF CLAY MINERALS BY GLYCEROL SORPTION ON A THERMOBALANCE

FRITZ T. MADSEN

Laboratory for Clay Mineralogy, Institute for Foundation Engineering and Soil Mechanics, Swiss Federal Institute of Technology, CH-8092 Zurich (Switzerland)

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ABSTRACT

Glycerol-treated montmorillonite gradually loses one layer of the two-layer glycerol complex upon heating to 150–200°C, forming a monolayer complex with a sharp X-ray reflection at about 14 Å. This complex is quite stable on further heating to about 230–250°C. Above 250°C the monolayer complex breaks down rapidly. A gravimetric method has been used to determine the weight of the glycerol monolayer. The procedure involves addition of a 10% glycerol solution to a dried and weighed sample of clay in a platinum crucible followed by a heating and weighing procedure in a thermoanalyzer (Mettler). The method was used to calculate the internal and external surface area of different clays.

INTRODUCTION

Various authors have investigated the possibility of carrying out surface measurements on clay minerals by glycerol sorption. In the procedure of Diamond and Kinter[1, 2] montmorillonites dried to constant weight at 110°C were wetted with a 2% solution of glycerol in water and then heated to constant weight at 110°C in an oven containing a source of free glycerol. The initial complex readily lost glycerol and formed a monolayer complex with *d*(001) spacing of about 14 Å persisting at constant weight for a considerable time. The weight of retained glycerol was used for calculating the surface area of montmorillonite. Details of this technique were modified by Mehra and Jackson[3] and Milford and Jackson[4] and were summarized by Jackson[5]. They recommend use of a Mg-saturated sample kept at 130°C in vacuum at a constant vapour pressure of glycerol. The disadvantages of the above-mentioned methods are the time-consuming weighing procedure and the uncertainty in the conditions forming the glycerol monolayer. In the method outlined below, the weighing procedure is simplified by using a thermoanalyzer and, continuous heating makes the need for a preselected equilibrium temperature superfluous.

METHOD

Amorphous coatings of iron oxides were removed by the method of Mehra and Jackson[6], followed by Ca-saturation and freeze-drying. The following unfractionated samples were investigated: 1. Kaolin, Georgia, low-crystl.; 2. Kaolin, Georgia, well-crystl.; 3. Montmorillonite, Wyo.; 4. Montmorillonite, Ariz.; 5. Montmorillonite, Texas; 6. Hectorite, Calif.; 7. Illite, France, Massif Central.

Samples 1–6: Source Clay Minerals Repository, Dept. of Geology, University of Missouri, Columbia, Miss.

Approximately 0.1 g of clay was placed on a plateshaped crucible (16 mm diameter) and weighed to 0.1 mg. To get the dry weight the sample was heated at 1 °C min^{-1} to 110°C to constant weight in the thermoanalyzer. After cooling to room temperature, 0.5 ml glycerol solution (10% glycerol in distilled water) were added and the sample kept in saturated glycerol vapour at 105°C overnight to form the two-layer glycerol complex. After cooling to room temperature, followed by weighing, the sample was heated in an air stream (1.9 l h^{-1}) at 1 °C min^{-1} until the monolayer complex was fully developed. Normally between 100 and 170°C a rapid loss of glycerol (about 0.5 mg min^{-1}) could be observed (Fig. 1). From 170 to 200°C the weight loss decreased and between 200 and 230°C it was only 0.08 mg mm^{-1} followed by an increase in weight loss above 230°C (about 0.15 mg min^{-1}). It was assumed that the monolayer glycerol complex was fully developed when the TG-curve approached a straight line, indicated in Fig. 1 by an arrow. Subtracting the weight loss during heating to this temperature the weight of the adsorbed monolayer complex was obtained from which the surface area in m^2 g^{-1} of the dry weight (110°C) of the sample could be calculated in the following way:

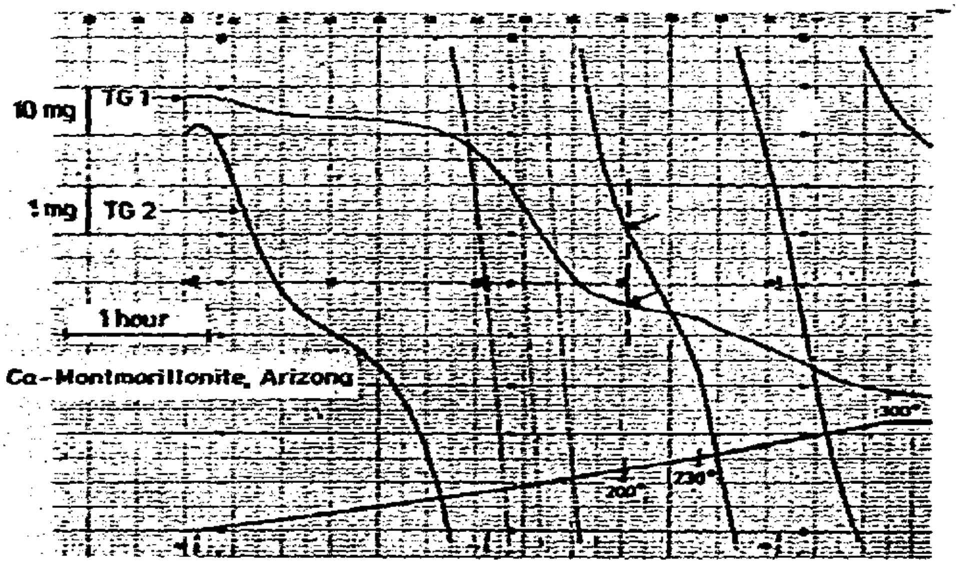

Fig. 1. TG run of a glycerol-treated Arizona montmorillonite on the Mettler thermoanalyzer. Heating rate, 1 °C min^{-1}.

$$\text{area of the glycerol monolayer at } 200^{\circ}\text{C} = \frac{0.885\ \text{cm}^3\ \text{g}^{-1}}{4.5 \cdot 10^{-8}\ \text{cm}} = 1967\ \text{m}^2\ \text{g}^{-1}$$

The density of glycerol at 200°C amounts to 1.13 g cm^{-3}. The thickness of the monolayer was assumed to be 4.5 Å. The glycerol retention of 1% is then equivalent to a monolayer area of 19.67 m^2. If the monolayer is between two unit layers of a swelling clay mineral the surface covered by the monolayer is twice the area of the monolayer itself, i.e., 3934 $\text{m}^2\ \text{g}^{-1}$. The following example shows the calculation of the total specific surface area of the montmorillonite from Wyoming (sample 3):
glycerol monolayer retention 17.61%
surface area of the monolayer = $17.61\% \cdot 39.34\ \text{m}^2\ \text{g}^{-1}\ \%^{-1} = 693\ \text{m}^2\ \text{g}^{-1}$
The external surface, determined by BET using nitrogen after drying at 150°C and 10^{-6} torr overnight, is calculated twice and should be subtracted to obtain the total surface of the montmorillonite:
$(693 - 31)\text{m}^2\ \text{g}^{-1} = 662\ \text{m}^2\ \text{g}^{-1}$.

RESULTS

The results of the determination of the specific surface area by glycerol sorption and by BET are presented in Table 1. Mean and standard deviation of three measurements.

TABLE 1

SPECIFIC SURFACE AREA BY GLYCEROL SORPTION AND BET

Sample	*Specific surface area ($m^2\ g^{-1}$)*		
	Glycerol retention (%)	*Total area by glycerol*	*Ext. area by BET*
1. Kaolin, Georgia, low-crystl.	1.26 ± 0.21	25 ± 4	24
2. Kaolin, Georgia, well-crystl.	0.81 ± 0.11	16 ± 2	10
3. Montmorillonite, Wyo.	17.61 ± 0.57	662 ± 22	31
4. Montmorillonite, Ariz.	23.19 ± 0.44	820 ± 18	92
5. Montmorillonite, Texas	17.30 ± 0.63	599 ± 24	82
6. Hectorite, Calif.	13.83 ± 0.30	486 ± 12	58
7. Illite, France	4.94 ± 0.16	97 ± 3	115

The TG-curve of the glycerol treated samples 4, 1 and 7 are represented in Figs. 1–3.

DISCUSSION

The most delicate part of the method will be to find the temperature at which the glycerol monolayer will be fully developed. It is assumed that the monolayer will be formed completely if the TG 2-curve, after decomposition of the two-layer

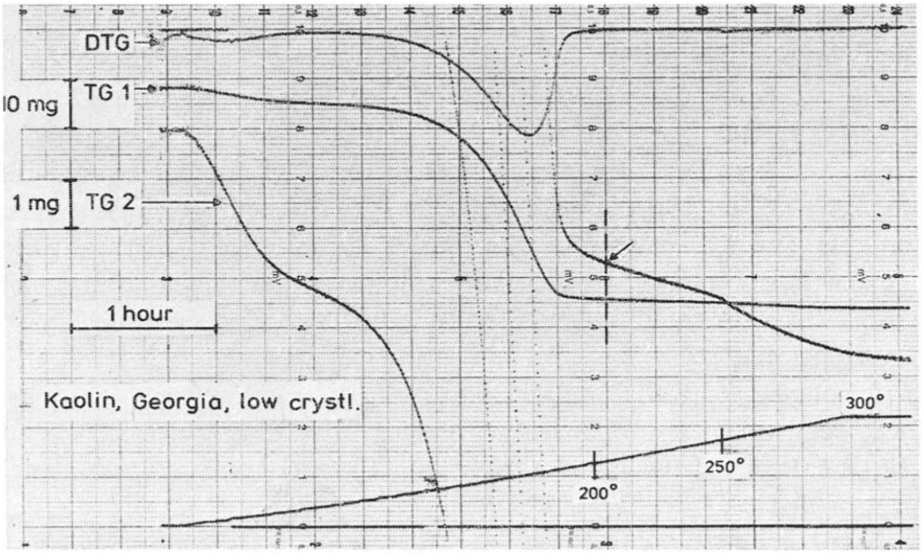

Fig. 2. TG run of a glycerol-treated Georgia kaolinite (low crystl.) on the Mettler thermoanalyzer. Heating rate, 1 °C min^{-1}.

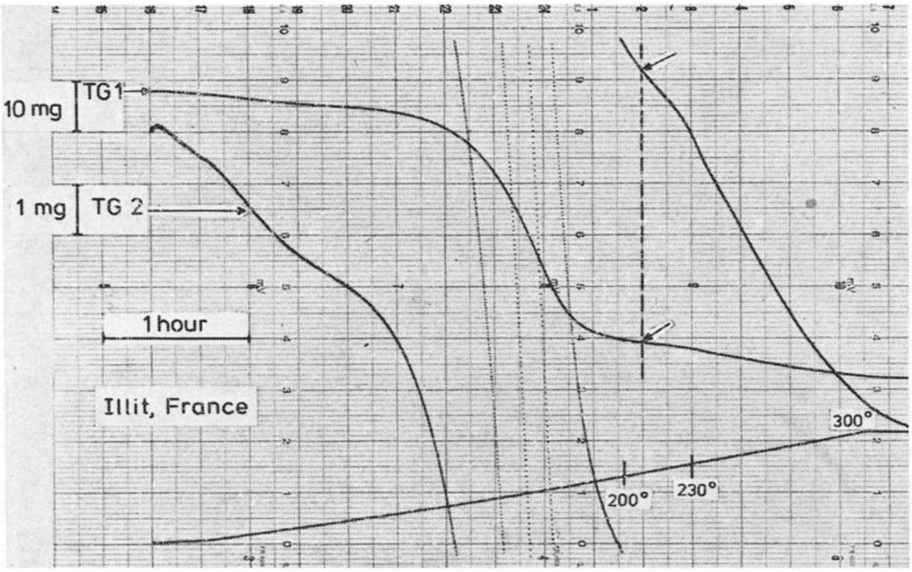

Fig. 3. TG run of a glycerol-treated illite (France) on the Mettler thermoanalyzer. Heating rate, 1 °C min^{-1}.

complex, approaches a straight line, forming some kind of a plateau before the decomposition of the monolayer complex starts. This temperature in most cases was about 200°C (Figs. 1–3). The weight of the monolayer is to be determined by subtracting the weight loss of the glycerol treated sample during heating to about 200°C and the weight of the dried (110°C) sample from the weight of the sample after glycerol treatment. Therefore, it is very important not to lose any of the freeze-dried clays. To avoid such an error, the clay has to be slightly compressed in the crucible. Furthermore, one has to take into consideration any change in the weight of the dried sample not treated with glycerol during heating from 110 to 200°C. Should there be any indication of such a change in weight, for instance the loss of water, it has to be determined and taken into account for the calculation of the specific surface area. For the determination of the dry weight (110°C) of the sample one has to use a clean oven, i.e., the adsorbed glycerol has to be removed by washing the oven with water, followed by acetone and drying in an air flow. Some clays partially lose their swelling properties during drying at 110°C. In such cases the dry weight has to be determined with separate samples.

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