



# The Amounts of Water Adsorbed to the Surface of Clay Minerals at the Plastic Limit

Aleksandra Gorączko\*, Andrzej Olchawa\*\*

\* Faculty of Civil and Environmental Engineering and Architecture, UTP University of Science and Technology, Al. Prof. S. Kaliskiego 7, 85-796 Bydgoszcz, Poland, e-mail: agora@utp.edu.pl;

\*\*The State University of Applied Sciences in Elbląg, ul. Grunwaldzka 137, 82-300 Elbląg, Poland, e-mail: andyolchawa@wp.pl

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## Abstract

The paper presents results of a study on the amount of water associated with the solid phase of the clay water system at the plastic limit. Two model monomineral clays, namely kaolinite, and montmorillonite, were used in the study. The latter was obtained by gravitational sedimentation of Na-bentonite (Wyoming).

The calculated mean number of water molecule layers on the external surface of montmorillonite was 14.4, and water in interlayer spaces constituted 0.3 of the water mass at the plastic limit.

The number of water layers on the external surface of kaolinite particles was 63, which was related to the higher density of the surface electrical charge of kaolinite compared to that of montmorillonite.

The calculations were made on the basis of the external surface area of clays and the basal spacing at the plastic limit measured by an X-ray diffraction test. The external surface area of clays was estimated by measuring sorption at a relative humidity  $p/p_0 = 0.5$ .

**Key words:** clays, liquid limit, plastic limit

## 1. Introduction

The Atterberg limits are characterized by plastic and liquid limits. The liquid limit represents the minimum water content at which soil particles flow under their own weight. The plastic limit is the minimum water content at which soil is moulded without breaking. The Atterberg limits are used in geotechnical engineering for the identification, description and classification of soils.

There are several papers discussing mechanisms controlling the liquid limit of soils (Sridharan and Rao 1975, Sridharan et al 1986, Muhuntanan 1991, Dolinar and Trauner 2004, 2005, Olchawa, Gorączko 2012). It has been found that the liquid limit is affected by the valency of exchangeable cations and by the specific surface area.

The conclusions with regard to the mechanism controlling the plastic limit are rather scarce.

White (1958) studied plastic limits in monomineral and monoionic clays – montmorillonite, illite and kaolinite. Plastic limits, depending on the exchangeable cation, ranged from 53 to 97% for montmorillonite, from 35 to 43% for illite and from 26 to 48% for kaolinite. The mean value of the plastic limit for  $\text{Ca}^{2+}$  montmorillonite was 68%, and that for  $\text{Na}^+$  montmorillonite was 91%. The corresponding values for  $\text{Ca}^{2+}$  and  $\text{Na}^{1+}$  kaolinites were 31% and 27%.

Paszyc (1960) studied the effect of the cationic composition of an exchangeable complex of bentonite from Zrecze Małe (Poland) on the plastic limit. The external specific surface area of the bentonite was  $\text{ESS} = 117 \text{ m}^2/\text{g}$ . Plastic limits determined for two monoionic  $\text{Na}^+$  and  $\text{Ca}^{2+}$  bentonites was  $69.9 \pm 0.3\%$  and  $66.1 \pm 0.3\%$ , respectively.

Yong and Warkentin's (1966) tests showed that the plastic limit varied much less than the liquid limit did. They also concluded that the plastic limit increased as the surface area of the clay increased, but not in a direct proportion.

Raymond et al (1975) studied the plastic limits of monoionic and monomineral clays (kaolinite, illite and montmorillonite). They showed that plastic limits increased with increasing external specific surface area.

Locat et al (1984) demonstrated a strong relationship between the specific surface area of Canadian marine clays and the plastic limit.

Sridharan et al (1986) showed that the cation valency and hydrated ionic radii influenced the plastic limit. The plastic limits of monoionic bentonites with  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  were 19.2, 40.6 and 57.8%, respectively.

Sridharan et al (1988) analysed plastic limits of nine kaolin soils with divalent cations and found that an increase in the plastic limit was accompanied by an increase in the specific surface area. Di Mao and Fenelli (1994) studied plastic limits of kaolinite, bentonite and mixtures of the two minerals. Plastic limits for kaolinite and bentonite were 37.8% and 55.2%, respectively. Plastic limits for mixtures with 25, 50, 60 and 75% of bentonite were 34.4, 37.8, 44.3 and 48.9%, respectively.

Grabowska-Olszewska (2003) investigated the physical properties of a mixture of two model clays – kaolinite and both  $\text{Ca}^{2+}$  and  $\text{Na}^+$  montmorillonites. Results of her study showed a significant influence of the specific surface area and a small effect of cationic composition on the value of the plastic limit.

Dolinar and Trauner (2004, 2005) determined the amounts of free water at the plastic limit and the amounts of firmly adsorbed water on the external surface area of clay minerals.

For minerals that do not swell internally, moisture is the sum of free water  $w_{ef/PL} = 23.16\%$  and firmly adsorbed water, whose thickness on the external surface of a particle is 2.7 nm (approx. 10 layers of water molecules). For swelling minerals, moisture is the sum of free water, adsorbed water and interlayer water. It was found in the previous studies that the plastic limit depends primarily on the external surface

area as well as on the type of the clay mineral (i.e. non-swelling or swelling) and its exchangeable cation composition.

The plastic limits of sodium montmorillonites are higher compared with calcium montmorillonites. This is certainly related to the higher content of water in the inter-layer spaces of sodium montmorillonites (Liu et al 2010, Yan et al 2012). The plastic limits of calcium kaolinites are slightly higher than those of sodium kaolinites, probably because of the radius of hydrated  $\text{Ca}^{2+}$  is larger than that of hydrated  $\text{Na}^{+}$  (Sridharan 2002).

The aim of the paper was to describe a method of determining the quantities of water bound to the surface of swelling and non-swelling clay minerals at the plastic limit.

## 2. Materials and Methods

Analyses of the amount of water in clays equal to the plastic limit were made for two standard clays: montmorillonite (W.B.) prepared by sedimentation of bentonite from Wyoming (USA) and kaolin from Sedlec (K.S.) (Czech Republic).

The plastic limit (*PL*) was determined by the rolling thread test (CEN ISO/TS 17892-12: 2004). A thread was rolled at a light pressure with the palm and fingers until its diameter reached 3 mm. This procedure of rolling and re-rolling was continued until the thread started to crumble, just when a diameter of 3 mm was reached. Plastic limits in clays were measured 12 times ( $N = 12$ ). The arithmetic mean of  $N$  determinations of *PL* was used for analyses. Particle size distribution was determined by the hydrometer method (CEN ISO/TS 17892-4:2004).

The bulk mineralogical composition of clays and the basal spacing were determined by means of X-ray diffraction (XRD). Oriented kaolin and montmorillonite samples with a water content equal to the plastic limit were scanned in a Seifert apparatus with a URD-6 goniometer using  $\text{CuK}\alpha$  radiation (working at  $\text{CuK}\alpha$  line) with an Ni filter. Figure 1 shows the diffraction patterns of the clays. The types and content of exchangeable cations in the kaolin were determined by the method described in detail by Yan Li et al (2012).

The physical and mineralogical characteristics of the clays are listed in Table 1. The content of exchangeable cations is given in Table 2.

**Table 1.** Physical and mineralogical characteristics of the clays

Clay	Plastic limit, <i>PL</i>	External surface area, ESS	Particle size distribution, %			X-ray diffraction mineralogy
	%		$\text{m}^2/\text{g}$	Sand	Silt	
W.B.	72.0	127.5	0	3.5	96.5	Montmorillonite, quartz
K.S.	33.1	19.8	0	37.0	63.0	Kaolinite, illite, quartz, montmorillonite

**Table 2.** The content of exchangeable cations [cmol/kg]

Clay	Na <sup>+</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>
K.S.	0.50	8.91	0.38	0.81
W.B.*	54.10	19.91	2.69	7.00

\* After Carlson (2004)

The external specific surface area (ESS) of clays was determined with the sorption test at a relative water vapour pressure  $p/p_0 = 0.5$  [Stępkowska 1977, Olchawa 1994] after a preliminary exchange of cations present in the natural complex for potassium ions K<sup>+</sup>. After such an exchange, the interlayer surface of clay minerals is unavailable for the molecules of sorbed water, and the sorption of water vapour may take place only on the external surface. The external specific surface area was calculated from the equation

$$ESS = \frac{WS(0.5)}{n \cdot \varphi \cdot \rho}, \quad (1)$$

where:

- $WS(0.5)$  – the hygroscopic water content determined at a relative water pressure  $p/p_0 = 0.5$ ,
- $n = 1.9$  – the number of layers of water molecules on the external surface of a particle at a relative humidity  $p/p_0 = 0.5$  (Stępkowska 1977),
- $\varphi = 2.76 \cdot 10^{-10}$  m – the diameter of a water molecule (Chełmicki 2003),
- $\rho = 1.27 \text{Mg} \cdot \text{m}^{-3}$  – the density of water adsorbed from the gas phase (Stępkowska 1977).

Based on the basal spacing  $d_{001}$ , the number of water layers in interlayer spaces was adopted after (Meunier 2005).

Assuming that the ratio of total (TSS) to external (ESS) specific surface areas measured by the adsorption or desorption of water is 5.5 (Olchawa 1998), the internal surface of montmorillonite  $ISS = 4.5 \text{ ESS}$ .

The mass of water in interlayer spaces of 1 g of clay was calculated according to the equation

$$w_{in} = 0.5 \cdot ISS \cdot n_i \cdot \varphi \cdot \rho, \quad (2)$$

where:

- $ISS$  – the internal surface area of clay;  $\text{m}^2/\text{g}$ ,
- $n_i$  – the mean number of layers of water molecules in interlayer spaces,
- $\varphi$  – the diameter of a water molecule adopted as  $2.76 \cdot 10^{-10}$  m,

$\rho$  – water density adopted as  $1 \text{ Mg} \cdot \text{m}^{-3}$  (water sorbed from the liquid phase).

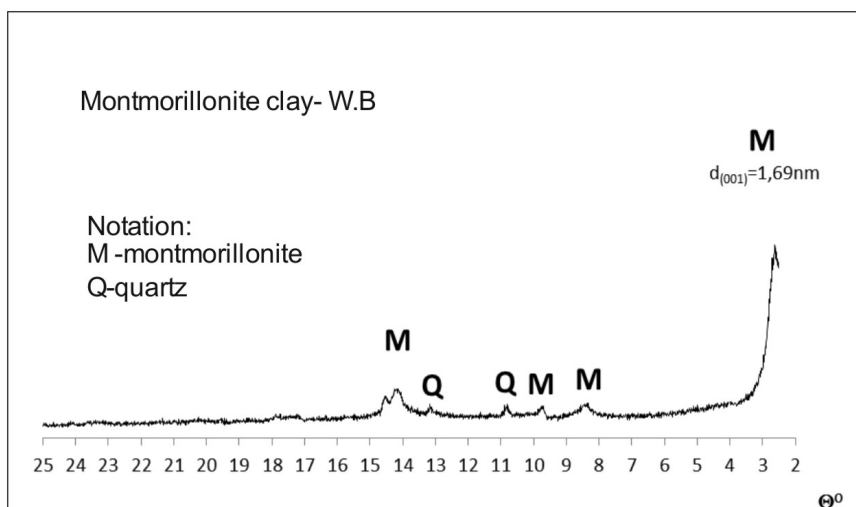
The mean number of layers of water molecules on the external surface of clay particles was calculated from the equation

$$n_e = \frac{w_p - w_{in}}{\varphi \cdot \rho \cdot ESS}. \quad (3)$$

Explanations as above.

### 3. Results

The X-ray diffraction pattern of W.B. clay showed that montmorillonite was the dominant clay mineral with quartz present in small amount. The XRD analysis of K.S. clay showed that kaolin is predominantly composed of kaolinite with trace amounts of illite, montmorillonite and quartz. (Fig. 1, 2).



**Fig. 1.** X-ray diffraction pattern of montmorillonite (W.B.) Soil sample moisture equal to the plastic limit

The basal spacing of montmorillonite determined in diffraction analyses was  $d_{001} = 1.69 \text{ nm}$ . The number of layers of water molecules in interlayer spaces was estimated after Meunier (2005). The mean number of layers of water molecules on the external surface calculated according to (3) was 13.7. The ratio of the mass of water on the external surface of particles to that in interlayer spaces was 2.07, and the ratio of the mass of water on the external surface area of particles to the total water mass was 0.3.

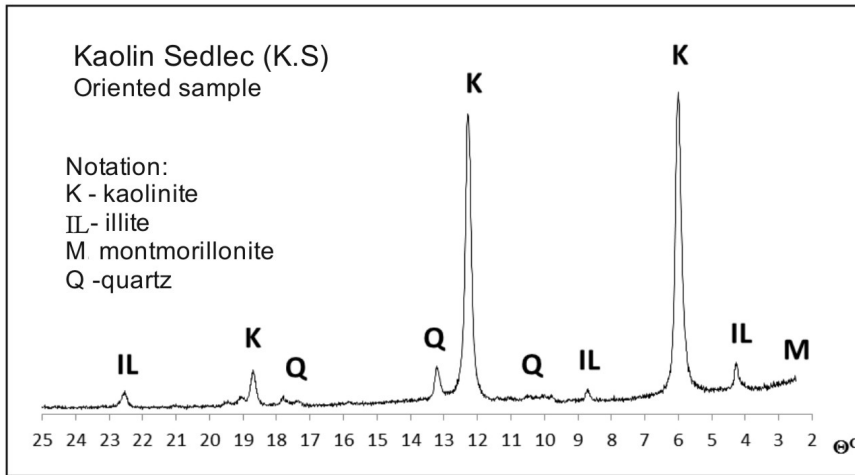


Fig. 2. X-ray diffraction pattern of kaolinite K.S.

What is worth noting that the ratio may assume a different value for another composition of exchangeable cations.

The mean number of layers of water molecules on the external surface of calcium kaolinite was 60.3. The ratio of the mass of water on 1 m<sup>2</sup> of the external surface of kaolinite to the mass of water on the same surface of montmorillonite was 4.7, which is probably related to the higher density of the surface electrical charge of kaolinite (Sheng et al 1994). The corresponding calculations are presented in Table 3. Figure 3 presents a scheme of water bound with particles of clay minerals in a water-clay system with a water content equal to the plastic limit.

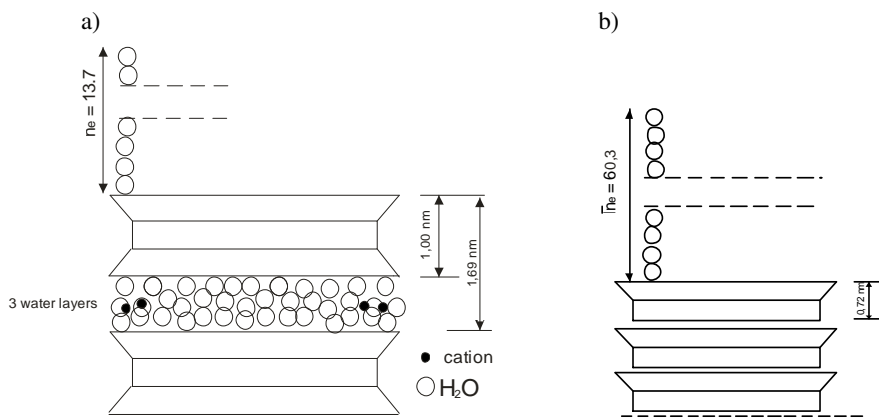
**Table 3.** Calculated quantities of water bound to external and internal surfaces of clay minerals with a water content equal to the plastic limit

Clay	ESS	ISS = 4.5 · ESS	$d_{001}$	$\Delta d_{001}$	$n_i^*$	$w_{in}$	$w_e = w_p - w_{in}$	$n_e$
	m <sup>2</sup> ·g	m <sup>2</sup> ·g	nm	nm	[–]	%	%	[–]
Montmorillonite – W.B.	127.5	573.7	1.69	0.690	3.00	23.7	48.3	13.7
Kaolinite – K.S.	19.8	–	0.73	0	0	0	34.0	60.3

\* after Meunier (2005)

Plastic limits calculated from external specific surfaces (ESS) of clays measured by water sorption and calculated with equations proposed by Dolinar (2012) were 79.0 and 28.5% for montmorillonite and kaolinite, respectively. These values are comparable with those measured experimentally in clays studied here.

The highest plastic limits are characteristic of montmorillonites saturated with Na<sup>+</sup> ions. If the theoretical surface of montmorillonite equals 771.4 m<sup>2</sup>/g (Meunier 2005), and particles are composed of 6 unit layers, the external specific surface area



**Fig. 3.** A scheme of the mean number of layers of water molecules in interlayer spaces and on the external surface of montmorillonite (a) and kaolinite (b) particles with a water content equal to the plastic limit

of such a particle is  $ESS = 128.6 \text{ m}^2/\text{g}$ . Assuming that the number of molecule layers in the interlayer spaces of monoionic sodium montmorillonites equals 3, the plastic limit estimated with the above equations should not exceed 73%. Higher values given in the literature for sodium montmorillonite (e.g. 91.0% in White 1958) may result from inaccurate measurements.

#### 4. Conclusions

The results obtained pertain to two monomineral clays with cationic composition given in Table 2. For the water content equal to the plastic limit, the water mass per  $1 \text{ m}^2$  of the external surface of kaolinite is 4.5 times the water mass per the same surface of montmorillonite. This is probably related to the higher density of the surface electrical charge of kaolinite. Charge density was not considered so far in the analyses of factors affecting the plastic limit.

The mass of water in the interlayer spaces of montmorillonite constitutes about 0.3 of the total water mass at the plastic limit. For another composition of exchangeable cations, the share of interlayer water in the total moisture might be different.

The theoretical plastic limit of Na-montmorillonite cannot be higher than 73%. Higher values given in the literature may result from inaccurate measurements.

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