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D – data interpretation
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The relationship between the liquid limit of clayey soils, external specific surface area and the composition of exchangeable cations

Andrzej OLCHAWA¹⁾ BDEF, Aleksandra GORĄCZKO²⁾ ACDF

¹⁾ University of Technology and Life Sciences, Department of Geotechnics, al. prof. S. Kaliskiego 7, 85-789 Bydgoszcz, Poland; tel. +48 52 340-84-08, e-mail: andyolchawa@wp.pl

²⁾ University of Technology and Life Sciences, Department of Geotechnics, al. prof. S. Kaliskiego 7, 85-789 Bydgoszcz, Poland; tel. +48 52 340-81-87, e-mail: agora@utp.edu.pl

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Abstract

The liquid limit – wL , the external surface area – S_e , the concentration of exchangeable cations – Z_i and the cation exchange capacity – CEC of seventeen clayey soils were determined. Finding the correlation between the liquid limit, external specific surface area and exchangeable cation concentration was the aim of this study. Experimental study performed using soils of the external surface area within the range of 4.1 to 118.5 m²·g⁻¹.

The relative content of sodium cation (i.e. Na⁺/CEC) varying between 0.03 and 1.0.

Obtained results point to statistically significant relationship between these three properties. The greatest predictive power of linear regression was found for soils of external specific surface area larger than 60 m²·g⁻¹.

For the soils of comparable external surface area, the liquid limit increase with increasing the ratio of the content of sodium cation to the cation exchange capacity – Na⁺/CEC. For the soils of comparable composition of exchangeable cations the liquid limit increase with increasing the external surface area.

These relationships indicates that interparticle forces have a prominent role in determining liquid limit of clayey soils.

Key words: cation exchange capacity, clayey soils, external surface area, exchangeable cations, liquid limit

INTRODUCTION

The Atterberg limits are widely used to classify soils and are correlated with other soil properties like swelling pressure, hydraulic conductivity, soil moisture after swelling process completion, shrinkage or shear strength [CHEN 1988; HEAD 1992; STĘPKOWSKA-PASZYC 1960; VAN DER MERWE 1964]. Studies on the factors affecting the liquid limits showed that the long-range interactions i.e. the diffusion double layer pressure and van der Waals attraction pressure play the decisive role [SRIDHARAN *et al.* 1988].

For constant composition of cations in natural exchangeable complexes of both natural and model soils, the liquid limit increases with the increase of specific surface area of the soil [LUTENEGGER, CERATO 2001; MUHUNTHAN 1991; YUKSELEN-AKSOY, KAYA 2010]. Since electro-kinetic processes in biphasic systems water – clayey soil proceed mainly in the diffusion layers of clay minerals, one may assume that the factor determining liquid limit will not be the total surface area of soil but their external specific surface area S_e .

In model soils with varying composition of exchangeable cations the liquid limits increase with the

increase of sodium content in relation to bi- and/or trivalent cations [STĘPKOWSKA-PASZYC 1966]. Based on literature data one may thus assume that the liquid limit depends on the external specific surface area of the soil and on the composition of exchangeable cations in natural exchangeable complex. An attempt to estimate these correlations based on experimental results was the aim of this study.

MATERIAL AND METHODS

Experimental studies were performed using two groups (natural and model) of soil samples. Model

soils were prepared by partial or total exchange of calcium ion for Na^+ , Mg^{2+} , Fe^{3+} , Al^{3+} in activated bentonite from Zrecz Mały (Z.M.) or for Na^+ in activated kaolinite from Sedlce (K.S.). A list of samples and places of their collection are given in Table 1.

The external specific surface area S_e of all soils, with the exception of clays from Bydgoszcz, was determined with the sorption test at the relative water vapour pressure $p/p_o = 0.5$ [OLCHAWA 1994; 2003] after preliminary exchange of cations present in natural complex for potassium ion K^+ . After such an exchange, the interlayer surface of clay minerals is unavailable for the molecules of sorbed water and the

Table 1. Set up of obtained results

Number of sample	Soil	Liquid limit w_L %	Plastic limit w_P %	External surface area S_e $\text{m}^2\cdot\text{g}^{-1}$	X-ray diffraction mineralogy	CEC $\text{mVal}\cdot\text{g}^{-1}$	Relative contents of cations				
							Na^+	Ca^{2+}	Mg^{2+}	Fe^{3+}	Al^{3+}
							Z_i/CEC				
1	Bentonite ¹⁾ Z.M. -1	176.5	109.1	117.2	montmorillonite	1.16	0.74	0.24	–	–	–
2	Bentonite ¹⁾ Z.M. -2	139.0	71.1			0.56	0.41	–	–	–	
3	Bentonite ¹⁾ Z.M. -3	99.1	28.9			0.04	0.95	–	–	–	
4	Bentonite ¹⁾ Z.M. -4	95.2	28.2			–	0.97	–	–	–	
5	Bentonite ¹⁾ Z.M. -5	95.5	23.3			–	–	–	0.96	–	
6	Bentonite ¹⁾ Z.M. -6	98.1	27.7			–	–	–	–	0.98	
7	Kaolin from Sedlce	68.5	34.1	19.8	kaolinite, micas, illite	0,18	–	1.00	–	–	–
8	Yoldia clay from near Elbląg	93.5	–	84.7	illite, montmorillonite, kaolinite, calcite, quartz	0.78	0.15	0.82	–	–	–
9	Pliocene clay Bydgoszcz	74.1	32.7	67.3	montmorillonite, kaolinite, illite, quartz	0.75	0.09	0.90	–	–	–
10	Kaolinitic clay Dommalur M. Bangalore, India	101.3	35.2	118.5	kaolinite, montmorillonite, muscovite, quartz	0.24	0.07	0.68	0.14	–	–
11	Spanish clay Almeria	43.3	–	11.9	kaolinite, montmorillonite	0.12	0.03	0.92	–	–	–
12	Dommalur clay M. Bangalore, India	47.0	20.9	13.0	kaolinite, montmorillonite, muscovite, quartz	0.12	0.18	0.58	0.23	–	–
13	Kaolinite clay Żarnowiec	18.8	–	4.1	–	0.38	0.13	0.85	–	–	–
14	Natural bentonite from near Chmielnik	94.0	–	69.3	montmorillonite, illite	0.63	0.11	0.77	0.11	–	–
15	Bentonite from Milowice	221.0	–	67.2	montmorillonite kaolinite, calcite quartz	68.2	0.98	0.01	–	–	–
16	Bentonite Z.M.	358.0	71.1	117.2	montmorillonite	1.156	0.98	0.02	–	–	–
17	Kaoline from Sedlce*	67.8	–	19.8	kaolinite, micas, illite	0.179	1.0	–	–	–	–

¹⁾ Model soils.

sorption of water vapour may take place only on the external surface. The external specific surface area was calculated from the equation:

$$S_e = \frac{10^{-2} WS(0.5)}{n \phi \rho} \quad (1)$$

where:

- n – the average number of layers of water molecules on the external surface of a particle, $n = 1.9$;
- ϕ – diameter of water molecule, $\phi = 0.276$ nm;
- ρ – density of water adsorbed from gas phase, $\rho = 1.27 \text{ Mg}\cdot\text{m}^{-3}$;
- $WS(0.5)$ – the sorption moisture of the soil, expressed in percent, at relative pressure of water vapour $p/p_o = 0.5$ and a temperature of 293 K.

After substitution of these values to eq. (1) the equation assumes its final form (2):

$$S_e = 15.01 \text{ m}^2\cdot\text{g}^{-1} WS(0.5) \quad (2)$$

The external specific surface area in clays from Bydgoszcz was determined with the BET method based on sorption analysis in liquid nitrogen [GRABOWSKA-OLSZEWSKA 1990]. Cation exchange capacity (CEC) was estimated based on the saturation of soil sample with barium in a triplicate extraction with triethylenamine buffered barium chloride solution. Then, a known excess of 0.02 M magnesium sulphate was added to the sample. This way, barium present in solution and that exchangeable adsorbed was precipitated as hardly soluble barium sulphate and ion exchanging centres were occupied by magnesium. Magnesium excess was determined with the flame atomic absorption spectrophotometry (FAAS) using PU-9100X, Philips spectrophotometer [PN-ISO 13536].

The types and content of exchangeable cations in all soil samples were determined with the method described in details by GRABOWSKA-OLSZEWSKA [1990].

Liquid limits in natural and model soil samples were determined in the Casagrande's apparatus according to standards [PN-88/B-04481]. At least 5 determinations were made for each sample.

RESULTS

The content of particular cations in the natural exchangeable complex with respect to the total cation exchange capacity is given in column 5 of Table 1. Figure 1 shows the relationship between liquid limit and the content of di- and trivalent cations in natural soils (no. 1–6) of

an external specific surface area $S_e = 117.2 \text{ m}^2\cdot\text{g}^{-1}$. The relationship demonstrates that in soils of the same content of exchangeable di- or trivalent cations the values of w_L are comparable. Increasing liquid limit with the decreasing content of di- or trivalent cations compared with monovalent ones is an evidence for significant impact of the diffuse layer repulsion pressure. Similar phenomena were observed by SRI DHARAN *et al.* [1988] who studied the effect of the composition of exchangeable cations on liquid limits in clayey soils.

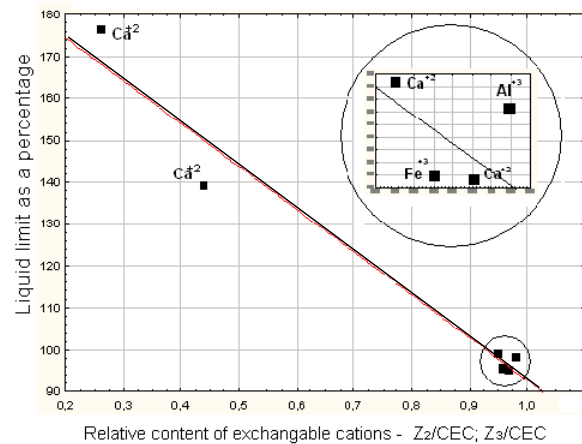


Fig. 1. The relationship between liquid limit and the content of di- and trivalent exchangeable cations in model soils

Figure 2 presents the relationship between liquid limit and the external specific surface area of studied soils. The relationships presented there show that the liquid limit increases with increasing external specific surface area. Coefficient of determination R^2 calculated with the least square method for linear equation $w_L = A S_e + B$ was 27.7%. It means that this linear regression should not be used as a predictor and indirectly indicates the effect of exchangeable cations on w_L .

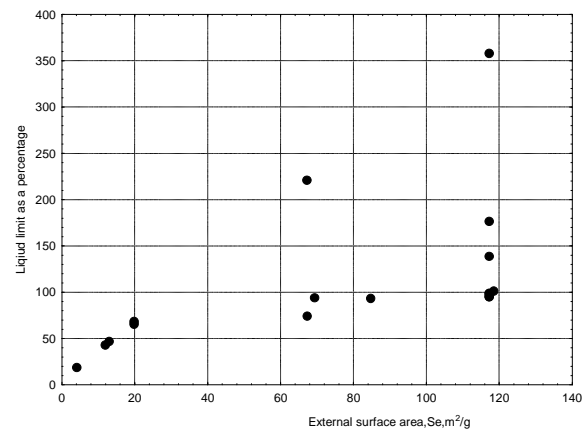


Fig. 2. Liquid limit versus the external specific surface area of the soils

To estimate the correlation between liquid limit w_L , the external specific surface area S_e and the relative content of exchangeable cations expressed as Z_i/CEC formulated as:

$$w_L = w_L(S_e; \frac{Z_i}{CEC}) \quad (3)$$

where Z_i is the content of an exchangeable cation of a valency of $i = 1, 2$ or 3 a regression was calculated from equation:

$$w_L = A \frac{S_e}{4 - 3n} + B \quad (4)$$

where n is the ratio of the content of sodium cation to the cation exchange capacity Na^+/CEC .

Constants A and B in equation (4) calculated with the least square method [NOWAK 2002] were: $A = 2.78$ and $B = 23.69$. Coefficient of determination was $R^2 = 97.5\%$ and Fischer-Snedecor coefficient $F = 291.4 > F_{crit} = 3.5$.

Hence, one may assume that equation (4) describes precisely enough the relationship between liquid limit, external specific surface area and the relative content of sodium cation.

After adopting the estimators of regression equation, the final form of correlation between liquid limit, external specific surface area and relative content of sodium cations is:

$$w_L = 2.78 \frac{S_e}{4 - 3n} + 23.69 \quad (5)$$

Figure 3 shows the liquid limit as a function of the expression $S_e/(4-3n)$. Comparison of measured and predicted values of liquid limits is presented in Figure 4. Figure 5 shows a plane mapping a set of S_e values and a set of Na^+/CEC values into a set of w_L values.

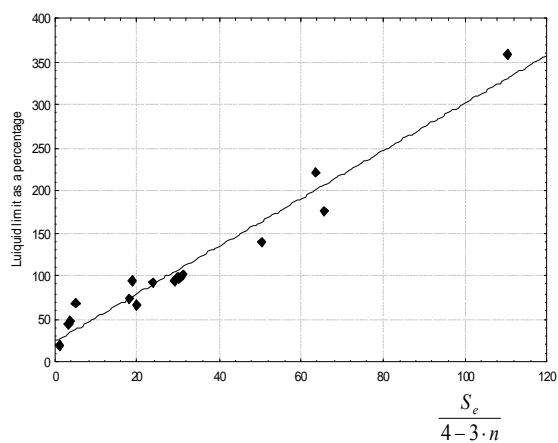


Fig. 3. Liquid limit w_L as a function of $S_e/(4-3n)$

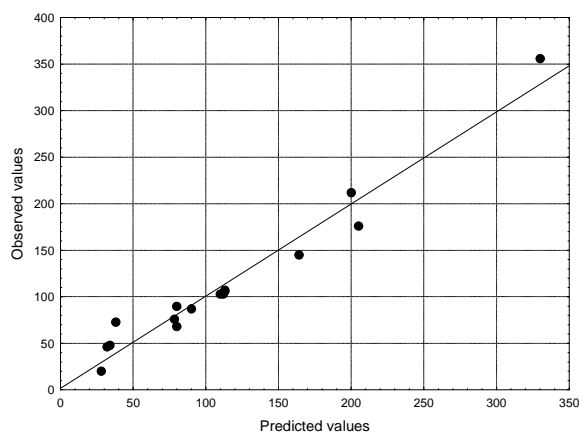


Fig. 4. Experimentally measured values of liquid limits and predicted from the regression

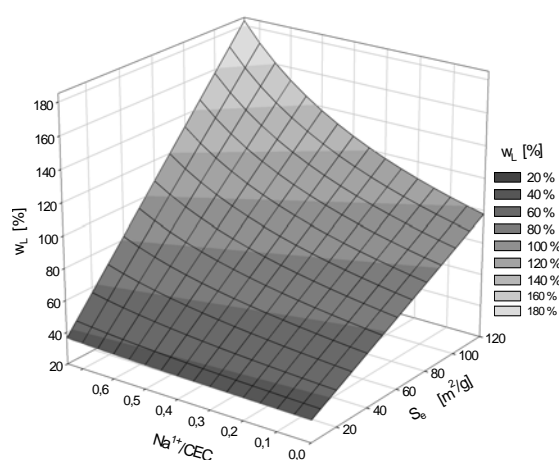


Fig. 5. A plane mapping (acc. to eq. 5) a set of S_e values and a set of Na^+/CEC into a set of w_L values

The relationship between the ratio of experimental to calculated liquid limit values and the external specific surface area is presented in Figure 6.

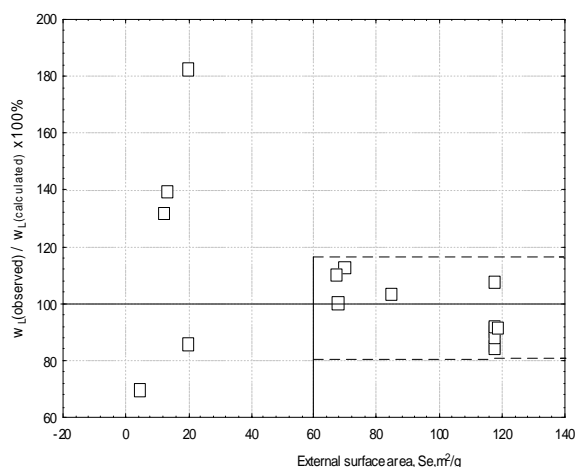


Fig. 6. The ratio of experimental to calculated liquid limits in relation to the external specific surface area

The greatest predictive power of linear regression was found for soils whose external specific surface area was larger than $60 \text{ m}^2 \cdot \text{g}^{-1}$. The highest absolute value of the deviation of the i -th observation from the predicted from eq. (5) was \hat{w}_{Li} , $|w_{Li} - \hat{w}_{Li}|_{\max} = 16\%$. For soils of the surface area less than $20 \text{ m}^2 \cdot \text{g}^{-1}$ $|w_{Li} - \hat{w}_{Li}|_{\max} = 82.5\%$.

A peculiar phenomenon is the comparable value of the liquid limit for kaoline from Sedlce (i.e. the Ca^{2+} kaoline) and the Na^+ kaoline (samples 7 and 17). This phenomenon may be an effect of a higher number of permanent edge to face bonds in the water- Na^+ kaoline compared with the number of the same bonds in the water - Ca^{2+} kaoline. These bonds, able to transfer the stretching tension, together with van der Waals attraction forces may compensate the repulsion pressure of diffusion layers thus decreasing their thickness.

CONCLUSIONS

Obtained results and their analysis allowed for formulating the following conclusions:

1. There is a functional relationship between liquid limit, external specific surface area of soils and relative content of sodium cation.
2. Predictive power of this relationship is the highest for soils of external specific surface area larger than c. $60 \text{ m}^2 \cdot \text{g}^{-1}$.
3. At a constant external surface area the liquid limit increases with increasing contribution of sodium cation in relation to di- and trivalent cations (except for low S_e values).
4. The external specific surface area may be an easy to estimate parameter in routine studies, especially when a great number of soil samples is to be analysed.
5. A factor not considered in the discussion is the mineralogical composition of soils. For soils of comparable external surface area and similar content of exchangeable cations the presence of montmorillonite would increase liquid limits due to the occurrence of water in its inter-layer spaces.
6. Further studies should focus on estimating the lower limit of the external surface area at which the functional relationship is a good predictor of liquid limit.

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Andrzej OLCHAWA, Aleksandra GORĄCZKO

Zależność granicy płynności od zewnętrznej powierzchni właściwej i składu kationów w naturalnym kompleksie wymiennym

STRESZCZENIE

Słowa kluczowe: granica płynności, grunty spoiste, pojemność wymiany kationowej, skład kationów wymiennych, zewnętrzna powierzchnia właściwa

W artykule przedstawiono wyniki badań związków korelacyjnych między granicą płynności – w_L , zewnętrzną powierzchnią właściwą – S_e i składem kationów w naturalnym kompleksie wymiennym siedemnastu wybranych gruntów, w tym siedmiu modelowych.

Zewnętrzna powierzchnia właściwa gruntów zawierała się w przedziale od 4,1 do 118,5 $m^2 \cdot g^{-1}$, a zawartość kationu sodowego Na^{1+} od 0,03 do 1,0. Na podstawie analiz wykazano istnienie statystycznych związków korelacyjnych między granicą płynności a zewnętrzną powierzchnią właściwą gruntu S_e i względną zawartością kationu sodowego w naturalnym kompleksie wymiennym, wyrażonym stosunkiem Na^{1+}/CEC .

Najlepszą zgodność korelacyjną wykazano w odniesieniu do gruntów, których zewnętrzna powierzchnia właściwa była większa od 60 $m^2 \cdot g^{-1}$.

Dla gruntów o takiej samej lub porównywalnej zewnętrznej powierzchni właściwej granica płynności przesuwa się w kierunku większych wartości wraz z większą względną zawartością kationu sodowego w naturalnym kompleksie wymiennym.

W gruntach o podobnym składzie kationów wymiennych granica płynności przyjmuje większe wartości w gruntach o większej zewnętrznej powierzchni właściwej.