

## SWELLING PRESSURE IN CLAYS

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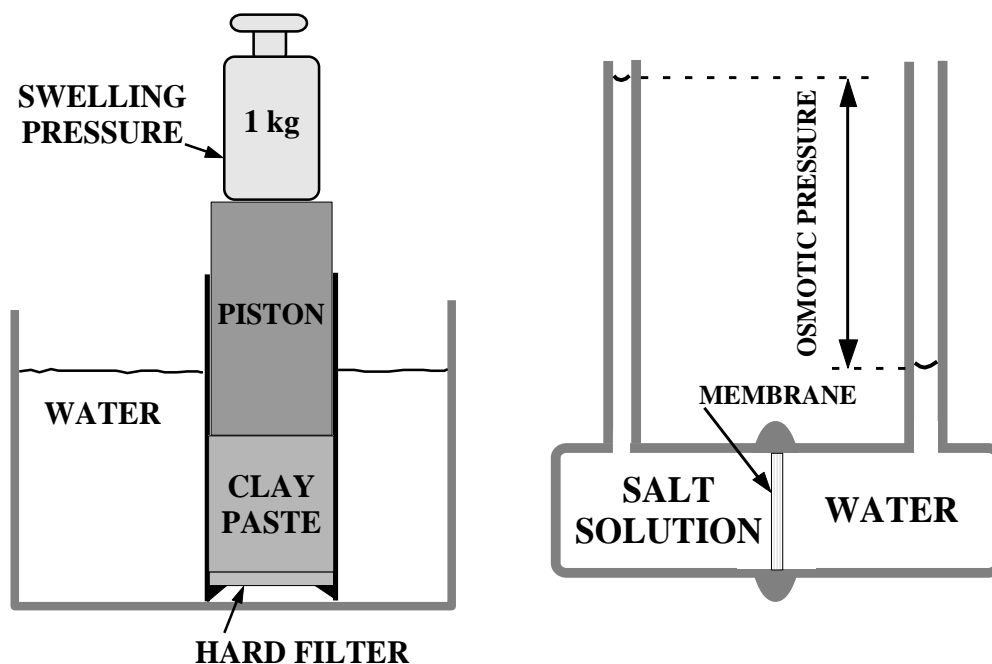
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### ABSTRACT

Paper presents brief summary of Gouy-Chapman-Stern model for swelling pressure in clays.

### INTRODUCTION

Electrostatic repulsion of charged particles in clay causes so-called swelling pressure. This factor gives significant contribution into total resistance of clay against compression forces. Pressure in the ionic atmosphere of charged surface is positive and it always increases to interface, similarly to pressure of gas atmosphere of planet. Swelling pressure is positive pressure, applied from clay paste to external boundaries. In equilibrium, swelling pressure of clay paste is equilibrated with external compression forces. In spite of pressure jump, in equilibrium state, there is no flux of water from clay paste to external bulk solution. This is because of electrostatic attraction of charged pore solution to charged clay particles. Sign of swelling pressure in clay paste is often mentioned as negative (“suction pressure”), because the swelling clay sucks water from external bulk solution, and it looks like an effect of negative pressure in clay. Because of this, there is mish-mush with sign of the effect. In general, there is close analogy between swelling pressure in clay and osmotic pressure between two solutions, separated by membrane (see Fig. 1). The difference is that the osmotic pressure arises due to retardation of ions by membrane, whereas swelling pressure is result of retardation of ions by electrostatic field of charged clay particles.



**Fig. 1** Swelling pressure in clay paste (left) and osmotic pressure in salt solution (right) in equilibrium with water.

In general case, pressure in the ionic atmosphere of charged surface may be found from:

$$|dP_x| = |E_x \times dQ_x| = |\{d\phi_x/dx\} \times \{\rho_x dx\}| = |\rho_x d\phi_x| \quad (1)$$

Here  $E_x = d\phi_x/dx$  and  $\phi_x$  are field strength and potential at distance  $x$  from the head of diffuse layer,  $dQ_x = \rho_x dx$  is charge of layer of the ionic atmosphere (with thickness  $dx$  and per unit of area),  $\rho_x$  is charge density of the ionic atmosphere at distance  $x$  from the head of diffuse layer:

$$\rho_x = 1000F \times \sum z_i c_i \exp(-z_i F \phi_x / RT) \quad (2)$$

Here constant factor is  $1000 \text{ dm}^3/\text{m}^3$ ,  $F = 96485 \text{ C/eq}$  is Faraday constant,  $z_i$  is charge of ion,  $c_i$  is molar concentration of ion (moles per liter) in the bulk solution,  $R = 8.3144 \text{ J/molK}$  is gas constant,  $T$  is absolute temperature.

From Eq. (1), pressure in the ionic atmosphere is:

$$P_x = \{1000RT\} \times \sum c_i \{ \exp(-z_i y_x) - 1 \} \quad (3) \text{ or}$$

$$P_x, \text{ bar} = 24.79 \times \sum c_i \{ \exp(-z_i y_x) - 1 \} \quad (3a)$$

Here  $y$  is scaled potential:

$$y = F\phi/RT \quad (4)$$

Note that Eq. (3) is valid for arbitrary shape of ionic atmosphere, e.g. for overlapped flat diffuse layers.

So on, swelling pressure in clay may be calculated from:

$$P_{sw}, \text{ bar} = 24.79 \times \sum c_i \{ \exp(-z_i y_m) - 1 \} = 24.79 \times \sum \{ c_{mi} - c_i \} = 24.79 \times \sum \Delta c_i \quad (5)$$

Here  $y_m = F\phi_m/RT$  is scaled mid-plane potential (in the middle between charged particles),  $\Delta c_i$  is difference between concentration of ion at mid-plane,  $c_{mi}$ , and its concentration in the bulk solution,  $c_i$ . Note that swelling pressure,  $P_{sw}$ , is difference between mid-plane pressure and pressure in the bulk solution (to obtain absolute pressure at mid-plane between particles, it is necessary to add pressure in the bulk solution).

As may be seen, Eq. (5) almost coincides with Van't Hoff equation for osmotic pressure:

$$P_{osm} = - \{ RT/V_w \} \times \omega \times \Delta \ln(a_w) \sim (1000RT) \times \omega \times v \times \Delta c \quad (6) \text{ or}$$

$$P_{osm}, \text{ bar} = - 1372 \times \omega \times \Delta \ln(a_w) \sim 24.79 \times \omega \times v \times \Delta c \quad (6a)$$

Here  $\Delta \ln(a_w)$  is difference (between more concentrated and less concentrated solutions) in natural logarithms of water activity, and  $\Delta c$  is difference in electrolyte concentrations between two solutions, separated by membrane;  $\omega$  is osmotic efficiency of membrane ( $\equiv$  reflection coefficient), which ranges from 0 to 1, and  $v$  is number of ions per formula of electrolyte (2 for NaCl, 3 for CaCl<sub>2</sub>, etc).

At the overlap of diffuse layers, surface charge and potential profile are defined by (Corkill and Rosenhead, 1939; Verwey, 1940; Verwey and Overbeek, 1948):

$$\sigma_s, \mu\text{eq/m}^2 = \text{sgn}(y_d) \times 0.608 \times [\sum c_i \{ \exp(-z_i y_d) - \exp(-z_i y_m) \}]^{0.5} \quad (7)$$

$$dy_x/dx, \text{ \AA}^{-1} = - \text{sgn}(y_d) \times (1/3.04) \times [\sum c_i \{ \exp(-z_i y_x) - \exp(-z_i y_m) \}]^{0.5} \quad (8)$$

Here  $y_d$  is scaled potential at the head of diffuse layer,  $\text{sgn}(y_d)$  is sign of  $y_d$ , factor  $0.608 = 10^6 \times (2000RT\varepsilon_0\varepsilon/F^2)^{0.5}$  is Gouy-Chapman constant, and  $3.04 = 5 \times 0.608 = 10^{10} \times (RT\varepsilon_0\varepsilon/2000F^2)^{0.5}$  is Debye constant,  $\varepsilon_0 = 8.8542 \times 10^{-12} \text{ C} \times \text{V}^{-1} \times \text{m}^{-1}$ ,  $\varepsilon$  is dielectric constant of water (78.47 at 25°C).

From Eq. (8), the distance between the heads of overlapped diffuse layers is:

$$h, \text{ \AA} = 6.08 \times \int_{y_m}^{y_d} [\sum c_i \{ \exp(-z_i y) - \exp(-z_i y_m) \}]^{-0.5} dy \quad (9)$$

In the limit  $y_d - y_m \rightarrow 0$ , Eq. (9) may be solved as (for symmetric z:z electrolyte):

$$h, \text{ \AA} \approx (6.08/zc^{0.5}) \times [2z(y_d - y_m)/\text{sh}(zy_m)]^{0.5} \quad (10)$$

Here  $z$  is valence of z:z electrolyte (i.e. “z” is always positive),  $\text{sh}(X) = 0.5 \{ \exp(X) - \exp(-X) \}$  is hyperbolic sinus. At zero ionic strength, if surface charge is compensated by the only kind of counter ion, Eq. (7) may be reduced to:

$$|\sigma_s|, \mu\text{eq/m}^2 = 0.608 \times [c_{d0} - c_{m0}]^{0.5} = 0.608 \times c_{m0}^{0.5} \times [\exp\{-z_c(y_d - y_m)\} - 1]^{0.5} \quad (11)$$

Here  $z_c$  is charge of counter ion,  $c_{d0}$  and  $c_{m0}$  are concentrations of counter ion at the head of diffuse layer and at mid-plane at zero ionic strength. Note here that sign of  $z_c$  is always opposite to that of  $\sigma_s$  and  $(y_d - y_m)$ . Thus,  $\{-z_c(y_d - y_m)\}$  is always positive. In the limit of zero ionic strength, both  $y_d$  and  $y_m$  approach to infinity (by modulus). Nevertheless, their difference at zero ionic strength is defined by (Langmuir, 1938; Verwey 1940; Verwey and Overbeek, 1948):

$$y_d - y_m = \{2/z_c\} \ln[\cos\{0.5z_c c_{m0}^{0.5}[h, \text{ \AA}]/6.08\}] \quad (12) \text{ or}$$

$$\exp\{-z_c(y_d - y_m)\} = 1/\cos^2\{0.5z_c c_{m0}^{0.5}[h, \text{ \AA}]/6.08\} \quad (12a)$$

Here  $\cos(X)$  is cosine  $X$ . From Eqs. (11) and (12a), concentration of counter ion at mid plane at zero ionic strength,  $c_{m0}$  (see **Tab. 1**), may be found via iterative solution of equation:

$$|\sigma_s|, \mu\text{eq/m}^2 = 0.608 \times c_{m0}^{0.5} \times \text{tg}\{0.5|z_c|c_{m0}^{0.5}[h, \text{ \AA}]/6.08\} \quad (13) \text{ or}$$

$$h, \text{ \AA} = \{2 \times 6.08/|z_c|c_{m0}^{0.5}\} \times \text{atg}\{[|\sigma_s|, \mu\text{eq/m}^2]/0.608c_{m0}^{0.5}\} \quad (13a)$$

Here  $\text{tg}(X)$  is tangent  $X$ , and  $\text{atg}(X)$  is arctangent  $X$ .

**Tab. 1** Molar concentration of counter ion with charge  $z_c$  at mid-plane at zero ionic strength. (No other ions present). Calculated from Eq. (13).

$ z_c  \times h, \text{ \AA}$	$c_{m0}, \text{ M}$			
	$ \sigma_s , \mu\text{eq/m}^2 = 0.1$	$ \sigma_s , \mu\text{eq/m}^2 = 1$	$ \sigma_s , \mu\text{eq/m}^2 = 2$	$ \sigma_s , \mu\text{eq/m}^2 = 3$
1	1.991015	19.12997	36.64018	52.69700
2	0.991048	9.160046	16.86230	23.38889
3	0.657746	5.855223	10.39506	13.97793
5	0.391143	3.241175	5.401974	6.913884
10	0.191300	1.350493	2.004618	2.377177
20	0.091601	0.501154	0.653689	0.724512
30	0.058552	0.264131	0.322005	0.346419
50	0.032412	0.111143	0.126603	0.132572
100	0.013505	0.031651	0.033932	0.034751

At any ionic strength, Eq. (13) is exact asymptotic relation for the function (for symmetric z:z electrolyte):

$$f_m = \{c_m - c^2/c_m\} \quad (14)$$

Approximation  $\{c_m - c^2/c_m\} \approx c_{m0}$  is almost exact up to  $h \sim 3.04/zc^{0.5}$  Å. The value  $f_m$  may be converted to  $c_m$  (for symmetric z:z electrolyte):

$$c_m = 0.5f_m + \{0.25f_m^2 + c^2\}^{0.5} \quad (15)$$

At  $h > \sim 12.16/zc^{0.5}$  Å, the exact asymptotic solution is (for symmetric z:z electrolyte):

$$f_m = \{c_m - c^2/c_m\} \approx 8 \times c \times \text{th}\{z|y_o|/4\} / \text{sh}\{zc^{0.5}[h, \text{Å}]/6.08\} \quad (16)$$

Here  $z$  is also positive,  $\text{th}(X) = \{\exp(X) - \exp(-X)\} / \{\exp(X) + \exp(-X)\}$  is hyperbolic tangent,  $\text{sh}(X) = 0.5\{\exp(X) - \exp(-X)\}$  is hyperbolic sinus, and  $y_o$  is scaled potential in the head of diffuse layer in the absence of overlap. In general case, value  $y_o$  is defined by Gouy-Chapman equation:

$$\sigma_s, \mu\text{eq/m}^2 = \text{sgn}(y_o) \times 0.608 \times [\sum c_i \{\exp(-z_i y_o) - 1\}]^{0.5} \quad (17)$$

For symmetric z:z electrolyte, Gouy-Chapman equation may be inversed as (here  $z > 0$ ):

$$y_o = \{2/z\} \ln\{0.5\alpha + (0.25\alpha^2 + 1)^{0.5}\} \quad (18)$$

$$\alpha = [\sigma_s, \mu\text{eq/m}^2] / \{0.608c^{0.5}\} \quad (19)$$

Eq. (16) is also exact asymptotic solution for  $\sigma_s \rightarrow 0$  (and at any  $h$ ).

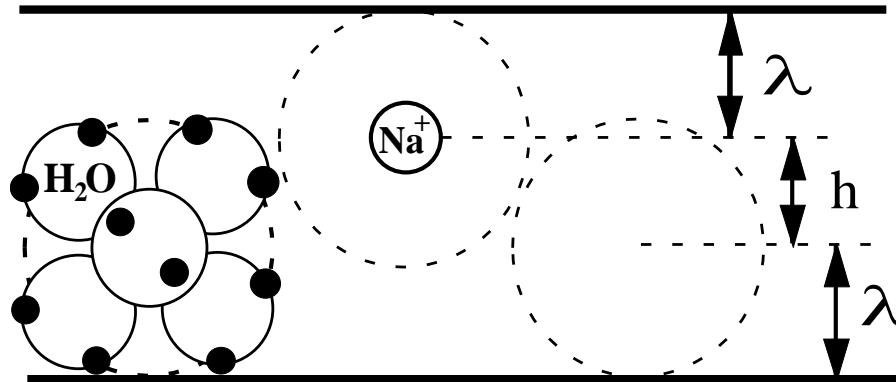
In general case, average distance between particles may be calculated from obvious relation:

$$d, \text{Å} = 2 \times 10^7 / \{[S, \text{m}^2/\text{g}][\text{Load}, \text{g/L}]\} \quad (20)$$

Here  $[S, \text{m}^2/\text{g}]$  is specific surface of clay, and  $[\text{Load}, \text{g/L}]$  is “solid load”, concentration of suspension or paste in grams of solid per liter of solution. The latter is related with porosity as:

$$[\text{Load}, \text{g/L}] \approx 1000 \times \{(100 - \theta) \times 2.78\} / \theta \quad (21)$$

Here  $\theta$  is porosity of clay (percent of total volume filled by solution), constant factor  $\sim 2.78$  is typical density of clay particles in grams per  $\text{cm}^3$ .



**Fig. 2** Layer of solution between two charged surfaces. Here  $h$  is distance between the heads of diffuse layers, and  $\lambda$  is radius of counter ion.

In accordance with original Gouy-Chapman approach, the head of diffuse layer coincides with solid-water interface, and thus,  $h = d$ . In accordance with Stern model, the head of diffuse layer is separated from charged surface by “radius of counter ion”. Thus, the distance between the heads of overlapped diffuse layers,  $h$ , is defined by (see **Fig. 2**):

$$h = d - 2\lambda \tag{22}$$

Here  $\lambda$  is radius of counter ion ( $2\lambda$  is diameter), and  $d$  is distance between charged surfaces. From common sense (see **Fig. 2**), parameter  $\lambda$  should be close to diameter of water molecule, and thus:

$$2\lambda \sim 6 \text{ \AA} \tag{23}$$

**SUBJECT OF PRESENT STUDY:** In order to obtain close approximation for concentrations of ions at mid-plane (and thus, for swelling pressure) numerical integration of Eq. (9) was performed for  $c = 0.1$  and  $1 \text{ M}$  (symmetric electrolyte).

## METHODS

The method of integration of Eq. (9) is the same as used in previous study (Pivovarov, 2014). Eq. (9) can not be integrated accurately near by  $y - y_m = 0$ . Thus, first ten steps of integration were approximated by Eq. (10):

$$\begin{aligned} \Delta h_{n=10}, \text{ \AA} &= 6.08 \times \int_{y_m}^{y_{n=10}} [\sum c_i \{ \exp(-z_i y) - \exp(-z_i y_m) \}]^{-0.5} dy \approx \\ &\approx \{ 6.08 / z c^{0.5} \} [2z(y_{n=10} - y_m) / \text{sh}(zy_m)]^{0.5} \end{aligned} \tag{24}$$

Here, as above,  $z$  is valency of symmetric  $z:z$  electrolyte. Other steps of integration were recovered using Simpson (parabolic) method:

$$h, \text{ \AA} \approx \Delta h_{n=10} + \{ 1/6 \} \sum_{n=11}^{n=1000000} \{ f_{n-1} + 4f_{n-0.5} + f_n \} \{ y_d - y_m \} / 1000000 \tag{25}$$

$$f_{n-1} = 6.08 \times [\sum c_i \{ \exp(-z_i y_{n-1}) - \exp(-z_i y_m) \}]^{-0.5} \tag{26}$$

$$f_{n-0.5} = 6.08 \times [\sum c_i \{ \exp(-z_i y_{n-0.5}) - \exp(-z_i y_m) \}]^{-0.5} \tag{27}$$

$$f_n = 6.08 \times [\sum c_i \{ \exp(-z_i y_n) - \exp(-z_i y_m) \}]^{-0.5} \tag{28}$$

$$y_{n-1} = y_m + (n-1) \times (y_d - y_m) / 1000000 \tag{29}$$

$$y_{n-0.5} = y_m + (n-0.5) \times (y_d - y_m) / 1000000 \tag{30}$$

$$y_n = y_m + n \times (y_d - y_m) / 1000000 \tag{31}$$

## RESULTS

**Tab. 2** Molar concentration of counter ion at mid-plane at  $c = 0.1$  M (symmetric z:z electrolyte).

$z \times h, \text{Å}$	$c_m, \text{M}$			
	$ \sigma_s , \mu\text{eq/m}^2 = 0.1$	$ \sigma_s , \mu\text{eq/m}^2 = 1$	$ \sigma_s , \mu\text{eq/m}^2 = 2$	$ \sigma_s , \mu\text{eq/m}^2 = 3$
1	1.995981	19.13045	36.64041	52.69716
2	1.000863	9.160977	16.86275	23.38918
3	0.672233	5.856588	10.39572	13.97837
5	0.414253	3.243393	5.403103	6.914696
10	0.231101	1.354998	2.007295	2.379348
20	0.149356	0.511721	0.661409	0.731414
30	0.124929	0.282827	0.337182	0.360525
50	0.107924	0.148831	0.160631	0.165389
100	0.100565	0.103073	0.103707	0.103954

**Tab. 3** Molar concentration of counter ion at mid-plane at  $c = 1$  M (symmetric z:z electrolyte).

$z \times h, \text{Å}$	$c_m, \text{M}$			
	$ \sigma_s , \mu\text{eq/m}^2 = 0.1$	$ \sigma_s , \mu\text{eq/m}^2 = 1$	$ \sigma_s , \mu\text{eq/m}^2 = 2$	$ \sigma_s , \mu\text{eq/m}^2 = 3$
1	2.403388	19.17789	36.66345	52.71217
2	1.603688	9.252265	16.90699	23.41832
3	1.369296	5.988832	10.46098	14.02253
5	1.194590	3.450743	5.513070	6.994396
10	1.068007	1.722577	2.251993	2.582933
20	1.012332	1.112563	1.181429	1.220502
30	1.002366	1.020843	1.032891	1.039527
50	1.000088	1.000769	1.001207	1.001446

Results of numerical integration of Eq. (9) are given in **Tabs 2, 3**. Because the Eq. (13) is exact in the limit  $c \rightarrow 0$ , it may be applied as a basis for general approximation. Close approximation for Eq. (13) is:

$$c_{m0} \approx \{20 \times [|\sigma_s|, \mu\text{eq/m}^2] / |z_c| [h, \text{Å}]\} / \{1 + 0.05488\alpha - 0.01008\alpha / (1 + 0.049\alpha)\} \quad (32)$$

$$\alpha = |z_c| \times [|\sigma_s|, \mu\text{eq/m}^2] \times [h, \text{Å}] \quad (33)$$

Up to  $h = 100$  Å, and  $|\sigma_s| = 3 \mu\text{eq/m}^2$ , maximum error of Eq. (32) for  $c_{m0}$  is 0.035 %.

At given ionic strength, concentration of counter ion at mid-plane,  $c_m$ , may be roundly estimated from:

$$c_m \sim (c_{m0}^2 + c^2)^{0.5} \quad (34)$$

Here  $c$  is concentration of counter ion in the bulk solution. Swelling pressure may be then calculated from (for symmetric z:z electrolyte):

$$P_{sw} = 24.79 \{c_m + c^2/c_m - 2c\} \quad (35)$$

Here  $c$  is concentration of bulk electrolyte, and  $c^2/c_m$  is concentration of co-ion at mid-plane. In the range of surface charge 1-3  $\mu\text{eq/m}^2$ , maximum error of Eq. (34) is 2.5 % for  $c_m$ . However, with Eq. (35), relative error of Eq (34) for swelling pressure in the limits  $h \rightarrow \infty$  and  $\sigma_s \rightarrow 0$  approaches to infinity. To obtain closer approach, Eq (32) may be combined with Eq (16).

More or less close approximation, consistent with Eqs (16, 32) is (for symmetric z:z electrolyte; here  $z > 0$ ):

$$f_m = c_m - c^2/c_m \approx \frac{(20 \times [|\sigma_s|, \mu\text{eq}/\text{m}^2] - B)(1 - \text{th}\{\beta g\})}{z[h, \text{\AA}]\{1 + g\}} + \frac{B\{c^{0.5}/6.08\}}{\text{sh}(zc^{0.5}[h, \text{\AA}]/6.08)} \quad (36)$$

$$B = 8 \times 6.08 \times c^{0.5} \times \text{th}(z|y_0|/4), \quad \text{where } y_0 \text{ is given by Eqs. (18, 19)} \quad (37)$$

$$\beta = B / (20 \times [|\sigma_s|, \mu\text{eq}/\text{m}^2] - B) \quad (38)$$

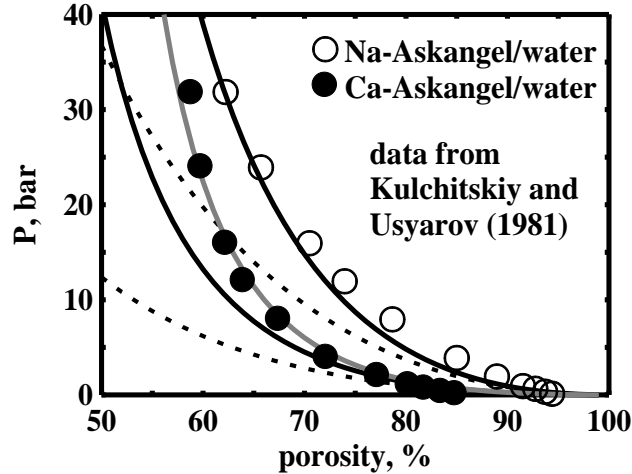
$$g = 0.05488\alpha - 0.01008\alpha / (1 + 0.049\alpha) \quad (39)$$

$$\alpha = z \times [|\sigma_s|, \mu\text{eq}/\text{m}^2] \times [h, \text{\AA}] \quad (40)$$

Maximum error of this approximation is 2.1 % for  $c_m$ , and, with Eq. (35), 4 % for swelling pressure.

### APPLICATION

**Figs. 3-4** show the compression curves for montmorillonite “Askangel” (Cihis-Ubanskoe part of Askanskoe deposit, Georgian Soviet Socialistic Republic, USSR) are shown, as measured by Kulchitskiy and Usyarov (1981). Each point was equilibrated under applied pressure for “several months”. The measured surface area of “Askangel” was  $646 \text{ m}^2/\text{g}$ , and measured exchange capacity was  $0.977 \text{ meq}/\text{g}$  on average ( $0.899$ - $1.025 \text{ meq}/\text{g}$  for various mono-cationic clay samples). Thus, surface charge of this clay is  $\sim -1.51 \mu\text{eq}/\text{m}^2$ .

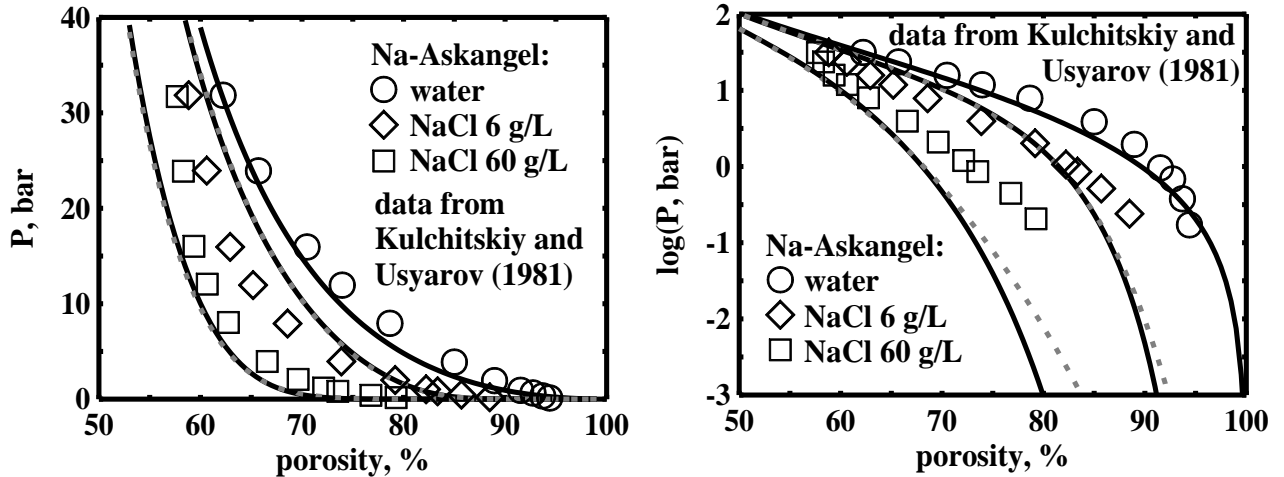


**Fig. 3** Compression curves for Na-Askangel (open circles) and Ca-Askangel (closed circles) in water. Data from Kulchitskiy and Usyarov (1981). Dashed curves: original Gouy-Chapman approach ( $\lambda = 0$ ). Black solid curves: Stern approach with radius of counter ion  $\lambda = 3 \text{ \AA}$ . Gray solid curve (for Ca-Askangel): Stern approach with  $\lambda$  adjusted to  $4.5 \text{ \AA}$ .

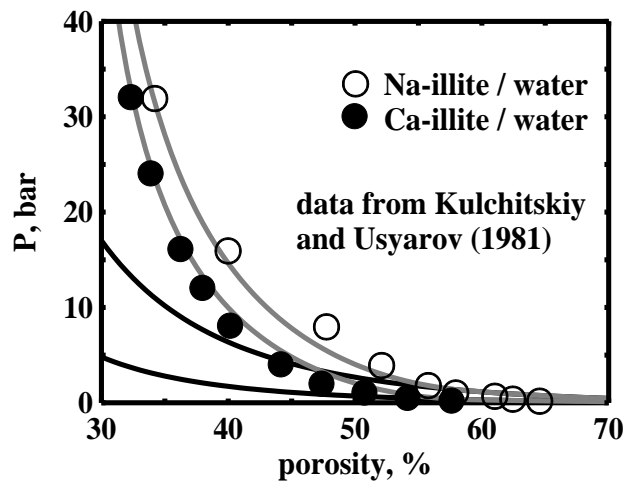
The dashed curves in **Fig. 3** were calculated with use of original Gouy-Chapman approach ( $h = d$ , see Eq. 20), whereas solid curves were calculated with use of Stern approach ( $h = d - 2\lambda$ , see Eqs. 20-22). As may be seen, size of counter ion is important factor for swelling pressure.

In Fig. 4, compression curves for Na-Askangel in 0.103 and 1.03 M NaCl are shown (clay pastes were prepared via coagulation in the same solutions). Gray dashed curves were calculated with use of approximation Eqs. (34) instead of Eqs (36-40). As may be seen, Eq. (34) is well applicable down to swelling pressures ~ 0.3-0.03 bar

One may see that the resistance of montmorillonite to compression is close to swelling pressure, and additional factors are of minor importance. However, for clays with smaller surface area, swelling pressure becomes secondary factor of total resistance.



**Fig. 4** Compression curves for Na-Askangel in water (circles), 0.103 M NaCl (diamonds), and 1.03 M NaCl (squares) with pressure on normal (left) and logarithmic (right) scales. Data from Kulchitskiy and Usyarov (1981). Black solid curves: Stern approach with  $\lambda = 3 \text{ \AA}$ . Gray dashed curves: the same approach but with use of Eq. (34) instead of Eqs. (36-40).



**Fig. 5** Compression curves for Na-illite and Ca-illite in water. Data from Kulchitskiy and Usyarov (1981). Black curves: swelling pressure (Stern approach with  $\lambda = 3 \text{ \AA}$ ). Gray curves: swelling pressure plus resistance of grain skeleton (Eq. 41).

Fig. 5 shows the compression curves for illite (Kudinovo, Moscow district, USSR), as measured by Kulchitskiy and Usyarov (1981). Again, each point was equilibrated under applied pressure for “several months”. Surface area of illite was measured at  $117.3 \text{ m}^2/\text{g}$ , and its exchange capacity was measured at  $0.308 \text{ meq/g}$  on average ( $0.280 - 0.335 \text{ meq/g}$  for various mono-cationic clay samples). Thus, surface charge of this clay is  $\sim -2.63 \text{ } \mu\text{eq/m}^2$ .



Black solid curves in **Fig. 5** were calculated using Stern approach with  $\lambda = 3 \text{ \AA}$ . As may be seen, model agrees with experimental data at lowest pressures. However, at highest applied pressure (32 bar), swelling pressure takes about 1/10 – 1/3 of total resistance. Thus, major factor of resistance for this clay is resistance of grain skeleton.

The uniform quartz sand in water may be easily compacted under its own weight (applying insignificant vibration) down to porosity  $\sim 40\%$ . This is average between simple cubic (48 %) and centered cubic (32 %) array of uniform spheres. Application of additional pressure to this sand gives no further compaction. Resistance of grain skeleton appears within some range of porosity. In this range, compaction is, in the main, result of ordering of array of particles (elasticity of grains is of minor importance). At upper limit of this range, resistance of grain skeleton is zero, and, at lower limit, until destruction of grains, resistance of grain skeleton approaches to infinity. Gray curves in **Fig. 5** were calculated with use of empirical approximation for skeletal resistance:

$$P_{sk, \text{ bar}} \sim 0.008 \times \{0.5(59-\theta) + 0.5|59-\theta|\}^2 / (1-26/\theta) \quad (41)$$

Here 0.008 is adjustable parameter, 59 and 26 are upper and lower limits of porosity for skeletal resistance. It should be noted, that the resistance of grain skeleton is peculiar property, and Eq. (41) is not applicable for all kinds of clay.

## CONCLUDING REMARKS

Gouy-Chapman-Stern approach gives close prediction for swelling pressure in clays.

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