

## IONIC EXCHANGE IN FLAT DIFFUSE LAYER AND IN CLAYS

Sergey Pivovarov

Institute of Experimental Mineralogy, Russian Academy of Sciences

E-mail: serg@iem.ac.ru

Published online 30.06.2013

### ABSTRACT

Paper presents numerical (for arbitrary salt medium) and analytical (for  $(M^+, Me^{2+})(A^-, An^{2-})$  salt medium) solution for the ionic sorption in flat diffuse layer. The results of calculations are compared with behavior of real systems: ionic exchange on montmorillonite and kaolinite.

### INTRODUCTION

Description of the ionic exchange in diffuse layer may be obtained from Poisson-Boltzmann equation. For flat diffuse layer, it is:

$$d^2\varphi_x/dx^2 = -\rho_x/\varepsilon_0\varepsilon = -(1000F/\varepsilon_0\varepsilon)\sum z_i c_i \exp(-z_i F\varphi_x/RT) \quad (1)$$

Here  $\varphi_x$  and  $\rho_x$  are potential (V) and charge density ( $C/m^3$ ) at distance  $x$  (meters) from the head of diffuse layer,  $\varepsilon_0$  is dielectric constant of free space ( $8.8542 \times 10^{-12} F/m = C \times V^{-1} \times m^{-1}$ ),  $\varepsilon$  is dielectric constant of medium (dimensionless; 78.47 for water at 25°C),  $z_i$  is charge of ion,  $c_i$  is molar concentration of ion in the bulk solution (moles per liter),  $F$  is Faraday constant (96485 C/mol),  $R$  is gas constant ( $8.314 J \times mol^{-1} \times K^{-1}$ ),  $T$  is absolute temperature (K).

Multiplying of both sides of Eq. (1) by  $2d\varphi_x$ , one may obtain

$$2d\varphi_x \times d^2\varphi_x/dx^2 = d(d\varphi_x/dx)^2 = -(2000F/\varepsilon_0\varepsilon) \sum z_i c_i \exp(-z_i F\varphi_x/RT) d\varphi_x \quad (2)$$

Integration gives the following relation:

$$d\varphi_x/dx = -\operatorname{sgn}(\varphi_x) \times (2000RT/\varepsilon_0\varepsilon)^{0.5} \times [\sum c_i \{ \exp(-z_i F\varphi_x/RT) - 1 \}]^{0.5} \quad \text{or} \quad (3)$$

$$dy_x/dx = -\operatorname{sgn}(y_x) \times \{ \kappa/I^{0.5} \} \times [\sum c_i \{ \exp(-z_i y_x) - 1 \}]^{0.5} \quad (3a)$$

Here  $y_x$  is scaled potential at distance  $x$  from the head of diffuse layer,  $\kappa$  is inversed Debye length, and  $I$  is ionic strength:

$$y_x = F\varphi_x/RT \quad (4)$$

$$\kappa = (2000F^2/RT\varepsilon_0\varepsilon)^{0.5} \times I^{0.5}, \quad \text{or} \quad (5)$$

$$\kappa^{-1}, \text{ \AA} = 3.04/I^{0.5} \quad (5a)$$

$$I = 0.5 \sum z_i^2 c_i \quad (6)$$

For symmetric z:z electrolyte, Eq. (3) may be simplified to:

$$dy_x/dx = - \{2\kappa/z\} \text{sh}\{zy_x/2\} \quad (7)$$

Here  $\text{sh}(X) = 0.5\{\exp(X) - \exp(-X)\}$  is hyperbolic sinus. Eq. (7) may be integrated analytically (for symmetric z:z electrolyte):

$$\text{th}\{zy_x/4\} = \text{th}\{zy_d/4\} \exp(-\kappa x) \quad (8)$$

Here  $\text{th}(X) = \{\exp(X) - \exp(-X)\}/\{\exp(X) + \exp(-X)\}$  is hyperbolic tangent, and  $y_d$  is value of scaled potential in the head of diffuse layer (i.e. at distance  $x = 0$  from the head of diffuse layer):

$$y_d = F\phi_d/RT \quad (9)$$

For small values of potential ( $|y_x| \ll 1$ ), the Eq. (8) is reduced to Debye-Hückel equation:

$$y_x = y_d \times \exp(-\kappa x) \quad (10)$$

It should be noted that Eq. (10) is valid for arbitrary salt medium.

In general case, there is no analytical solution for Eq. (3), and it should be solved numerically:

$$x = \{I^{0.5}/\kappa\} \left| \int_{y_x}^{y_d} [\sum c_i \{\exp(-z_i y) - 1\}]^{-0.5} dy \right| \quad (11)$$

If the potential profile is known, sorption of ion in diffuse layer may be calculated in accordance with:

$$[D\text{Ion}], \mu\text{mol}/\text{m}^2 = 0.1c_i \int_0^\infty \{\exp(-z_i y_x) - 1\} d[x, \text{Å}] \quad (12)$$

The numerical solution, based on Eq. (12), may be extended to various approaches, accounting for different sizes of ions, density oscillations, changes of dielectric constant and in activity coefficients of ions near the surface, etc. (see Neal and Cooper, 1983). However, this method requires double integration. Within the original Gouy-Chapman approach, more simple way (see Borkovec and Westall, 1983) is to combine Eqs. (12) and (3):

$$[D\text{Ion}], \mu\text{mol}/\text{m}^2 = \text{sgn}(y_d) \times 0.304c_i \int_0^{y_d} [ \{\exp(-z_i y) - 1\} / \{\sum c_i (\exp(-z_i y) - 1)\}^{0.5} ] dy \quad (13)$$

The Eq. (13) may be solved analytically for symmetric z:z electrolyte:

$$\begin{aligned} [D\text{Ion}], \mu\text{mol}/\text{m}^2 &= 0.608 \times \{c/I^{0.5}\} \times \{\exp(-z_i y_d/2) - 1\} = \\ &= 0.608 \times \{c^{0.5}/z\} \times \{\exp(-z_i y_d/2) - 1\} \end{aligned} \quad (14)$$

Here  $z_i$  is charge of ion, and  $z = |z_i|$ .

At small  $y_d$ , the exponent term is  $\exp(-z_i y_d/2) \approx 1 - z_i y_d/2$ , and Eq. (14) may be reduced to:

$$[D_{Ion}], \mu\text{mol}/\text{m}^2 = 0.608 \times \{c_i/\Gamma^{0.5}\} \times \{-z_i y_d/2\} = -0.304 \times \{z_i c_i/\Gamma^{0.5}\} \times y_d \quad (\text{at } y_d \ll 1) \quad (15)$$

Note that Eq. (15) is valid for arbitrary salt medium.

Charge of diffuse layer is related with field strength in the head of diffuse layer as:

$$\sigma_d, \text{C}/\text{m}^2 = \varepsilon_o \varepsilon E_d = \varepsilon_o \varepsilon (d\phi_x/dx)_d \quad (16)$$

In the absence of outer-spherical complexes, charge of diffuse layer is equal by modulus to surface charge ( $\sigma_d = -\sigma_s$ ).

Combining with Eq. (3), one may obtain the charge-potential relation:

$$\sigma_d, \text{C}/\text{m}^2 = -\text{sgn}(\phi_d) \times (2000RT\varepsilon_o\varepsilon)^{0.5} \times [\sum c_i \{ \exp(-z_i y_d) - 1 \}]^{0.5} \quad \text{or} \quad (17)$$

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

For symmetric z:z electrolytes, Eq. (17) may be simplified to:

$$\sigma_d, \mu\text{eq}/\text{m}^2 = -0.608 \times c^{0.5} \times \{ \exp(z y_d/2) - \exp(-z y_d/2) \} = -0.608 \times \Gamma^{0.5} \times \{ 2/z \} \text{sh}(z y_d/2) \quad (18)$$

In general case, Eq. (17) may be rearranged as

$$\sigma_d, \mu\text{eq}/\text{m}^2 = -0.608 \times I_{\text{eff}}^{0.5} \times (P_d^{0.5} - 1/P_d^{0.5}) \quad (19)$$

$$P_d = \exp(F\phi_d/RT) = \exp(y_d) \quad (20)$$

$$I_{\text{eff}} = 0.5 \{ [A^-] + [An^{2-}](2 + 2P_d) + \dots [An^n](n + 2(n-1)P_d + \dots 2P_d^{n-1}) + \\ + [M^+] + [Me^{2+}](2 + 2/P_d) + \dots [Me^{n+}](n + 2(n-1)/P_d + \dots 2/P_d^{n-1}) \} \quad (21)$$

Here and below  $[M^+]$ ,  $[Me^{2+}]$ ,  $[Me^{n+}]$ ,  $[A^-]$ ,  $[An^{2-}]$  and  $[An^n]$  are molar concentrations in the bulk solution (moles per liter). Another variant of Eq. (17) is:

$$\sigma_d, \mu\text{eq}/\text{m}^2 = -0.608 \times \{ 1/I_{\text{eff}}^{0.5} \} \times \left( [A^-]P_d^{0.5} + [An^{2-}](P_d^{0.5} + P_d^{1.5}) + \dots [An^n](P_d + P_d^2 + \dots P_d^n)/P_d^{0.5} \right. \\ \left. - [M^+]/P_d^{0.5} - [Me^{2+}](1/P_d^{0.5} + 1/P_d^{1.5}) - \dots [Me^{n+}]P_d^{0.5}(1/P_d + 1/P_d^2 + \dots 1/P_d^n) \right) \quad (22)$$

As may be seen from Eq. (22), the charge of diffuse layer may be represented by additive function of composition of solution. This gives possibility to calculate contribution of each ion into the total charge of diffuse layer (Pivovarov, 2009, 2010). However, the values of diffuse sorption, which may be guessed from structure of Eq. (22) are very approximate.

For  $M^+A^- + Me^{2+}An^{2-}$  salt mixture,  $M^+/Me^{2+}$  and  $A^-/An^{2-}$  exchange in diffuse layer may be described by Eriksson equation (Eriksson, 1952):

$$E(M^+A^-) = \{ 0.304/[\sigma_d, \mu\text{eq}/\text{m}^2] \} \times \{ [M^+A^-]/[Me^{2+}An^{2-}]^{0.5} \} \times \ln \{ \alpha + (\alpha^2 + 1)^{0.5} \} , \quad \text{where} \quad (23)$$

$$\alpha = \{ [\sigma_d, \mu\text{eq}/\text{m}^2]/0.304 \} \times [Me^{2+}An^{2-}]^{0.5} / \{ [M^+A^-] + 4[Me^{2+}An^{2-}] \} \quad (24)$$

Here  $E(M^+A^-) = \{[DM^+] - [DA^-]\}/\sigma_d$  is equivalent fraction of surface charge balanced by positive adsorption of univalent counter ion and negative adsorption of univalent co-ion, and  $[M^+A^-]$  and  $[Me^{2+}An^{2-}]$  are molar concentrations of 1:1 and 2:2 salts (moles per liter). On this basis,  $E(M^+A^-) + E(Me^{2+}An^{2-}) = 1$ . Neglecting the difference between  $(M^+, Me^{2+})A^-$  and  $(M^+, Me^{2+})An^{2-}$  solutions, one may obtain from Eq. (23) close description of cationic exchange on clays (see Bower, 1959). At  $I = 0.1$  M and less, and at substantially negative surface charge ( $1 \mu\text{eq}/\text{m}^2$  and more), the error is negligible ( $E(M^+A^-) \sim E(M)_{\text{as}}$ , see section “Non-specific ionic exchange” and Eq. 52 below). For  $M^+A^- + Me^{2+}An^{2-}$  salt mixture, Eriksson equation is exact relation.

In general case, there is no analytical solution of Eq. (13). In present study, the exact analytical description of diffuse sorption in arbitrary  $(M^+, Me^{2+})(A^-, An^{2-})$  salt medium was deduced, and convenient method of numerical solution of Eq. (13) was suggested. The results of calculations are compared with ionic exchange on clays.

## ANALYTICAL SOLUTION

The Eq. (13) may be rearranged as:

$$[DM^+], \mu\text{mol}/\text{m}^2 = -0.304 \times [M^+] \times \int_0^{y_d} \left( \{1/P^{0.5}\}/I_{\text{eff}, y}^{0.5} \right) dy \quad (25)$$

$$[DMe^{2+}], \mu\text{mol}/\text{m}^2 = -0.304 \times [Me^{2+}] \times \int_0^{y_d} \left( \{1/P^{0.5} + 1/P^{1.5}\}/I_{\text{eff}, y}^{0.5} \right) dy \quad (26)$$

$$[DMe^{n+}], \mu\text{mol}/\text{m}^2 = -0.304 \times [Me^{2+}] \times \int_0^{y_d} \left( \{1/P + 1/P^2 \dots 1/P^n\} \{P/I_{\text{eff}, y}\}^{0.5} \right) dy \quad (27)$$

$$[DA^-], \mu\text{mol}/\text{m}^2 = 0.304 \times [A^-] \times \int_0^{y_d} \left( P^{0.5}/I_{\text{eff}, y}^{0.5} \right) dy \quad (28)$$

$$[DAn^{2-}], \mu\text{mol}/\text{m}^2 = 0.304 \times [An^{2-}] \times \int_0^{y_d} \left( \{P^{0.5} + P^{1.5}\}/I_{\text{eff}, y}^{0.5} \right) dy \quad (29)$$

$$[DAn^{n-}], \mu\text{mol}/\text{m}^2 = 0.304 \times [An^{2-}] \times \int_0^{y_d} \left( \{P + P^2 + \dots P^n\}/\{P \times I_{\text{eff}, y}\}^{0.5} \right) dy \quad (30)$$

$$P = \exp(y) \quad (31)$$

$$I_{\text{eff}, y} = 0.5 \{ [A^-] + [An^{2-}](2 + 2P) + \dots [An^{n-}](n + 2(n-1)P + \dots 2P^{n-1}) + [M^+] + [Me^{2+}](2 + 2/P) + \dots [Me^{n+}](n + 2(n-1)/P + \dots 2/P^{n-1}) \} \quad (32)$$

For arbitrary  $(M^+, Me^{2+})(A^-, An^{2-})$  salt mixture, Eq. (32) is:

$$I_{\text{eff}, y} = [Me^{2+}]/P + N + [An^{2-}]P \quad (33)$$

$$N = [M^+] + 2[Me^{2+}] = [A^-] + 2[An^{2-}] \quad (34)$$

For this case, Eqs. (25, 26, 28, 28) may be solved analytically. The result may be presented as:

$$[DM^+], \mu\text{mol}/\text{m}^2 = 0.608 \times \{(I_{\text{eff}}/P_d)^{0.5} - I^{0.5}\} \quad (\text{at } [Me^{2+}] = 0) \quad (35)$$

Here  $P_d$  and  $I_{\text{eff}}$  are defined by Eqs. (20) and (21); and, if  $[Me^{2+}] > 0$ :

$$[DM^+], \mu\text{mol}/\text{m}^2 = 0.304 \times \{[M^+]/[Me^{2+}]^{0.5}\} \times \ln[\{2([Me^{2+}]I_{\text{eff}}/P_d)^{0.5} + 2[Me^{2+}]/P_d + N\}/\{2([Me^{2+}]I)^{0.5} + 2[Me^{2+}] + N\}] \quad (36)$$

$$[DMe^{2+}], \mu\text{mol}/\text{m}^2 = 0.304 \times \{(I_{\text{eff}}/P_d)^{0.5} - I^{0.5}\} - 0.5[DM^+] \quad (37)$$

Here  $P_d$ ,  $I_{\text{eff}}$ , and  $N$  are defined by Eqs. (20), (21), and (34) correspondingly. Similarly, for anions:

$$[DA^-], \mu\text{mol}/\text{m}^2 = 0.608 \times \{(I_{\text{eff}}P_d)^{0.5} - I^{0.5}\} \quad (\text{at } [An^{2-}] = 0) \quad (38)$$

If  $[An^{2-}] > 0$  then

$$[DA^-], \mu\text{mol}/\text{m}^2 = 0.304 \times \{[A^-]/[An^{2-}]^{0.5}\} \times \ln[\{2([An^{2-}]I_{\text{eff}}P_d)^{0.5} + 2[An^{2-}]/P_d + N\}/\{2([An^{2-}]I)^{0.5} + 2[An^{2-}] + N\}] \quad (39)$$

$$[DAn^{2-}], \mu\text{mol}/\text{m}^2 = 0.304 \times \{(I_{\text{eff}}P_d)^{0.5} - I^{0.5}\} - 0.5[DA^-] \quad (40)$$

## NUMERICAL SOLUTION

The numerical integration of Eq. (13) may be performed in accordance with, e.g.:

$$[DIon], \mu\text{mol}/\text{m}^2 = \sum_{n=1}^{n=100} \Delta[DIon]_n \quad (41)$$

$$\Delta[DIon]_n, \mu\text{mol}/\text{m}^2 \approx 0.304 \times c_i \times f_i(y) \times \Delta y \quad (42)$$

$$y = (n-0.5) \times \Delta y \quad (n = 1 \text{ to } 100) \quad (43)$$

$$\Delta y = y_d/100 \quad (44)$$

$$f_i(y) = \text{sgn}(y_d) \times \{\exp(-z_i y) - 1\} / [\sum c_i \{\exp(-z_i y) - 1\}]^{0.5} \quad (45)$$

However, near the zero charge point, Eq. (45) leads to instability and failure of calculations due to division by operational zero. Similar problems may be caused by small deviations of the bulk solution from electroneutrality (e.g., “1e-6 M Ca in 0.1 M NaCl”). To avoid these

problems, it is better to rearrange Eq. (45). The variable  $f_i(y)$  for cations may be rearranged as:

$$f_i(y) \text{ (for } M^+) = - (1/P^{0.5})/I_{\text{eff}, y}^{0.5} \quad (46)$$

$$f_i(y) \text{ (for } Me^{2+}) = - (1/P^{0.5} + 1/P^{1.5})/I_{\text{eff}, y}^{0.5} \quad (47)$$

$$f_i(y) \text{ (for } Me^{n+}) = - (1/P + 1/P^2 + \dots 1/P^n) \times \{P/I_{\text{eff}, y}\}^{0.5} \quad (48)$$

Similarly, for anions:

$$f_i(y) \text{ (for } A^-) = P^{0.5}/I_{\text{eff}, y}^{0.5} \quad (49)$$

$$f_i(y) \text{ (for } An^{2-}) = (P^{0.5} + P^{1.5})/I_{\text{eff}, y}^{0.5} \quad (50)$$

$$f_i(y) \text{ (for } An^{n-}) = \{P + P^2 + \dots P^n\}/(P \times I_{\text{eff}, y})^{0.5} \quad (51)$$

Here  $P$  and  $I_{\text{eff}, y}$  are defined by Eqs. (31) and (32). This solves problem.

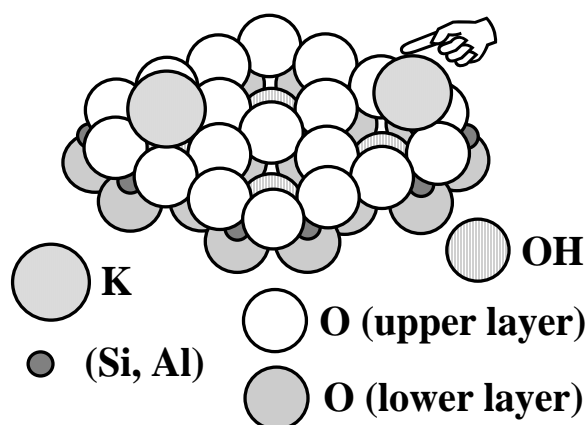
The algorithm of numerical calculation of diffuse sorption at given  $y_d$ , and composition of solution, e.g.,  $[H^+]$ ,  $[Na^+]$ ,  $[K^+]$ ,  $[Ca^{2+}]$ ,  $[Cd^{2+}]$ ,  $[Al^{3+}]$ ,  $[Eu^{3+}]$  and  $[NO_3^-]$  is:

- Define  $f_{M(I)} = 0$ :  $f_{M(II)} = 0$ :  $f_{M(III)} = 0$ :  $f_{A(I)} = 0$
- Calculate  $[M^+] = [H^+] + [Na^+] + [K^+]$   
 $[Me^{2+}] = [Ca^{2+}] + [Cd^{2+}]$   
 $[Me^{3+}] = [Al^{3+}] + [Eu^{3+}]$
- Cycle. From  $n = 1$  to 100, step 1; Calculate  
 $y = (n-0.5)y_d/100$ :  $P = \exp(y)$   
 $I_{\text{eff}, y} = 0.5 \{ [M^+] + [Me^{2+}] \times (2+2/P) + [Me^{3+}] \times (3+4/P + 2/P^2) + [NO_3^-] \}$   
 $f_{M(I)} = f_{M(I)} - (1/P^{0.5}) \times \{1/I_{\text{eff}, y}^{0.5}\} \times \{y_d/100\}$   
 $f_{M(II)} = f_{M(II)} - (1/P^{0.5} + 1/P^{1.5}) \times \{1/I_{\text{eff}, y}^{0.5}\} \times \{y_d/100\}$   
 $f_{M(III)} = f_{M(III)} - (1/P^{0.5} + 1/P^{1.5} + 1/P^{2.5}) \times \{1/I_{\text{eff}, y}^{0.5}\} \times \{y_d/100\}$   
 $f_{A(I)} = f_{A(I)} + P^{0.5} \times \{1/I_{\text{eff}, y}^{0.5}\} \times \{y_d/100\}$   
 Next  $n$
- Calculate  
 $[DH^+], \mu\text{mol}/\text{m}^2 = 0.304 \times [H^+] \times f_{M(I)}$   
 $[DNa^+], \mu\text{mol}/\text{m}^2 = 0.304 \times [Na^+] \times f_{M(I)}$   
 $[DK^+], \mu\text{mol}/\text{m}^2 = 0.304 \times [K^+] \times f_{M(I)}$   
 $[DCa^{2+}], \mu\text{mol}/\text{m}^2 = 0.304 \times [Ca^{2+}] \times f_{M(II)}$   
 $[DCd^{2+}], \mu\text{mol}/\text{m}^2 = 0.304 \times [Cd^{2+}] \times f_{M(II)}$   
 $[DAl^{3+}], \mu\text{mol}/\text{m}^2 = 0.304 \times [Al^{3+}] \times f_{M(III)}$   
 $[DEu^{3+}], \mu\text{mol}/\text{m}^2 = 0.304 \times [Eu^{3+}] \times f_{M(III)}$   
 $[DNO_3^-], \mu\text{mol}/\text{m}^2 = 0.304 \times [NO_3^-] \times f_{A(I)}$

The maximum error of this algorithm in the range  $|y_d| < 6$  is 0.034 % (error is approximately  $(zy_d/n_{\text{tot}})^2$  %, where  $z$  is charge of counter ion, and  $n_{\text{tot}}$  is number of integration steps).

## SURFACE STRUCTURE OF CLAY

The surface structure of clay minerals may be considered on example of muscovite,  $\text{KAl}_2[\text{Si}_3\text{Al}]\text{O}_{10}(\text{OH})_2$ . The structure of basal face of muscovite is sketched in Fig. 1. As may be seen, the major motive is formed by holes, which are located in the nodes of right triangle net. The distance between holes in Fig. 1 is 5.2 Å and 9.0 Å (lattice parameters  $a_0$  and  $b_0$ ). Thus total number of holes is 4.27 per  $\text{nm}^2$  or  $7.1 \mu\text{mol}/\text{m}^2$ . In the bulk lattice, all these holes are filled by potassium ions. If to divide the muscovite crystal along the basal face, the potassium ions will be equally distributed between two new surfaces. Because of this, a half of holes in Fig. 1 are free. One may suggest that the holes of



**Fig. 1** Structure of basal face of muscovite

muscovite surface are specific sites. However, these holes are not identical. The surface charge of muscovite is generated by replacement of quarter of all silicon atoms in tetrahedrons by aluminum. Each aluminum atom, located in tetrahedron, is surrounded by 3 holes. A half of these holes is coordinated by one aluminum atom, whereas another half is doubly coordinated by aluminum atoms. Thus, more realistic surface speciation of muscovite is a following: by  $3.55 \mu\text{mol}/\text{m}^2$  of  $(\ )^{1/3-}$  and  $(\ )^{2/3-}$  positions. Note that the number of strongly charged positions coincides with surface charge of muscovite. Thus, the site density of muscovite is  $3.55 \mu\text{eq}/\text{m}^2$ . The surface area of muscovite one-unit-cell crystal is  $a_0b_0N_A = 282000 \text{ m}^2/\text{mole}$  or  $708 \text{ m}^2/\text{g}$  (formula weight is 398.31 g/mole).

The surface of montmorillonite contain similar holes as muscovite ( $\sim 7.1 \mu\text{mol}/\text{m}^2$ ) and has similar surface area of one-unit-cell crystal ( $282000 \text{ m}^2/\text{mol}$ ). Due to smaller lattice charge, montmorillonite has smaller formula weight. For example, for Wyoming montmorillonite,  $\text{M}^{\text{I}}_{0.31}(\text{Al}_{1.64}\text{Fe}^{\text{III}}_{0.15}\text{Fe}^{\text{II}}_{0.02}\text{Mg}_{0.19})[\text{Si}_{3.9}\text{Al}_{0.1}]\text{O}_{10}(\text{OH})_2$  (Weaver and Pollard, 1973) it is 371.7 g/mol (for sodium form). Thus, “total surface area” of Wyoming montmorillonite is about  $282000/371.7 = 759 \text{ m}^2/\text{g}$ . The montmorillonite is expandable clay. The interlayer distance of montmorillonite varies from  $\sim 9.3 \text{ Å}$  for completely dehydrated samples to  $\sim 20 - 200 \text{ Å}$  in aqueous solutions, depending on concentration and composition of salts; dispersion of montmorillonite in deionized water leads to complete decomposition of crystals (Brindley, 1981). Because of these peculiarities, “total surface area” of monmorillonite is independent of particle size and is close to theoretical surface of one-unit-cell crystal. The whole of this surface is well accessible for ionic exchange.

It should be noted that “dry” montmorillonite contains significant number of physically sorbed water. At typical content of water, 4 per formula unit, its formula weight changes to  $\sim 444 \text{ g/mol}$ , and specific surface area decreases to  $\sim 635 \text{ m}^2/\text{g}$ . If properties of montmorillonite are related to weight of calcinated sample, formula weight decreases to  $\sim 354 \text{ g/mol}$ , and specific surface increases to  $\sim 797 \text{ m}^2/\text{g}$ . In general case, any property of montmorillonite, measured “per gram”, is dependent on drying procedure.

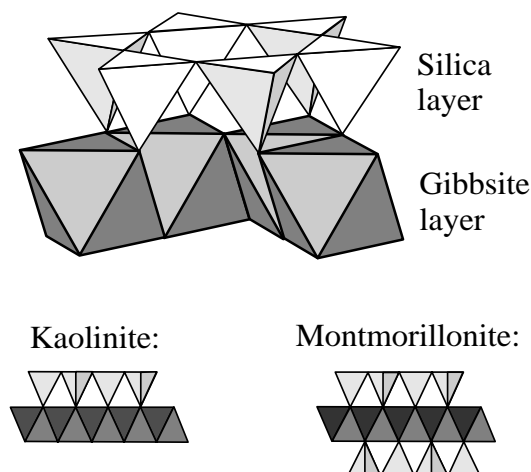
The Wyoming montmorillonite is close to “ideal montmorillonite” with lattice charge  $1/3$  per formula unit, or  $3.55/3 = 1.18 \mu\text{eq}/\text{m}^2$ . The exchange capacity of nominal ideal montmorillonite is  $0.90 \text{ meq}/\text{g}$ . On weight basis of calcinated sample (i.e. decomposed to mixture of oxides), exchange capacity of ideal montmorillonite is  $0.94 \text{ meq}/\text{g}$ . For air dry sample with  $\sim 4$  water molecules per formula unit (referred below as “tetrahydrate”), this value is close to  $\sim 0.75 \text{ meq}/\text{g}$ .



Perhaps, the ideal montmorillonite with surface charge  $1.18 \mu\text{eq}/\text{m}^2$  has the following surface speciation:  $3.55 \mu\text{mol}/\text{m}^2$  of “active positions”  $(\text{O})^{1/3-}$  and  $3.55 \mu\text{mol}/\text{m}^2$  of “inert positions”  $(\text{O})^0$ . However, it is likely that the “active positions” do not act as independent surface species, and specific site of montmorillonite is  $\text{Al}(\text{O})_3^-$ . This site (below designed as  $\text{X}^-$ ) may attach up to 3 exchange cations (note that the distance between the holes is about  $5.2 \text{ \AA}$ , and the exchange cation cannot occupy two holes simultaneously). However, upon adsorption of one potassium ion, the site loses its charge, and thus, formation of complexes such as  $\text{XK}_2^+$  and  $\text{XK}_3^{2+}$  should be negligible. Thus, it is possible, that the site density of montmorillonite is equal to surface charge, and this rule may be extended to all clay minerals.

In addition to “exchange surface”, there is also “oxide surface” of clay. **Fig. 2** shows structure of kaolinite in comparison with montmorillonite. As may be seen, crystal of kaolinite looks like muscovite on one side, and like gibbsite on another side. Thus, fraction of “oxide area” of kaolinite is close to a half of total area. Kaolinite is not expandable clay, and its area coincides with geometric surface of crystal. From its nominal chemical composition,  $\text{Al}_4(\text{OH})_8[\text{Si}_4\text{O}_{10}]$ , lattice charge of kaolinite is zero. Nevertheless, it has exchange capacity of unknown genesis. In case of montmorillonite, the “oxide area” is roundly equal to external area of montmorillonite “quasi-crystal”.

Some properties of typical kaolinite and montmorillonite, relevant to surface modeling, are summarized in **Tab. 1**.



**Fig. 2** Structure of kaolinite, and comparison with montmorillonite

**Tab. 1** Some properties of Wyoming montmorillonite SWy-1 and Georgia kaolinite KGa-1.

Clay	External area, $\text{m}^2/\text{g}$	Exchange area, $\text{m}^2/\text{g}$	Oxide area, $\text{m}^2/\text{g}$	Total area, $\text{m}^2/\text{g}$	Surface charge of exchange area, $\mu\text{eq}/\text{m}^2$	Exchange capacity, $\text{meq}/\text{g}$
Wyoming montmorillonite SWy-1 (Na-form, nominal)	36 <sup>a</sup>	759 <sup>b</sup>	36 <sup>c</sup>	795 <sup>d</sup>	-1.18 <sup>e</sup>	0.90 <sup>f</sup>
Wyoming montmorillonite SWy-1 (Na-form, tetrahydrate)	30 <sup>a</sup>	635 <sup>b</sup>	30 <sup>c</sup>	665 <sup>d</sup>	-1.18 <sup>e</sup>	0.75 <sup>f</sup>
Georgia kaolinite, KGa-1	$\sim 10^g$	$\sim 5^h$	$\sim 5^h$	$\sim 10^i$	-2.6 <sup>j</sup>	$\sim 0.013^k$

<sup>a</sup> from BET analysis, the external area of Wyoming montmorillonite SWy-1 is  $35 \text{ m}^2/\text{g}$  (Baeyens and Bradbury, 1997), or  $31 \text{ m}^2/\text{g}$  (McKinley et al 1995; Zachara et al 1993),

<sup>b</sup> theoretical values

<sup>c</sup> assumed to be equal to external surface area

<sup>d</sup> sum of exchange and oxide surface; from ethylene glycol monoethyl ether adsorption, it is  $662 \text{ m}^2/\text{g}$  (Zachara et al 1993), or  $753 \text{ m}^2/\text{g}$  (Amrhein and Suarez 1991)

<sup>e</sup> surface charge of “ideal” montmorillonite

<sup>f</sup> calculated from surface charge and exchange area; from  $^{22}\text{Na}^+/\text{Na}^+$  exchange measurements, the exchange capacity of Wyoming montmorillonite SWy-1 is  $0.87 \text{ meq}/\text{g}$  (Baeyens and Bradbury, 1997),  $0.75 \text{ meq}/\text{g}$  (McKinley et al 1995), or  $0.82$  (Zachara et al 1993).

<sup>g</sup> from BET analysis, the external area of Georgia kaolinite KGa-1 is  $15.6 \text{ m}^2/\text{g}$  (Zachara et al. 1992),  $10.2 \text{ m}^2/\text{g}$  (Schindler et al 1987), or  $8.2 \text{ m}^2/\text{g}$  (Huertas et al 1999)

<sup>h</sup> estimated as a half of external surface

<sup>i</sup> total and external surfaces of kaolinite are equal

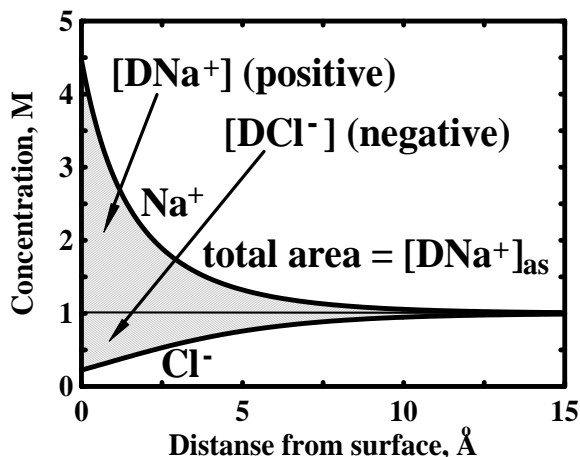
<sup>j</sup> best fit value (present study)

<sup>k</sup> calculated from exchange area and surface charge; as measured by  $^{22}\text{Na}/\text{Na}$  exchange (Zachara et al, 1992), it is  $0.015\text{-}0.018 \text{ meq}/\text{g}$



## NON-SPECIFIC IONIC EXCHANGE

The value of cation sorption, as measured in the ion exchange experiment, often differs from real one. For instance, the values of cation sorption are often normalized on condition: adsorption of anions is zero (see Fig. 3). For example, the precipitate is separated from solution, the exchangeable cations are extracted from precipitate (e.g., by 1 M NH<sub>4</sub>NO<sub>3</sub>, several times), and then, the total amount of extracted cations is corrected on their quantity in the solution remaining in the wet clay prior to extraction. For the chloride medium, this may be determined by total amount of chloride ions in the extracts. The conventional sorption of cation, defined on basis of anion subtraction may be calculated from:



**Fig. 3** Sodium and chloride concentration in 1 M NaCl solution near the surface with charge minus 1 μeq/m<sup>2</sup> (solid curves). Hatched areas correspond to diffuse sorption. Total hatched area (= 1 μeq/m<sup>2</sup>) is conventional sorption of sodium ion

$$[DMe]_{as}, \mu\text{mol/m}^2 = [DMe] - \{[Me]/[A^-]\} \times [DA^-] \quad (52)$$

The conventional equivalent fraction of cation in clay is then defined by:

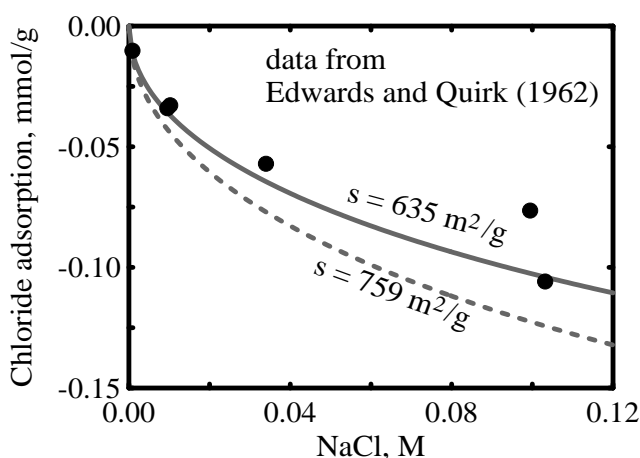
$$E(\text{Me})_{as} = z_i [DMe]_{as} / \sum z_i [DMe]_{as} = - z_i [DMe]_{as} / \sigma_s \quad (53)$$

Another method of correction is based on difference between the weight of precipitate, and weight of dry sample (i.e. weight of water in precipitate). Potentially, it gives real values, [Dion] (see Fig. 3), consistent with classical difference method. In this case, the exchange fraction of metal ion in clay may be defined by:

$$E(\text{Me}) = z_i [DMe] / \sum z_i [DMe] \quad (54)$$

The sum  $\sum z_i [DMe]$  is dependent on composition of solution, and is smaller than total exchange capacity of clay. This is because the negative adsorption of negative ion (anion) gives positive contribution to total charge of diffuse layer.

In Fig. 4, the chloride sorption on montmorillonite is shown (data from Edwards and Quirk, 1962). These values were measured in accordance with classic difference method. At the dispersion of Na-montmorillonite in the NaCl solution, concentration of chloride increases due to repulsion from negatively charged surface. Thus, the difference between initial and final concentration of chloride is negative.



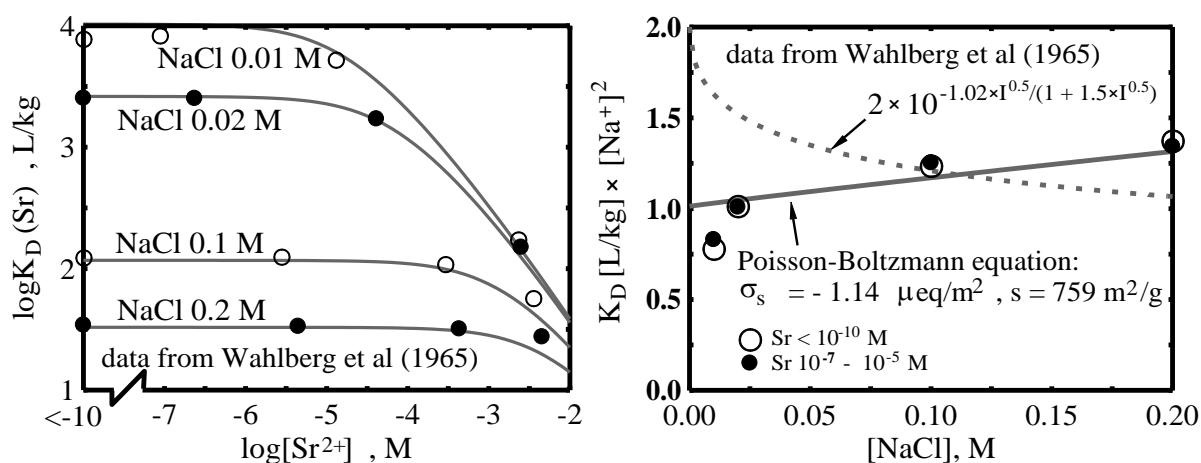
**Fig. 4** Adsorption of chloride ion on Wyoming montmorillonite. Data from Edwards and Quirk (1962).

Note that the concentration of sodium ion in solution also increases. However, the difference between total sodium (initial electrolyte concentration plus sodium in clay related to volume of solution) and final concentration of sodium in solution is positive. The curves in **Fig. 4** were calculated in accordance with Eqs (14, 18), i.e.

$$[\text{DCl}^-], \mu\text{mol/m}^2 = 0.608 \times I^{0.5} \{P_d^{0.5} - 1\} \quad (55)$$

$$P_d^{0.5} = 0.5[\sigma_s, \mu\text{eq/m}^2] / (0.608 \times I^{0.5}) + \left( \{0.5[\sigma_s, \mu\text{eq/m}^2] / (0.608 \times I^{0.5})\}^2 + 1 \right)^{0.5} \quad (56)$$

The surface charge  $\sigma_s$  was set equal to  $-1.18 \mu\text{eq/m}^2$ , and specific surface area was set to  $759 \text{ m}^2/\text{g}$  (for nominal montmorillonite) or to  $635 \text{ m}^2/\text{g}$  (for tetrahydrate, see **Tab. 1**). As may be seen, contribution of chloride into total exchange capacity increases with ionic strength. At low ionic strengths, negative adsorption of anions is small, and difference between  $E(\text{Me})_{\text{as}}$  and  $E(\text{Me})$  may be neglected.



**Fig. 5** Sr distribution coefficient on Burns montmorillonite (left) and that multiplied by square of ionic strength (right). Data from Wahlberg et al (1965). Curves were calculated for surface charge  $-1.14 \mu\text{eq/m}^2$  and exchange area  $759 \text{ m}^2/\text{g}$

**Fig. 5** (left) shows the Sr distribution coefficient on Burns montmorillonite (Wahlberg et al., 1965). Solid curves were calculated in accordance with Eqs. (41-44, 46, 47), assuming surface charge  $-1.14 \mu\text{eq/m}^2$  and specific surface area  $759 \text{ m}^2/\text{g}$ . The same data at trace Sr concentrations, multiplied on square of ionic strength (as NaCl) are shown in right panel of **Fig. 5**. As may be seen, selectivity of clay for bivalent cation increases slightly with ionic strength (see solid curve in right panel of Fig. 5). For comparison, the data are modeled also with use of Gaines-Thomas exchange model (dashed curve in **Fig 5**, right):

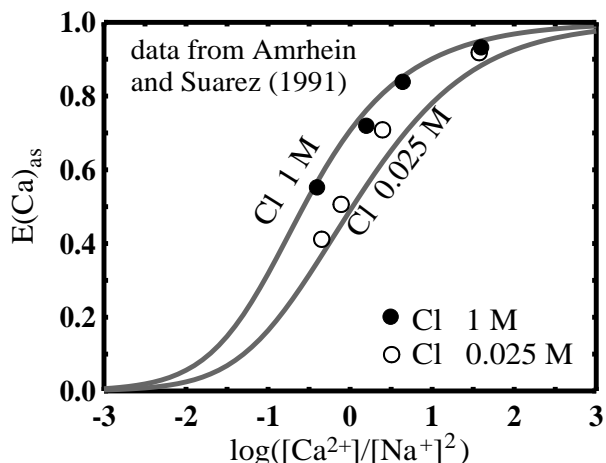


$$K_{\text{Sr/Na}}^0 = \{2[\text{X}_2\text{Sr}]/[\text{XNa}]^2\} \times \{a_{\text{Na}}^2/a_{\text{Sr}}\} = 4.6 \text{ and, for trace Sr,} \quad (58)$$

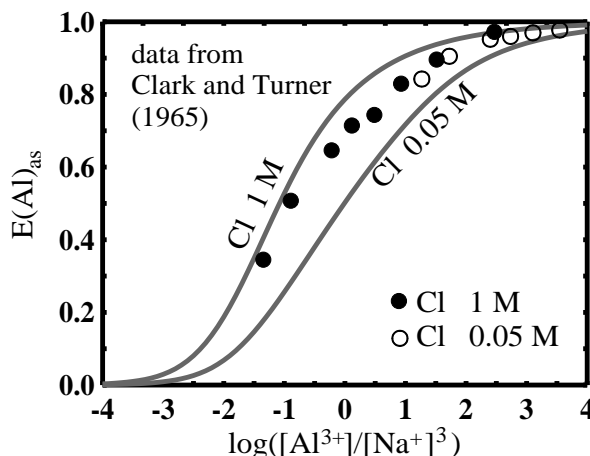
$$K_d(\text{Sr, L/kg}) \times [\text{Na}^+]^2 = 0.5 \times K_{\text{Sr/Na}}^0 \times [\text{Exchange capacity, eq/kg}] \times \{\gamma_{\text{Sr}}/\gamma_{\text{Na}}^2\} \sim \sim 2 \times 10^{-1.02 \times I^{0.5} / (1 + 1.5 \times I^{0.5})} \quad (59)$$

Here  $a_{\text{Sr}}$  and  $a_{\text{Na}}$  are activities of ions in solution.

Thus, on operational basis, the activity coefficient of ion in diffuse layer is close to that in the bulk solution.



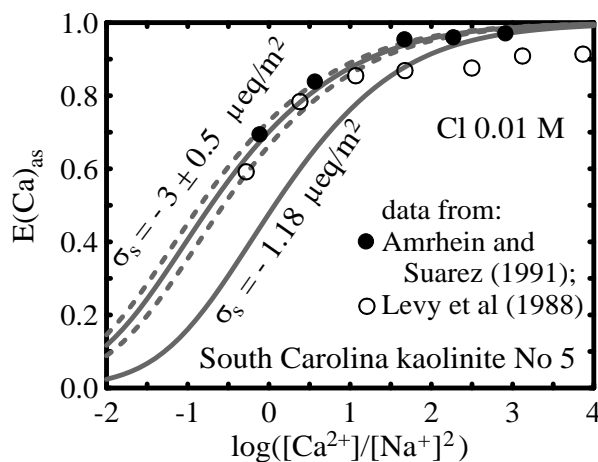
**Fig. 6** Na/Ca exchange on Wyoming montmorillonite. Data from Amrhein and Suarez (1991). Curves were calculated for surface charge - 1.18  $\mu\text{eq}/\text{m}^2$



**Fig. 7** Na/Al exchange on Wyoming montmorillonite. Data from Clark and Turner (1965). Curves were calculated for surface charge - 1.18  $\mu\text{eq}/\text{m}^2$

The selectivity of clay for polyvalent metal ion, as measured in common exchange experiment, also increases with ionic strength. However, this effect seems to be less pronounced than expected from Poisson-Boltzmann equation (see Fig. 6, 7).

The value of surface charge acts as selectivity constant. Thus, the surface charge may be estimated from selectivity of non-equivalent ionic exchange. In Fig. 8, the Na/Ca exchange on kaolinite is shown (kaolinite № 5 from Lamar pit, South Carolina; data from Amrhein and Suarez, 1991, and from Levy et al, 1988). The solid curves in Fig. 8 were calculated for surface charge - 3  $\mu\text{eq}/\text{m}^2$  and - 1.18  $\mu\text{eq}/\text{m}^2$ . As may be seen, selectivity of kaolinite for polyvalent cations is higher than for “ideal montmorillonite”, which may be caused by larger surface charge.



**Fig. 8** Na/Ca exchange on kaolinite. Data from Amrhein and Suarez (1991) and from Levy et al (1988)

## EXTENSION TO STERN MODEL AND SPECIFIC IONIC EXCHANGE

Some ions are preferred by “muscovite-like” surface of clay due to formation of weak complexes with atoms of clay surface. In accordance with the Stern model, the head of diffuse layer is separated from the surface by some distance  $\lambda$  (familarly, it is radius of counter ion). Thus, the chemical (specific) sorption leads to formation of “inner-“ and “outer-sphere” complexes. The charge of ion in the “inner-spheric” complex (e.g.,  $\text{XC}_s^0$  or  $\text{XPb}^+$ ) is located in surface plane. The charge of ion in the “outer-spheric” complex (e.g.,  $\text{X}^-\dots\text{Cs}^+$  or  $\text{X}^-\dots\text{Pb}^{2+}$ ) is located in the head of diffuse layer. The charge of inner (surface) plane plus charge of outer plane is equal by modulus to charge of diffuse layer, e.g.:

$$\sigma_s + \sigma_{\text{out}} = -\sigma_d \quad (60)$$

$$\sigma_s = -[\text{X}^-] - [\text{X}^-\dots\text{Cs}^+] - [\text{X}^-\dots\text{Pb}^{2+}] + [\text{XPb}^+] \quad (61)$$

$$\sigma_{\text{out}} = [\text{X}^-\dots\text{Cs}^+] + 2[\text{X}^-\dots\text{Pb}^{2+}] \quad (62)$$

In accordance with the formula for flat capacitor, the surface potential is related with potential at the head of diffuse layer as

$$\varphi_s = \varphi_d + \{\sigma_s/\varepsilon_0\varepsilon\} \times \lambda = \varphi_d + \sigma_s/C \quad (63)$$

Here  $C$  ( $C \times \text{m}^{-2} \times \text{V}^{-1} = \text{F}/\text{m}^2$ ) is electric capacitance. Consequently, the factor  $P_s = \exp(F\varphi_s/RT)$  is related with  $P_d$  as

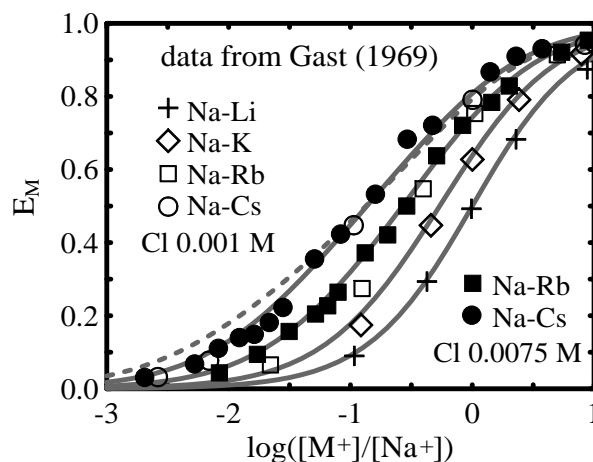
$$P_s = P_d \exp\left(\{F\sigma_s/RT\varepsilon_0\varepsilon\} \times \lambda\right) \quad (64)$$

$$P_s = P_d \exp\left(0.541 \times [\sigma_s, \mu\text{eq}/\text{m}^2] \times [\lambda, \text{\AA}]\right) \quad (64a)$$

Note that the Coulomb’s law factor 0.541 is numerically related with Gouy-Chapman factor 0.608 as  $0.541 = 0.2/0.608^2$ .

In **Fig. 9**, the data on Na-Li, Na-K, Na-Rb, and Na-Cs exchange are shown (Gast, 1969). Solid curves were calculated assuming formation of outer-spheric complexes  $\text{X}^-\dots\text{M}^+$  with formation constant  $K_{\text{X}^-\dots\text{M}^+}^0 = 0$  ( $\text{Li}^+$ ), 0.35 ( $\text{K}^+$ ), 1.6 ( $\text{Rb}^+$ ) and 4.5 ( $\text{Cs}^+$ ). Calculations were performed for the ionic strength 0.0075 M (the results for 0.001 M are closely similar). As may be seen, the slope of calculated exchange curves is closely consistent with experiment. For the comparison, the dashed curve was calculated assuming formation of inner-sphere complex  $\text{XC}_s^0$  ( $K_{\text{XC}_s^0}^0 = 1.5$  and  $\lambda = 3 \text{\AA}$ ). Obviously, the inner-sphere complexation is absent.

The algorithm of calculations at given composition of solution ( $[\text{Na}^+]$ ,  $[\text{K}^+]$ ,  $[\text{Ca}^{2+}]$ ,  $[\text{Al}^{3+}]$ ,  $[\text{Cl}^-]$ ), total number of surface  $\text{X}^-$  groups ( $\text{TX} = |\sigma_s|$ ,  $\mu\text{mol}/\text{m}^2$ ), constant of outer-spheric complex  $\text{X}^-\dots\text{K}^+$  ( $K_{\text{X}^-\dots\text{K}^+}^0$ ), constant of inner-spheric complex  $\text{XK}^0$  ( $K_{\text{XK}^0}^0$ ), and radius of counter ion  $\lambda$  ( $\text{\AA}$ ):



**Fig. 9**  $\text{Na}^+ - \text{M}^+$  exchange on Wyoming montmorillonite. Data from Gast (1969). Solid curves were calculated assuming formation of outer-spheric complexes  $\text{X}^-\dots\text{M}^+$  with formation constant 0 ( $\text{Li}^+$ ), 0.35 ( $\text{K}^+$ ), 1.6 ( $\text{Rb}^+$ ) and 4.5 ( $\text{Cs}^+$ ).

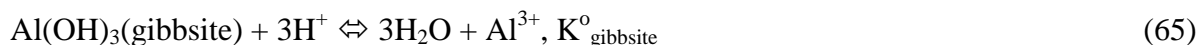
- Define:  $P_d = 1, [X^-] = TX$   
 $P_s = 1, B = 0$  (\*see note below)
- Calculate:  $I = 0.5\{[Na^+] + [K^+] + 4[Ca^{2+}] + 9[Al^{3+}] + [Cl^-]\}$   
 $\gamma_{\pm} = 10^{-0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5})}$
- Cycle. Calculate:  
 $P_s = P_d \times \exp(B)$  (\*see note below)  
 $I_{eff} = 0.5\{[Na^+] + [K^+] + [Ca^{2+}](2 + 2/P_d) + [Al^{3+}](3 + 4/P_d + 2/P_d^2) + [Cl^-]\}$   
 $[X^-] = TX / (1 + K_{X...K}^0 \times \gamma_{\pm} \times [K^+] / P_d + K_{XK}^0 \times \gamma_{\pm} \times [K^+] / P_s)$   
 $[X^- \dots K^+] = K_{X...K}^0 \times \gamma_{\pm} \times [X^-][K^+] / P_d$   
 $[XK^0] = K_{XK}^0 \times \gamma_{\pm} \times [X^-][K^+] / P_s$  (\*see note below)  
 $PLUS = 0.608 \times \{I_{eff} / P_d\}^{0.5}$   
 $MINUS = [X^-] + 0.608 \times \{I_{eff} P_d\}^{0.5}$   
 $P_{d1} = P_d \{PLUS / MINUS\}$   
 $P_d = \{P_d \times P_{d1}\}^{0.5}$
- Compare  $P_d$  and  $P_{d1}$ ; if necessary, repeat cycle
- Calculate:  $B_1 = 0.541 \times \{-[X^-] - [X^- \dots K^+]\} \times [\lambda, \text{\AA}]$  (\*see note below)  
 $B = (3 \times B + B_1) / 4$  (\*see note below)  
 - Compare  $B_1$  and  $B$ ; if necessary, repeat cycle (\*see note below)
- Calculate  $y_d = \ln(P_d)$  and (see algorithm on page 39)  $[DNa^+], [DK^+], [DCa^{2+}], [DAl^{3+}], [DCl^-]$  (in case of  $K^+$ , total sorption is  $[DK^+] + [X^- \dots K^+] + [XK^0]$ ).

\*Note that the surface potential  $y_s = \ln(P_s)$  is necessary for calculations with inner-sphere complexes (such as  $XK^0$ ). Because of evident absence of such complexes, marked lines of algorithm may be omitted together with variables  $P_s, B, [XK^0]$ , and parameters  $\lambda$  and  $K_{XK}^0$ .

## CONCENTRATION OF DISSOLVED ALUMINUM IN CLAY

The ionic exchange in clays is affected by presence of aluminum ions. Because of this, it is necessary to estimate concentration of aluminum ions in solution.

Dry clay contains significant amount of “active” aluminum (adsorbed ions plus hydroxide precipitates). The amount of “active” aluminum is variable and dependent on pre-history of clay. In contact with solution, “active” aluminum dissolves very fast. Nevertheless, it is almost impossible to remove it from clay. Acid treatment leads to slow conversion of clay into Al-form, whereas saturation with index cation and replacement of exchangeable Al leads to formation of Al hydroxide precipitates. In the range of pH ~ 5-10, the amount of aluminum is enough for the formation of gibbsite precipitates:



In accordance with measurements, performed by Peryea and Kittrick (1988), the constant of this reaction is  $K_{\text{gibbsite}}^0 = 10^{7.76 \pm 0.14}$ . This reaction gives the following relationship for concentration of aluminum in solution:

$$[Al^{3+}] = K_{\text{gibbsite}}^0 \times 10^{-3pH} / \gamma_{\pm}^9 \quad (66)$$

Here  $\gamma_{\pm}$  is activity coefficient of univalent ion ( $\gamma_{Al} \approx \gamma_{\pm}^9$ ), which may be estimated from:

$$\gamma_{\pm} \approx 10^{-0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5})} \quad (67)$$

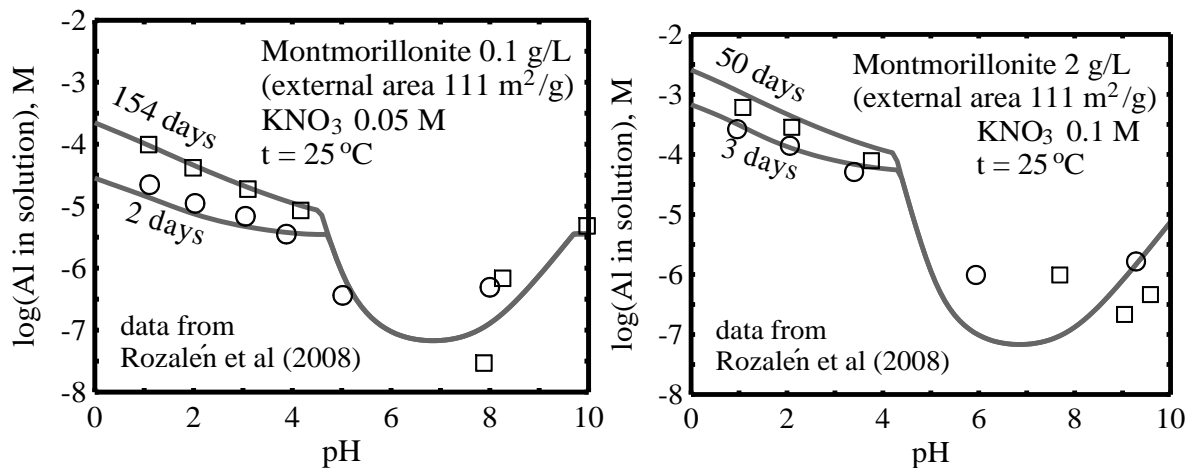
Total aluminum in solution may be calculated as:

$$\text{Al in solution, } M = [\text{Al}^{3+}] \times \{1 + a\text{Al}\} \quad (68)$$

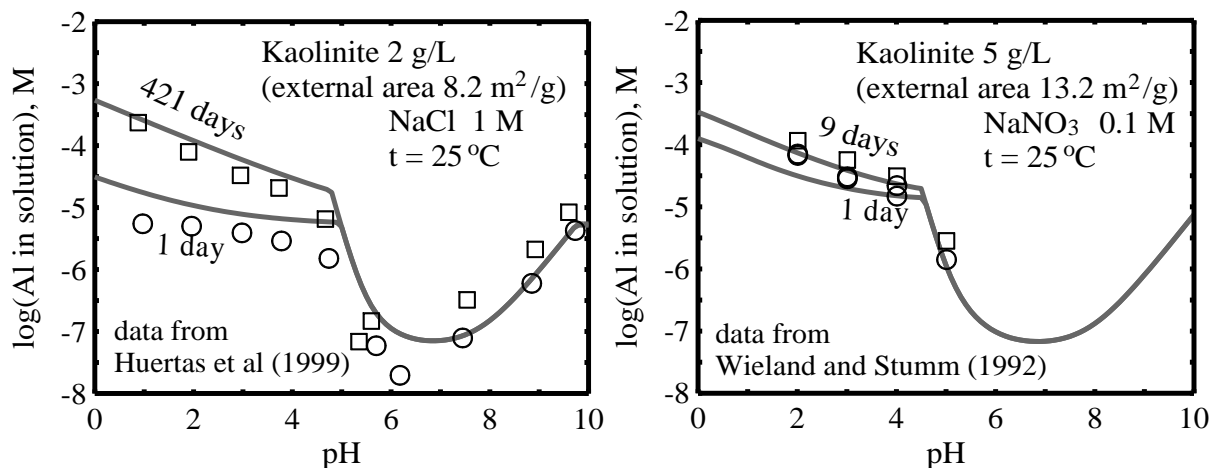
$$a\text{Al} = K_{\text{AlOH}}^0 \times \gamma_{\pm}^5 \times 10^{\text{pH}} + K_{\text{Al(OH)2}}^0 \times \gamma_{\pm}^8 \times 10^{2\text{pH}} + K_{\text{Al(OH)3}}^0 \times \gamma_{\pm}^9 \times 10^{3\text{pH}} + K_{\text{Al(OH)4}}^0 \times \gamma_{\pm}^8 \times 10^{4\text{pH}} \quad (69)$$

Here  $K_{\text{AlOH}}^0 = 10^{-4.97}$ ,  $K_{\text{Al(OH)2}}^0 = 10^{-9.3}$ ,  $K_{\text{Al(OH)3}}^0 = 10^{-15}$ ,  $K_{\text{Al(OH)4}}^0 = 10^{-23}$  are hydrolysis constants of aluminum (see Baes and Mesmer, 1976).

The surface of clay acts as precursor, and precipitation/dissolution of gibbsite is a fast process. However, in acidic and alkaline range, the amount of “active” aluminum is too small for precipitation of gibbsite, and the concentration of dissolved aluminum is controlled by intrinsic solubility of clay mineral.



**Fig. 10** Concentration of aluminum in KCl solutions in presence of Cabo de Gata (Spain) montmorillonite at solid load 0.1 g/L (left) and 2 g/L (right). Data from Rozalén et al (2008).



**Fig. 11** Concentration of aluminum in NaCl solution in presence of Georgia kaolinite (KGa-1). Data from Huertas et al (1999).

**Fig. 12** Concentration of aluminum in NaNO<sub>3</sub> solution in presence of Cornish china kaolinite. Data from Wieland and Stumm (1992).



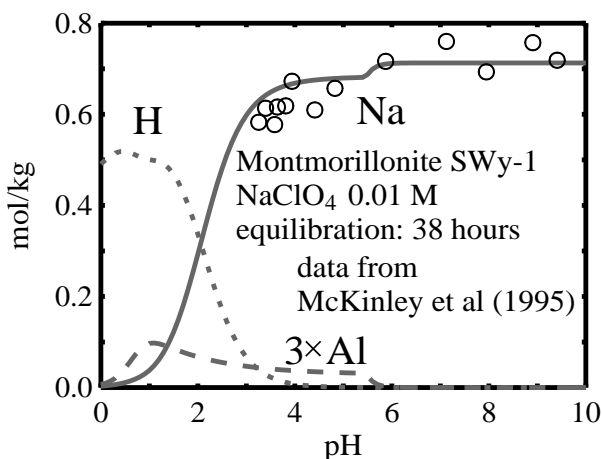
Dissolution of clay minerals is extremely slow process. Besides, the rate of dissolution decreases with time, which may be caused by adsorption of silica and capsulation of “gibbsite” layers. In general case, concentration of aluminum in suspension of clay may be roundly estimated from:

$$\begin{aligned} \text{Total Al, } M &= [\text{Al}^{3+}] \times \{1 + a_{\text{Al}}\} + g_{\text{ex}} \times [\text{DAI}^{3+}, \mu\text{mol/m}^2] \sim \\ &\sim [\text{Clay, g/L}] \times [\text{External area, m}^2/\text{g}] \times \{10^{-6.5} + [\text{Time, days}]^{0.5} \times 10^{-5.8 - \text{pH}/3}\} \end{aligned} \quad (70)$$

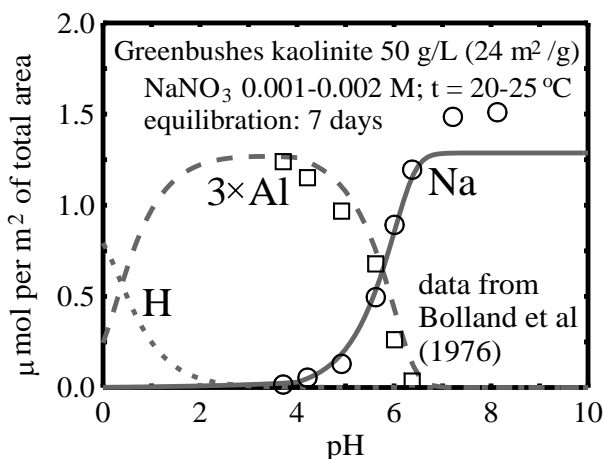
Here  $g_{\text{ex}}$  is conversion factor (from  $\mu\text{mol/m}^2$  to moles per liter):

$$g_{\text{ex}} = 10^{-6} \times [\text{Clay, g/L}] \times [\text{Exchange area, m}^2/\text{g}] \quad (71)$$

The accuracy of this correlation is about 0.3 log units. In **Figs. 10-12**, the data on solubility of montmorillonite and kaolinite are shown. Solid curves were calculated as minimum between Eqs. (66) and (70). It should be noted that Eq. (70) ignores dissolution of clay in alkaline range. However, at  $\text{pH} > 7$ , the aluminum ions are completely hydrolyzed and have no influence on ionic exchange.



**Fig. 13** Exchangeable Na in Wyoming montmorillonite SWy-1 in equilibrium with 0.01 M NaClO<sub>4</sub> solution. Data from McKinley et al (1995). Curves (for solid load > 0.5 g/L) were calculated, assuming parameters for tetrahydrate of Wyoming montmorillonite (see **Tab. 1**)



**Fig. 14** Exchangeable Na and Al in Greenbushes kaolinite in equilibrium with 0.001-0.002 M NaNO<sub>3</sub> solutions. Data from Bolland et al (1976). Curves were calculated, assuming that the concentration of NaNO<sub>3</sub> is 0.002 M, the surface charge of exchange area is -2.6  $\mu\text{eq/m}^2$ , and the exchange area is 50 % of total area

The clay dissolves on edges, and dissolution is roundly proportional to external area (see Eq. 70 and **Tab. 1**). In case of montmorillonite, external area is about 5-10 % of total area. Total aluminum, released from external surface of montmorillonite, is enough to fill 5-20 % of exchange capacity (see **Fig. 13**). Because of this, ionic exchange on montmorillonite surface is almost independent of pH. In suspensions of kaolinite, total aluminum (adsorbed plus dissolved plus precipitated as hydroxide) is close to exchange capacity. In acidic field, the exchange capacity of kaolinite is almost completely filled by aluminum ions (see **Fig. 14**).



## MASS BALANCE EQUATION FOR DIFFUSE SORPTION

If the amount of some component in the system is defined by its total concentration, it is necessary to introduce the mass balance equation. In case of aluminum (outside the range of gibbsite precipitation) it is given by left side of Eq. (70), i.e.

$$\text{Total Al, } M = [\text{Al}^{3+}] \times \{1 + a_{\text{Al}}\} + g_{\text{ex}} \times [\text{DAI}^{3+}, \mu\text{mol/m}^2] \quad (72)$$

For successful solution of mass balance equation, all its terms should be positive. However, the diffuse sorption may be positive and negative as well. Because of this, mass balance equation, such as Eq. (72), may lead to failure of calculations. To avoid this problem, it is better to rearrange Eq. (72):

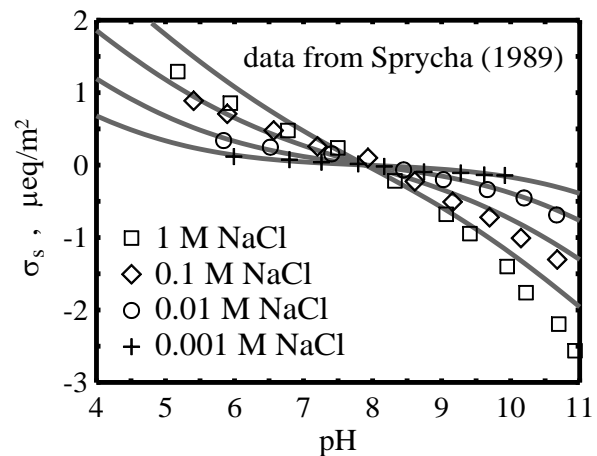
$$\begin{aligned} [\text{Total Al, } M] + 0.5g_{\text{ex}} \times \{ |[\text{DAI}^{3+}, \mu\text{mol/m}^2]| - [\text{DAI}^{3+}, \mu\text{mol/m}^2] \} = \\ = [\text{Al}^{3+}] \times \{1 + a_{\text{Al}}\} + 0.5g_{\text{ex}} \times \{ |[\text{DAI}^{3+}, \mu\text{mol/m}^2]| + [\text{DAI}^{3+}, \mu\text{mol/m}^2] \} \end{aligned} \quad (73)$$

This kind of mass balance equation solves the problem.

## REACTIONS ON GIBBSITE-LIKE SURFACE OF CLAY

To account for specific sorption on “gibbsite-like” surface of clay, it is necessary to consider sorption on alumina.

**Fig. 15** shows surface charge of  $\gamma$ - $\text{Al}_2\text{O}_3$  (data from Sprycha 1989). As may be seen, surface charge of alumina varies with pH. The intersection point near  $\text{pH} \sim 8$  indicates zero surface charge. This behavior may be explained by dissociation of surface hydroxyl groups:



**Fig. 15** Surface charge of  $\gamma$ - $\text{Al}_2\text{O}_3$ . Data from Sprycha (1989)

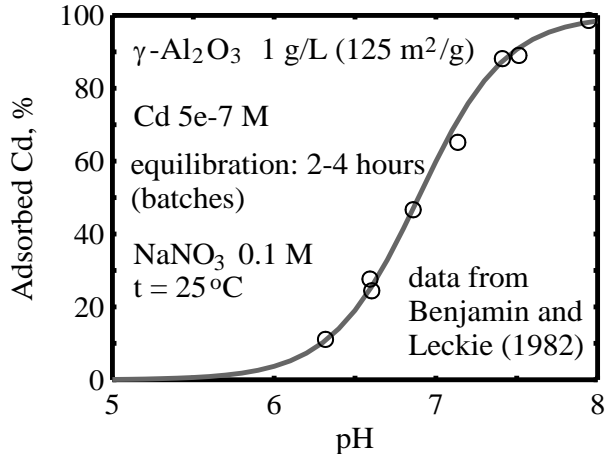


$$K_{\text{SOH}_2}^0 = [\text{SOH}_2^+] \times 10^{\text{pH}} \times P_s / [\text{SOH}^0] = 10^{6.8} \quad (75)$$

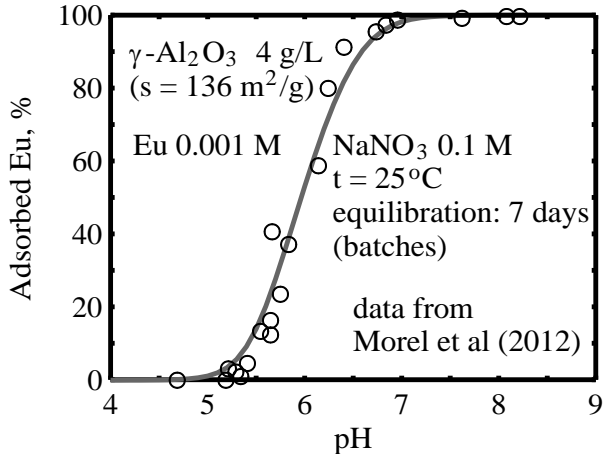


$$K_{\text{SO}^-}^0 = [\text{SO}^-] \times 10^{\text{pH}} / \{P_s[\text{SOH}^0]\} = 10^{-9} \quad (77)$$

Here  $P_s = \exp(y_s)$ , and  $y_s$  is scaled surface potential of oxide surface. The modeling of oxides is always overparameterized, and some parameters of model should be taken arbitrarily. The solid curves in **Fig. 15** were calculated, assuming that the site density ( $\text{TSOH} = [\text{SOH}_2^+] + [\text{SOH}^0] + [\text{SO}^-]$ ) is  $4 \mu\text{mol/m}^2$ , and the radius of counter ion  $\lambda$  is  $2 \text{ \AA}$ .

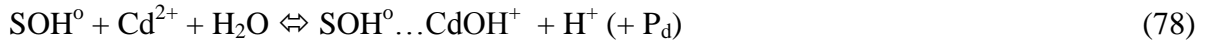


**Fig. 16** Cd adsorption on  $\gamma\text{-Al}_2\text{O}_3$ . Data from Benjamin and Leckie (1982)



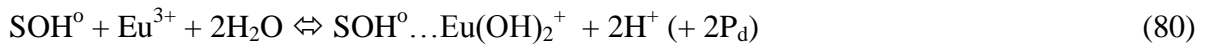
**Fig. 17** Eu adsorption on  $\gamma\text{-Al}_2\text{O}_3$ . Data from Morel et al (2012)

In **Fig. 16**, the adsorption of cadmium on  $\gamma\text{-Al}_2\text{O}_3$  is shown (data from Benjamin and Leckie, 1982). As may be seen, adsorption increases from zero to 100% in very narrow pH range. The solid curve in **Fig. 16** was calculated assuming formation of outer-spheric complex:



$$K^0(\text{SOH}^0 \dots \text{CdOH}^+) = \frac{[\text{SOH}^0 \dots \text{CdOH}^+]}{[\text{SOH}^0][\text{Cd}^{2+}]} \times 10^{-\text{pH}} / \{P_d[\text{SOH}^0][\text{Cd}^{2+}]\gamma_{\text{Cd}}\} = 10^{-2.45} \quad (79)$$

Similar data for europium (Morel et al, 2012) are shown in **Fig. 17**. The solid curve in **Fig. 17** was calculated assuming reaction:



$$K^0(\text{SOH}^0 \dots \text{Eu}(\text{OH})_2^+) = \frac{[\text{SOH}^0 \dots \text{Eu}(\text{OH})_2^+]}{[\text{SOH}^0][\text{Eu}^{3+}]} \times 10^{-2\text{pH}} / \{P_d[\text{SOH}^0][\text{Eu}^{3+}]\gamma_{\text{Eu}}\} = 10^{-6.5} \quad (81)$$

Due to overparametrization, the surface complexation model gives no definite information on real processes at interface. However, this method is more accurate than approximation of experimental distribution coefficients by some empirical function.

The algorithm of calculation of, e.g., Cd sorption on oxide (neglecting, for clarity, solubility of oxide) at given total concentration of cadmium (TCd, M), solid load (SL, g/L), specific area of oxide ( $s_{\text{ox}}$ ,  $\text{m}^2/\text{g}$ ), site density of oxide ( $\text{TSOH}$ ,  $\mu\text{mol}/\text{m}^2$ ), acid-base constants ( $K^0_{\text{SOH}_2}$  and  $K^0_{\text{SO}}$ ), radius of counter ion ( $\lambda$ , Å), constant of cadmium adsorption ( $K^0_{\text{SOH}^0 \dots \text{CdOH}^+}$ ) and hydrolysis ( $K^0_{\text{CdOH}} = 10^{-10.08}$ ,  $K^0_{\text{Cd}(\text{OH})_2} = 10^{-20.35}$ ,  $K^0_{\text{Cd}(\text{OH})_3} = 10^{-33.3}$ ,  $K^0_{\text{Cd}(\text{OH})_4} = 10^{-47.35}$ , as given by Baes and Mesmer, 1976), pH, and composition of bulk solution ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ ):

- Define:  $[Cd^{2+}] = TCd; P_d = 1; P_s = 1; B = 0$
- Calculate:  $g_{ox} = 10^{-6} \times [SL, g/L] \times [s_{ox}, m^2/g]$

- Cycle.

- Calculate:

$$[NO_3^-] = [Na^+] + 2[Ca^{2+}] + 2[Cd^{2+}]$$

$$I = 0.5 \{ [Na^+] + 4[Ca^{2+}] + 4[Cd^{2+}] + [NO_3^-] \}$$

$$\gamma_{\pm} = 10^{\{-0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5})\}}$$

(Subprogram)

Define:  $f_{M(II)} = 0$

Calculate:  $y_d = \ln(P_d)$

From  $n = 1$  to 100, step 1; Calculate:

$y = (n-0.5) \{ y_d / 100 \}; P = \exp(y)$

$I_{eff, y} = 0.5 \{ [Na^+] + \{ [Ca^{2+}] + [Cd^{2+}] \} \times (2 + 2/P) + [NO_3^-] \}$

$f_{M(II)} = f_{M(II)} - (1/P^{0.5} + 1/P^{1.5}) \times \{ 1/I_{eff, y}^{0.5} \} \times \{ y_d / 100 \}$

Next  $n$

(End of subprogram)

- Calculate:

$P_s = P_d \times \exp(B)$

$bSOH = K_{SOH2}^o \times 10^{-pH} / P_s + K_{SO}^o \times 10^{pH} \times P_s + K_{SOH...CdOH}^o \times [Cd^{2+}] \times \gamma_{\pm}^4 \times 10^{pH} / P_d$

$[SOH^o] = TSOH / (1 + bSOH)$

$[SOH_2^+] = K_{SOH2}^o \times [SOH^o] \times 10^{-pH} / P_s$

$[SO^-] = K_{SO}^o \times [SOH^o] \times 10^{pH} \times P_s$

$aCd = K_{CdOH}^o \times \gamma_{\pm}^3 \times 10^{pH} + K_{Cd(OH)2}^o \times \gamma_{\pm}^4 \times 10^{2pH} +$   
 $+ K_{Cd(OH)3}^o \times \gamma_{\pm}^3 \times 10^{3pH} + K_{Cd(OH)4}^o \times 10^{4pH}$

$bCd = K_{SOH...CdOH}^o \times g_{ox} \times [SOH^o] \times \gamma_{\pm}^4 \times 10^{pH} / P_d$

$dCd = 0.304 \times g_{ox} \times f_{M(II)}$

$[Cd^{2+}] = \{ TCd + [Cd^{2+}] \times (|dCd| - dCd) / 2 \} / \{ 1 + aCd + bCd + (|dCd| + dCd) / 2 \}$

$[SOH...CdOH^+] = K_{SOH...CdOH}^o \times [SOH^o] \times [Cd^{2+}] \times \gamma_{\pm}^4 \times 10^{pH} / P_d$

$I_{eff} = 0.5 \{ [Na^+] + \{ [Ca^{2+}] + [Cd^{2+}] \} (2 + 2/P_d) + [NO_3^-] \}$

PLUS =  $[SOH_2^+] + [SOH...CdOH^+] + 0.608 \times \{ I_{eff} / P_d \}^{0.5}$

MINUS =  $[SO^-] + 0.608 \times \{ I_{eff} P_d \}^{0.5}$

$P_{d1} = P_d \{ PLUS / MINUS \}$

$P_d = \{ P_d \times P_{d1} \}^{0.5}$

- Compare  $P_d$  and  $P_{d1}$ ; if necessary, repeat cycle

- Calculate:  $B_1 = 0.541 \times \{ [SOH_2^+] - [SO^-] \} \times [\lambda, \text{Å}]$

$B = (3 \times B + B_1) / 4$

- Compare  $B_1$  and  $B$ ; if necessary, repeat cycle

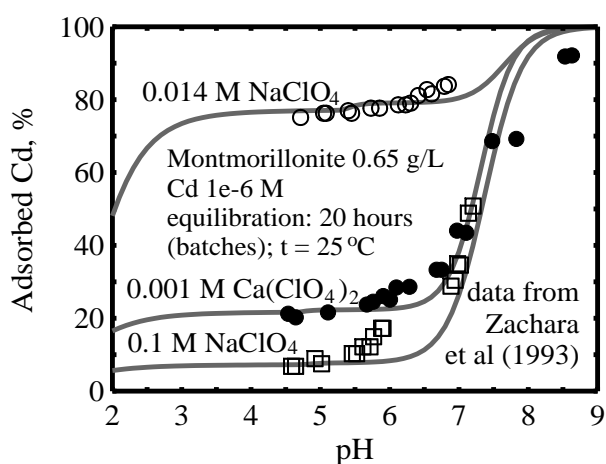
- Calculate: Adsorbed Cd, % =  $100 - 100 \times [Cd^{2+}] \times (1 + aCd) / TCd$  or, the same:

Adsorbed Cd, % =  $100 \times [Cd^{2+}] \times (bCd + dCd) / TCd$

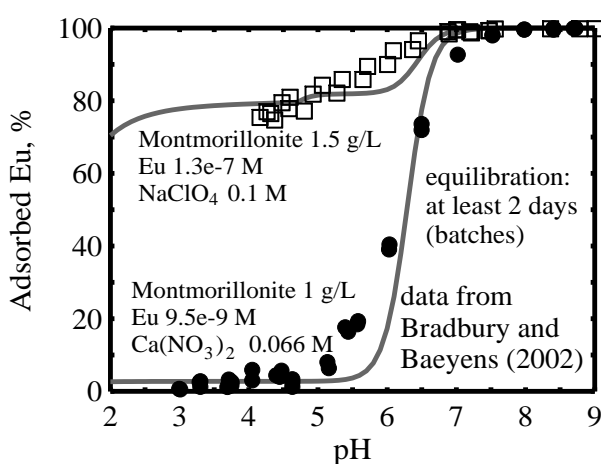
It should be noted that the diffuse sorption of polyvalent ions on oxides (except silica, see Pivovarov, 2010), as compared with specific sorption, is negligible. In case of data in Figs. 16, 17, the diffuse sorption accounts for less than 0.03 % of total Cd, and less than 0.15 % of total Eu. Because of this, subprogram for calculation of diffuse sorption may be omitted together with variables  $f_{M(II)}$  and  $dCd$ . Besides, up to  $pH = 9$ , the hydrolysis of Cd in solution may be neglected.

## EXCHANGE AND SPECIFIC SORPTION IN CLAYS

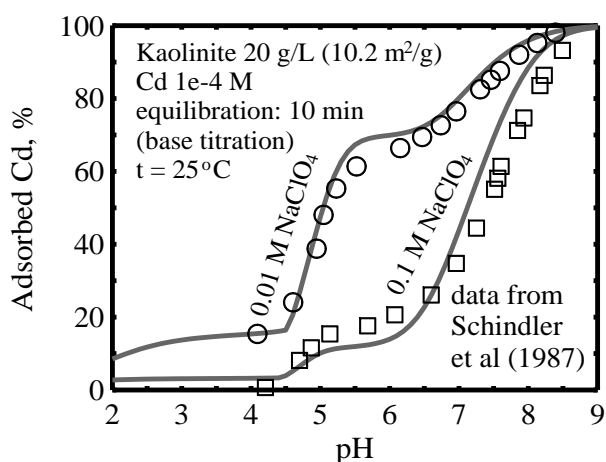
“Gibbsite-like” and “muscovite-like” surfaces of clay are separated each of other (see Fig. 2). Thus, potentials of the “oxide” and “exchange” surfaces are independent variables. Therefore, adsorption of ions on clay may be considered as adsorption on mechanical mixture of “exchanger” and “oxide”. Solid curves in Figs. 18-21 were calculated for sorption of metal ion on mechanical mixture of  $\gamma\text{-Al}_2\text{O}_3$  and “exchanger” having constant surface charge ( $-1.18 \mu\text{eq}/\text{m}^2$  for montmorillonite and  $-2.6 \mu\text{eq}/\text{m}^2$  for kaolinite). The “exchange” and “oxide” surface of kaolinite are equal to a half of total surface. In case of montmorillonite, parameters for nominal montmorillonite were used (see Tab. 1). As may be seen, this is good approach. There is the only unexpected effect: “oxide-like” sorption curves on montmorillonite are gentler (see Figs 18, 19) than these on  $\gamma\text{-Al}_2\text{O}_3$  (see Figs 16, 17). Perhaps, this is caused by curvature of interface on edges, or by interference between potentials of “oxide” and “exchange” area.



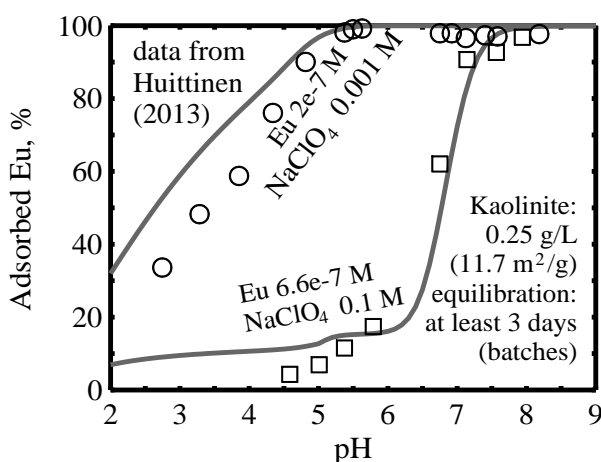
**Fig. 18** Cd adsorption on Wyoming montmorillonite SWy-1. Data from Zachara et al (1993)



**Fig. 19** Eu adsorption on Wyoming montmorillonite SWy-1. Data from Bradbury and Baeyens (2002)



**Fig. 20** Cd adsorption on Georgia kaolinite KGa-1. Data from Schindler et al (1987)



**Fig. 21** Eu adsorption on St. Austell (UK) kaolinite. Data from Huittinen (2013)

The algorithm of calculation of, e.g., Eu sorption on clay at given total concentration of europium (TEu, M), solid load (SL, g/L), oxide area ( $s_{ox}$ ,  $m^2/g$ ), exchange area ( $s_{ex}$ ,  $m^2/g$ ), external area ( $s_{ext}$ ,  $m^2/g$ ), surface charge of exchange area ( $\sigma_{ex}$ ,  $\mu eq/m^2$ ), site density of exchange area ( $TX = |\sigma_{ex}|$ ,  $\mu mol/m^2$ ), site density of oxide surface (TSOH,  $\mu mol/m^2$ ), acid-base constants ( $K_{SOH2}^o$  and  $K_{SO}^o$ ), radius of counter ion ( $\lambda$ , Å), constants of europium adsorption ( $K_{SOH...Eu(OH)2}^o$ ) and hydrolysis ( $K_{EuOH}^o = 10^{-7.64}$ ,  $K_{Eu(OH)2}^o = 10^{-15.2}$ ,  $K_{Eu(OH)3}^o = 10^{-23.7}$ ,  $K_{Eu(OH)4}^o = 10^{-36.2}$ , as given by Hummel et al, 2002), equilibration time (Time, days), solubility product of gibbsite ( $K_{gibbsite}^o$ ), constants of aluminum hydrolysis ( $K_{AlOH}^o$ ,  $K_{Al(OH)2}^o$ ,  $K_{Al(OH)3}^o$ ,  $K_{Al(OH)4}^o$ ), constant of potassium sorption ( $K_{X...K}^o$ ), pH, and composition of bulk solution ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Cl^-$ ) is given below. Subscripts “ex” and “ox” specify variables, related to “exchanger” and “oxide” surfaces of clay.

- Calculate:  $g_{ox} = 10^{-6} \times [SL, g/L] \times [s_{ox}, m^2/g]$   
 $g_{ex} = 10^{-6} \times [SL, g/L] \times [s_{ex}, m^2/g]$   
 $TAl = [SL, g/L] \times [s_{ext}, m^2/g] \times \{10^{-6.5} + [Time, days]^{0.5} \times 10^{-5.8-pH/3}\}$

- Define:  $[Al^{3+}] = TAl$ ,  $[Eu^{3+}] = TEu$ ;  $P_{d(ex)} = 1$ ;  $P_{d(ox)} = 1$ ;  $P_{s(ox)} = 1$ ;  $B_{ox} = 0$ ;  $\gamma_{\pm} = 1$

- Cycle.

- Calculate:

$$[H^+] = 10^{-pH} / \gamma_{\pm}$$

$$[Cl^-] = [H^+] + [Na^+] + [K^+] + 2[Ca^{2+}] + 3[Al^{3+}] + 3[Eu^{3+}]$$

$$I = 0.5 \{ [H^+] + [Na^+] + [K^+] + 4[Ca^{2+}] + 4[Al^{3+}] + 9[Eu^{3+}] + 9[Al^{3+}] + [Cl^-] \}$$

$$\gamma_{\pm} = 10^{\{-0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5})\}}$$

(Subprogram)

Define:  $f_{M(III)ox} = 0$ ;  $f_{M(III)ex} = 0$ :

Calculate:  $y_{d(ox)} = \ln(P_{d(ox)})$ ;  $y_{d(ex)} = \ln(P_{d(ex)})$

From  $n = 1$  to 100, step 1; Calculate:

$y_{ox} = (n-0.5) \{ y_{d(ox)} / 100 \}$ ;  $P_{ox} = \exp(y_{ox})$

$I_{eff, y_{ox}} = 0.5 \{ [H^+] + [Na^+] + [Ca^{2+}] \times (2 + 2/P_{ox}) + \{ [Al^{3+}] + [Eu^{3+}] \} \times (3 + 4/P_{ox} + 2/P_{ox}^2) + [Cl^-] \}$

$f_{M(III)ox} = f_{M(III)ox} - (1/P_{ox}^{0.5} + 1/P_{ox}^{1.5} + 1/P_{ox}^{2.5}) \times \{ 1/I_{eff, y_{ox}} \}^{0.5} \times \{ y_{d(ox)} / 100 \}$

$y_{ex} = (n-0.5) \{ y_{d(ex)} / 100 \}$ ;  $P_{ex} = \exp(y_{ex})$

$I_{eff, y_{ex}} = 0.5 \{ [H^+] + [Na^+] + [Ca^{2+}] \times (2 + 2/P_{ex}) + \{ [Al^{3+}] + [Eu^{3+}] \} \times (3 + 4/P_{ex} + 2/P_{ex}^2) + [Cl^-] \}$

$f_{M(III)ex} = f_{M(III)ex} - (1/P_{ex}^{0.5} + 1/P_{ex}^{1.5} + 1/P_{ex}^{2.5}) \times \{ 1/I_{eff, y_{ex}} \}^{0.5} \times \{ y_{d(ex)} / 100 \}$

Next n

(End of subprogram)

- Calculate:

$P_{s(ox)} = P_{d(ox)} \times \exp(B_{ox})$

$bSOH = K_{SOH2}^o \times 10^{-pH} / P_{s(ox)} + K_{SO}^o \times 10^{pH} \times P_{s(ox)} + K_{SOH...Eu(OH)2}^o \times [Eu^{3+}] \times \gamma_{\pm}^9 \times 10^{2pH} / P_{d(ox)}$

$[SOH^o] = TSOH / (1 + bSOH)$

$[SOH_2^+] = K_{SOH2}^o \times [SOH^o] \times 10^{-pH} / P_{s(ox)}$

$[SO^-] = K_{SO}^o \times [SOH^o] \times 10^{pH} \times P_{s(ox)}$

$bX = K_{X...K}^o \times [K^+] \times \gamma_{\pm} / P_{d(ex)}$

$[X^-] = TX / (1 + bX)$

$$\begin{aligned}
 aAl &= K^o_{AlOH} \times \gamma_{\pm}^5 \times 10^{pH} + K^o_{Al(OH)_2} \times \gamma_{\pm}^8 \times 10^{2pH} + \\
 &\quad + K^o_{Al(OH)_3} \times \gamma_{\pm}^9 \times 10^{3pH} + K^o_{Al(OH)_4} \times \gamma_{\pm}^8 \times 10^{4pH} \\
 dAl &= 0.304 \times \{g_{ox} \times f_{M(III)ox} + g_{ex} \times f_{M(III)ex}\} \\
 [Al^{3+}] &= \{TAl + [Al^{3+}] \times (|dAl| - dAl) / 2\} / \{1 + aAl + (|dAl| + dAl) / 2\} \\
 \text{If } [Al^{3+}] > K^o_{gibbsite} \times 10^{-3pH} / \gamma_{\pm}^9, &\text{ then } [Al^{3+}] = K^o_{gibbsite} \times 10^{-3pH} / \gamma_{\pm}^9
 \end{aligned}$$

$$\begin{aligned}
 aEu &= K^o_{EuOH} \times \gamma_{\pm}^5 \times 10^{pH} + K^o_{Eu(OH)_2} \times \gamma_{\pm}^8 \times 10^{2pH} + \\
 &\quad + K^o_{Eu(OH)_3} \times \gamma_{\pm}^9 \times 10^{3pH} + K^o_{Eu(OH)_4} \times \gamma_{\pm}^8 \times 10^{4pH} \\
 bEu &= K^o_{SOH...EuOH} \times g_{ox} \times [SOH^o] \times \gamma_{\pm}^9 \times 10^{pH} / P_{d(ox)} \\
 dEu &= 0.304 \times \{g_{ox} \times f_{M(III)ox} + g_{ex} \times f_{M(III)ex}\} \\
 [Eu^{3+}] &= \{TEu + [Eu^{3+}] \times (|dEu| - dEu) / 2\} / \{1 + aEu + bEu + (|dEu| + dEu) / 2\} \\
 [SOH...Eu(OH)_2^+] &= K^o_{SOH...Eu(OH)_2} \times [SOH^o] \times [Eu^{3+}] \times \gamma_{\pm}^9 \times 10^{2pH} / P_{d(ox)}
 \end{aligned}$$

$$\begin{aligned}
 I_{eff, ox} &= 0.5 \{ [Na^+] + [Ca^{2+}] \times (2 + 2/P_{d(ox)}) + \{ [Al^{3+}] + [Eu^{3+}] \} \times (3 + 4/P_{d(ox)} + 2/P_{d(ox)}^2) + [Cl^-] \} \\
 PLUS_{ox} &= [SOH_2^+] + [SOH...Eu(OH)_2^+] + 0.608 \times \{ I_{eff, ox} / P_{d(ox)} \}^{0.5} \\
 MINUS_{ox} &= [SO^-] + 0.608 \times \{ I_{eff, ox} \times P_{d(ox)} \}^{0.5} \\
 P_{d(ox)1} &= P_{d(ox)} \{ PLUS_{ox} / MINUS_{ox} \} \\
 P_{d(ox)} &= \{ P_{d(ox)} \times P_{d(ox)1} \}^{0.5}
 \end{aligned}$$

$$\begin{aligned}
 I_{eff, ex} &= 0.5 \{ [Na^+] + [Ca^{2+}] \times (2 + 2/P_{d(ex)}) + \{ [Al^{3+}] + [Eu^{3+}] \} \times (3 + 4/P_{d(ex)} + 2/P_{d(ex)}^2) + [Cl^-] \} \\
 PLUS_{ex} &= 0.608 \times \{ I_{eff, ex} / P_{d(ex)} \}^{0.5} \\
 MINUS_{ex} &= [X^-] + 0.608 \times \{ I_{eff, ex} \times P_{d(ex)} \}^{0.5} \\
 P_{d(ex)1} &= P_{d(ex)} \{ PLUS_{ex} / MINUS_{ex} \} \\
 P_{d(ex)} &= \{ P_{d(ex)} \times P_{d(ex)1} \}^{0.5}
 \end{aligned}$$

- Compare  $P_{d(ox)}$  and  $P_{d(ox)1}$ ,  $P_{d(ex)}$  and  $P_{d(ex)1}$ ; if necessary, repeat cycle
- Calculate:  $B_{ox1} = 0.541 \times \{ [SOH_2^+] - [SO^-] \} \times [\lambda, \text{Å}]$   
 $B_{ox} = (3 \times B_{ox} + B_{ox1}) / 4$
- Compare  $B_{ox1}$  and  $B_{ox}$ ; if necessary, repeat cycle
- Calculate: Adsorbed Eu, % =  $100 - 100 \times [Eu^{3+}] \times (1 + aEu) / TEu$  or, the same:  
 Adsorbed Eu, % =  $100 \times [Eu^{2+}] \times (bEu + dEu) / TEu$

## CONCLUDING REMARKS

It looks like a miracle that, knowing the Boltzmann law and Coulomb law (Poisson equation), one may predict chemical equilibria in clays. Nevertheless, that is so.

## REFERENCES

- Amrhein C. and Suarez D.L. (1991) Sodium-calcium exchange with anion exclusion and weathering corrections. *Soil Science Society of America Journal*, 55, 698-706.
- Baes C.F and Mesmer R.F (1976) *The hydrolysis of cations*. Wiley.
- Baeyens B. and Bradbury M.H. (1997) A mechanistic description of Ni and Zn sorption on Na-montmorillonite Part I: Titration and sorption measurements. *J. Contaminant Hydrol.* 27, 199-222.
- Benjamin M.M, and Leckie J.O. (1982) Effects of complexation by Cl, SO<sub>4</sub>, and S<sub>2</sub>O<sub>3</sub> on adsorption behavior of Cd on oxide surfaces. *Environ Sci. Technol.* 16, 162-170.
- Bolland M.D.A, Posner A.M. and Quirk J.P. (1976) Surface charge on kaolinites in aqueous suspensions. *Aust. J. Soil Sci.* 14, 197-216.
- Borkovec M. and Westall J. (1983) Solution of the Poisson-Boltzmann equation for surface excesses of ions in the diffuse layer at the oxide-electrolyte interface. *J. Electroanal. Chem.* 150, 325-337.
- Bower C.A. (1959) Cation exchange equilibria in soils affected by sodium salts. *Soil Sci.* 88, 32-35.
- Bradbury M.H. and Baeyens B. (2002) Sorption of Eu on Na- and Ca-montmorillonites: experimental investigations and modeling with cation exchange and surface complexation. *Geochim. Cosmochim. Acta* 66, 2325-2334.
- Brindley G.W. (1981) Clays, clay minerals. In: *The Encyclopedia of Mineralogy* (ed. K. Frye). Hutchinson Ross Publishing Company, Stroudsburg, Pennsylvania.
- Clark J.S. and Turner R.C. (1965) Extraction of exchangeable cations and distribution constants for ion exchange. *Soil Science Society of America Journal*, 29, 271-274.
- Edwards D.G. and Quirk J.P. (1962) Repulsion of chloride by montmorillonite. *Journal of Colloid Science*, 17, 872-882.
- Eriksson E. (1952) Cation exchange equilibria on clay minerals. *Soil Science*, 74, 103-118.
- Gast R.G. (1969) Standard free energies of exchange for alkali metal cations on Wyoming bentonite. *Soil Science Society of America Journal*, 33, 37-41.
- Huertas F.J., Chou L., Wollast R. (1999) Mechanism of kaolinite dissolution at room temperature and pressure. Part II: Kinetic study. *Geochim Cosmochim Acta* 63, 3261-3275.
- Huittinen N.M. (2013) Sorption of trivalent actinides onto gibbsite,  $\gamma$ -alumina, and kaolinite. PhD thesis, Univ. of Helsinki.
- Hummel W., Berner U., Curti E., Pearson F. J., and Thoenen T. (2002) *Nagra/PSI Chem. Thermodynamic Data Base 01/01. NAGRA Technical Report NTB 02-16*, Nagra, Wettingen, Switzerland and Universal Publishers/uPublish.com, Parkland, Florida, USA
- Levy G.J., van der Watt H.v.H., Shainberg I., and du Plessis H.M. (1988) Potassium-calcium and sodium-calcium exchange on kaolinite and kaolinitic soils. *Soil Sci. Soc. Am. J.* 52, 1259-1264.
- McKinley J.P., Zachara J.M., Smith S.C., and Turner G.D. (1995) The influence of uranyl hydrolysis and multiple site-binding reactions on adsorption of U(VI) to montmorillonite. *Clays and Clay Miner.* 43, 586-598.
- Morel J.-P., Marmier N., Hurel Ch., Morel-Desrosiers N. (2012) Effect of temperature on sorption of europium on alumina: microcalorimetry and batch experiments. *J. Colloid Interface Sci.* 376, 196-201.
- Neal C. and Cooper D.M. (1983) Extended version of Gouy-Chapman electrostatic theory as applied to the exchange behavior of clay in natural waters. *Clays and Clay Mineralogy*, 31, 367-376.



- Peryea F.J. and Kittrick J.A. (1988) Relative solubility of corundum, gibbsite, boehmite, and diasporite at standard state conditions. *Clays and Clay Miner.* 36, 391-396.
- Pivovarov S. (2009) Diffuse sorption modeling: apparent H/Na, or the same, Al/Na exchange on clays. *Journal of Colloid and Interface Science*, 336, 898-901.
- Pivovarov S. (2010) Diffuse sorption modeling: ionic adsorption on silica. *Journal of Colloid and Interface Science*, 352, 158-162.
- Rozalén M.L., Huertas F.J., Brady P.V., Cama J., Garsía-Palma S., and Linares J. (2008) Experimental study of the effect of pH on the kinetics of montmorillonite dissolution at 25°C. *Geochim Cosmochim Acta* 72, 4224-4253.
- Schindler P.W., Liechti P. and Westall J.C. (1987) Adsorption of copper, cadmium and lead from aqueous solution to the kaolinite/water interface. *Neth. J. Agric. Sci.* 35, 219-230.
- Sprycha R. (1989) Electrical double layer at alumina/electrolyte interface. I. Surface charge and zeta potential. *J. Colloid Interface Sci.* 127, 1-11.
- Wahlberg J.S., Baker J.H., Vernon R.V. and Dewar R.S. (1965) Exchange adsorption of strontium on clay minerals. *Geological Survey Bulletin* 1140-C. US Government Printing Office, Washington.
- Weaver C.E. and Pollard L.D. (1973) *The chemistry of clay minerals*. Elsevier Sci. Publ. Co., Amsterdam.
- Wieland E. and Stumm W. (1992) Dissolution kinetics of kaolinite in acidic aqueous solutions at 25°C. *Geochim Cosmochim. Acta* 56, 3339-3355.
- Zachara J.M., Smith S.C., Resch Ch.T., Cowan C.E. (1992) Cadmium sorption to soil separates containing layer silicates and iron and aluminum oxides. *Soil Sci. Soc. Am. J.* 56, 1074-1084.
- Zachara J.M., Smith S.C., McKinley J.P., and Resch C.T. (1993) Cadmium sorption on specimen and soil smectites in sodium and calcium electrolytes. *Soil Sci. Soc. Am. J.* 57, 1491-1501.