J. Mater. Environ. Sci. 5 (5) (2014) 1541-1550
ISSN : 2028-2508
CODEN: JMESCN

Potassium-Calcium exchange in clays of selected Moroccan vertisols

Yamina Moujahid[1], Rachid Bouabid[2]
1 –Centre Régional de la Recherche Agronomique, Meknès, Morocco
2- Ecole Nationale d'Agriculture, Meknès, Morocco

Received 18 July 2013, Revised 5 July 2014, Accepted 5 July 2014
** Corresponding author. E mail: moujahidy@yahoo.fr ; Tel: 06 79668168*

Abstract

The Clay fractions of five Moroccan vertisols (Chaouia, Gharb, Doukalla, Zair, and Sais) as well as a reference smectite (montmorillonite SWY-1) were Ca-saturated and dispersed in $K^+ \leftrightarrow Ca^{2+}$ binary exchange solutions with constant ionic forces of 10^{-2} at 25°C. Exchange isotherms established showed that K is preferentially adsorbed compared to Ca^{2+} in all soil clays and the reference smectite. The clay fraction of the Ch-Chaouia soil, which is dominantly beidellitic, represents the highest affinity for K^+. For all other soil clays, the values of the Vanselow (K_V) exchange selectivity coefficient, Gaines and Thomas (K_{GT}), and Gapon (K_G) were higher than 1. This corroborates the fact that clays fractions of vertisols dominated by smectites are highly selective to K^+ compared to Ca^{2+}. The regression coefficient show that a two-site adsorption model predicts well the adsorption parameters α, K_{V1}, K_{V2} and N_0. The site 1 (α) portion is more important in the Chaouia soil clay (α = 0.248) and the least in the Doukkala soil clay (α = 0.078). The selectivity coefficient of sites 1 (K_{V1}) is less important for the reference Montmorillonite SWY-1 compared to all soil clays. For sites 2, the selectivity coefficients (K_{V2}) are of less importance and vary from 1.77 $(mole/l)^{-1}$ for SWY-1 to 12.54 $(mole/l)^{-1}$ for the Chaouia soil clay. The equilibrium constants (Kéq) of the K-Ca exchange at 25°C are greater than 1. They are highest for the Chaouia clay and the lowest for the SWY-1 reference montmorillonite. For all clays, the standard free enthalpy ($\Delta G°$) has negative values varying from -5 to 0 KJ/éq.

Key words: soil clays, exchange, potassium, calcium, selectivity, adsorption, models.

1. Introduction

In the arid and semi arid countries of North Africa and the Middle East, the exchange complex of most soils is saturated. The calcium constitutes the main exchangeable cation occupying the exchange sites. When potassium is applied as fertilizer to the soil, or when Ca is depleted, the process of ionic exchange of K-Ca is triggered to re-equilibrate the soil solution concentrations of these two elements. Therefore, the K-Ca exchange is of major importance in the understanding of the potassium dynamics (K) in soil and its availability for the plants, especially for countries like Morocco, where this element is entirely imported and relatively expensive.

Studies undertaken on the ionic exchange in clays and soils were based on the coefficients of selectivity defined by three the models: Vanselow, Gaines and Thomas, and Gapon. These models vary as a function of the cation assortment of the exchanger and the availability of the sites presenting differentiated affinities for K. Such heterogeneity of sites has been revealed long time ago in the case of the adsorption of K by soils and clays [1-3].

In the reaction of exchange between K and another major cation of soils as Ca, the selectivity for potassium compared to that for Ca decreases when the soil K assortment increases: the K ions occupies in priority the more selective preferential sites [3-5]. These observations exclude all possibility of modelling of the K-Ca exchange with only one value of the selectivity coefficient for the entire interval of the K saturation on the exchange matrix. Therefore, a model involving double-sites of exchange of different selectivities has been proposed by Dufey and Delvaux (1989). In the same line of thinking, the present work has been conducted with the main objective to study the variation of the coefficients of selectivity of the K-Ca exchange and the possibility of modelling of the double-sites of this exchange in clays of vertisols from Morocco as a function of their K content.

2. Review of the K-Ca exchange theory

2.1 K-Ca exchange selectivity coefficient

The reaction of K-Ca exchange can be written as:

$$\text{Clay-Ca}\ (\mathrm{S}) + 2\ K^{+}(L) \leftrightarrow Clay - 2K\ (S) + Ca^{2+}\ (L)$$

where (S) and (L) indicate the solide and liquide (solution) phases respectively. The exchange selectivity can be determined by one the following 3 formalisms:
The Vanselow selectivity coefficient $\mathrm{K_v}$ [28] is defined as:

$$\mathrm{K_v} = \frac{\mathrm{M_K^2\ (S)\ .\ \ a_{Ca}\ (L)}}{\mathrm{M_{Ca}\ (S).\ \ a_K^2\ (L)}} \quad (1)$$

where M (S) is the molar fraction in the clay and a (L) is the activity of the ion in solution.

- The Gaines & Thomas selectivity coefficient $\mathrm{K_{GT}}$ [14] is defined as:

$$\mathrm{K_{GT}} = \frac{\mathrm{E_K^2\ (S)\ .\ \ a_{Ca}\ (L)}}{\mathrm{E_{Ca}\ (S)\ .\ \ a_K^2\ (L)}} \quad (2)$$

where E (S) is the equivalent fraction of the cation on the clay.

- The Gapon selectivity coefficient $\mathrm{K_G}$ [12-13-25] is based the following exchange reaction:

$$\text{Clay-}\,{}^{1}\!/_{2}\ \text{Ca (S)} + K^{+}(L) \leftrightarrow Clay - K\ (S) + {}^{1}\!/_{2}\,Ca^{2+}\ (L)$$

where $\mathrm{K_G}$ is defined as:

$$\mathrm{K_G} = \frac{\mathrm{E_K\ (S)\ \ .\ a_{Ca}^{1/2}\ (L)}}{\mathrm{E_{Ca}^{1/2}(S)\ .\ a_K\ (L)}} \quad (3)$$

The $\mathrm{K^+}$ and Ca^{2+} ion activities in the equilibrium solution are:

$\mathrm{a_K\ (L) = \gamma_K\ \ C_K(L)}$ (4) and $\mathrm{a_{Ca}\ (L) = \gamma_{Ca}\ C_{Ca}\ (L)}$ (5), where γ_K and γ_{Ca} are the activities coefficients and $\mathrm{C_K(L)}$ and $\mathrm{C_{Ca}(L)}$, are the concentrations (mole/l) in the equilibrium solution for $\mathrm{K^+}$ and Ca^{2+} respectively.

The total normality of the equilibrium solutions $\mathrm{N_0(eq/L)}$ is defined as:

$$\mathrm{N_0 = C_K(L) + 2\ C_{ca}\ (L)} \quad (6)$$

The ionic force of the equilibrium solution I when the counter anion is monovalent is given as:

$$\mathrm{I = C_K(L) + 3C_{Ca}\ (L)}\ (7)$$

The equivalent fractions of $\mathrm{K^+}$ and Ca^{2+} in solution are defined as:

$$\mathrm{E_K(L)} = \frac{\mathrm{C_K(L)}}{\mathrm{C_K(L){+}2C_{Ca}\ (L)}}\ (8)\ \text{and}\ \mathrm{E_{Ca}\ (L)} = \frac{\mathrm{2C_{Ca}\ (L)}}{\mathrm{C_K(L){+}2C_{Ca}\ (L)}}\ (9)$$

With $\mathrm{N_0 = C_K(L) + \ 2C_{ca}\ (L)}$ and $\mathrm{E_K(L) + \ E_{Ca}\ (L) = 1}$

Thus $\mathrm{C_K(L) = N_0E_K(L)}$ and $\mathrm{C_{Ca}(L) = {}^{1}\!/_{2}\,N_0\ [1 - E_K\ (L)]}$
The ion activities of $\mathrm{K^+}$ and Ca^{2+}become:

$$\mathrm{a_{K^+}(L) = \gamma_K N_0 E_K\ (L)} \qquad (10)$$

$$a_{Ca^{2+}}(L) = \gamma_{Ca}(N_0/2)[1 - E_K(L)] \qquad (11)$$

Commonly we designate the Potassium Adsorption Ratio (KAR) as:

$$KAR = \frac{a_{K^+}(L)}{(a_{Ca^{2+}}(L))^{1/2}} = \frac{{\gamma_K}^2}{\gamma_{Ca}} 2N_0 \frac{{E_K}^2(L)}{1 - E_K(L)} \qquad (12)$$

The equivalent fractions of $K^+$and Ca^{2+}adsorbed by the clay are defined as:

$$E_K(S) = \frac{C_K(S)}{C_K(S) + 2C_{Ca}(S)} \ (13) \text{ and } E_{Ca}(S) = \frac{2C_{Ca}(S)}{C_K(S) + 2C_{Ca}(S)} \ (14)$$

The molar fractions of $K^+$and Ca^{2+} adsorbed by the clay correspond to:

$$M_K(S) = \frac{C_K(S)}{C_K(S) + C_{Ca}(S)} \ (15) \text{ and } \ M_{Ca}(S) = \frac{C_{Ca}(S)}{C_K(S) + C_{Ca}(S)} \ (16)$$

Consequently the three selectivity coefficients K_v, K_{GT} and K_G became:

$$K_V = \frac{4{E_K}^2(S)}{1 - {E_K}^2(S)} \cdot \frac{1}{(KAR)^2} \qquad (17)$$

$$K_{GT} = \frac{{E_K}^2(S)}{1 - E_K(S)} \cdot \frac{1}{(KAR)^2} \qquad (18)$$

$$K_G = \frac{E_K(S)}{1 - E_K(S)} \cdot \quad \frac{1}{KAR} \qquad (19)$$

2.2 Theoritical considerations of the double-sites model

The main hypothesis of the model is that the cation exchange capacity of the clay remains constant during the ionic exchange regardless of composition of the exchange complex by K and Ca:

$$CEC = C_K(S) + 2C_{Ca}(S) \qquad (20)$$

The second hypothesis consists in considering that the soil clays have two exchange sites of varying proportions and of different selectivitys with respect to K^+ [11]. To these two sites are associated constant average selectivity coefficients: K_{V1} and K_{V2} when for instance one adopts the Vanselow model.

To the constant of an exchange solution of total normality N_0 and of K^+ constant (L) equivalent fraction E_K, the two types of sites will carry the K^+ fractions, $E_{K1}(S)$ and $E_{K2}(S)$ expressed as follow:

$$E_{K1}(S) = \frac{C_{K1}(S)}{C_{K1}(S) + 2C_{Ca1}(S)} = \frac{C_{K1}(S)}{CEC_1} \ (21)$$

Where $C_K(S) = C_{K1}(S) + C_{K2}(S)$ and $C_{Ca}(S) = C_{Ca1}(S) + C_{Ca2}(S)$

$$E_{K2}(S) = \frac{C_{K2}(S)}{C_{K2}(S) + 2C_{Ca2}(S)} = \frac{C_{K2}(S)}{CEC_2} \ (22)$$

and $CEC = C_K(S) + 2C_{Ca}(S) = CEC_1 + CEC_2 \qquad (23)$

The equivalent fraction of K adsorbed by the clay $E_K(S)$:

$$E_K(S) = \frac{C_K(S)}{C_K(S) + 2C_{Ca}(S)} = \frac{C_{K1}(S) + C_{K2}(S)}{CEC} = \frac{CEC_1 .\ E_{K1}(S) + CEC_2 .\ E_{K2}(S)}{CEC} \ (24)$$

If α designates the fraction of CEC occupied by sites of type 1:

$\alpha = CEC_1/CEC$ and $(1-\alpha) = CEC_2/CEC$

Then, $E_K(S) = \alpha\ E_{K1}(S) + (1-\alpha)\ E_{K2}(S)$ (25)

With $E_{K1}{}^2(S) = \frac{K_{V1}(KAR)^2}{4 + K_{V1}(KAR)^2}$ (26) and $E_{K2}{}^2(S) = \frac{K_{V2}(KAR)^2}{4 + K_{V2}(KAR)^2}$ (27)

The exchange experiment allow to get the value of $E_K(S)$ corresponding to every $E_K(L)$. The couples of data obtained permit to explicitly lay the expression $E_K(S) = \alpha\ E_{K1}(S) + (1-\alpha)\ E_{K2}(S)$ as a system of equations, whose variables are α, K_{V1} and K_{V2}. By a non linear regression procedure, one calculates these parameters that permit to redefine the theoretical values of the coefficients K_v, K_{GT} and K_G . The correspondence between the calculated and the experimental values constitutes the main criteria of validity of the double-sites model.

2.3 Equilibrium constant (K_{eq}), standard enthalpy (ΔG^0) of the exchange reaction, and $K^+$and Ca^{2+} *activity coefficients on the clay*

The model allows the determination of K_V for a given $E_K(S)$. The integral of the curve $Ln\ K_V = f\ [E_K(S)]$(28) between $E_K(S) = 0$ and 1 is [26]:

$A = \int_0^1 Ln\ K_V\ d\ E_K\ (S) = Ln\ K_{eq} = -\Delta G^0/RT$ (28) ; we obtain:

$K_{eq} = e^A$ (29) and $\Delta G^0 = -ART$ (30)

The activity coefficients of K and Ca on the surface (g_K and g_{Ca}) are given as follow:

$$Ln\ g_{Ca} = E_K(S).Ln\ K_V - \int_0^{E_K(S)} Ln\ K_V\ dE_K(S) \quad (31)$$

$$Ln\ g_K = 1/2\ [-LnK_V + Lng_{Ca} + LnK_{eq}] \quad (32)$$

3. Materials and Methods

The clay fraction (<2µm) from the surface horizons of representative vertisols of five major agricultural regions of Morocco (Chaouia (CH), Gharb (GH), Doukkala (DK), Zaer (ZR) and Saïs (SA)) have been sampled for this study. These soils are clay rich and present important swelling and shrinking characteristic (Table 1). A reference clay, Wyoming montmorillonite (SWY-1; Clays Minerals Society), has been also included in the study for comparison.

Table1: Total cation exchange capacity (CEC_T), tetrahedral CEC (CEC_{Tetra}), Interlayer charge (IC), % smectite, and smectite nature (Beidellite (B), montmorillonite (M)) in the soil clays and reference montmorillonite.

	CH	ZR	GH	SA	DK	SWY-1
CEC_T(meq/100g)	108.5	102.2	94.3	91.6	85.3	90.4
CEC_{Tetra} (meq/100g)	76.4	70.6	50.8	56.3	45.8	30.1
IC (mol(c)/½ cell)	0.57	0.44	0.45	0.39	0.36	0,36 [29]
% de Smectite	83	89	74	>90	90	100
Nature of Smectite	B	B+M	B+M	B+M	B+M	M

3.1 Preparation of Ca-saturated clay

Soil samples were air dried at room temperature. The 2 mm fraction was subject to carbonates elimination according to [24], organic matter and oxides removal according to [17], and to a densimetric clay fraction separation according to [16].

The clay fractions were saturated first with Ca concentrated solutions using 0.5 M $CaCl_2$, and shaking during two hours, and subsequently saturated with a dilute solution of 0.01M $CaCl_2$. They were then washed four times to eliminate the excess salt, and kept as moist past (with known water content proportion).

3.2 K-Ca Exchange on the clays

K and Ca solutions were prepared with a constant ionic force (I) of 10^{-2}, with $I = C_K(L) + 3C_{Ca}(L)$ where $C_K(L)$ and $C_{Ca}(L)$ are the K and Ca molar concentrations of the exchange solutions. The equivalent fractions of K of these solutions are: 0, 0.1, 0.2, 0.4, 0.6, 0.8 et 1.0, with $E_K(L) = \frac{C_K(L)}{C_K(L)+2C_{Ca}(L)}$.

A mass of Ca saturated clay past corresponding to a dry weight of clay 0.5g is put in suspension in 100 ml of exchange solution. The suspension is maintained under shaking during 24 hours to a stationary temperature of 25°C. At equilibrium, the exchange solutions are recovered by centrifugation. The quantity of K retained due to Ca exchange on the clays corresponds to the difference of the concentrations in K of the initial solutions. K concentrations were determined by atomic absorption spectroscopy. The Ca adsorbed by the clays (exchangeable Ca) is determined by exchange with solutions of 1M ammonium acetate and analyzed by atomic absorption spectroscopy.

4. Results and discussion

4.1 Exchange isotherms at 25°C

According to the model of Gaines et Thomas, the exchange isotherms of Ca^{+2} by K^+, correspondent to the plot of the equivalent fractions of K^+ on the clays $E_K(S)$ as a function of its equivalent fractions in the exchange solutions at equilibrium $E_K(L)$ at 25°C. Figure 1 shows that the K-Ca exchange isotherms of all the clays studied are situated below the isotherm of non-preference (INP), given by the following equation [26]:

$$E_K\,(S) = [1 + 2/\Gamma N_0(2/E_K^2\,(S) - 1/E_K\,(L))]$$

Where Γ is the ration activity coefficient of K and Ca in the solution and N_0 is the total normality of the exchange solutions.

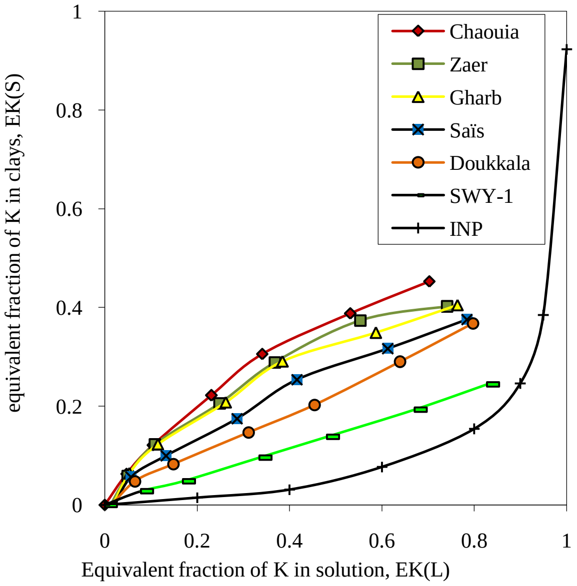

Figure 1: K-Ca exchange isotherms at 25°C of the soil clays and the reference montmorillonite (SWY-1) studied and isotherm of non-preference (INP)

K^+ is preferentially exchanged with respect to Ca on all the soils clays studied as well as on the reference montmorillonite. Similar results have been reported by [2-9-18-23]. This preference is nonetheless more marked for the vertisol clays than for the reference clay. The Chaouia clay (CH) showed the highest K preference. Similar results have been reported by [4-6-15] for swelling soil smectites.

4.2 K-Ca exchange selectivity at 25°C

For all clays, the values of the Vanselow (K_V) selectivity coefficient were greater than 1. Therefore, these clays are more selective with respect to K^+ compared to Ca^{2+}. On the other hand, the values of K_V decreased for all clays from 430 (mole/l)$^{-1}$ to 2.5 (mole/l)$^{-1}$ when the equivalent fraction of K^+ of the initial solution goes from 0.1 to 1 (Table 2). The Chaouia vertisol clay is distinctly more selective to K^+ than all other clays studied, whereas the Wyoming montmorillonite (SWY-1) was the least selective. The other soil clays, Zaïr, Gharb, Saïs and Doukkala have intermediate degrees of selectivity.

Table 2: Vanselow (K_V) selectivity coefficient of K-Ca exchange at 25°C for the soil clays and the reference montmorillonite.

Initial E_K	CH	ZR	GH	SA	DK	SWY-1
0.0	0. ∞	425.2	491.6	524.0	559.7	0. ∞
0.1	431.0	319.5	314.0	217.4	114.6	26.5
0.2	289.3	267.3	238.5	111.5	61.7	15.0
0.4	155.4	111.4	100.3	57.3	32.6	11.3
0.6	117.3	84.9	77.6	46.5	22.9	8.3
0.8	49.2	41.7	28.6	20.1	14.2	4.7
1.0	24.3	14.4	12.7	9.2	7.9	2.5

Figure 2 illustrates the variation of the Logarithmic function of the Vanselow coefficient (ln K_V) an Gaines and Thomas (ln K_{GT}) selectivity coefficients and the Gapon (K_G) selectivity coefficient with respect to the equivalent fraction of K^+ exchanged to Ca^{2+} $E_K(S)$. This figure shows a reduction of the selectivity of the clays to K^+ when their rate of saturation with K^+ increases. Similar findings have been reported by [1-3]. This decease is more marked for the soil clays (Ln K_V decreases from 6 to 2) than for the reference montmorillonite. This trend can be attributed to heterogeneity of the exchange sites on soil clays compared to the reference clay.

The selectivity coefficient of Gaines and Thomas Ln K_{GT} also presents a reduction when the fraction of K^+ adsorbed by the clays increases. This reduction is slightly weaker than that of Ln K_V. For soils rich in kaolinite, [27] found that Ln K_{GT} decreases from 5 to 1. Also, [22] showed that Ln K_V and Ln K_{GT} vary from 4 to 1 and 2.5 to 0 respectively, when the equivalent fraction in K^+ in the clays ($E_K(S)$) increases. A similar behaviour has been revealed by [20] on kaolinites and kaolinitic soils.

The Gapon selectivity coefficient K_G is 2 to 4 times greater for the soil clays compared to the reference montmorillonite. K_G varies between 2 to 12 mole/l^{-1}, which is in agreement with the results obtained by [8-19]. The decrease of K_G is weaker than those of K_V and K_{GT}. K_G is the one that varies the least with K^+ saturation of the clays.

The clay of the Chaouia vertisol is the most selective to K^+. This is due to its high charge and to the beidellitic nature of the smectites (Figure 2). However, the reference montmorillonite (SWY-1), mainly octahedraly charged, is the least selective to K.

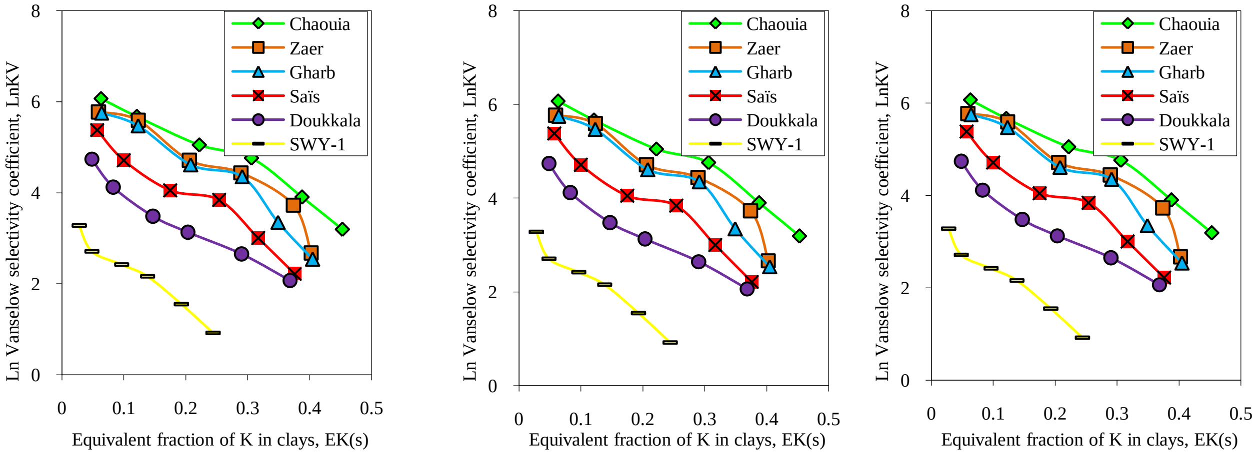

Figure 2: Relationship between K-Ca exchange selectivity coefficients of Vanselow (ln K_V), Gaines et Thomas (ln K_{GT}) and Gapon (K_G) and the K equivalent fraction in the soil clays and reference montmorillonite at 25°C.

To assess the relation between the nature of the clays and their selectivity to K, linear regressions were performed between the Vanselow selectivity coefficient and the CEC_T, CEC_{Tetra}, IC, and the equivalent fractions of K^+ of the initial solutions equal to 0.1, 0.4 and 1.
The correlation coefficients of the 3 regressions were all significant (Table 3) indicating a strong relationship between the selectivity of these clays to K and their CEC_T, CEC_{Tetra} and IC of the smectite. Furthermore, the r values indicate that the selectivity to K is more explained by the CEC_{Tetra} and the IC than with CEC_T. This result confirms the fact that the selective adsorption or fixation of potassium is more controlled by the charges emanating from the tetrahedral than from the octahedral sheets of clay [6-21].

Table 3: Correlation coefficients (r) for [K_V= b.CEC_T + a], [K_V = b.CEC_{Tetra} + a] and [K_V = b.IC+ a] for the K equivalent fractions in the initial solutions (E_K(L)) equal to 0.1, 0.4 et 1.0

Fraction	CEC_T	CEC_{Tetra}	IC
E_K (L) = 0.1	0.854*	0.915*	0.963**
E_K (L) = 0.4	0.912*	0.908*	0.972**
E_K (L) = 1	0.882*	0.912*	0.981**

4.3 K-Ca modelling in the clays

The double sites model consist at considering that K exchange is occurring in the clays on two types of sites: site 1, of α proportion, and of selectivity to the K^+ given by K_{V1}, and site 2, of (1-α) proportion, and of selectivity to the K^+ given by K_{V2}. The parameters of the model α, K_{V1}, K_{V2} and N_0 are determined by a non linear regression procedure. The data to introduce are: the experimental couples of the K equivalent fractions adsorbed E_K(S) and in solution E_K(L), the equation that relates E_K(S) and E_K(L), the intervals and the steps of variation of these parameters.
The values of the correlation coefficients of the non linear regressions giving the parameters of modelling of the K exchange are given in the Table 4. With the exception of the Gharb vertisol clay and the reference montmorillonite (SWY-1), the double sites model can predict α, K_{V1}, K_{V2} and N_0 with a good precision. The non linear correlation coefficients serving to determine these parameters are in generally greater than 0.8. The double sites model doesn't seem to be adapted to the Gharb vertisol clay (r<0.3) and to the reference montmorillonite (infinite r). The weakness of the correlation may be attributed to the fact that the model is not well adapted to clays with a single site nor to clays with a mixed mineralogy of montmorillonite and beidellite (including interstratified) which is the case of the Gharb soil clays [6-15].

Table 4: Correlation coefficients of the non linear regressions giving the α, K_{V1}, K_{V2} and N_0 parameters of K-Ca exchange at 25°C

	Chaouia	Zair	Gharb	Sais	Doukkala	SWY-1
α	0.964	0.964	0.192	0.957	0.923	-
K_{V1}	0.877	0.846	0.209	0.910	0.922	-
K_{V2}	0.834	0.832	0.271	0.846	0.638	-
N_0	0.815	0.853	0.126	0.439	0.849	-

When referring to the isotherm curves of modeled and experimental exchange corresponding to the Chaouia and Gharb clays (Figure 3), one may conclude that the double site model is adapted to both clay types. The same results have been reported by [1]. However, the parameter in Table 4 showed that the double site model is not adapted to the Gharb. This means that the exchange isotherms may not be revelatory for the presence of two sites in clays dominated by montmorillonite. The same observation can be deducted when examining the curves of the K_V,
The fraction of the site 1 (α) is important in the Chaouia clay and weak in the Doukkala clay. It is important to notice that the highly selective sites for K represent less than 25% of the exchange sites (α <0.25) [1]. The selectivity coefficient of the site 1, K_{V1}, is weaker for the reference montmorillonite than for the soils clays. For sites 2, their selectivity coefficients are very weak, they vary between 1.77 $(molel^{-1})^{-1}$ for SWY-1 and 12.54 $(molel^{-1})^{-1}$ for the Chaouia clay. The values of K_{V1} are greater than those calculated from the experimental data for low K^+ molar fractions in the exchange solutions. The values of K_{V2} are in the same order of magnitude compared

to experimental values for the high K^+ molar fractions in the exchange solutions. The total normality N0 of the equilibrium solutions is nearly constant for all clays, with a value ranging between 7 and 8 cmoll^{-1}.

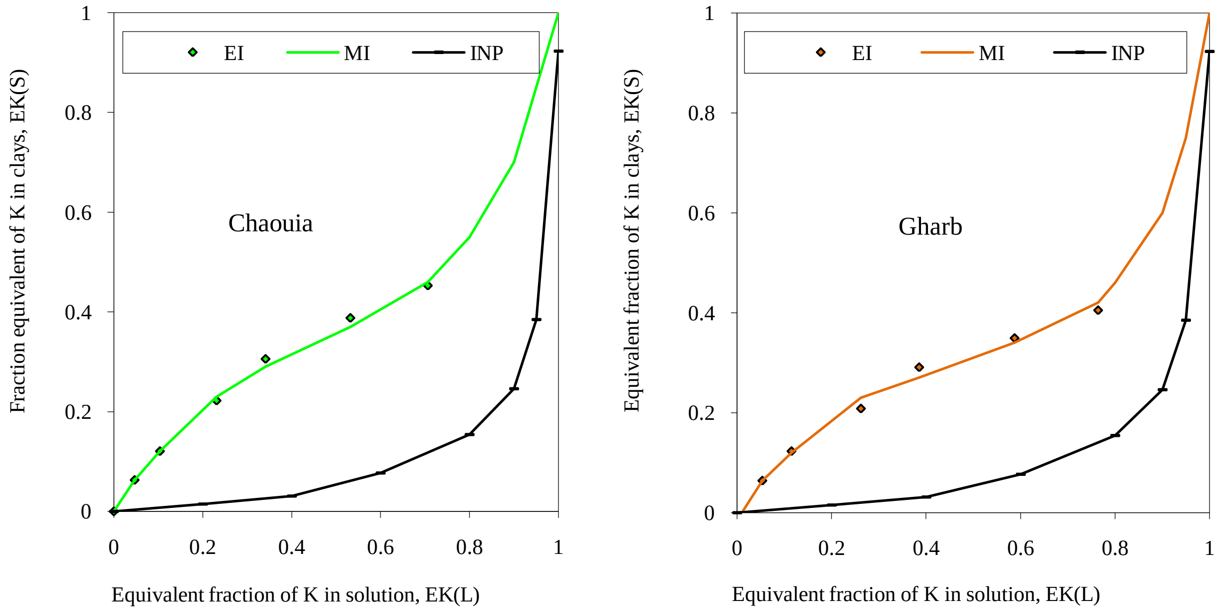

Figure 3: Double sites experimental (E) and modelled (M) K-Ca exchange isotherms (I) of the Chaouia and Gharb soil clays 25°C

Values of K-Ca exchange modeling in the soils clays and reference montmorillonite given in Table 5. K_v, K_{GT} and K_G selectivity coefficients as a function of the K^+ equivalent fractions adsorbed for these same clays are giving in Figure 4.

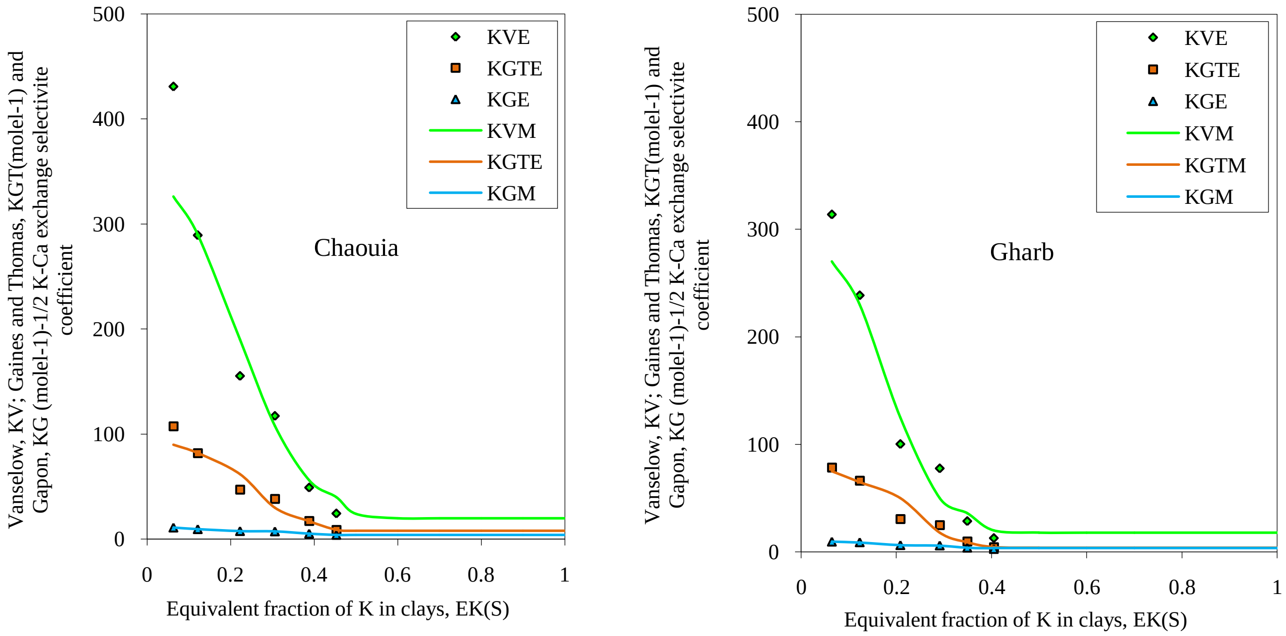

Figure 4 : Double sites experimental (E) and modelled (M) K-Ca selectivity coefficients for the Chaouia and Gharb soil clays 25°C

Table 5: Values of α, K_{V1}, K_{V2} and N_0 parameters of the double sites K-Ca exchange model for the soil clays and reference montmorillonite at 25°C

	CH	ZR	GH	SA	DK	SWY-1
α	0.248	0.245	0.229	0.156	0.078	0.091
K_{V1} (mole $l^{-1})^{-1}$	4144	3645	4481	5457	10620	1237
K_{V2} (mole $l^{-1})^{-1}$	12.54	5.81	5.95	7.52	9.43	1.77
N_0 (coml.(c)l^{-1})	7.35	7.99	7.33	7.03	7.44	7.81

4.4 Equilibrium constant (Keq), standard free entalpy (ΔG°) at 25°C of K-Ca exchange and K , Ca ion activity coefficient K^+ et Ca^{2+} in the clays studied

Table 6 presents the values of the equilibrium constants (Keq), the standard free enthalpies ΔG° (KJ/eq) of the K-Ca exchange as well as the K and Ca activity coefficients in the soil clays and reference montmorillonite studied.
The equilibrium constant for K-Ca exchange at 25°C for the clays was superior to 1. It was the highest for the CH clay and the lowest for the SWY-1 clay. The standard free enthalpy ΔG° had negative values, varying between 0 and -5 KJ/eq for the Chaouia, Zaer, Gharg, Sais, Doukkala and Montmorillonite clays. The Chaouia clay, the most selective to K^+, had the highest absolute value of ΔG°. On the other hand, ΔG° was the highest (absolute value) for the SWY-1 montmorillonite, indicating its weak affinity for K in comparison to the other clayey fractions.

Tableau 6: Equilibrium constants (Keq), and standard free enthalpies ΔG° (KJ/eq) of the K-Ca exchange as well as the K and Ca ion activity coefficients in the soil clays and reference montmorillonite studied. at 25°C

	$E_K(S)$	CH	ZR	GH	SA	DK	SWY-1
Kéq		52.7	28.1	27.1	20.9	16.3	3.2
ΔG°(KJ/eq)		-4.9	-4.1	-4.1	-3.8	-3.5	-1.4
g_{Ca}	0.025	1	1	1	1	1	1
	0.525	0.476	0.410	0.410	0.525	0.690	0.677
	0.975	0.327	0.280	0.286	0.430	0.624	0.624
g_K	Al values $E_k(S)$	1.007	1.007	1.007	1.008	1.011	1.011

The values of the Ca^{2+} activity coefficient (g_{Ca}) in the clays decrease with respect to the K^+ equivalent fractions, and vary between 1 and 0.28. The K^+ activity coefficients in the clays g_K are constant and equal to 1, which is in agreement with the results of [1-22]. These authors showed that the K^+ activity coefficient in two studied soils increase slightly for the low K^+ fractions until it reaches 1, and then remains nearly constant. [10] observed that K^+ activity coefficients, calculated by the model of Gaines and Thomas, had values slightly greater than 1 for British soils.

Conclusion

With the exception of the Gharb vertisol, the K-Ca exchange in the soil clays studied is well described by the double sites model. The K^+ is selectively adsorbed first by the type 1 sites having high K affinity, then by type 2 sites with lower K affinity. The fractions of the selective sites are determined with a good precision between 0 and 0.25. The number of highly selective sites for K^+ is the greatest for the Chaouia clay, and the lowest for the Doukkalas clay. The values of the thermodynamic equilibrium constants Keq and ΔG° confirmed the findings concerning the selectivity of the clays for K^+.
The K^+ activity coefficient (gK) is independent of the amount of K on the clay phase; its value is constant and equal to 1. On the other hand, the Ca^{2+} activity coefficient (gCa) decreases from 1 to 0.28 when the saturation of the clays with K^+ increases from 0 to 1.
The exchange selectivity for K in relation to that of Ca is largely determined by the tetrahedral charge fraction of the clay. Consequently, beidellitic soils will adsorb K more energetically than montmorillonitic soils. The proximity of the tetrahedral charge to the interlayer space explains the strong K selectivity of beidellites compared to montmorillonites.

Acknowledgment-The authors wish to thank the department of soil science of IAV Hassan II for their help in achievement tests and chemical analysis

References

1. Alves M.E., Lavorenti A., *Australian Journal of Soil Research*, 41 (2003) 1423.
2. Appel C., Ma, L.Q., Rhue, R. D., Reve W., *Soil Science Society of America Journal*, 67 (2003) 1707.
3. Badreddine R., Le Dred, R., Prost, R. *Clay Minerals*, 37 (2002) 59.
4. Bar A., Banin, A.Y. and Chen. *20th colloquium of the international: Potash Institute Baben bei wein Austria* (June 23 to 25, 1987), Bernl/Switzerland.
5. Bekett P.H.T., *Soil Science*, 97 (1964) 376.
6. Bouabid R., Badraoui, M. Bloom, P.R,. *Soil Science Society of America Journal*, 55 (1992) 1493.
7. Bolt G.H., Summer, M.E., Kemphorst., *Soil Science Society of America Proceedings*, 27 (1963) 294.
8. Carson B., Dixon, G.P., *Soil Science Society of America Proceedings*, (1972) p.36.
9. Cofie O.O., Pleysier, *Journal Soil Science and Plant Analysis*, 35 (2005) 17.
10. Deist J., Talibudeen, O., *Journal of Soil Science*, 18 (1967) 138.
11. Dufey J.E., Delvaux, B. *Soil Science Society of America Journal*, 53 (1989) 1297.
12. Evangelou V.P., Coale, F.J., *Soil Science Society of America Journal*, 51 (1987) 68.
13. Evangelou V.P., Philips, R.E. *Soil Science Society of America Journal*, 52 (1988) 379.
14. Gaines G.L., Thomas, H.C., *Journal of Chemical Physics*, 21 (1953) 714.
15. Goulding K. W. T., Talibudeen O., *Journal Colloid and interface Science*, 78 (1980) 15.
16. Holtzapffel T. *Société Géologique du Nord*, 12 (1985) 95.
17. Jackson M.L. *2nd Ed, 11th printing, Published by the Author, University of Winsconsin, Madison* (1979) 53705.
18. Kalu G.I. *Nigerian Journal of Science*, 41 (2007) 30.
19. Knibbe W.G.J., Thomas, G.W., *Soil Science Society of America Journal*, 36 (1972) 568.
20. Levy, G. J., Van der Watt, H.V.H., Shainberg, I., Du Plessis, H.M. *Soil Science Society of America Journal*, 52 (1988).
21. Ndayiragije S., Delvaux, B., *Catena*, 56 (2004) 1.
22. Ogwada R.A., Sparks, *Soil Science*, 141 (1986), N°4, USA.
23. Parfitt R.L. *Australian Journal of Soil Research*, 30 (1992) 145.
24. Robenhorst R.D., Wilding, L.P. *Soil Science Society of America Journal*, 48 (1984) 216.
25. Shainberg I., Oster, J. D., Wood, J. D., 1980. *Soil Science Society of America Journal*, 44 (1980) 960.
26. Sposito G., 1981. *University of California, Riverside Oxford, Clarendon, Press*, (1981)
27. Udo E.J. *Soil Science Society of America Journal*, 42 (1978) 556.
28. Vanselow A.P., *Soil Science*, 33 (1932) 95.
29. Eberl D.D., Srodon, J., Nortrop R., *American chemical Society*, 323 (1986) 296.