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# Swelling clays and salt-affected soils : demixing of Na / Ca clays as the rationale for discouraging the use of sodium adsorption ratio (SAR)

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## Abstract

Sodium adsorption ratio SAR defined as $SAR = (Na)/\sqrt{(Ca+Mg)/2},$ where concentrations of cations in solution are expressed in meq L−1 has long been considered as correlated to exchangeable sodium percentage (ESP) on clay minerals or soil exchange complex, and as the key concept to explain swelling of clay minerals and the difficulties of reclaiming salt-affected soils. Though its basis is empirical, it was alleged to be theoretically justified on the basis of ion exchange, derived from the Gapon convention. However, it has long been challenged on the basis of both field observations and experimental evidence : it fails to account for the fact that calcium and magnesium do not play the same role, while potassium is absent from the formula ; calcium concentration must be “corrected “when calcite is present etc. There exist specific ion effects. Experimental measurements of the decrease of permeability when solutions are diluted led Quirk and Schofield (1955) to define the concept of critical threshold, and to show that potassium and magnesium play an intermediate role between sodium and calcium. This threshold is simply determined by the concentration of calcium, irrespective of the value of SAR or ESP. Indeed, demixing of Ca-Na clay minerals during ion exchange, a phenomenon well known since Glaeser and Mering (1954), implies that there exists an interaction between adjacent sites. This undermines the theoretical basis of SAR : the derivation of SAR from ion exchange equilibria implies to use an equilibrium constant. This parameter is no more constant if demixing occurs. The results obtained are positive : demixing leads to expulsion of sodium from inner exchange surfaces and its replacement by calcium, according to the “three crystals pore”proposed by Quirk (2003b). Sodium can then be more easily leached, as permeability is maintained by clusters of Ca-sites. Calcium concentration in solution appears thus as the simpler parameter to guide saltaffected soils reclamation when swelling clays are present.

**Keywords**: SAR, sodium, calcium, clay, swelling, ESP, demixing, sodium adsorption ratio.

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## Introduction

Increasing population and food demand, combined with urbanization result in diet modification with an increasing proportion of animal proteins, while simultaneously arable lands are sealed by urban sprawl. Intensification of agriculture implies irrigation while water resources are scarce (Meigs 1977/1979; UNESCO, 1995). Irrigation will thus increasingly rely on non conventional water resources, either recycled treated wastewater (“water reuse”) or non phreatic groundwater bodies, with a risk of overexploitation of water resources. However, irrigation without drainage leads to accumulation of salts in the topsoil and land degradation. This has long been studied and especially when swelling clay minerals, such as smectites, are present. The adverse effects of sodium and calcium on soil structure have been largely documented, and

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classical guidelines for salt-affected soils devised (U.S. Salinity Laboratory Staff, 1954). These guidelines have been extensively used, though they fail to account for many field and laboratory observations (Rimmer et al., 2013). Indeed, in the same years when these guidelines were proposed, Quirk and Schofield (1955) demonstrated that soil permeability could be maintained in a satisfactory range without large additions of gypsum, introducing the concept of critical threshold of calcium concentration in solution, while evidence for the underlying mechanism of clay minerals swelling was brought by Glaeser and Mering (1954). This mechanism implies demixing of cations, *i.e.* Ca- and Na-smectites do not form a continuous solid solution.

The aim of this paper is thus to discuss why the widely used sodium adsorption ratio (SAR) fails to account for swelling phenomena and permeability decrease, and why specific ion effects dominate, that are not correctly taken into account either in classical SAR concept or in diffuse double layer (ddl) and DLVO theories. The three-pores model by Quirk (2003b) and demixing phenomena form a better, and simpler rationale to explain the adverse roles of calcium and sodium in swelling of clay minerals and soils.

## Sodium adsorption ratio and exchangeable sodium percentage

According to U.S. Salinity Laboratory Staff (1954), the effect of water quality (irrigation water) on sodicity hazard can be assessed by considering mainly two phenomena:

- the effect of sodium on swelling, expressed by the *sodium adsorption ratio*;
- the effect of electrolytes on flocculation expressed by the *electrical conductivity* of the solution.

The sodium adsorption ratio (SAR) is defined as:

$$SAR \equiv \frac{[\mathrm{Na}^+]}{\sqrt{\frac{[\mathrm{Ca}^{2+}]+[\mathrm{Mg}^{2+}]}{2}}}, \tag{1}$$

where brackets designate concentrations in mmolc $L^{-1}$.

Electrical conductivity EC is either directly measured in the solution, or estimated from the analysis, *e.g.* by a polynomial fit (McNeal et al., 1970). Due to the existence of ion pairs, it is better correlated with the *true* ionic strength of the solution than with the *stoichiometric* ionic strength (Griffin and Jurinak, 1973).

From the analysis of solution, SAR and EC can be calculated. Exchangeable sodium ratio Res, and exchangeable sodium percentage ESP are defined as:

$$R_{es} \equiv \frac{[\mathrm{Na}^+]_x}{[\mathrm{Ca}^{2+}]_x + [\mathrm{Mg}^{2+}]_x}, \tag{2}$$

$$ESP \equiv 100 \cdot \frac{[\mathrm{Na}^+]_x}{CEC}, \tag{3}$$

When $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ are dominant, CEC = $[Na^+]_x + [Ca^{2+}]_x + [Mg^{2+}]_x$, so that:

$$ESP \equiv 100 \cdot \frac{R_{es}}{1 + R_{es}}. \tag{4}$$

$R_{es}$ was statistically shown to be well correlated with SAR (U.S. Salinity Laboratory Staff 1954):

$$R_{es} = 0.01475 \cdot SAR - 0.0126, \tag{5}$$

so that ESP can be estimated as:

$$ESP = 100 \cdot \frac{0.01475 \cdot SAR - 0.0126}{1 + (0.01475 \cdot SAR - 0.0126)}. \tag{6}$$

According to Suarez (1981), "the objective of determining SAR is usually to predict the ESP of a soil. The SAR expression implicitly assumes that calcium and magnesium have equal selectivity for exchange. Also, the exchange phase composition is fixed by the total concentrations of the exchangeable ions rather than their activities. Despite these simplifications, the SAR expression can predict ESP for a range of solution compositions and concentration."

ESP measured is generally well correlated with ESP calculated from eq.6, but wide differences were observed in Algeria by Durand (1958): in 40% of cases, this difference varied between 100 and 200% (Kovda et al., 1967).

For red brown earths from Australia, a different relation was obtained (Rengasamy et al., 1984):

$$ESP = 1.95 \cdot SAR + 1.8 \; (R^2 = 0.82, N = 138). \qquad (7)$$

The empirical relations between ESP and SAR are thus largely variable.

### Permeability decrease and specific effets of ions

For reclamation of salt-affected soils, we are primarily interested in soil permeability, which is strongly sensitive to small modifications of pore space. The question is then: are ESP and SAR as a proxy of ESP good parameters to estimate the risk of permeability decrease ?. In this respect, Quirk and Schofield (1955) defined the threshold concentration (TEconc) as the value of the concentration of electrolyte that results in a 10–15% decrease from its initial value during dilution. This is relevant for permeability changes due to input of irrigation water or even more of rainwater.

### Single ion electrolyte solutions

In single cation solutions of monovalent and divalent chlorides, the electrolyte concentration necessary to prevent a 10 to 15% decrease of permeability increases in the classical order Na > K > Mg > Ca (Table 1).

Table 1. Threshold Concentrations TEconc_ and pH values for Sawyers I, and corresponding values of ionic strength (Table I, from Quirk and Schofield, 1955).

| Salt | TE conc*/mol $L^{-1}$ | pH | I **/ mol $L^{-1}$ |
|---|---|---|---|
| NaCI | $2.5 \times 10^{-1}$ | 5.2 | $2.5 \times 10^{-1}$ |
| KCI | $6.7 \times 10^{-2}$ | 5.4 | $6.7 \times 10^{-2}$ |
| $MgCI_2$ | $1 \times 10^{-3}$ | 5.4 | $3.0 \times 10^{-3}$ |
| $CaCI_2$ | $3 \times 10^{-4}$ | 5.4 | $9.0 \times 10^{-4}$ |

*Threshold concentration; **Stoichiometric ionic strength (this paper).

The main clay mineral in Sawyers I soil is montmorillonite. Magnesium effect on swelling is not the same as calcium effect, and indeed it is intermediate between sodium and calcium. When considering the ionic strength (last column of Table 1), it appears that the threshold concentration does not correspond to a constant value of ionic strength.

### Mixed Na - Ca electrolyte solutions

In mixed NaCl–$CaCl_2$ electrolytes, the threshold concentrations are *the same* as in homoionic solution of the divalent cation, *i.e.* 2.5 x$10^{-4}$ mol/L of $Ca^{2+}$, while ESP is largely variable (Table 2).

Table 2. Threshold concentrations of mixed NaCl–CaCl2 solutions, ESP and Ionic strength.

| $ESP$ /% | $TE_{conc}$* /mol $L^{-1}$ | NaCl /mol $L^{-1}$ | $CaCl_2$ /mol $L^{-1}$ | $I$** /mol $L^{-1}$ |
|---|---|---|---|---|
| 5.8 | $2.3 \times 10^{-3}$ | $1.79 \times 10^{-3}$ | $2.5 \times 10^{-4}$ | $2.54 \times 10^{-3}$ |
| 8.9 | $4.1 \times 10^{-3}$ | $3.58 \times 10^{-3}$ | $2.5 \times 10^{-4}$ | $4.33 \times 10^{-3}$ |
| 21.0 | $9.5 \times 10^{-3}$ | $9.0 \times 10^{-3}$ | $2.5 \times 10^{-4}$ | $9.75 \times 10^{-3}$ |
| 35.0 | $18.6 \times 10^{-3}$ | $18.0 \times 10^{-3}$ | $2.5 \times 10^{-4}$ | $18.75 \times 10^{-3}$ |

* Given by Quirk and Schofield 1955, it is the total cation concentration TCC;
** Stoichiometric ionic strength (this paper).

This means that the threshold concentration corresponds to a fixed concentration of $Ca^{2+}$ in the bulk solution, irrespective of the ESP or SAR. The most relevant conclusion of the experimental work by Quirk and Schofield (1955) seems to be that the concentration of calcium in solution must be larger than about 3 x $10^{-4}$ M to prevent a significant decrease of permeability.

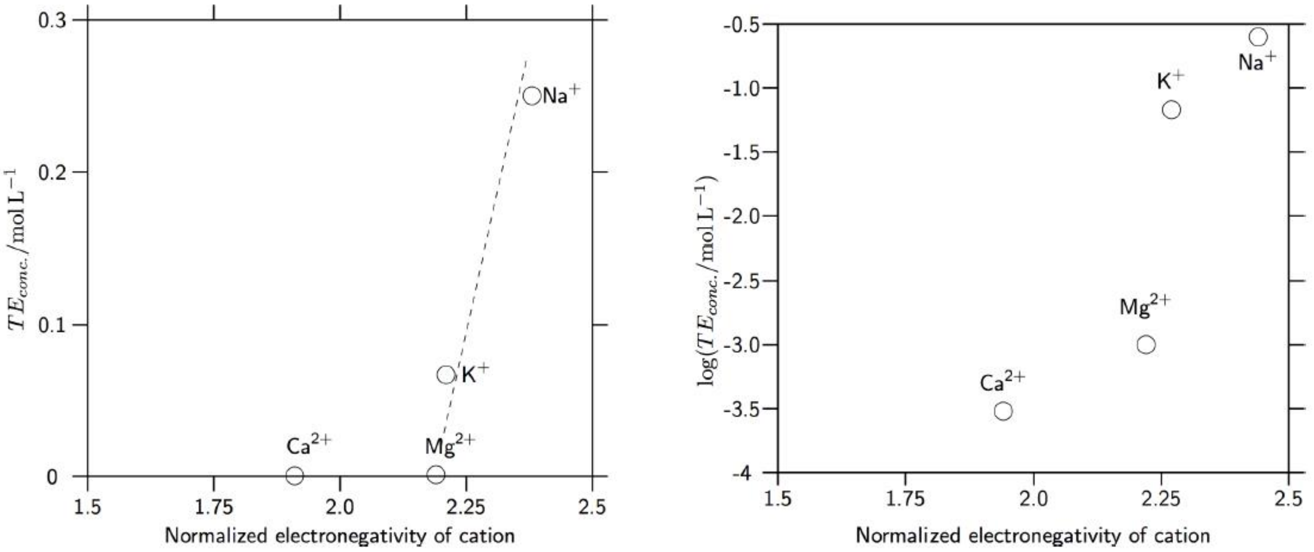
## Role of magnesium and potassium

Simply adding magnesium and calcium concentrations appears as an oversimplification. The threshold concentration is about three times larger for Mg2+ saturated clays than for $Ca^{2+}$ saturated clays (Table 1). This is confirmed by experimental results obtained in soils containing smectite, kaolinite, vermiculite and illite (Zhang and Norton, 2002), which was ascribed to the greater hydration energy and larger hydration shell of $Mg^{2+}$ as compared to $Ca^{2+}$. A reduction of soil structural stability was observed when the ratio $Mg^{2+}/Ca^{2+}$ increases (Arienzo et al., 2012), while the hydraulic conductivity was reduced in Vertisols when exchangeable magnesium increased (Pal et al., 2006).

Potassium is not considered in SAR, and PAR, defined by substituting K for Na in the expression was used, especially in vinery wastewaters where large K concentrations are observed. On clayey calcareous soils, hydraulic conductivity measurements by Arienzo et al. (2012) showed a significantly smaller decrease with K as compared to Na. As a conclusion, "there are no unique relationships between TEconc and the SAR or PAR solutions in mixed cation systems. This relationship is dependent on the relative amounts of different cation combinations" (Arienzo et al. 2012). This confirms *qualitatively* the classical order, but shows there are *specific counterion effects*.

## Relation between threshold concentration and electronegativity of the cation

As interactions between clay minerals and cations are mainly of electrostatic origin, the changes in threshold concentrations can be related with a suitable parametre depending on the natüre of the cation. In Figure 1, the Allred-Rochow electronegativity of the cation was checked as an explanatory factor, as it proved to be successfully correlated with Gibbs free energies and enthalpies of formation of isostructural compounds such as green rusts, oxides and hydroxides (Bourrié et al., 2004; Trolard and Bourrié, 2008; Trolard and Bourrié, 2012). While $Ca^{2+}$ and $Mg^{2+}$ are very close in the arithmetic plot, they are separated in the semi-logarithmic plot.



(a) Arithmetic plot (b) Semi-logarithmic plot

Figure 1. Relation between threshold concentration of electrolyte limiting the permeability decrease to less than 10–15% and the normalized Allred-Rochow electronegativity of the cation. The Allred-Rochow electronegativity of the cation is normalized by dividing it by the electric charge as a bivalent cation occupies half of the sites occupied by a monovalent. The values are: $Ca^{2+}$: 1.94; $Mg^{2+}$: 2.22; $K^+$: 2.27, $Na^+$: 2.44.

## Diffuse double layer and DLVO theories

### Diffuse double layer theory

*Specific counterion effects* are not taken into account by Diffuse Double Layer (ddl) theory where the only parametre is the valence of the electrolyte, so there should be no difference between Na and K, or between Ca and Mg, which does not explain the results obtained by Quirk and Schofield (1955), but ddl gives a partial insight in the phenomena and leads to correct order of magnitude of swelling pressure.

The counterions equilibrating the excess charge of clay minerals tend to diffuse in the bulk electrolyte solution, while they are retained close to it to compensate the charge of the surface. The solution of the Poisson-Boltzmann differential equation leads to the variation of the electrical potential and the concentrations of ions as a function of the distance to the charged surface. While some ions are tightly held close to the surface (Helmholtz or Stern layer), or expelled from it (same charge ions), the remainder are distributed as an exponentially decreasing function, which constitutes the *diffuse double layer* (ddl). The parameter of this exponential function, *i.e.* the "characteristic length" of the phenomenon is the *Debye length* $K^{-1}$ such that:

$$\psi = \psi_0 \, e^{-\kappa x}, \tag{8}$$

$$\kappa = \sqrt{\frac{e^2}{\epsilon_r \epsilon_0 kT} \sum_i z_i^2 n_{i\infty}}, \tag{9}$$

where e is the charge of the electron, k the Boltzmann constant, T the absolute temperature, $e_r$ the dielectric constant of the solvent, $e_0$ the permittivity of vacuum, $z_i$ the charge of ion i, and $n_{i\infty}$ its concentration at infinity, *i.e.* in the bulk solution. The summation in this expression is twice the ionic strength of the solution. In water, in a 0.01 M solution of a 1:1 electrolyte, $K^{-1}$ = 3.04 nm (Hiemenz and Rajagopalan, 1997).

For a Na-montmorillonite $[(Si_8)(Al_{3.33}Mg_{0.67})O_{10}(OH)_4]Na_{0.67}$, in a 1:1 electrolyte solution 0.1 M, $\psi_0$ = 95.6 mV; in a 1:1 electrolyte solution 1 x $10^{-5}$ M, $\psi_0$ = 332 mV. Those values are halved with a 2:1 electrolyte. The surface charge is compensated by an excess cations and a deficit anions, this latter increasing relatively with the concentration of the electrolyte (about 14% at 0.1 M).

The overlapping of the ddl of two planar surfaces leads to a repulsive force. For two charged surfaces at distance d, the Poisson-Boltzmann still holds, with different limiting conditions, and the solution for symmetric electrolytes is (Quirk, 1986):

$$\kappa x = 2e^{-\frac{U}{2}}\{F(e^{-U}, \pi/2) - F(e^{-U}, arcsin(e^{-(Z-U)/2})\}, \tag{10}$$

where F is an elliptic integral of the first kind (Legendre 1826), Z and U are the reduced potentials at x and at the mid-plane (x = 0), such that:

$$Z(x) \equiv \frac{\nu e \psi(x)}{kT}, \tag{11}$$

$$U \equiv \frac{\nu e \psi_0}{kT}, \tag{12}$$

where _ is the valence of the electrolyte.

"Swelling pressures in excess of 1 bar are only developed at relatively close approach (*ca.* 1 nm) and high potentials. A hydrostatic suction, when this exists in the system, opposes this swelling pressure. Similarly a mechanical load operates to resist expansion." (Quirk, 1986).

## The Deryaguin-Landau-Vervey-Overbeek theory

Hydration of ions tend to separate surfaces and swelling is explained by repulsion between adjacent diffuse double layers. The ddl is larger with monovalent ions than with divalent ions, which is qualitatively in agreement with larger swelling of Na-smectite as compared to Ca-smectite.

At close distances, Van-der-Waals attractive forces dominate. According to the DLVO theory (Deryaguin and Landau,1941; Vervey et al., 1948), the variation of interaction energy with the distance to the surface may present a minimum or two minima. The Van-der-Waals forces depend on a constant specific of the interacting materials, the Hamaker constant. The larger the Hamaker constant, the larger the attraction (Hiemenz and Rajagopalan, 1997). For Limontmorillonite, DLVO theory combined with the hypernetted chain formalism for electrolyte solution satisfactorily explains the interactions between close lamellae from

$1 \times 10^{-4}$ M to 0.1 M (Quirk and Marčelja, 1997). They conclude that no structural perturbation of interfacial water is responsible for swelling. This is consistent with the classical results that water structure is not modified except the first or two water layers adjacent to clay minerals (Keren and Shainberg, 1975; Keren and Shainberg, 1979; Keren and Shainberg, 1980; Prost, 1975). There are two interfaces: between the anhydrous mineral and the water layers, and between hydrated mineral and pore water, the limit corresponding to water activity $a_w = 0.97$, separating dessiccation from ultra-dessiccation. The tightly held water layers that are only removed for $a_w < 0.97$ are indeed part of the mineral, that must be considered as an hydrate (Bourrié et al., 1983).

DLVO theory works reasonably for concentrations < $5 \times 10^{-2}$ M), but fails for electrolyte concentrations larger than 0.1 M (Boström, 2001): it does not properly take into account *specific ion effects*, as Hamaker constant ($\approx 1 \times 10^{-20}$ J), is a characteristic of the solid (clay mineral here).

The surface charge density is considered, but not the origin of the electric charge, whether it is due to tetrahedral or octahedral substitutions, which is important for swelling, which depends on the stacking order of interlayers (Glaeser, 1953).

## Ion exchange equilibria: a not so sound basis for SAR

Though it was empirically defined, SAR was tentatively related to ion exchange and equilibrium constants or selectivity constants, following different conventions for activities of ions in solution, mole fractions of $Na_{exch.}$, $Ca_{exch.}$.

Strictly speaking, only products or ratios of activities are defined, *i.e.* algebraic sums of chemical potentials (Gibbs free energies). SAR when restricted to binary system Na-Ca is thus physically defined, but when extended to ternary system such as Na-Ca-Mg, or quaternary Na-K-Ca-Mg system, sums of activities are physically meaningless. When concentrations are substituted for activities, the link with thermodynamics is lost, and if sums of concentrations are physically meaningful, however, as shown before, the role of Mg is ambiguous.

The Ca/Na exchange on an anionic exchanger X– can be written as:

$$\mathrm{Ca}_{0.5}\mathrm{X} + \mathrm{Na}^+ \rightleftarrows \mathrm{NaX} + \frac{1}{2}\mathrm{Ca}^{2+}, \tag{13}$$

which leads at equilibrium to:

$$\frac{\{NaX\}\sqrt{\{\mathrm{Ca}^{2+}\}}}{\{Ca_{0.5}X\}\{\mathrm{Na}^+\}} = K_{Na-Ca}, \tag{14}$$

where { } designate activities.

If $Ca^{2+}$ and $Mg^{2+}$ are not separable, as isotopes of the same element, activity coefficients for them are identical and the sum of concentrations of calcium and magnesium can be substituted for calcium concentration. This implies that $K_{Ca\text{-}Mg} = 1$, and one obtains eventually:

$$\frac{\{NaX\}}{\{Ca_{0.5}X\} + \{Mg_{0.5}X\}} = K_{Na-Ca}\frac{\gamma_{Na+}}{\sqrt{\gamma_{Ca}}} \cdot \frac{[\mathrm{Na}^+]}{\sqrt{[\mathrm{Ca}^{2+}] + [\mathrm{Mg}^{2+}]}} \tag{15}$$

where the SAR term appears.

## Demixing phenomena

For the derivation above to be valid, $K_{Na\text{-}Ca}$ must be constant throughout all the Exchange reaction from pure $Ca_{0.5}X$ to pure NaX. This implies not only that $Na^+$ and $Ca^{2+}$ occupy the same sites, with different energies of course, but that *there is no lateral interaction between adjacent sites*. This does not hold if there is demixing: above a critical demixing threshold, adjacent calcium ions expel sodium ions, and clusters are formed where calcium dominates in some layers and sodium in other sites. This phenomenon was observed in Na-Ca montmorillonites very early (Glaeser, 1953; Glaeser and Mering, 1954) and confirmed by numerous authors since, both in the first stage of hydration (aw < 0:97) and in water-saturated systems: "In montmorillonite systems saturated with a mixture of Na- and Ca- ions, demixing of the adsorbed ions takes place, which means that Ca-ions are concentrated on some interlayers while Na-ions are adsorbed on other interlayers. The demixing phenomenon is energetically favorable and amounts to 1.4 kcal per equivalent of exchangeable ions."(Keren and Shainberg, 1979).

According to Pils et al. (2007), the evolution from the Ca-smectite with increasing Na, and the reverse evolution, show demixing and quasi-crystals (QCs) breakup and formation: "In low ionic strengths systems, demixing with monovalent cations on the external surfaces and divalent cations on the internal surfaces of QCs largely controls the average size of QCs in suspensions. In high ionic strength systems, both monovalent and divalent cations are found in the interlayers. The average size of QCs is controlled by the monovalent to divalent cation ratio, the hydration energies of the cations, and the ionic strength of the system." Moreover, demixing of Ca-Na smectites imply that activity coefficients for the solid end members are not unity. Referring to equation 15, two assumptions fail:

- $K_{Na\text{-}Ca}$ is no more constant;
- activities of the solid end-members $\{Ca_{0.5}X\}$ and $\{NaX\}$ are no more identical to the exchangeable mole fractions, including ESP.

Another consequence of demixing, underlined by Quirk (1986) is that "a threshold exchangeable sodium percentage (e.s.p.) of 15 for sodic soils is somewhat arbitrary and that the onset of adverse behaviour at lower values of e.s.p. may be closely related to clay microstructure."

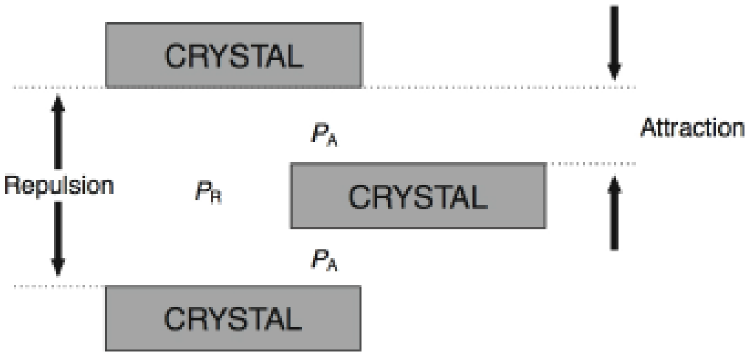


Figure 2. Three pores model by Quirk (2003b) showing geometris favourable to attraction and to repulsion.

### The geometry of pores

Permeability is sensitive to small changes in pore organization. The preceding theories (DDL and DLVO) imply separating forces (hydration, Van-der-Waals…), adding them and solving the equations for electric potential and then distances. However, all these forces are merely due to electromagnetic interaction and one can start instead from distances (Henry, 2008). This is the basis of considerations by Quirk and Schofield 1955, Ca-smectite forming stable entities ("clay domains"). The "slit-shaped pores" and the "overlap pores" are the two associated geometries in the three-crystal model (Quirk, 2003b) that explain best the swelling of smectite,

and the limited swelling of Ca-smectite: in the region of crystal overlap, the attractive pressure dominates. It can be as large as 1.5 MPa for a separation of 1 nm (Quirk, 2003a). Conversely, in slit-shaped pores, distances are larger and repulsive pressure dominates. When Na substitutes for Ca, the attractive pressure decreases and smectite starts to swell. This explains the concept of threshold concentration.

While the calcium concentration is larger than the threshold concentration, attraction by calcium dominates.

Starting from the opposite situation is important in salt-affected soils: when calcium concentration increases, calcium ions tend to form clusters and expel sodium ions to external pores, which facilitates drainage and sodium leaching.

## Conclusion

In order to predict, or prevent, swelling and degradation of soil structure, SAR and ESP are bad predictors. This has been verified by numerous studies since the last 60 years, and indeed the fundamental reasons were already known when it was proposed. Permeability is the most sensitive indicator of changes of soil structure, which explains the associated metrological difficulties. Calcium concentration in solution and ionic strength appear as the most relevant parameters that explain the swelling behaviour, with due consideration to clay mineralogy and clay microstructure. The threshold concentration concept remains a key of the processes. Its

value is around 2.5 x $10^{-4}$ M to 3 x $10^{-4}$ M, which is largely exceeded in solutions in equilibrium with calcite, that will vary from 5 x $10^{-4}$ M to 1 x $10^{-2}$ M, depending on the value of pCO2. Things are thus both simpler and more complex than thought in 1954. Calcium concentration is simpler to obtain and control than ESP or SAR. Specific ion effects on swelling are not taken into account by ddl or DLVO theories.

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