PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Soil Permeability in Relation to Sodicity and Salinity [and Discussion]

J. P. Quirk, Charles Pereira and T. W. Tanton

Phil. Trans. R. Soc. Lond. A 1986 **316**, 297-317
doi: 10.1098/rsta.1986.0010

Phil. Trans. R. Soc. Lond. A **316**, 297–317 (1986)
Printed in Great Britain

Soil permeability in relation to sodicity and salinity

By J. P. Quirk

Director's Research Unit, Waite Agricultural Research Institute, University of Adelaide,
Glen Osmond, South Australia 5064

Difficulties encountered in the irrigation of sodium-affected soils or in the reclamation of sodic–saline soils can be circumvented by controlling the electrolyte level in the irrigation water, which prevents deterioration of the soil structure. The threshold concentration concept simply expresses the minimum level of electrolyte required to maintain the soil in a permeable condition for a given degree of sodium saturation of the soil colloids.

It is shown that decreases in permeability at concentrations below the threshold concentration are occasioned by increased clay-particle interaction owing to the extensive development of diffuse double layers which give rise to enhanced swelling. Mechanical failure is associated with this swelling and deflocculation of clay particles. This behaviour of sodium-affected soils is considered in relation to the operation of van der Waals forces, hydration forces and osmotic repulsive forces arising from the development of diffuse double layers on particle surfaces.

Considerations of ion-exchange equilibria between particle surfaces and the soil solution (irrigation water) are discussed in relation to the threshold concentration concept, and the application of the concept in irrigation practice is illustrated by reference to several case histories.

INTRODUCTION

In most general terms soil structure is defined as the arrangement of soil particles (Baver 1940); however, remarkably little quantitative information exists either in terms of particle arrangement or its complement, pore-size distribution. For a considerable period it has been customary to discuss soil structure in terms of macropores, i.e. those drained at 0.1 bar† of water suction (with an equivalent cylindrical radius greater than 15 μm), and micropores (the remainder of the total porosity). Such a separation into two broad pore classes relates to the fact that two to three days after irrigation the macropores have drained and the downward movement of water has become so slow that a quasi-equilibrium state is considered to exist. This is referred to as 'field capacity', which is regarded as the upper limit of plant-available water in the soil. In the laboratory, 'field capacity' is estimated by using natural soil aggregates, slowly wetted and drained to equilibrium with 0.05–0.1 bar suction. The lower limit for plant availability is defined as water held in the pore space with a suction greater than 15 bar, as a result of capillary forces or osmotic forces between contiguous clay surfaces, arising from the presence and distribution of ions balancing the surface charge.

Because permeability is a function of the square of the pore radius and the porosity or cross-sectional area available for flow, it follows that any treatment that decreases or even eliminates macroporosity will have a dramatic effect on soil permeability and hence water entry during irrigation.

---

† 1 bar = 10^5 Pa.

If processes associated with soil structure are to be understood in their appropriate context, it is necessary to define not only pore-size distribution but also the probability of continuity of a particular pore-size class (Childs & Collis-George 1950; Millington & Quirk 1961, 1964). Quirk & Williams (1974) inferred that the 30–15 μm pore radius class was not randomly distributed and that there is a high probability that this pore class is interconnected within loam-textured soil aggregates. They found that organic polymers stabilize soil structure by strengthening this pore class within the macropore category.

For the purpose of this paper it is more convenient and appropriate that the total soil pore space be simply considered as consisting of structural and textural porosity; the structural porosity may be affected by mechanical treatment of a particular soil and its cropping history, whereas the textural porosity, in the main, may be considered to be an intrinsic property arising from the arrangement of the fundamental particles. Those of colloidal dimensions, the clay-size particles, are especially significant; the clay fraction in a soil is referred to as the 'active' fraction on account of its large surface area (of magnitude *ca.* 100 $m^2\ g^{-1}$), the lamellar nature of the particles, and the negative crystal lattice charge which is balanced by exchangeable cations on the surface of the particles. The interaction of the clay particles in the presence of water leads to swelling which, for lighter textured soils, may be accommodated within the structural porosity, giving rise to decreased permeability. The relative abundance of clay particles in a soil is indicated by textural classes such as sandy loam, loam, clay loam and clay.

For many soils the dominant ion balancing the lattice charge is calcium. However, soils developed in arid or semi-arid environments may have appreciable quantities of sodium ions balancing the charge. Because the presence of significant quantities of exchangeable sodium ions may adversely affect the physical properties of a soil including permeability, a special class of soils, sodic soils, has been defined as those with more than 15% exchangeable sodium (Richards 1954). McIntyre (1979) studied the hydraulic conductivity of 71 Australian soils and as a result proposed an exchangeable sodium percentage (e.s.p.) of five as being more appropriate for separating normal from sodic soils. Such definitions of a sodic soil are somewhat arbitrary in that there is no sharp change in the properties of a particular soil as the degree of saturation of the exchange complex with sodium increases. Furthermore, soils will vary in texture, structural porosity and in the abundance of organic matter and oxides of iron and aluminium, which may significantly modify particle interactions that would otherwise lead to enhanced swelling and deflocculation (Quirk & Schofield 1955).

The mechanism of the decrease in permeability of sodic soils involves the blocking or part blocking of conducting pores owing to swelling, which may also cause failure as a result of an unequal distribution of stress within the soil mass. At lower electrolyte levels, dispersion of the clay may result from the dominance of long-range repulsive interparticle forces.

Particle interaction in a sodic soil can be appreciably influenced by the presence of electrolyte either in the soil as salts or in the irrigation water. The use of electrolyte level to control soil permeability is the central focus of this paper, and the way in which such control can assist in the reclamation and management of irrigated soils is discussed.

THE NATURE AND ARRANGEMENT OF CLAY PARTICLES IN SOILS

Before presenting the physico-chemical basis for clay-particle interaction in the presence of water, it is necessary to consider the nature of clay particles (Brindley & Brown 1980) and their surface properties as well as their organization or arrangement within a soil.

The principal features of the lamellar clay minerals occurring in soils can be illustrated by reference to the ideal structural formulae of the following minerals:

muscovite mica	$(Si_6Al_2)^{IV}(Al_4)^{VI}O_{20}(OH)_4\cdots K_2$;
montmorillonite	$(Si_8)^{IV}(Al_{3.34}Mg_{0.66})^{VI}O_{20}(OH)_4\cdots Na_{0.66}$;
kaolinite	$(Si_4)^{IV}(Al_4)^{VI}O_{10}(OH)_8$.

In these structures the ions Si^{4+}, Al^{3+} and Mg^{2+} occur within the interstices of an anionic framework made up of O^{2-} and OH^-. The aluminosilicate layer for muscovite is not electrically neutral, because of the replacement of $2Si^{4+}$ by $2Al^{3+}$ in the tetrahedral (IV) layer; this deficiency in charge is balanced by potassium ions which are too large to be accommodated within the tetrahedral (IV) or octahedral (VI) layer. The potassium is accommodated between the 10 Å† thick aluminosilicate layers. Similarly, in the ideal montmorillonite structure one aluminium ion in six is replaced by a magnesium ion in the octahedral layer and, in this example, the deficiency in the lattice charge is balanced by sodium ions. The formula given for kaolinite is electrically neutral and it is difficult to detect isomorphous replacement in this group of minerals by total analysis. However, Bolland *et al.* (1976) concluded that most of the negative surface charge on kaolinites is independent of pH and is thus likely to be a result of isomorphous replacement.

The crystals of the above minerals are made up of elementary silicate sheets or lamellae stacked in the direction of the *c*-axis; these sheets have considerable lateral extent in the *a*- and *b*-directions varying from *ca.* 10^3 Å to many times this magnitude in well crystallized materials. For montmorillonite and mica these lamellae are about 9.5–10 Å thick and for kaolinite they are 7 Å thick. The mica crystals and kaolinite crystals do not expand in water and thus have a fixed *c*-axis spacing, whereas for montmorillonite and related smectite minerals the crystals swell as a result of hydration of the cations balancing the charge of the elementary silicate sheets. As a consequence all the metal ions balancing the montmorillonite lattice charge are exchangeable and can be replaced by leaching with a salt solution. Thus, for montmorillonite, the exchange capacity corresponds to the deficiency of lattice charge arising from isomorphous replacement of Al^{3+} by Mg^{2+} in the lattice. The surface area available for the adsorption of water by montmorillonite can be calculated from crystallographic parameters to be about 750 $m^2\ g^{-1}$.

By contrast, for mica-type minerals the exchange capacity is considerably less than the extent of isomorphous replacement, because only those ions that are on the external crystal surfaces are exchangeable. For fine-grained mica-like materials (for example, Willalooka illite; see Aylmore & Quirk (1962)), the exchange capacity may be 0.40 meq g^{-1} and the extent of isomorphous replacement may be in the vicinity of 2 meq g^{-1}. Such lamellar crystals may have an external surface area of about 150 $m^2\ g^{-1}$ and would therefore, on average, have five elementary silicate sheets per crystal, as the fully cleaved area for these minerals is in the vicinity of 750 $m^2\ g^{-1}$. Thus the thickness of the crystals would be 50 Å on average, and the lateral extent observed by electron microscopy is of the magnitude of 500–1000 Å.

Low-temperature nitrogen desorption isotherms of Willalooka illite have been used to demonstrate that the dominant pore size in Willalooka illite is 35 Å (Aylmore & Quirk 1960, 1962, 1967). The origin of this pore size is the near-parallel alignment of the individual clay

---

† $1\ Å = 10^{-10}\ m = 10^{-1}\ nm$.

crystals to provide slit and acute wedge-shaped pores; the pores result from the imperfect stacking of the clay crystals. Electron microscopy was used to confirm this interpretation and revealed a long-range order extending for several microns and giving compound particles, which Aylmore & Quirk (1960) have described as domains. Because clay materials frequently exhibit isotropic swelling at the macroscopic level, the domains were described as being in turbostratic array. The long-range order of the domain structure, extending over distances in excess of 5 μm (or 50 times the lateral dimensions of individual crystals), is a result of the interleaving of the crystals in which the thinner crystals are considered to play a significant role.

Similar considerations pertain to montmorillonite or smectitic materials in which the 10 Å elementary silicate sheets are condensed to give particles 40–100 Å thick and several microns in lateral extent (Fitzsimmons *et al.* 1970); these particles have been described as quasi-crystals by Quirk & Aylmore (1971). In the electron micrographs of Tessier (1984) the quasi-crystals are seen to have an even greater extent and form part of a network within a clay mass.

In an illitic soil in which the charge is almost entirely balanced by calcium, the domains, as assemblages of crystals, are the functional particles rather than the crystals themselves; however, interaction between the crystals in a domain causes an appreciable volume change. Similarly, in Ca montmorillonite or montmorillonitic soils the quasi-crystals are the functional particles within which the elementary silicate sheets are separated by 10 Å of water, irrespective of electrolyte concentration. However, when considerable quantities of sodium ions are present, the increased interaction in water, between the illite crystals within a domain and between the elementary silicate sheets within a quasi-crystal of montmorillonite, becomes a dominant factor in determining physical behaviour.

FILM THICKNESS ON CLAY PARTICLES IN RELATION TO ELECTROLYTE CONCENTRATION

The swelling of soil and clay materials is mediated by the development of water films at the clay–solution interface. The thickness of the water film which develops on an isolated surface as a function of electrolyte concentration and cation charge will be considered. Attention will then be given to the swelling pressures which develop when two such films interact at different distances of approach of two parallel plates or clay crystals.

The manner in which film thickness (X) on a single plate varies with concentration is provided by

$$X = \frac{2}{\nu\sqrt{(\beta c)}}\,\mathrm{arccot}\,\frac{2\sqrt{c}}{\Gamma\sqrt{\beta}} \tag{1}$$

(Schofield 1946), where c is the ionic concentration at the outer surface of the film, ν is the valency of the ions balancing the surface charge, Γ (equivalents per unit area) is the density of charge on the clay surface and β is a factor comprising physical constants ($8\pi F^2/\epsilon RT = 1.06\times10^{16}\ \mathrm{mmol}^{-1}$ at 20 °C).

For large values of Γ, X has a limiting value given by

$$X_{\max} = \pi/[\nu\sqrt{(\beta c)}], \tag{2}$$

from which it may be noted that at high charge densities the film thickness is inversely proportional both to $c^{\frac{1}{2}}$ and to the valency of the attracted ion. These equations are derived for symmetric electrolytes in which the valency of cation and anion are equal.

Streaming potential measurements (Kemper & Quirk 1972) and Gouy potentials derived from co-ion exclusion (Chan *et al.* 1984) indicate that clays should be treated as constant potential surfaces with respect to electrolyte concentration. When (1) is substituted into (7), the film thickness is given by

$$X = \frac{2}{\nu\sqrt{(\beta c)}}\,\operatorname{arccot}\left[\frac{1}{4\sinh^2\frac{1}{2}Z}\right] \tag{3}$$

in which Z, the reduced surface potential $(-\nu e\psi_0/kT)$, represents the balance of the electrical and thermal forces on an ion at an interface with a diffuse double layer or Gouy potential ψ_0. For a constant-surface potential, (3) shows that the film thickness is linear in $c^{-\frac{1}{2}}$; as Z increases, the film thickness at a given concentration approaches the limiting value of π/κ, in which κ^{-1} is the characteristic length in the Debye–Hückel theory of strong electrolytes. It is noteworthy that for a given value of Z, the film thickness for a divalent ion system is half that for a monovalent ion system.

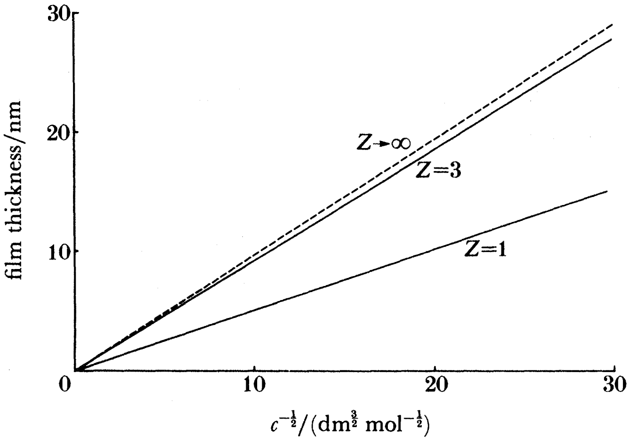

FIGURE 1. The relation (equation (3)) between the thickness of a water film developed on a surface of constant potential $(Z = -\nu e\psi_0/kT)$ and the concentration of monovalent cations in the bulk solution; note the limiting film thickness at large surface potentials. For divalent cations at the same reduced potential the film thickness is halved.

Figure 1 shows the magnitude of film thickness developed on clay surfaces in relation to surface potential and electrolyte concentration. It is relevant that the surface potential reported (Chan *et al.* 1984) for a Ca illite was -10 mV ($Z = 0.8$), and for a Na montmorillonite was -70 mV ($Z = 2.8$), so that the Z values in figure 1 would fall within the range of values found experimentally.

PARTICLE INTERACTION

Introduction

The Derjaguin–Landau (1941) and Verwey & Overbeek (1948) theory of particle interaction (D.L.V.O) has two principal elements involving London or van der Waals attractive forces and diffuse double-layer repulsive forces. The cations associated with a clay surface immersed in water are subjected to an electrostatic force of attraction towards the clay surface as well as a tendency to diffuse into the bulk. The net result of this competition is to establish a dynamic equilibrium in which the concentration of cations diminishes exponentially as a function of distance from the clay surface. This partition of cations between surface adsorption (the Stern or Helmholtz layer) and solution (the Gouy layer) is the electrical double layer and leads to the mutual osmotic repulsion of opposing surfaces in dilute electrolyte solutions. At higher concentrations the diffuse component of the double layer recedes and ultimately vanishes, as does the double-layer repulsive force.

The separation of contiguous clay surfaces which results from the adsorption of water attests to the existence of a repulsive force that is superior to van der Waals attraction at small separations (less than 1 nm). A familiar example of this is provided by the crystalline swelling of smectite minerals, for example, montmorillonite in concentrated electrolyte solutions (Posner & Quirk 1964*a*). The process responsible for this behaviour is hydration, the strong electrostatic interaction between exchangeable surface cations and the highly polar water molecule. Israelachvili & Adams (1978) have described such repulsive forces between mica plates as 'hydration forces' and have measured these forces. It should be noted, however, that these relatively short-range forces are observed as the difference between the total measured force and that obtained by extrapolation of the observed double-layer repulsion to small separations.

Diffuse double-layer forces between clay particles

A parallel plate model is adopted to examine particle interaction. In an extension of the Gouy diffuse-layer theory, Verwey & Overbeek (1948) presented the following equation for symmetric electrolytes:

$$Z'(x) = \kappa(2\cosh Z(x) - 2\cosh U)^{\frac{1}{2}}, \tag{4}$$

where $Z(x) = -\nu e\psi(x)/kT$ is the reduced potential, $\psi(x)$ is the electrical potential at a distance x from the mid-plane, U is the reduced potential at the mid-plane (where $Z'(x) = 0$), ν is the valency of the cation, e is the electronic charge,

$$\kappa = \left(\frac{8\pi F^2\nu^2 c}{\epsilon RT}\right)^{\frac{1}{2}} = \nu(\beta c)^{\frac{1}{2}} \tag{5}$$

and c is the bulk solution concentration.

Equation (4) can be rearranged and integrated from the mid-plane of the film towards the surface and provides, for any plane distant x from the mid-plane, the relation between x, $Z(x)$ and U in the form of an elliptic integral of the first kind:

$$\kappa x = 2\mathrm{e}^{-\frac{1}{2}U}\{F(\mathrm{e}^{-U}, \tfrac{1}{2}\pi) - F[\mathrm{e}^{-U}, \arcsin(\mathrm{e}^{-\frac{1}{2}(Z-U)})]\}. \tag{6}$$

This equation can be solved numerically or by use of a nomogram (Kemper & Quirk 1970).

If the surface charge density, σ $(= F\Gamma)$ is known, then the reduced surface potential can be calculated from the relation

$$\sigma = [(2\epsilon RTc)/\pi]^{\frac{1}{2}}\sinh\tfrac{1}{2}Z. \tag{7}$$

Having obtained Z, (6) can be solved for a given distance of separation and electrolyte concentration to furnish a value of U, the mid-plane potential. The swelling or disjoining pressure is then provided by the relation (Langmuir 1938)

$$P = 2RTc(\cosh U - 1). \tag{8}$$

Thus a relation between the distance of separation, swelling pressure and electrolyte concentration can be established for a given surface density of charge.

Figure 2 demonstrates the magnitude of the osmotic repulsive pressures under particular

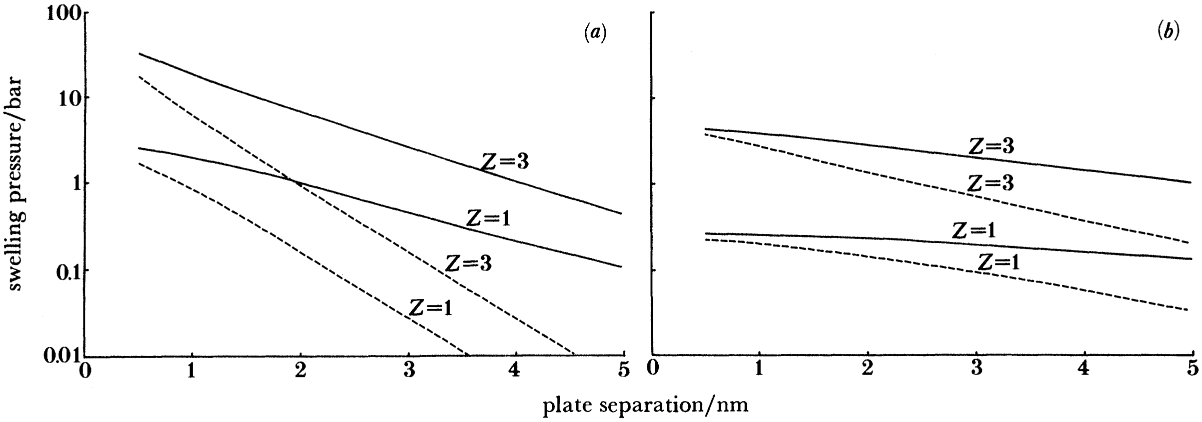

FIGURE 2. The relation between the diffuse double-layer component of swelling pressure and the separation of two surfaces with various constant surface potentials in (*a*) 0.1 mol $\mathrm{dm^{-3}}$ and (*b*) 0.01 mol $\mathrm{dm^{-3}}$ solutions of 1:1 (solid lines, e.g. NaCl) and 2:1 (broken lines, e.g. $\mathrm{CaCl_2}$) electrolytes.

conditions. It may be noted that 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.

In applying diffuse double-layer theory to the swelling of clay–water systems, it is important to distinguish broadly between irreversible shrinkage that is due to rearrangement of particles and reversible shrinkage (or swelling) associated with the dependence of film thickness on pressure or electrolyte concentration.

Van der Waals forces

The cohesion of clay particles and particulate materials is generally dominated by van der Waals forces. These attractive forces have their origin in the mutual polarization of atoms and molecules by the rapidly fluctuating charge distributions of their neighbours. Although the attractive potential between any two atoms diminishes very rapidly as the inverse sixth power of the separation, summation of these forces over all possible interactions leads to somewhat less dramatic behaviour for two quasi-infinite parallel plates of thickness t and separation D; this potential is given by

$$V_A = -\frac{A}{12\pi}\left[\frac{1}{D^2}+\frac{1}{(D+2t)^2}-\frac{1}{(D+t)^2}\right], \tag{9}$$

in which the Hamaker constant, A (*ca.* 10^{-20} J) reflects the polarizability and density of the atoms in the materials of interest as well as the dielectric properties of the intervening medium. At large separations, the finite velocity of propagation of electromagnetic fluctuations leads to retardation, a more rapid diminution of the force with distance than is implied by (9). These forces are non-retarded at separations below about 6 nm (Israelachvili & Adams 1978).

The interactions discussed here are expressed as potential energies relative to infinite separation, the derivatives of which, with respect to distance, yield the forces (figure 3).

Hydration forces

The magnitudes of the hydration potentials reflect, as might be expected, the electric field strength at the ion surface, that is, the square of the ion charge per ionic radius. The gross dependence of this potential (which is relatively insensitive to concentration) on distance has been reported for sodium and calcium muscovite mica by Pashley & Quirk (1984); their results are expressed in the form of a repulsive pressure against distance curve in figure 3. It may be noted from this figure that at separations up to 2 nm the hydration forces are at least 10 times greater than those arising from the diffuse double-layer repulsion. However, closer examination of the magnitude of these forces at separations below 1.5 nm (so far for potassium mica only) has revealed a series of deep, discrete potential energy minima, at intervals of about 0.28 nm (i.e. about the diameter of the water molecule), corresponding to the presence of integral numbers of water layers between the mica sheets (Israelachvili & Pashley 1983). This observation is readily reconciled with the existence of discrete, stable, interlayer hydrates of clay minerals (Norrish 1954) and their transitions in concentrated electrolyte solutions (Posner & Quirk 1964*a*, *b*).

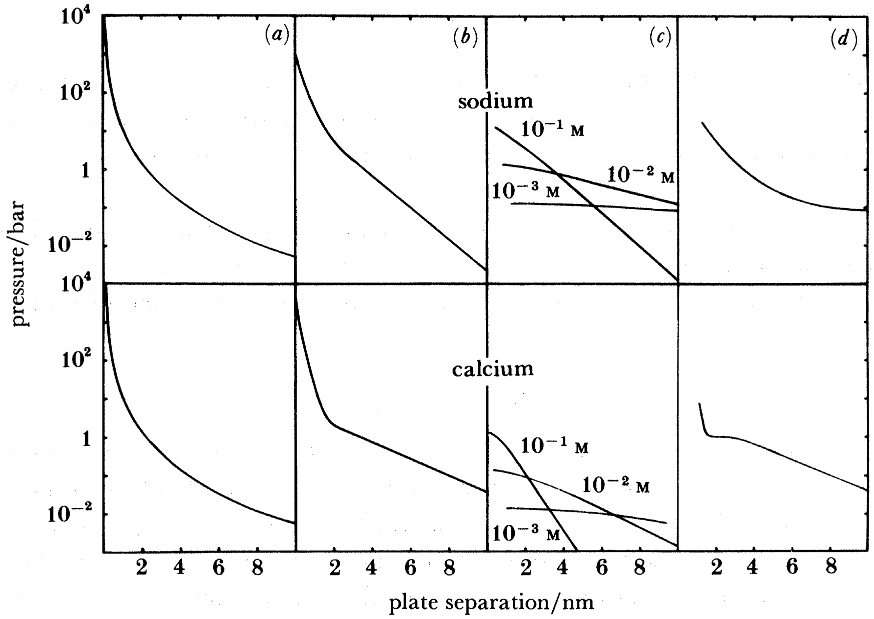

FIGURE 3. Components of the swelling pressure between two homo-ionic illite sheets calculated as a function of separation from the data of Pashley & Quirk (1984) for muscovite mica. (*a*) The non-retarded, attractive van der Waals pressure for sheets 4 nm thick; (*b*) the repulsive hydration pressure; (*c*) the repulsive diffuse double-layer pressure at various electrolyte concentrations, with the use of representative surface potentials from Chan *et al.* (1984) of −50 and −10 mV for sodium and calcium respectively; and (*d*) the total repulsive swelling pressure at 10^{-3} M.

Resultant forces

It may be noted from figure 3 that the resultant of the attractive and repulsive forces indicates that at all separations and concentrations the forces between two parallel illite plates is repulsive, indicating that in the absence of other factors, one would expect calcium and sodium clay systems to behave in an essentially similar fashion. However, consideration needs to be given to the character of a mass of illite particles and their organization into domains. In such a mass, although the pore size will approximate the thickness of the individual clay crystals, there will be significant areas of overlap in which separations of less than 1 nm and, indeed, areas of adhesive contact are to be found.

Potential minima

That calcium montmorillonite exists in a primary potential minimum was first demonstrated by Quirk (1952) with the use of permeability measurements (table 1); this was confirmed by X-ray diffraction measurements, which revealed that in calcium chloride solutions less concentrated than about 1 mol dm^{-3}, the $d(001)$ X-ray spacing remained at 19 Å (i.e. about 9 Å separation of the elementary silicate surfaces). This contrasted with the behaviour of sodium montmorillonite, for which the spacing in molar NaCl was 19 Å and increased to 40 Å in 0.3 M NaCl (Norrish & Quirk 1954).

TABLE 1. PERMEABILITY AND X-RAY SPACING FOR Na AND Ca MONTMORILLONITE IN NaCl AND CaCl$_2$ SOLUTIONS[a]

solution	10^5 permeability / cm s^{-1}	X-ray spacing/Å
0.1 M CaCl$_2$	1.7	19.0
$< 10^{-5}$ M CaCl$_2$	1.4	19.0
1.0 M NaCl	1.8	18.7
0.5 M NaCl	0.4	18.9
0.3 M NaCl	*ca.* 0	43

[a] From Quirk (1952).

TABLE 2. WATER CONTENT OF MINERALS IN RELATION TO ELECTROLYTE CONCENTRATION

concentration / mol dm^{-3}	montmorillonite		illite	
	Na$^+$	Ca^{2+}	Na$^+$	Ca^{2+}
1.0	0.95	0.58	0.57	0.45
0.1	4.9	0.68	0.77	0.45
0.01	7.7	0.71	1.60	0.47
$< 10^{-5}$	18.0	0.71	$\geqslant 2.0$	0.47

Water content (g g^{-1}) at 0.01 bar suction. Results from Aylmore & Quirk (1962).

In table 2, results are presented for the swelling of sodium and calcium montmorillonite (Wyoming) and illite (Willalooka) in relation to electrolyte concentration at 0.01 bar suction. The water contents for calcium montmorillonite change relatively little over a wide concentration range, whereas those for sodium montmorillonite vary markedly as a result of the development of diffuse double-layer repulsive pressures. The behaviour of sodium illite is similar, but clearly diffuse double-layer theory cannot be so readily applied to the calcium illite. Aylmore & Quirk (1962), Bolt & Koenigs (1972) and Murray & Quirk (1985) have interpreted this as being a result of the existence of potential barriers at regions of overlap where there is close interparticle approach. Thus the behaviour of this part of an illite clay–water system resembles that of calcium montmorillonite, which retains a fixed spacing.

Table 3 shows that for the natural aggregates of two clay soils, at least three-quarters of the porosity is in pores of size less than 10 nm, and that for the montmorillonite soil about 70% of the surface area is in pores with walls separated by less than 2 nm; for the predominantly illitic soil, 40% of the surface area is in pores smaller than 2 nm.

If a part of the surface of two contiguous clay surfaces are separated in the dry state by distances of about 1 nm or less they will be prevented from expansion beyond the potential

Table 3. Distribution of surface area within the microstructure of natural aggregates of two Australian soils

soil[a]	porosity cm^3 g^{-1} total	porosity cm^3 g^{-1} < 10 nm	surface area m^2 g^{-1}	percentage surface area in pores < 2 nm	percentage surface area in pores 2–3 nm	percentage surface area in pores 3–10 nm
I	0.144	0.108	154	68	29	2
II	0.175	0.155	116	39	23	37

[a] Soil I is a Queensland vertisol, Darling Downs, Queensland (Murray *et al.* 1985); soil II is Urrbrae B, the subsoil of a South Australian red-brown earth (Murray & Quirk 1980).

minimum resulting from the interplay of strong short-range forces. However, the monotonic repulsive forces that characterize greater distances of separation act to overcome this effect, and may remove some or all the surfaces from within potential minima.

This operation of the potential minimum needs some consideration with respect to sodic soils for which the behaviour would be expected to be intermediate between that of the sodium and calcium clays. In a system comprising only sodium and calcium as exchangeable cations, a random distribution of ions on the clay surface can be seen to act in two ways. In regions of close approach the presence of sodium ions may act to reduce the depth of the adhesive potential energy well, while in coarser voids the significant enhancement of surface potential would lead to increased repulsion. In this way, the stable regions of overlap existing between surfaces saturated with calcium would be rendered metastable by the introduction of sodium, and the cooperative creation of coarser voids would become a self-sustaining process driven by the enhanced Gouy potentials of surfaces bearing sodium ions. Furthermore, the extent of sodium saturation required to produce a given behavioural change in a soil is clearly seen to be very sensitive to microstructure (Murray & Quirk 1985). An additional complication arises if the segregation of exchangeable cations on the clay surface is considered. The preferential adsorption of either cation in regions of close approach would be expected to lead to complex swelling behaviour. These considerations confirm that a threshold exchangeable sodium percentage (e.s.p.) of 15 for sodic soils is somewhat arbitrary and that the onset of adverse soil behaviour at lower values of e.s.p. may be closely related to clay microstructure.

McNeal & Coleman (1966) found that replacing about 15% of the adsorbed calcium with sodium had little effect on the swelling of the clay. With a further increase in the e.s.p. of the soil, a very sharp increase in macroscopic swelling was found for montmorillonite soils (Gila clay and Waukena clay loam). At the high e.s.p. range (over 50), such soils swell almost as much as sodium-saturated materials. Glaeser & Mering (1954) suggested that 'demixing' of the cations occurs so that some interlayer spaces contain mainly sodium ions and others mainly calcium ions. They also showed that complete mixing occurs in the first stages of substitution of calcium for sodium. The demixing started at about 30% calcium and was complete at 40%. If, as these results suggest, the exchangeable sodium ions accumulate on the external surfaces of quasi-crystals, then the effective e.s.p. will be much higher than if the sodium ions were uniformly associated with the whole surface area, and as a result the physical behaviour will resemble a soil with a much higher e.s.p.

CATION-EXCHANGE ISOTHERMS – THE GAPON EQUATION

The thermodynamic exchange equilibrium constant for the binary stoichiometric exchange reaction

$$2\mathrm{NaX(s)} + \mathrm{CaCl_2(aq)} = \mathrm{CaX_2(s)} + 2\mathrm{NaCl(aq)}$$

is represented by

$$K = \frac{(\mathrm{Na^+})^2(\mathrm{CaX_2})}{(\mathrm{NaX})^2(\mathrm{Ca^{2+}})}, \tag{10}$$

where X is one equivalent of the anionic clay surface and the quantities in parentheses refer to the activity of the chemical species, that is the ion concentration multiplied by the activity coefficient (i.e. $a_i = m_i \gamma_i$). The activities of the exchangeable ions in the Gaines & Thomas treatment of (10) is taken as the equivalent fraction and in the Vanselow treatment as the mole fraction (Sposito 1981).

The Gapon exchange equation has been widely used in saline and sodic soil studies (Richards 1954); the exchangeable cations are shown as reacting in equivalents thus:

$$\mathrm{NaX(s)} + \tfrac{1}{2}\mathrm{CaCl_2(aq)} = \mathrm{Ca_{\frac{1}{2}}X(s)} + \mathrm{NaCl(aq)};$$

and the Gapon equilibrium constant is

$$K_\mathrm{G} = \frac{[\mathrm{Ca^{2+}}]^{\frac{1}{2}}\,(\mathrm{NaX})}{[\mathrm{Na^+}]\,(\mathrm{Ca_{\frac{1}{2}}X})}, \tag{11}$$

or alternatively,

$$\frac{E_\mathrm{Na}}{E_\mathrm{Ca}} = K_\mathrm{G}\frac{[\mathrm{Na^+}]}{[\mathrm{Ca^{2+}}]^{\frac{1}{2}}}, \tag{12}$$

in which E_Na and E_Ca are the equivalent fraction of sodium and calcium ions on the exchange complex and the square brackets refer to concentrations in solution rather than activities. The ratio of the ion concentrations is of a similar magnitude to the corresponding ratio of the ion activities over the concentration ranges common to salt-affected soils, even though the activities themselves are quite different. In considering K_G for individual soils it is important to realize that soil clays are frequently a mixture of clay mineral types and contain at least four cationic species: sodium, potassium, magnesium and calcium. Furthermore, in the field there is point-to-point variation of a soil over small distances and a temporal variation in water content.

Equation (12) may be expressed as

$$R_\mathrm{es} = K_\mathrm{G}(R_\mathrm{sa}), \tag{13}$$

in which R_es is the exchangeable sodium ratio (e.s.r.) and R_sa is referred to as the sodium adsorption ratio (s.a.r.) (Richards 1954). In calculating the e.s.r. the calcium and magnesium are, as a matter of practice, included in the denominators of both sides of the equation. In (12) and (13) the cation concentration in the solution phase (s.a.r. term) is expressed in mol m^{-3} (mmol dm^{-3}), and the exchangeable ion equivalent fraction is given in milliequivalents per hundred grams for each ion divided by the exchange capacity of the clay in the same units.

The United States Salinity Laboratory (Richards 1954) has examined a large number of soils from the Western United States and have obtained the following relation to describe their results:

$$R_\mathrm{es} = 0.01475\ R_\mathrm{sa} - 0.0126. \tag{14}$$

This relation is an empirical form of the Gapon equation with $K_G \approx 0.015$. A useful rule of thumb is that over the range 0–30 the s.a.r. values are approximately equal to the e.s.p. values.

For a particular soil on which detailed studies are to be performed it would be advisable to determine K_G because considerable variation has been reported (see, for example, Levy & Hillel 1968).

The occurrence of $(Ca^{2+})^{\frac{1}{2}}$ in the Gapon equation has two interesting features. First, if a soil is equilibrated with a solution having a given $Na^+/(Ca^{2+})^{\frac{1}{2}}$ value, and it is desired to percolate the soil with a more dilute solution and at the same time maintain the ratio of sodium to calcium on the soil surface constant, then if the sodium ion concentration is reduced by a factor the calcium ion concentration must be reduced by the square of that factor. Stated more directly, if the sodium ion concentration is halved, then the calcium ion concentration should be reduced by a factor of four to maintain the exchangeable sodium percentage at the same value. Secondly, if water being used to reclaim a sodic soil is diluted, this dilution decreases the s.a.r. and thus favours the adsorption of calcium on the soil surfaces, so that the exchangeable sodium percentage is reduced and reclamation is assisted.

THRESHOLD CONCENTRATION CONCEPT

In a recent review, Shainberg & Lety (1984) noted that the basic approach of Quirk & Schofield (1955) has been extended to a large number of additional soils. To describe the relation between soil permeability and solution composition, Quirk & Schofield developed the concept of 'threshold concentration'. This was defined as the concentration in the percolating solution that would give rise to a 10–15% decrease in relative permeability at a given e.s.p. value. They demonstrated that soil permeability can be maintained at a high and stable level, even for a sodium-saturated soil or at large e.s.p. values, provided the salt concentration of the water is above a critical (threshold) value.

Figure 4 shows the effect of sodium chloride concentration on the permeability of a Na-saturated Rothamsted soil (Sawyers I); it may be observed that the threshold concentration is 250 meq dm^{-3}. It may also be observed that there are large decreases in permeability when solutions containing 50 and 10 meq dm^{-3} are used.

Dispersed clay first appeared when the percolating solution contained 25 meq dm^{-3}. These observations indicate that considerable decreases in permeability with respect to electrolyte concentration take place as a result of swelling and swelling-induced effects before dispersed clay particles appear in the percolate. This has been confirmed by the experiments of Rowell *et al.* (1967). Thus the decreases in permeability are a result of an enhanced interaction between clay particles, beyond that which occurs in more concentrated electrolyte solutions when the permeability is stable. Quirk & Schofield (1955) recognized that swelling, failure and deflocculation or dispersion were involved.

The effect of electrolyte concentration on the permeability of the Ca-saturated soil is not great (figure 4); the threshold concentration is 0.6 meq dm^{-3}. The permeability of the system does not decrease more than about 20%, even when distilled water is the permeant. Slight turbidity appeared at 0.2 meq dm^{-3}; however, flocculation did not occur in the soil suspension until the concentration exceeded 2 meq dm^{-3} (Quirk 1952), emphasizing the important role of the potential barrier at distances of close approach of clay particles within the aggregates. This barrier is an important determinant of behaviour, as opposed to the situation in a

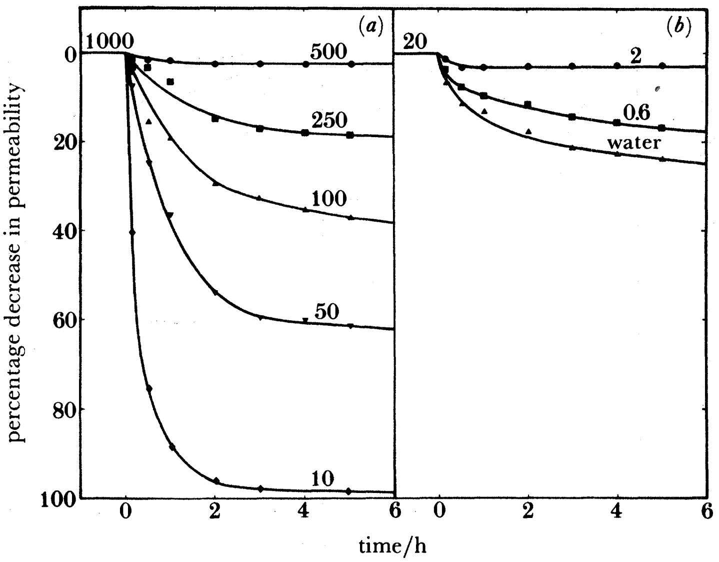

FIGURE 4. The loss of permeability from a homo-ionic Rothamsted soil (Sawyers 1) saturated with (*a*) sodium or (*b*) calcium during percolation of successively more dilute solutions of the chloride salt. The numbers on the curves are concentrations in milliequivalents per cubic decimetre.

suspension in which the particles have been well separated as a result of the mechanical work in preparing the suspension.

To determine the threshold concentration for various degrees of exchangeable sodium saturation, Quirk & Schofield (1955) brought the Rothamsted soil to equilibrium with relatively concentrated mixed solutions of NaCl and $CaCl_2$ having different values of $Na^+/(Ca^{2+})^{\frac{1}{2}}$ (i.e. s.a.r. values). When ionic equilibrium was established between a particular solution and the soil surfaces then the permeability was determined for successively more dilute solutions having the same s.a.r. value as the original solution, as required by the Gapon equation. The threshold concentrations determined in this manner are plotted against the exchangeable sodium percentage (figure 6). The relative permeability measurements for e.s.p. values of 9 and 21 are shown in figure 5 and can be contrasted with the results obtained when the soil was saturated with sodium or with calcium (figure 4).

The curve in figure 6 divides the figure into two parts; on the right-hand side the concentrations are greater than the threshold concentration for a given e.s.p. and the permeability is stable, whereas on the left-hand side of the curve permeability decreases owing to increased particle interaction. The usefulness of such a relation may easily be seen by referring to a soil with an e.s.p. value of 20; if this soil were to be irrigated with water containing less than 9 meq dm^{-3} of electrolyte, then structural disruption would take place and the extent of this disruption would be greater, the lower the electrolyte concentration.

In figure 7 it can be seen that when the threshold concentration is plotted against s.a.r. (i.e. $Na^+/(Ca^{2+})^{\frac{1}{2}}$), a linear relation emerges (Quirk 1971):

$$c_t = 0.56Na^+/(Ca^{2+})^{\frac{1}{2}} + 0.6, \tag{15}$$

in which c_t is the electrolyte concentration required to prevent increased particle interaction for a particular s.a.r. value. It may be noted that (15) does not contain any parameters characteristic of the soil so that when the s.a.r. value of the saturated extract is known, then

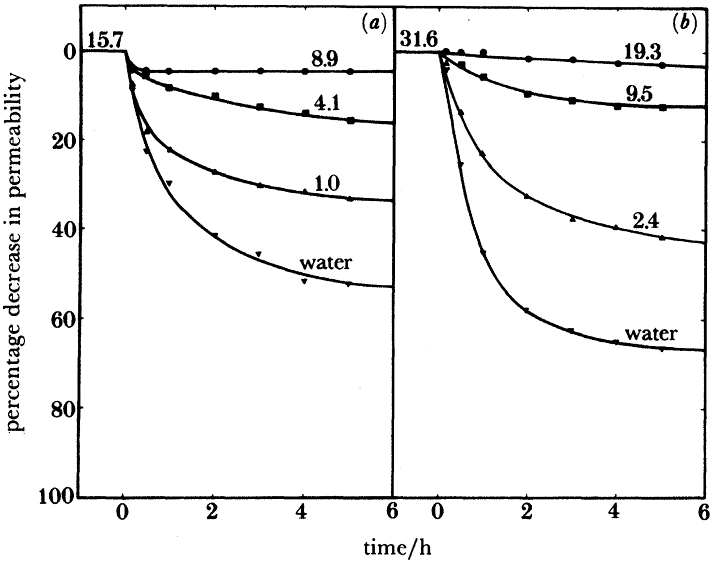

FIGURE 5. The loss of permeability from a hetero-ionic Rothamsted soil (Sawyers 1), initially in equilibrium with a mixed sodium chloride and calcium chloride solution during percolation of successively more dilute solutions with the same s.a.r. (i.e. $Na^+/(Ca^{2+})^{\frac{1}{2}}$). (*a*) $R_{sa} = 6.3$, (*b*) $R_{sa} = 15.8$. The numbers on the curves are total concentrations in milliequivalents per cubic decimetre.

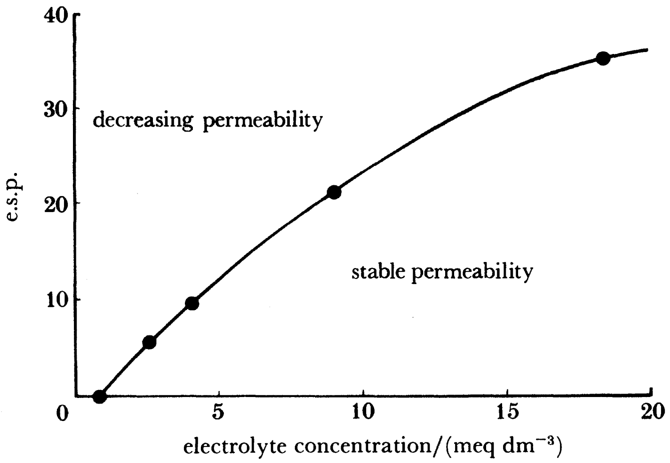

FIGURE 6. The relation between threshold electrolyte concentration and exchangeable sodium percentage for a Rothamsted soil (Sawyers 1) (Quirk & Schofield 1955).

the required electrolyte level in the irrigation water to maintain the permeability can be predicted. If a non-sodic soil is being irrigated with water of a quality which is likely to increase the exchangeable sodium percentage, then (15) can be used to assess the likely effect that such an irrigation water will have on the soil permeability as the soil approaches equilibrium with the s.a.r. value of the water.

In figure 7 some results of McNeal & Coleman (1966) are presented; they determined the salt concentration for which there was a 25% reduction in permeability for a number of Californian soils, including Oasis clay loam, Pachappa sandy loam, Waukena clay loam and Grangeville sandy loam. In the region where comparisons can be made, that is up to an s.a.r. value of 30, the agreement is reasonable.

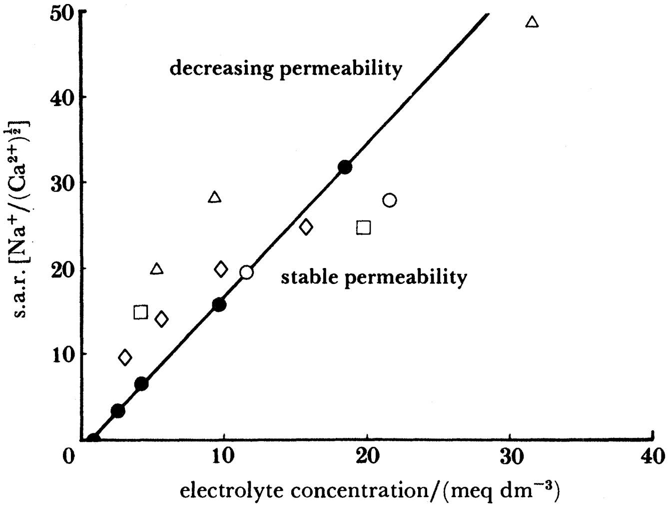

FIGURE 7. A graphical representation of (15) (filled circles show data of Quirk (1971)) with additional experimental points (open symbols) from McNeal & Coleman (1966): ○, Grangeville sandy loam; □, Oasis clay loam; △, Pachappa sandy loam; ◊, Waukena clay loam.

The presence of iron oxides and amorphous materials as stabilizing agents can largely prevent the unfavourable physical effects arising from the presence of exchangeable sodium (McNeal & Coleman 1966). Gila clay, which contains 60% clay and appreciable quantities of montmorillonite, requires much higher concentrations of electrolyte to maintain permeability. This may be associated with the nature of the textural porosity and of the structural porosity of the material.

Rengasamy *et al.* (1984) examined the spontaneous dispersion of a large number of Australian red-brown earth soils and found that only 28 of the 106 soils examined dispersed without mechanical agitation, that is, spontaneously; none with an s.a.r. less than 3 dispersed spontaneously. For the soils that dispersed they obtained an equation relating C_{tc} the total cation concentration (t.c.c.) for dispersion to the s.a.r. of the solution, and found that

$$C_{tc} = 0.16\,R_{sa} + 0.14. \tag{16}$$

This equation can be related to the observations of Quirk & Schofield, who showed in their permeability experiments that dispersed clay first appeared in the percolate at concentrations which, in total electrolyte level, were about one-quarter of the threshold concentration given by (15); thus (16) is in good agreement with the observations of these authors on the appearance of turbidity. Rengasamy *et al.* also made field observations for the turbidity of water on the surface of red-brown earth soils under pasture following a rainfall of 2.5 cm in 1 h. The values obtained for the presence and absence of turbidity related closely to that determined in the laboratory and represented by (16). The significance of the presence of pasture is that it protected the surface soil from the energetic action of raindrops. Their field observations of bare cultivated soils conformed closely with the laboratory-determined relation

$$C_{tc} = 1.21\,R_{sa} + 3.3, \tag{17}$$

which was based on flocculation of a suspension formed by mechanical stirring. These authors claimed that the mechanical stirring used by them simulated the energetic action of falling raindrops on the bare soil surface. The rainfall before the field observations was 2.5 cm in an hour, and it is relevant that Quirk & Panabokke (1962) have reported that, for rates of wetting (rainfall intensity) greater than 1 cm h^{-1}, 'incipient failure' took place for red-brown earth soils from narrow rotations; it follows that (17) would be appropriate for high rainfall intensities or for rapid wetting with flood irrigation.

In discussing the reclamation of sea-flooded soils in The Netherlands, van Beekom *et al.* (1953) observed that 'The typical heavy decline in structure begins in the first winter after drainage when the soluble salts are largely removed from the top soil', and 'The crumb structure is only lost if the soil is stirred; therefore this only occurs in the layer that is ploughed and especially at the surface which is exposed to the devastating influence of falling raindrops'. It is obvious from their work that soils with high organic matter or soils just out of grass have more favourable physical properties when saturated to varying degrees with exchangeable sodium than other arable soils in a similar condition. It is also important to recognize that disturbance of the soil by cultivation is likely not only to diminish the favourable conditions conferred by organic polymers but also to cause structural damage through mechanical work. The underlying principle is that the particles are provided with opportunities for separation by shearing or lateral movement which do not occur naturally. Lateral movement of particles is a considerably less energetic way of separating particles in potential minima.

Application of the threshold concentration concept

In their review Shainberg & Letey (1984) remarked that the following statement of Quirk & Schofield (1955) is still relevant today: 'Despite the obvious effect of electrolyte on soil permeability, the main emphasis has been given to the exchangeable sodium percentage and (electrical) conductivity of the irrigation water as an index of the degree to which sodium will occupy exchange positions on the clay surface. Soils in arid and semi-arid regions often have a high e.s.p. before being irrigated, and for this reason the quantity of electrolyte in the irrigation water should be given greater consideration.'. This statement forms the background to the examples to be discussed here. Cajon sandy loam in Arizona was usually irrigated with Colorado River water, but during the years 1946 to 1948, little river water was available, and as a result it was necessary to rely on underground water. This water contained 50 meq dm^{-3} of sodium and 8 meq dm^{-3} of calcium (plus magnesium). After irrigation with this water for three years the e.s.p. value was reported as varying between 19 and 34 with 25 as the mean. Such a soil would have a threshold concentration of 11 meq dm^{-3} of irrigation water to maintain a stable permeability (figure 6). The underground water, although it would have provided a very saline environment, exceeded this concentration. However, the river water contained 3.9 meq dm^{-3}, which is considerably less than the threshold concentration. In their paper McGeorge & Fuller (1950) reported that when river water was again available in 1949 its use caused the soil to become impermeable and to develop unsatisfactory physical conditions: the soil 'froze up'. If the river water had been modified by the addition of 8 meq dm^{-3} of calcium ions, or, alternatively, if as little as one-seventh of the underground water had been mixed with the river water, this problem could have been avoided. This would have given an electrolyte concentration of about 11.6 meq dm^{-3}, which could have been progressively reduced by monitoring the e.s.p. value until it fell to a level that would have allowed the use of river water alone.

Reeve & Bower (1960) remarked that 'the use of waters of poor quality, that is those having a high salt content and a high proportion of sodium, for reclamation has been unthinkable in the past, and at first thought such use would seem to be questionable practice'. However, these authors used sea water mixed with river water to maintain a high permeability, to shorten the reclamation time and to make use of the 'valence-dilution effect' which, as indicated earlier, makes use of dilution as favouring the exchange of calcium for sodium.

The soil used by Reeve & Bower was from Coachella Valley, California and has an e.s.p. value of 37. To sustain the permeability of a soil at this level of exchangeable sodium, the level of electrolyte should be 20 meq dm^{-3}. In their experiments they added Salton sea water (560 meq dm^{-3}) to Colorado River water (11 meq dm^{-3}) to ensure that the electrolyte level was always above the threshold concentration. Decreasing amounts of sea water were added as the reclamation progressed. The use of river water alone reduced the permeability to 0.02 cm h^{-1}, whereas with the appropriate mixtures the permeability was maintained at 0.50 cm h^{-1}. The most efficacious treatment involved the successive use of waters containing one part of sea water to 3, 15 and 63 parts of river water. The final part of the reclamation was done with river water alone. With this treatment reclamation was achieved in 12 days, with only 6 % of the total water used being sea water. The soil in equilibrium with the Colorado River water would have had an e.s.p. value of 2.

Gypsum ($CaSO_4 \cdot 2H_2O$) has been widely used in agriculture to replace exchangeable sodium by calcium in sodic soils or to adjust unfavourable s.a.r. values of irrigation waters. The amount of gypsum required to replace the exchangeable sodium in the top 10 cm of soil may be many tonnes per hectare and in some circumstances would not be considered economic. The use of gypsum in irrigated agriculture has been discussed by Oster (1982).

Attention has been given to developing models for the composition of soil solutions (Dutt *et al.* 1972; Bresler *et al.* 1982), taking into account various factors such as leaching by excess water or rainfall, drainage conditions, and the solubility of soil constituents. Gypsum dissolution follows first-order reaction kinetics and the electrolyte concentration in the soil pores may (depending on the particle size of gypsum, the flow rate through the soil, and other factors) be less than 10 meq dm^{-3} (Keisling *et al.* 1978); the concentration of calcium in a saturated gypsum solution is almost 20 meq dm^{-3} at 20 °C. It is thus possible that addition of gypsum to a sodic soil may not be as effective, as far as the electrolyte effect is concerned, as adding the gypsum or another soluble calcium salt to the irrigation water, when procedures can be adopted to ensure that the desired concentrations are achieved.

Because it would not have been economic to add large quantities of gypsum to soils used for pasture development in western New South Wales, Davidson & Quirk (1961) added gypsum to the irrigation water to assist pasture-plant establishment on Riverina clay. This soil (with an e.s.p. value of 20) and the irrigation water had an electrolyte concentration of about 1 meq dm^{-3}, and as a result deflocculation took place when the soil was irrigated; water entry was poor and very few pasture plants emerged because of the hard surface crusts that developed between irrigations. These difficulties were overcome when 10 meq dm^{-3} (*ca.* 0.6 t ha^{-1}) was added to the irrigation water. It was only necessary to add gypsum to the first irrigation to achieve satisfactory pasture establishment and development.

In this paper the specific topic of the effect of electrolyte level on permeability has been discussed together with a consideration of the surface and colloid chemistry of clay-particle interaction which leads to enhanced swelling, failure of aggregates and deflocculation. Other aspects of the management of saline and sodic soils are extensively discussed by Bresler *et al.* (1982).

It is a pleasure to acknowledge the helpful discussions and assistance provided by Dr R. S. Murray during the preparation of this paper.

REFERENCES

Aylmore, L. A. G. & Quirk, J. P. 1960 Domain or turbostratic structure of clays. *Nature, Lond.* **187**, 1046–1048.

Aylmore, L. A. G. & Quirk, J. P. 1962 The structural status of clay systems. *Clays Clay Miner.* **9**, 104–130.

Aylmore, L. A. G. & Quirk, J. P. 1967 The micro-pore size distribution of clay mineral systems. *J. Soil Sci.* **18**, 1–17.

Baver, L. D. 1940 *Soil physics.* New York: John Wiley.

van Beekom, C. W. C., van der Berg, C., de Boer, Th. A., van der Molen, W. H., Verhoeven, B., Westerhof, J. J. & Zuur, A. J. 1953 Reclaiming land flooded with salt water. *Neth. J. agric. Sci.* **1**, 153–163 and 225–244.

Bolland, M. D. A., Posner, A. M. & Quirk, J. P. 1976 Surface charge on kaolinites in aqueous suspension. *Aust. J. soil Res.* **14**, 197–216.

Bolt, G. H. & Koenigs, F. F. R. 1972 Physical and chemical aspects of the stability of soil aggregates. *Meded. Fac. Landbouwwet., Rijksuniv. Gent* **37**, 955–973.

Bresler, E., McNeal, B. L. & Carter, D. L. 1982 (ed.) *Saline and sodic soils – principles – dynamics – modelling.* Berlin: Springer-Verlag.

Brindley, G. W. & Brown, G. 1980 *Crystal structures of clay minerals and their identification.* London: Mineralogical Society.

Chan, D. Y. C., Pashley, R. M. & Quirk, J. P. 1984 Surface potentials derived from co-ion exclusion measurements on homoionic montmorillonite and illite. *Clays Clay Miner.* **32**, 131–138.

Childs, E. C. & Collis-George, N. 1950 The permeability of porous materials. *Proc. R. Soc. Lond.* A **201**, 392–405.

Davidson, J. L. & Quirk, J. P. 1961 The influence of dissolved gypsum on pasture establishment on irrigated sodic clays. *Aust. J. agric. Res.* **12**, 100–110.

Derjaguin, B. V. & Landau, L. 1941 Theory of the stability of strongly charged lyophobic sols and the adhesion of strongly charged particles in solutions of electrolytes. *Acta Phys.-chim. URSS* **XIV**, 633–662.

Dutt, G. R., Terkeltoub, R. W. & Rauschkolb, R. S. 1972 Prediction of gypsum and leaching requirements for sodium-affected soils. *Soil Sci.* **114**, 93–103.

Fitzsimmons, R. F., Posner, A. M. & Quirk, J. P. 1970 Electron microscopic and kinetic study of the flocculation of calcium montmorillonite. *Israel J. Chem.* **8**, 301–314.

Glaeser, R. & Mering, J. 1954 Isothermes d'hydratation des montmorillonites bi-ioniques (Na, Ca). *Clay Miner. Bull.* **2**, 188–193.

Israelachvili, J. N. & Adams, G. E. 1978 Measurement of forces between two mica surfaces in aqueous electrolyte solutions. *J. chem. Soc. Faraday Trans.* I **74**, 975–1001.

Israelachvili, J. N. & Pashley, R. M. 1983 Molecular layering of water at surfaces and origin of repulsive hydration forces. *Nature, Lond.* **306**, 249–250.

Keisling, T. C., Rao, P. S. C. & Jessup, R. E. 1978 Pertinent criteria for describing the dissolution of gypsum beds in flowing water. *Soil Sci. Soc. Am., J.* **42**, 234–246.

Kemper, W. D. & Quirk, J. P. 1970 Graphic presentation of a mathematical solution for interacting diffuse layers. *Soil Sci. Soc. Am., Proc.* **34**, 347–351.

Kemper, W. D. & Quirk, J. P. 1972 Ion mobilities and electric charge of external clay surfaces inferred from potential differences and osmotic flow. *Soil. Sci. Soc. Am., Proc.* **36**, 426–433.

Langmuir, I. 1938 Role of attractive and repulsive forces in the formation of tactoids, thixotropic gels, protein crystals and coacervates. *J. chem. Phys.* **6**, 873–896.

Levy, R. & Hillel, D. 1968 Thermodynamic equilibrium constants of sodium-calcium exchange in some Israeli soils. *Soil Sci.* **106**, 393–398.

McGeorge, W. T. & Fuller, W. H. 1950 Relation between the Na:Ca ratio in the saturation extract and the percentage sodium in the exchange complex. *Trans. 4th Int. Congr. Soil Sci., Amsterdam* (ed. F. A. Van Baren *et al.*), vol. 1, pp. 400–403. Groningen: Hoitsema Brothers.

McIntyre, D. S. 1979 Exchangeable sodium, subplasticity and hydraulic conductivity of some Australian soils. *Aust. J. soil Res.* **17**, 115–120.

McNeal, B. L. & Coleman, N. T. 1966 Effect of solution composition on soil hydraulic conductivity. *Soil Sci. Soc. Am., Proc.* **30**, 308–312.

Millington, R. J. & Quirk, J. P. 1961 Permeability of porous solids. *Trans. Faraday Soc.* **57**, 1200–1207.

Millington, R. J. & Quirk, J. P. 1964 Formation factor and permeability equations. *Nature, Lond.* **202**, 143–145.

Murray, R. S. & Quirk, J. P. 1980 Clay water interactions and the mechanism of soil swelling. *Colloids Surf.* **1**, 17–32.

Murray, R. S., Coughlan, K. J. & Quirk, J. P. 1985 Nitrogen sorption isotherms and the microstructure of vertisols. *Aust. J. soil Res.* **23**, 137–149.

Murray, R. S. & Quirk, J. P. 1985 Interparticle forces in relation to the stability of soil aggregates. *ISSS Commission II. The nature and properties of soil colloids.* (In the press.)

Norrish, K. 1954 The swelling of montmorillonite. *Discuss. Faraday Soc.* **18**, 120–134.

Norrish, K. & Quirk, J. P. 1954 The crystalline swelling of montmorillonite – use of electrolytes to control swelling. *Nature, Lond.* **173**, 255–256.

Oster, J. D. 1982 Gypsum usage in irrigated agriculture: a review. *Fert. Res.* **3**, 73–89.

Pashley, R. M. & Quirk, J. P. 1984 The effect of cation valency on DLVO and hydration forces between macroscopic sheets of muscovite mica in relation to clay swelling. *Colloids Surf.* **9**, 1–17.

Posner, A. M. & Quirk, J. P. 1964*a* The adsorption of water from concentrated electrolyte solutions by montmorillonite and illite. *Proc. R. Soc. Lond.* A **278**, 35–56.

Posner, A. M. & Quirk, J. P. 1964*b* Changes in basal spacing of montmorillonite in electrolyte solutions. *J. Colloid Sci.* **19**, 798–812.

Quirk, J. P. 1952 *Deflocculation of soil colloids*. Ph.D. thesis, University of London.

Quirk, J. P. 1971 Chemistry of saline soils and their physical properties. In *Salinity and water use* (ed. T. Talsma & J. R. Philip), pp. 79–91. London: MacMillan.

Quirk, J. P. & Aylmore, L. A. G. 1971 Domain and quasi-crystalline regions in clay systems. *Soil Sci. Soc. Am., Proc.* **35**, 652–654.

Quirk, J. P. & Panabokke, C. R. 1962 Incipient failure of soil aggregates. *J. Soil Sci.* **13**, 60–70.

Quirk, J. P. & Schofield, R. K. 1955 The effect of electrolyte concentration on soil permeability. *J. Soil Sci.* **6**, 163–178.

Quirk, J. P. & Williams, B. G. 1974 The disposition of organic materials in relation to stable aggregation. In *Trans. 10th Int. Congr. Soil Sci., Moscow*, (ed. F. R. Zaidelman, I. I. Sudnitsin & E. A. Dmitriev), vol. 1, pp. 165–171. Moscow: Nauka Publishing House.

Reeve, R. C. & Bower, C. A. 1960 Use of high-salt waters as a flocculant and source of divalent cations for reclaiming sodic soils. *Soil Sci.* **90**, 139–144.

Rengasamy, P., Greene, R. S. B., Ford, G. W. & Mehanni, A. H. 1984 Identification of dispersive behaviour and the management of red-brown earths. *Aust. J. soil. Res.* **22**, 413–431.

Richards, L. A. 1954 (ed.) Diagnosis and improvement of saline and alkali soils. *U.S.D.A. agriculture handbook 60.* Washington: U.S.D.A.

Rowell, D. L., Payne, D. & Ahmad, N. 1967 The effect of the concentration and movement of solutions on the swelling, dispersion and movement of clay in saline and alkali soils. *J. Soil Sci.* **20**, 176–188.

Schofield, R. K. 1946 Ionic forces in thick films of liquid between charged surfaces. *Trans. Faraday Soc.* **XLIIB**, 219–225.

Shainberg, I. & Letey, J. 1984 Response of soils to sodic and saline conditions. *Hilgardia* **52**, 1–57.

Sposito, G. 1981 *The thermodynamics of soil solutions.* Oxford: Clarendon Press.

Tessier, D. 1984 *Etude experimental de l'organization des materiaux argileux.* Doctorat d'Etat, Université de Paris.

Verwey, E. J. W. & Overbeek, J. Th. G. 1948 *Theory of the stability of lyophobic colloids.* Amsterdam: Elsevier.

Discussion

Sir Charles Pereira (*Maidstone, Kent*). The need to understand the soil science to achieve practical improvements in management is very well illustrated by the decision to add 25% of seawater to river irrigation supplies to flocculate a soil rendered impervious by sodium. Can Professor Quirk suggest how this could be solved in an inland situation?

J. P. Quirk. The example cited in my paper concerns the reclamation of a saline-sodic soil in the Imperial Valley in California by the use of Salton sea water, and its progressive dilution with river water. The Salton Sea is an area of internal drainage in the Imperial Valley and the salinity of the water exceeds that of seawater. This is perhaps an extreme example of the application of the threshold concentration concept.

The information I provided about the management of Cajon sandy loam in Arizona is a more likely situation as here the soil that had become sodic by the use of underground water developed adverse physical conditions when the river water became available, because the concentration of the irrigation water was considerably less than the threshold concentration for the degree of sodium saturation. The physical condition of the soil could have been maintained by irrigating with a mixture of river water and underground water, and reducing with each irrigation the proportion of underground water as the exchangeable sodium percentage was progressively decreased; the appropriate dilution is determined by reference to figure 7.

The threshold concentration concept is now an important feature of the strategies for the efficient use of water in the San Joaquin Valley and elsewhere in California. This has been discussed in a recent issue of a University extension journal by Oster *et al.* 1984).

One example concerns the re-use of drainage water. As a water conservation measure, drainage water is used in the later stages of the growth of a salt-tolerant crop, and before a less tolerant crop is grown the soil is irrigated with the river water, which has a relatively low salt concentration. To monitor the suitability of the water used in irrigation, figure 7 is used to ensure that the threshold concentration is exceeded. It is relevant that the sodium adsorption ratio in figure 7 can be used to refer to the irrigation water or to the solution in the soil pores, and can thus be used to judge the 'compatibility' of an irrigation water and a soil in relation to the use of a particular water, or the need to modify that water.

The tolerance of crops to various soil salinity levels is defined in terms of the electrical conductivity of the solution in the soil pores; this solution is referred to as the saturation extract.

Reference

Oster, J. D., Hoffman, G. J. & Robinson, F. E. 1984 *Calif. Agric.* **38**, 29–32.

T. W. Tanton (*Institute of Irrigation Studies, University of Southampton*). The data presented relate the Na:Ca ratio to the soil's stability. Worldwide, many of the irrigated soils have a high magnesium content (in excess of 40% of exchangeable cations). Because many magnesium soils, such as the Mapane soils of Africa, are known to have poor stability, what effect is a high level of magnesium expected to have on the monovalent and divalent cation relations presented?

This is of particular importance to us at Southampton because we are working on the instability of a clay soil. The soil is a montmorillonitic clay (80%) clay with a c.e.c. of about 30 meq per 100 g, which is made up of 40% Mg, 10% Na and 50% Ca.

The saline water dilution method of reclaiming sodic soils theoretically appears to be of value for many soil types. However, the practical problems encountered in carefully controlling and monitoring the rate of dilution could well present a major problem in applying this method to the less developed world. Poor soil permeability could also be a major factor restricting its use.

J. P. Quirk. The matter of the effects of a high exchangeable magnesium content has often been discussed in general terms, and indeed some people have even suggested that the magnesium ion has an effect on some soils similar to that of sodium ions. The solid evidence is that magnesium clays do not swell to an appreciably greater extent than calcium clays. The crystalline swelling of magnesium montmorillonite does not extend beyond 19 Å, and in this respect is similar to calcium, and is thus clearly different from sodium montmorillonite. The threshold concentration for the magnesium soil I discussed is only a little greater than that for the calcium soil. It may be that when soils are disturbed the greater hydration energy for the magnesium ion may lead to less favourable conditions than for the same soil dominated by calcium as the exchangeable ion.

Without examining the details of the Southampton clay soil, I cannot comment on the matter.

With respect to the second part of Dr Tanton's remarks, I have already commented, in my reply to Sir Charles, that the threshold concentration concept is not only useful in reclaiming soils, but has an important role to play in maintaining and monitoring the behaviour of soils within an irrigation scheme. Once the sodium adsorption ratio or the exchangeable sodium percentage of a soil is determined, then the threshold concentration is indicated. Because high precision in mixing waters is not required, and dilutions can be readily monitored by conductivity methods, I do not see this as constituting any major impediment to a wider application of the concept.

Dr Tanton's comment on poor permeability is correct. Whether poor water transmission arises in the surface soil or results from impeded profile drainage, each case needs to be considered on its merits. It may be necessary in the circumstances he raises to couple appropriate surface cultivation or deep-ripping treatments with the appropriate threshold concentration.