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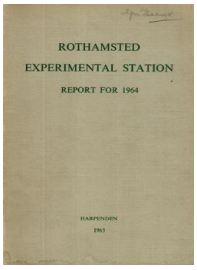

Electrical Charges on Clay

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ELECTRICAL CHARGES ON CLAY

G. H. CASHEN

A review by R. K. Schofield in the *Rothamsted Report* for 1947 gave a concise account of several new ideas that he had put into the subject. Since then the ideas have been tested at Rothamsted and elsewhere on a scale too big to summarise in a short article: the present review is restricted to work done here, or at least recognisably started here.

Clay lattices have a permanent negative charge because cations of the ideal structure are replaced by others of lower valency, and electrical neutrality is maintained by cations held outside the lattice. These are the exchangeable cations, important in many aspects of soil fertility and soil management. The edges of the clay crystals are not inert, and study of reactions at the edge faces is a necessary part of the study of the clays, but it is the nature and behaviour of the exchangeable cations that determine the suitability of soils for successful plant growth.

When clays are immersed in water or dilute salt solutions the exchangeable cations can dissociate from the particle surfaces to form diffuse double layers. This leaves the surface negatively charged and sets up a potential difference between the surface and the bulk solution, the concentration of the cations decreasing with distance from the surface. The effective thickness of the diffuse double layer is smaller the greater the concentration of the salt solution, and a quantitative study by Gouy (1910) was revived and greatly extended by Schofield (1948).

Ratio Law

When the salt solution contains ions of different kinds the distribution of cations away from the face depends upon their valencies: Schofield's ratio law (1947a) states the condition for equilibrium between the cations in the exchange complex and a smaller number in solution: equilibrium will be maintained if the concentrations of monovalent ions are changed in one ratio, those of divalent ions in the square of that ratio and those of trivalent ions in the cube of that ratio. As an example, if the concentration of a monovalent ion is halved the concentrations of divalent and trivalent ions must be decreased to one-quarter, and one-eighth of their former values. (One practical aspect of this is the possible effects of percolating rain or irrigation water on the nutrient balance of the soil, and on its permeability—see below.) For a calcium clay in equilibrium with a solution of calcium chloride the ratio of the square root of the calcium concentration to that of hydrogen ion should not alter. To test the law over a wide range of concentrations it is better to use "activities"—*a*—rather than concentrations, and as a ratio is not altered by multiplying both terms by the same quantity, the equilibrium condition can be written

$$\mathrm{pH}-\tfrac{1}{2}p\,\mathrm{Ca} = p(\mathrm{HCl}) - \tfrac{1}{2}p(\mathrm{CaCl_2}) = \tfrac{1}{2}\log a_{\mathrm{Ca(OH)_2}} + 14{\cdot}2$$

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where p denotes the negative of a common logarithm and 14·2 is the negative logarithm of the ionisation product of water. This is the form of the relationship expressed in activities of neutral substances and gives an estimate of the activity of $Ca(OH)_2$ in the system. Schofield and Taylor (1955a) confirmed the accuracy of the equation for calcium clays over a wide range of concentrations of $CaCl_2$, and made similar measurements on aluminium, potassium and sodium clays. They (1955b) also extended the general reasoning to normal non-saline soils where the chief exchangeable cations are calcium and magnesium, recognising that pH as ordinarily determined will depend on the activities of other ions in the system. They found that constant values of the quantity $pH - \frac{1}{2}p(Ca + Mg)$—the so-called "lime potential"—were obtained in solutions of calcium chloride up to 3×10^{-2} M. From this they suggested that for routine measurements of soil pH, $M/100$-$CaCl_2$ solution should be used instead of water, and a soil/solution ratio of 1/2 was recommended, though the exact value is not critical. The suggestion and the recommendation are widely used.

Negative adsorption and swelling pressure. As cations are attracted to the negatively charged surface, so anions are repelled—so-called "negative adsorption"—and the increased concentration of a solution in contact with clay can be used to measure the surface area of the clay (Schofield 1947b). When the clay particles are so close together that their diffuse double layers interact, new aspects of charge distribution become important. For two fixed parallel clay plates the combination of attracted cations and repelled anions produces a total ionic concentration at the mid-plane greater than that in the bulk solution. For equilibrium of the water throughout the system some water must attempt to move into the space between the parallel plates to compensate for the lowering of the free energy by the additional ions there: squeezing more water in increases the hydrostatic pressure, and unless there is some cohesive force to counteract the pressure (one of the attributes of a soil with stable structure), the clay will swell and ultimately deflocculate. Alternatively, suction can be applied to the bulk solution. From measurements on sodium montmorillonite, Warkentin and Schofield (1960, 1962) concluded that the osmotic pressure of the ions in the diffuse layer accounts satisfactorily for swelling pressures in dilute salt solutions ($<10^{-3}N$-NaCl): for more concentrated solutions the observed pressures were relatively higher than those calculated, and this was explained by a higher activity of the ions in the diffuse double layer, as compared with the neutral equilibrium solution. Assuming the repulsive force was correctly estimated, there was no evidence for attractive forces of the order of magnitude of the osmotic repulsive force. However, the measured X-ray spacings for sodium montmorillonite in salt solution, e.g., Norrish (1954), are usually considered as representing an equilibrium between the repulsive pressure and attractive forces, and it seems there are still some difficulties to be resolved.

In most agricultural soils the predominant cations are calcium and magnesium. When they are partly or wholly replaced by sodium, as by sea-water flooding, or by the use of unsuitable irrigation water, there may be unfortunate effects on the stability of the soils. The structure is stable

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provided the electrolyte concentration is great enough, but loss of permeability, caused by swelling and deflocculation, occurs when attempts are made to wash out the salt, unless the sodium is replaced by calcium in the exchange complex. Quirk and Schofield (1955) measured the changes in permeability of soils saturated with one ion only, using solutions of the chloride of that ion, and made similar measurements on sodium–calcium clays with differing degrees of sodium saturation, using solutions of mixed chlorides diluted according to the ratio law. The results showed the importance of knowing the values of $[Na]/[Ca + Mg]^{\frac{1}{2}}$ for the soil and water to decide whether the water was safe to use. For sites already damaged, Schofield and Taylor (1961) devised a quick method of estimating how much gypsum must be added to soil affected by sea-water to prevent structure being damaged by the leaching action of rain water. This was used by Advisory Officers after the North Sea floods of 1953.

Soil Structure

Seedbed preparation, and other aspects of soil management, are designed to produce a good "crumb" structure—open agglomerations of sand, silt and clay particles held together in some way, or ways. In a soil with good natural structure the crumbs are resistant to slaking, i.e., dry crumbs do not disrupt on wetting and, when wet, they remain strong enough to resist destruction by mechanical disturbance. The necessary cohesion to withstand swelling pressure can come from organic matter, and knowledge of the electrical properties of the clays provided useful guidance in the design and interpretation of experiments on soil structure (Emerson, 1957). Emerson and his colleagues sought for the type of bonding possible in natural soils by studying the action of synthetic polymers, ionic and non-ionic, in modifying the swelling behaviour of sodium-saturated crumbs (in effect, using the swelling pressure as a calibrated hammer to try to disrupt the crumbs). The results showed that polyvinyl alcohol was taken up by the planar faces by hydrogen bonding, whereas carboxylated compounds formed complexes on the edge faces of clay crystals. Crumbs from pasture land are stronger than those from arable land, but differ little in rate of uptake of water, degree of swelling or in appearance in thin sections (Emerson and Dettmann, 1959). Emerson (1959) therefore concluded that the clay crystals in crumbs form domains of oriented crystals free from organic matter, but these domains are linked to the quartz particles by organic matter, mainly at the planar faces, but carboxylated compounds could also link with the edge faces of the domains. The domains themselves could be linked to each other, to give an open structure amid the mineral particles but still able to restrain diffuse double layer swelling of the clay when sodium-saturated. Flocculation by edge-to-face attraction between clay units is considered unlikely.

Measurement of Electric Charge

The possibility of such edge-to-face attraction depends on the fact that in some conditions the edges of the clay crystals do carry a positive charge:

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the presence of the negative charge on the planar faces would then provide an electrostatic mechanism for flocculation and structure building. Schofield (1949), working with a clay subsoil, found that the total charge varied with the pH of the clay suspension. An increase in the negative charge with alkalinity was explained as caused by dissociation of hydrogen from hydroxyl groups attached to silicon. In an acid medium (pH 2·5) chloride ions were attracted to the clay, showing that it carried a positive charge, but after chemical treatment that removed free oxides chloride ions were repelled at pH 2·5. Schofield concluded that the positive charges were carried by the free oxides. Later, Schofield and Samson (1953, 1954) found that sodium kaolins were firmly flocculated in distilled water and absorbed chloride from neutral sodium chloride solutions; they explained their results by the formation of positive charges on the edges of the clay, produced by proton transfer to oxygen atoms or hydroxyl groups on the exposed edges. Adding alkali caused deflocculation, and this was explained by neutralisation of the positive edge charge and the loss of edge-to-face attraction. The implications for anion adsorption and other aspects of the electro-chemistry of the surface were discussed by Fieldes and Schofield (1960). As subsequent work has produced a very different explanation, a brief note on technique is necessary. The kaolin was prepared by first washing with *N*-NaC1 adjusted to pH 3 with HC1 in the belief that the dilute acid would remove all aluminium external to the lattice, without causing any significant breakdown: the kaolin was then washed with distilled water until free from chloride. The assumption was that the system was electrically neutral, the zero charge balance being made up of permanent negative charge on the planar faces incompletely balanced by sodium ions—and only sodium ions—with permanent positive charges on the edges to account for the remainder. There is now little doubt (Cashen, 1961) that the assumption was wrong: kaolins prepared in this way contain considerable quantities of exchangeable aluminium, produced by acid attack, and this can account for the observed flocculation, and for other properties of the treated clay, without invoking any permanent edge charge.

Reactions of clays with acids. Acid treatment will produce a hydrogen clay, but in agricultural research it has long been known that such clays, however prepared, are unstable, and, in time, change to the aluminium form. The process is probably controlled by diffusion of hydrogen and aluminium ions to and from the edges of the crystals, and will be irreversible. As first proposed by Paver and Marshall (1934), it is reasonable to suppose that the presence of a positive charge on an edge represents an intermediate stage in the release of aluminium ion from the lattice; also that protons transferred from the surrounding electrolyte will act more quickly than hydrogen ions that have to diffuse from the planar faces. For *N*-NaC1 at pH 3 the ratio of sodium to hydrogen ions is 1,000 and there should be very few exchangeable hydrogen ions, yet a positive charge is formed in such a strong salt solution. It is possible that the assumed "permanent" model of Schofield and Samson is, in fact, a good description of a transient state, after washing with distilled water, in which the

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incompletely sodium-saturated clay has equal amounts of unbalanced negative and positive charge (faces and edges). The electrical stress between the faces and edges might produce physical breakdown at the edges releasing aluminium to replace the missing cations on the planar faces and so discharging the edge faces (Cashen 1959). The detritus would contain other lattice components, notably potassium, and similar processes in the soil, acting very much more slowly, of course, might account for some release of non-exchangeable potassium from mica-type minerals in the soil, as measured by P. W. Arnold and B. M. Close (*Rothamsted Report* for 1961, p. 57). Further, an initially neutral soil that had become acid because of decomposing organic matter could not have its acidity washed out if there are exchangeable aluminium ions present: these can supply hydrogen ions on hydrolysis.

Hydrolysis of aluminium ion. In addition to its bearing on the permanence and importance of edge charges, the behaviour of aluminium in the soil is clearly the key to problems of soil acidity. As part of recent work on clays (Cashen, in preparation), experiments with dilute solutions of alum ($2{\cdot}78 \times 10^{-4}$ *M* in Al) have followed the changes in electrical conductivity as solutions are titrated with dilute alkali. There is some evidence —perhaps significant—of the formation of an ion $AlOH^{2+}$ as an intermediate stage in the formation of a complex ion $Al_6(OH)_{15}^{3+}$ (or one with the same OH/Al ratio) already suggested by Brosset, Biedermann and Sillén (1954) as the main product of the hydrolysis of aluminium in the acid region. The reactions are

$$6Al^{3+} + 6H_2O \longrightarrow 6Al(OH)^{2+} + 6H^+$$
$$6Al(OH)^{2+} + 9H_2O \longrightarrow Al_6(OH)_{15}^{3+} + 9H^+$$

At this stage the aluminium is five-sixths neutralised. Electro-chemically, the new complex ion is equivalent to one aluminium ion; physically—in the clay—it produces some striking effects.

Continued titration takes the system through the neutral point without very clear evidence of where it is, and the next clear singular point is assumed to correspond to the formation of aluminate, according to

$$Al_6(OH)_{15}^{3+} + 3OH^- \longrightarrow 6Al(OH)_3$$
$$6Al(OH)_3 + 6OH^- \longrightarrow 6Al(OH)_4^-$$

The important quantities of alkali additions are: to aluminate, total 24 OH^-; to hydroxide, 18 OH^-; to complex ion, 15 OH^-; giving ratios of 4/3:1:5/6, or 8/5:6/5:1.

The same three phases were detected in similar experiments with the ions displaced from an aluminium kaolin by a solution of cetyl trimethyl ammonium bromide. After necessary corrections the ratio of hydroxyl additions for the aluminate stage and the complex ion was between 1·57 and 1·62, close enough to 8/5 to show that the ions displaced from the kaolin, prepared by acid washing, were Al^{3+} and not others hydrolised during the preparation of the clay.

In a direct titration of the aluminium kaolin the three phases were not so

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clearly differentiated, but the ratio of additions for aluminate and hydroxide was near 1·33. The very close agreement with the ratio 4/3 is probably fortuitous, but this is the ratio to be expected if the edge charges are playing no significant part in the neutralisation. It is concluded that the effects of the edge charge are small compared with those of the permanent charge on the planar faces.

Physical Properties of Suspensions

Schofield and Samson (1954) found that a "sodium" kaolin was flocculated in electrolyte-free conditions, and explained a completely unexpected result by invoking edge-to-face bonding dependent on a permanent positive edge charge. It now seems clear that the clay was a sodium/aluminium clay, that the flocculation is attributable to the aluminium and that behaviour after adding alkali can be accounted for by the hydrolysis of the aluminium. One of these effects is the extremely large decrease in viscosity of the suspension, which occurs after the five-sixths stage of a neutralisation of the aluminium. With their "sodium" kaolin the decrease was to a thousandth when 1·0 milli-equivalents of alkali had been added (per 100 g clay); with the pure aluminium clay the amount needed was 2·5 milli-equivalents. It is a fair inference that the sodium clay was 40% saturated with aluminium ion, and all the electro-chemistry and rheology can be explained on this basis.

Buzágh and Szántó (1960) found that "hydrogen" montmorillonite exhibited thixotropic behaviour when 80–90% neutralised. As bonding between particles is usually a requisite for gel formation, Cashen (1963) suggested that the clay was an aluminium clay, and that the bonds were formed by shared complex ions. The maximum opportunity for such bonding should occur at the 5/6 stage of neutralisation (83%) when all the aluminium initially present is still there, retained as complex ions balancing one-sixth of the charge: the remaining five-sixths of the permanent negative charge is balanced by sodium ions, capable of exerting diffuse double-layer repulsion in the ordinary way. The distribution of sodium and aluminium at this five-sixths stage may be random, but because the aluminium ions have to move to form the complex ions, the same mobility may permit them to take up positions corresponding to minimum energy, i.e., as far apart as possible under their mutual repulsions. This might produce a tendency to move towards the periphery of the surfaces, producing a polarisation of the particles.

Whatever the explanation, the effect is real. Simple experiments on aluminium kaolin and aluminium montmorillonite show that the viscosity is maximum near 83% neutralisation. Elsewhere, Nash (1960) reports a maximum near 80% for aluminium montmorillonite. Nor need the effect be peculiar to aluminium and sodium: Cashen (1963), in discussion, suggests that it might apply to other mixed ionic systems with the ions greatly different, so explaining the rheological behaviour of materials free from clay or aluminium.

As indicated previously, the effect of swelling pressure can be balanced by applying suction to the external liquid. New measurements of this

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equilibrium suction (Cashen, in preparation) on five-sixths neutralised aluminium clays show that the responses of suspensions of montmorillonite and kaolin to shearing stress are not always the same.

Conclusion

All of this work grew out of the pioneer activity of Schofield, and it is appropriate to return to a sentence from his 1947 review. "The undertaking is formidable, and much groundwork is needed before results can be obtained that bear directly on the very complex conditions existing in field soil." Under nearly every heading in the present review there is evidence, or a hint, of progress towards Schofield's goal. The ideas behind the ratio law are relevant to many aspects of the percolation of rain or irrigation water, both in chemical effects (leaching and cation exchange) and in physical effects (swelling and decrease in permeability): our knowledge of how soil structure is produced and maintained is better than it was, with understanding of the role of organic matter; there is a clue to one aspect of weathering that may release the stored potash reserves of the soil; in the study of this the problem of soil acidity is clearly revealed as the problem of aluminium in the soil, and in measuring acidity for research and advisory work it is worth while using the régime of stable lime potential. The newest work, here only mentioned in advance of publication, brings the department back to topics that were major projects before 1937—the flow properties of clays. Fresh thinking about these with new ideas may help in problems of soil management both in agriculture (e.g., cultivation operations) and in civil engineering (e.g., foundation problems).

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