



Some interactions of salts and clays upon diffusivity and ion movement
by Donald Robert Christenson

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

The effects of clay type, electrolyte concentration and adsorbed sodium upon diffusivity and ion movement were studied. Prepared soils containing 17.6% dickite, illite or montmorillonite clay minerals were equilibrated with solutions of sodium adsorption ratios of 0, 7, 18 or 40. Calcium chloride concentrations of 0, 0.005 or 0.015 normal were applied to soil columns at a tension of 2 millibars. Diffusivities were calculated from moisture content vs distance curves. Diffusivity was increased by a factor of two or more with 0.015 N CaCl₂ over distilled water on all soil sodium levels except the montmorillonite soil equilibrated with SAR 40. Sodium was displaced from the first 4 centimeters of the column and was moved with the wetted front by 0.015 N CaCl₂. Distilled water displaced small amounts of Na⁺ due to hydrolysis of CaCO₃.

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ABSTRACT

The effects of clay type, electrolyte concentration and adsorbed sodium upon diffusivity and ion movement were studied. Prepared soils containing 17.6% dickite, illite or montmorillonite clay minerals were equilibrated with solutions of sodium adsorption ratios of 0, 7, 18 or 40. Calcium chloride concentrations of 0, 0.005 or 0.015 normal were applied to soil columns at a tension of 2 millibars. Diffusivities were calculated from moisture content vs distance curves. Diffusivity was increased by a factor of two or more with 0.015 N CaCl_2 over distilled water on all soil sodium levels except the montmorillonite soil equilibrated with SAR 40. Sodium was displaced from the first 4 centimeters of the column and was moved with the wetted front by 0.015 N CaCl_2 . Distilled water displaced small amounts of Na^+ due to hydrolysis of CaCO_3 .

INTRODUCTION

The effects of sodium salt accumulation can be seen in many arid regions of the world. When wet these soils are more impermeable to air and water than similar soils not containing sodium. When dry these soils form hard clods which are difficult to till for seed bed preparation. These physical effects reduce production.

Although Way (1850) showed that base exchange takes place in soils, it was not until 1912 that Gedroiz, as cited by Kelley (1951), showed its importance in alkali soils of dry regions. The first systematic investigation into the effects of salts on permeability was made by Gedroiz in 1924 (Kelley, 1951). He showed that the permeability of the soil is greatly reduced by replacing naturally occurring ions (chiefly Ca^{++}) with Na^+ .

Alkali soils having similar exchangeable sodium levels may vary considerably with respect to water permeability. Several soil characteristics may modify the effects of sodium.

Texture has a direct bearing on water permeability. In general, the physical properties of fine textured soils are affected more adversely at a given sodium level than those of coarse textured soils.

Clay type is an important factor in the effects of sodium on physical properties and water permeability. Soils containing expanding type clays are less permeable to water than soils containing an equal amount of non expanding type clay. It appears that this is especially true at higher exchangeable sodium percentages.

Adsorbed cations, soluble salts and electrolyte present in irrigation waters influence the effects of sodium upon permeability. High concentrations of

adsorbed calcium and magnesium reduce the effects of sodium upon infiltration (Kelley, 1951). Kelley further shows that on soils containing both soluble salts and adsorbed sodium, permeability will decrease as the soluble salts are leached due to deflocculation of the soil. High electrolyte concentrations in irrigation waters aid in maintaining permeability. Moreover, water with high sodium content may increase permeability, however, it will tend to decrease with time due to sodium adsorbing on the colloids (Kelley, 1951).

Most of the studies on water movement in soils with respect to salts have been conducted in saturated systems. It appears that very few studies have been made on the influence of salts on unsaturated flow. Furthermore, this author found no studies published on the effect of clays or the interaction of salts and clays on unsaturated water flow. A thorough understanding of how unsaturated water flow is influenced by clay type, exchangeable ions, soluble salts and water quality should be useful in irrigation and reclamation. Even under conditions where free water stands on the soil surface, as in flood irrigation, most water movement downward is thought to occur as unsaturated flow.

This study was conducted to measure the interaction of clay type, exchangeable sodium, and quality of irrigation water on unsaturated flow and ion movement.

LITERATURE REVIEW

Diffusivity is a basic characteristic of soils which describes the tendency of a soil to conduct water in the unsaturated state (Bruce & Klute, 1956). At a given water content it may be expected to be largely influenced by pore size distribution and thus, by factors affecting pore size distribution. Clay type, aggregate stability, swelling pressures, exchangeable cations, soluble salts and quality of irrigation water might be expected to influence diffusivity.

Theory:

Diffusion theory has been applied to the capillary movement of water in the soil. It is assumed that the capillary flow of moisture in soils is analagous to heat transmission in solids or molecular diffusion of gases. The diffusivity term in the heat flow and diffusion equation is present in a flow equation for an unsaturated porous media. This term is required for the complete treatment of transient flow systems.

The flow equation has been derived (Klute, 1952) by combining the equation of continuity, $\frac{\partial(\rho_s \theta)}{\partial t} = -\nabla \cdot v$ and Darcy's law, $v = -K \nabla \Phi$, where; ρ_s = bulk density, θ = moisture content, v = mass flux of moisture, t = time, v = volume flux of moisture, Φ = total moisture potential and K = coefficient of aqueous conductivity. This yields the general flow equation with ρ representing fluid density:

$$\frac{\partial}{\partial t} (\rho_s \theta) = \nabla \cdot (\rho K \nabla \Phi) \quad [1]$$

If θ may be regarded as a single valued function of the capillary potential, then the right side of equation [1] may be written for the horizontal case of flow in one dimension as:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \theta}{\partial x} \right) \quad [2]$$

where; x = distance. This is a nonlinear diffusion equation with a diffusivity term, D , and is impossible to solve unless one has some knowledge of the way D varies with moisture content.

Bruce and Klute (1956) applied the Boltzmann transformation, $\lambda = \frac{1}{2} x t^{\frac{1}{2}}$, to obtain a measure of diffusivity. By substitution of λ , a concentration function, into equation [2], the equation is reduced to the ordinary differential equation:

$$-\frac{\lambda}{2} \frac{d\theta}{d\lambda} = \frac{d}{d\lambda} \left(D(\theta) \frac{d\theta}{d\lambda} \right) \quad [3]$$

Upon integration in terms of x and t at constant t , equation [3] becomes:

$$D(\theta_x) = -\frac{1}{2t} \left(\frac{dx}{d\theta} \right)_{\theta_x} \theta_x \quad [4]$$

Bruce and Klute showed that equation [4] can be evaluated by:

(1) Obtaining a moisture content-distance curve from an unsaturated flow system, i.e., θ as a function of distance at a constant value of time, t .

(2) From the plot of θ versus x , evaluate the integral and the derivative of equation [4] at a series of values of θ_x .

(3) Calculate D at the values of θ_x , used in step 2.

The Effects of Salts Upon Saturated Permeability

Several workers (Brooks et al., 1956; Fireman, 1944; Fireman and Bodman, 1939; Quirk and Schofield, 1955; Reeve et al., 1954) have studied the effect of exchangeable ions and/or water quality on saturated permeability. In all cases with low electrolyte concentration in the water, saturated permeability decreased as exchangeable sodium increased.

Fireman (1944) found that the permeability of a sandyloam soil was initially high to water containing 4,500 ppm. sodium chloride, but decreased with time. On the other hand, Quirk and Schofield (1955) found that waters containing greater than 14,500 ppm. sodium chloride maintained high permeability in sodium soils. Apparently the electrolyte level used by Fireman was not sufficient to depress the diffuse double layer. In the same paper, Quirk and Schofield reported that as the sodium content of the soil increased, the electrolyte concentration required to maintain a given permeability also increased. For example, when the exchangeable sodium percentage (ESP) equalled six, the electrolyte concentration required was 130 ppm. At an ESP of 35, the electrolyte concentration was 1070 ppm. This can be attributed to difficulty in depressing the diffuse double layer at the higher sodium levels.

The Effects of Salts Upon Aggregate Stability

Aggregate stability, as affected by salts, has an influence on the permeability of a soil. Collis-George and Smiles (1963) found that as sodium content increased, the total cation concentration in suspension that was required to maintain aggregate stability also increased. At a sodium adsorption ratio (SAR) of 10 the aggregates were dispersed when the total cation concentration was 2 me/l and flocculated at 20 me/l, while at SAR 40 the aggregates were dispersed at 10 me/l and flocculated at 40 me/l. Rowell (1963) studied the effect of total electrolyte concentration on the aggregate stability of montmorillonite at various levels of sodium and calcium. He found that at a high SAR, aggregates deflocculated at higher electrolyte concentrations than aggregates at a low SAR. For example, at SAR 2.5; ESP 54,

$\frac{3000}{200} = 15$
 3000 10

deflocculation took place with a concentration of 5×10^{-2} eq/l, whereas, at SAR 0.25; ESP 12.5, deflocculation occurred at 2×10^{-5} eq/l. The flow of water can be expected to be reduced when deflocculation occurs.

The Effects of Salts Upon Swelling Pressure

Soluble salts and adsorbed ions influence swelling pressure. Swelling pressure in turn influences diffusivity. Adsorbed cations which cause a high zeta potential increase swelling pressure due to increased d spacings and distance between particles. Soluble salts, present in large concentrations depress the diffuse double layer and decrease the swelling pressure. Norrish (1954) found a linear relation between d spacing of montmorillonite and $C^{-\frac{1}{2}}$ (concentration, g solute/l.) for LiCl, HCl, NaCl and Na_2SO_4 at $C^{-\frac{1}{2}}$ values of 2-10 over which range the d spacings varied from 40-13 Å. Warkentin and Schofield (1962) found that swelling pressures increased with decreasing sodium chloride concentrations on sodium montmorillonite in equilibrium with sodium chloride solutions. Emerson (1962) found that oriented Ca-montmorillonite flakes increased in volume as they were brought into equilibrium with successively more dilute calcium chloride solutions. However, this effect could not be reversed by increasing the concentration of calcium chloride. The observed swelling did not increase the d spacing. He concluded that this was due to the formation of tactoids by Ca-montmorillonite crystals. Swelling was due to the development of double layers within the pores of the tactoid.

The Effect of Clay Type on Saturated Permeability

Fireman and Bodman (1939) found greater permeability on a clay loam soil containing predominately kaolinitic clay than on another containing

predominantly montmorillonitic clay. It is interesting to note that both soils showed very similar initial permeability values to distilled water. But, as time progressed the permeability decreased more rapidly on the soil containing montmorillonitic clay than the one containing kaolinitic clay. This decrease in permeability can be attributed to the swelling of the montmorillonitic clay.

The Effects of Sodium and Electrolyte Concentration Upon Diffusivity

Gardner et al. (1959) measured the diffusivity of two soils with various exchangeable sodium to calcium ratios. They found that when the exchangeable sodium percentage was above 25, the diffusivity was reduced as much as one-thousand fold when the electrolyte concentration was decreased from 300 to 3 me/l. It was also found that diffusivity increased as the electrolyte concentration increased, regardless of exchangeable sodium percentage.

The data from Gardner indicate the same type of effects from adsorbed sodium and electrolyte concentration could be expected in unsaturated flow as is found in saturated flow.

*But not to
a reduced
state*

Ion Movement

Ion movement within soil columns is complex. Bower and Goertzen (1958) derived a Langmuir adsorption formula for the prediction of sodium movement in calcareous soils. Bower et al. (1957) used partial differential equations to predict ion distribution as functions of depth and volume of solution applied when two cations were present. Dutt (1962) developed a computer program for calculating the ionic composition of percolating waters.

