



**Behaviour of Alkaline Sodic Soils and Clays  
as Influenced by  
pH and Particle Charge**

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## Abstract

Sodic soils occur in about 30% of the total land area in Australia and 86% of these sodic soils are alkaline ( $\text{pH} > 8.4$ ), particularly in dense clayey subsoils (Rengasamy and Olsson 1991). Many of these alkaline soils also contain lime ( $\text{CaCO}_3$ ) ranging from 10 to 2000  $\text{t ha}^{-1}$  up to a metre depth. In spite of the presence of calcium compound, sodicity is highly prevalent and affects soil physical properties related to transport of air and water. High pH of these soils also interferes with nutrient availability. These constraints are considered to reduce the potential yields of crops to less than half.

The objective of this thesis is to investigate the factors affecting swelling and dispersion of alkaline sodic soils containing lime and the ways to manage these soils to improve their physical conditions. Studies on pure clay systems have been included to understand the fundamental process involved in swelling and dispersion of pure and soil clays.

The literature review has identified soil pH as an important factor affecting these properties. Therefore, the mechanisms by which pH controls swelling and dispersion as well as how to reduce soil pH by utilising the native  $\text{CaCO}_3$  are the foci of this thesis.

The investigations of this study are described in the following chapters dealing with:

- 1) Dispersion and zeta potential of pure clays
- 2) Dispersion of soil clays as influenced by pH and net particle charge
- 3) Changing particle charge and altering clay behaviour
- 4) Influence of amendments on the behaviour of an alkaline sodic soil

The effect of changing pH and electrolyte concentration on the dispersion and zeta potential of Na- and Ca- forms of kaolinite, illite and smectite was investigated in relation to changes in their net negative charge. The percentage of dispersible Na-clay and the percentage increase in net negative charge was positively correlated with pH, but the slopes varied from clay to clay. In general, the net negative charge was the primary factor in clay dispersion, and the pH affected clay dispersion by changing the net charge on clay particles. Na-smectite had larger net charge at all pHs than Na-illite and Na-kaolinite, and it always had larger flocculation values. The role of electrolyte concentration could be due to its effect both on flocculation and variable charge component of the clay minerals. The zeta potential at different pHs also reflected the same trend of clay dispersion with net particle charge.

In Ca-clays the trends were similar to Na-clays up to pH 7.0. In more alkaline solution  $\text{CaCO}_3$  formation led to charge reduction on clay particles, resulting in flocculation and reduction of zeta potential. At similar pHs the electrophoretic mobilities of all the clays showed constant potential behaviour. However, the zeta potentials of Ca-clays were always smaller than those of sodic clays because the clays were more aggregated. Net particle charge was the most important factor in controlling clay dispersion for the whole range of pH and ionic strength and for all types of cations.

The effect of changing pH on the dispersion of clay from sodic soils was investigated in relation to changes in net charge on clay particles. Positive relationship was obtained between pH and the percentage of dispersible clay for each soil clay. The percentage increase in net negative charge was also positively correlated with pH. However, the slopes of these relationships varied between soil clays. In comparing the values for pure clay minerals quoted in the literature with soil clays having similar mineralogy, it was found that soil clays had higher flocculation values. This is shown to be due to higher



net negative charge on soil clays than the corresponding values for pure clay minerals found in the literature. The effect of soil organic matter in enhancing the net negative charge probably contributes to the higher charge on soil clays.

The critical dispersion concentration (CDC) for clay dispersion from soil aggregates was lower than the flocculation values observed for the separated soil clays. The separated soil clays had high negative charge due to exposure of surfaces which were originally bonded in the aggregates. The dispersive potential of a number of Alfisols, Oxisols, Aridisols (calcareous soils) and Vertisols collected from different parts of Australia was highly correlated with soil pH. The relationship with CEC was poor because CEC was estimated at a pH different to the natural pH of the soil. This study has brought out the importance of pH in the management of dispersive soils.

The effect of heat treatments on the swelling, dispersion, particle charge and particle aggregation of Li-, Na-, K-, Mg-, Ca- and Al-Wyoming bentonite was investigated. Before thermal treatment, unheated (25°C) Li-, Na- and K-clays showed increased  $d_{001}$  spacings on glycerol solvation and dispersed spontaneously in water. Mg-, Ca- and Al-clays did not disperse spontaneously in water, but the  $d_{001}$  spacing increased on glycerol solvation. After heating at 300°C or above, none of these clays dispersed spontaneously. However, swelling varied with the type of cation and the temperature of heating.

The results generally suggested that swelling and dispersion of homoionic Wyoming bentonite after heating at various temperatures depended on the nature of bonding between clay particles and the cations. Enhanced swelling and dispersion of clays indicate the more ionic character of the cationic bonding than in the cases where heating resulted only in swelling, with polar covalent bonding of cations to clay surfaces allowing limited hydration. It is also suggested that in case of absence of both swelling and dispersion as a

result of thermal treatment, a covalent bond is formed between cation and clay surface.

Thermal treatment apparently affect the bonding in different ways. It appears that the smaller cations (ionic radius  $< 0.7\text{\AA}$ ) Li, Mg and Al migrate to octahedral vacant sites and form covalent bonds after heating at  $400^{\circ}\text{C}$ ; this reduces the negative charge drastically. This process for Li-clays occurred even at  $200^{\circ}\text{C}$ . The larger cations (ionic radius  $> 0.9\text{\AA}$ ) Na, K and Ca ions apparently did not migrate to octahedral vacant sites after heating up to  $400^{\circ}\text{C}$ ; a high proportion of them being exchangeable. The data on exchangeable cation, particle charge and clay particle size were consistent with the postulated effect of the nature of cationic bonding on swelling and dispersion properties.

Slaking and dispersion of Georgia kaolinite and Grundite illite were studied after heating the cations (Li, Na, K, Mg and Ca) saturated samples up to  $400^{\circ}\text{C}$ . The results on spontaneous dispersion, mechanical dispersion and particle size after thermal treatment, are consistent with the hypothesis that heating alters the nature of bonding between cations and clay surfaces. Thus, in Li-, Na- and K-clays on heating up to  $100^{\circ}\text{C}$  reduces the ionicity of bonding and hence spontaneous dispersion. Heating above  $200^{\circ}\text{C}$  increases polar covalency and covalency of bonding and prevents spontaneous dispersion. Divalent cations form predominantly polar covalent bonds with clay surfaces. The freeze dried Mg- and Ca-kaolinites and illites slake in water. On heating these clays, covalency of bonding is increased and slaking is proportionally reduced.

On heating CEC is reduced progressively with temperature; with increasing polar covalency and covalency of cationic bonding, cations become difficult to be exchanged. Mechanical dispersion decreases proportionate to the charge reduction (CEC decrease). The mean diameter of particles also increases

because of the aggregation of particles as reflected by charge reduction. The dissociation of cations in water and clay dispersion results indicate that cation bonds are weaker in illite than kaolinite samples.

Studies on pure clays and soil clay have clearly shown that particle charge, when altered either by heating or by changing pH, influences swelling and dispersion properties. Therefore, a greenhouse study was conducted to evaluate the effects of a few amendments viz. gypsum, green manure and glucose on the physical properties of Natrixeralf (with alkaline pH of 9.4 and 5%  $\text{CaCO}_3$  content) by influencing pH, carbonate chemistry and particle charge.

Gypsum reduced the pH from 9.38 to 7.89, increased  $\text{Ca}^{2+}$  in soil solution and reduced SAR from 11.6 to 1.2. Green manure, due to increased  $\text{CO}_2$  production, reduced pH to 8.68 and SAR to 7.52. Green manure plus gypsum reduced pH to 7.67 and SAR to 0.91. The interactive effect of gypsum and green manure on all soil properties was highly significant as shown by ANOVA analysis. Reduction of soil pH was also reflected in the levels of carbonates in soil solution.

Addition of glucose increased the microbial activity and produced fatty acids. The drastic reduction of pH ( $< 6.0$ ) was related to the amount of glucose added. The concentration of  $\text{Ca}^{2+}$ , carbonates and SAR values were inversely related to the soil pH after glucose addition. The data on soluble  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ , zeta potential, mechanical dispersion, aggregate stability and saturated hydraulic conductivity confirm the effects of pH reduction and carbonate solubility as influenced by the amendments in alkaline sodic soil.

Thus, particle charge emerges as the primary factor in controlling swelling and dispersion of soil clays in alkaline sodic soils. This study has shown that, under natural conditions, when these soils contain native lime, particle charge can be manipulated by aiming to reduce alkaline pH to the

values < 8.4. Future studies should concentrate on how organic matter can be used to manipulate particle charge of sodic soils even when lime is absent.