Effect of cations on structural stability of salt-affected soils

Alla Marchuk

In the fulfilment of the degree of

DOCTOR OF PHILOSOPHY

A thesis by prior publications submitted to

Discipline of Soil Science

School of Agriculture, Food and Wine

The University of Adelaide

March 2013

Dedication

To my Father

Table of Contents

Acknowledgement

I am truly grateful to my **Principal Supervisor Dr Rengasamy** for his inspiring scientific ideas, being ever helpful and available for discussion and advice, encouragement, guidance and patience.

I would like to express my gratitude and appreciation to my **Co-Supervisor**, **Associate Professor Ann McNeill** for the continuing support, valuable advice, help and understanding.

I am very grateful to **Dr Jock Churchman** for stimulating discussions, questions and valuable advice on different aspects of this research.

My thanks to **Dr Peter Self** for help with XRD analysis on soil clays used in this research; to the Waite Institute Analytical Services team, **Teresa Fowles** and **Dr Lyndon Palmer** for their help and advice throughout my PhD candidature; to the staff in Adelaide Microscopy and in particular to **Dr Benjamin Wade** for help with TEM and **Ms Aoife McFadden** for help with CT scanning.

My deep gratitude to my husband **Serhiy Marchuk** for continuous support, patience and encouragement; and my son **Aleksandr Tsiboulski** for being an inspiration of my life.

Abstract

About 35% of the total land area in Australia is affected by different categories of salt-affected soils. Apart from natural salinity, a significant proportion of the cultivated land has become saline due to irrigation, particularly where groundwater or recycled waters were used. Sodium salts tend to dominate salt affected soils and groundwater in Australia, therefore sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) are currently used to assess the effects of sodium on soil structure.

However, the literature review has identified that the solutions of salt–affected and fresh water or wastewater irrigated soils may contain elevated concentrations of potassium and/or magnesium, which may affect the levels of soluble and exchangeable cations, and lead to soil structural deterioration due to clay dispersion and swelling.

Traditional indices SAR and ESP, used for assessing soil structure, do not take into account the effects of K on soil clay dispersion and swelling. Furthermore, although exchangeable Mg has not been included within the common definition of sodicity, there has been disagreement concerning its influence on the behaviour of sodic soils. In addition, in the SAR model Ca^{2+} is equated to Mg^{2+} in flocculating power.

Consequently the use of SAR and ESP, as the indices of soil structural stability, can be misleading when soil structure is negatively affected by the high amount of monovalent K^+, and the concentration of Mg in soil solution and exchange sites is higher than that of Ca.

In the research reported in this thesis, a newly developed concept of CROSS (cation ratio of soil structural stability) has been used, instead of SAR, as an index for assessing soil structural changes affected by different cations in soils.

Traditional index SAR is defined as $$\mathbf{SAR}=\frac{\mathbf{Na}}{\sqrt{(\mathbf{Ca}+\mathbf{Mg})/2}}$$

New index, CROSS is defined as : $$\mathbf{CROSS}=\frac{\mathbf{Na}+0.56\mathbf{K}}{\sqrt{(\mathbf{Ca}+0.6\mathbf{Mg})/2}}$$

where the concentrations of these ions (Na, K, Ca and Mg) are expressed in milli moles of charge/L.

While SAR as a measure of soil structural stability is only applicable to sodium dominant soils, CROSS derived from the ionicity of clay-cation bond is better suited to soils containing multiple cations in various proportions. In contrast to SAR, the differential effects of Na and K in dispersing soil clays and the differential effects of Mg and Ca in flocculating soil clays are considered in the CROSS model.

The main objectives of this thesis were to investigate the effects of elevated concentration of K and Mg on soil structure in combination with the other cations, and to assess the applicability of CROSS as an index of structural stability for salt-affected soils by using soils of different clay mineralogy, texture, electrolyte concentration, pH and organic matter. Further, to identify potential ways to manage structural stability of these soils and to improve their physical condition. Studies on pure clay systems have been included to understand the fundamental processes involved in dispersion in soil clays.

The primary outcomes of this research were a series of peer reviewed scientific papers, which centred on the following key findings:

1. The deleterious effects of increasing concentration of K on clay dispersion and hydraulic conductivity were confirmed for three soil types of different clay mineralogy, pH EC and organic matter. Non- destructive X-ray CT scanning provided a means of measuring changes in soil porosity and pore connectivity.
2. The ionicity indices of the cations Li^+, Na^+, $K^{+,}$ Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} were theoretically derived using their ionisation potentials and charge. The behaviour of two pure clays (illite and bentonite) and two soil clays in aqueous suspension was investigated. As the ionicity index decreased in the following order $Li^+ > Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ the tendency to covalency increased and, hence, the predisposition to break the clay-cation bonds in water decreased. Strong and significant relationships between ionicity indices of cations in clay–cation bonds and clay behaviour such as dispersivity (r^2=0.93) and zeta potential (r^2=0.84) confirm that the degree of ionicity in these bonds dictates the water interaction with clay particles, leading to their separation from the clay aggregates. The strong relationships between zeta potential and the degree of dispersivity (r^2=0.78) suggests that surface charge on clays is responsible for the variations in correlations between ionicity indices and clay behaviour among the four types of clays.
3. Effects of clay-cation bonding on soil structure were further validated by non destructive X-ray computed tomography (μCT) scanning of the cation treated soil samples. Changes in pore architecture as influenced by the proportion of cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) bonded to soil particles were characterised. All the structural parameters, studied by μCT scanning, were highly correlated with the ionicity indices of dominant cations, confirming that the structural changes during soil-water interaction depend on the ionicity of clay cation bonding. Saturated hydraulic conductivity of cation treated soils dominated by a single cation were

dependant on the observed structural parameters, and were significantly correlated with active porosity (r^2=0.76) and pore connectivity (r^2=0.97) characterised by μCT scan.

4. Applicability of CROSS as a new index of soil structural stability was methodically validated and confirmed in series of studies for a range of soils containing varying quantities of Na, K, Mg, and Ca. The effects of CROSS were highly dependent on the total electrolyte, soil texture, clay mineralogy, pH and organic matter content.
5. Useful threshold values of the electrolyte concentration required to flocculate the dispersed suspension were derived. Threshold electrolyte concentration (TEC) of the flocculated suspensions of three soils were significantly correlated with CROSS of the dispersed suspensions (r^2=0.93). Again, when the individual soil type was considered, smectitic clay with high negative charge had lower TEC than the illitic or kaolinitic clay. The cationic flocculating charge of the flocculated suspensions (CFC), which incorporate the individual flocculating power of the cations, was significantly correlated with CROSS. However, these types of relationships will depend on several factors even within the given soil class. Therefore, the dispersive potential (P_{dis}) of the individual soil was derived, from which the required amount of the cationic amendments can be calculated to maintain flocculated soils and their structural integrity.
6. The research results presented within this thesis clearly demonstrate that clay dispersion influenced by CROSS values depends on the unique association of soil components affecting the net charge (measured as negative zeta potential) available for clay-water interaction, rather than the charge attributed to the clay mineralogy and/or organic matter. Soil with smectitic mineralogy and high cation exchange capacity dispersed less than soils dominant in illitic and kaolinitic clays. In

successive experiments, soils differing in clay mineralogy, organic carbon and pH were treated with solutions of varying CROSS, NaOH and sodium hexa- meta phosphate (calgon) respectively. Where the high organic carbon of the soil was bonding with clay surface, the charge was reduced considerably. Treating this soil with NaOH led to the dissolution of organic carbon and increased the pH, thereby increasing the net charge and clay dispersion. The treatment with calgon did not dissolve the organic carbon or increase the pH. Nevertheless, the attachment of hexa-meta phosphate with six negative charges on each molecule greatly increased the negative zeta potential and clay dispersion. A high correlation (r^2=72) was obtained between the dispersed clay content and zeta potential of all soils with different treatments confirming that the net charge on the soil surface available for water interaction controls the dispersion-flocculation phenomena.

The research outcomes presented in this thesis have significantly contributed to theoretical and practical knowledge concerning the effects of cations in soils and irrigation waters on soil structure. The new structural stability index, CROSS, validated in this thesis, provides a far more comprehensive assessment of the structural stability of soils affected by salinity, naturally or due to different quality of irrigation waters, than the traditionally used indices such as sodium adsorption ration (SAR), monovalent cation ratio (MCAR) or potassium adsorption ratio (PAR).

Furthermore, CROSS provides an accurate and more suitable guideline for the use of irrigation water of different cation composition (e.g. recycled water), which enables management decisions on the suitability and the rate of irrigation water. The dispersive

potential for individual soils, derived in this research, will facilitate calculation of the required cationic amendments to maintain flocculated soils and their structural integrity.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

In addition, I certify that no part of this work will, in the future, be used in a submission for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

The author acknowledges that copyright of published works contained within this thesis resides with the copyright holder(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library catalogue and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Alla Marchuk

List of publications by Candidate

Marchuk A, Rengasamy P and McNeill A., (2012) Effect of soil potassium concentration on soil structure. *Geoderma.* Under review (submitted February 2012).

Marchuk A, Rengasamy P., (2011) Clay behaviour in suspension is related to the ionicity of clay–cation bonds. *Applied Clay Science* **53** (4), 754-759

Marchuk A, Rengasamy P, McNeill A, Kumar A., (2013) Nature of the clay–cation bond affects soil structure as verified by X-ray computed tomography. *Soil Research* 50 (8), 638-644

Rengasamy P, **Marchuk A.**, (2011) Cation ratio of soil structural stability (CROSS). *Soil Research* **49**(3), 280-285.

Marchuk A, Rengasamy P (2012)., Threshold electrolyte concentration and dispersive potential in relation to CROSS in dispersive soils. *Soil Research* **50**(6), 473-481.

Marchuk A, Rengasamy P and McNeill A. (2013) The influence of organic matter, clay mineralogy and pH on the effects of CROSS on soil structure is related to the zeta potential of the dispersed clay. Soil Research **51**(1).

Chapter 1 Introduction

Of the elements sustaining human life on earth, the quality of soil and water are the two most crucial. Poor management of the soil water system threatens the survival of the human population by making it much harder to produce food.

Soil structure and associated architecture is a key factor in the functioning of soil, its ability to support plant and animal life, and moderate environmental quality with particular emphasis on soil carbon (C) sequestration and water quality (Bronick and Lal, 2005; Pagliai et al., 2004; Passioura, 1991; Warkentin, 2008). Soil quality is strongly related to soil structure and much of the environmental damage in intensive arable lands such as erosion, desertification and susceptibility to compaction, originate from soil structure degradation.

There is no more damaging threat to soil quality than the spread of salinity (Beresford et al., 2001). Salt-affected soils are naturally present in more than 100 countries of the world where many regions are also affected by irrigation-induced salinization. Different types of salinization with a prevalence of sodium salts affect about 30% of the land area in Australia (Rengasamy, 2006b).

Australia is the driest inhabited countries on earth, with the territory equal to 5% of global area, but only 1% of global river runoff (Anderson and Davis, 2006). The fact that irrigation is vital for increasing productivity is well appreciated by farmers and governments. However, the expansion of irrigation, which has been the principal focus of agricultural development in the recent years, has lately been offset due to the depletion of groundwater resources and salinisation. The prospects of climate change further calls for skilful management as well as proactive environmental strategies (Braimoh and Vlek, 2007).

This necessitates finding other sources of water for irrigation such as industrial effluent and recycled water from urban sources. However, using industrial effluent (with high pH and salinity) and recycled water for irrigation potentially can have an adverse impact on soil structure and permeability due to the development of salinity, and the accumulation of sodium (Bond and Smith, 2006; Halliwell et al., 2001; Kunhikrishnan et al., 2012; Rengasamy, 2006a; Toze, 2006).

Most irrigated soils in Australia are sodic (Rengasamy and Olsson, 1991; Szabolcs, 1989), with low hydraulic conductivity increasing the problem of salt build up over time (Rengasamy, 2006b). The main concern for using different quality water for irrigation is the presence of different ions, which have a deleterious effect on soil structural stability.

The integrity of soil aggregates on contact with water, during rain or irrigation, is important in maintaining favourable soil structure in agricultural soils. On interaction with water, the clay particles with high adsorbed monovalent cations are separated from the aggregates to form a dispersive phase. This phenomena reduce soil porosity affecting water and air movement in agricultural soils and the possibility of their erosion (Shainberg and Letey, 1984).

Dispersive soil behaviour has been hypothesised to involve various electrical diffused double layer forces generated between colloidal particles suspended in water (Quirk, 2001). However, clay particles in soil aggregates exist as a complex heterogeneous compound without being in colloidal suspension in water. Rengasamy and Sumner (1998) suggested that stability of these aggregates when in contact with water depends on the nature and persistence of linkages between the particles which, in turn, are functions of the type of bonding such as covalent or ionic. Furthermore, the degree of ionicity (or covalency) of these bonds depend on the nature of cations (inorganic or organic) found on clay surfaces. Therefore, interactions between water molecules and charged clay particles are functions of the ionicity of bonding involved. Several studies have attempted to describe the partial ionic character of covalent bonds (Baird and Whitehead, 1964; Pauling, 1967). However, no quantitative index for the ionic character of clay-cation bonds has been developed.

Adsorbed sodium is traditionally considered to be a primary cause for poor soil structural stability. Sodium Adsorption Ratio (SAR) or Exchangeable Sodium Percentage (ESP) are used as the indicators for soil sodicity and the effect of sodium on soil structure.

$$\mathbf{SAR=\frac{Na}{\sqrt{(Ca+Mg)/2}}}$$

where the concentrations of these ions (Na, K, Ca and Mg) are expressed in milli moles of charge/L

$$\textbf{ESP= Exchangeable } \left(\frac{Na}{CEC}\right) \textbf{ X 100}$$

where CEC –cation exchange capacity and the quantities of the exchangeable cations are expressed in cmol_c/kg.

However, there is a knowledge gap in understanding the effect of potassium and magnesium on soil structural stability. Recent reports have drawn attention to elevated concentrations of potassium and/or magnesium in some soils naturally and also as a result of increasing irrigation with waste or effluent water or recycled water in Australia. The ionic composition of these waters depends on the source and, in many instances they contain significant amounts of potassium or magnesium in addition to sodium and calcium. Furthermore, there is also a tendency in industries to use potassium or magnesium salts instead of sodium during production processes to prevent the increase in sodium concentration in effluents.

Potassium, being a monovalent cation, can cause swelling and dispersion, appears not equivalent to sodium in causing structural problems in soils (Rengasamy and Sumner, 1998). Early basic colloidal studies showed an extremely strong correspondence between the effect of sodium and potassium in aqueous suspensions of lyophobic colloids (Hunter, 1993).

Therefore, there is a need to derive and define a new ratio of these cations in place of SAR, which will indicate the effect of Na, K, Ca and Mg on soil structural stability.

Rengasamy and Sumner (1998) derived the flocculating power values of these cations on the basis of Misono softness parameter responsible for hydration reaction and the ionic valence, which respectively are for Na=1.0; K=1.8; Mg=27 and Ca=45.

Based on this concept Rengasamy suggested that the cation ratio of structural stability (CROSS) could be an index which would be analogous to SAR, but the differential effects of Na and K in dispersing soils, and the differential effects of Ca and Mg in flocculating soil clays.

Cation ratio of structural stability (CROSS) was defined as:

$$\mathbf{CROSS}=\frac{\mathbf{Na+0.56K}}{\sqrt{(\mathbf{Ca}}\mathbf{+0.6Mg)/2}}$$

where the concentrations of these ions (Na, K, Ca and Mg) are expressed in milli moles of charge/L.

The total concentration of the cations, together with this formula should parameterize soil structural effects of the relative amounts of monovalent and divalent cations in the soil solution more comprehensively than any previous approach.

1.1 Research aims and objectives

1. To confirm the effects of increasing amount of potassium on clay dispersion and hydraulic conductivity in soil.
2. To develop the ionicity and covalency indices for monovalent and divalent cations bonded to clay surface and to investigate the relationships of those indices with clay dispersion – flocculation.
3. To validate experimentally cation ratio of soil structural stability (CROSS) and to investigate the relationships between CROSS and soil exchangeable cation ratio (ECR)
4. To investigate the relationships between CROSS and clay dispersion in relation to clay mineralogy, organic matter and pH in soils
5. To establish the threshold electrolyte concentration (TEC) in relation to values of CROSS using soils with varying clay content and mineralogy
6. To investigate structural differences induced by different cations, as indicated by changes in pore architecture identified by using non-destructive X-Ray CT scanning.

1.2 Linkage of Scientific Papers

Paper 1 (*The effect of soil potassium on soil structure*) investigated the effects of increasing the amount of potassium on clay dispersion and hydraulic conductivity. The changes to soils characteristics after treatments with different amounts of potassium were directly related to the increasing concentration of potassium in treatment solutions. The difference in soil porosity and pore connectivity were also confirmed by using X-ray CT scanning, which allowed visualisation and quantification of the changes in three dimensions.

Paper 2 (*Clay behaviour in suspension is related to the ionicity of clay- cation bonds*) investigates the hypothesis that water interaction with clay is dictated by the degree of ionicity of clay-cation bonds. The ionicity indices of the cations were derived using their ionisation potentials and charge and found to decrease in the following order $Li^+ > Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. The study confirmed the difference in the dispersive effects of monovalent cations and the difference in flocculating effects of divalent cations on soil clays which in contact with water was related to the iconicity indices. This paper further confirmed the effect of K on clay dispersion as observed in **Paper 1.**

Paper 3 (*Nature of clay –cation bond affects structure as verified by X-ray computed tomography*) provided visual and quantitative evidences of changes in soil pore architecture as influenced by the proportion of cations (Na, K, Mg and Ca) bonded to soil particles. Pore architectural parameters such as effective porosity and pore connectivity, as characterised by micro CT scans, were influenced by the cations dominated in the soil in the following order Na > K > Mg > Ca, confirming that structural changes during soil-water interaction depends on the ionicity of clay-cation bonding. All of the structural parameters studied in **Paper 1**, **Paper 2** and **Paper 3** were highly correlated with the ionicity indices of dominant cations, providing strong scientific evidence that water interaction with clay is dictated by the degree of ionicity of clay-cation bonds.

Paper 4 (*Cation ratio of soil structural stability (CROSS).* The concept of CROSS has been developed as an alternative to SAR to accommodate the difference in the dispersive power of Na and K and the different flocculating power of Ca and Mg, and has been based on the theory that the degree of ionicity in a bond involving a metal cation is characterised by its ionisation and ionic potentials, validated by the outcomes of **Paper 2**. The results of **Papers 1** and **Paper 3** and **Paper 4** highlighted the importance of considering K in the assessment of soil structural stability. Hydraulic conductivity experiments have shown that CROSS is more suitable than SAR for evaluating soil structural behaviour.

Paper 5 (*Threshold electrolyte concentration and dispersive potential in relation to CROSS*) established the relationships between the threshold electrolyte concentration (TEC) of the flocculated suspension with CROSS of the dispersed suspension. Statistical results of linear regression between TEC of the soil solution and CROSS and TEC and exchangeable cation ratio were highly significant. Furthermore, the dispersive potential for an individual soil was derived which allowed calculation of the required cationic amendments to maintain soil structural integrity.

Paper 6 (The influence of organic matter, clay mineralogy and pH on the effects of CROSS on soil structure is related to the zeta potential of the dispersed clay) provided more detailed discussion on how the degree of clay dispersion influenced by CROSS values depended on the net charge (measured as negative zeta potential) on dispersed clays rather than the charge attributed to clay mineralogy and /or organic matter. This paper, a logical continuation of the series of experiments, described in Papers 1, 3, 4 and 5, focussed on the comprehensive validation of a newly developed concept of CROSS to use instead of SAR for the assessment of soil structural behaviour.

Chapter 2 Literature review

This literature review discusses soil structure, structural stability and how it can be assessed chemically and physically. It focuses on cation balance in soils and in particular on the factors that affect clay dispersion in saline soils.

2.1 Soil Structure

Soil structure is a crucial soil property in the functioning of several processes important to soils productive capacity, environmental quality, and agricultural sustainability (Bronick and Lal, 2005; Lal, 1991; Munkholm, 2011). There seems to be no single definition of soil structure, and several are presented in Table 1.

Table 1 Definitions of soil structure by different authors

Source	Definition
Bradfield (1950)	“Soil structure is arrangement of the solid particles in the soil profile.”
Oades (1984)	“Soil structure is defined as the size and arrangement of particles and pores in soils.”
Lal (1991)	“The size shape and arrangement of solids and voids, continuity of pores and voids, their capacity to retain and transmit fluids and organic and inorganic substances, and ability to support vigorous root growth and development.”
Ball (2007)	“Soil structure is a complex soil property, partly related to inherent characteristics of particle size and clay mineralogy and partly to anthropogenic influences related to land use and management. “

All these definitions are similar and relate to the arrangement of soil particles which determine the size and distribution of pores.

Good structure for plant growth refers to the presence of pores for the storage of water available to plants, pores for the transmission of water and air, and pores in which roots can grow (Oades, 1984) and therefore, describes the arrangement and size of inter-and intra-aggregate pores. Table 2 provides a modified classification of the pore size diameters given by Oades (1984)

Table 2 Soil pore diameters and functions

Source: Modified (Oades, 1984)

Pore diameter(µm)	Function	Terminology
<0.2	Residual (very strong bound water, unavailable to plants)	Bonding pores, very fine and fine pores
0.2-2.5	Storage of water available to plants	Effective pores
25-100	Infiltration, permeability	Water transmission pores
>100	Aeration, fast drainage, root growth	Root pores, drainage

2.1.1 Soil structural stability

Structural stability describes the ability of the soil to retain its arrangement of solid (i.e., aggregates) and pore space when exposed to external force (e.g., tillage, wetting).

In the arid and semi arid regions, the stability of soil aggregates is an important issue to address because problems arise from intensive agricultural practices, land use change, low content organic matter, and high content of sodium in the soil.

The stability of soil effective pores (see Table 2) depends on the stability of soil aggregates and strength of bonds between different soil structural units on contact with water, during either rainfall or irrigation, and is an important characteristic of the soil structural stability.

During wetting, aggregates on the soil surface are broken down to primary particles which results in loss of macroporosity (Rengasamy and Olsson, 1991).

Many physical, chemical and biological properties of soils are affected by soil clay dispersion, both directly and indirectly. These include hardsetting, low water and nutrient movement, poor soil aeration, unfavourable soil hydraulic conductivity, reduced plant and shoot growth, difficulty in preparation of seedbeds and high soil erodibility (Greene et al., 2002; Nelson et al., 1999; Nguetnkam and Dultz, 2011; Oades, 1984; Oster, 2001; Rengasamy and Olsson, 1991).

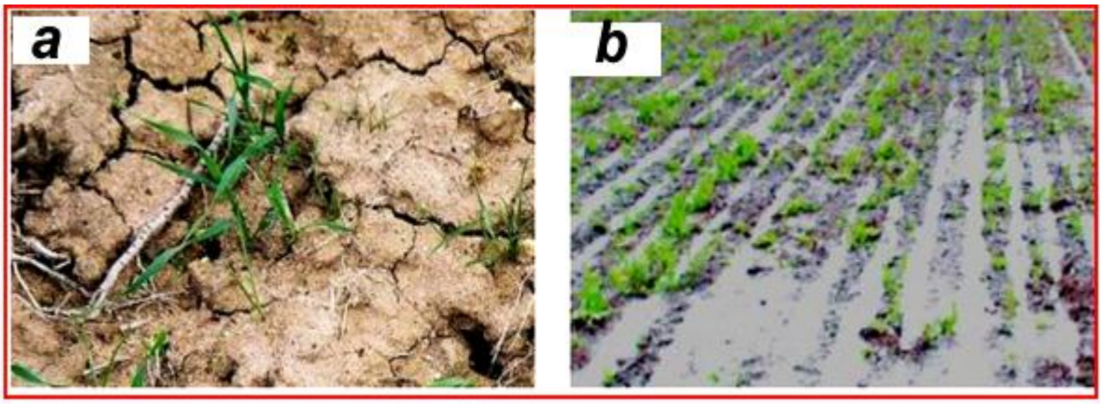


Figure 1 Symptoms of poor soil structure in the field due to soil clay dispersion: (a) soil crusting; (b) waterlogging

Thus, dispersion of clay particles is one of the major processes responsible for the degradation of soil structure (Chorom et al., 1994; Rengasamy, 2002a). Figure 1 depicts poor soil structure due to clay dispersion in salt affected soil.

Structural stability of soils is controlled by a number of factors including the concentration of the electrolytes in soil water system (electrical conductivity), type and proportion of cations, clay mineralogy, pH, organic matter and management system. It is important to note, one parameter cannot be considered without considering the interaction with other parameters.

2.1.2 Assessment of soil structure attributes

Quantifying soil structure within the tilled layer of cultivated fields is necessary to evaluate the impact of management practices on the soil environment (Pagliai et al., 2004). However, direct measurement of soil structure is difficult and there is no unique method of measurement that can satisfy requirements of all objectives for structural assessment (Lal, 1991). Therefore, the numerous methods proposed for characterizing soil structure are indirect methods and designed to measure soil attributes depending on soil structure, rather than the structure per se (Hillel, 1998).

In the 1950s and 1960s many indices of soil structure were developed, based on laboratory tests for stability of soil aggregates, their dispersion in water and pore size distribution (Childs et al., 1957; Currie, 1965; Low, 1954). Aspects of soil structure are commonly described and quantified from water retention, water and gas permeability, porosity and aggregate stability (Ball et al., 2007; Churchman and Payne, 1983; Gaskin and Raymond, 1973). More recently, methods involving micromorphology (Ringrose-Voase, 1991; RingroseVoase, 1996) and 3D visualisation (Taina et al., 2008; Vergés et al., 2011; Young et al., 2001) have been used as non destructive techniques for structural assessments.

Sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) are currently used as indices for assessing soil structural stability of salt affected soils on interaction with water (Kopittke et al., 2006; Rengasamy and Churchman, 1999; Rengasamy and Olsson, 1991; USSL, 1954; Viviani and Iovino, 2004).

2.2 Salt affected soils

Soil salinity is one of the most common soil-degrading processes and is especially prevalent in arid and semiarid areas (Rengasamy, 2008). The growth of most crops in salt affected soils is adversely affected by soluble salts. Such soil includes both saline and sodic soils. A saline–sodic soil contains both soluble and exchangeable sodium (Evangelou, 1998).

Salinity–sodicity effects on the physical, chemical and hydraulic properties of the soil are very complicated processes and can be influenced by many factors, among which are soil type and texture (Greene et al., 1978; Quirk and Schofield, 1955), concentration and proportion of monovalent and divalent cations in soil solution and on exchange sites (Gillman and Sumner, 1987; Schofield, 1947; van de Graaff and Patterson, 2001) clay mineralogy and content (Frenkel et al., 1978; Goldberg et al., 1988; Nelson et al., 1997), pH of soil solution (Chorom and Rengasamy, 1997; Chorom et al., 1994; Suarez et al., 1984; Sumner, 1993), the initial water content in soil (Rengasamy and Sumner, 1998) and organic matter (Barzegar et al., 1997; Nelson and Oades, 1998).

Saline -sodic soils are subject to severe structural degradation and show poor soil–water and soil–air relations. Swelling and dispersion of sodic aggregates destroy soil structure, reduce the porosity and permeability of soils and increase the soil strength even at low suction (Rengasamy, 2002b). Plant growth in saline-sodic soils can be severely constrained due to waterlogging, which leads to plant aeration stress (Jayawardane and Chan, 1994). The effective management of these soils require adequate understanding of not only how water, and hence, solutes are transported within the soil, but also how soil salinity and sodicity interact to determine soil structural changes (Rengasamy and Sumner, 1998).

2.2.1 Salinity

Soil salinity is a characteristic of soils that relates to their content of total dissolved solids in water and soil (Charman and Murphy, 2007). Usually, inorganic salts are crystalline ionic compounds, which dissociate in water to form cations. The major ions present in water are the cations of sodium (Na^{+}), potassium (K^{+}), calcium (Ca^{2+}), magnesium (Mg^{2+}), aluminium (Al^{3+}), iron (Fe^{2+}) and anions of chloride (Cl^{-}), nitrate (NO^{3-}), phosphate (PO^{3-}), sulphate (SO^{4-}), carbonate ($CO3^{2-}$), bicarbonate (HCO^{3-}) (McBride, 1994; Patterson, 2006; White, 2006). Soil solutions have the same elements that are in water. The proportion of cations and anions in natural soil-water is a product of soil type, climate and land use. Generally, salinity is described as a total concentration of salts, irrespective of its components.

2.2.2 Processes leading to soil salinity

Salinity in the landscape has developed under different environmental conditions over many geological periods. Even though many Australian soils are naturally saline and are found predominantly in arid and semi-arid regions, all soil types with diverse morphological, chemical and biological properties may be affected by salinity (Rengasamy, 2010).

Three main processes, which lead to saline land all over the world, have been distinguished by Rengasamy (2006): groundwater associated, non-groundwater associated and irrigation associated salinity (Figure 2). Dry land associated salinity is caused through the salt input by natural processes of precipitation or the movement of saline groundwater. Whereas, irrigation salinity is induced by the salt content in irrigation water. Transient salinity is caused by the temporal and special variations of salt accumulation in root zone, not influenced by ground water or rising saline water table and mostly occurs in areas dominated by sodic subsoils (Rengasamy, 2002b).

The other source of accumulation of salts is deposition of the oceanic and terrestrial salts carried by wind and rain. Rain water contains 6-50 mg/kg of sodium chloride: the concentration decreasing with distance from the coast. Rain containing 10mg/kg of sodium chloride would deposit 10kg/ha of salt for each 100ml of rain (Munns and Tester, 2008). Oceanic influence decrease rapidly with distance from the coast, and the increasing proportion of cations such as calcium and potassium in rain water suggest the influence of terrestrial sources on rainwater composition (Isbell et al., 1983)

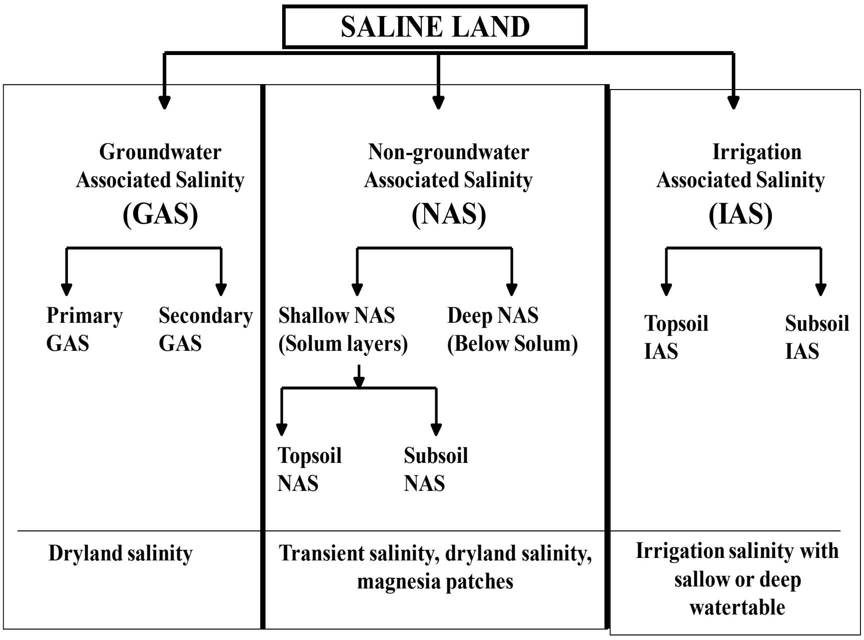


Figure 2 Formation of saline land by three different processes

Source: Rengasamy, (2006a)

2.2.3 Classification of salt affected soils

An overview of the classification of salt affected soils shows that a number of attempts have been made in the past to characterise such soil into different categories (Gupta and Arbol, 1990; McIntyre, 1979; Northcote and Skene, 1972; Rengasamy, 2010; Rengasamy et al., 1984a; Rengasamy et al., 1992; Shainberg and Letey, 1984; Sumner et al., 1998). The United States Department of Agriculture devised a classification that is widely used in many countries (Table 3). A tentative correlation of the most widely used classification systems of salt affected soils has been proposed by Szabolcs (1989) using terms like sodic, alkali, solonchak, solonetz and solodized solonetz. It is the complex interrelationship between those classifications which makes comparison between sodic soils difficult (Rengasamy, 2006a; Rengasamy and Olsson, 1991).

Table 3 Classification of saline and sodic soils

Source: US Salinity Laboratory Staff (1954)

Soil classification	Parameters
Saline, non-sodic soils	Exchangeable sodium percentage (ESP)<15, electrical conductivity in saturated paste extract ($EC_{e)}$>4dS/m)
Sodic, non- saline	ESP>15 and EC_e <4dS/m
Saline, Sodic	ESP>15 and EC_e>4dS/m
Non-saline, non sodic	ESP<15 and EC_e<4dS/m

Northcote and Skene (1972) proposed a classification for Australian sodic soils (Table 4), where soils with an ESP greater than 6 are considered to be sodic.

Table 4 Sodicity ratings and ESP for Australian soils

Source: Northcote and Skene (1972)

Ratings	ESP
Non sodic	0-6
Marginally sodic to sodic	6-14
Strongly sodic	>14

The reason for the difference in critical sodium level between Australia and America is necessary to clarify an understanding of dispersive soils. In the U.S. Salinity Laboratory, the hydraulic conductivity of disturbed soil samples were measured using tap water with an electrolyte concentration of 5-10 mmolc /l (Shainberg and Letey, 1984). At these electrical conductivities, relatively high ESP values are needed to reduce hydraulic conductivity (Shainberg et al., 1981). Conversely, in Australia, distilled water with electrical conductivity of 0.7mmolc /l was used (McIntyre, 1979).

It has been widely observed in Australia, on the basis of clay dispersion and reduced hydraulic conductivity, that some soils can be considered to be sodic, when the soil ESP <6 (McIntyre, 1979; Rengasamy, 2006a). Therefore, the definition of sodicity, in addition to ESP, needs to be based on the dispersive behaviour of soil.

For Australian salt affected soils, Rengasamy and Olsson (1991) have proposed a simple classification based on the key soil properties: SAR, EC and pH (1:5 soil/water suspensions) (Table 5). Where: SAR (sodium adsorption ration) is a measure of relative dominance of dissolved sodium in water compared to the amount of dissolved calcium and magnesium;

TEC (threshold electrolyte concentration) is a minimum concentration of salts required to maintain the soil in permeable condition.

Table 5 A simple classifications of Australian sodic soils

Source: Rengasamy and Olsson (1991)

Saline-sodic	Sodic	
(SAR1:5 >3, EC 1:5 >TEC)	(SAR1:5 >3, EC 1:5 <TEC)	
Alkaline sodic	Neutral sodic	Acidic sodic
(pH>8.0)	(pH 6.0-8.0)pH	(pH <6.0)

2.2.4 Distribution of saline and sodic soils

Agricultural losses caused by salinity are difficult to assess but estimated to be substantial and expected to increase with time. Saline and sodic soils cover more than 6% of the world total area of land, which counts for 800 million ha worldwide (Munns and Tester, 2008). At least 20% of all irrigated lands are salt-affected, with some estimates being as high as 50% (Pitman and Läuchli, 2004). Table 6 summarises the global distribution of salt affected soils across several continents of the world.

Table 6 Global distribution of salt affected soils (10^{3}km^2)

Source: Rengasamy and Olsson (1991)

Continent	Saline	Sodic	Sodic/Saline ratio
Australia	386.3	1997.0	5.17
North America	81.6	95.6	1.17
South America	694.1	595.7	0.86
Asia	1949.2	1218.6	0.63
Africa	534.9	269.5	0.50

Salinity problems in Australia are already significant and expected to increase as a result of past and present practices. The National Land and Water Resources Audit estimates that 5.7 million hectares have a high potential for the development of dryland salinity, and predicts this to rise to 17 million hectares by 2050. The value of agricultural productivity lost due to salinity in Australia has been estimated at $200 million (NLWRA, 2002). Furthermore over 60% of soils in Australian agricultural zones are sodic (Rengasamy, 2006a), and cost associated loss of productivity to sodicity estimated at $1 billion (NLWRA, 2002).

2.2.5 Irrigation and salinity

The National Land and Water Audit (2001) estimated that approximately 5.7 x104 km^2 of Australian agricultural and pastoral land has a high potential for developing salinity. The report advised that this area could increase to 17x104 km^2 by 2050, unless effective solutions are found and applied. Irrigation in Australia has been developing over a wide range of climatic zones and uses over 10.2 million mega litres of water annually on 1.84 million ha (Rengasamy and Olsson, 1993). Major irrigation development in Australia has been taking place within the Murray Darling Basin. Generally the quality of irrigation water from the river sources is good (EC 0.1-0.6 dS/m-1), however the discharge from effluent and drainage waters into the river increase salinity of irrigated water. Recent developments using industrial effluent and recycled water for irrigation may result in addition of a large amount of salt to the soil if an environmentally sustainable reclaimed water scheme is not developed and implemented (Bond and Smith, 2006; Laurenson et al., 2012; Stevens et al., 2006; Stevens et al., 2003) Considering that most of the irrigated soils in Australia are sodic, with low hydraulic conductivity, probability of salt build up due to irrigation over time increases. Furthermore, salinity of the water-table has increased in recent years, ranging between 4 and 150 dS/m^{-1}, due to recharge of water from the flat irrigated areas (Rengasamy and Olsson, 1993).

2.2.6 Effect of salinity and sodicity on plants

Soil salinity becomes a major issue for global agriculture when the accumulation of salts in soil reaches a level that adversely affects crop production (Rengasamy, 2010).

Munns and Tester (2008) elucidated the following two phases of crop growth responses to salinity:

1) a continuous osmotic phase that prevents water uptake by plants due to osmotic pressure of saline soil solution

2) a slower ionic phase when the accumulation of specific ions in the plant over a period of time leads to ion toxicity or ion imbalance.

These factors limit plant growth through poor seedling emergence, and root growth as well as limit plant nutrition by restricting water and nutrient uptake and gaseous exchange (Qadir and Schubert, 2002).

Rengasamy (2010) categorised salt affected soils in relation to the range of the possible impact on plant growth (Figure 3) and took into account the ionic composition of irrigation water and soil solution to allow full interpretation of soil-plant interactions. Furthermore, he pointed out that toxicity, deficiency or ion-imbalance due to other elements (e.g. B, K, N, P) will depend on the ionic composition of the soil solution.

The diagram also shows the cyclic changes of the categories as influenced by climatic factors and land management. It is important to note that in Australia, 1:5 soil/water suspension is commonly used for measurements of EC (and also for SAR) because of the ease of measurements. Saturation extract is more prevalent in USA and other parts of the world and therefore to compare the research data, particularly salt tolerance thresholds for crops based on EC_e, conversion of $EC_{1:5}$ to EC_e has become a necessity (Rengasamy 2010b).

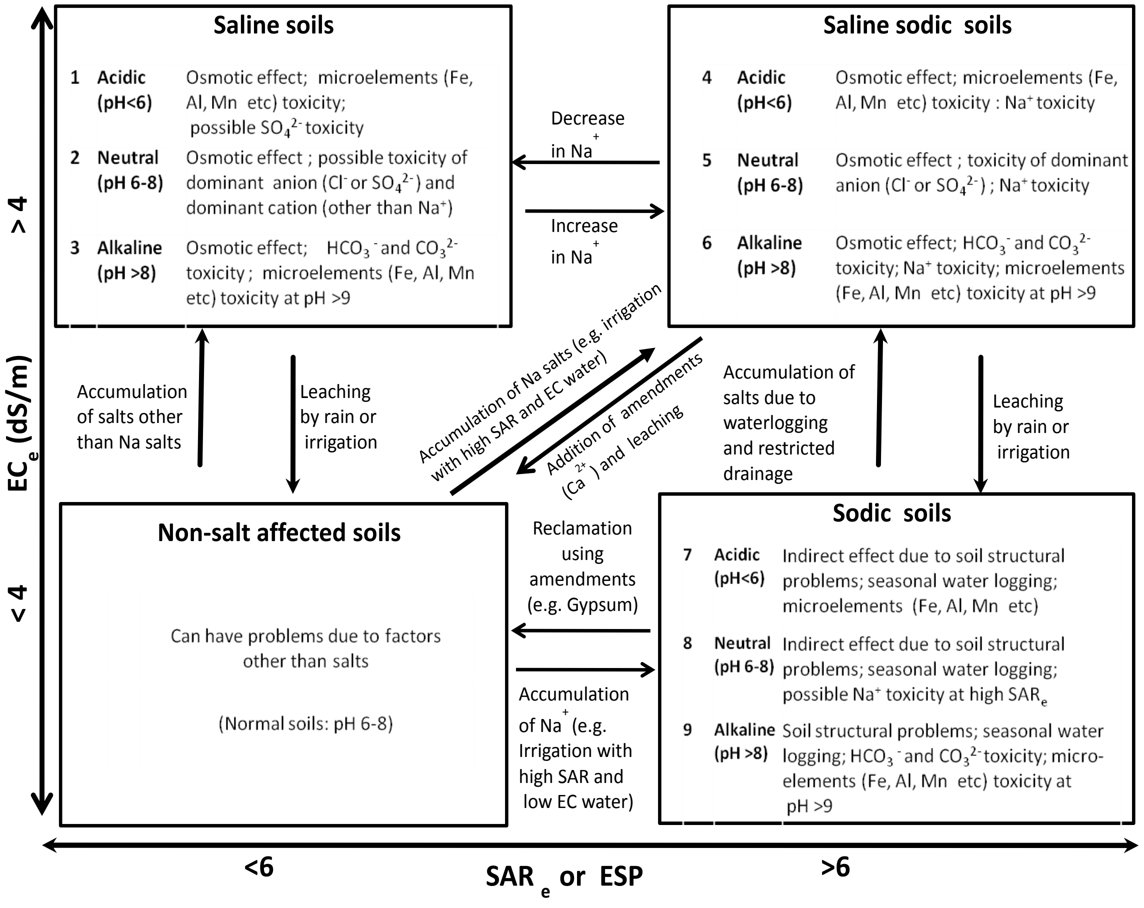


Figure 3 Categories of salt affected soils based on Na+ adsorption ratio (SARe) and electrical conductivity (EC_e) measured in soil saturation extract and pH1:5 measured in soil water suspension and possible mechanisms of impact on plants

Source: Rengasamy (2010)

2.2.7 Salinity assessment

The amount of dissolved salts is usually expressed as total soluble salts (TSS) and the units are mg/kg (parts per million) or g/100g (%) (Hazelton and Murphy, 2007). The conductivity of soil solution is directly related to the amount of salts present in solution, although relationships can vary depending on the type or species of cations and anions present. The conversion is influenced by the atomic weight of the cations and ions present in soil solution and will vary depending on the type of salts present.

These conversions are based on salts dominated by sodium chloride.

TSS (mg/kg) = 640 X EC $_{(1:5)}$ (dS/m)

TSS (g/100g) = 0.064 X EC$_{(1:5)}$ (dS/m)

The relationships between the cations concentration TCC (mmol (+)/L) and EC dS/m is linear for solutions with EC<10 dS/m

TCC (mmol (+)/L≈10 EC (dS/m)

Traditionally the electrical conductivity of saturated extracts (EC$_{e)}$ is measured, reflecting soil water content in the field conditions, though the method is considered to be tedious. The electrical conductivity measured in 1:5 soil/water suspension is a rapid method of estimation of soil salt content, though the suspension is much more diluted than field conditions. The common units for electrical conductivity are deciSiemen per metre (dS/m).

Multiplier factors are used for converting EC$_{1:5}$ (dS/m) to EC$_e$ value (dS/m). Slavich and Paterson proposed the conversion of EC$_{1:5}$ to EC$_e$ values using an estimated water holding capacity of the soil based on the texture of the soil. Rengasamy et al. (2006a) derived a conversion equation between EC$_e$ and EC$_{1:5}$ by using 40 soil samples collected from different types of soil with clay content ranging from 6% to 60%:

EC$_e$ = (0.14 - 0.13 X clay %) X EC $_{1:5}$

This simple conversion is not always ideal, but generally enables an assessment of the salinity in soils. Also, it must be noted that these relationships are largely based on chloride salts, so where a large quantity of sulphate or carbonate salts are present, some errors may occur using these conversions (Shaw, 2005).

2.3 Sodic soils and sodicity

The soil is considered to be sodic when free salts are leached from the soil layer and only exchangeable sodium remains adsorbed on the soil particles at concentrations adversely affecting the structure of soils (Charman and Murphy, 2007; Rengasamy, 2002b).

The distinction between saline and sodic soils arises as the attractive and repulsive forces vary depending on whether the soil solution is concentrated (saline) or diluted with a high proportion of Na to divalent cations sufficient to cause swelling and dispersion (sodicity) (Rengasamy and Sumner, 1998).

Due to high sodium and low salt levels, sodic soils have extremely poor physical properties manifested in degradation of aggregate structure, loss of macroporosity, which lead to a severe imbalance between water and air movement within the soil. This imbalance stems from restricted water infiltration and transmission properties which result in soil being too wet or too dry for much of the time (Brady and Weil, 2008; Rengasamy and Olsson, 1991; Shainberg and Letey, 1984). Lack of structural stability in these soils promotes seal and crust formation at the soil surface resulting in erosion (Rengasamy and Olsson, 1991). Sodic soils are formed as a result of the adsorption of sodium ions (Na^+) by the negatively charged sites on soil particles, mostly soil clays, from soil solution containing free sodium salts such as sodium chloride ($NaCl$), sodium carbonate (Na_2CO_3) sodium bicarbonate ($NaHCO_3$) and sodium sulphate (Na_2SO_4).

Swelling, dispersion and slaking are the major mechanisms by which the structure of sodic soils collapses during rain or irrigation, resulting in a poor physical condition (Brady and Weil, 2008; Cass, 1999; Rengasamy and Olsson, 1991; Rengasamy and Sumner, 1998). Firstly, exchangeable sodium increases the tendency of aggregates to disintegrate or slake upon wetting. The clay and silt particles released by slaking aggregates clog soil pores as they washed down the profile. Secondly, when clay that is prone to expansion, such as montmorillonite, become saturated with Na^+ their degree of swelling is increased, shutting large pores responsible for water drainage in the soil. Third and the most important condition – the combination of high sodium and low dissolved salt concentration leads to soil clay dispersion (Brady and Weil, 2008; Nguyen et al., 2009; Rengasamy, 2002a).

2.3.1 *Sodicity assessment: ESP, SAR*

Exchangeable sodium percentage (ESP) is often used as a measure of sodicity. ESP is determined by measuring concentration of all the exchangeable cations in the soil and expressing the amount of exchangeable sodium Na_x (cmol/kg) as a proportion of sum of all the exchangeable cations or cation exchange capacity (CEC), (Brady and Weil, 2008; Charman and Murphy, 2007; Hazelton and Murphy, 2007).

Exchangeable sodium percentage is determined by soil extraction techniques as described in the *Soil Chemical Methods Australasia* chapter 15 (Rayment and Lyons, 2011):

$$\mathbf{ESP = (Exch\ (Na+ X\ 100)\ /CEC_{eff}}$$

where CEC_{eff} is the sum exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+.

The sum of the major exchangeable cations ($\sum Exch.(Ca + Mg + Na + K)$) is referred to as total exchangeable bases (TEB) or base saturation (BS), similar to CEC value and called effective CEC (Hazelton and Murphy, 2007).

Patterson (2006) underlined the importance of understanding the difference between the measurement of exchangeable cations Ca^{2+}, Mg^{2+}, Na^+ and K^+ (effective cations exchange capacity CEC_{eff}) in the soil with or without inclusion of the soluble salts in soil solution, and measurements made for the same four cations plus the H^+ and Al^{3+} cations (Cation exchange capacity CEC).

Sodicity can be measured indirectly by measuring the concentrations of all cations in the soil solution (1:5 soil/water suspensions). These concentrations are used to measure sodium adsorption ratio (SAR), which describes concentration of the sodium ion relative to that of calcium and magnesium, defined as:

$$\mathbf{SAR= Na+ / \sqrt{(Ca^{2+}+Mg^{2+})},}$$

with all the cation concentrations expressed in mmol/L.

SAR is becoming more widely used than ESP, because of its high correlation with ESP and because it is practically more easily measured. Also, SAR can be determined from the same soil-water extract used to evaluate the EC in soil solution (Qadir and Schubert, 2002).

Both, the ESP and SAR are related to the process of cation exchange (Rengasamy and Olsson, 1991; So and Aylmore, 1993; Sumner, 1993). ESP values can be expressed as an SAR equivalent by a number of relationships. For example, the ESP of a soil can be estimated from SAR of the saturated extract using the following equation (USSL, 1954):

$$\mathbf{ESP=1.475(SAR) / (1+1.0147SAR)}$$

Rengasamy et al (1984a) suggested that ESP can be estimated from the SAR of the 1:5 soil water extract using the following equation:

$$\mathbf{ESP=1.95\ (SAR)\ +1.8}$$

However, such relationships can vary with clay content and mineralogy, salinity of equilibrium solution and saturation percentage of the soils (Sumner et al., 1998).

2.4 Effect of potassium and magnesium on soil structure

2.4.1 Potassium

Potassium exists in soils in structural, non-exchangeable, exchangeable and water soluble forms (Sekhon, 1999). The major mechanisms involved in the decrease in permeability due to monovalent exchangeable cations are swelling, dispersion and clay migration which affect hydraulic conductivity of the soil (Quirk and Schofield, 1955). Irrigation with wastewaters from agri-industry processes is commonplace nowadays and these wastewaters all have high concentrations of potassium (K). Long term application of such wastewaters may lead to build up of potassium in soil resulting in a decrease in the hydraulic conductivity of the receiving soils (Arienzo et al., 2009).

Reported results on the effect of exchangeable potassium on soil permeability differ or are conflicting, which may be attributed to differences in clay mineralogy and sample preparation procedures (Holthusen et al., 2012; Levy and Torrento, 1995; Shainberg and Levy, 1992). Some studies have found that exchangeable sodium and exchangeable potassium had similar deleterious effects on hydraulic conductivity of the soil (Quirk and Schofield, 1955). Other researchers have reported that the effect of exchangeable potassium on soil permeability was not as negative as that of Na, but not as favourable as that of divalent cations (Ca and Mg) (Reeve et al., 1954). The literature shows a broad spectrum of possibilities for potassium's effect on infiltration, ranging from being similar to sodium (negative effect) to being similar to calcium (positive effect).

However, it seems that the overall effect of increasing exchangeable potassium can negatively impact on soil hydraulic conductivity. For example, it was reported that soil permeability relates to exchangeable cations in the following order: Ca ≈ Mg>K>Na (Chen et al., 1983), although difference in the relative values of permeability have been reported: Mg>K>Na (Reeve et al., 1954), Ca>Mg>Na=K (Quirk and Schofield, 1955); Ca>K>Na

(Gardner et al., 1959); NH_4=K>Na; Ca=Mg>K>Na (clay loam); Ca>Mg>K=Na (clay) (Swaify et al., 1970). Levy and van der Watt (1990) observed that an increased amount of exchangeable K^+ in soil clay resulted in a decrease in hydraulic conductivity. These authors commented that the extent of this phenomena depended on the clay mineralogy of the particular soil. The smallest effect was found in kaolinites and the greatest in the illitic soils. In contrast Cecconi et al. (1963) suggested greater stability in K^+ saturated soils than in those saturated with divalent cations; K>Ca=Mg>Na. Furthermore, Chen et al. (1983) reported that an exchangeable potassium percentage (EPP) in the range of 10-20, improved the hydraulic conductivity in some Israeli soils. Shainberg et al. (1987 a, b) concluded that effect of K depends on charge density of the smectitic clay. They found that the higher the charge density of the clay the more favourable the effect of K^+ on hydraulic conductivity.

In some soils potassium effects on hydraulic conductivity were intermediate between Ca^{2+} and Na^+, whereas in others K^+ improves permeability. It seems that potassium fixation could be a possible mechanism that affects permeability.

Potassium K^+ is a major nutritional element for plants and enrichment of K^+ in the exchange sites due to fertiliser practice can be expected. Therefore it is important to understand the effect of potassium on soil structure and its role and position in the exchange complex (Table 7).

Potassium, a cation with low hydration energy (Sawhney, 1972), produce interlayer dehydration and layer collapses and therefore is fixed in interlayer positions. The degree of cation fixation depends on the layer charge of the mineral. In vermiculite, K^+ saturation effects interlayer collapse producing 10A° structure, but in montmorillonite with a smaller layer charge than vermiculite, K^+ saturation produces only a partial layer collapse. (Sawhney, 1972).

Table 7 The influence of dominant clay minerals on the amount of the exchangeable, water soluble and total potassium in soils Source: Brady and Weil (2008)

	Dominant clay mineralogy of soils, mg K/kg soil		
Potassium pool	Kaolinitic	Mixed	Smectitic
Total potassium	3340	8920	15780
Exchangeable potassium	45	224	183
Water soluble potassium	2	5	4

Certain minerals have a specific preference for potassium, such as vermiculite, as shown on Figure 4, where the release of potassium proceeds to the right, while the fixation process proceeds to the left. The dehydrated potassium ion is much smaller than the hydrated ions of Ca^{2+}, Mg^{2+}, Na^{+}. When potassium is added to soil containing 2:1 type minerals such as vermiculite, the reaction goes to the left and potassium ions are tightly held (fixed) in between layers within the crystal, producing a fine grain mica structure (Brady and Weil, 2008). In strongly acidic soils the tightly held H^{+} and hydroxy aluminium ions prevent potassium ions from being closely associated with the colloidal surface, which reduce their susceptibility to fixation. As the pH increases, the H^{+} and hydroxy aluminium ions are removed or neutralised, making it easier for potassium ions to move closer to the colloidal surface, where they are susceptible to fixation (Brady and Weil, 2008).

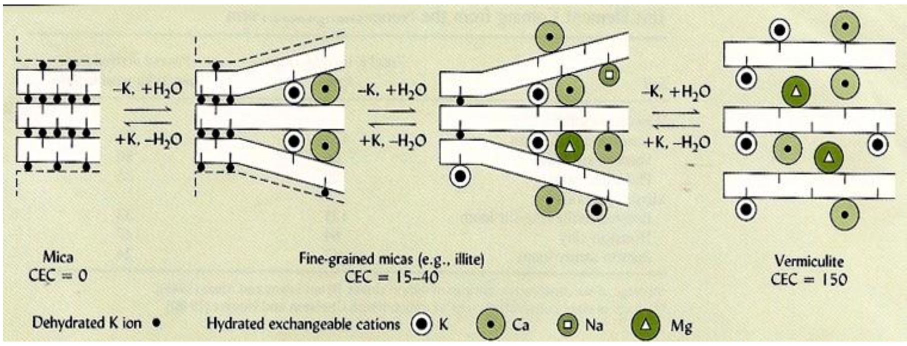


Figure 4 The release and fixation of potassium between primary micas, fine grained mica (Illite) and vermiculite Modified from McLean (1978) Brady and Weil (2008)

2.4.2 Magnesium

Traditionally, the negative effect on hydraulic conductivity and infiltration rate due to soil chemistry has been attributed to exchangeable sodium, or low irrigation water salinity, or both. However, magnesium may have been partially responsible (Emerson and Smith, 1970; Oster, 2001; Rengasamy et al., 1986).

Some of the irrigation water in many regions of the world contains a high concentration of Mg, which results in increased concentration of exchangeable Mg in the soil. In some soils the exchangeable Ca/Mg ratio is less than 1 (Shainberg and Levy, 1992). Ca and Mg, have, for practical purpose, generally been grouped together as similar ions in maintaining soil structure when quantifying sodicity of soil and irrigation water (US Salinity laboratory Staff, 1954).

While several reports on laboratory experiments have shown little or no differential effect of Mg and Ca on soil structure, a few laboratory studies have shown that exchangeable magnesium can cause structural deterioration in some soils under specific conditions (Dontsova and Norton, 1999; Rahman and Rowell, 1979; Zhang and Norton, 2002). Quirk and Schofield (1955) observed that saturated hydraulic conductivity (Ks) of Mg saturated illitic soils was much lower than Ca saturated soils. Emerson and Smith (1970) reported a difference in the ease of dispersion of surface soils when saturated with Ca or Mg ions. Aggregates of a kaolinitic red earth were washed with either $CaCl_2$ or $MgCl_2$. Dispersion was visually assessed using the scale 0-4, where 4 includes complete dispersion into primary particles. Figure 5 shows that Mg washed soil exhibited signs of dispersion when remoulded at a water content of 15 percent by weight, whereas Ca soil started to disperse at 20 percent, which is a significant difference considering that the field capacity of the soil is about 20 percent by weight (Emerson and Smith, 1970).

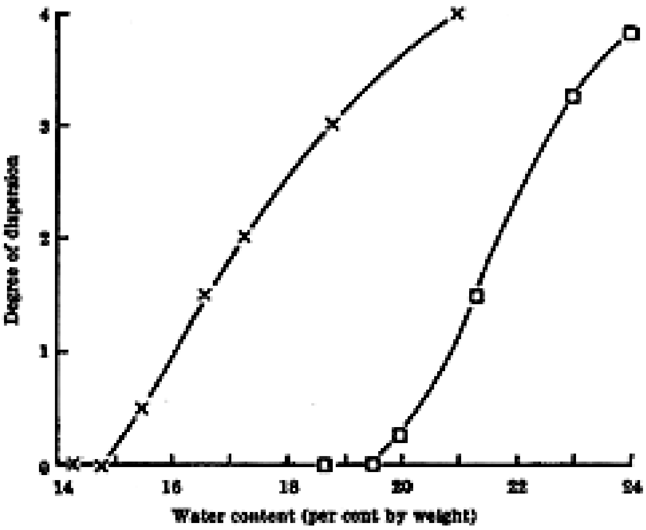


Figure 5 Visual dispersion in water of surface aggregates of a red brown earth remoulded at various water contents. X- washed $MaCl_2$; ◊-washed $CaCl_2$

Source: Emerson and Smith, (1970)

Alperovitch (1981), found that in a calcareous soil exchangeable Mg had no specific adverse effect on the hydraulic conductivity whereas in non-calcareous soils Mg cause a decrease in hydraulic conductivity.

Exchangeable magnesium in soil can directly influence soils structural properties: the effect is known as a “specific effect’, which has been reported in soils dominant in clay mica, but not in smectitic and kaolinitic soils (Emerson, 1977; Emerson and Bakker, 1973; Rahman and Rowell, 1979). Direct negative effect results from the hydrated radius of Mg ion are 50% greater than that of Ca ion. Therefore, soil surface, where exchangeable Mg is present, will tend to absorb more water than where exchangeable Ca is present, which will tend to weaken forces that keep soil particles together, resulting in increase in clay swelling and dispersion (Oster, 2001).

Magnesium can have an indirect effect on soil structural properties by influencing higher adsorption of sodium than in calcium dominant soils (Rahman and Rowell, 1979).

Keren (1991) studied the effect of adsorbed Mg and Ca on soil erosion and infiltration rate on two soils exposed to rainfall, in the presence and absence of adsorbed Na. The author concluded that the erosion rate of the soils was higher for the Mg soils than for the Ca soils. Moreover, the infiltration rate and the cumulative water depth required to reach a steady state infiltration rate were lower for Mg soils than for Ca soils. Adsorbed Mg by the montmorillonitic soil increased erosion and lower infiltration rate, regardless of $CaCO_3$ present. The Ca aggregates were more stable than Mg aggregates, even in the presence of Na. The specific effect of Mg on soil erosion was explained by the presence of Mg ions on external surfaces of the clay tactoids, and the wider hydration shell of Mg as opposed to that of the Ca ion (Keren, 1991).

Shainberg et al, (1988) concluded that the low hydraulic conductivity values of the Na-Mg smectite systems compared to the Na-Ca system are related to the effect of Mg on hydrolysis of these clays. These conclusions were based on the findings of Kreit et al. (1982) who showed that the presence of a high concentration of Mg at the clay surface slowed down the release of octahedral Mg from the lattice (Kreit et al., 1982) and lowered the EC of Na-Mg clay solution (Shainberg et al., 1988). In order to prevent structural problems in sodic soils, the high level of exchangeable Mg (Ca/Mg <1) needs to be minimised to maintain an electrolyte level above the threshold value for a particular soil (Rengasamy et al., 1986). In fact, Rengasamy et al. (1986), observed that red-brown earth soils with an exchangeable Ca/Mg ratio less than 0.5 have an adverse permeability problem in the presence of sodium.

2.5 Cation Ratio of Soil Structural Stability (CROSS)

2.5.1 Problems associated with the use of ESP and SAR as structural stability indices.

Several problems can be associated with the use of ESP and SAR used as structural stability indices:

1. ESP and SAR can be misleading when used as indices of soil structural stability where soil structure is negatively affected by a high amount of monovalent ions such as K^+, rather than sodium. Excessive potassium originates from irrigation water, soil minerals and potassium fertiliser or manure generated by animals fed in high potassium diet, such as alfalfa-rich diets used by dairy farms (Brady and Weil, 2008).
2. Although exchangeable Mg has not been included within the common definition of sodicity, there has been disagreement concerning its influence on the behaviour of sodic soils (Rengasamy and Churchman, 1999). Furthermore, in SAR model Ca^{2+} is equated to Mg^{2+} in their flocculating effects.

The role of Mg in enhancing the dispersive potential, compare to Ca, is explained by the lower degree of covalence in Mg than in Ca when bonded to exchangeable sites (Rengasamy, 1996).

Therefore there is a need to modify SAR, firstly to include K^+ in the equation, and secondly, to incorporate the differences in dispersive effects of Na and K on the one hand and the flocculating effects of Ca and Mg on the other. ESP needs to include exchangeable K, along with Na in the numerator.

2.5.2 CROSS- concept development

As was discussed in previous sections, sodium adsorption ratio (SAR) or exchangeable sodium percentage (ESP) is used as an index of sodicity effects on soil structure (Rengasamy and Churchman 1999). The SAR model was originally developed on the basis of ratio law of Schofield (1947) to predict the adsorption of sodium on soil exchange sites in relation to the cation concentrations in soil solutions. SAR is estimated from the concentrations of Na, Mg and Ca in soil solutions and has been found to be correlated with ESP. Potassium is not considered in the SAR model.

Smiles and Smith (2004) suggested a “monovalent cation ratio” (MCAR), which includes Na+K in the calculation of SAR and where Mg is treated as equal to Ca.

A Monovalent Cations Adsorption Ratio (MCAR), is defined as:

$$\mathbf{MCAR = (Na+K)/[(Ca + Mg)/]^{1/2}}$$

where concentrations of Na, K, Ca and Mg are expressed as mill moles of charge/L.

This ratio may predict the adsorption of monovalent ions by soil colloids on the basis of cation exchange isotherms, but it fails to weight the relative efficacies of Na and K in the numerator and of Ca and Mg in the denominator, and treats members of each pair as identical.

There are numerous reports, (Section 2.4.2), that Mg is aiding dispersion in a similar way to sodium and exhibiting the lower flocculating effect compared with Ca.

Therefore, there is a need to derive and define a new ratio of these cations in place of SAR, which will indicate the effects of Na, K, Mg and Ca on soil structural stability while taking into consideration soil pH, texture and clay mineralogy. This will be achieved using a formula analogous to the SAR but which selectively incorporates the dispersive effects of Na and K and the flocculating effects of Ca and Mg.

Rengasamy and Sumner (1998) derived the flocculating power of these cations on the basis of Misono softness parameter responsible for hydration reactions and the ionic valence. They defined the flocculating power as:

Flocculating power = $100(I_z / I_{z+1})^2$

where I_z and I_{z+1} are z^{th} and z+1 ionisation potential of a cation with valence Z. Thus, the relative flocculating power of cations is: Na=1, K=1.8, Mg=27 and Ca=45 (Rengasamy, 2002a).

Flocculating power gives the reverse of dispersive effects. Based on these notions a ratio analogous to the MCAR but which incorporates the differential effects of Na and K in dispersing soil clays, and the differential effects of Ca and Mg in flocculating soil clays, may be written as:

***Cations Ratio of Structural Stability*(CROSS) = (Na+0.56K) / [(Ca +0.6 Mg)/2]$^{1/2}$**

where the concentrations of these ions (Na, K, Ca and Mg) are expressed in milli moles of charge/L.

The total concentration of the cations, together with this formula should parameterize soil structural effects of the relative amounts of monovalent and divalent cations in the soil solution more comprehensively than any previous approach.

Furthermore, the research on salinity effect on plant growth is mainly concentrated on sodium and chloride ions. It is important to know how different cations, such as K, Ca, Mg in addition to Na, and anions such as sulphate and carbonate in addition to chloride, affect plant growth when salinity is dominated by salts other than NaCl.

This development is critically important in view of current concerns about salinity definition and management in Australia.

2.6 Processes involved in the dispersive behaviour of soils

In the past, soil scientists have used a model involving Lifshitz-van der Waals, ion correlation, hydration and electrical diffused double layer forces generated between colloidal clay minerals suspended in water to explain sodic soil behaviour (Quirk, 1994; Sumner, 1993).

DLVO theory was considered as the centrepiece of colloid science for over 50 years (Derjaguin and Landau, 1941; Israelachvili, 1992; Verwey and Overbeek, 1948b). DLVO theory is used to predict whether the long-range forces between any pair of colloids will be attractive or repulsive, and hence whether or not a given suspension of colloids will be stable against aggregation. The theory states that long-range forces are dominated by two interactions: double-layer repulsion and van der Waals attraction. The first of these arises when the cloud of ions surrounding any charged particle in an electrolyte, its so-called double layer, overlaps with the double layer of another particle, driving them apart. The second is caused by the quantum fluctuations in the electrons of one particle inducing correlated fluctuations in another particle-the resulting dipoles cause an attraction between the particles.

However, DLVO theory has several flaws. Firstly, the identity of the ions only enters the theory through their valence, so according to the theory any electrolyte with the same valence will behave the same way, something that is not the case (Edwards and Williams, 2004; Güven, 1992; Rengasamy and Sumner, 1998). Secondly, clay particles are bound together with silt, sand particles and organic matter into aggregates of various sizes are confined and not readily suspended in water. Consequently, for clay in soil to become dispersed, forces other than those which operate in colloidal suspension must be overcome (Rengasamy and Sumner, 1998).

In addition most investigations on clay dispersion and flocculation were conducted on pure clay minerals rather than on soil clay systems and the organisation of clay crystals and the separation of their surfaces in soil is very different from that in dilute clay suspension (Quirk, 2003).

The origin of non-DLVO forces lies in solvation reactions where polar solvents react with polar surfaces. Slaking, swelling and dispersion of soil aggregates are not influenced by non-polar solvents (Murray and Quirk, 1982), the polar (electrical) nature of water molecules is crucial for determining the patterns of behaviour of clays in dispersed soils (Table 8).

Table 8. Slaking and spontaneous dispersion of Alfisols aggregates at two levels of sodicity in various solvents   Source: Murray and Quirk, (1982)

	Dielectric constant	Slaking <2µm		Dispersed clay %of total clay	
		ESP 1	ESP 20	ESP 1	ESP 20
Water	6	67	80	0	26
Ethanol	24.3	24	12	0	6
Benzene	2.3	0	0	0	0
N-Hexanol	1.9	0	0	0	0

Furthermore, clay particles are bound together by inorganic and organic compounds involving several mechanisms and types of bonding (Table 9) which produce strong attractive forces (Rengasamy and Olsson, 1991).

Thus, the water stability of the aggregate depends on these linkages, which are functions of the type of bonding.

According to Pauling (1967), a bond between two atoms may be said to have a certain amount of covalency or ionicity. The covalency and ionicity of a bond are very useful quantitative concepts based on electronegativity differences of the atoms involved in the bond.

Table 9 Types of bonding and mechanisms involved in the linkages between clay particles in an aggregate Source: Rengasamy and Olsson (1991)

Type of bond	Mechanism
Van der Waals forces	bonding between permanent of induced polar units
Ionic bonds	cation and anion exchange, cation bridging
Hydrogen bond	water bridging, H-bond with oxygen the silicate sheet, proton mediated H-bond
Coordination complex	ion-dipole interaction, ligand exchange, inner and outer sphere complexation
Covalent bond	O-H, Al-O, Si-O bonding, inner and outer sphere complexation
Hydrophobic bond	interaction between the hydrophobic portion of the clay surface and non-polar groups of organic molecules

Bond strength in the presence of water decreases in the order: covalent, hydrophobic, van der Waals, coordination complexing, hydrogen and ionic boding (Table 9). When the cation and the surface atoms are mutually polarised it results in polar covalent bond. If the cation has no polarizing effect on the clay surface atoms, the bond is ionic (Figure 6).

Fajans (1970) considered the effect of a highly charged cation on an anion. If the anions were large and soft enough, the cations should be capable of polarising it and in the extreme cases would virtually penetrate the anionic electron cloud giving a covalent bond.

It is probable that every heteronuclear bond contains a mixture of ionic and covalent character (Huheey et al., 1993).

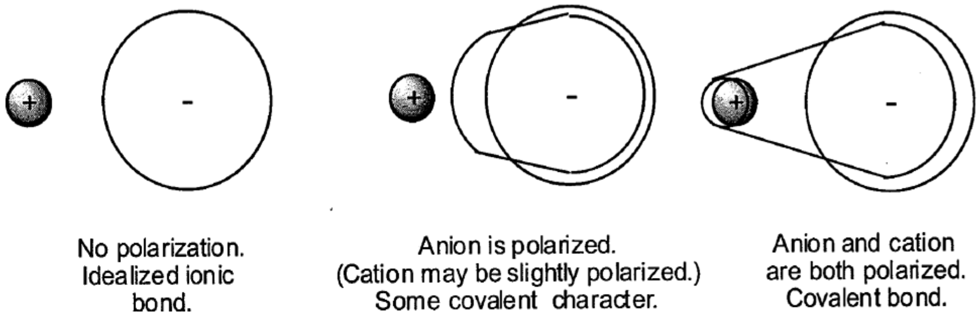


Figure 6 Schematic picture of ionic, partially covalent and covalent bonds between anion and cation Source: Huheey (1993)

The degree of covalency in a bond involving metal cations is quantified by the Misono softness parameter Y derived from ionisation and ionic potentials (Misono et al., 1967). Misono factor Y expresses the tendency of metal ion to form a dative π-bond and corresponds to its "softness" or the ability to enter into electron acceptor and electron donor (EAED) or hard soft acid base (HSAB) reactions (Figure 7).

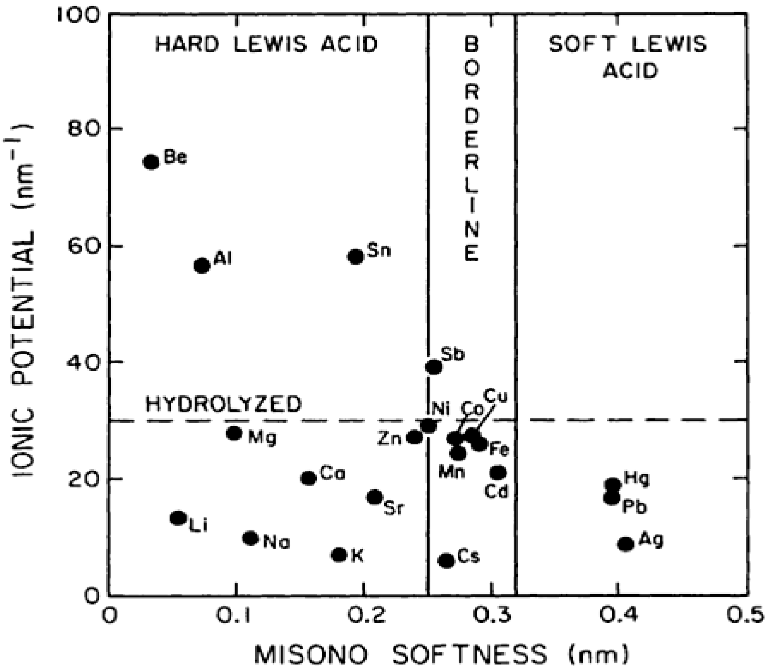


Figure 7 Lewis Classification of some metals according to ionic potential, Lewis acid softness parameter and Misono softness parameter Source: Sposito (1994)

In quantitative terms, a hard Lewis base is “a molecular unit of high electronegativity and low polarizability” (Sposito, 1994). Examples of hard Lewis bases are cations of the metals Na, K, Mg and Ca.

However, Sposito (1994) pointed out that even with the set of hard Lewis acid there is a spectrum of hardness instead of a single degree of hardness, applicable to all members. Although Li, Na,K, Mg, Ca, Cs and Be are all classified as hard Lewis acids, Cs and Be are much softer than Li and Mg. These relationships between the metal ions can be quantified as the Misono softness parameter Y:

$$\mathbf{Y= 10\ (I_z\, R\ /\ Z^{1/2}\, I_{z+1})}$$

Where: R- ionic radius of metal ion; z - its formal charge; I_Z-ionization potential;
I_{z+1}- ionization potential when the valence of the cation changes to Z+1.

Rengasamy and Sumner (1998) concluded that the attractive forces between clay particles depend on the nature of bonding mediated through the cations commonly found in soils (Na, K, Mg, Ca, Fe, and Al) and the tendency to form covalent bonding and complexes increases in the order: $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$.

2.6.1 Mechanism of structural changes in dispersive soils

The stability of soil aggregates, and therefore that of pore systems, depends upon attractive and repulsive forces arising from intermolecular and electrostatic interactions between the soil solution and soil particles. Rengasamy and Sumner (1996) described the changes in particle association in clay aggregates with wetting and drying, contrasting sodic and calcic systems. Figure 8 shows schematically the magnitude and direction of pressure changes taking place during wetting of aggregates, involving slaking, spontaneous and mechanical dispersion, and flocculation of dispersed clay by electrolytes. The organic and inorganic compounds, which bind together clay particles in dry aggregates (stage 1), produce strong attractive pressure of the magnitude measured in megapascals. On wetting, initial forces are generated, and initial attractive forces between clay particles in aggregates decrease distinctly.

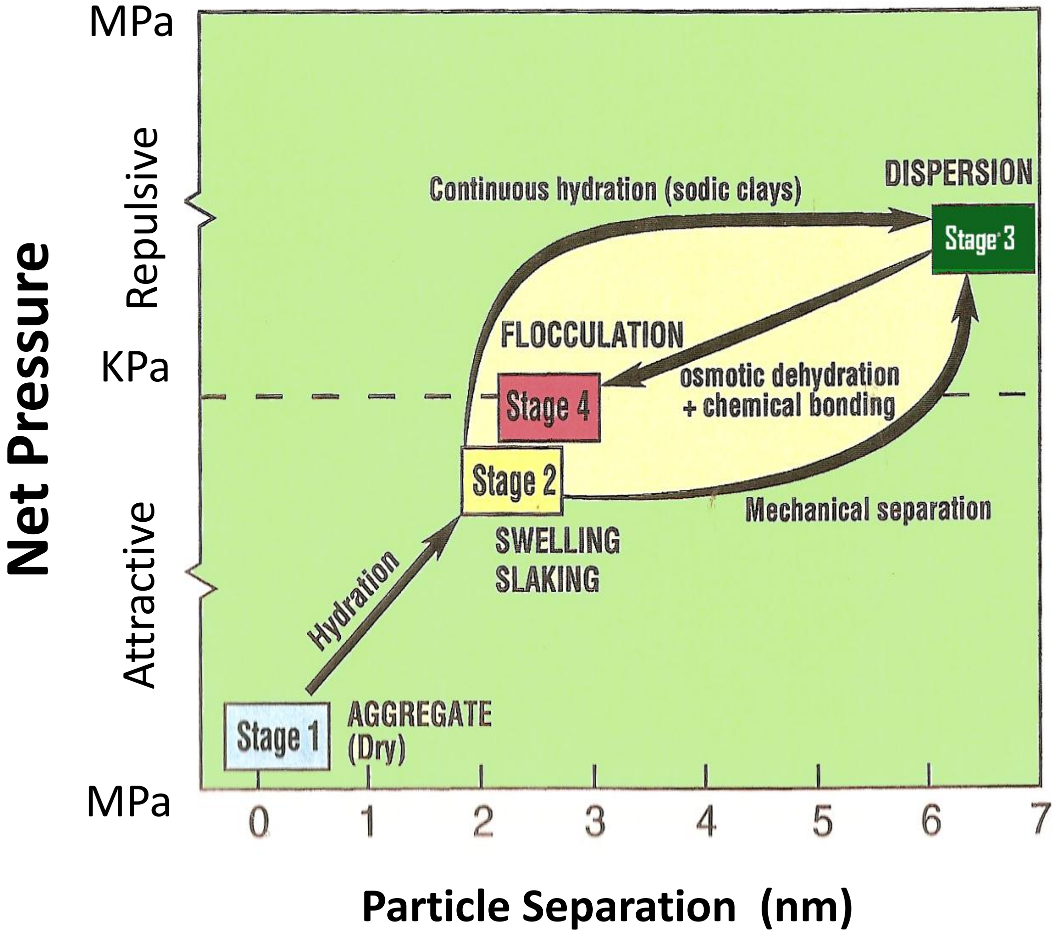


Figure 8 Schematic illustration of the process taking place when a dry aggregate is wetting Source: Rengasamy and Sumner (1998)

As hydration continues, the distance between these particles increases. If the clay particles are Ca- or Mg saturated, further wetting does not increase the interparticle distance beyond 2-3nm whereas in monovalent cation saturated clay, particles continue to separate.

The swelling due to hydration of divalent cations, called crystalline swelling (stage 2), occurs in clay particles even at high electrolyte concentration. When the ionic strength of the equilibrium solution is decreased, water molecules enter between the clay particles, increasing the distance between the clay particle beyond 7nm (Stage 3), resulting in clay dispersion (Rengasamy and Sumner, 1998). Once the complete clay dispersion takes place, electrostatic repulsive forces are operative and, at this stage, van der Waals attractive forces become insignificant. Stage 4 represents the point of net zero pressure, meaning that the attractive and repulsive forces are balanced. The attractive pressure necessary to bring the clay particles closer to each other is provided by the electrolyte concentration in soil solution. A threshold electrolyte concentration (TEC) is necessary for the clay particles to flocculate.

2.7 Factors affecting clay dispersion

2.7.1 Electrolyte concentration

Many authors (Agassi et al., 1981; Fireman and Bodman, 1939; Quirk, 2001; Quirk and Schofield, 1955; Rengasamy et al., 1984a; Rengasamy and Olsson, 1991), have reported that intensity of dispersion depend on soil ESP and electrolyte concentration in the applied water. Fireman and Bodman (1939) demonstrated that increasing electrolyte concentration in irrigation water applied to non-sodic soils increased hydraulic conductivity.

Infiltration rate and hydraulic conductivity are adversely affected if electrolyte concentration is insufficient to compensate for the deleterious effect of Na^+ , i.e. the concentration of soil solution decreases below critical flocculation concentration (CFC), an electrolyte concentration above or at which clay minerals flocculate (Goldberg and Forster, 1990; Shainberg and Letey, 1984).

Soils with low rate of mineral dissolution are the most susceptible to sodicity induced aggregate deterioration when leaching with low electrolyte water. Whereas, soils that readily release salts during leaching are less susceptible to disaggregation (Shainberg et al., 1981). Arora and Coleman (1979) found sodium saturated clay minerals to differ in their sensitivity to flocculation by $NaHCO_3$ in the decreasing order: illite > vermiculite > smectite >kaolinite, with the critical salt concentration (CSC), 185, 58, 28 and 8 meq/L respectively, for the above clays. The role of $NaHCO_3$ is to maintain the pH in the alkaline range.

In southern Australia, soils often become waterlogged during the winter rains, when early rainfall has leached the small amount of salts present in the surface soil, causing the clay to disperse and the soil to seal (Fitzpatrick et al., 1994). It is necessary to maintain adequate electrolyte concentration in the soil that in turn, depends on irrigation water salinity, ionic composition of irrigation water, presence of soluble minerals in soils and associated chemical equilibria that involves the composition of the solid, liquid and gaseous phases of the soil. Occurrence of calcite, gypsum or both in sodic soils can maintain Ca^{2+}, HCO_3^+ and SO_4^{2-} at adequate level, depending on the exchangeable ion composition and the partial pressure of carbon dioxide (Qadir and Schubert, 2002).

Ayers and Westcote (1985) proposed water quality guideline for the combined effect of SAR and EC of a soil or irrigation water on the likelihood of problems associated with low infiltration rate or hydraulic conductivity (Table 10). However, such guidelines have a limited ability to predict hydraulic conductivity under different conditions (Oster and Jayawardane, 1998).

Table 10 Guideline for interpretation of water quality for irrigation by using combine effects of SAR and EC of irrigation water

Source: adapted from Ayers and Westcote (1985)

SAR	Severe problem	Slight to moderate problem	No problem
	EC(dS/m)		
0-3	<0.2	0.2-0.7	>0.7
3.0-6.0	<0.3	0.3-1.2	>1.2
6.0-12.0	<0.5	0.5-1.9	>1.9
12.0-20.0	<1.3	1.3-2.9	>2.9
20.0-40.0	<2.9	2.9-5.0	>5

2.7.1.1 Threshold electrolyte concentration

Quirk and Schofield (1955) introduced the concept of threshold electrolyte concentration (TEC), the electrolyte concentration in the percolating solution that may cause a 15 percent decrease in hydraulic conductivity of a soil at a given SAR or ESP values. A systematic study was carried out by these authors on the effect of electrolyte concentration on the permeability of soil when saturated with Na, K, Mg, Ca ions. The key finding from this experiment was that permeability of the Na saturated soil can be maintained provided the electrolyte concentration was sufficiently large ($5X10^{-1}$M NaCl). TEC varies from soil to soil, and cannot generally be forecast without empirical tests, even for soils of similar clay content and type (Rhoades and Ingvalson, 1969).

Rengasamy et al (1984a) measured the TEC for spontaneous and mechanical dispersions in a red-brown earth soil. These authors obtained linear relationships between ESP, SAR $_{1:5}$ and EC $_{1:5}$ demonstrating the importance of the total electrolyte concentration for preventing clay dispersion from soil aggregates (Figure 9).

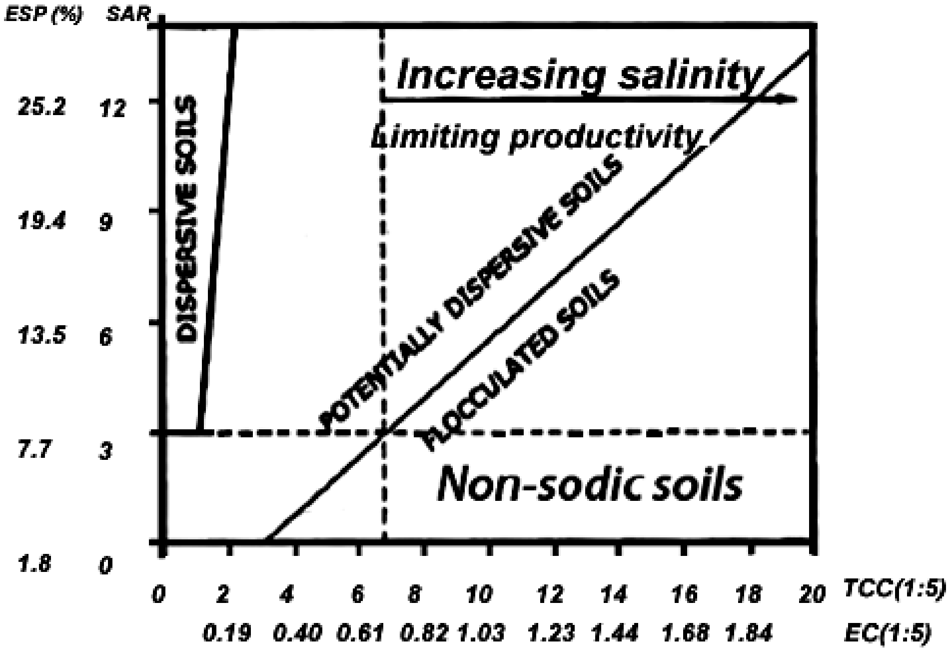


Figure 9 The relationships between ESP/SAR and EC/TEC for preventing clay dispersion Source: Modified from Rengasamy et.al. (1984a)

As a result, dispersion can be prevented though the application of water at the appropriate electrolyte level, depending of the values of SAR or ESP. However, even though the extent of dispersion is due to a high level of Na^+ in a soil, the presence of another monovalent cation K^+ in soil solution or/and on exchange sites, can promote dispersion (Chen et al., 1983; Subba Rao and Rao, 1996).

2.7.1.2 Dispersive potential (P_{dis})

Most of the investigations on clay dispersion have concentrated on soils with high exchangeable Na, and Ca as the other complementary cation. However, as the literature review (Section 3.4.1 and 3.4.2) clearly indicates, magnesium and potassium in the exchange complex can enhance the degree of clay dispersion. Furthermore, as mentioned earlier, dispersion of clay in soil is influenced by several other factors (i.e. mineralogy, pH, EC, clay content).

In order to derive a single parameter that will combine the effect of a number of factors causing clay dispersion, Rengasamy at al.(1991) proposed the use of dispersive potential (P_{dis}), which is derived from the electrolyte concentration.

Dispersive potential indicates the energy associated with the dispersive reactions in soil water system and because it is determined using a particular soil, it eliminates the differences due to soil factors such as mineralogy, organic matter etc.

P_{dis} is defined as the difference in the osmotic pressure between that at the threshold electrolyte concentration (P_{tec}) and that required to achieve a complete flocculation of the clay particles and the given soil solution concentration (P_{sol}):

$$\mathbf{P_{dis}\,(kPa) = P_{tec} - P_{sol}}$$

Osmotic pressure (P_{tec} or P_{sol}) is calculated from the corresponding EC values using the following relationships:

1dS /m =10mmol$_c$ /L

P_{osm}=3.6 kPa per mol$_c$ m^3 (mol$_c$ m^3=mmol$_c$/L)

Using the flocculating powers of the common cations theoretically derived and experimentally verified by Rengasamy and Sumner (1998), P_{tec} and P_{sol} can be calculated using the following equation:

P_{tec} or P_{sol}= 3.6x (45 x C_{Ca}+27 x C_{Mg} +1.8 x C_K + C_{Na})

where C is the concentration of Ca, Mg, K and Na (mmol$_c$/L) in equilibrium solution which contains threshold electrolyte concentration (TEC) or the original solution in which clay dispersion is observed. 45, 27, 1.8 and 1 are the flocculating powers of Ca, Mg, K and Na respectively (Rengasamy and Sumner 1998).

2.7.3 Clay mineralogy

Minerals in the clay (<2 μm) fraction dominate the contribution of soil minerals to many soil physical and chemical properties. Table 2.8 shows the main types of aluminosilicate minerals found in soil clay fractions and some of their properties relevant to their reaction to sodic conditions (Brady and Weil, 2008; Churchman et al., 1995). Of the entire types presented in Table 2.8, kaolinite, smectite and illite are the most common in soils. Interstratifications of kaolinite or illite with smectite are also a common phenomena (Churchman et al., 1995).

2.7.3.1 Clay minerals

To understand the behaviour of soil clays, it is necessary to consider both the crystal structure of clay minerals and the surface chemistry of clay–water suspensions.

The kaolinite structure is based on a single sheet of silicon tetrahedral combined with a single sheet of aluminium octahedra. These two sheets are tightly bound by sharing oxygen atoms. Most of the sorption activity occurs in kaolinite along the edges and outside surfaces. Soil with a large amount of kaolinite usually has a low percolation rate due to the compact structure.

Kaolinite is considered the least active clay compared to other types of clay and has relatively low capacity to adsorb exchangeable cations, 5-10milliequivalents of a cation charge per 100g , (Table 11) due to un-terminated bonds on crystal edges (Velde, 2010).

Table 11 Major properties of selected silicate clay minerals and humus

Source: Brady and Weil (2008)

Colloid	Type	Size, µm	Shape	Surface area, m^2/g		Net Charge
				External	Internal	cmol$_c$ /kg
Smectite	2:1 silicate	0.01-1.0	Flakes	80-150	550-650	(-80) to (-150)
Illite (mica)	2:1 silicate	0.2-2.0	Flakes	70-175		(-10) to (-40)
Kaolinite	1:1 silicate	0.1-5.0	Hexagonal crystals	5.0-30		(+10) to (-5)
Humus	Organic	0.1-1.0	Amorphous	Variable		(-100) to (-500)

Illite structure is based on layers consisting of octahedral sheet of alumina sandwiched between tetrahedral sheets of silica. In the octahedral sheets there is a partial substitution of Al^{+3} by Mg^{+2} or Fe^{+} and in the tetrahedral sheet there is a partial substitution of silicon by aluminium.

Soils that contain illite have a higher cation exchange capacity than kaolinite due to their surface charge. The soils dominated by illite clays have a high K^{+} fixing capacity (Velde, 2010).

Smectites are minerals with low layer charges that have cation attractions (exchange capacity) of near 135 milli equivalents. The amount of ions attracted are a function of the amount of substitutional charge but also the site of the charge (Velde, 2010).

2.7.3.2 Surface area

The smaller the size of a particle in a given mass of soil, the greater the surface area exposed for adsorption, catalysis, precipitation, microbial colonisation and other surface phenomena (Brady and Weil, 2008). Some clays also have an extensive internal surface area. The total surface area of clay minerals ranges from the 1:1 layer clays such as kaolinite, with external surface areas of around 10 metres square per gram to more than 800 metres square per gram for the 2:1 clays such as montmorillonite with large internal as well as external surface area. Figure 10 shows the difference in surface area between the 1:1 and 2:1 layer clays.

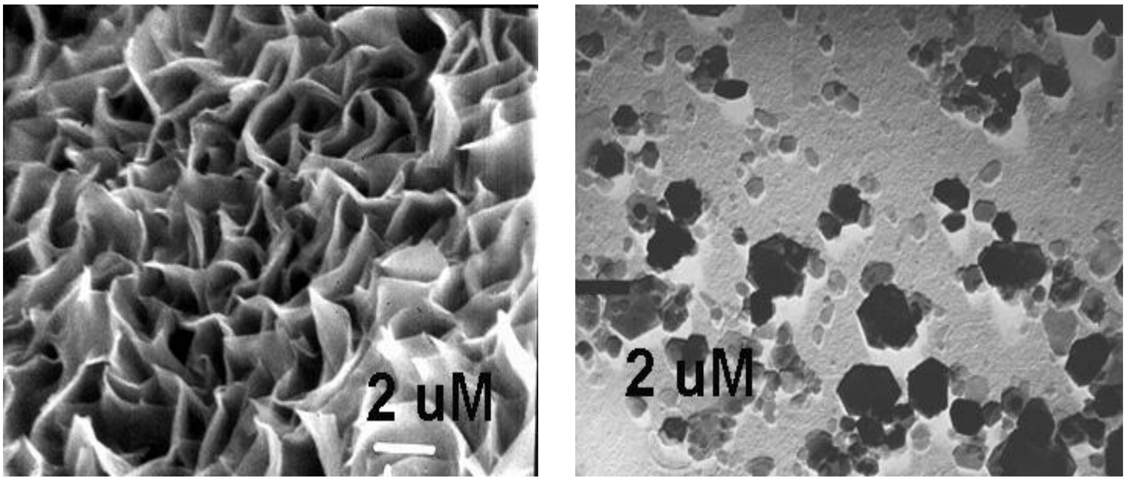


Figure 10 Electron micrographs of the clay minerals montmorillonite (left) and kaolinite (right) show the different surface area between the two clay types

Source: Department of Crop and Soil Environmental Sciences, Virginia Polytechnic Institute and State University

2.7.3.3 Origin of charge –summary points

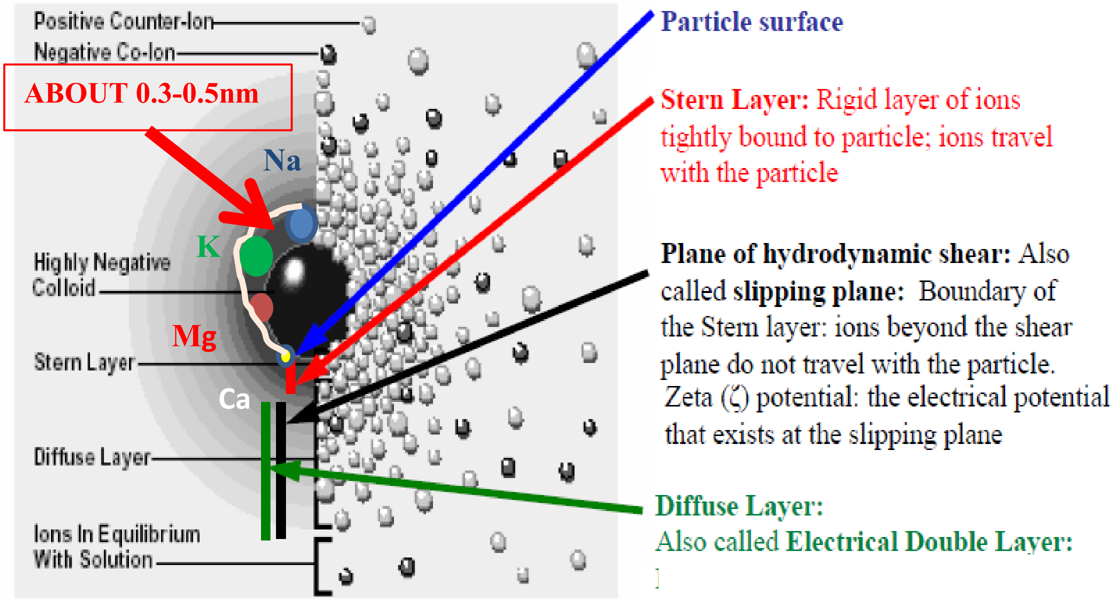
- Isomorphic substitution of original lattice elements with elements of lower valency, e.g. substitution of Al^{3+} with Mg^{2+} or Si^{4+} with Al^{3+} will produce a negative charge known as pH permanent charge. This mechanism has the most significant influence on the overall mineral charge (Chorom and Rengasamy, 1995)
- Lattice defects-the empty spaces within mineral lattice where an ion was removed leaving an unbalanced charge (Chorom and Rengasamy, 1995)
- Formation of pH dependant charge on mineral oxides by adsorption of proton hydroxyl groups to form positive or negative sites respectively. The pH dependant charge of minerals oxides depends on which of two species dominates. Therefore H^+ and OH^- ions are known as potential determining ions (Chorom and Rengasamy, 1995)
- Broken bonds-when the surface of minerals is fractured the bonds connecting elements can be broken leaving atoms with unsatisfied valence. The resulting charge can be negative or positive depending on the type of the bond that was broken (Chorom and Rengasamy, 1995)

When charged particles are suspended in solution, ions of opposite charge surround the surface of the particle resulting in an increasing concentration of counterions close to the surface (Figure 11).

2.7.3.4 Zeta potential

In many practical situations the value of zeta potential (ζ) obtained from electrophoresis experiments can be important in assessing the tendency for the soil colloids to disperse (Aydin et al., 2004).

Although zeta potential is not a direct measure of surface charge density-most surfaces are too complicated for such a direct proportionality to exist-it changes when the surface charge changes. Even a small percent of a component, if preferentially adsorbed at the surface of the particle, will largely determine the surface charge density, the resulting zeta potential, and the stability, or lack thereof, of the dispersion. Colloidal system are thought to be stable when the ζ-potential of particles is smaller than -30mV or greater than +30mV (Kirby and Hasselbrink, 2004). A reduction of the negative charge of minerals: a destabilisation of colloidal systems, decrease the affinity for nutrients and metals, etc. influencing agricultural unity of soil as well as performance of many technological processes employing suspension of minerals (Markiewicz et al.).



Particle surface

Stern Layer: Rigid layer of ions tightly bound to particle; ions travel with the particle

Plane of hydrodynamic shear: Also called **slipping plane:** Boundary of the Stern layer: ions beyond the shear plane do not travel with the particle.
Zeta (ζ) potential: the electrical potential that exists at the slipping plane

Diffuse Layer:
Also called **Electrical Double Layer:**

Figure 11 Two ways to visualize the Double Layer: the left view shows the change in charge density around the colloid; the right shows the distribution of positive and negative ions around the charged colloid Modified from Zeta Master Manual(1999)

As was mentioned in Section 2.5, forces between charged surfaces are mostly correctly described by DLVO theory. The exception is the last nm, 0.3-0.5 nm from the particle surface, which corresponds to the diameters of the hydrated counterions. Only several molecular layers remaining between the surfaces and the solvent structure become important. The thickness of this layer depends upon the type and concentration of ions in solution (Figure 11) (Edwards and Williams, 2004).

2.7.3.5 Effect clay mineralogy on dispersion

The effect of pH and exchangeable cations and electrolytes the stability of soil clay-water systems largely depends on the dominant type of clay mineral present in soil. Schofield and Samson, (1954) found that pure sodium kaolinite suspensions flocculated at pH<7, but illite and montmorillonite under these conditions dispersed. They showed that kaolinite edge faces are positively charges at low pH (pH around 4) and the system is partially flocculated. At high pH it was completely deflocculated, which they attribute to the loss of positive edge charge. Kaolinite exhibits a much greater variable charge which is pH dependant. At low levels of exchangeable sodium, and in weak electrolyte solutions, smectitic and micaceous soils disperse more than kaolinitic soils (Velasco-Molina et al., 1971). These authors concluded that, in the absence of electrolytes, the dispersion of a soil is related to the dominant clay mineral in the order: montmorillonite > hallyosite > mica. However, at low ESP values, micaceous soils sometimes disperse more than hallyosite-kaolinite soils. Using Australian soils, Emerson, (1983), found that soil dominated by clay sized mica (illite) dispersed easily. Oster et al (1980) found more dispersibility for illitic clay than for montmorillonitic clay. Australian soils (red-brown earths) dominated by illite are susceptible to dispersion even at low ESP and under weak mechanical forces (Rengasamy et al., 1984b). Illitic soils are more sensitive to dispersion and clay movement than are soils dominant in smectites because of the different shape and size of the illite clay particles, and the lower strength of edge-to face attraction (Greene et al., 1978). The surface area is inversely related to the thickness of particles. Smectites have a larger total surface area than other clay minerals (see Table 11). Therefore, when the particles are large in size, (and thus lower in surface area) there will be fewer points of contact between particles (Greene et al., 1978). Hence, these particles will disperse even with low sodium levels on their surface (Rengasamy et al., 1984b).

Goldberg et al. (1990) treated the soil with oxalate for removal of amorphous aluminium and iron oxides, and with dithionite for removal of crystalline aluminium and iron oxides, which resulted in increased clay dispersibility. These results indicate an important role of amorphous and crystalline oxides in stabilising soil clay against dispersion. The role of organic anions such as citrate and oxalate in increasing dispersion was explained by Durgin and Chaney (1984). These authors concluded that the size of an organic anion determines its influence. The stabilising effect on soil structure produced by the presence of Al and Fe oxides was demonstrated by Deshpande et al. (1964) and Shanmuganathan and Oades (1982). Deshpande et al.(1964) found that Al oxide reduces swelling, but Fe oxide did not. They concluded that Al oxide was acting as cement and that Fe oxide was present as a discrete particle. El Rayah and Rowell (1973) reported that Al hydroxide was more effective than Fe hydroxide in preventing swelling and dispersion. Frenkel and Shainberg (1980) found that Al polymers could stabilise a montmorillonite suspension against the adverse effect of Na ions better than Fe polymers.

Moreover, Oades (1984) found Al polymers could be more efficient than Fe polymers in reducing the swelling of montmorillonite. He suggested that this difference was a result of polymer morphology. Aluminium polymers occur as sheets and can, therefore, neutralise clay layer charge more completely than can the spherical Fe polymers. Goldberg et al. (1988) suggested that aluminium and iron oxides play an important role as binding agents in the structure of arid soils. McNeal et al.(1968) showed that iron oxides stabilise soil against dispersion under high-sodium and low salt conditions.

2.7.4 Effect of pH on soil structure

The pH of a soil has an impact on clay dispersion, which is governed by the size and nature of the surfaces of soil clay particles, particularly their charge (cation exchange capacity) and surface area (Rengasamy and Churchman, 1999). Table 12 presents charge characteristics of representative colloids showing comparative levels of permanent (constant) and pH-dependant negative charges as well as pH-dependant positive charges. Isomorphous substitution is the mechanism of charge generation in permanently charged minerals, where surface charge is independent of pH. In contrast, for variable charge surfaces, the charge is mostly dependent on the pH of the equilibrium solution (Sumner, 1993).

Table 12 Charge characteristics of some representative colloids showing comparative levels of permanent (constant) and pH-dependant negative charges as well as pH-dependant positive charges

Source: Brady and Weil, (2008)

	Negative charge			Positive charge
Colloidal type	Total at pH 7 (cmol$_c$) kg^{-1})	Constant (%)	Variable (%)	(cmol$_c$ kg^{-1})
Organic	200	10	90	0
Smectite	100	95	5	0
Vermiculite	150	95	5	0
Fine-grained micas	30	80	20	0
Kaolinite	8	5	95	2

Suarez et al. (1984) have shown that at constant SAR and electrolyte levels, clay dispersion increased with the increasing pH for predominantly kaolinitic soils. Chorom et al, (1994), in a study of three soils, dominated by illite, kaolinite and smectite, have found that pH affects clay dispersion by changing the net negative charge on clay particles. With the increase of pH, all three soils showed an increase in net negative charge and zeta potential, corresponding with an increase in clay dispersion. Figure 12 gives a schematic representation of the effect of pH on clay particles. In nature, strongly alkaline soils invariably exhibit high sodicity; on the other hand, a sodic soil with a soil solution of high SAR does not necessarily have a high pH (Van Beek and Van Breeman, 1973). In calcareous soils, high pH and high ESP nearly always occur together, and it is difficult to separate their effect on the resultant poor physico-chemical conditions and consequently on crop growth. In many saline sodic soils that do not contain sodium carbonate, the saturation paste pH is observed to be less than 8.2-8.3. For subsurface soils, the zero point of charge (ZPC) and charge reversal usually occurs around pH 7 to 9 (Bowden et al., 1980), depending on structural composition and degree of crystallinity of the variable charge components.

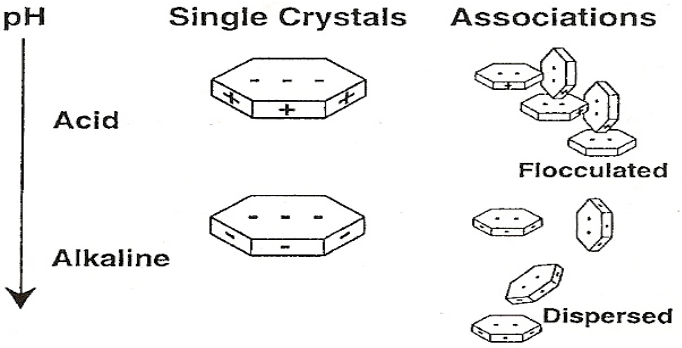


Figure 12 Schematic representation of the effect of pH upon kaolinites and their associations. Left: effect of pH on the individual crystals. Edges become positively charged at low pH, negatively charges at high pH. Right; consequent effect of pH upon associations of kaolinites Source: Churchman et al. (1993)

2.7.5 Effect of organic matter on soil structure

Organic matter comprises 1-10% of soil mass, which is approximately 1-5% microbial biomass. To understand the effect of organic matter on soils, it is important to know the form in which organic matter is added, and the way it is distributed within the soil (Nelson and Oades, 1998). There is some disagreement in the literature in respect to the effect of organic matter on the dispersion of sodic soils, as organic matter may enhance dispersion or prevent it, depending on circumstances. Na ions have direct chemical and physical effect on soil organic matter, as well as affecting links between minerals and organic matter (Churchman et al., 1993). Furthermore, Nelson et al. (1999) concluded that dispersibility of clay fractions was a function of the amount and type of organic matter they contained, selectivity of cations and their particle size.

The three physico-chemical types of organic matter in soil can be considered: soluble/dispersible (fulvic acid and humic acid), clay associated humic acid plus fine particulate organic matter and largely unaltered organic debris. The first type is readily extracted by NaOH; the second is recovered along with clay fraction, while the third type is recovered with sand fractions. Increased sodicity has a potential to mobilize up to 40% of organic matter in soil either as colloidal organic matter or as clay organic matter complexes (Churchman et al., 1993).

Organic matter influences sodicity through its CEC and the selectivity of exchange sites for Ca and Na, as well as its ability to donate protons. CEC of soil organic matter ranges from 60 to 300 cmol_c/kg with value up to 1400 cmol_c/kg of total acidity being recorded to fulvic and humic acids. Figure 13 demonstrates that organic matter has greater CEC than most soil minerals. Negatively charged sites on organic matter interact with positive sites on inorganic colloids, especially oxides, thereby reducing the CEC of organic matter and the amount of positive charge in the soil (Oades et al., 1989).

Organic anions can enhance dispersion by increasing the negative charge on clay particles and by complexing Ca^{2+} and other polyvalent cations (such as Al), thereby reducing their activity in soil solution (Oades, 1984). In their experiment, Nelson et al. (1999) observed that organic matter in the easily dispersed clay fraction of all soils contained a large proportion of amino acids and proteins, suggesting that these materials acted as dispersants.

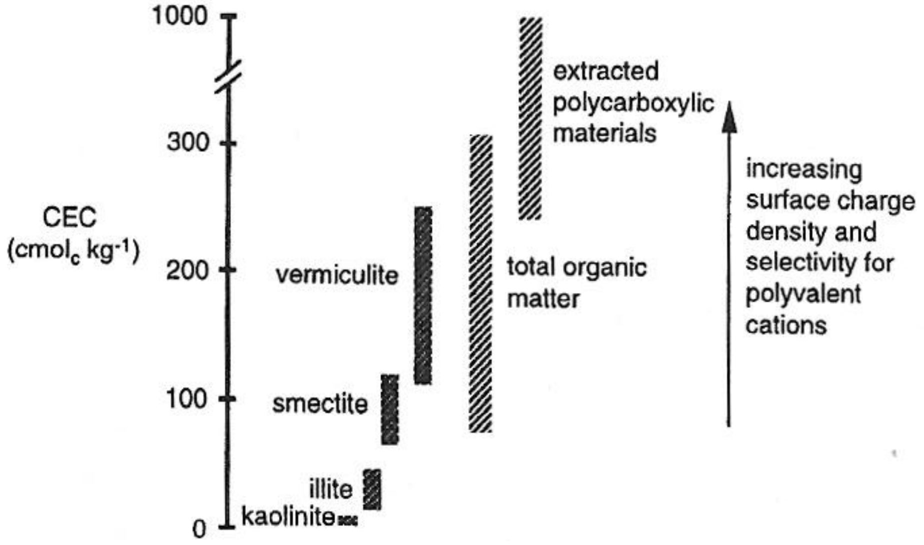


Figure 13 CEC and selectivity of soil clay minerals and organic matter.

Source: Nelson and Oades (1998)

Large organic polyanions can bind clay particles together into stable microaggregates. Barzegar et.al., (1997) found that the addition of plant residues had a positive effect on stability of soil aggregates in water irrespective of clay type or sodicity in the SAR range of 0-30. Organic material such as fungal hyphae and fine roots can help prevent dispersion by stabilizing microaggregates and thereby reducing the surface area from which clay may disperse (Tisdall, 1996).

Sodicity strongly affects biological activity, with nitrification inhibited completely at ESP >70. The ratio of humic to fulvic acids increased with ESP and carbon becomes more easily extractable at high ESP values (Laura, 1976.)

Effect of sodicity on organic matter composition further complicates any attempts to predict the behaviour of soils on the basis of sodicity (Churchman et al., 1993).

2.8 Assessment of soil structure by µCT scanning

Knowledge of soil structure and pore connectivity is vital to understand and predict changes in soil aeration, hydraulic conductivity and sequestration or emission of greenhouse gases. Porosity plays a crucial role in facilitating numerous physical, chemical and biological processes occurring in soil. However, despite the significance of pore structure, it has historically been difficult to quantify (Cárdenas et al., 2012; Vogel, 2000; Vogel et al., 2010). Traditional testing methods for pore architecture include the gas adsorption method, mercury intrusion porosimetry and permoporometry (Churchman and Payne, 1983; Gaskin and Raymond, 1973; Lipiec et al., 2012).Paradoxically, the majority of the tests destroy or alters the very parameters they are supposed to measure. Additionally, the toxicity of mercury is a concern for the well-being of the user.

High resolution X-ray computed tomography (µCT) is a technique which can provide valuable information in the analysis of soil pore architecture, and which can reliably describe the pore structure and connectivity of an undisturbed soil entity (Turner et al., 2003). A µCT scan with subsequent 3D reconstruction of serial images enables the visualisation of isolated pores not visible externally due to the opaque nature of the soil medium, and therefore can be used to determine parameters such as total porosity, closed porosity, pore interconnectivity and overall 3D micro-architecture (Cárdenas et al., 2012; Darling and Sun, 2004; Vergés et al., 2011).

Computed tomography became feasible with the development of modern computer technology in the 1960s, but some of the ideas on which it is based can be traced back to the first half of that century. In 1917 the Bohemian mathematician Radon (1917) proved in a research paper of fundamental importance that the distribution of a material or material property in an object layer can be calculated if the integral values along any number of lines passing through the same layer are known. The first applications of this theory were developed for radio astronomy by Bracewell (1956), but they met with little response and were not exploited for medical purposes. X-ray computed tomography (CT) was first developed in the medical field and largely attributed to Hounsfield (Hounsfield, 1973).

The first result of CT in soil science was reported by Petrovic (1982) in the experiments where an x-ray transmission computed tomography (CT) scanner was evaluated as a tool to determine soil bulk density. Over the past three decades, there has been considerable interest in the application of CT scanning to understand many different aspects of soil. Among the pioneers of the use of micro μCT scans in soil science were Hainsworth and Aylmore in Australia (Aylmore, 1993; Hainsworth and Aylmore, 1983) and Silvio Crestana in Brazil (Crestana et al., 1986). Principals of μCT operations in soil and plant sciences are comprehensively detailed by Taina et al. (2008), Mooney et al. (2012), Vogel et al. (2010), and Basile (2012).

Microtomography uses X-rays to create cross-sections of a 3D-object that later can be used to recreate a virtual model without destroying the original model. The term *micro* is used to indicate that the pixel sizes of the cross-sections are in the micrometer range. These pixel sizes have also resulted in the terminology micro-computed tomography, micro-ct, micro-computer tomography, high-resolution X-ray tomography, and similar terminologies. All of these names generally represent the same class of instruments. By rotating the sample 360° in the X-ray cone beam the system acquires N numbers of images, called projections. The TeraRecon filtered back projection with Feldkamp Algorithm reconstructs the μCT absorption coefficient visible in 2D oblique slice cuts or in a 3D volumen by loading all reconstructed 512 (1024, 2048 = voxel number) slices.

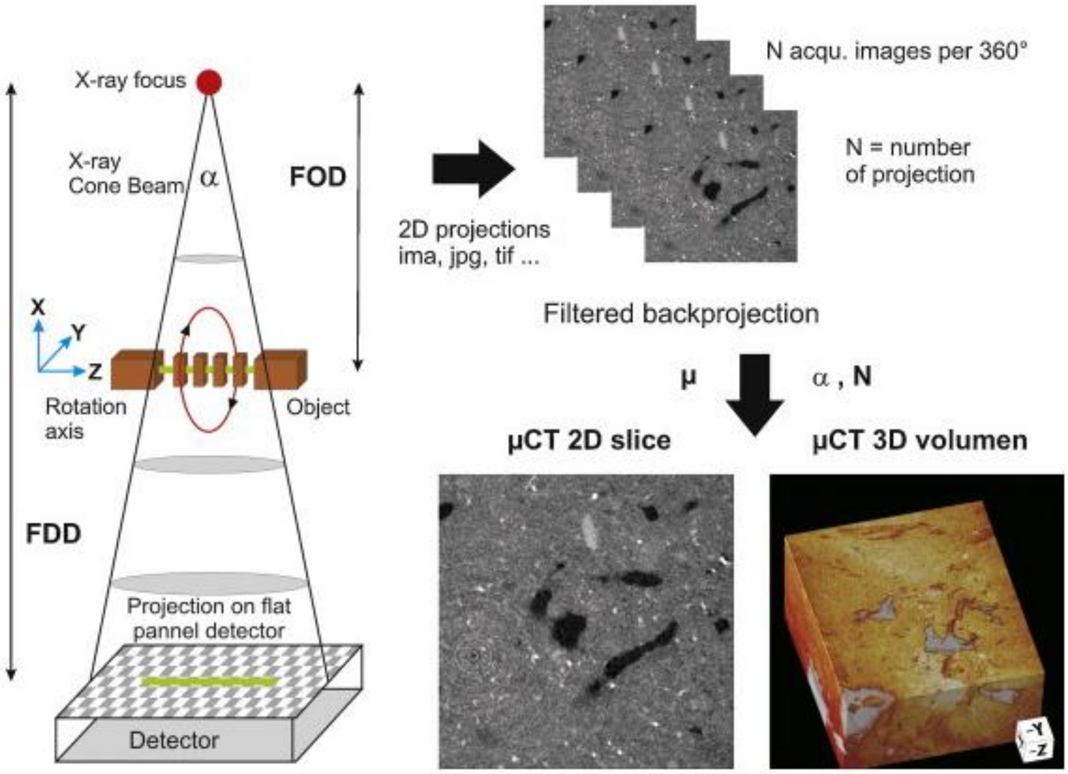


Figure 14 Schematic illustration of an axial microfocus computed tomography system (μCT) Source: Russ (2011)

The resulting voxel size is calculated from FOD, FDD, detector size, detector pitch, and voxel number (FOD = focus object distance, FDD = focus detector distance) (Tippkötter et al., 2009).

Completion of a μCT scan consists of two main processes: data collection and image reconstruction. During data collection, a specimen is digitally photographed from multiple angles as it is exposed to X-rays. During the reconstruction phase, many individual x-ray photographs are superimposed in such a way that their resulting image describes the interior structure of the specimen. X-rays are invisible, high energy electromagnetic waves that are able to pass through the objects (Figure 14). As a beam of X-rays penetrates the object, some of the x-rays are absorbed by the object's matter.

Dense matter (e.g. rock, wood) absorbs more x-rays than less dense materials (e.g. plastic, water). A digital camera is used to capture the image on the screen, which replicates the x-ray penetration pattern of the object.

The data collection phase of a CT scan occurs after the object is viewed with x-rays from many different directions (Figure 2.18). In traditional two dimensional CT scanning, the object is scanned through a single "slice" and each of the individual images consists of the object's x-ray penetration pattern through the location of the slice. Some three dimensional CT scanning techniques use individual images consisting of broad sections of the object's x-ray penetration pattern. In either case, the object must be photographed as it rotates at least one-half of a full rotation relative to the X-ray trajectory and detector screen (Russ, 2011). The details of the data collection and reconstruction phases, and mathematical analysis of the process are given in Russ (2011).

2.9 Conclusion from Literature Review

This Literature Review has highlighted several important issues which needed to be investigated in order to develop a robust, scientifically based assessment of the effect of cations on soil structural stability.

These issues are:

- Identifying and quantifying the deleterious effects of increasing concentration of K on clay dispersion and hydraulic conductivity for different type of soils;
- An in depth understanding of the complex physico-chemical soil processes that influence the effect of cations in soils and irrigation water on soil structure;
- More comprehensive assessment and evaluation of soil structural stability and quality of irrigation water based on scientific investigation is required to insure adequate management of the salt -soils, and
- Developing improved methods of measuring and understanding the function of cations and cation-clay interactions for soil structural responses to irrigation or rainfall.

The following peer reviewed scientific papers explore these issues and contribute to understanding and developments in this area with the respective outcomes used for the development of the assessment criteria to predict behaviour of salt affected soils.

Chapter 3 Effect of soil potassium concentration on soil structure

Alla Marchuk, Pichu Rengasamy and Ann McNeill

Soil Science, The University of Adelaide, SA 5064, Australia.

Submitted to *Geoderma*, February 2012.

Statement of Authorship

Marchuk, Alla (Candidate)

Established methodology, data collection and analysis, preparation of the tables and figures, writing and compilation of the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed Date

Rengasamy, Pichu (Principal Supervisor)

Supervised and assisted in establishing the methodology, writing and editing of manuscript.

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed Date

McNeill, Ann (Co-Supervisor)

Supervised manuscript evaluation, reviewed and edited manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed Date

This chapter is an exact copy of the journal paper referred to above.

Effect of soil potassium concentration on soil structure

Alla Marchuk*, Pichu Rengasamy and Ann McNeill

Soil Science, Waite Campus, The University of Adelaide, South Australia, 5068, Australia.

[a]* Corresponding author. *Soil Science, Waite Campus, The University of Adelaide, South Australia, 5068, Australia.*

Tel: +61-8-83037398 Fax: +61-8-83036511

E-mail address: alla.marchuk@adelaide.edu.au (Alla Marchuk).

Abstract.

Re-use of industrial and agricultural wastewater for irrigation can increase the concentration of potassium ions in soil solutions and affect soil structure. The objective of this study was to assess the effect of increasing concentration of potassium (K) on soil structure and permeability. Traditional indices for assessing soil structural stability, sodium adsorption ratio (SAR) and exchangeable sodium percentages (ESP) do not take into account the effects of K on soil clay dispersion and swelling. Therefore, a new quantitative index, cation ratio of structural stability (CROSS), was used as an alternative of SAR, to take into account the differential effects of Ca, Mg, Ma and K on soil structural stability. Two soils of different clay mineralogy (illite –kaolinite and smectite), soil texture, net charge, pH and EC were treated with three wetting and drying cycles using treatment solutions with increasing K concentration ($CROSS_{tr}$ 6,8,11,15, but SAR of 1.2) for each soil. Saturated hydraulic conductivity (HC_s) measurements were taken at the end of the experiment. Significant reductions in HC_s were observed in both soils at the high $CROSS_{tr}$ values (11 and 15), while HC_s

increased slightly (11%) for illitic- kaolinitic soil treated with CROSS$_{tr}$ 8. Replicate columns for each treatment were analysed for soluble and exchangeable cations. The significant relationships between CROSS of the treatment solution, CROSS of the soil solution and exchangeable cation ratio (ECR) were established. X-ray computed tomography (CT) scanning of the replicate columns provided a means of measuring changes of soil structure in two (2D) and three (3D) dimensions. 2D and 3D images reconstructed from CT scans allowed visualisation of the structural effects of high potassium concentration and quantification of reduced porosity and connectivity due to high potassium in soils. CT scan results confirmed that the soils treated with the solutions of low K concentration (CROSS$_{tr}$6) had an increased porosity than the soils leached with water only.

Keywords: Potassium; Soil structure; Clay dispersion, CROSS; X-ray computed tomography

1. Introduction

Wastewaters from urban and agricultural sources have a great potential for re-use in irrigating horticultural and agricultural crops. These wastewaters can have high concentration of cations such as sodium and potassium and long term application of such wastewaters may affect the levels of both soluble and exchangeable cations and lead to soil structural deterioration and salt accumulation in soils. The soil solution of salt-affected or irrigated soils may contain a range of dissolved salts, comprising a set of different cations and anions. Globally, more attention is given to the levels of sodium in relation to its deleterious effects on soil structure because of the predominance of sodium in salt-affected soils (Rengasamy, 2010). However, recent reports suggest the occurrence of high levels of potassium in some regional soils and recycled waters used for irrigation. Arienzo et al. (2009) gave an account of high concentrations of both potassium (250- 200,000 mg.L^{-1}) and sodium (120-400 mg.L^{-1}) in various effluents from dairy, piggery, winery and cooking oil processing industries. Smiles (2006) reported that on average there is more water soluble and exchangeable potassium than sodium across a range of soils in the Murray-Darling Basin in Australia. The potassium status of some Indian soils is categorized as medium to high (Subba Rao and Rao, 1996). High inputs of potassium in agricultural soils in the United States irrigated with waters from different sources have been documented by Robbins (1984)

Potassium, being a monovalent cation, can cause soil clay swelling and dispersion similar to sodium. The role of potassium in affecting soil structure has been debated in the literature, its effects found to be equal to or less than that of sodium (El Swaify et al., 1970; Chen et al., 1983; Robbins, 1984 ; Smiles and Smith, 2004). Rengasamy and Sumner (1998) hypothesised that the ionicity of clay-cation bonds determine the dissociation of clay particles on interacting with polar water molecules and on this basis derived flocculating and dispersive powers of cations. Recently, Marchuk and Rengasamy (2011) derived ionicity indices of the cations Na^+, K^+, Mg^{2+} and Ca^{2+} using their ionisation potentials and charge. Their studies on homoionic pure and soil clays confirmed that clay behaviour such as dispersivity was dictated by the degree of ionicity of clay-cation bonds.

Currently, sodium adsorption ratio (SAR) or exchangeable sodium percentage (ESP) is used as an index of sodicity effects on soil structure (details in Rengasamy and Churchman 1999). The SAR model was originally developed on the basis of ratio law of Schofield (1947) to predict the adsorption of sodium on soil exchange sites in relation to the cation concentrations in soil solutions. SAR is estimated from the concentrations of Na, Mg and Ca in soil solutions and has been found to be correlated with ESP. Potassium is not considered in the SAR model. Smiles and Smith (2004) suggested a "monovalent cation ratio" (MCAR), which includes Na+K in the calculation of SAR and where Mg is treated as equal to Ca. However, the ionicity indices of Mg and Ca are different (Marchuk and Rengasamy 2011) and hence, their flocculating powers will differ. Similarly, the ionicity indices of Na and K are also different with different effects on clay dispersion. Based on these notions, Rengasamy and Marchuk (2011) proposed a new ratio "CROSS" (cation ratio of soil structural stability) analogous to SAR but which incorporates the differential effects of Na and K in dispersing soil clays, and also the differential effects of Mg and Ca in flocculating soil clays, and is defined as: $\text{CROSS} = (\text{Na} + 0.56\text{K}) / [(\text{Ca} + 0.6\text{Mg})/2]^{0.5}$ where the concentrations of these ions are expressed in millimole of charge/L.

In their preliminary studies, Rengasamy and Marchuk (2011) found CROSS to be superior to SAR and MCAR in predicting clay dispersion in a number of soils. These authors also found that CROSS measured in soil solutions was strongly correlated to the ratio of exchangeable cations.

In the present study, we aimed to confirm the effects of increasing levels of potassium on clay dispersion from soils and their hydraulic conductivity. Further, we also examined the changes in soil structure after treating with different levels of potassium by using X-ray CT scanning to acquire serial images of soils so as to visualise and quantify the changes in soil structure in three dimensions. In these experiments, instead of using potassium adsorption ratio (PAR) in which K replaces Na in the formula for SAR, or monovalent cation adsorption ratio (MCAR), we focused on using CROSS which takes into account the different effects of all of all major cations in soil solution.

2. Materials and methods

2.1. Soils used

Two soils viz. Urrbrae and Claremont were used in the present study. Selection of these soils was based on differences in their clay mineralogy, texture, pH, EC, effective cation exchange capacity (CEC_{eff}) and zeta potential measured on clay < 2μm clay fractions obtained from the soils without preliminary chemical treatment by the method described in Churchman (2002). The soil samples were taken by a hand auger, air-dried, sieved to 2 mm particle diameter and analysed for physical and chemical characteristics. Physico-chemical properties and locations of the soils are presented in Table 1.

2.2. Saturated Hydraulic conductivity

Percolating solutions were prepared using 0.1M chloride solutions of Ca, Mg, K and Na at predetermined concentrations to obtain $CROSS_{tr}$ values of 6, 8, 11, 15, but all having the same SAR of 1.2. The cation concentration of the treatment solutions are presented in Table 2. Soil samples were evenly packed into Plexiglas columns (6 cm in diameter and 10 cm long) at a bulk density of 1.33 Mg/m^3.Both column ends were fitted with nylon mesh screens with a double disk of a gaze mesh on the top of the soil to reduce surface disturbance. Initially the columns were wetted with the treatment solutions to saturation for 24 hours from the base by slow capillary rise and then the flow direction was reversed.

Table 1 Selected physical and chemical properties, main clay minerals, classification and location of the soils used

Soil properties	Units	Soil	
		Urrbrae	Claremont
Depth	cm	15-40	15-40
pH (1:5 soil water solution)		6.7	8.3
EC(1:5 soil water solution)	dS/m	0.06	1.03
CROSS (Cation ratio of structural stability)	$mol^{05}\ m^{-1.5}$	0.24	0.32
Total carbon	%	1.5	4.0
Organic carbon	%	1.4	2.2
CEC_{eff}	cmol kg^{-1}	7	30
Zeta potential	mV	-38	-19
Major clay minerals		Illite-kaolinite	Smectite
Taxonomic class *(Australian Soil Classification (Isbell, 2002)*		Red Chromosol	Vertisol
Clay content (Gee and Bauder, 1986)	%	30	60
Clay content (water dispersible)	%	26	6
Location in South Australia		34°58’00.41” S 138°38’03.29” E Elevation: 109 m Waite Research Institute	34°58’20.7” S 138°38’11.87” E Elevation 137 m Waite Research Institute

he columns were percolated with three wetting, draining and drying cycles using each of four CROSS treatment solutions ($CROSS_{tr}$) for each soil. For each cycle, 1 L of one of the $CROSS_{tr}$ solutions was percolated and then the soils were allowed to drain and dry for 1 week. Saturated hydraulic conductivity measurements were taken at the end of the last cycle with the deionised water passing through the columns to simulate the infiltration of the soil with rain water. The experiments were conducted using triplicate samples.

After hydraulic conductivity measurements, the soils from the first and second replicates were removed from the columns, air dried, crushed and passed through a 2-mm sieve. These final soils were then analysed for spontaneous dispersion, Zeta potential on separated clays and other selected properties such as $EC_{1:5}$, pH $_{1:5}$, CROSS of soil solutions ($CROSS_{ss}$) and exchangeable cation ratio (ECR %).

Table 2 Attributes of each treatment solution ($CROSS_{tr}$) and potassium concentration in $CROSS_{tr}$ solutions

Treatment No	Cations in treatment solutions (mmol$_c$/L)				TCC (mmol$_c$/L)	SAR_{tr} $mol^{0.5}m^{-1.5}$	$CROSS_{tr}$
	K	Na	Ca	Mg			
1	20	3.2	5.4	10	38.6	1.2	6.0
2	30	3.2	5.4	10	48.6	1.2	8.4
3	42	3.2	5.4	10	60.6	1.2	11.2
4	60	3.2	5.4	10	78.6	1.2	15.4

2.3. Soluble and Exchangeable cations

The EC, pH and soluble cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) concentrations (mmol$_c$ /L^{-1}) were determined using extracts from 10g of final soil in 50ml deionised water, and $CROSS_{ss}$ of the final soil solutions were calculated using the following equations:

$$CROSS_{ss} = (Na + 0.56K) / [(Ca + 0.6Mg)/2]^{0.5} \qquad (1)$$

where the concentrations of the corresponding ions are expressed in millimole of charge/L.

The exchangeable cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) were determined after soluble salts were removed by washing each of soil sample with 250ml of 60% ethanol until the electrical conductivity of the soil suspensions was below 0.05dS m^{-1}.

The exchangeable cations were extracted with 250 ml of 0.1MNH_4Cl adjusted to pH 7 for the Urrbrae soil and to pH 8.2 for the Claremont soil. The process was repeated a further two times and all the extracts collected and analysed for the exchangeable cations by inductively coupled plasma –atomic emission spectroscopy (ICP-AES) (Jackson, 2005; Rayment and Lyons, 2011). Subsequently, the effective cation exchange capacities (CEC_{eff}) and exchangeable cation ratio percentage (ECR %) were calculated as:

$$CEC_{eff} = (\Sigma \text{ exch } Na^+, K^+, Mg^{2+} \text{ and } Ca^{2+}) \quad (4)$$

$$ECR\ \% = [(Na^+ + K^+) / CEC_{eff})] \times 100 \quad (5)$$

where the quantities of the exchangeable cations are expressed in $cmol_c/kg$.

2.4. Spontaneous dispersion and turbidity measurements

Spontaneous dispersion was assessed by a modification of the method described by Rengasamy (2002). Samples (20g) of dry final soils were placed into 250 ml transparent measuring cylinders and 200 ml of distilled water was added slowly down the sides of the cylinders, taking care to avoid disturbance of the soil. After approximately 5 hr, any particles which had dispersed from the soils were gently stirred into suspension and left to stand for 2 hours. Suspensions were pipetted out from 10 cm depth for turbidity measurements.

To quantify the amount of < 2μm particles dispersed, measurements were made on a Hach 2100N Laboratory Turbidimeter at 25°C and recorded in Nephelometric Turbidity Units (NTU). A standard suspension of Formazin was used to calibrate the instrument. The 2100N is equipped with a stable halogen-filled, tungsten filament lamp to meet the reporting requirements of EPA Method 180.1(ASTM, 1976; Eaton and Franson, 2005). The method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspensions. The higher the intensity of scattered light, the higher is the turbidity.

2.5. Electrophoretic mobility and zeta potential

The zeta potential (*ζ)* was measured on < 2μm particles by laser Doppler velocimetry on a Malvern Zeta master Particle Electrophoresis Analyser. The correlation functions were measured automatically and zeta potential calculated by Malvern Control Software v1.23a. Prior to injection of the sample, cell alignment and set up of the system were performed and the operating conditions of the instrument were checked and calibrated using a DTS 5050 Electrophoretic Standard. The intensity (kilo counts/second) of each clay sample was measured prior to the readings to ensure the compatibility of the samples. The zeta potentials (ζ) were calculated as the mean of ten runs, each of which was averaged over 25 individual measurements performed automatically by the instrument.

2.6. X-ray CT scan

X-ray computed tomography (CT) scanning is a non-invasive imaging technique that allows the three dimensional, non-destructive examinations of heterogeneous materials, whereby a large number of transmission measurements of an x-ray beam are used to reconstruct an image of a scanning object. Using digital image processing, it is possible to create 3-D visualisations derived from 2-D scans, and hence examine the undisturbed soil pore network in 3D.

The soil samples from the third set of replicate columns were dissected by a scalpel into a small parallelepiped piece of 30x20x10 mm each and scanned using a SkyScan-1076 in vivo micro-CT system (Belgium). The scans were performed at a pixel resolution of 18μm using 100kV and 100μA, with a 1.0mm Al filter inserted. The scan used 180° rotation and a step size of 0.8°. The resultant radiographs were reconstructed into 2D slices using the "NRecon" software. 3D models of the soils and pore space were visualised using the "CTVol" software (Version1.10.10.2).The porosity, 3D pore size distribution, numerical density (i.e. the number of pore per volume of soil) was calculated by a SkyScan CT Analyser program (“CTAn”). Illustrative 3D visualisation of half reconstructed pore space (coloured in white) was made by applying a visual cut away of the solid region that occluded the pores.

2.7. Statistical analysis

Statistical calculations and linear regression analysis were performed with the programme GraphPad Prism Instat version 5.01 (GraphPad Software, Inc., San Diego, USA).

3. Results and discussions

The degree of ionicity of a clay-cation bond determines the ease of water molecules breaking the bond. Marchuk and Rengasamy (2011) derived the ionicity indices of various cations involved in clay bonding from their ionisation potentials and ionic charge, and thus the ionicity indices of Na, K, Mg and Ca were 0.89, 0.86, 0.73 and 0.67 respectively. Based on this concept, Rengasamy and Marchuk (2011) comprehensively indicated that the dispersive effect of K is 0.56 times the dispersive effects of Na. Therefore, in explaining the soil structural deterioration caused by the combination of monovalent cations, the factor Na+0.56 K should be taken into account. Experiments reported in this paper deal with the changes in soil structural parameters associated with increasing levels of K while the concentrations of Na, Mg and Ca are kept constant in the treatments.

3.1. The treatment effects on changes in soluble and exchangeable cations

The effect of the increased K^+ concentrations in treatment solutions on the final soil solution compositions, exchange complex, turbidity, zeta potential for the soils used in this study are shown in Table 3. CROSS of the treatment solutions ($CROSS_{tr}$) were of high total cation concentrations (0.1M) and adsorption of cations in the exchange complex occurred under these conditions. When leaching occurs during measurements of K_s by using de-ionised water, changes take place in cationic composition of soil solution and hence, we measured the composition of the final soil solution and calculated $CROSS_{SS}$.

Although values of $CROSS_{ss}$ were lower than $CROSS_{tr}$ (Table 3), both these parameters were highly related in each soil as shown in Table 4. There is also a good correlation between $CROSS_{ss}$ and ECR% with R^2 value of 0.90 when combining data from both soils (Figure1).

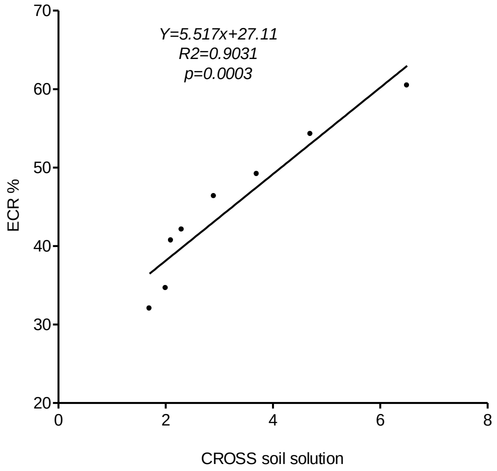


Fig.1. Relationships between the final soil cation ratio ($CROSS_{ss}$) and exchangeable cation ratio (ECR %) for the Urrbrae and Claremont soils.

Generally, electrolyte concentration of soil solution determines SAR-ESP relation. For example, ESP is approximately equal to SAR measured in saturation extracts while in dilute extracts (e.g. 1:5 extracts) ESP is more than twice the SAR (Rengasamy et al., 1984; Hazelton and Murphy, 2007). Similarly, the relation between CROSS_{ss} and ECR% will depend on the electrolyte concentration of the soil solution. This is confirmed by a different slope of the regression equation between CROSS_{tr} and ECR% as given below:

$\text{ECR\%}=5.52\ \text{CROSS}_{ss} + 27.1$ (low EC)

$\text{ECR\%}=1.39\ \text{CROSS}_{tr} + 30.3$ (high EC)

3.2. Effect K^+ on dispersion and zeta potential

Dispersible clay is considered as a measure of soil structural stability in water (Sumner, 1993; Rengasamy and Marchuk, 2011). In this study, the turbidity values (Table 3) are the quantitative evaluation of the changes in the dispersion of soil clays which occurred following the treatment cycles. As the concentration of K^+ increases in final soil solution and on exchange sites, the turbidity increases in both soils. This is confirmed by the high correlation between turbidity and CROSSss when the results for both soils were combined together, with the R^2 value 0.97 (Figure 2a)

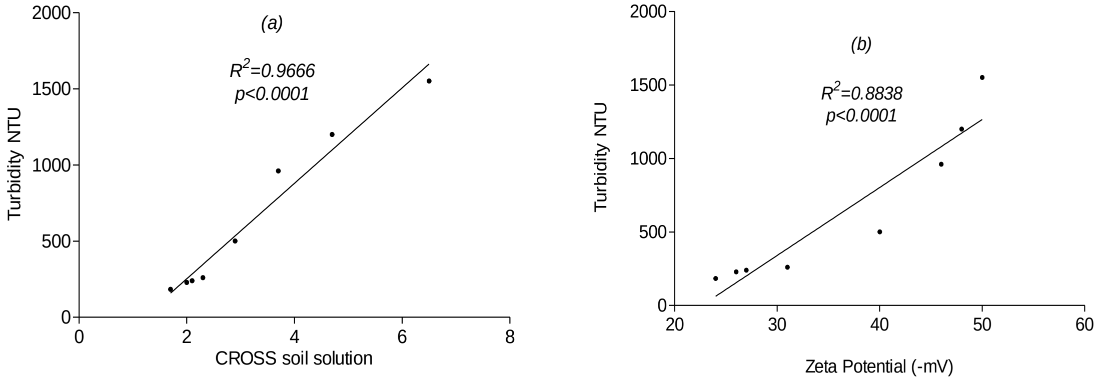


Fig.2. The relationships between (a) $CROSS_{SS}$ and (b) Zeta Potential of dispersed particles and the turbidity of final soil suspensions.

Measurement of the electrophoretic mobility of dispersed clay particles gives a measure of net charge on the solid clay particles (Hunter, 1981).The effect of K^+ on zeta potential was evaluated by measuring the electrophoretic mobility on dispersed clay from which zeta potential was derived. Table 1 shows the difference in zeta potential values between the two soils used in this study. The values of zeta potential of Urrbrae and Claremont soil clays are -38.0 and -19.0 mV respectively, while the cation exchange capacity values are 7 and 30 $cmol_c$ kg^{-1}. Zeta potential represents the charge on the dispersed clay particles only. In Claremont soil, with higher organic matter, clays are bound strongly together hence, the quantity and charge of dispersed clays are lower. Despite these differences, the zeta potential steadily increased with the increase in K^+ concentration in $CROSS_{SS}$, as well as ECR % and

turbidity in both the soils (Table3).

The difference in soil clay dispersion is naturally influenced by the clay type and the organic matter content (Tisdall and Oades, 1982).Claremont soil, with the predominantly smectitic clay and organic carbon content of 4%, disperses less than Urrbrae soil with illitic-kaolinitic clay and the organic carbon content of 1.49%. However, the close relationships between the zeta potential and turbidity, Fig.2b (R^2 value of 0.88), show that the differences due to clay type are mainly due to the charge on the surface of dispersed clay, confirming the findings by Marchuk and Rengasamy (2011).

3.3. Hydraulic conductivity in relation to CROSS$_{ss}$

Soil hydraulic conductivity depends on cations and the composition and concentraion of the electrolytes in soil solutions (Reeve et al., 1954; Quirk and Schofield, 1955). Earlier reports (e.g. Rengasamy and Sumner 1998) have shown that the threshold electrolyte concentration for clay flocculation varies with soil types, particularly clay content and composition. Therefore, as the measurements of hydraulic conductivity were done at different electrolyte concentrations for each soil, the relationships between $CROSS_{ss}$ and K_{sr} are highly dependent on the soil type. The value of relative hydraulic conductivity (H_{sr}) as influenced by K^+ in $CROSS_{tr}$ solutions are given in Table 3.Generally, the two soil samples, although different in soil type, exhibited the decrease of H_{rs}, as the concentration of K^+ in soil solutions increased. However, the correlations between $CROSS_{ss}$ and K_{sr} and as well between ECR% and K_{sr} are significant only for individual soils (Fig. 3a and 3b).

It seems that for the illite-kaolinite soil (Urrbrae), low level of K^+ may have positive effects on hydraulic conductivity, possibly due to interlyer adsorption of K^+ resulting in the stabilisation of the aggregates. Similar results were obtained earlier by Reeve at al. (1954) and Chen at al. (1983).

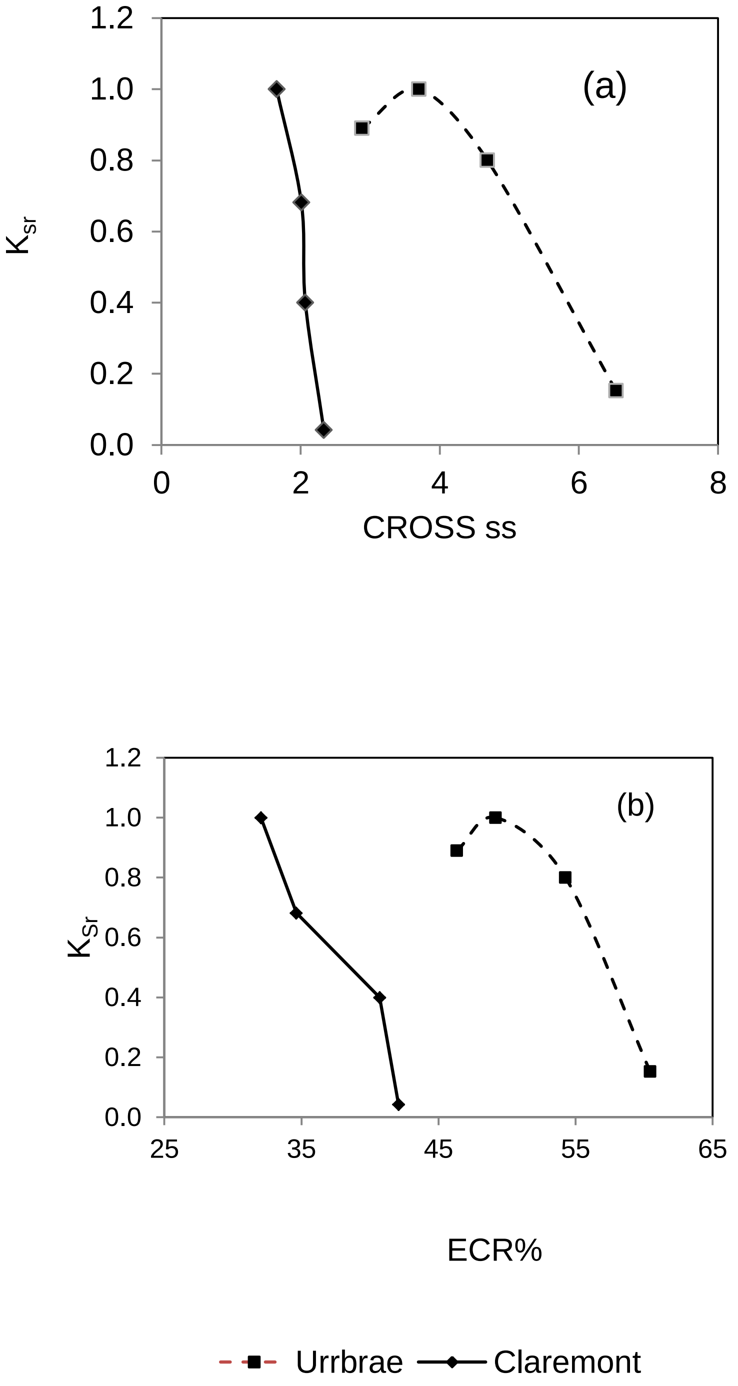


Fig.3. Relative hydraulic conductivity of each soil as a function of (a) CROSS_{ss} and (b) ECR%.

Table 3 Relative hydraulic conductivity (K_{sr}), pH, EC, soluble and excahngeable cations, $CROSS_{ss}$, CEC_{eff} and ECR, Zeta potential and turbidity measured on the final soils.

CROSS tr	Ksr	pH (1:5)	EC (1:5)	Soluble cations				Exchangeable cations				CROSS $_{ss}$	ECR	Zeta potential	Turbidity
				Ca	Mg	Na	K	Ca	Mg	Na	K				
	rel		dS/m	meq/l				meq/100g					%	mV	NTU
Urrbrae soil															
6	0.89	7	0.29	0.30	0.30	0.30	1.97	1.47	1.35	0.08	2.36	2.9	46	-40	500
8	1.00	7.1	0.29	0.27	0.16	0.35	2.19	1.62	1.04	0.08	2.50	3.7	49	-46	960
11	0.80	7.3	0.32	0.22	0.19	0.33	2.82	1.59	0.94	0.08	2.92	4.7	54	-48	1200
15	0.15	7.4	0.34	0.15	0.06	0.31	3.05	1.51	0.64	0.09	3.21	6.5	61	-50	1551
Claremont soil															
6	1.00	8.6	0.54	1.65	0.83	0.78	1.67	11.7	6.0	0.2	8.1	1.7	32	-24	184.0
8	0.68	8.7	0.51	1.69	0.84	0.96	2.05	12.1	5.4	0.2	9.0	2.0	35	-26	229.0
11	0.40	8.8	0.59	1.63	0.78	0.91	2.15	12.0	4.3	0.3	10.9	2.1	41	-27	240.0
15	0.04	8.9	0.60	1.67	0.76	0.87	2.74	10.3	5.0	0.3	10.9	2.3	42	-31	260.0

In contrast, Claremont soil is a smectite rich Vertisol with high clay content, high electrolyte concentration (EC) and high pH. Despite the relatively high electrolyte concentration, ($EC_{1:5}$=0.6 dS/m), of the final soil solution and low turbidity, hydraulic conductivity of Claremont soil reduced significantly after the treatment with $CROSS_{tr}$15, owing to a shrink- swell behaviour typical of smectite rich Vertisol (Barzegar et al., 1995). Regardless of the individual differences, the statistical analysis confirmed the strong correlation between the relative hydraulic conductivity and the increase in concentration of potassium in $CROSS_{ss}$ (Table 4). Our further studies will focus on establishing the relationships between threshold electrolyte concentrations for flocculation and $CROSS_{ss}$ as influenced by mineralogy and soil type.

3.4. Statistical results of linear regressions

Table 4 presents the summary of statistical results of linear regressions between $CROSS_{ss}$ and other parameters such as $CROSS_{tr}$, ECR%, turbidity and zeta potential for the individual soils. The R^2 values are higher for the individual soils than for both soils combined together indicating the influence of soil types on soil behaviour.

Table 4 Statistical results of linear regression between $CROSS_{ss}$ of the final soil solutions and $CROSS_{tr}$, exchangeable cation ration (ECR%), turbidity and Zeta

Soil	x	y	n	Regression equation	R^2
Urrbrae	$CROSS_{tr}$	CROSS ss	12	2.52x-1.20	0.99
	ECR %		12	0.25x-8.69	0.99
	Turbidity		12	0.003x+0.87	0.93
	Zeta potential		12	0.32x-10.34	0.80
Claremont	$CROSS_{tr}$	CROSS ss	12	14.93x-20.24	0.91
	ECR %		12	0.05x+0.22	0.86
	Turbidity		12	0.007x+0.26	0.99
	Zeta potential		12	0.08x-0.16	0.90

3.5. CT scans and soil structural change

In recent years, CT scan has provided a valuable tool for soil scientists to observe soil sturcture, especially pore size distribution and connectivity in relation to soil aeration and moisture relationships, as well as for evaluating root proliferation, soil permeability and hydraulic properties (Vogel, 2000; Mooney, 2002; Jassogne et al., 2007; Dexter and Richard, 2009).

In the present study, X-ray computer tomography (CT) scanning was used to acquire serial 2-D and 3-D images of two contrasting soil types to study changes in porosity, pore size distribution and the connectivity of the soil pores after treatment. The cost constrains led us to limit the number of treatments to water only, $CROSS_{tr}6$ and $CROSS_{tr}15$.

3.5.1 2D and 3D images and cross sections of the reconstructed soils

2D and 3D visualisations from the CT images for Urrbrae and Claremont soils after treatment cycles and saturated hydraulic conductivity measurements are presented in Figure 4. Comparison of the images illustrates clearly the differences in the sizes, connectivity and quantities of the pores between the treatments. As the K concentration increased in $CROSS_{tr}15$, most of the effective pores decreased dramatic in both soils were destroyed and their vertical continuity reduced.

3. 5.2. Porosity and connectivity analysis

The effect of soil K concentration on the soil structure is illustrated using interconnected porosity and connectivity data calculated from 3D CT scan images. When the pores connectivity decreases, there is a decrease in air porosity and increase in bulk density leading to soil structural degradation (Speirs et al., 2011). Table 5 shows the calculated porosity and connectivity for treatments. Porosity and connectivity in $CROSS_{tr}$ 6 treated soils was higher compared with the water- treated soils, confirming the hydraulic conductivity results that at the low level of K^+, there is a beneficial effect on soil structure.However, there was a significant decrease in porosity and connectivity when $CROSS_{tr}$ 15 was applied to the soils.

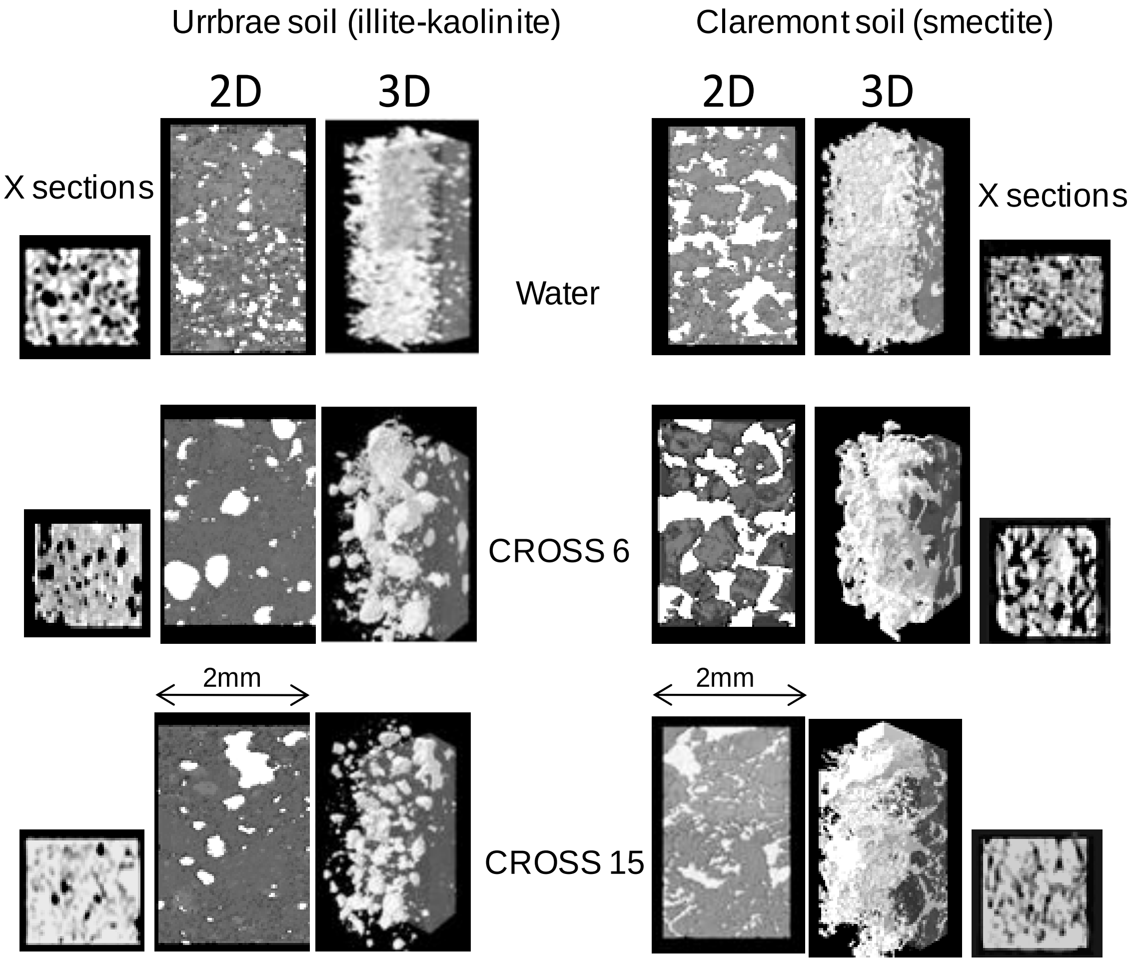


Fig.4. 2 D and 3D CT images and the cross sections (small blockes) showing pore space (white colour) for Urrbrae and Claremont soils treated with: (a)-deionised water, (b)- CROSS$_{tr}$ 6, (c)- CROSS$_{tr}$ 15.

Table 5 Pore size distribution, total porosity % and pore connectivity from quantified 3-D CT scan results, showing for Urrbrae and Claremont soils treated with water, CROSS$_{tr}$ 6 and CROSS$_{tr}$ 15.

Soil	Treatment	K^+ concentration	Total	Connectivity
Urrbrae	Water	0	23.5	39584
	CROSS$_{tr}$ 6	20	40.9	50438
	CROSS$_{tr}$ 15	60	20.6	21005
Claremont	Water	0	39.0	20313
	CROSS$_{tr}$ 6	20	51.0	24395
	CROSS$_{tr}$ 15	60	38.0	15182

3. 5.3. Comparison of soil pore sizes between the treatments

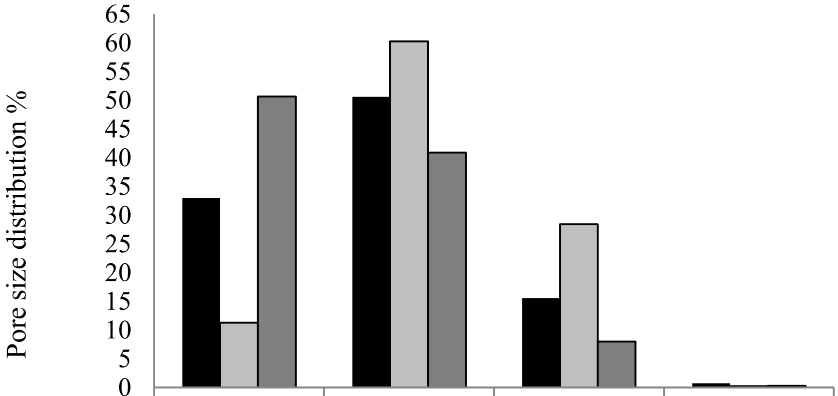
The desirable range of pore sizes and a good soil structure for plant glowth can be defined in terms of the presence of pores for the storage of water available to plants, pores for transmission of water and air, and pores in which roots can grow. However, there is little or no consensus for the definition and termonology used to classify micropore and macropores in the soil literature (Kwiecien, 1987; Perret et al., 1999).

Table 6 Soil pore diameters and functions Source: Oades (1984)

Pore diameter (µm)	Function	Terminology
0-17.4	Residual (very strong bound water, unavailable to plants)	Bonding pores, very fine and fine pores
17.4-69.2	Water holding capacity, plant available water	Effective pores
69.2-500	Infiltration, permeability	Water transmission pore
> 500		Fissures

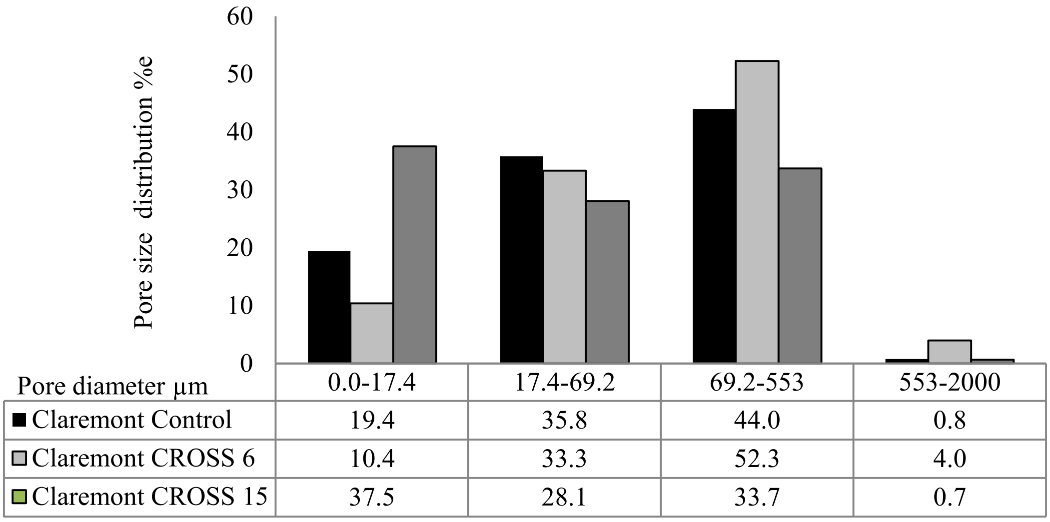
Table 6 provides a modified classification of the pore size diameters given by Oades (1984) on the basis of their functions in the soil system. This classification allowed assembly of the CT scan pore size distribution data into the functional groups. The groups were compared for the changes in soil pore structure between the treatments for Urrbrae and Claremont soils (Fig 5 and 6). The percentage of the effective pores (17.4-69.2μm) decreased dramatically with the increase in K^+ concentration in treatment solution ($CROSS_{tr}$ 15) while the percentage of the water bonding pores (0-17.4 μm) increased, indicating deterioration of soil structure in both soils. Treatment with $CROSS_{tr}$6 resulted in increased number the effective pores in both soils as compared to the treatment with water only.

All the results obtained from X-ray CT scan confirm the structural deterioration with the high concentration of K^+ in treatment solution in the both soils. The results also confirm that in soils treated with low K solutions had better structure than the soils treated with water only.



Pore diameter μm	0-17.4	17.4-69.2	69.2-553	553-2000
■ Urrbrae Control	33	50.6	15.6	0.73
□ Urrbrae CROSS 6	11.3	60.3	28.4	0.24
▨ Urrbrae CROSS 15	50.7	40.9	8.0	0.32

Fig.5. Pore size diameter distribution of the Urrbrae soil.



Pore diameter µm	0.0-17.4	17.4-69.2	69.2-553	553-2000
■ Claremont Control	19.4	35.8	44.0	0.8
□ Claremont CROSS 6	10.4	33.3	52.3	4.0
🟩 Claremont CROSS 15	37.5	28.1	33.7	0.7

Fig.6. Pore size diameter distribution of the Claremont soil.

4. Conclusions

Results obtained for hydraulic conductivity, turbidity, zeta potential, porosity and connectivity all confirm that increasing levels of potassium in soil solutions affect soil structure. There is an indication that at low levels of potassium soil structure may not be affected. The good correlations obtained between CROSS measured in soil solutions ($CROSS_{ss}$) and the parameters like turbidity and zeta potential support its use instead of SAR, PAR or MCAR in identifying soil structural stability influenced by cations. The present study also indicates the influence of soil type, especially clay content and mineralogy, in changing the effcts of potassium. Future studies are necessary to establish these influnces as well the role of electrolyte concentration in affecting soil structure in relation to CROSS.

Acknowledgements

We are grateful to Dr Jock Churchman of The University of Adelaide for several helpful discussions and comments.

Aoife McFadden of Adelaide Microscopy is thanked for her help with X-ray CT scan.

References

Arienzo, M., Christen, E.W., Quayle, W., Kumar, A., 2009. A review of the fate of potassium in the soil-plant system after land application of wastewaters. Journal of Hazardous Materials 164, 415-422.

ASTM, 1976. Annual Book of ASTM Standards, Part 31. Water", Standard D1889-71, p. 223.

Barzegar, A.R., Rengasamy, P., Oades, J.M., 1995. Effects of clay type and rate of wetting on the mellowing of compacted soils. Geoderma 68, 39-49.

Chen, Y., Banin, A., Borochovitch, A., 1983. Effect of potassium on soil structure in relation to hydrolic conductivity. In: Bisdom, E.B.A., Ducloux, J. (Eds.), Submicroscopic studies of soils. Elsevier, Amstetrdam-Oxford-new York-Tokyo, pp. 135-147.

Churchman, G.J., 2002. Formation of complexes between bentonite and different cationic polyelectrolytes and their use as sorbents for non-ionic and anionic pollutants. Applied Clay Science 21, 177-189.

Dexter, A.R., Richard, G., 2009. The saturated hydraulic conductivity of soils with n-modal pore size distributions. Geoderma 154, 76-85.

Eaton, A.D., Franson, M.A.H., 2005. Standard Methods for the Examination of Water & Wastewater. American Public Health Association.

El Swaify, S.A., Ahmed, S., Swindale, L.D., 1970. Effect od adsorbed cations on physiscal properties of tropical red and tropical black earths. Journal of Soil Science 21, 188-198.

Gee, G.W., Bauder, J.W., 1986. Particle Size Analysis. In: A.Klute (Ed.), Method of Soil Analysis. Madison, Wisconsin USA, Wisconsin, USA, pp. 383-411.

Hazelton, P., Murphy, B., 2007. Interpreting soil test results: what do all the numbers mean? CSIRO Publishing, Australia.

Hunter, R.J., 1981. Zeta Potential in Colloid Science principles and applications. Academic Press, London, New York.

Isbell, R.F., 2002. The Australian Soil Classification. Australian Soil and Land Survey Handbook Series 4. CSIRO Publishing, Melbourne.

Jackson, M.L., 2005. Soil Chemical Analysis: Advanced course. University of Wisconsin–Madison.

Jassogne, L., McNeill, A., Chittleborough, D., 2007. 3D-visualization and analysis of macro- and meso-porosity of the upper horizons of a sodic, texture-contrast soil. European Journal of Soil Science 58, 589-598.

Kwiecien, M.J., 1987. Determination of pore size distribution of berea sandstone through three dimentional reconstruction. M.S.thesis. Univ. Waterloo Ontario, Canada.

Marchuk, A., Rengasamy, P., 2011. Clay behaviour in suspension is related to the ionicity of clay–cation bonds. Applied Clay Science 53, 754-759.

Mooney, S.J., 2002. Three-dimensional visualization and quantification of soil macroporosity and water flow patterns using computed tomography. Soil Use and Management 18, 142-151.

Oades, M., 1984. Soil organic matter and structural stability: mechanisms and implications for management Plant and Soil.

Perret, J., Prasher, S.O., Kantzas, A., Langford, C., 1999. Three-Dimensional Quantification of Macropore Networks in Undisturbed Soil Cores. Soil Science Society of America Journal 63, 1530-1543.

Quirk, J.P., Schofield, R.K., 1955. The Effect of Electrolyte Concentration on Soil Permeability. European Journal of Soil Science 6, 163-178.

Rayment, G., Lyons, D., 2011. Soil Chemical Methods-Australasia. CSIRO Publishing, Collingswood.

Reeve, R.C., Bower, C.A., Brooks, R.H., Gschwend, F.B., 1954. A Comparison of the Effects of Exchangeable Sodium and Potassium upon the Physical Condition of Soils. Soil Sci Soc Am J 18, 130-132.

Rengasamy, P., 2002. Clay Dispersion. In: McKenzie, B.M., Coughlan, K., Cresswell, H. (Eds.), Soil Physical Measurement and Interpretation for Land Evaluation. CSIRO Publishing, Collingwood, pp. 200-210.

Rengasamy, P., 2010. Soil processes affecting crop production in salt-affected soils. Functional Plant Biology 37, 613-620.

Rengasamy, P., Churchman, G.J., 1999. Cation exchange capacity, exchangeable cations and sodicity. In: Peverill, K., Sparrow, L., Reuter, D. (Eds.), Soil Analysis and Interpretation Manual. CSIRO Australia, pp. 147-155.

Rengasamy, P., Greene, R., Ford, G.W., Mehanni, A.H., 1984. Identification of dispersive behaviour and the management of red- brown earths. Australian Journal of Soil Research 22, 413-431.

Rengasamy, P., Marchuk, A., 2011. Cation ratio of soil structural stability (CROSS). Soil Research 49, 280-285.

Rengasamy, P., Sumner, M.E., 1998. Processes Involved in Sodic Behaviour. In: Sumner, M.E., Naidu, R. (Eds.), Sodic Soils. Distribution, Properties, Management, and Environmental Consequences. New York Press., New York, pp. 35-50.

Robbins, C.W., 1984. Sodium adsorption ratio-exchangeable sodium percentage

Robbins, W., 1984 Sodium Adsorption Ratio-Exchangeable Sodium Percentage Relationships in a High Potassium Saline-Sodic Soil. Irrigation Science., 173-179.

Schofield, R.K., 1947. A ratio law governing the equilibrium of cations in soil solutions. Proc. 11th Int.Cogr.Pure Appl. Chem. 3, 257-61.

Smiles, D., Smith, C., 2004. A survey of the cation content of piggery effluents and some consequences of their use to irrigate soil. Australian Journal of Soil Research 42, 231-246.

Smiles, D.E., 2006. Sodium and potassium in soils of the Murray-Darling Basin: a note. Australian Journal of Soil Research 44, 727-730.

Speirs, S.D., Cattle, S.R., Melville, G.J., 2011. Impact of sodium adsorption ratio of irrigation water on the structural form of two Vertosols used for cotton production. Soil Research 49, 481-493.

Subba Rao, A., Rao, C.S., 1996. Potassium Status and Crop Response to Potassium on the Soils of Agro-ecological Regions of India. International Potash Institute. IPI Research Topics No 20, pp. 1-57.

Sumner, M.E., 1993. Sodic soils - New perspectives. Australian Journal of Soil Research 31, 683-750.

Tisdall, J.M., Oades, J.M., 1982. Organic matter and water-stable aggregates in soils. Journal of Soil Science 33, 141-163.

Vogel, H.J., 2000. A numerical experiment on pore size, pore connectivity, water retention, permeability, and solute transport using network models. European Journal of Soil Science 51, 99-105.

Chapter 4 Clay behaviour in suspension is related to the ionicity of clay –cation bonds

Alla Marchuk and Pichu Rengasamy

Soil Science, The University of Adelaide, SA 5064, Australia.

Published in Applied Clay Science 53, (2011) 754-759

Statement of Authorship

Marchuk, Alla (Candidate)

Contributed to the quantitative theoretical development, established the methodology, data collection and analysis, preparation of the tables and figures, writing and compilation of the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 21 \ 02 \ 2013

Rengasamy, Pichu (Principal Supervisor)

Contributed to the theoretical and quantitative developments, supervised, reviewed and edited manuscript.

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 22/02/2013

This chapter is an exact copy of the journal paper referred to above.

Marchuk, A. & Rengasamy, P. (2011) Clay behaviour in suspension is related to the ionicity of clay-cation bonds.
Applied Clay Science, v. 53(4), pp. 754-759

NOTE:
This publication is included on pages 95-100 in the print copy of the thesis held in the University of Adelaide Library.

It is also available online to authorised users at:

http://doi.org/10.1016/j.clay.2011.05.019

Chapter 5 Nature of the clay-cation bond affects soil structure as verified by X-ray computed tomography

Alla Marchuk [a], *Pichu Rengasamy* [a], *Ann McNeill* [a] *and Anupama Kumar* [b]

[a] Soil Science, School The University of Adelaide, SA 5064, Australia.

[b] CSIRO Land and Water, Waite Campus, PMB2, Glen Osmond, SA 5064, Australia.

Published in Soil Research 2012, 50 pp. 638-644

Statement of Authorship

Marchuk, Alla (Candidate)
Established the methodology, laboratory and CT scanning data collection and analysis, preparation of the tables and figures, writing and compilation of the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 21\02\2013

Rengasamy, Pichu (Principal Supervisor)
Supervised and assisted in establishing the methodology, writing and editing of manuscript.

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 22/02/2013

McNeill, Ann (Co-Supervisor)
Supervised evaluation of CT scanning, reviewed and edited manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 21/02/2013

Kumar, Anupama
Contributed to the progress of CT scanning, reviewed the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 21|02|2013

This chapter is an exact copy of the journal paper referred to above.

Marchuk, A. Rengasamy, P., McNeill, A. & Kumar, A. (2012) Nature of the clay-cation bond affects soil structure as verified by x-ray computed tomography.
Soil Research, v. 50(8), pp. 638-644

Chapter 6 Cation ratio of soil structural stability

Pichu Rengasamy and Alla Marchuk

Soil Science, The University of Adelaide, SA 5064, Australia.

Published in Soil Research, 2011, 49, p 280-285

Statement of Contribution of Joint Authorship

Rengasamy, Pichu (Principal Supervisor)

Formulation of the theoretical concept of the CROSS, writing and editing of manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 22/02/2013

Marchuk, Alla (Candidate)

Experimental work, data collection and analysis, preparation of tables and figures

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 21\02\2013

This chapter is an exact copy of the journal paper referred to above.

Rengasamy, P. & Marchuk, A. (2011) Cation ratio of soil structural stability (CROSS).
Soil Research, v. 49(3), pp. 280-285

Chapter 7 Threshold electrolyte concentration and dispersive potential in relation to CROSS in dispersive soils

Alla Marchuk, Pichu Rengasamy and Ann McNeill
Soil Science, The University of Adelaide, SA 5064, Australia.

Published in Soil Research, 2012, 50, 6, 473-481.

Statement of Authorship

Marchuk, Alla (Candidate)

Established methodology, data collection and analysis, preparation of the tables and figures, writing and compilation of the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 21\02\2013

Rengasamy, Pichu (Principal Supervisor)

Supervised and assisted in establishing methodology, writing and editing of manuscript.

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 22/02/2013

McNeill, Ann (Co-Supervisor)

Supervised manuscript evaluation, reviewed and edited manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date**

21/02/2013

This chapter is an exact copy of the journal paper referred to above

Marchuk, A. & Rengasamy, P. (2012) Threshold electrolyte concentration and dispersive potential in relation to CROSS in dispersive soils.
Soil Research, v. 50(6), pp. 473-481

Chapter 8 The influence of organic matter, clay mineralogy and pH on the effects of CROSS on soil structure is related to the zeta potential of the dispersed clay

Alla Marchuk,, Pichu Rengasamy and Ann McNeill,

Soil Science The University of Adelaide, SA 5064, Australia.

Submitted to Soil Research in January 2013. In Press.

Statement of Authorship

Marchuk, Alla (Candidate)

Established methodology, data collection and analysis, preparation of the tables and figures, writing and compilation of the manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 21\02\2013

Rengasamy, Pichu (Principal Supervisor)

Supervised and assisted in establishing the methodology, writing and editing of manuscript.

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 22/02/2013

McNeill, Ann (Co-Supervisor)

Supervised manuscript evaluation, reviewed and edited manuscript

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed **Date** 21/02/2013

This chapter is an exact copy of the journal paper referred to above.

Influence of organic matter, clay mineralogy and pH on the effects of CROSS on soil structure is related to the zeta potential of the dispersed clay

Alla Marchuk, Pichu Rengasamy and Ann McNeill,

Soil Science, School of Agriculture, Food and Wine, Waite Campus, The University of Adelaide, SA 5064, Australia.

Abstract

The high proportion of adsorbed monovalent cations in soils in relation to divalent cations affects soil structural stability in salt-affected soils. Cationic effects on soil structure depend on the ionic strength of the soil solution. The relationships between CROSS (cation ratio of soil structural stability) and the threshold electrolyte concentration (TEC) required for the prevention of soil structural problems vary widely for individual soils even within a soil class, usually attributed to variations in clay mineralogy, organic matter and pH. The objective of the present study was to test the hypothesis that clay dispersion influenced by CROSS values depends on the unique association of soil components, including clay and organic matter, in each soil affecting the net charge available for clay-water interactions.

Experiments, using four soils differing in clay mineralogy and organic carbon, showed that clay dispersion at comparable CROSS values depended on the net charge (measured as negative zeta potential) of dispersed clays rather than the charge attributed to the clay mineralogy and/or organic matter. The effect of pH on clay dispersion was also dependant on its influence on the net charge. Treating the soils with NaOH dissolved the organic carbon and increased the pH, thereby increasing the negative zeta potential and hence, clay dispersion, whereas, treatment with calgon (sodium hexa-meta phosphate) did not dissolve organic carbon significantly or increase the pH. However, the attachment of hexa-meta phosphate with six charges on each molecule greatly increased the negative zeta potential and clay dispersion. A high correlation (R^2 =0.72) was obtained between the relative clay content and relative zeta potential of all soils with different treatments, confirming the hypothesis that clay dispersion due to adsorbed cations depends on the net charge available for clay-water interactions. The distinctive way in which clay minerals and organic matter are associated and the changes in soil chemistry affecting the net charge cause the CROSS-TEC relationship to be unique for each soil.

Additional keywords: cation ratio of soil structural stability, SAR, turbidity

Introduction

High proportions of monovalent cations, sodium (Na) and potassium (K), in relation to divalent ions, calcium (Ca) and magnesium (Mg), in salt-affected soils affect soil structural integrity and cause severe constraints to crop production when the ionic strength of the soil solution is lower than that causing osmotic stress to the plants (Rengasamy 2010). Currently, in evaluations of the effect of salt on soil structure, the focus is mainly on the concentration of Na with the usage of parameters sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP). However, recent reports on the occurrence of significant amounts of K in soils and waste waters used for irrigation in Australia (e.g. Smiles 2006; Arienzo *et al*. 2009; Laurenson *et al*. 2012), encourage attention on the effects of K on soil structure. Further, the differential effects of Ca and Mg in their flocculating powers are also known (e.g. Rengasamy and Sumner 1998). Marchuk and Rengasamy (2011), on the premise that water stability of soil aggregates depends on the degree of ionicity of clay-cation bonding, derived the ionicity indices of monovalent and divalent cations in relation to their bonding with clay particles and showed that these indices dictate clay behaviour in aqueous suspensions. Due to differences in ionicity indices, the dispersive effects of Na and K, and the flocculating powers of Ca and Mg will differ. Based on these concepts a new ratio 'CROSS' (cation ratio of soil structural stability) analogous to SAR was proposed (Rengasamy and Marchuk, 2011) which incorporates the differential effects of Na and K in dispersing soil clays, and also the differential effects of Mg and Ca in flocculating soil clays. This is defined as: CROSS = (Na + 0.56K) / $[(\mathrm{Ca} + 0.6\mathrm{Mg})/2]^{0.5}$ where the concentrations of these ions are expressed in millimole of charge/L. The coefficient of K was based on the ratio of the dispersive powers (reciprocal of flocculating powers) of Na and K, and the coefficient of Mg was based on the ratio of flocculating powers of Ca and Mg. The flocculating powers of all these cations have been derived theoretically and verified experimentally by Rengasamy and Sumner (1998).

Cationic effects on soil structural features such as clay dispersion and hydraulic conductivity are dependent on the ionic strength of the soil solution. Threshold electrolyte concentration (TEC) which completely prevents dispersion for a given cationic suite defined by SAR or CROSS (e.g. Quirk and Schofield 1955; Rengasamy *et al.*1984; Marchuk and Rengasamy 2012) allows one to distinguish osmotic salinity effects from the soil structural stability effects in salt-affected soils. However, TEC obtained by relating SAR or CROSS with EC (electrical conductivity) in solutions of dispersed and flocculated soils differs widely for soils even within a soil type because of the differences in soil factors including clay mineralogy, organic matter and pH (Rengasamy and Olsson 1991; Marchuk and Rengasamy 2012). Similarly, the slope of the correlations between CROSS (or SAR) and the amount of dispersed clay vary with clay type, organic matter and pH (Marchuk and Rengasamy 2011; Chorom and Rengasamy 1995; Emerson and Smith 1970). Net charge on soil particles is responsible for water interaction leading to structural instability (Rengasamy and Sumner 1998). Non-charged soil components including organic moieties do not react with water. Similarly, in variable charge soils, the clay particles do not disperse at pH values where net charge is zero.

Generally, the cation exchange capacity (CEC) reflecting the charge on soil depends on clay minerals and organic matter contents. Modification of this charge by pH variations is also well known (e.g. Chorom and Rengasamy 1995). However, the methods of estimating CEC destroy the natural soil aggregation, and hence the real charge available on natural aggregates for water interaction will not be indicated by CEC or the charge estimated by individual clay minerals or organic matter. Previous studies (Chorom and Rengasamy 1995; Marchuk and Rengasamy 2011) have shown that zeta potential of the dispersed clays is closely related to the dispersion-flocculation phenomena.

The present investigation aimed to define the relationship between CROSS and clay dispersion in relation to mineralogy, organic matter and pH in four soils with different mineralogical composition and organic matter content. The relevance of the zeta potential of the dispersed clays to the relationship between CROSS and dispersed clay was also investigated.

Materials and methods.

Soils used

Four soils viz. Urrbrae, McLaren, Claremont and Keilira were used in the present study. Selection of these soils was based on differences in their clay mineralogy, texture, pH, EC, effective cation exchange capacity (CEC_{eff}) and zeta potential measured on clay < 2μm clay fractions obtained from the soils without preliminary chemical treatment by the method described in Churchman (2002). The soil samples were taken by a hand auger, air-dried, sieved to 2 mm particle diameter and analysed for physical and chemical characteristics.

Soil particle size distribution (Gee and Bauder 1986), soluble and exchangeable cations (Rayment and Lyons 2011), total carbon by Dumas high temperature combustion method (Rayment and Lyons 2011), organic carbon (Walkley and Black 1934), clay mineralogy by X-ray diffraction and zeta potential of dispersed clays (Marchuk and Rengasamy 2011) were measured and are presented in Table 1. Water dispersible clay (WDC) was determined in the same way as particle size analysis except that the samples were dispersed with water without any pre-treatment to remove cementing compounds, and without use of dispersive agents.

Physico-chemical properties and locations of the soils are presented in Table 1.

Experiment 1 *Soil pre- treatment*

Two soils were chosen for the experiment 1: Urrbrae and Claremont. Percolating solutions were prepared using 0.1M chloride solutions of Ca, Mg, K and Na at predetermined concentrations to obtain $CROSS_{tr}$ values of 6, 8, 11, 15, but all having the same SAR of 1.2.

Soil samples were evenly packed into Plexiglas (Evonik Industries, Essen, Germany) (6 cm in diameter and 10 cm long) at a bulk density of 1.33 Mg/m^3. Both column ends

Table 1. Selected physical and chemical properties, main clay minerals, and soil location of the soils used

Soil properties	Units	Soil			
		Urrbrae	Mc Laren	Claremont	Keilira
Depth	cm	15-40	15-40	15-40	15-40
pH (1:5 soil water)		6.7	7.3	8.3	9.7
EC (1:5 soil water)	dS/m	0.061	0.139	1.03	1.03
Total carbon	%	1.5	0.8	4.0	4.6
Organic carbon	%	1.4	0.3	2.2	2.4
CEC_{eff}	cmol kg^{-1}	8	10	33	30
Zeta potential	mV	-38	-42	-19	-25.6
Dominant clay minerals		Illite-kaolinite	Illite -kaolinite	Smectite	Smectite
Taxonomic class [A]		Red Chromosol	Red-Brown Earth	Vertisol	Vertisol
Texture		Sandy loam	Clay-loam	Clay	Clay
Clay content	%	40	45	60	40
Water dispersible clay (WDC)	%	26	32	6	26
Location in South Australia		34°58’S 138°38’ E Waite Research Institute	35°15’ S 138°33’ E McLaren Vineyard	34°58’” S 138°38’” E Waite Research Institute	36°71’S 140°16’ E Keilira District South Australia

[A] Australian Soil Classification (Isbell 2002)

were fitted with nylon mesh screens with a double disk of gauze mesh on the top of the soil to reduce surface disturbance. Initially the columns were wetted with the treatment solutions to saturation for 24 hours from the base by slow capillary rise and then the flow direction was reversed. The columns were percolated with three wetting, draining and drying cycles using each of four CROSS treatment solutions (CROSS_{tr}) for each soil. For each cycle, 1 L of one of the CROSS_{tr} solutions was percolated and then the soils were allowed to drain and dry for 1 week. The experiments were conducted using triplicate samples. The cation concentration of the treatment solutions are presented in Table 2.

Table 2 Attributes of each treatment solution ($CROSS_{tr}$) and potassium concentration in $CROSS_{tr}$ solutions.

Treatment No	Cations in treatment solutions (mmol$_c$/L)				TCC (mmol$_c$/L)	SAR_{tr}	$CROSS_{tr}$
	K	Na	Ca	Mg			
1	20	3.2	5.4	10	38.6	1.2	6.0
2	30	3.2	5.4	10	48.6	1.2	8.4
3	42	3.2	5.4	10	60.6	1.2	11.2
4	60	3.2	5.4	10	78.6	1.2	15.4

*$CROSS_{tr}$ was calculated from the cation concentrations

After completion of the treatment cycles, the soils were removed from the columns, air dried, crushed and passed through a 2-mm sieve. These final soils were then analysed for spontaneous dispersion, Zeta potential on separated clays and other selected properties such as $EC_{1:5}$, pH $_{1:5}$, CROSS of soil solutions ($CROSS_{ss}$) and exchangeable cation ratio (ECR %).

Soluble and Exchangeable cations

The EC, pH and soluble cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) concentrations (mmol$_c$ /L^{-1}) were determined using extracts from 10g of final soil in 50ml deionised water, and $CROSS_{ss}$ of the final soil solutions were calculated using the following equations:

$$CROSS_{ss} = (Na + 0.56K) / [(Ca + 0.6Mg)/2]^{0.5} \qquad (1)$$

where the concentrations of the corresponding ions are expressed in millimole of charge/L.

The exchangeable cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) were determined after soluble salts were removed by washing each of soil sample with 250ml of 60% ethanol until the electrical conductivity of the soil suspensions was below 0.05dS m^{-1}.

The exchangeable cations were extracted with 250 ml of 0.1MNH_4Cl adjusted to pH 7 for the Urrbrae soil and to pH 8.2 for the Claremont soil. The process was repeated a further two times and all the extracts collected and analysed for the exchangeable cations by inductively coupled plasma –atomic emission spectroscopy (ICP-AES) (Jackson 2005; Rayment and Lyons 2011). Subsequently, the effective cation exchange capacities (CEC_{eff}) and exchangeable cation ratio percentage (ECR %) were calculated as:

$$CEC_{eff} = (\sum \text{exch } Na^+, K^+, Mg^{2+} \text{ and } Ca^{2+}) \qquad (2)$$

$$ECR\ \% = [(Na^+ + K^+) / CEC_{eff})] \times 100 \qquad (3)$$

where the quantities of the exchangeable cations are expressed in $cmol_c/kg$.

Spontaneous dispersion and turbidity measurements

Spontaneous dispersion was assessed by a modification of the method described by Rengasamy (2002). Samples (20g) of dry final soils were placed into 250 ml transparent measuring cylinders and 200 ml of distilled water was added slowly down the sides of the cylinders, taking care to avoid disturbance of the soil. After approximately 5 hr, any particles which had dispersed form the soils were gently stirred into suspension and left to stand for 2 hours. Suspensions were pipetted out from 10 cm depth for turbidity measurements.

To quantify the amount of < 2µm particles dispersed, measurements were made on a Hach 2100N Laboratory Turbidimeter at 25°C and recorded in Nephelometric Turbidity Units (NTU).

Electrophoretic mobility and zeta potential

The zeta potential (*ζ)* was measured on < 2μm particles by laser Doppler velocimetry on a Malvern Zeta master Particle Electrophoresis Analyser. The correlation functions were measured automatically and zeta potential calculated by Malvern Control Software v1.23a. Prior to injection of the sample, cell alignment and set up of the system were performed and the operating conditions of the instrument were checked and calibrated using a DTS 5050 Electrophoretic Standard. The intensity (kilo counts/second) of each clay sample was measured prior to the readings to ensure the compatibility of the samples. The zeta potentials (ζ) were calculated as the mean of ten runs, each of which was averaged over 25 individual measurements performed automatically by the instrument.

Experiment 2

Soil samples of Urrbrae and Claremont soils pre-treated with the CROSS_{tr} 11 were dried and resuspended at 10g in distilled water and adjusted to the 4 desired pH values with 0.1M HCl and NaOH (Chorom and Rengasamy 1995). After 14 hours the suspension pH was measured. Turbidity and zeta potential were measured as described above.

Experiment 3

Four soils, McLaren, Urrbrae, Claremont and Keilira were used in this study. 40 g of soil was treated with different treatment solutions, intended to change organic carbon content, as described in Table 6 and shaken for 24 hours. The solutions were transferred to measuring cylinders and made up to 1000ml with water, allowing to stand for 30 minutes to thermally equilibrate. A hydrometer was used on the suspension and a readings taken after 5 hours to determine clay content (Gee and Bauder, 1986). Zeta potential was measured on clays particles < 2µm. Dissolved organic carbon was measured using Shimadzu UV-1601 spectrophotometer at 254nm by the method described in Deflandre and Gagne (2001). Clay content estimated as a measure of clay dispersion. Relative zeta potential (ζ_{rel}) and relative clay content were calculated in relation to the highest value for each four soil to compare the effect of treatments.

Results and Discussion

Relationships between CROSS, Turbidity and Zeta potential

The two soils, Urrbrae and Claremont, were treated with solutions of different CROSS_{tr} values, viz. 6,8,11 and 15 and after equilibrium, the excess salts were washed. The values of different parameters meseaured in the treated soils are given in Table 3. The CROSS_{ss} values in 1:5 extracts are lower than the values of corresponding treatment solutions while pH remains nearly constant. The turbidity, ECR% and zeta potential increase with increasing CROSS_{ss} while the changes in SAR and ESP are not significant. In individual soil, CROSS_{ss} is highly correlated with turbidity, zeta potential and ECR% (Table 4), as observed in previous work (Marchuk and Rengasamy 2012). The results in the present study also confirm that these relationships are unique to each soil. Claremont soil with smectite as the major component of the clay fraction and higher CEC than the Urrbrae soil with illite and kaolinite dispersed less than Urrbrae soil at comparable CROSS_{ss} values. This was reflected in the zeta potential values of dispersed clays from Claremont soil and it was hypothesised that high organic carbon in

Claremont soil had a role in reducing the net charge on soil surfaces and influencing the clay dispersion. Hence, experiment 3 was undertaken.

Table 3 pH, Electrical conductivity (EC), cation ratio of structural stability (CROSS), Excahngeable cation ratio (ECR %), Sodium Adsorption Ratio (SAR), exchangeable sodium percentage (ESP), Turbidity and zeta potential measured in the treated soils

Soil	CROSS$_{tr}$	pH (1:5)	EC (1:5) dS/cm	CROSS$_{ss}$ in soil solution	ECR (%)	SAR	ESP (%)	Turbidity (NTU)	Zeta(ζ) mV
Urrbrae	6	7.5	0.04	1.2	41.4	0.36	1.65	980	-51
	8	7.2	0.06	1.5	46.9	0.48	2.26	1270	-55
	11	7.3	0.04	1.5	52.1	0.47	2.54	2680	-59
	15	7.3	0.05	1.9	61.4	0.66	2.51	3980	-62
Claremont	6	8.6	0.18	1.7	18.1	0.69	0.39	560	-27
	8	8.7	0.2	1.9	20.7	0.67	0.53	876	-29
	11	8.8	0.26	2.8	26.2	0.92	0.53	1560	-32
	15	8.9	0.32	3	31.6	0.45	0.53	2270	-34

Table 4 Statistical results of linear regression between CROSS$_{ss}$ of the final soil solutions and exchangeable cation ratio (ECR%), turbidity and Zeta potential

Soil	X	Y	Regression equation	R^2
Urrbrae	CROSS ss	Turbidity	4462.2X-4493	0.81
		Zeta potential (ζ)	16.07X+32	0.88
		ECR %	29.48X+5.9	0.94
Claremont	CROSS ss	Turbidity	1131.6X-1348.3	0.91
		Zeta potential (ζ)	4.63X+19.5	0.96
		ECR %	8.98X+2.9	0.92

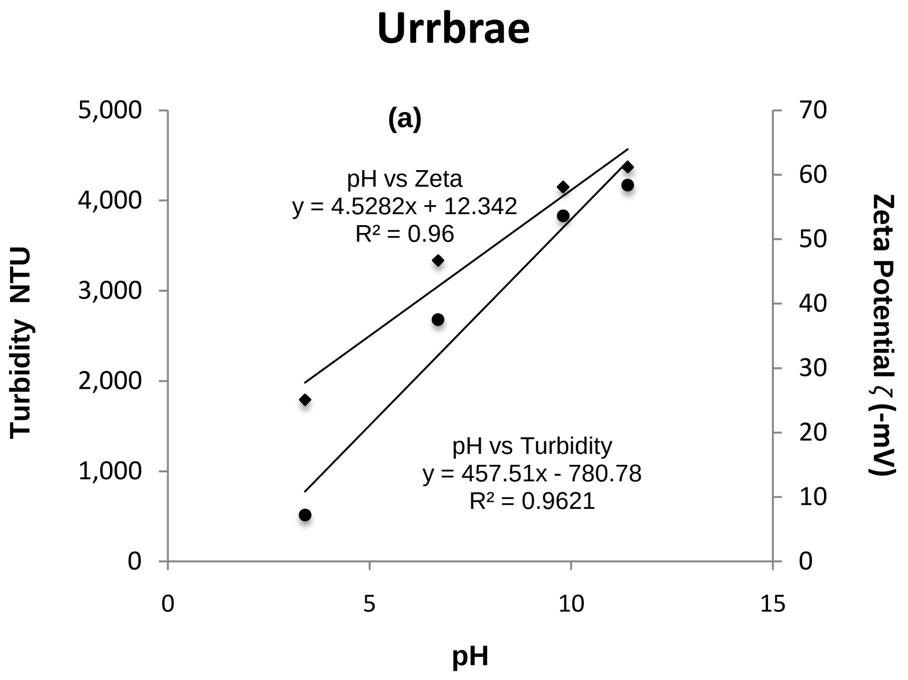
*Statistical calculations and linear regression analysis were performed with the programme Graphpad Prism version 5.01(GraphPad Software, Inc., San Diego, USA).

The effect of pH on clay dispersion and zeta potential

Variations in pH have been found to affect clay dispersion in pure clay minerals (e.g. Arora and Coleman 1979; Chorom and Rengasamy 1995) and in soils (e.g. Suarez *et al.* 1984; Chorom *et al.*1994). The effect of pH on the electrical potential of the clay surfaces can be related to the amount of variable charge on the external surface of the clay particles. Earlier studies (Chorom *et al*. 1994) have shown that net negative charge is the primary factor in clay dispersion, and that pH affects clay dispersion by changing the net charge on clay particles. While the previous studies focussed on sodium saturated clays or soils, in the present experiment we used soils treated with a solution of multiple cations including higher concentration of potassium and low levels of sodium. The results (Table 5) clearly show that in both soils (Urrbrae and Claremont), as the pH increases both turbidity (clay dispersion) and negative zeta potential (reflecting the net charge on clay particles) increase. Higher negative charge with increasing pH in Claremont soil could be also due to high organic carbon content. Helling *et al*. (1964), analysing 60 Wisconsin soils, showed a linear increase in CEC contributed by organic matter with increasing pH. Figure 1 shows the significant correlation between pH and turbidity as well as between pH and zeta potential, for both soils Urrbrae and Claremont. The slopes of these regressions for each soil are different indicating that the pH effect is controlled by the type of clay minerals and perhaps, organic matter.

Table 5 Effect of pH of soils treated with the solution of CROSS 11 on clay dispersibility (measured as turbidity) and zeta potential

Soil	pH (1:5)	Turbidity (NTU)	Zeta (ζ) (mV)
Urrbrae	3.4	517	-25.1
	6.7	2680	-46.7
	9.8	3830	-58.1
	11.4	4170	-61.2
Claremont	6.9	200	-15.6
	7.7	1230	-21.7
	9.3	3047	-28.6
	11.6	9760	-38.8



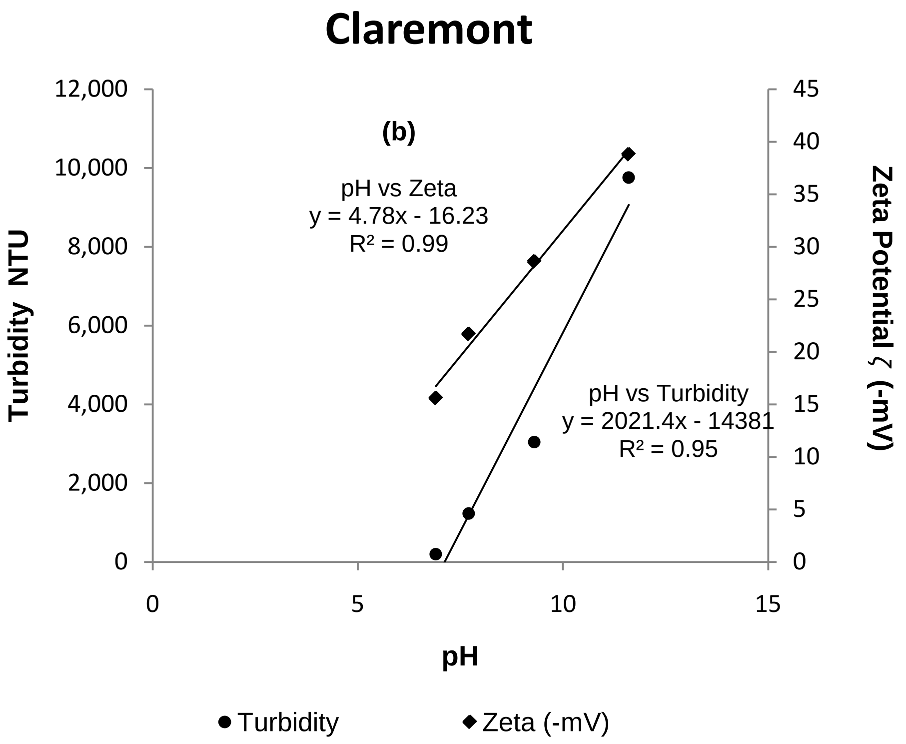


Fig. 1 Turbidity and Zeta potential as a function of the pH in suspension for (a) Urrbrae soil, (b) Claremont soil.

The role of organic matter in clay dispersion

While both organic matter and clay contribute to the CEC of soils and hence, promote water interactions, they cannot be considered as uniform entities and interactions between them have major influence on clay dispersion (Nelson and Oades 1998). An earlier report (Marchuk and Rengasamy 2012) and the results in the present study (Table 3) indicate that in Claremont soil, despite smectite mineralogy, clay dispersion was lower than in the soils with illite-kaolinite mineralogy. The negative zeta potential of the dispersed clay was also lower than expected for smectite minerals. Previous work (Marchuk and Rengasamy 2012) hypothesized that when organic matter is high in soils, water interaction leading to clay dispersion is minimal because charge on clays is reduced by clay-organic bonds, which are mostly covalent, or soil aggregates are enveloped by organic materials formed by covalent bonding. To test this hypothesis, four soils with different organic carbon content were treated with different solutions which can affect the solubility of organic matter and subsequently the amount of clay dispersed, the zeta potential of dispersed clay and the residual organic carbon were measured (Table 6).

Treatments with NaCl or KCl caused minor dissolution of organic carbon in all four soils. The exchange of Na from NaCl led to higher clay content (due to dispersion) compared to the exchange of K from KCl. This confirmed earlier observations in this work that exchangeable K leads to dispersion but less than the effects of Na.

However, when treated with NaOH, in all four soils, organic carbon dissolved to a great extent with an increase in pH >10.5. This caused to the increase in clay content by 1.6 times in Claremont soil and 2.7 times in Keilira soil, compared to NaCl treatment. These two soils were high in organic carbon and NaOH treatment reduced organic carbon by 8.6 times in Claremont and 4.1 times in Keilira soils. Correspondingly, negative zeta potential of the dispersed clays increased 1.2 times in Claremont and 1.13 times in Keilira soils. Whereas, in McLaren and Urrbrae soils with illite-kaolinite mineralogy and low organic carbon, NaOH treatment dissolved larger proportions of organic carbon with simultaneous increase in clay content and negative zeta potential of the dispersed clay. The dissolution of organic carbon in all these soils has exposed the negative charge on clays by removing clay-organic bonds. The increase in negative charge, also contributed to by the increased pH, is reflected in the increase in negative zeta potential of the dispersed clays and is responsible for the increase in clay dispersion.

The treatment with calgon (sodium hexa-meta phosphate) solutions, in all four soils, increased clay dispersion, which became greater with increasing amount of calgon added, and concurrently the negative zeta potential increased. The dissolution of organic carbon with calgon alone was very low compared to NaOH treatments. Notably, the negative zeta potentials of the dispersed clays in all soils from calgon treatments were very high although the pH of these soils did not increase significantly from those of the original soils (Table 6). The six negative charges on each molecule of sodium hexa- meta phosphate attached to the clay surfaces increased the net charge to very high values and the clay dispersion.

For NaOH treatment, the pH values were higher in McLaren and Urrbrae soils than for the Claremont and Keilira soil, however, the clay content of the McLaren and Urrbrae were very low comparing to the Claremont soil, the results were inverse for Keilira. The reason may be that McLaren and Urrbrae soils had illite and kaolinite which had high pH-dependant charge, while Claremont soil has smectite which does not have high pH-dependant charge. Dissolution of more organic matter in Claremont soil compared to Keilira soil can partially explain the difference in clay content between them (Table 6).

Thus, the role of organic matter in reducing clay dispersion due to adsorbed monovalent cations appears to be in reducing the negative charge available for water interactions. The high correlation ($R^2 = 0.72$; Figure 2) between relative clay content (dispersed clay) and the relative zeta potential, including the data for all soils and all treatments, confirm the hypothesis that clay dispersion due to adsorbed cations depends on the charge available for water interactions irrespective of mineralogy, organic matter and pH of the soils (Figure 2). The net charge on soil surfaces, available for water interaction, depends on the unique association of clay minerals and organic matter in addition to the pH effects on the net charge.

Table 6 Selected properties of soils after treated with different solutions: electrical conductivity (EC), pH, Clay content % , relative clay content compared to NaOH treatment, Zeta potential, relative zeta potential and residual organic carbon (OC)%

Treatment	EC	pH	Clay content ^{A} %	Zeta(ζ) (-mV)	Zeta (ζ) $_{rel}$	Clay $_{rel}$	Residual OC %
McLaren							
20 ml NaOH	1.16	11.7	32.5	73.9	1.00	0.72	0.03
5 ml calgon	0.43	6.9	32.5	71.9	0.97	0.72	0.06
10ml calgon	0.78	6.7	30.0	70.2	0.95	0.72	0.07
25 ml calgon	1.80	6.5	30.0	71.6	0.97	0.83	0.05
0.1M NaCl	0.36	6.8	22.5	48.5	0.66	0.61	0.26
0.1M KCl	0.61	6.6	8.8	41.4	0.56	0.28	0.30
Urrbrae							
20 ml NaOH	1.05	11.4	35.5	68.0	0.87	0.92	0.10
5 ml calgon	0.42	6.7	33.8	72.0	0.93	0.99	0.87
10ml calgon	0.81	6.6	35.0	74.6	0.96	1.08	0.85
25 ml calgon	1.46	6.6	37.5	75.0	0.96	1.02	1.32
0.1M NaCl	0.27	6.1	22.8	66.3	0.85	0.84	1.40
0.1M KCl	0.71	5.8	16.3	61.7	0.79	0.66	1.43
Claremont							
20 ml NaOH	1.80	10.5	40.0	34.9	0.63	0.62	0.30
5 ml calgon	0.30	7.9	41.0	33.3	0.59	0.68	2.50
10ml calgon	0.66	8.1	46.0	38.2	0.68	0.77	2.35
25 ml calgon	1.36	8.2	50.0	46.0	0.81	0.83	2.12
0.1M NaCl	0.53	9.2	25.0	29.0	0.51	0.42	2.57
0.1M KCl	0.73	9.2	21.0	28.0	0.50	0.35	2.90
Keilira							
20 ml NaOH	1.80	10.5	30.0	34.9	0.63	0.62	0.48
5 ml calgon	0.86	9.4	30.0	38.2	0.69	0.75	1.56
10ml calgon	1.29	9.4	33.0	41.5	0.75	0.83	0.96
25 ml calgon	2.20	9.3	36.0	48.0	0.87	0.90	0.56
0.1M NaCl	1.01	9.7	11.0	30.8	0.56	0.28	1.98
0.1M KCl	1.09	9.7	10.0	29.7	0.54	0.25	2.10

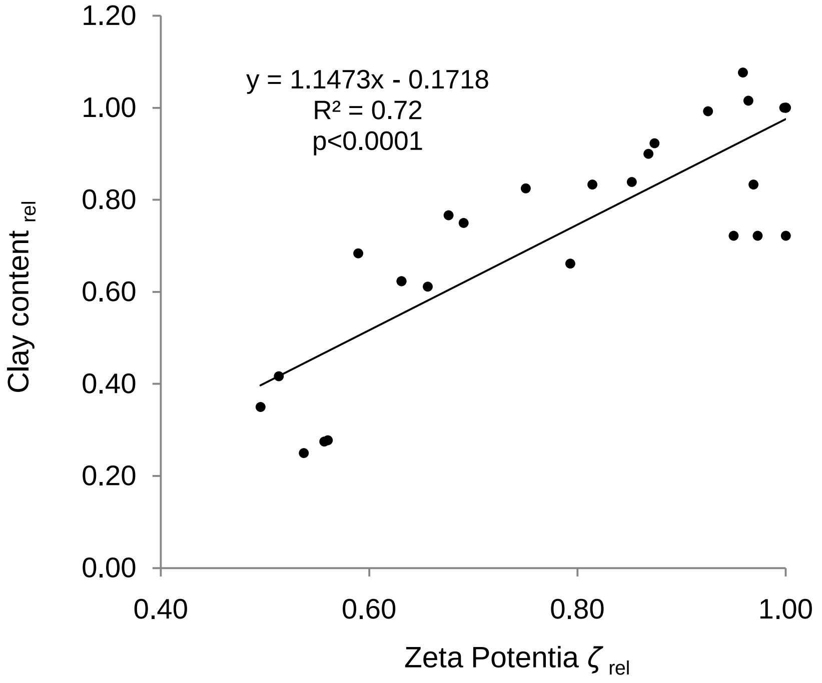


Fig. 2 Relationships between relative zeta potential (and relative clay content for four soils subjected to each of the treatment solutions (relative clay content and ζ values were calculated to eliminate the effect of individual soil characteristics when the results of all soils ware combined together)

Conclusions

Experiment one clearly demonstrated that the dispersibility of clay was a function of the CROSS values and depended on the unique association of soil components affecting the net charge available for clay-water interactions.

Claremont soil with smectite mineralogy and higher CEC than Urrbrae soil with illite and kaolinite dispersed less than Urrbrae soil at comparable CROSS values.

The results of the second and third experiments independently confirmed that clay dispersion depended on the net charge as influenced by pH.

The high correlation between the relative clay content (a measure of clay dispersion) and relative zeta potential for all soils and all treatments in the third experiment confirm the hypothesis that clay dispersion due to adsorbed cations depend on the charge available for water interaction irrespective of mineralogy, organic matter and pH of the soils.

The fact that CROSS (or SAR) relationships with threshold electrolyte concentrations in dispersive soils are unique for each soil can be attributed to the distinctive way in which clay minerals and organic matter are associated in each soil and how this affects the net charge.

References

Arienzo M, Christen EW, Quayle W, Kumar A (2009) A review of the fate of potassium in the soil-plant system after land application of wastewaters. *Journal of Hazardous Materials* **164,** 415-422.

Arora HS, Coleman NT (1979) The Influence of Electrolyte Concentration on Flocculation of Clay Suspensions. *Soil Science* **127**, 134-139.

Chorom M, Rengasamy P (1995) Dispersion and zeta potential of pure clays as related to net particle charge under varying pH, electrolyte concentration and cation type. *European Journal of Soil Science.* **46**, 657-665.

Chorom M, Rengasamy P, Murray RS (1994) Clay dispersion as influenced by pH and net particle charge of sodic soils. *Australian Journal of Soil Research* **32**, 1243-1252.

Churchman GJ (2002) Formation of complexes between bentonite and different cationic polyelectrolytes and their use as sorbents for non-ionic and anionic pollutants. *Applied Clay Science* **21**, 177-189.

Deflandre B, Gagne JP (2001) Estimation of dissolved organic carbon (DOC) concentrations in nanoliter samples using UV spectroscopy. *Water Research* **35**, 3057-3062.

Emerson W, Smith BH (1970) Magnesium, Organic Matter and Soil structure. *Nature* **228**, 453-454.

Gee GW, Bauder JW (1986) Particle-size analysis. In 'Methods of Soil Analysis: Part 1. Physical and Mineralogical Methods. Vol. 9.' 2 edn. Ed. A Klute) pp. 383- 411. (ASA, SSSA, : Madison, WI)

Helling CS, Chesters G, Corey RB (1964) Contribution of Organic Matter and Clay to Soil Cation-Exchange Capacity as Affected by the pH of the Saturating Solution1. *Soil Sci. Soc. Am. J.* **28**, 517-520.

Isbell RF (2002) 'The Australian Soil Classification. Australian Soil and Land Survey Handbook Series 4.' (CSIRO Publishing: Melbourne)

Jackson ML (2005) 'Soil Chemical Analysis: Advanced course.' Revised second edition edn. (University of Wisconsin–Madison)

Laurenson S, Bolan NS, Smith E, McCarthy M (2012) Review: Use of recycled wastewater for irrigating grapevines. *Australian Journal of Grape and Wine Research* **18**, 1-10.

Marchuk A, Rengasamy P (2011) Clay behaviour in suspension is related to the ionicity of clay–cation bonds. *Applied Clay Science* **53**, 754-759.

Marchuk A, Rengasamy P (2012) Threshold electrolyte concentration and dispersive potential in relation to CROSS in dispersive soils. *Soil Research* **50**, 473-481.

Nelson PN, Oades JM (1998) Organic matter, sodicity and soil structure. . In 'Sodic soils : distribution, properties, management and environmental consequences.'. (Eds ME Sumner and R Naidu) pp. 51-75. (Oxford University Press: New York, USA)

Quirk JP, Schofield RK (1955) The Effect of Electrolyte Concentration on Soil Permeability. *European Journal of Soil Science* **6**, 163-178.

Rayment G, Lyons D (2011) 'Soil Chemical Methods-Australasia.' (CSIRO Publishing: Collingswood)

Rengasamy P (2002) Clay Dispersion. In 'Soil Physical Measurement and Interpretation for Land Evaluation.' (Eds BM McKenzie, K Coughlan and H Cresswell) pp. 200-210. (CSIRO Publishing: Collingwood)

Rengasamy P (2010) Osmotic and ionic effects of various electrolytes on the growth of wheat. *Australian Journal of Soil Research* **48**, 120-124. [In English]

Rengasamy P, Greene R, Ford GW, Mehanni AH (1984) Identification of dispersive behaviour and the management of red- brown earths. *Australian Journal of Soil Research* **22**, 413-431.

Rengasamy P, Marchuk A (2011) Cation ratio of soil structural stability (CROSS). *Soil Research* **49**, 280-285.

Rengasamy P, Olsson KA (1991) Sodicity and soil structure. *Australian Journal of Soil Research* **29**, 935-952.

Rengasamy P, Sumner ME (1998) Processes Involved in Sodic Behaviour. In 'Sodic Soils. Distribution, Properties, Management, and Environmental Consequences.'. (Eds ME Sumner and R Naidu) pp. 35-50. (New York Press.: New York)

Smiles DE (2006) Sodium and potassium in soils of the Murray-Darling Basin: a note. *Australian Journal of Soil Research* **44**, 727-730.

Suarez DL, Rhoades JD, Lavado R, Grieve CM (1984) Effect of pH on Saturated Hydraulic Conductivity and Soil Dispersion. *Soil Sci Soc Am J* **48**, 50-55.

Walkley A, Black IA (1934) An Examination of the Degtjareff Method for Determining Soil Organic Matter, and A Proposed Modification of the Chromic Acid Titration Method. *Soil Science* **37**, 29-38.

Chapter 9 Conclusion

The solutions of salt–affected, fresh water or wastewater irrigated soils contain a range of dissolved salts, and may have an elevated concentration of sodium, potassium and magnesium, which may affect the levels of both, soluble and exchangeable cations and lead to soil structural deterioration due to clay dispersion and swelling (Arienzo et al., 2009; Rahman and Rowell, 1979; Smiles, 2006; Zhang and Norton, 2002). However, most investigations of clay dispersion have been focused on high exchangeable sodium, with sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) currently used as indices for assessing soil structural stability on interaction with water. The main focus of this research project was to investigate the effects of increased input of potassium and magnesium on clay dispersion and hydraulic conductivity of soils and, to experimentally validate the new structural stability index CROSS using soils of different clay mineralogy, pH, EC, net charge and organic matter.

With respect to the effect of potassium on soil structural stability, the studies reported in this thesis (Chapter 3, 5 and 6) highlighted two important points:

- High concentration of potassium in soils leads to soil structural deterioration
- Soil type , mineralogy, organic matter content and pH influence the effect of K on soil structure
- 2D and 3D image reconstructions from X-ray CT scan allowed visualisation of the structural changes as the effect of high potassium concentration in soil and quantification of reduced porosity and pore connectivity
- A new quantitative index, CROSS, accurately accounts for the influence of all major cations on soil structural stability when used as an alternative to SAR.

Dispersive behaviour of soils has been explained by soil scientists using an hypothesis involving various electrical diffused double layer forces generated between colloidal particles suspended in water (e.g. Quirk, 2001). The DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948a) has served since the 1950s as the main theoretical framework for analysing the properties of colloidal and biocolloidal systems. However, Israelachvili and McGuiggan (1988) stated that solvation and hydration forces are more important in swelling than DLVO forces. Further, Rengasamy and Sumner (1998) proposed that HSEB (Hard-Soft Acid -Base) reactions lead to different types of bonding between clay surfaces and cations, namely covalent and ionic which control hydration and therefore swelling and dispersion properties of soil clays. These same authors (Rengasamy and Sumner, 1998) also stated that the tendency to form covalent bonding and complexes increases in the order: Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+} for example, although quantitative comparison between the theory and experiment was yet to be developed.

The ionicity indices of the cations Li^+ Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} were derived theoretically using their ionisation potentials and charge. In all homoionic clays, used in the experimental part of this study, highly significant relationships between ionicity indices of cations in clay- cation bonds and the clay behaviour such as dispersivity and zeta potential confirmed that the degree of ionicity of these bonds dictate the water interaction with clay particles leading to clay dispersion.

Non destructive X-ray micro computed tomography scanning (Chapter 5) was used to characterise the changes in pore architecture as influenced by the proportion of cations (Na, K, Mg, and Ca) bonded to soil particles. The results of this study confirmed that structural changes during soil water interaction depend on the ionicity indices of dominant cations. Pore architecture parameters, such as total and closed porosity and pore connectivity as characterised by µCT scans, were influenced by the valence of cations. The degree of ionicity of an individual cation also explained the different effects caused by cations within a monovalent and divalent category.

The results of the laboratory experiments confirmed that hydraulic conductivity, clay dispersion and the negative charge of the dispersed clays (measured as zeta potential) of cation- treated soils decreased in the order Ca>Mg>K>Na.

Linear regression analysis between active porosity, pore connectivity, hydraulic conductivity, turbidity and zeta potential significantly correlated with the ionicity index of clay cation bonds.

The theory of the degree of ionicity in a clay- cation bond was followed in the study reported in Chapter 6. The concept of CROSS has been developed in place of SAR to reflect the different dispersive power of Na and K and the different flocculating power of Ca and Mg. The correlations between percentage of dispersed clay and SAR (r^2=0.70) and between the percentage of dispersible clay and CROSS (r^2=0.95) indicated: (a) the importance of including K in the equation; (b) the superiority of CROSS over SAR in determining the dispersive clays in soils. It was also found that CROSS measured in 1:5 soil/water extracts was strongly related to the ratio of exchangeable cations (ECR), used in this study in place of a traditional ESP.

The relationships between CROSS and ECR will depend on soil type, organic matter and mineralogy of clay. Differently treated soils of three soil types, pH, EC, organic matter and clay mineralogy were used to determine threshold electrolyte concentration of the flocculated suspensions, and to establish relationships between CROSS and TEC for those soils. TEC was significantly correlated with CROSS of the dispersed suspensions. The cationic flocculating charge (CFC) of the flocculated suspensions, which incorporates the individual flocculating power of cations, also significantly correlated with CROSS. However, those relationships depend on several soil factors even within the same soil type. The dispersive potential of the individual soils was derived from which allowed to calculate the required cationic amendments to maintain soils structural integrity.

The role of the net charge on dispersed clays in relation to clay dispersion of the soils with different clay mineralogy, pH and organic matter content was investigated during the final experimental stage of this research. The high correlations between the relative clay content and relative zeta potential which included data for all soil and all treatments confirmed that clay dispersion due to adsorbed cations depend on the net charge available for water interaction, irrespective of mineralogy, organic matter or pH of the soils.

Chapter 10 Future research opportunities

Differing from the use of SAR, the CROSS ratio was developed to include quantitative influence of K in addition to Na and the differential effects of Ca and Mg on soil structural stability. In this research, the CROSS of the soils of three soil types with varying soil characteristics, treated with solutions of varying concentrations of Na, K, Mg and Ca, was highly correlated with the clay dispersion induced by cations, highlighting the potential of using CROSS for predicting the effects of cations on soil structure.

Future research is recommended to investigate the effect of CROSS in irrigation water, soil type, mineralogy and pH on predictability of exchangeable cation ratio (ECR). This research may be important in certain irrigation areas where irrigation water in use have higher potassium and magnesium than most typical irrigation waters.

The theoretical derivation of ionicity indices of cations in clay –cation bonding and their relation to clay behaviour in aqueous suspensions established in this research validate the formulation of CROSS concept. However, the results presented in this thesis are based only on a limited number of soils and clays. In order to derive general guidelines for soil structural stability in salt-affected soils and irrigation water quality on the basis of CROSS, future work using a number of soils with different characteristics belonging to different regions is necessary.

The major phenomenon when using irrigation water is the adsorption of cations in the exchange sites. In sodium dominated systems, the adsorption of sodium is well defined by SAR which has been found to predict soil ESP reasonably. Strong relationship between CROSS and ECR have been presented in this thesis, but the relationships are unique for each soil. Since some clays can fix potassium in addition to exchange reactions, it is not clear whether exchange potassium can be predicted by CROSS in soils containing-fixing minerals, and this needs further investigation.

The results presented in this thesis clearly indicated that the net charge available for water interaction is highly related to the clay dispersion induced by the cations. Irrespective of clay mineralogy, organic matter and pH, how these components together uniquely lead to the net charge seems to be important. Therefore, it should be possible to include a third factor of net charge in the relationships between CROSS and dispersible clay, and then derive a common relation applicable to all soils. Future research should focus on this to derive appropriate guidelines.

Chapter 11 References

Agassi M., Shainberg I., Morin J. (1981) Effect of Electrolyte Concentration and Soil Sodicity on Infiltration Rate and Crust Formation. Soil Sci Soc Am J 45:848-851.

Alperovitch N., Shainberg I., Keren R. (1981) SPECIFIC EFFECT OF MAGNESIUM ON THE HYDRAULIC CONDUCTIVITY OF SODIC SOILS. European Journal of Soil Science 32:543-554.

Anderson J., Davis C. (2006) An overview of Australia and reclaimed water, in: D. Stevens (Ed.), Growing crops with reclaimed wastewater, CSIRO publishing. pp. 1-5.

Arienzo M., Christen E.W., Quayle W., Kumar A. (2009) A review of the fate of potassium in the soil-plant system after land application of wastewaters. Journal of Hazardous Materials 164:415-422.

Arora H.S., Coleman N.T. (1979) The Influence of Electrolyte Concentration on Flocculation of Clay Suspensions. Soil Science 127:134-139.

ASTM. (1976) Annual Book of ASTM Standards, Part 31, Water", Standard D1889-71. pp. 223.

Aydin M., Yano T., Kilic S. (2004) Dependence of zeta potential and soil hydraulic conductivity on adsorbed cation and aqueous phase properties. Soil Science Society of America Journal 68:450-459.

Ayers R.S., Westcote D.W. (1985) Water quality for agriculture. food and Agriculture Organisation, Rome.

Aylmore L.A.G. (1993) The use of computer assisted tomography in studying water movement around plant roots Academic Press Inc., London.

Baird N.C., Whitehead M.A. (1964) Ionic character. Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta) 2:259-264. DOI: 10.1007/bf00527052.

Ball B.C., Batey T., Munkholm L.J. (2007) Field assessment of soil structural quality – a development of the Peerlkamp test. Soil Use and Management 23:329-337. DOI: 10.1111/j.1475-2743.2007.00102.x.

Barzegar A.R., Nelson P.N., Oades J.M., Rengasamy P. (1997) Organic Matter, Sodicity, and Clay Type: Influence on Soil Aggregation. Soil Sci Soc Am J 61:1131-1137.

Barzegar A.R., Rengasamy P., Oades J.M. (1995) Effects of clay type and rate of wetting on the mellowing of compacted soils. Geoderma 68:39-49. DOI: Doi: 10.1016/0016-7061(95)00022-g.

Basile A., Buttafuoco G., Mele G., Tedeschi A. (2012) Complementary techniques to assess physical properties of a fine soil irrigated with saline water. Environmental Earth Sciences 66:1797-1807. DOI: 10.1007/s12665-011-1404-2.

Beresford Q., Bekle H., Phillips H., Mulcock J. (2001) The Salinity Crisis: Landscapes, Communities and Politics University of Western Australia Press.

Bond W., Smith C. (2006) Environmental Implication of reclaimed water use for irrigated agriculture., in: D. Stevens (Ed.), Growing Crops with Reclaimed Wastewater, CSIRO Publishing, Collingwood. pp. 171-178.

Bowden J.W., Posner A.M., Quirk J.P. (1980) Adsorption and charging phenomena in variable charge soils, in: B. K. G. Theng (Ed.), Soils with Variable Charge., New Zealand Society of Soil Science., Lower Hutt. pp. 147-166.

Bradfield R. (1950) Soil Structure, 4th International Congress of Soil Science, Amsterdam. pp. 9-19.

Brady N.C., Weil R.R. (2008) The Nature and Properties of Soils. 14th ed. Pearson Prentice Hall, New Jersey.

Braimoh A., Vlek P. (2007) Impact of Land Use on Soil Resourses, in: A. Braimoh and P. Vlek (Eds.), Land Use and Soil Resourses, Springer, Stockholm.

Bronick C.J., Lal R. (2005) Soil structure and management: a review. Geoderma 124:3-22.

Cárdenas J.P., Santiago A., Tarquis A.M., Losada J.C., Borondo F., Benito R.M. (2012) Community Structure in a Soil Porous System. Soil Science 177:81-87 10.1097/SS.0b013e318245d3ec.

Cass A. (1999) Interpretation of Some Soil Physical Indicators for Assessing Soil Physical Fertility, in: K. Peverill, et al. (Eds.), Soil Analysis and Interpretation Manual, CSIRO Publishing, Collingswood.

Cecconi S., Salazrand A., Martelli M. (1963) The effect of different cations on the structural stability of some soils. Agrochemica.

Charman P.E.V., Murphy B., W. (2007) Soils, Their properties and Management. Oxford University Press.

Chen Y., Banin A., Borochovitch A. (1983) Effect of potassium on soil structure in relation to hydrolic conductivity, in: E. B. A. Bisdom and J. Ducloux (Eds.), Submicroscopic studies of soils, Elsevier, Amstetrdam-Oxford-new York-Tokyo. pp. 135-147.

Childs E.C., Collis-George N., Holmes J.W. (1957 Permeability measurements in the field as an assessment of anisotropy and structure development. Journal of Soil Science 8:27-41. DOI: 10.1111/j.1365-2389.1957.tb01865.x.

Chorom M., Rengasamy P. (1995) Dispersion and zeta potential of pure clays as related to net particle charge under varying pH, electrolyte concentration and cation type. European Journal of Soil Science. 46:657-665.

Chorom M., Rengasamy P. (1997) Carbonate chemistry, pH, and physical properties of an alkaline sodic soil as affected by various amendments. Australian Journal of Soil Research 35:149-161.

Chorom M., Rengasamy P., Murray R.S. (1994) Clay dispersion as influenced by pH and net particle charge of sodic soils. Australian Journal of Soil Research 32:1243-1252. DOI: doi:10.1071/SR9941243.

Churchman G.J. (2002) Formation of complexes between bentonite and different cationic polyelectrolytes and their use as sorbents for non-ionic and anionic pollutants. Applied Clay Science 21:177-189.

Churchman G.J., Payne D. (1983) Mercury intrusion porosimetry of some New-Zealand soils in relation to clay mineralogy and texture. Journal of Soil Science 34:437-451.

Churchman G.J., Skjemstad J.O., Oades J.M. (1993) Influence of clay minerals and organic matter on effects of sodicity on soils. Australian Journal of Soil Research 31:779-800. DOI: doi:10.1071/SR9930779.

Churchman G.J., Skjemstad J.O., Oades J.M. (1995) Effect of clay minerals and organic matter on Sodicity., in: R. Naidu, et al. (Eds.), Australian Sodic Soils: Distribution, Properties and Management, CSIRO Publications, Melbourne, Victoria.

Crestana S., Cesareo R., Mascarenhas S. (1986) Using a computed-tomography miniscanner in soil science. Soil Science 142:56-61. DOI: 10.1097/00010694-198607000-00008.

Currie J.A. (1965) Diffusion within soil microstructure a structural parameter for soils.Journal of Soil Science 16:279-289. DOI: 10.1111/j.1365-2389.1965.tb01439.x.

Darling A.L., Sun W. (2004) 3D microtomographic characterization of precision extruded poly-epsilon-caprolactone scaffolds. Journal of Biomedical Materials Research Part B-Applied Biomaterials 70B:311-317. DOI: 10.1002/jbm.b.30050.

Derjaguin B., Landau L. (1941) Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. Acta Physico Chemica 14.

Deshpande T.L., Greenland D.J., Quirk J.P. (1964) Role of Iron Oxides in the Bonding of Soil Particles. Nature 201:107-108.

Dexter A.R., Richard G. (2009) The saturated hydraulic conductivity of soils with n-modal pore size distributions. Geoderma 154:76-85. DOI:10.1016/j.geoderma.2009.09.015.

Dontsova K.M., Norton D. (1999) Effects of exchangeable Ca:Mg ratio on soil clay flocculation, infiltration and erosion., in: D. E. Scott, et al. (Eds.), 10th International Soil Conservation Organization Meeting, May 24-29, 1999 at Perdue University and USDA-ARS National Soil Research Laboratory.

Durgin P.B., Chaney J.G. (1984) Dispersion of kaolinite by dissolved organic matter from Douglas-fir roots. . Canadian Journal. of Soil Science. :445-455.

Eaton A.D., Franson M.A.H. (2005) Standard Methods for the Examination of Water & Wastewater. 21 ed. American Public Health Association.

Edwards S.A., Williams D.R.M. (2004) Hofmeister effects in colloid science and biology explained by dispersion forces: analytic results for the double layer interaction. Current Opinion in Colloidal and Interface Science Volume 9, Issues 1–2, Pages 139–144.

El Swaify S.A., Ahmed S., Swindale L.D. (1970) Effect od adsorbed cations on physiscal properties of tropical red and tropical black earths. Journal of Soil Science 21:188-198. DOI: 10.1111/j.1365-2389.1970.tb01167.x.

Emerson W. (1983) Inter-particle bonding., in: C. A. d. o. Soils. (Ed.), Soils; an Australian Viewpoint., Academic Press London. pp. 477-498.

Emerson W., Smith B.H. (1970) Magnesium, Organic Matter and Soil structure. Nature 228:453.

Emerson W.W. (1977) Physical properties and structure., in: J. S. Russel and Greacen, E.L. (Eds.), Soil factors in crop production in a semi-arid environment., University of Queensland Press. pp. 78-104.

Emerson W.W., Bakker A.C. (1973) The comparative effects of exchangeable calcium, magnesium, and sodium on some physical properties of red-brown earth subsoils. II. The spontaneous dispersion of aggregates in water. Australian Journal of Soil Research 11:151-157. DOI: doi:10.1071/SR9730151.

Evangelou V.P. (1998) Environmental Soil and Water Chemistry: Principles and Applications John Wiley &Sons, Inc., New York.

Fajans K. (1970) Polarizability of alkali and halide ions, especially fluoride ion. The Journal of Physical Chemistry 74:3407-3410

Fireman M., Bodman G.B. (1939) The effect of saline irrigation water upon the permeability and base status of soils. Soil Science Society of America Proceedings. 4:71-77.

Fitzpatrick R.W., Boucher S.C., Naidu R., Fritsch E. (1994) Environmental consequences of soil sodicity. Australian Journal of Soil Research 32:1069-1093. DOI: doi:10.1071/SR9941069.

Frenkel H., Goertzen J.O., Rhoades J.D. (1978) Effects of Clay Type and Content, Exchangeable Sodium Percentage, and Electrolyte Concentration on Clay Dispersion and Soil Hydraulic Conductivity. Soil Sci Soc Am J 42:32-39.

Frenkel H., Shainberg I. (1980) The Effect of Hydroxy-Al and Hydroxy-Fe Polymers on Montmorillonite Particle Size. Soil Sci Soc Am J 44:626-629.

Gardner W.R., Mayhugh M.S., Goertzen J.O., Bower C.A. (1959) Effect of Electrolyte Concentration and Exchangeable Sodium Percentage on Diffusivity of Water in Soils. Soil Science 88:270&hyhen;274.

Gaskin P.N., Raymond G.P. (1973) Pore Size Distribution as a Frost Susceptibility Criterion Frost Action on Roads: Proceedings of the Symposium on Frost Action on Roads, Norwegian Road Research Laboratory, Oslo:76-78.

Gee G.W., Bauder J.W. (1986) Particle Size Analysis, in: A.Klute (Ed.), Method of Soil Analysis, Madison, Wisconsin USA, Wisconsin, USA. pp. 383-411.

Gillman G.P., Sumner M.E. (1987) Surface Charge Characterization and Soil Solution Composition of Four Soils from the Southern Piedmont in Georgia. Soil Sci. Soc. Am. J. 51:589-594. DOI: 10.2136/sssaj1987.03615995005100030007x.

Goldberg S., Forster H.S. (1990) Flocculation of the reference clay and arid-zone clays. Soil Science Society of America Journal 54:714-718.

Goldberg S., Kapoor B.S., Rhoades J.D. (1990) Effect of Aluminium and Iron Oxides and Organic Matter on Flocculation and Dispersion of Arid Zone Soils. Soil Science 150:588-593.

Goldberg S., Suarez D.L., Glaubig R.A. (1988) Factors Affecting Clay Dispersion and Aggregate Stability of Arid-Zone Soils. Soil Science 146:317-325.

Greene R.S.B., Eggleton R.A., Rengasamy P. (2002) Relationships between clay mineralogy and the hardsetting properties of soils in the Carnarvon horticultural district of Western Australia. Applied Clay Science 20:211-223.

Greene R.S.B., Rosner A.M., Quirk J.P. (1978) A study of the Coagulation of Montmorillonite and Illite Suspension by Calcium Chloride Using the Electron Microscope., in: W. W. Emerson, et al. (Eds.), Modification of Soil Structure., John Wiley and Sons: Chichester. pp. 35-40.

Güven N. (1992) Molecular aspects of clay- water interaction, in: N. Güven and R. M. Pollastro (Ed.), Clay-water interface and its rheological implications, Clay Mineral Society, Boulder.

Gupta R.K., Arbol I.P. (1990) Salt-affected soil: Their reclamation and management for crop production. Advances in Soil Science. 11:224-288.

Hainsworth J., Aylmore L. (1983) The use of computer assisted tomography to determine spatial distribution of soil water content. Soil Research 21:435-443. DOI: http://dx.doi.org/10.1071/SR9830435.

Halliwell D.J., Barlow K.M., Nash D.M. (2001) A review of the effects of wastewater sodium on soil physical properties and their implications for irrigation systems. Australian Journal of Soil Research 39:1259-1267.

Hazelton P., Murphy B. (2007) Interpreting soil test results: what do all the numbers mean? 2nd ed. CSIRO Publishing, Australia.

Hillel D. (1998) Envoronmental soil physics Academic Press, San Diego.

Holthusen D., Peth S., Horn R., Kuhn T. (2012) Flow and deformation behavior at the microscale of soils from several long-term potassium fertilization trials in Germany. Journal of Plant Nutrition and Soil Science 175:535-547. DOI: 10.1002/jpln.201100073.

Hounsfield G.N. (1973) Computerized transverse axial scanning (tomography): Part 1. Description of system. British Journal of Radiology (1973) 46, 1016-1022

Huheey J., Keiter E., Keiter R. (1993) Inorganic Chemistry: Principles of Structure and Reactivity Harper Collins College Publishers.

Hunter R.J. (1981) Zeta Potential in Colloid Science principles and applications Academic Press, London, New York.

Hunter R.J. (1993) Introduction to modern colloid science Oxford University Press, Oxford, New York

Isbell R.F. (2002) The Australian Soil Classification. Australian Soil and Land Survey Handbook Series 4. CSIRO Publishing, Melbourne.

Isbell R.F., Reeve R.C., Hutton J.T. (1983) Salt and Sodicity, in: A. Press (Ed.), Soils: an Australian viewpoint., Division of Soil, CSIRO, Melbourne. pp. 107-118.

Israelachvili J.N. (1992) ntermolecular and surface forces. 2nd ed ed. Academic, London.

Israelachvili J.N., McGuiggan P.M. (1988) Forces Between Surfaces in Liquids. Science 241:795-800. DOI: 10.1126/science.241.4867.795.

Jackson M.L. (2005) Soil Chemical Analysis: Advanced course. Revised second edition ed. University of Wisconsin–Madison.

Jassogne L., McNeill A., Chittleborough D. (2007) 3D-visualization and analysis of macro- and meso-porosity of the upper horizons of a sodic, texture-contrast soil. European Journal of Soil Science 58:589-598. DOI: 10.1111/j.1365-2389.2006.00849.x.

Jayawardane N.S., Chan K.Y. (1994) The management of soil physical properties limiting crop production in Australian sodic soils - a review. Australian Journal of Soil Research 32:13-44. DOI: doi:10.1071/SR9940013.

Keren R. (1991) Specific Effect of Magnesium on Soil Erosion and Water Infiltration. Soil Sci Soc Am J 55:783-787.

Kirby B.J., Hasselbrink E.F. (2004) Zeta potential of microfluidic substrates: 1. Theory, experimental techniques, and effects on separations. ELECTROPHORESIS 25:187-202. DOI: 10.1002/elps.200305754.

Kopittke P.M., So H.B., Menzies N.W. (2006) Effect of ionic strength and clay mineralogy on NaCa exchange and the SAR- ESP relationship. European Journal of Soil Science 57:626-633.

Kreit J.F., Shainberg I., Herbillon A.J. (1982) Hydrolysis and decomposition of hectorite in dilute salt solutions. Clays and Clay Minerals. 30.

Kunhikrishnan A., Bolan N.S., Muller K., Laurenson S., Naidu R., Kim W.I. (2012) THE INFLUENCE OF WASTEWATER IRRIGATION ON THE TRANSFORMATION AND BIOAVAILABILITY OF HEAVY METAL (LOID)S IN SOIL, in: D. L. Sparks (Ed.), Advances in Agronomy, Vol 115, Elsevier Academic Press Inc, San Diego. pp. 215-297.

Kwiecien M.J. (1987) Determination of pore size distribution of berea sandstone through three dimentional reconstruction. M.S.thesis, Univ. Waterloo Ontario, Canada.

Lal R. (1991) Soil Structure and Sustainability. Journal of Sustainable Agriculture 1:67-92. DOI: 10.1300/J064v01n04_06.

Laura R.D. (1976.) Effect of alkali salts on carbon and nitrogen mineralization of organic matter in soils. Plant and Soil. :587-596.

Laurenson S., Bolan N.S., Smith E., McCarthy M. (2012) Review: Use of recycled wastewater for irrigating grapevines. Australian Journal of Grape and Wine Research 18:1-10. DOI: 10.1111/j.1755-0238.2011.00170.x.

Levy G.J., Torrento J.R. (1995) Clay Dispersion and Macroaggregate Stability As Affected By Exchangeable Potassium and Sodium. Soil Science 160:352-358.

Levy G.J., Van Der Watt H.V.H. (1990) Effect of Exchangeable Potassium on the Hydraulic Conductivity and Infiltration Rate of Some South African Soils. Soil Science 149:69-77.

Lipiec J., Hajnos M., Swieboda R. (2012) Estimating effects of compaction on pore size distribution of soil aggregates by mercury porosimeter. Geoderma 179:20-27. DOI: 10.1016/j.geoderma.2012.02.014.

Low A.J. (1954) A study of soil structure in teh field and the laboratory. Journal of Soil Science 5:57-74.

Marchuk A., Rengasamy P. (2011) Clay behaviour in suspension is related to the ionicity of clay–cation bonds. Applied Clay Science 53:754-759. DOI: 10.1016/j.clay.2011.05.019.

Markiewicz M., Mrozik W., Rezwan K., Thöming J., Hupka J., Jungnickel C. Changes in zeta potential of imidazolium ionic liquids modified minerals – Implications for determining mechanism of adsorption. Chemosphere. DOI: 10.1016/j.chemosphere.2012.09.053.

Master Z. (1999) Zeta Master Manual, Staunton VA 24402 USA.

McBride M.B. (1994) Environmental Chemistry. Oxford University Press, New York, Oxford.

McIntyre D.S. (1979) Exchangeable sodium, subplasticity and hydraulic conductivity of some Australian soils. Australian Journal of Soil Research.:115-120.

McNeal B.L., Layfield D.A., Norvell W.A., Rhoades J.D. (1968) Factors Influencing Hydraulic Conductivity of Soils in the Presence of Mixed-Salt Solutions. Soil Sci Soc Am J 32:187-190.

Misono M., Ochiai E., Saito Y., Yoneda Y. (1967) A new dual parameter scale for the strength of lewis acids and bases with the evaluation of their softness. Journal of Inorganic and Nuclear Chemistry 29:2685-2691.

Mooney S., Pridmore T., Helliwell J., Bennett M. (2012) Developing X-ray Computed Tomography to non-invasively image 3-D root systems architecture in soil. Plant and Soil:1-22. DOI: 10.1007/s11104-011-1039-9.

Mooney S.J. (2002) Three-dimensional visualization and quantification of soil macroporosity and water flow patterns using computed tomography. Soil Use and Management 18:142-151. DOI: 10.1111/j.1475-2743.2002.tb00232.x.

Munkholm L.J. (2011) Soil friability: A review of the concept, assessment and effects of soil properties and management. Geoderma 167-68:236-246. DOI: 10.1016/j.geoderma.2011.08.005.

Munns R., Tester M. (2008) Mechanisms of Salinity Tolerance. Annual Review of Plant Biology 59:651-681. DOI: doi:10.1146/annurev.arplant.59.032607.092911.

Murray R.S., Quirk J.P. (1982) The physical swelling of clays in solvents. Soil Science Society of America Journal 46:865-868.

Nelson P.N., Baldock J.A., Clarke P., Oades J.M., Churchman G.J. (1999) Dispersed clay and organic matter in soil: Their nature and associations. Australian Journal of Soil Research 37:289-315.

Nelson P.N., Barzegar A.R., Oades J.M. (1997) Sodicity and Clay Type: Influence on Decomposition of Added Organic Matter. Soil Sci. Soc. Am. J. 61:1052-1057. DOI: 10.2136/sssaj1997.03615995006100040010x.

Nelson P.N., Oades J.M. (1998) Organic matter, sodicity and soil structure. , in: M. E. Sumner and R. Naidu (Eds.), Sodic soils : distribution, properties, management and environmental consequences., Oxford University Press, New York, USA. pp. 51-75.

Nguetnkam J.P., Dultz S. (2011) Soil degradation in Central North Cameroon: Water-dispersible clay in relation to surface charge in Oxisol A and B horizons. Soil and Tillage Research 113:38-47. DOI: 10.1016/j.still.2011.01.006.

Nguyen M.N., Dultz S., Kasbohm J., Le D. (2009) Clay dispersion and its relation to surface charge in a paddy soil of the Red River Delta, Vietnam. Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde. 172:477-486. DOI: 10.1002/jpln.200700217.

NLWRA. (2002) National Land and Water Resource Audit.Commonwealth od Australia. A.C.T.

Northcote K.H., Skene J.K.M. (1972) Australian Soils with Saline and Sodic Properties. Commonwealth Scientific and Industrial Research Organisation (CSIRO) Publishing, Melbourne.

Oades J.M., Gillman G.P., Uehara G. (1989) Interaction of soil organic matter and variable charge clays., in: N. T. Coleman, et al. (Eds.), Dynamic of Soil organic Matter in Tropical Ecosystems., Niftal project, University of Hawaii., HI.

Oades M. (1984) Soil organic matter and structural stability: mechanisms and implications for management Plant and Soil.

Oster J.D. (2001) Exchangeable sodium percentage, ESP-zeolite material., in: SLPHYCHM. (Ed.), Available online at http://esce.ucr.edu?oster/SLPHY5.html

Oster J.D., Jayawardane N.S. (1998) Agricultural management of sodic soils., in: M. E. Sumner and R. Naidu (Eds.), Sodic Soils: Distribution, management and Environmental Consequences., Oxford University Press., New York. pp. 125-147.

Oster J.D., Shainberg I., Wood J.D. (1980) Flocculation Value and Gel Structure of Sodium/Calcium Montmorillonite and Illite Suspensions. Soil Sci Soc Am J 44:955-959.

Pagliai M., Vignozzi N., Pellegrini S. (2004) Soil structure and the effect of management practices. Soil and Tillage Research 79:131-143. DOI: http://dx.doi.org/10.1016/j.still.2004.07.002.

Passioura J. (1991) Soil structure and plant growth. Australian Journal of Soil Research 29:717-728. DOI: doi:10.1071/SR9910717.

Patterson R. (2006) Consideration of soil sodicity when assessing land application of effluent or graywater. Technical Sheet Reference.

Pauling L. (1967) The Chemical Bond. Cornell University Press, Ithaca, New York.

Perret J., Prasher S.O., Kantzas A., Langford C. (1999) Three-Dimensional Quantification of Macropore Networks in Undisturbed Soil Cores. Soil Science Society of America Journal 63:1530-1543.

Petrovic A.M., Siebert J.E., Rieke P.E. (1982) Soil Bulk Density Analysis in Three Dimensions by Computed Tomographic Scanning1. Soil Sci. Soc. Am. J. 46:445-450. DOI: 10.2136/sssaj1982.03615995004600030001x.

Pitman M.G., Läuchli A. (2004) Global Impact of Salinity and Agricultural Ecosystems. Salinity: Environment - Plants - Molecules Salinity: Environment - Plants - Molecules

Qadir M., Schubert S. (2002) Degradation processes and nutrient constraints in sodic soils. Land Degradation & Development 13:275-294.

Quirk J.P. (1994) Interparticle forces:a basis for the interpretation of soil physical behaviour. Advanced Agronomy.:121-183.

Quirk J.P. (2001) The significance of the threshold and turbidity concentrations in relation to sodicity and microstructure. Australian Journal of Soil Research. 39:1185-1217.

Quirk J.P. (2003) Comments on "Diffuse double-layer models, long-range forces, and ordering of clay colloids". Soil Sci Soc Am J 67:1960-1961.

Quirk J.P., Schofield R.K. (1955) The Effect of Electrolyte Concentration on Soil Permeability. European Journal of Soil Science 6:163-178.

Rahman W.A., Rowell D.L. (1979) The influence of magnesium in saline and sodic soils. A specific effect or a problem of cation exchange? European Journal of Soil Science 30:535-546. DOI: 10.1111/j.1365-2389.1979.tb01007.x.

Rayment G., Lyons D. (2011) Soil Chemical Methods-Australasia CSIRO Publishing, Collingswood.

Reeve R.C., Bower C.A., Brooks R.H., Gschwend F.B. (1954) A Comparison of the Effects of Exchangeable Sodium and Potassium upon the Physical Condition of Soils. Soil Sci Soc Am J 18:130-132.

Rengasamy P. (1996) Dispersive potential of soil clays as influenced by cations. Proceedings, Australia and New Zealand National Soil Conference.

Rengasamy P. (2002a) Clay Dispersion, in: B. M. McKenzie, et al. (Eds.), Soil Physical Measurement and Interpretation for Land Evaluation, CSIRO Publishing, Collingwood. pp. 200-210.

Rengasamy P. (2002b) Transient salinity and subsoil constraints to dryland farming in Australian sodic soils: an overview. Australian Journal of Experimental Agriculture 42:351-361. DOI: 10.1071/ea01111.

Rengasamy P. (2006a) Soil salinity and sodicity, in: D. Stevens (Ed.), Growing crops with reclaimed wastewater, CSIRO. pp. 125-137.

Rengasamy P. (2006b) World salinization with emphasis on Australia. Journal of Experimental Botany 57:1017-1023.

Rengasamy P. (2008) Salinity in the landscape: A growing problem in Australia. Geotimes 53:34-39.

Rengasamy P. (2010) Soil processes affecting crop production in salt-affected soils. Functional Plant Biology 37:613-620.

Rengasamy P., Churchman G.J. (1999) Cation exchange capacity, exchangeable cations and sodicity, in: K. Peverill, et al. (Eds.), Soil Analysis and Interpretation Manual, CSIRO Australia. pp. 147-155.

Rengasamy P., Greene R., Ford G.W., Mehanni A.H. (1984a) Identification of dispersive behaviour and the management of red- brown earths. Australian Journal of Soil Research 22:413-431.

Rengasamy P., Greene R.S.B., Ford G.W. (1984b) The Role of Clay Fraction in the Particle Arrangement and Stability of Soil Aggregates-a Review. Clay Research 3:53-67.

Rengasamy P., Greene R.S.B., Ford G.W. (1986) Influence of magnesium on aggregate stability in sodic red-brown earths. Australian Journal of Soil Research 24:229-237.

Rengasamy P., Kempers J., Olsson K. (1991) Dispersive potential of Natrixeralfs and their crusting strength. Clay Research 10:6-10.

Rengasamy P., Marchuk A. (2011) Cation ratio of soil structural stability (CROSS). Soil Research 49:280-285.

Rengasamy P., Olsson K.A. (1991) Sodicity and soil structure. Australian Journal of Soil Research 29:935-952.

Rengasamy P., Olsson K.A. (1993) Irrigation and sodicity. Australian Journal of Soil Research 31:821-837. DOI: doi:10.1071/SR9930821.

Rengasamy P., Olsson K.A., Kirby J.M. (1992) Physical constraints to root growth in the subsoil., National Workshop on Subsoil Constraints to Root Growth and High Soil Water and Nutrient Use by Plants. , Tanunda, South Australia. pp. 84-91.

Rengasamy P., Sumner M.E. (1998) Processes Involved in Sodic Behaviour., in: M. E. Sumner and R. Naidu (Eds.), Sodic Soils. Distribution, Properties, Management, and Environmental Consequences., New York Press., New York. pp. 35-50.

Rhoades J.D., Ingvalson R.D. (1969) Macroscopic Swelling and Hydraulic Conductivity Properties of Four Vermiculite Soils. Soil Sci Soc Am J 33:364-369.

Ringrose-Voase A.J. (1991) Micromorphology of soil structure-Description, quantification, application. Australian Journal of Soil Research 29:777-813. DOI: doi:10.1071/SR9910777.

RingroseVoase A.J. (1996) Measurement of soil macropore geometry by image analysis of sections through impregnated soil. Plant and Soil 183:27-47. DOI: 10.1007/bf02185563.

Robbins C.W. (1984) Sodium adsorption ratio-exchangeable sodium percentage relationships in a high potassium saline-sodic soil. Irrigation Science 5:173-179. DOI: 10.1007/bf00264606.

Robbins W. (1984) Sodium Adsorption Ratio-Exchangeable Sodium Percentage Relationships in a High Potassium Saline-Sodic Soil. Irrigation Science.:173-179.

Russ J.C. (2011) The Image Processing Handbook. 6 ed. Boca Raton, CRC Press.

Sawhney B. (1972) Selective sorption and fixation of cations by clay minerals: a review. Clay and Clay Minerals 20:93-100.

Schofield R.K. (1947) A ratio law governing the equilibrium of cations in soil solutions. Proc. 11th Int.Cogr.Pure Appl. Chem. 3, 257-61.

Sekhon G.S. (1999) Potassium in Indian Soils and Crops. PINSA 83-108.

Shainberg I., Alperovitch N., Keren R. (1988) Effect of magnesium on the hydraulic conductivity of Na-smectite-sand mixtures. Clays Clay Miner 36:432-438.

Shainberg I., Letey J. (1984) Response of Soils to Sodic and Saline Conditions. Hilgardia. 52:1-57.

Shainberg I., Levy G.J. (1992) Physico-Chemical Effect of Salts upon Infiltration and Water Movement in Soils., in: R. J. Wagenet, et al. (Eds.), Interacting Processes in Soil Science., Lewis Publishers, Boca Raton. pp. 37-146.

Shainberg I., Rhoades J.D., Prather R.J. (1981) Effect of Low Electrolyte Concentration on Clay Dispersion and Hydraulic Conductivity of a Sodic Soil. Soil Sci Soc Am J 45:273-277.

Shanmuganathan R.T., Oades J.M. (1982) Effect of dispersible clay on the physical properties of the B horizon of a red-brown earth. Australian Journal of Soil Research 20:315-324.

Shaw R., J. (2005) Soil Salinity - Electrical Conductivity and Chloride., in: K. I. Peverill (Ed.), Soil Analysis: an Interpretation Manual., CSIRO, Collingwood. pp. 129-144.

Smiles D., Smith C. (2004) A survey of the cation content of piggery effluents and some consequences of their use to irrigate soil. Australian Journal of Soil Research 42:231-246.

Smiles D.E. (2006) Sodium and potassium in soils of the Murray-Darling Basin: a note. Australian Journal of Soil Research 44:727-730. DOI: doi:10.1071/SR06057.

So H.B., Aylmore L.A.G. (1993) How do sodic soils behave - the effects of sodicity on soil physical behavior. Australian Journal of Soil Research 31:761-777. DOI: doi:10.1071/SR9930761.

Speirs S.D., Cattle S.R., Melville G.J. (2011) Impact of sodium adsorption ratio of irrigation water on the structural form of two Vertosols used for cotton production. Soil Research 49:481-493. DOI: http://dx.doi.org/10.1071/SR11083.

Sposito G. (1994) Chemical Equilibria and Kinetics in Soils Oxford University Press, New York Oxford.

Stevens D., Kelly J., McLaughlin M., UNkovich M. (2006) Growing cropswith reclaimed wastewater CSIRO Publishing.

Stevens D.P., McLaughlin M.J., Smart M.K. (2003) Effects of long-term irrigation with reclaimed water on soils of the Northern Adelaide Plains, South Australia. Australian Journal of Soil Research 41:933-948. DOI: doi:10.1071/SR02049.

Suarez D.L., Rhoades J.D., Lavado R., Grieve C.M. (1984) Effect of pH on Saturated Hydraulic Conductivity and Soil Dispersion. Soil Sci Soc Am J 48:50-55.

Subba Rao A., Rao C.S. (1996) Potassium Status and Crop Response to Potassium on the Soils of Agro-ecological Regions of India. International Potash Institute. IPI Research Topics No 20:pp. 1-57.

Sumner M.E. (1993) Sodic soils - New perspectives. Australian Journal of Soil Research 31:683-750. DOI: doi:10.1071/SR9930683.

Sumner M.E., Rengasamy P., Naidu R. (1998) Sodic soils: a reappraisal. Sodic Soils - Distribution, Properties, Management and Environmental Consequences / Sumner, M.E. and Naidu, R.(eds), pp. 3-17.

Swaify S.A.E., Ahmed S., Swindale L.D. (1970) Effect of adsorbed cations on physical properties of tropical red and tropical black earths. European Journal of Soil Science 21:188-198.

Szabolcs I. (1989) Salt-Affected Soils. CRC Press, Boca Raton, F.I.

Taina I.A., Heck R.J., Elliot T.R. (2008) Application of X-ray computed tomography to soil science: A literature review. Canadian Journal of Soil Science.

Tippkötter R., Eickhorst T., Taubner H., Gredner B., Rademaker G. (2009) Detection of soil water in macropores of undisturbed soil using microfocus X-ray tube computerized tomography (μCT). Soil and Tillage Research 105:12-20. DOI: 10.1016/j.still.2009.05.001.

Tisdall J.M. (1996) Formation of soil aggregates and accumulation of soil organic matter., in: M. R. Carter and B. Stewart (Eds.), Structure of Organic Matter Storage in Agricultural Soils., Lewis Publishers., Boca Raton. pp. 57-96.

Tisdall J.M., Oades J.M. (1982) Organic matter and water-stable aggregates in soils. Journal of Soil Science 33:141-163. DOI: 10.1111/j.1365-2389.1982.tb01755.x.

Toze S. (2006) Reuse of effluent water--benefits and risks. Agricultural Water Management 80:147-159.

Turner M., Sakellariou A., Arns C., Sok R., Limaye A., Senden T., Tiacktedt M. (2003) Towards measuring regolith permiability with high resolution x-ray tomography., in: I. C. Roach (Ed.), Advances in Regolith, CRC LEME, Adelaide. pp. 421-425.

USSL. (1954) Diagnosis and improvement of saline and alkali soils. United States Salinity Laboratory Handbook No.60.

Van Beek C.G.E.M., Van Breeman N. (1973) The Alkalinity of Alkali soils. European Journal of Soil Science 24:129-136.

van de Graaff R., Patterson R.A. (2001) Exlaining the Mystery of Salinity, Sodocity, SAR and ESP, in: R. A. Patterson and J. M.J. (Eds.), On-site Practice in proceedings of On-site 01 Conference: Advancing on-site Wastewater Systems Lanfax Laboratories, Armidale. pp. 361-368.

Velasco-Molina H., Swoboda A., Godfrey C. (1971) Dispersion of Soils of Different Mineralogy in Relation To Sodium Adsorption Ratio and Electrolytic Concentration. Soil Science 111:282-287.

Velde B. (2010) Soils, Plants and Clay Minerals. Mineral and Biological interactions Springer Verlag Heidelberg, Berlin

Vergés E., Tost D., Ayala D., Ramos E., Grau S. (2011) 3D pore analysis of sedimentary rocks. Sedimentary Geology 234:109-115. DOI: 10.1016/j.sedgeo.2010.12.005.

Verwey E.J.W., Overbeek J.T.G. (1948a) Theory of Stability of Lyophobic Colloids Eldevier, Amsterdam.

Verwey E.J.W., Overbeek J.T.G. (1948b) Theory of the Stability of Lyophobic Colloids North Holland, Amsterdam.

Viviani G., Iovino M. (2004) Wastewater Reuse Effects on Soil Hydraulic Conductivity. Journal of Irrigation and Drainage Engineering 130:476-484. DOI: 10.1061/(asce)0733-9437(2004)130:6(476).

Vogel H.J. (2000) A numerical experiment on pore size, pore connectivity, water retention, permeability, and solute transport using network models. European Journal of Soil Science 51:99-105. DOI: 10.1046/j.1365-2389.2000.00275.x.

Vogel H.J., Weller U., Schlüter S. (2010) Quantification of soil structure based on Minkowski functions. Computers & Geosciences 36:1236-1245. DOI: 10.1016/j.cageo.2010.03.007.

Warkentin B.R. (2008) Soil structure: A history from tilth to habitat, Advances in Agronomy, Vol 97, Elsevier Academic Press Inc, San Diego. pp. 239-272.

White E.R. (2006) Principles and Practice of Soil Science Bleckwell Science Ltd, Carlton, Victoria, Australia.

Young I.M., Crawford J.W., Rappoldt C. (2001) New methods and models for characterising structural heterogeneity of soil. Soil & Tillage Research 61:33-45. DOI: 10.1016/s0167-1987(01)00188-x.

Zhang X.C., Norton L.D. (2002) Effect of exchangeable Mg on saturated hydraulic conductivity, disaggregation and clay dispersion of disturbed soils. Journal of Hydrology 260:194-205.