

# **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*

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## **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  $\text{Ca}^{2+}$  is equated to  $\text{Mg}^{2+}$  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  $\text{K}^+$ , 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 
$$\text{SAR} = \frac{\text{Na}}{\sqrt{(\text{Ca} + \text{Mg})/2}}$$

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

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  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  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  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$  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 ( $\mu\text{CT}$ ) scanning of the cation treated soil samples. Changes in pore architecture as influenced by the proportion of cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) bonded to soil particles were characterised. All the structural parameters, studied by  $\mu\text{CT}$  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  $\mu$ CT 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.

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