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

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Abstract

Sodic soils occur in about 30% of the total land area in Australia and 86% of these sodic soils are alkaline (pH> 8.4), particularly in dense clayey subsoils (Rengasamy and Olsson 1991). Many of these alkaline soils also contain lime ($CaCO_3$) ranging from 10 to 2000 t ha^{-1} up to a metre depth. In spite of the presence of calcium compound, sodicity is highly prevalent and affects soil physical properties related to transport of air and water. High pH of these soils also interferes with nutrient availability. These constraints are considered to reduce the potential yields of crops to less than half.

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

The literature review has identified soil pH as an important factor affecting these properties. Therefore, the mechanisms by which pH controls swelling and dispersion as well as how to reduce soil pH by utilising the native $CaCO_3$ are the foci of this thesis.

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

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

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

In Ca-clays the trends were similar to Na-clays up to pH 7.0. In more alkaline solution $CaCO_3$ formation led to charge reduction on clay particles, resulting in flocculation and reduction of zeta potential. At similar pHs the electrophoretic mobilities of all the clays showed constant potential behaviour. However, the zeta potentials of Ca-clays were always smaller than those of sodic clays because the clays were more aggregated. Net particle charge was the most important factor in controlling clay dispersion for the whole range of pH and ionic strength and for all types of cations.

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

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

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

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

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

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

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

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

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

Studies on pure clays and soil clay have clearly shown that particle charge, when altered either by heating or by changing pH, influences swelling and dispersion properties. Therefore, a greenhouse study was conducted to evaluate the effects of a few amendments viz. gypsum, green manure and glucose on the physical properties of Natrixeralf (with alkaline pH of 9.4 and 5% $CaCO_3$ content) by influencing pH, carbonate chemistry and particle charge.

Gypsum reduced the pH from 9.38 to 7.89, increased Ca^{2+} in soil solution and reduced SAR from 11.6 to 1.2. Green manure, due to increased CO_2 production, reduced pH to 8.68 and SAR to 7.52. Green manure plus gypsum reduced pH to 7.67 and SAR to 0.91. The interactive effect of gypsum and green manure on all soil properties was highly significant as shown by ANOVA analysis. Reduction of soil pH was also reflected in the levels of carbonates in soil solution.

Addition of glucose increased the microbial activity and produced fatty acids. The drastic reduction of pH (< 6.0) was related to the amount of glucose added. The concentration of Ca^{2+}, carbonates and SAR values were inversely related to the soil pH after glucose addition. The data on soluble Na_2CO_3 and $NaHCO_3$, zeta potential, mechanical dispersion, aggregate stability and saturated hydraulic conductivity confirm the effects of pH reduction and carbonate solubility as influenced by the amendments in alkaline sodic soil.

Thus, particle charge emerges as the primary factor in controlling swelling and dispersion of soil clays in alkaline sodic soils. This study has shown that, under natural conditions, when these soils contain native lime, particle charge can be manipulated by aiming to reduce alkaline pH to the values < 8.4. Future studies should concentrate on how organic matter can be used to manipulate particle charge of sodic soils even when lime is absent.

Statement

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university. To best of author's knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

I give consent to this copy of my thesis, when deposited in the University Library, being available for photocopying and loan.

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Publications from the Thesis

(a) Refereed articles

1. Chorom M., Rengasamy, P., and Murray, R. S. (1994). Clay dispersion as influenced by pH and net particle charge of sodic soils. *Australian Journal of Soil Research* **32**, 1243-52.

2. Chorom M., Rengasamy, P., and Murray, R. S. (1995). The effect of pH and electrical charge on clay dispersion. In 'Sealing, Crusting and Hardsetting Soils: Productivity and Conservation. (Eds H. B. So, G. D. Smith, S. R. Raine, B. M. Schafer and R. J. Loch) pp. 431- 35. (Australian Society of Soil Science Inc. : Queensland)

3. Chorom, M., and 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- 65.

4. Chorom, M., and Rengasamy, P. (1996). Effect of heating on swelling and dispersion of different cationic forms of a smectite. *Clays and Clay Minerals* **44**, (in press).

5. Chorom, M., and Rengasamy, P. (in press). Slaking and dispersion of different cationic forms of illite and kaolinite as influenced by heating. *Applied Clay Science*

6. Chorom, M., and Rengasamy, P. (in press). Carbonate chemistry, pH and physical properties of an alkaline sodic soil as affected by various amendments. *Australian Journal of Soil Research*

7. Chorom, M., Janik, L. J., and Rengasamy, P. (in review). Infrared spectra of homoionic clays heated up to 400°C in relation to swelling, dispersion and net particle charge.

(b) Conference poster

8. Chorom, M., and Rengasamy, P. (1996). Clay swelling and dispersion as affected by thermal energy. In 'Proceedings of the Australian and New Zealand National Soils Conference' Vol. 3, pp. 41-42 (Melbourne; Australia)

CHAPTER 1

INTRODUCTION

Sodic soils exhibit physical and nutritional problems due to poor soil-water and soil-air relations. The problems of low crop production on sodic soils are mainly associated with their low macro-porosity and poor stability of macropores. Often sodic soils exhibit surface sealing, crusting and hardsetting (Rengasamy *et al.* 1993) and these processes commonly restrict infiltration, induce waterlogging, increase runoff and erosion (Jayawardane and Chan 1994), reduce seedling emergence and crop establishment. Alkaline pH values, found in many of these soils, exacerbate these problems in addition to affecting plant nutrition.

The distribution of sodic soils is generally related to the pattern of average annual rainfall (Northcote 1988). Soils that are sodic throughout the profile seldom occur where average annual rainfall exceeds 500 mm. The majority of salt-affected soils in Australia consist of different types of alkaline sodic soils. Many of the alkaline sodic soils also contain lime ($CaCO_3$) in quantities ranging from 10 to 2000 t ha^{-1} at up to a metre in depth. Sodic soils cover 30% of the Australian land (Northcote and Skene 1972) and a large proportion (86%) of these soils have dense subsoils with an alkaline pH (8 - 9.5), (Rengasamy and Olsson 1991). The predominance of sodic soils in Australia is revealed by the high sodic/saline soils ratio of 5.17 compared to < 1.0 in other parts of the world. Rengasamy and Olsson (1991) suggested that the relatively high ratio of sodic/saline soils in Australia was due to the higher ratio of Na/(Na+ Ca) in the soil solution and ground water, compared with other countries.

Because salinity in soil environments in Australia is dominated by NaCl, any process that accumulates NaCl salt in the soil profile inevitably leads to soil sodification unless soluble calcium or magnesium minerals are present in the profile (Rengasamy and Olsson 1991). Sodium salts are deposited in soil layers when the rain and irrigation waters (which derive sodium salts from different sources) are lost by evaporation and transpiration. These salts accumulate in the soil layer if they are not dissolved and are either leached to depth or exported in the drainage water. The degree of sodification of soil layers depends on the proportion of sodium to multivalent ions in the soil solution; this is generally measured as the sodium adsorption ratio (SAR).

Two processes, namely swelling and dispersion are responsible for the physical behaviour of sodic soils during wetting. Both swelling and dispersion behaviour are governed by the balance between attractive and repulsive forces arising from intermolecular and electrostatic interactions involving solution and solid phases in the soil. Recent studies have shown that clay dispersion is influenced by a range of soil properties such as clay mineralogy, sodicity, electrolyte levels and composition, clay content, charge density and organic matter (Emerson 1977; Quirk 1977; Rengasamy and Olsson 1991; Sumner 1993). These studies have neglected the influence of soil pH on clay dispersion. Sodic soils all over the world vary widely in their pH values, usually ranging from 4 to 10 (Szabolcs, 1989). Flocculation experiments, conducted at different pH values, have reported highly variable flocculation values (Sumner, 1993), without emphasising the effect of varying pH. The pH influences clay dispersion by changing the charge on soil particles (Sumner 1993). The particle charge of sodium-saturated clays depends on the degree of protonation of aluminol and silanol groups as affected by pH and, as a result, clay dispersion-flocculation behaviour is also altered (Thellier *et al.* 1992).

Alteration of particle charge and the resultant clay behaviour have not been investigated quantitatively. Studies of the swelling and dispersion of pure clays under different conditions of pH, SAR, cation type and electrical conductivity (EC) in solution are essential to understand the mechanisms of these processes. The models derived from pure clays will enable rationalisation of the behaviour of soil clays which are heterogenous in nature.

The main objective of this thesis is to investigate the factors affecting swelling and dispersion of alkaline sodic soils containing native lime and ways of managing these soils to improve their physical conditions. The literature review has identified the soil pH as an important factor affecting swelling and dispersion properties of alkaline sodic soils. Therefore, the mechanisms by which pH controls swelling and dispersion, as well as how to reduce soil pH by utilising the native $CaCO_3$, are the foci of this thesis.

The investigations in this study have the following aims:

i) To establish how dispersion and zeta potential of pure clays are related to net particle charge.

ii) To understand how dispersion of soil clays are influenced by pH and net particle charge

iii) To study the clay behaviour by changing particle charge

iv) To study how different amendments influence the behaviour of an alkaline sodic soil so that management strategies may be devised.

CHAPTER 2

Review of Literature

2.1 Sodic soils

2.1.1 Nature of sodic soils

Sodic soils have extremely poor physical properties which lead to an inadequate balance between water and air within the soil. This imbalance stems from restricted water infiltration and transmission properties which result in the soil being too wet or too dry for much of the time; this is leads to poor root development and crop growth (Shainberg and Letey 1984). In addition, sodic soils are difficult to cultivate and have poor load bearing characteristics. The lack of structural stability in these soils promotes seal and crust formation at the soil surface resulting in soil erosion (Rengasamy and Olsson 1991).

Two processes, namely swelling and dispersion are responsible for the physical behaviour of sodic soils during wetting. Both swelling and dispersion behaviour are governed by the balance between attractive and repulsive forces arising from intermolecular and electrostatic interactions involving solution and solid phases in the soil.

When sodium is involved in the association between clay particles, soils tend to form massive structures without the normal hierarchical arrangement of different particle size ranging into micro- and macro-aggregates (Barzegar *et al.* 1994). Slaking, swelling and clay dispersion are the major mechanisms by which the massive structure of sodic soils disintegrates during rain or irrigation resulting in the observed poor physical condition (Rengasamy and Olsson 1991). Poorly structured sodic soils constrain crop productivity firstly by restricting the growth and function of roots and secondly, by restricting gas exchange and the storage and transport of water through the characteristically low porosity of the soil. Figure 2.1 illustrates, for sodic and non-sodic soils, the range of soil water content over which roots are able to grow and in which they are not limited by aeration and strength (Rengasamy *et al.* 1992). As a general approximation, a penetrometer resistance of < 1 MPa and an air-filled porosity of > 15% may be considered to be non-limiting for root growth. For sodic soil, the soil has to be dried to the point B over a longer time period in order to meet the specification for air-filled porosity. By this time, increasing soil strength is a limitation for root growth. In contrast, the relatively higher macro-porosity of non-sodic soils allows the aeration specification to be met quickly after only a small amount of water withdrawal, to D. The strength becomes limiting at the much lower water content C, allowing a wider range of water content as well as a longer period for root growth in rapidly drying soil.

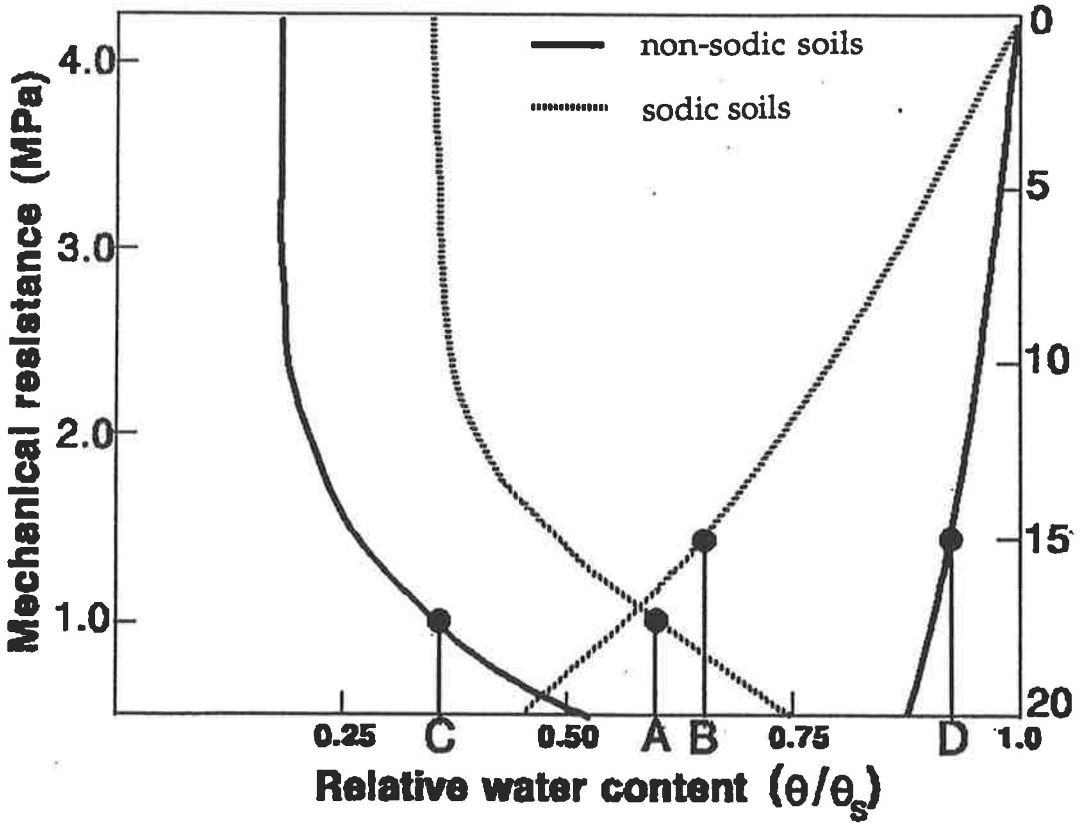

Fig. 2.1. Ranges of water content (volumetric) in sodic and non-sodic soils where soil aeration and strength are non-limiting for root growth (after Rengasamy *et al.* 1992).

2.1.2 *World distribution of saline and sodic soils*

Saline and sodic soils cover about 10% of the world's arable land and exist in over 100 countries. Salt-affected soils are not limited to semi-arid or arid regions. In several other regions, the climate and mobility of salts produce saline water and soil seasonally. Table 2.1 (after Szabolcs 1989; Gupta and Abrol 1990) shows that salt-affected soils are to be found to various extents, on all continents. For example, in Australia they contribute to a much higher percentage of the total surface than anywhere else.

Table 2.1. World distribution of salt-affected soils

	Area in thousands of hectares			
Continent	Saline	Sodic	Total	Sodic/saline ratio
North America	6,191	9,564	15,755	1.55
Mexico and Central America	1,965	-	1,965	-
South America	69,410	59,573	129,163	0.86
Africa	53,492	26,946	80,438	0.5
South Asia	83,312	1,798	85,110	0.02
North and Central Asia	91,621	120,065	211,686	1.31
Southeast Asia	19,983	-	19,983	-
Australia	17,269	339,971	357,971	5.17

In Asia the greatest occurrence of salt-affected soils after the U.S.S.R., China, India, and Pakistan can be found in Iran. The arid conditions of this country contribute to the formation of saline soils, which are very common in several areas. Alkaline soils are also frequent and gypsiferous soils particularly so; acid sulfate soils also occur. They are either poorly drained or have developed under poor drainage conditions. Saline soils contain large quantities of soluble salts, are usually light-coloured and poor in organic matter, and have a slightly crusted, friable granular structure. The salts in saline soils are mainly dominated by chlorides, but sulphates are also present in considerable quantities, being found as sodium sulphate in saline soils and as calcium sulphate in gypsiferous soils (Szabolcs 1989). Sodic soils are the products of the partial leaching and alkalisation of saline soils, often due to irrigation without proper drainage and management. Sodic soils frequently develop in spots, scattered throughout saline or other soil types. They have a surface layer of light-coloured leached material over a darker subsoil.

2.1.2.1 Australia

Australia has the highest ratio of salt-affected soils in relation to the total surface of the continent. About one third of this continent is covered by salt-affected soils of various types (Northcote and Skene 1972). The large area of salt-affected soils in Australia can be explained partly by the fact that this is the driest continent in the world. Due to the climatic conditions, 87% of the average annual rainfall, which totals 420 mm, is lost into the atmosphere due to evaporation and transpiration. Consequently, accumulation of salts in the soils is very pronounced. A great part of the Australian continent consists of deserts and semi-deserts, where saline soils are very widespread. Table 2.2 shows the areas of salt-affected soils in Australia according to Northcote and Skene (1972). Table 2.2 indicates that the majority of salt-affected soils in Australia consist of different types of alkaline and sodic soils. The predominance of sodic soils in Australia is revealed by the high sodic/saline soils ratio of 5.17 compared to 0.50 to 1.55 in other parts of the world (Table 2.1).

Table 2.2. Area of saline sodic soils in Australia

Saline sodic soil category	Area (Km^2)	Area (% total)
Saline soils	386,300	5.3
Alkaline strongly sodic to sodic clay Soils with uniform texture profiles	666,400	9.2
Alkaline strongly sodic to sodic coarse and medium textured soils with uniform and gradational texture	600,700	8.3
Alkaline strongly sodic to sodic duplex soils	454,400	6.3
Non alkaline sodic and strongly sodic neutral duplex soils	134,700	1.9
Non alkaline sodic acid duplex soils	140,700	1.9
Total		**32.9**

2.1.3 Classification of saline and sodic soils

Sodic soils occur both naturally and as a result of irrigation practices which permit the mobilisation of salt within the soil body and the transport to new locations. Such soils are usually separated into two groups, namely, saline soils on the one hand, and alkaline and/or sodic soils, on the other (Shainberg and Letey 1984; Gupta and Abrol 1990).

2.1.3.1 Saline soils

Saline soils, often recognised by the presence of salt encrustations on the surface, predominantly contain chlorides and sulphates of Na^+, Ca^{2+} and Mg^{2+}. Soils with neutral soluble salts have a saturation paste $pH < 8.2$. The electrical conductivity of saturation extracts of saline soils is generally more than 4 dS m^{-1} at 25°C. When chlorides and sulphates of Ca and Mg are the predominant salts, the sodium adsorption ratio (SAR) of the soil solution is usually less than 15. If soils contain neutral salts and hence high SAR (SAR>15) they are termed saline-sodic (U.S. Salinity Laboratory Staff 1954).

2.1.3.2 Alkaline sodic soils

Alkaline soils frequently have poor physical properties due to high sodicity and high pH, resulting in restricted water and air movement (Acharya and Abrol 1978). Plants in alkaline soils commonly lack an adequate and continuous water supply due to low infiltration rates. This results in shallow wetting and temporary waterlogging problems, diminished water storage in the rhizosphere due to cracking, extremely low water conductivity, and narrow available moisture range. Leaching alkaline soils with waters having electrolyte concentrations insufficient to maintain flocculated conditions cause hydraulic conductivity reductions due to clay swelling, dispersion and movement and consequent blockage of water-conducting pores (Frenkel *et al.* 1978).

The alkalinity of a sodic soil solution (Sposito 1989) is represented by:

$$\text{Alkalinity} = [HCO_3^-] + 2\,[CO_3^{2-}] + [H_2PO_4^-] + 2\,[HPO_4^{2-}] + 3\,[PO_4^{3-}] + [B(OH)_4^-] + [L^-] + [OH^-] - [H^+] \qquad [2.1]$$

where L^- denotes organic ligands with negatively charged functional groups. Partial pressure of CO_2 and the concentration of CO_3^{2-} and HCO_3^- ions are the principal factors responsible for alkaline pH (Beek and Breeman 1973; Mashhady and Rowell 1978) and this relationships are as follows:

$$pH = 7.83 + \log\,[HCO3] - \log P_{CO2} - 0.51\mu^{0.5} \qquad [2.2]$$

$$\text{Log(Alkalinity)} = pH + \log P_{CO2} - 7.82 \qquad [2.3]$$

where μ refers to the ionic strength of the soil solution.

As the concentration of CO_3^{2-} and HCO_3^- increase with drying by evaporation in arid and semi-arid climates (annual precipitation<500 mm), soluble calcium and magnesium become low and sodium and potassium accumulate in the soil solution. The resulting increase in SAR is associated with an increase in pH caused by the formation of $NaHCO_3$ and $NaCO_3$.

USSL Staff (1954) defined a non saline-alkali soil as one in which the ESP>15, EC of the saturation extract is <4 dS m^{-1}, and pH is between 8.5 and 10. In the mid 1960s, the term sodic began to be used instead of 'alkaline' with the definition "a soil having an ESP>15%" (Anon 1965). The influence of texture was recognised by Greene *et al.* (1978) who changed the critical ESP to 10 for fine-textured and 20 for coarse-textured sodic soils.

For Australian saline and sodic soils, Rengasamy and Olsson (1991) have proposed a classification (Figure 2.2) based upon the key soil properties; sodium adsorption ratio (SAR), electrolyte concentration measured as electrical conductivity (EC) and pH of 1:5 (W/V) soil:water suspension. These key properties were selected since they are the major factors involved in the deleterious effects of sodicity on soil structure. The ESP of the soil is approximately twice the SAR of the 1:5 soil water extract, and hence is consistent with the widely used Northcote and Skene (1972) threshold value of ESP 6.

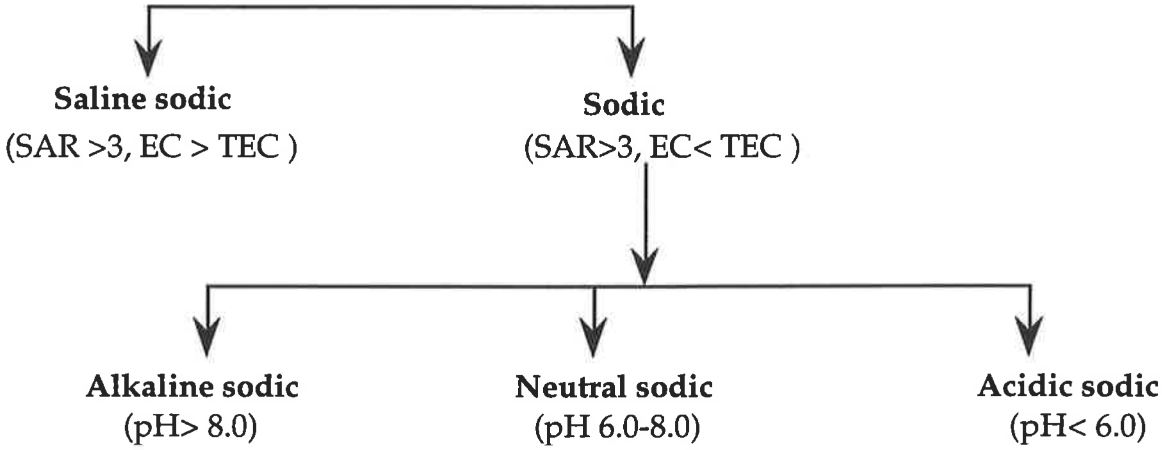

Fig. 2.2. Proposed classification of sodic soils by Rengasamy and Olsson (1991), TEC denotes threshold electrolyte concentration

In the new Australian national classification system (Isbell 1995) sodicity is used at several hierarchical levels (Table 2.3). Those soils with a strong texture contrast and B horizons in which the upper part has pH ≥5.5 and ESP >6 are separated at the highest categorical level (order) and are termed Sodosols. Further subdivision is then made at the great group level into three classes: subnatric (ESP 6-14), mesonatric (ESP 15-25) and hypernatric (ESP >25). In seven other orders, B-horizon sodicity is used to create classes at the great group or subgroup level.

Table 2.3. Use of sodicity in the new Australian soil classification proposed by Isbell (1995)

Order	Great group	Subgroup
Sodosols (texture contrast with upper B horizon pH 5.5 or more and ESP ≥6)	Subnatric (ESP 6-14) Mesonatric (ESP 15-25) Hypermatric (ESP >25)	
Kurosols texture-contrast, upper B horizon pH <5.5	Natric (ESP ≥6) in upper B horizon	
Hydrosols (prolonged seasonal saturation of profile)	Sodosolic (as for Sodosol definition)	Sodic (ESP ≥6 in lower B horizon)
Chromosols (texture-contrast with upper B horizon pH 5.5 or more and non-sodic)		Sodic (ESP ≥6 in lower B horizon)
Dermosols (no strong texture-contrast, structured B horizon)		Sodic (ESP ≥6 in lower B horizon)
Kandosols (no strong texture-contrast, massive B horizon)		Sodic (ESP ≥6 in lower B horizon)
Calcarosols (calcareous throughout, no strong texture-contrast)		Epihypersodic (ESP ≥15 in upper 0.5 m) Endohypersodic (ESP ≥15 below 0.5 m)
Vertosols (cracking clay, ≥35%, with slickensides)		Episodic (ESP ≥6 in upper 0.1 m) Epihypersodic (ESP ≥15 in upper 0.5 m) Endohypersodic (ESP ≥15 below 0.5 m)

2.1.3.3 Calcareous soils

Calcareous soils are found in arid, semi-arid and humid regions of the world. Soils that develop from calcareous parent material often have calcium carbonate somewhere in the profile. The physical condition of calcareous soils is usually satisfactory, because the exchange complex is usually saturated with Ca^{2+}. There are calcareous soils which are poorly structured, although they appear to have sufficient calcium carbonate present to maintain the stability of soil aggregates. This indicates that some factors can operate in soils that reduce the efficiency of $CaCO_3$ by decreasing its solubility. Calcareous soils containing soluble carbonates and having ESP>15 and saturated paste pH>8.2 manifest problems associated with alkalinity. These soils contain soluble salts in variable quantities. A large number of researchers have reported a direct positive relation between ESP and soil pH for calcareous sodic soils (Gupta and Abrol 1990).

2.1.3.4 Measuring salinity and sodicity

The chemical and physical properties of a salt-affected soil reflect the amount and type of salt present One of the methods for determining the amount of dissolved salts is called the total dissolved solids (TDS) and the used units are mg l^{-1} (p.p.m).

$$\text{TDS (mg l}^{-1}\text{)} = 640^{*}\ \text{EC(dS m}^{-1}\text{)} \qquad [2.4]$$

$$\text{TDS (mmol}_c\text{ l}^{-1}\text{)} = 10^{*}\ \text{EC(dS m}^{-1}\text{)} \qquad [2.5]$$

(Note that: dS m^{-1}=mS cm^{-1}=mmhos cm^{-1})

Determinations of sodicity and alkaline status of soils are important for assessing amendment requirements. It has been observed that different methods of determining cation-exchange capacity and exchangeable sodium generally yield differing results.

The first parameter of importance is the exchangeable sodium percentage (ESP) which can be defined as:

$$\text{ESP} = (100^{*}\ \text{Exchangeable Na}^{+})/\text{cation exchange capacity or} \quad [2.6]$$

$$\text{ESP} = (100\text{x Ex. Na}^{+}) \ / \ \text{Ex. } (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^{+} + \text{Na}^{+} + \text{Al}^{3+}) \quad [2.7]$$

Sodium adsorption ratio (SAR) is another parameter for definition of sodic soils which can be defined as :

$$\text{SAR} = \frac{[\text{Na}^{+}]}{\sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})}} \quad [2.8]$$

Where all concentrations are in mmol l^{-1}. SAR therefore has the unit (mmol $l^{-1})^{0.5}$.

Exchangeable sodium ratio [ESR = Ex.Na /(CEC- Ex.Na)] [2.9]

is another parameter for definition of sodic soils.

The ESP of a soil can be estimated from the SAR of the water with which it is in equilibrium using the following equation (USSL Staff, 1954):

$$\text{ESP} = 1.475\ (\text{SAR}) / \ (1 + 0.0147\ \text{SAR}) \quad [2.10]$$

Rengasamy *et al.* (1984a) suggested that ESP can be estimated from the SAR of soil solution using the following equation when more dilute extracts such as 1:5 soil:water extract, are used:

$$\text{ESP} = 1.95\ (\text{SAR}) + 1.8 \quad [2.11]$$

2.2 Dispersion of sodic soils

Dispersion of clay particles is the primary process responsible for the degradation of physical properties of sodic soils. Clay dispersion is defined as the formation of a stable suspension of particles in water. It is caused by the mutual repulsion between clay particles which results from the presence of an extensive negative electric field surrounding them (van Olphen 1977; Rengasamy and Olsson 1991). When a clay system is dispersed, particles frequently collide under the influence of Brownian motion, but repulsive forces in the diffuse double layer cause them to separate again. When electrolyte concentration is increased, repulsive forces are reduced allowing the van der Waals forces of attraction to prevail. Under such conditions, the system flocculates. The minimum concentration of electrolyte solution which is required to maintain flocculation is called the threshold electrolyte concentration (TEC).

2.2.1 Spontaneous dispersion

Clay dispersion occurs by two mechanisms; (a) spontaneously on wetting and (b) via mechanical processes on application of external energy. At low electrolyte concentrations when sodium is the principal adsorbed cation, the distance between the particles continuously increases, with reduced soil water suction, to beyond about 7 nm and clay particles become completely independent of each other (Rengasamy and Olsson 1991). Soils with an exchangeable sodium percentage (ESP) >6 and electrolyte concentration (EC) less than the threshold electrolyte concentration (TEC) disperse spontaneously (Rengasamy *et al.* 1984a). At moderate to high ESP values, clays from soil aggregates may spontaneously disperse when placed in distilled water provided that their salt contents are sufficiently low (Emerson and Bakker 1973). Under such conditions, the repulsive energy within the double layer is so much larger than the van der Waals force of attraction and the clay particles are able to overcome the energy barrier and move apart. With progressive reduction in ESP, these two opposing forces become more nearly equal and increasingly, to achieve dispersion, energy (e.g. shaking, sonication) must be supplied to promote the separation of the particles. When particles are bonded together by organic or inorganic cements or when the attractive forces between particles are dominant (low ESP and TEC values) stable dispersion will not be achieved no matter what quantity of energy is applied and the system remains flocculated.

Spontaneous dispersion can occur at ESP levels as low as 10 to 20 if the electrolyte level is <10 meq l^{-1} (Felhendler *et al.* 1974).

2.2.2 *Mechanical dispersion*

Mechanical dispersion is defined as the additional mechanical work required for dispersion in order to overcome the attractive forces between clay particles. Emerson (1967) and Rengasamy *et al.* (1984a) clearly demonstrated the importance of mechanical stress in influencing dispersion. Rengasamy *et al.* (1984a) analysed 138 Australian soil samples and showed that nearly 80% of the samples dispersed after mechanical shaking even with SAR values less than 3. Spontaneous dispersion occurred in only 20% of the samples with equilibrium $SAR_{1:5}$ values greater than 3.

2.2.3 *Factors affecting clay dispersion*

Recent evidence shows that dispersion of soil colloids is influenced by a range of soil properties such as pH, clay mineralogy, sodicity, clay content, charge density, clay-organic interaction and electrolyte levels (Emerson 1977; Quirk 1977; Frenkel *et al.* 1978; Gupta *et al.* 1984; Goldberg *et al.* 1991; Sumner 1993).

2.2.3.1 The influence of electrolyte concentration on dispersible clay

Several studies have been conducted on the effect of electrolyte concentration on clay dispersion. Quirk and Schofield (1955) reported that the amount of dispersed clay decreased with increasing electrolyte concentration. Soil can be maintained in a flocculated state, even at high ESP values, provided that the EC of the solid solution is above a critical (threshold) level (Quirk and Schofield 1955). Shainberg *et al.* (1981) showed that clay dispersion was very sensitive to the level of exchangeable sodium and to the salt concentration of the soil solution. When the concentration of salt in the soil solution was 3.0 meq l^{-1}, spontaneous clay dispersion occurred only if ESP values exceeded 12%. Conversely, when the concentration of the soil solution was maintained at ~ 0.5 meq l^{-1} spontaneous clay dispersion occurred at ESP values as low as 1 to 2% because the electrolyte concentration of the soil solution was below the threshold value. Shainberg *et al.* (1981) concluded that mineral soils which release salt at a rate sufficient to maintain the soil solution concentration above the flocculation value of the clay at its given ESP level will not disperse. However, mineral soils that do not release enough salt in the soil solution will be dispersed, and they will also be very sensitive to low levels of ESP.

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, and kaolinite. These authors concluded that critical coagulation concentrations (CCC) were 185, 52, 28 to 60 and 8 meq l^{-1}, respectively, for the above clays. The role of $NaHCO_3$ is to keep the pH in the alkaline range. Threshold electrolyte concentrations vary from soil to soil, however, and cannot generally be forecast without empirical tests, even for soils of similar clay content and type (Rhoades and Ingvalson 1969).

2 sentences

Even though, for a given soil type, clay dispersion is controlled by sodicity (SAR) and salinity (EC) as defined by TEC (threshold electrolyte concentration) lines (Quirk and Schofield 1955). Several other factors which affect the negative charge on soils also change the slopes and intercepts of these lines (Rengasamy and Olsson 1991). Figure 2.3 shows, schematically, the factors affecting the changes in TEC lines. For a given SAR, the line A-B in Figure 2.3 predicts the TEC necessary to prevent spontaneous clay dispersion in the soils. With increasing negative charge, the slope and intercept of the line A-B relating SAR and EC increase toward a line C-D as shown in Figure 2.3. For a given soil, increase in pH, broken bonds of organic and bio-polymers, adsorbed organic molecules and exposure of particle surfaces due to fragmentation of aggregates, causes an increase in the nagative charge (Rengasamy and Olsson 1991). The line C-D represents the TEC necessary to prevent mechanical dispersion in the soils. The TEC necessary to prevent mechanical dispersion is always higher than that required to prevent spontanous dispersion. This is due to the increased negative charge on surfaces exposed during mechanical agitation (Rengasamy and Olsson 1991). These are several factors such as increase in pH, broken bonds of organic and bio-polymers, adsorption of organic molecules, exposure of surfaces, all lead to change in negative charge and hence threshold electrolyte concentration needed for flocculation.

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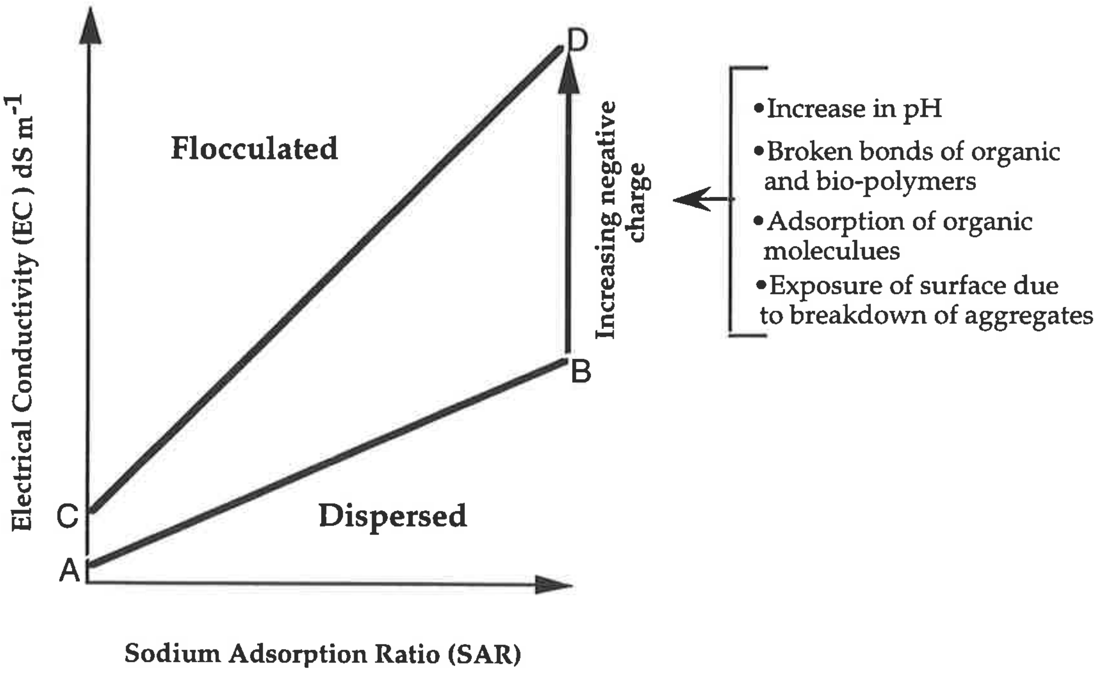

Fig. 2.3. Factors influencing threshold electrolyte concentration (after Rengasamy and Olsson 1991).

2.2.3.2 Sodicity and soil pH

In calcareous soils, high ESP and high pH nearly always go together, and it is often difficult to apportion their effects on the resulting poor physico-chemical conditions and consequently on crop growth. As an example, Gupta *et*

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al. (1984) observed increased dispersible clay both with high pH and high sodicity.

An excess of exchangeable sodium and high pH caused by the presence of sodium bicarbonate or carbonate impart poor physical conditions to these soils, and adversely affect plant growth. 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 (Beek and Breeman 1973). 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. Gupta and Khosla (1982) indicated that pH, with its intimate relationship with sodicity of calcareous soils, is likely to affect the whole range of physico-chemical and surface properties of soils.

Variations in pH have been found to affect dispersion in many pure clay minerals (Schofield and Samson 1954; Arora and Coleman 1979; Goldberg and Forster 1990; Thellier *et al.* 1992) and in soils (Gupta *et al.* 1984; Suarez *et al.* 1984). Depending on clay mineralogy and oxide contents, soils may exhibit a net negative charge or positive charge at high or low pH respectively. For example, Suarez *et al.* (1984) showed that at constant SAR and electrolyte levels, clay dispersion increased with increasing pH for two arid-zone soils, one predominantly kaolinitic and the other smectitic.

Clay minerals have negative charges, while their edges and the surfaces of the sesquioxides can have either charge depending on conditions in the equilibrium solution. Isomorphous substitution is the mechanism of charge generation in permanently charged minerals, where surface charge is independent of pH, whereas, for variable charge surfaces, the charge is entirely dependent on the pH of the equilibrium solution (Sumner 1993).

Changes in pH affect the edge charge on clays and the surface charge of oxide minerals such as iron and aluminium oxides. Soils having large amounts of variable charge minerals should be most susceptible to pH effects (Suarez *et al.* 1984). They found that dispersion increased with increasing pH for both kaolinitic and montmorillonitic soil. In this regard, these authors suggested that the pH effect in their soil was due to the presence of variable charge minerals and organic matter. At low pH these materials are positively charged and bonded to the negatively charged faces of the phyllosilicates. At high pH, however, they underwent charge reversal, contributed negative charge to the system, and thereby increased dispersion. The predominant variable-charge minerals in soils are the Al and Fe oxides (Bohn *et al.* 1979).

For surface soils , the zero point of charge (ZPC) and charge reversal usually occurs around pH 7 to 9 (Bowden *et al.* 1980), but may vary depending on the structural composition and degree of crystallinity of the variable charge components. At low pH values (lower than the ZPC), the positive charge on edge surfaces leads to edge-to-face association which inhibits dispersion. When the pH exceeds the ZPC, increase in negative charge results in increased dispersion. Adsorption of various anions can increase the net negative charge in the clay system and hence its dispersion (Shanmuganathan and Oades 1983).

Arora and Coleman (1979) observed that increasing the pH (from 7 to 9.5) resulted in increasing dispersion of their soil clays, but for specimen clays, maximum dispersion occurred at pH 8.3. They found that increasing the pH of a Georgia kaolinite from 7 to 8.3 made the soil more dispersive than any of the other samples, including pure clays such as smectites, illites and vermiculites.

From these results, it was concluded that the role of pH in promoting dispersion is very important. At high and low pH, soils (depending on clay mineralogy and the presence of oxides) would be expected to exhibit negative and positive charge respectively. In both systems, one would expect to have dispersion under acid and alkaline rather than under neutral conditions.

2.2.3.3 Clay mineralogy

The effect of exchangeable cations and electrolytes in increasing swelling and dispersion in aggregates is largely dependent on the dominant type of clay mineral present in soil. Schofield and Samson (1954) found that a pure sodium - kaolinite flocculated at pH<7 which illite and montmorillonite under these conditions dispersed. They showed that kaolinite edge faces are positively charged at low pH (pH approximately 4) and the system is partially flocculated. At high pH, it was completely deflocculated, which they attributed to the loss of positive edge charges. Kaolinite exhibits a much greater variable charge which is pH dependent. At low levels of sodium and in weak electrolyte solutions smectitic and micaceous soils disperse more than kaolinitic soils as showen by Velesco-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 > halloysite > mica. However, at low ESP values, micaceous soil sometimes dispersed more than the halloysitic-kaolinitic soils. Using Australian soils, Emerson (1983) found that soils dominated by clay sized mica (illite) dispersed easily. Oster *et al.* (1980) found much greater 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.* 1984a). 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 e*t al.* 1978). The surface area is inversely related to the thickness of the particles. Smectites have larger total surface area than other clay minerals (e.g. clay-sized micas). 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 surfaces (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. The removal of amorphous and/or crystalline oxides increased the clay dispersibility. These results indicate an important role for both 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 the 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); El Rayah and Rowell (1973) and Shanmuganathan and Oades (1982). Deshpande *et al.* (1964) found that Al oxide reduced swelling but Fe oxide did not. They concluded that Al oxide was acting as a cement and that Fe oxide was present as discrete particles. 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 effects of Na ions better than Fe polymers. Moreover, Oades (1984) found Al polymers to be more efficient than Fe polymers in reducing the swelling of montmorillonite. He suggested that this difference was a result of polymer morphology. Aluminum polymers occur as sheets and can, therefore, neutralise clay layer charge more completely than can the spherical Fe polymers. Shanmuganathan and Oades (1982) showed that by applying iron polycations, the amount of dispersible clay in an illitic soil decreased because arid zone soils are usually low in organic matter, and aluminium and iron oxide content. Goldberg *et al.* (1988) suggested that aluminium and iron oxides play an important role as binding agents in the structure of arid zone soils. McNeal *et al.* (1968) showed that iron oxides stabilise soils against dispersion under high-sodium and low-salt conditions.

2.2.3.4 Effect of organic matter on clay dispersion

Sodicity is generally associated with poor soil structure whereas, organic matter has good effects to improve soil structure. The interactions between organic matter and sodicity are much less well understood (Emerson *et al.* 1986; Mullins *et al.* 1990 and Churchman *et al.* 1993). Grierson (1975) and Aylmore and Sills (1982) found that there is a negative correlation between the organic matter content of soils and sodicity effects for Australian soils.

The well-known positive effect of organic matter on soil structure probably occurs through binding of soil particles by roots and hyphae at the aggregate level, but at the clay-particle level the negative charge of organic anions enhances clay dispersion. Shamuganathan and Oades (1983) observed that addition of organic anions (fulvate, citrate, oxalate, tartrate, salicylate, aspirate, lactate and acetate) increased clay dispersion in an Australian soil. The role of organic matter in the soil was explained by Emerson (1983) as follows: organic bonds stabilise aggregates against slaking and disaggregation; however, once these bonds are broken and disaggregation has occurred, the organic matter acts as a deflocculating agent.

Goldberg *et al.* (1990) showed that the removal of organic matter from Spell sodiun saturated clay by hypochlorite, decreased the clay dispersion. They suggested that the effect of organic matter on soil structure is also a function of the size scale of the soil particles investigated. An explanation for this phenomenon has been proposed by Durgin and Chaney (1984). These authors indicated that if the organic anion is greater in length than the edge of the clay particle, its specific adsorption offsets the positive charge at the adsorption site, provides excess negative charge to the particle, and leads to dispersion. If, on the other hand, the organic anion is shorter than the clay edge, it will attach to the edges of several clay particles and bind them together. Gupta *et al.* (1984) demonstrated that increasing soil organic matter applied as farmyard manure under moderate to high sodic conditions (ESP=10-30) promoted clay dispersion in calcareous and non-calcareous soils. Goldberg *et al.* (1988) also showed that organic matter in arid zone soils in which the organic carbon content was below 1%, appears to promote clay dispersion. They observed that addition of farmyard manure increased clay dispersion of a salt-affected soil at high ESP.

2.3 Flocculation of dispersed clays

2.3.1 Introduction

Flocculation is an important step in many solid-liquid separation processes and is widely used in water treatment. Flocculation occurs only if particles (1) collide with each other and (2) can adhere when brought together by collision (i.e. the particles have low colloid stability). Although flocculation of clays in soil system is of a different nature, the forces operating are similar to that in pure clay suspensions.

When two particles approach each other, several types of interaction can come into play which may have a major effect on the flocculation process. The two most familiar kinds of colloidal interaction are van der Waals attraction and electrical repulsion which form the basis of the well known DLVO theory (Deryagin and Landau and Verwey and Overbeek) of colloid stability. While these enable a large amount of experimental flocculation data to be explained, at least in a semi quantitative manner (Gregory 1989), there are many cases where other types of interaction have to be invoked.

2.3.2 *Critical coagulation concentration*

When the repulsive force within a diffuse double layer is less than the attractive force, the particles will flocculate. Thus the balance between the attractive and repulsive forces determines whether a system will be dispersed or flocculated. The electrolyte concentration at this point, called the critical coagulation concentration (CCC), is inversely proportional to the sixth power of the valency of the counter ion. Thus, as the valency of the counter ion increases, the CCC decreases very rapidly (Sumner 1993). The flocculation value or CCC is the minimum electrolyte concentration required to cause flocculation of a given colloidal dispersion in a given time (van Olphen 1977). Conversely, if the salt concentration is below the CCC, dispersion occurs. The CCC is operationally defined by Goldberg and Glaubig (1987) as the salt concentration at which percent transmittance (%T) corresponds to 20% of the clay remaining in solution after 3 hours. The CCC values for Na-montmorillonite range from 7 to 20 meq l^{-1} NaCl (Arora and Coleman 1979), and those for Ca-montmorillonite range from 0.17 meq l^{-1} (van Olphen 1977) to 0.25 meq l^{-1} of $CaCl_2$ (Greene *et al.* 1978; Oster *et al.* 1980). For Na-kaolinite, CCC values range from 0 to 5 meq l^{-1} NaCl; however, Ca-kaolinite is flocculated even in distilled water (Arora and Coleman 1979). The CCC values for Na-illite range from 7 meq l^{-1} (Rengasamy 1983) to 55 meq l^{-1} of NaCl(Oster *et al.* 1980). The CCC for Ca-illite range from 0.25 mmol l^{-1} (Oster *et al.* 1980) to 1mmol l^{-1} of $CaCl_2$ (Greene *et al.* 1978).

2.3.3 *Flocculation of pure clays as related to pH and SAR*

The flocculation /dispersion behaviour of reference clay minerals has been found to be pH dependent (Swartzen- Allen and Matijevic 1976; Arora and Coleman 1979; Goldberg and Glaubig 1987). Dispersion of pure clay systems, particularly montmorillonite and illite, has been studied by many investigators (van Olphen, 1977; Emerson and Chi 1977; Greene *et al.* 1978; Arora and

Coleman 1979; Goldberg *et al.* 1991). Schofield and Samson (1954) found that a pure sodium -kaolinite flocculated at pH<7 under conditions that dispersed illite and montmorillonite. Arora and Coleman (1979) and Frenkel *et al.* (1978) found kaolinite with montmorillonite impurities to be more dispersive than pure kaolinite. The effect of pH and SAR on the flocculation of a reference kaolinite, montmorillonite and illite were investigated by Goldberg and Forster (1990). They found that the CCC values of all three clay minerals increased with increasing pH and SAR value. The CCC for kaolinite and illite were more pH dependent than those for montmorillonite at all SAR values. Moreover, they reported that the CCC values for kaolinite and illite were more dependent on SAR than those for montmorillonite, especially at high pH. The CCC values for Na-montmorillonite, Na-kaolinite and for Na-illite increased when pH increased from 2 to 12 in NaCl solution respectively (Swartzen-Allen and Matijevic 1976; Goldberg and Glaubig 1987). The CCC values for Ca-montmorillonite and Ca-kaolinite increased when the pH increased from 5.5 to 9.3 in $CaCl_2$ solution (Goldberg and Glaubig 1987).

The effect of the presence of Al or Fe oxides on CCC of the clay and clay mixtures as a function of pH was investigated by Goldberg and Glaubig (1987). They found that the CCC of all clays, clay mixtures, oxides and oxide-clay mixtures were pH dependent. The pH dependence for kaolinite was greater than that for montmorillonite, with the 50/50 mixture behaving more like montmorillonite. The same amount of oxide material was more effective in promoting flocculation in the Ca system than in the Na system. The ameliorative effect of Al oxide was greater than that of Fe oxide, probably because of the size and the morphology of the oxide particles.

Flocculation of illite/kaolinite and illite/montmorillonite mixtures as affected by SAR and pH was studied by Goldberg *et al.* (1991). They found that the CCC values of illite/kaolinite and illite/montmorillonite increased with increasing pH and SAR. The 50/50 illite/kaolinite mixture showed greater pH dependence than the 50/50 illite/montmorillonite mixture, especially at high SAR. This result is attributed to the greater proportion of pH-dependent charge of kaolinite. They concluded that the presence of illite did not play a dominant role in determining flocculation behaviour of the 50/50 clay mixture. At the agriculturally desirable ESP and SAR values of 0 to 15, all the clays and 2:1 clay mixtures demonstrated similar CCC values.

2.4 Interactions between particles in aqueous suspensions

The nature and strength of interactions between particles in contact with aqueous solutions are the resultant of attractive and repulsive forces. They each show a variation with distance of separation between interacting particles (Churchman *et al.* 1994). Possible forces of attraction between distinct particles which are not bonded chemically include van der Waals interatomic forces, interaction of diffuse double layers for particles and bridging by polymers. The forces of repulsion between particles include: hydration of exchangeable cations on clay surface and osmotic pressure (Churchman *et al.* 1994).

2.4.1 van der Waals interaction

The universal attractive forces between atoms and molecules, known as van der Waals forces, also operate between macroscopic objects and play a very important part in the interaction of colloidal particles. Indeed, without these forces, aggregation of particles would usually be prevented by the hydrodynamic interaction (Hunter 1981). The interaction between two particles is calculated simply by summing the interactions of all molecules in one particle with all of the molecules in the other. For two spheres, radii a_1 and a_2, separated by a distance d (see Figure 2.4), the interaction energy at close approach ($d<<a$) is given by Hamaker expressions:

$$V_A = -(A_{12}/6d)a_1a_2/(a_1 + a_2) \qquad [2.12]$$

where V_A is the attraction energy between the two spheres and A_{12} is the Hamaker constant. For equal spheres, radius a_1, the result is simply

$$V_A = -A_{12}\,a_1/12d \qquad [2.13]$$

For practically all aqueous dispersions, Hamaker constants lie in the range 0.3 to 10x 10^{-20} J (Gregory 1989). Dense mineral particles have higher values than this range, whereas low density, especially biological, materials have quite low values.

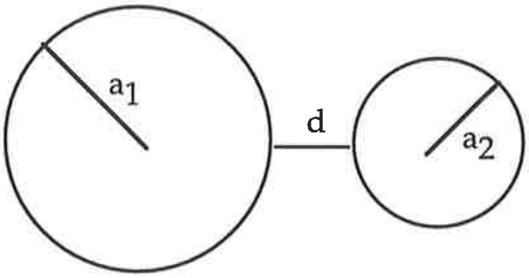


Fig. 2.4. Model for the interaction of two particles at close approach (after Gregory 1989)

2.4.2 *Electrical interaction*

2.4.2.1 Electrical double layers

Most particles in aqueous media are charged for various reasons, such as the ionisation of surface groups, specific adsorption of ions, etc. In an electrolyte solution, the distribution of ions around a charged particle is not uniform and gives rise to an electrical double layer (Hunter 1981). The essential point is that the charge on a particle surface is balanced by an equivalent number of oppositely charged counterions in solution. These counterions are subject to two opposing influences: electrostatic attraction tending to localise the counterions close to the particles and the tendency of ions to diffuse randomly throughout the solution due to their thermal energy. The surface charge on a particle and the associated counterions together constitute the electrical double layer. A widely accepted model for the double layer is that due to Stern, in which part of the counterion charge is located close to the particle surface (the so called Stern layer) and the remainder is distributed more broadly in the diffuse layer.

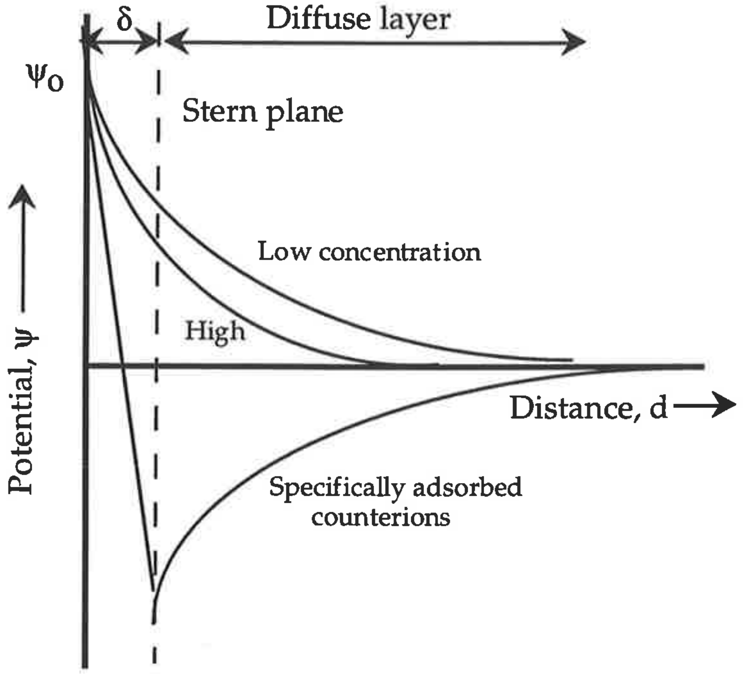


Fig. 2.5. The Stern model of the electrical double layer (after Gregory 1989).

The interaction between charged particles is governed predominantly by the overlap of diffuse layers, so the potential most relevant to the interaction is that at the boundary between the Stern and diffuse layers (the Stern potential, ψ_δ), rather than the potential at the particle surface (see Figure 2.5). This boundary (the Stern plane) is generally considered to be at a distance of about 0.3 to 0.5 nm from the particle surface, corresponding to the diameter of an hydrated counterion. There is no direct experimental method for determining the Stern potential, but there is good reason to believe (Lykiema 1977) that the electrokinetic or zeta potential, is an adequate substitute. The zeta potential is that at the plane of shear, between a particle and a fluid, when there is relative motion between them. The two major influences on electrical interaction between particles are the magnitude of the effective surface potential (generally assumed to be the zeta potential) and the extent of the diffuse layer since the latter governs the range of the interaction. Surface potential can be modified in two distinct ways. If the ionic strength is raised, then a greater proportion of the potential drop occurs across the Stern layer, giving a smaller Stern potential. This effect can be produced by adding salt, and those which act only in this way are known as indifferent electrolytes. The extent of the diffuse layer is also dependent on the ionic strength. The initial electric potential at the colloidal surface is maximum and decreses exponentially with distance from the surface as shown by Poisson-Boltzmann expression equation (Tan 1993):

$$\psi = \psi_\delta \exp(-\kappa d) \qquad [2.14]$$

where, ψ is electric potential at distance d, ψ_δ is surface potential, κ is constant associated with concentration, valence of ions, dielectric constant, and temperatute; At room temperature, $\kappa = 3 \times 10^7 z \pm C^{0.5}$ where, z is valence of the ion, C is concentration of the bulk solution in moles per liter. The value $1/\kappa$ is usually used as a measure of the thickness of the double layer. Addition of excess salt can cause restabilization of the particles because counterions are adsorbed to such an extent that the particle charge is reversed (Figure 2.7) causing a repulsion between the particles.

2.4.2.2 Double layer interaction

Double layer charge depends on the potential and charge at the particle surface, whereas double layer interaction depends on the potential at the Stern plane, which may respond quite differently to the approach of another particle.

When two charged particles approach each other in an electrolyte solution, their diffuse layers overlap and, in the case of identical particles, a repulsion is experienced between them. The potential energy, V_E of this repulsive interaction as given by Gregory (1989):

$$V_E = 32\pi \varepsilon a_1 (kT/ze)^2 \gamma^2 \exp^{(-\kappa d)} \qquad [2.15]$$

where, ε is the permittivity of the medium, a_1 is a ion radius, k is Boltzmann's constant, T is the absolute temperature, z is the valency of the ions, and e is the elementary charge and γ is dimensionless function of the surface potential, $\gamma = \tanh -(ze\psi_\delta /4kT)$.

2.4.3 *Combined interaction and colloid suspension stability*

Classical DLVO approach to colloid stability, which is based only on van der Waals and electrical interactions, assuming that these contributions are additive and may be simply combined to give the total interaction:

$$V_T = V_A + V_E \qquad [2.16]$$

$$V_T = 32\pi\varepsilon a_1(kT/ze)^2 \gamma^2 \exp^{(-\kappa d)} - A_a/12d \qquad [2.17]$$

In Figure 2.6a, the repulsion and attraction energies are plotted against separation distance, as is the total interaction. When $V_T = 0$ by reducing the electrical repulsion, the above equation leads to the following expression for the critical flocculation concentration (CFC),

$$\text{CFC (or CCC)} = K\,(\gamma^4 / A^2Z^6) \qquad [2.18]$$

where K is constant which depends only on the properties of the dispersion medium, A is the appropriate Hamaker constant and Z is the valency of the ions. When the surface potential (zeta potential) is very high, the term γ approaches unity and the critical concentration becomes inversely proportional to the sixth power of the valency, z. This dependence of CFC on $1/Z^6$ has become known as the Schulze-Hardy rule, and it is found that the counterion charge has the dominant effect, so that, for negative particles, $CaCl_2$ would be much more effective than $NaSO_4$. Flocculation of silver iodide by similar salts (Frens and Heuts 1988) show rather lower CFC values, which, for K^+, Ba^{2+}, and La^{3+} were in the ratios 1; 0.021; 0.001, which do not follow the $1/Z^6$ law. So, the theoretical basis for the $1/Z^6$ behaviour seems doubtful (Gregory 1989).

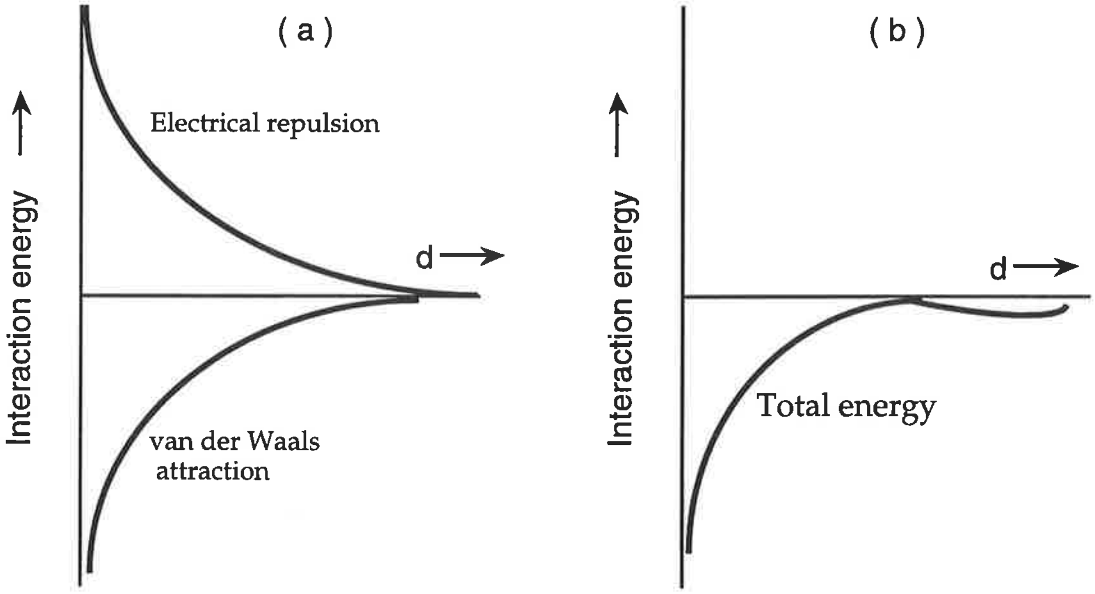


Fig. 2.6. (a) Potential energy diagram for the interaction of colloidal particles. (b) The total interaction energy, when the particles are at the onset of rapid flocculation (after Gregory 1989).

2.4.4 *Hydration effects*

The nature of water close to a particle surface can be very different from bulk water for a variety of reasons. Since ions in aqueous solution tend to be hydrated, it is reasonable to suppose that surface ions are also associated with a certain amount of ' bound water '. The major consequence of hydration at a particle surface is an increased repulsion between approaching particles, because of the need for ions to lose their water of hydration if contact between particles is to be achieved. The most direct evidence for hydration effects comes from measurements of the force between mica sheets in various electrolyte solutions (Pashley and Israelachvili 1984). At low ionic strengths, the repulsion follows the expected exponential form for double layer interaction. The range of these hydration forces is quite appreciable in relation to the range of double layer repulsion, and they may be expected to have an effect on colloid stability, especially at high ionic strength.

2.4.5 *Ion-ion correlation forces*

The attraction forces experienced in divalent clay systems at low separations were explained recently by introducing the concept of ion-ion correlation forces. This theory has been used by Kjellander *et al.* (1988) to calculate the attractive pressure between clay surfaces for close distances of approach (about 10Å or less) when the surface charge is balanced by a divalent ions (radius < 3Å) and in the absence of electrolyte in the bulk solution. The net internal pressure between two charged plates is given by

$$P_{net} = P_{ionic} + P_{vw} - P_{bulk} \qquad [2.19]$$

in which P_{bulk} refer to the bulk solution, P_{vw} is the van der Waals contribution, and P_{ionic} is made up of a number of components as follows:

$$P_{ionic} = kT \sum_i n_i(m) + P_{el} + P_{core} + P_{im} \qquad [2.20]$$

where k is the Boltzmann constant, T is the temperature (°K), $n_i(m)$ is the number concentration of ions at the midplane which gives the Langmuir pressure, P_{el} is the electrostatic force across the midplane due to ion-ion interactions, P_{core} is the pressure component due to core-core interactions across the midplane, and P_{im} is the electrostatic interaction due to the difference in dielectric constant between water and the interacting particles.

The kjellander-Marcelja theory, as it exists, does not provide for differences in the surface interaction of cation species of the same valency. For a 1:1 electrolyte a moderate attractive pressure is predicted only for a large surface density of charge and for concentration of about 1 M (Quirk 1994).

2.4.6 Polymer bridging

Long chain polymers may be adsorbed on particles at many points along the chain, and it can happen that a single polymer molecule becomes attached to more than one particle. In that case, the particles may be said to be bridged by adsorbed polymer and this mechanism is of great practical importance in a number of applications. Polymer bridging was postulated by Ruehrwein and Ward (1952) to account for the aggregation of clay particles by poly-electrolytes, and the concept has been widely accepted since then. For bridging flocculation to occur, the polymer needs to be of quite high molecular weight and to adsorb in such a way that a significant fraction of segments is not in contact with the particle surface, but extend some distance into the aqueous phase (Gregory 1989). Also, the adsorbed amount should not be too great, so that a significant fraction of the surface remains free of adsorbed polymer. In this way, contact can occur between unoccupied areas of a particle surface and extended segments of chains adsorbed on other particles, as illustrated schematically in Figure 2.7a. When excess polymer is adsorbed, bridging is prevented because there is insufficient free particle surface for bridging contacts to occur and the adsorbed layers may also cause repulsion (see Figure 2.7b). For these reasons, there is an optimum dosage of polymer to give good bridging flocculation, and this is usually found to depend on the particle concentration (Gregory 1989). Bridging flocculation can give much stronger aggregates than when particles are destabilised by simply reducing the repulsion between them (usually by adding salt), and the resulting stronger aggregates are larger.

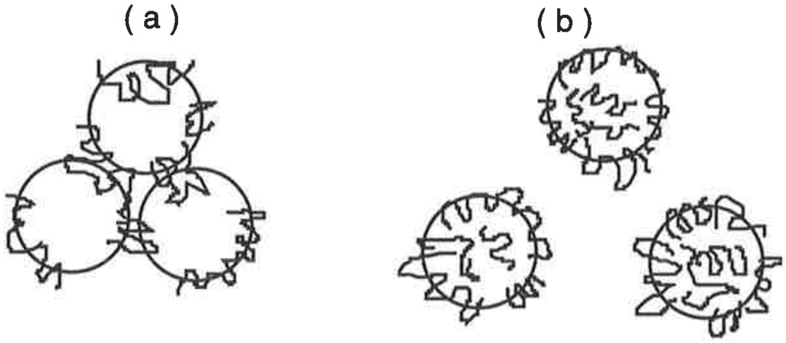


Fig. 2.7. Schematic illustration of (a) bridging flocculation and (b) destabilisation by excess adsorbed polymer (after Gregory 1989).

Many colloid scientists use different terms such as suspension, coagulation and flocculation to describe destabilisation of colloids. Coagulation refers to aggregation caused by reducing double layer repulsion (like adding salt) and flocculation refers to that caused by polymer bridging (Gregory 1989). Interpretation of flocculation by polymers is often complicated by the fact that many of the polymeric flocculants used in practice are charged (i.e. they are poly-electrolytes). When particle and polymer are of opposite sign (as in the common case of negative particles and cationic poly-eletrolytes), charge effects cannot be ruled out. In fact, the action of the poly-electrolyte can be explained simply by the fact that it adsorbs very strongly and neutralises the particle charge (Gregory 1989). In soil science, as well as in this thesis, both terms are used synonymously.

2.5 Mechanisms of structural change in sodic soils

The stability of soil aggregates, and hence that of pore systems, depends to a large extent upon the 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 assemblage in clay aggregates with wetting and drying, contrasting sodic and calcic systems. Figure 2.8 shows schematically the magnitude and direction of pressure changes taking place during wetting of an aggregate involving slaking, dispersion (spontaneous and mechanical) and flocculation of dispersed clay by electrolytes. The clay particles in air-dry aggregates in stage 1 are linked by strong attractive pressures of the magnitude of megapascals (MPa). On wetting, repulsive forces are generated, and the initial attractive force between clay particles in the aggregate decreases markedly. As the 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 2-3 nm whereas in monovalent cation saturated clays, 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 concentrations. When the ionic strength of the equilibrium solution is decreased, water molecules enter between the clay particles (Rengasamy and Sumner 1996). When sodium is the principal adsorbed cation, the interparticle distance continuously increases with continued wetting to beyond 7 nm and the clay particles become completely independent of each other, resulting in clay dispersion (stage 3). The proportion of clay particles thus separated depends on the SAR. Stage 4 represents the point of net zero pressure, that is, the stage at which the forces of attraction and repulsion are balanced. The attractive pressure (in the range of Pa to kPa) necessary to bring the clay particles closer together is provided by the electrolyte concentration of soil solution (Figure 2.8). A threshold electrolyte concentration (TEC) is necessary for flocculation. In sodic soils, TEC increases with increasing SAR.

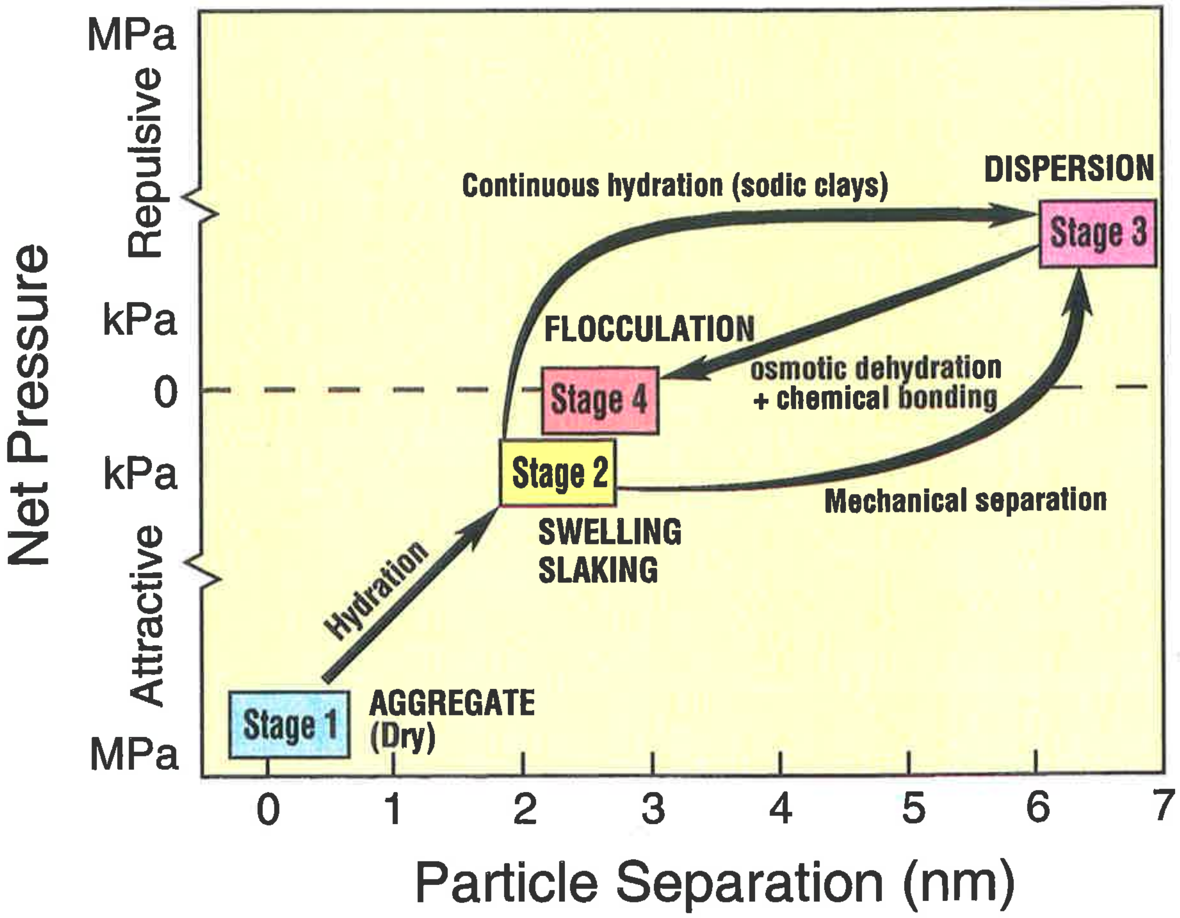


Fig. 2.8. Schematic representation of changes in clay particles association as influenced by attractive and repulsive pressure (after Rengasamy and Sumner 1996)

2.6 Particle charge and clay behaviour

2.6.1 Net charge and charge location effect

Suquet *et al.* (1975) and Horvath and Novak(1976) found that total layer charge plays a major role in the expansion properties of layer silicates. In recent works, Glaeser and Mering (1968); Suquet *et al.* (1977), and Sato *et al.* (1992) estimated the effects of interlayer cations, net layer charge and charge location (octahedral or tetrahedral) on the expansion properties. In these works it was generally found that the expansion of tetrahedrally-charged smectites were smaller than those of the octahedrally-charged smectites under the same hydration and solvation conditions.

Jenkins and Hartman (1979, 1982) considered all possible factors influencing the expansion properties of layer silicates. They concluded that the energy required to expand the octahedrally-charged layer silicates was larger than that of the tetrahedrally-charged layer silicates. Kjellander *et al.* (1988) demonstrated that the amount of intercrystalline swelling decreased as surface density of charge increased. Sato *et al.* (1992) observed that smectites having similar layer charge, showed differences in the expansion. Their results showed that the expansion was larger when the layer charge was located in octahedral sites than when it was in tetrahedral sites. Slade *et al.* (1991) reported that Na-Nibost montmorillonite and Na-Drayton montmorillonite, both with tetrahedral charge, did not exhibit swelling or dispersion in dilute solutions or even in distilled water. This suggests that expansion of layer silicates is due to the combined effects of the charge location and amount.

The effects of layer charge magnitude and location on expansion can be represented by an energy change (expansion energy: ΔE_r) during the hydration and solvation processes. Interlayer solvation (or hydration) exerts a repulsive force between the silicate layers and leads to expansion. On the other hand, if electrostatics attractive forces between the negatively-charged silicate layers and the positively-charged interlayer cations dominate, the repulsive forces do not lead to expansion. The tendency of the interlayer cations to hydrate is accompanied by an interlayer expansion that is opposed by electrostatic attraction between the cations and the clay surfaces (Norrish and Quirk 1954). Therefore, the expansion reaction is determined by a balance between the opposing forces. Crystalline swelling occurs in steps, corresponding to one to four layers of water between the silicate layers, and the pressure, producing such swelling can be very large, up to several hundred MPa (Slade and Quirk 1991).

Calvet and Prost (1971) presented data to show that the adsorption of a polar solvent on a clay surface depends on the nature of the polar solvent and the number of exchangeable cations. They concluded that these factors have a interdependence which can be a useful source of information concerning the mechanisms of swelling. Low (1981) concluded that swelling is due primarily to the interaction between water and the adjacent mineral surfaces. A balance between cation hydration forces, interlamellar electrostatic forces, and van der Waals forces was apparently the basis of the relationship between surface charge and swelling.

Charged clay particles exhibit swelling and dispersion which depend on the ability of water molecules to solvate the cations or anions involved in clay-clay bonding (Rengasamy and Sumner 1996). The attractive forces between clay particles depend on the nature of bonding mediated through the cations. In hydration reactions, it is convenient to be able to characterise the bond as an intermediate. Three types of bonds between clay surfaces and cations can be presented (Rengasamy and Sumner 1996):

1) Covalent bond, like the linkage between Al-hydroxy cations and clay surfaces which is dominated by covalency because of the high polarising power of Al. Hence, hydration of Al in such linkage becomes difficult.

2) Calcium forms polar covalent bonds in which the hydration of Ca is limited and determined by the polarity of the bond.

3) Ionic bond, like bonding between sodium and clay surfaces which is ionic and hence, hydration is extensive. If the cation has no polarising effect on clay surface atoms, the bond is essentially are ionic. When the cation and the surface atoms are mutually polarising, the resultant bond is polar covalent. The degree of ionicity (or covalency) of such bonds depends on the nature of cations as characterised by Misono's factor (Rengasamy and Sumner 1996).

2.6.2 *Effect of heating on particle charge*

The study of the properties of heated clays saturated with monovalent, divalent and trivalent cations show some important features of the clay structure and cation system dynamics. The mechanism of swelling and dispersion can be understood by studying the features of heated clays.

Hoffmann and Klemen (1950) have shown that a dioctahedral clay saturated with small cations such as Li^+ (ionic radius 0.68Å) loses both cation exchange capacity (CEC) and swelling capacity after heating at 250°C for 24 hours. The suggested interpretation is the migration of Li^+ cations toward the vacant octahedral layer charge. Therefore, the three conditions necessary to obtain the so-called Hoffmann- Klemen effect are:

1) exchangeable cation with radius smaller than 0.7Å;

2) vacancies in the octahedral sheets;

3) at least a fraction of the lattice charge originating from substitution in the octahedral sheet.

Jaynes and Bigham (1987) found that charge reduction could be induced in hectorite by heat treatment (250°C) of a Mg-saturated sample. They attributed the charge reduction in hectorite to the migration of Mg^{2+} ions into octahedral sites. Brindley and Ertem (1971) and Clementz *et al.* (1974) examined the hydration of Na-montmorillonite as the CEC of the clay was reduced by the Hofmann-Klemen technique. They found that free swelling of the clay in water was inhibited completely after the CEC had been reduced to about 68% of its initial value and that water vapour adsorption was diminished significantly. This behaviour of the clay is consistent with the view that swelling is associated with the solvation properties of the exchangeable cations (Sposito *et al.* 1983).

A decrease in CEC of the montmorillonite after heating may be ascribed to three interdependent factors (Bishop *et al.* 1994):

1- an increase in dissociation of the water directly coordinating with the cations, due to the polarizing power of these cations and the action of the surface electric fields.

2- dehydration: as water is lost, the polarizing effects of the cation are concentrated on fewer water molecules, thus dehydration increases hydrolysis

3- partial destruction of the montmorillonite structure.

A rough estimate of the polarizing power of the cations was calculated by dividing the charge on the cation by the radius of the hexa-coordinated metals. This approximate polarizing power increases from Na^+ (0.86 charge/Å)< Ca^{2+} (1.75 charge/Å)< Mg^{2+} (2.33 charge/Å)> Fe^{3+} (3.82 charge/Å) (Bishop *et al.* 1994).

Bishop *et al.* (1994) studied montmorillonite saturated with exchangeable Na^+, Ca^{2+}, Mg^{2+} and Fe^{3+} at a range of moisture contents. They found the amount of moisture lost from each sample on subsequent heating to 500°C was 6% for Na^+, 8% for Fe^{3+}, 9.5% for $Ca^{2+}$and 11% for Mg^{2+} -exchanged samples.

Their thermal analyses confirm that the interlayer cations influence the character of the interlayer water and that two or more forms of water exist in the interlayer region.

2.6.3 Infrared spectra of clays as related to hydration

The thermal treatment of Li, Na, K, Mg, Ca and Al-montmorillonite give rise to a decrease in cation exchangeability. This decrease can be measured either through direct determination of the exchangeable cations or, through estimates of the cations amount present in the structure by IR spectroscopy (Green-kelly 1955a). Infrared spectroscopy can be a useful tool for studying bonding of water molecules on surfaces. Water exhibits three vibrational modes: a symmetric stretch, an asymmetric stretch and an H-O-H bending. The symmetric stretching modes are much stronger and more sensitive to bonding with the interlayer cations than the asymmetric stretching modes. The asymmetric stretching mode requires forces of opposite directions along the H-bending axes and motion lateral to the cation bound to the O atom, which implies that the cation may not have a strong influence on this vibration (Bishop *et al.* 1994). Both symmetric and asymmetric H-O-H stretching vibrations are predicted in this region (3700 to 3300 cm^{-1}). Infrared spectroscopy provides data on the arrangements of atoms in the structural OH groups, which makes it possible to probe the inner structure of the clay. It has been established that the low-frequency stretching band in IR patterns of kaolin-group minerals is related to internal OH groups, or inner-hydroxyls (Farmer and Russell 1964; Ledoux and White 1965; Cruz-Cumplido *et al.* 1982). The high-frequency stretching bands are generally attributed to external OH groups which correspond, according to Ledoux and White (1965), to outer- and inner- surface hydroxyls.

Prost *et al.* (1987) showed that temperature is an important parameter in the study of structural OH groups of 1:1 dioctahedral minerals. They found dichroite components which is the result of coupling phenomena, was at 3692 cm^{-1} and also the shift of the high-frequency components to higher frequencies and of the low-frequency components to lower frequencies as the temperature decreases from 600 to 5°K lead to changes in the resolution.

Sposito *et al.* (1983), showed using IR studies that adsorbed water on Na-montmorillonite is primarily solvation water of the exchangeable cations, with the silicate surface playing a lesser role in determining the arrangements of the water molecules. Peaks in montmorillonite spectra have been attributed to structural OH in the octahedral layer, water adsorbed on layer surfaces and water adsorbed or bound in the interlayer regions. The character of these interlayer water molecules is greatly dependent on the moisture level and the nature of the interlayer cations (Farmer and Russell 1971; Sposito *et al.* 1983 and Bishop *et al.* 1993). Their experiments suggest at least two kinds of interlayer water in smectites: water that is readily removable through drying or heating to ~ 105°C, and water that is held more firmly. The firmly bound water molecules are thought to form the inner hydration sphere of the interlayer cations (water bound directly to cations), while the readily removable water consists of outer sphere water molecules H-bonded to each other in the interlayer region (Farmer and Russell 1971).

Schultz (1966) found that ions affected H_2O vibrational modes by polarization of the water molecules and distortion of the H_2O structure. Factors influencing these effects include ionic size, the magnitude of the ionic charge and other properties of the ion such as polarizability. Schultz (1966) also observed a decrease in the stretching frequencies corresponding to an increase in H-bonding of the H_2O molecule.

2.7 Reclaiming Alkaline Sodic Soils

2.7.1 *Introduction*

Reclamation of alkaline sodic soils requires removal of part or most of the exchangeable sodium and its replacement by the calcium ions in 'at least' the root zone soil. This can be accomplished in many ways, best dictated by local conditions, available resources, and the kinds of crops to be grown during reclamation. For quick results, cropping must be preceded by the application of a chemical amendment followed by leaching for removal of soluble salts and other reaction products of the amendments. Amendments are materials that directly or indirectly, through chemical or microbial action, furnish divalent cations (usually Ca^{2+}) for replacement of exchangeable sodium. Inorganic Chemical amendments for reclaiming alkaline sodic soils have been broadly grouped into two categories:

1- Soluble calcium salts: $CaSO_4 . 2H_2O$; $CaCl_2$, phospho-gypsum

2- Acids or acid forming agents: H_2SO_4, iron and aluminium sulfates, elemental sulphur and pyrite, etc.

All amendments, when used under appropriate soil conditions, have a common characteristic: they supply soluble calcium. Acid amendments react immediately with lime, naturally present in alkaline sodic soils, to produce soluble calcium. Materials such as sulphur or iron pyrite must first be oxidised to produce sulphuric acid, which in turn produces calcium sulphate; they are consequently less effective than gypsum or sulphuric acid. It is clear that sulphuric acid is more effective than gypsum in reclaiming calcareous sodic soils (Yahia *et al.* 1975; Prather *et al.* 1978).

Several chemical amendments have been used to reclaim alkaline sodic soils, but the most commonly used material is gypsum ($CaSO_4.2H_2O$). Shainberg *et al.* (1982) found that $CaCl_2$ and $CaSO_4$ had similar reclamation effects, but $CaSO_4$ had a longer electrolyte effect. In contrast, Prather *et al.* (1978) found that on calcareous soils H_2SO_4 was more effective in reducing soil ESP than either $CaSO_4$ or $CaCl_2$. The combination of either $CaCl_2$ or H_2SO_4 with $CaSO_4$ hastened reclamation, compared with $CaSO_4$ alone. Since H_2SO_4 reacts with soil $CaCO_3$ to produce $CaSO_4$, it effectively increases water penetration and works toward reclaiming sodic calcareous soils (Yahia *et al.* 1975; Miyamoto *et al.* 1975).

Recent developments in the reclamation of sodic soils include the possibility of using various polymers added to irrigation water for the purposes of stabilising the hydraulic properties of the soil (El-Morsy *et al.* 1991) or for crack stabilisation (Kamphorst 1990). Aly and Letey (1990) demonstrated that polyacrylamide (PAM) was effective in promoting flocculation of mildly sodic soils at low EC values while El-Morsy *et al.* (1991) found that PAM, added to the water used for leaching disturbed sodic soil columns, was effective in increasing the hydraulic conductivity after the soil had been dried. Oxides of iron and aluminium act as polycations, linking clay particles and promoting flocculation and stabilisation of soil structure (Rengasamy and Oades 1977).

2.7.2 *Chemical amendment*

2.7.2.1 Gypsum application

Gypsum directly prevents excessive swelling and dispersion, and indirectly increases porosity, structural stability, permeability, drainage, leaching, soil tilth and reduces dry soil strength. With regard to soil tilth, gypsum-induced improvements include a wider range of water contents at which tillage can be performed, and greater ease and effectiveness of tillage for seedbed preparation and for weed control (Milthorpe and Newman 1979). Surface crust strength is very largely dependent on moisture content and, because gypsum treatment slows the rate of surface drying (Loveday and Scotter 1966), strength is reduced.

Gypsum added to an alkaline sodic soil can increase permeability by means of both electrolyte concentration and cation exchange effects (Loveday 1976). The relative importance of the two effects is of interest for several reasons. If the electrolyte effect is sufficiently great to prevent clay dispersion and swelling, surface application of gypsum may be worthwhile. In this case, the amount of gypsum required depends on the amount of high-quality water applied and the rate of gypsum dissolution (Shainberg *et al.* 1989).

2.7.2.2 Gypsum dissolution

The rate of gypsum dissolution is an important parameter affecting the efficiency of gypsum as an amendment. Gypsum ($CaSO_4.2H_2O$) and its dehydration products are slightly soluble in aqueous solution, dissolving to an extent of approximately 2.5 g l^{-1} or 15 mmole per litre. This level of solubility is a substantial contribution to the ionic strength of most soil solutions. The dissolution-exchange reactions, represented as:

$$CaSO_4.\ 2H_2O(s) = CaSO_4(aq.) \qquad [2.21]$$

$$CaSO_4(aq.) + 2NaX = CaX_2 + Na_2SO_4 \qquad [2.22]$$

appear simple, but the actual process involves simultaneous mineral dissolution, cation exchange, and solute and water movement. Gypsum dissolution is a linear function of the exchangeable sodium content of the soils (Abrol *et al.*, 1979; Hira and Singh 1980; Gupta and Aborol 1990). Dissolution also increases with SAR, ionic strength, ion-pair association, and Mg/Ca ratio (Oster 1982).

For rapid and sustained dissolution of gypsum and to avoid reduction by formation of $CaCO_3$ coatings (Keren and Kauschansky 1981), it has been recommended to have a mix of gypsum particle sizes. Thus, dual benefits of initial fast dissolution rates at high sodicity followed by longer sustained release of calcium are possible. Surface-applied gypsum generally increases infiltration rates and reclaims sodic soils, but the process is sometimes rather slow because the gypsum moves only slowly into the soil. Field studies and backup laboratory investigations have shown that mixing the gypsum requirement in the desired reclamation depth proved more beneficial than mixing at greater depths. Khosla *et al.* (1973) found that increasing the depth of mixing of gypsum reduces its reclamation efficiency due to a dilution effect (large soil: gypsum ratio). In areas with surface crusting and infiltration problems, shallow mixing of the gypsum in the surface layer is considered best (Loveday 1984).

2.7..2.3 Gypsum requirement

The amount of gypsum per unit of land area needed (GR) to replace exchangeable sodium and to reduce sodicity to an acceptable level can be calculated using the equation (Gupta and Aborol 1990):

$$GR\ (Mg\ ha^{-1}) = 0.172 * 104 * \rho_b * d_s * n * (CEC)\ (ENa_i - ENa_f) \qquad [2.23]$$

where

ρ_b = bulk density (Mg m^{-3})

Mg = metric tons

ds = depth of soil (m)

CEC = cation exchange capacity (mole Mg^{-1} soil)

ENa_i, ENa_f = initial and desired final fractions of exchangeable Na

The Na-Ca exchange inefficiency factor (n) is usually taken as 1.20 (U.S. Salinity laboratory staff 1954).

2.7.3 Biological reclamation

2.7.3.1 Introduction

Biological reclamation is most successful in desodification of alkaline sodic soils (Robbins 1986). The biotransformation of organic matter into organic acids and CO_2 by microorganisms in sodic soil causes a reduction in soil pH, and eventually sodicity. Organic acids such as carbonic acid react with $CaCO_3$ within the soil, freeing Ca^{2+} ions.

2.7.3.2 Green manure

The benefits of adding organic matter such as green manure are:

1- Increased P_{CO_2} due to plant root respiration and decomposition of organic matter (Robbins 1986; Gupta *et al.* 1989), which in turn increases soil EC and decreases soil pH.

2- In-situ production of polysaccharides, which in conjunction with differential dewatering at the root/soil interface, promotes aggregate stability (Boyle *et al.* 1989).

3- The physical effects of root action, including removal of entrapped air from the larger conducting pores and creating of macropores and release of CO_2 upon decomposition (McNeal *et al.* 1966).

The production of both CO_2 and organic acids is favoured by the addition of fresh, readily decomposable material rather than more decomposed material. Organic acids are also weak acids, but they are stronger than carbonic acid and are an important source of protons in soils when they dissociate. In anaerobic incubation, Tsutsuki and Ponnamperuma (1987) found that amendment with rice straw or green manure enhanced the formation of CO_2, CH_4 and acetic acid. The production of organic acids and maintenance of high P_{CO_2} is also maximised under anaerobic, eg. waterlogged conditions (Gupta and Abrol 1990). Another probable beneficial effect of anaerobic conditions is the mobilization of Fe as Fe^{2+} (Puttaswamygowda and Pratt 1973). Excretion of protons from plant roots can be a major acidification mechanism in soils.

The addition of readily decomposable organic matter, whether by deliberate addition or by the growth of plants, especially legumes, tends to favour acidification and thus the desodification of calcareous sodic soils. In green manure treated soils, active biodegradation and the resultant extensive production of CO_2 can lead to the dissolution of Ca and Mg carbonates. Biomass production of green manure crops varies widely according to the legumes species, environmental conditions and crop management practices (Nelson and Oades 1996).

As a green manure crop grows, its protein content decreases and soluble carbohydrates, cellulose and C:N ratio increase resulting in less decomposable material (Ishikawa 1988). Organic matter additions in the form of green manure affect the chemical and electrochemical properties of soils such as pH, redox potential, partial pressure of CO_2, and soil particle surface properties (Singh *et al.* 1992). Green manuring effects soil pH change in two ways. Organic acids and CO_2 produced during decomposition of green manure can furnish protons to the soil, inducing a decrease in pH. During green manuring, anions become separated from H^+ ions by being returned to the surface soil layers than to the subsoil, where the majority of roots originally released the H^+ ions.

The addition of green manure to waterlogged soils will enhance the rate of O_2 consumption (in microbiological respiration and chemical oxidation of organic reducing substances) resulting in CO_2 accumulation. This leads to a lower redox potential.

Katyal (1977) observed higher and sharper peaks of P_{CO_2} in waterlogged soils amended with green manure. The initial rise in P_{CO_2} after flooding is brought by aerobic respiration followed by the anaerobic decomposition of organic matter. Sadana and Bajwa (1985) found marked increase in $P_{CO_2}$with the addition of green manure. The P_{CO_2} in the root zone is a dynamic parameter which depends on microbial and root respiration and on soil water content. Values may range from 0.32 kPa near the soil surface to about 10 kPa in the lower portions of rapidly respiring root systems (Buyanovsky and Wagner 1983).

Increasing pH from acidic to neutral values also increases the rate of decomposition, probably mainly due to its positive effect on microbial and faunal activity (Baldock *et al.* 1994). In alkaline sodic soils with increasing pH, they increase the mineralisation of organic matter.

The relative selectivity of organic matter for Ca over Na increases with increasing pH due to increasing CEC (Gupta *et al.* 1984). Organic exchange sites tend to hold more Ca and less Na than clay exchange sites (Nelson and Oades 1996). The selectivity of Ca over Na for organic exchange sites increases with:

1- Increasing CEC of the organic matter, especially in the presence of carboxylate groups.

2- Increasing degree of cross-linking of the organic matter.

3- Increasing solution pH and

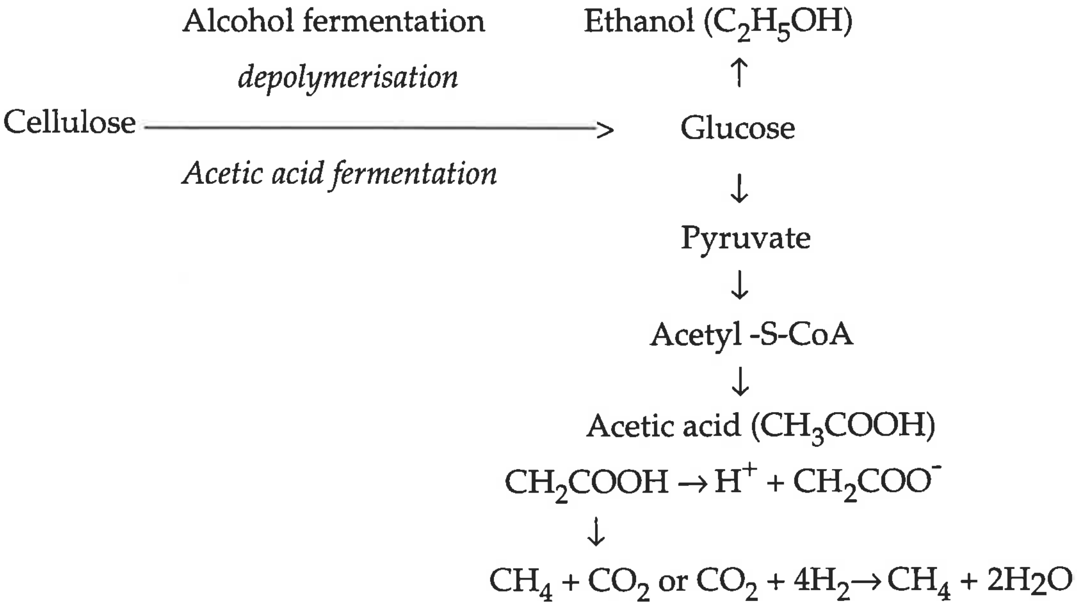
4- Decreasing Ca activity (increased ESP).

Robbins (1986) demonstrated that the solubility of calcite under cropping conditions can be sufficient to reclaim a nonsaline calcareous sodic soil. He measured the partial pressure of CO_2 in the root zone during reclamation of a nonsaline sodic calcareous silt loam under cropping conditions and demonstrated conclusively the benefits of increased soil atmosphere CO_2 for maintaining adequate levels of electrolyte and calcium with reduction of exchangeable sodium. Sufficient information is not available on the effect of organic matter in combination with gypsum in controlling the precipitation and dissolution of Ca and carbonates and preventing sodification in the soils.

2.7.3.3 Microbial reclamation through glucose application

Microorganisms can be one of the most useful resources for introducing protons to alkaline sodic soils and lowering their pH. Under anaerobic condition, simple water soluble organic compounds such as fats, carbohydrates and proteins are released during the microbial breakdown of organic materials and converted into volatile fatty acids (commonly acetic acid) acetates, and eventually H_2, CO_2 and CH_4 (Ponnameruma 1972). Production of these end-products is dependent on the microbial flora present within the soil and on the soil environment itself (Polprasert 1989). Therefore, biological proton injection may be a way to reclaim sodic soil by reducing pH below 8.5 and releasing calcium from $CaCO_3$ for exchange with sodium.

Consequences of anaerobiosis in soils can be explained by the following sequences of reactions:



Acetic acid $pK_a = 4.75$ and similarly produced butyric acid are weak acids. Although nearly 90% of acetic acid is undissociated at pH 4, only 5% is undissociated at pH 6. One would therefore, expect any phytotoxic effects of acetic acid to be minimal in most arable soils where pH is maintained close to neutrality (Cresser *et al.* 1993). The phytotoxic effects of acetic acid, produced by organic matter fermentation under anaerobic conditions, are strongly pH dependent. Consequently, methane is a most important product of acetate fermentation in water-logged soils. Approximately 25 to 50% of total global CH_4 emissions are from flooded rice and natural wetland soils (Bouwman 1990).

2.8 Further research needed

It is clear that sodicity is a widespread environmental problem affecting crop productivity in many countries, particularly in arid and semi-arid Australia. Sodic soils with pH> 8.4 containing varying amounts of native lime ($CaCO_3$) in the profile, are predominant in these countries. These soils have extremely poor physical properties leading to an inadequate balance between water and air within the soil.

Two processes, namely swelling and dispersion, are responsible for the physical behaviour of sodic soils. There are various factors in soils which affect these phenomena. All the published reports concluded that swelling and dispersion of clays in alkaline sodic soils are influenced by soil pH in addition to SAR and EC values of the soil solution. Soil pH indirectly affects these phenomena by altering the particle charge. Therefore, it is essential to quantity the effects of pH and particle charge on sodicity related problems.

Soil particle charge is mainly due to the clay minerals and the oxide components, the contribution from organic matter being low. It is important to know how the manipulation of particle charge will alter the clay behaviour. A knowledge on how the particle charge alters the effect of sodicity will facilitate the management of sodic soils in novel ways.

Alkaline sodic soils invariably contain native $CaCO_3$. Reduction of pH in these soils is a logical step towards mobilizing Ca^{2+} stored as $CaCO_3$ and causing exchange with Na and a stabilizing electrolyte effect. Therefore, the quantification of pH-carbonate interaction is necessary for the management of alkaline sodic soils.

It is also economical to ameliorate sodic soils by biological reaction or organic matter addition to generate protons and to solubilize native $CaCO_3$. Research is needed to explore possible amendments which will reduce soil pH by these mechanisms.

The literature review, so far, has identified the soil pH as an important factor in the management of alkaline sodic soils. Therefore, the mechanisms by which pH controls swelling and dispersion of soil clays and pure clays are targeted in this thesis. As seen in previous sections, particle charge is a primary factor in the soil physical properties and clay behaviour when SAR and pH are large. This prompted the design of experiments on pure clays where alteration of particle charge was achieved by thermal treatment. How to reduce soil pH and sodicity by utilising native $CaCO_3$ is another aspect covered in this project.

CHAPTER 3

Dispersion and Zeta Potential of Pure Clays

3.1 Introduction

Studies of dispersion and flocculation behaviour of sodium and calcium clay minerals are regarded as important because these clays have been considered as models for the behaviour of sodic and calcareous soils. Clay dispersion is governed by the attractive and repulsive forces in the electrical double layer at the surface of charged colloids (Sumner 1992). The balance between these forces is determined by factors such as exchangeable cations and the ionic strength of the soil solution (Rengasamy and Olsson 1991). The behaviour of calcium-clay is very different from that of sodium-clay, and electrostatic forces in addition to those normally in diffuse double layers are thought to operate. When calcium ions dominate the exchange phase, they probably have an orienting effect on clay platelets, and under such conditions quasi-crystals or tactoids have been reported to develop, particularly in smectite clay minerals (Emerson 1962; O'Connor and Kemper 1969; Greene *et al.* 1978).

The particle charge of sodium-saturated clays depends on the degree of protonation of aluminol and silanol groups as affected by pH and as a result, clay dispersion-flocculation behaviour is also altered (Thellier *et al.* 1992). Although the influence of pH on clay dispersion is widely known, flocculation experiments, conducted at different pH values, have reported highly variable flocculation values for clay minerals and soil clays (see Sumner 1993).

The study of the influence of pH is of great interest in the analysis of the electrokinetic properties of clays due to its effect on the charge distribution on the particle surface. It is known that pH is an important determinant of the electrical potential of the clay surface. The effect of pH on the electrical potential of the clay surface when SAR is high can be related to the amount of variable charge available on the external surface of the particle. Therefore, we can expect that the variable charge in single crystals is bigger than in domain. In this regard, Lebron *et al.* (1993) found that changes in pH affect the mobility of individual crystals more than the mobility of domains.

Dixit (1982) showed that increases or decreases in electrophoretic mobility (EM) of Na-clays depended on pH; this, in turn, was responsible for the development of surface charge. Lebron *et al.* (1993) found that the EM of Silver Hill illite was doubled when the pH increased from 5 to 9 at SAR >15. The influence of the exchangeable cation upon the zeta potential was studied by several workers (Delgado *et al.* 1985; Lebron *et al.* 1993). The distribution of sodium and calcium ions on particle surfaces affects the electrical potential because the thickness of the diffuse double layer is affected by the type of cation.

While all these studies indicate the importance of individual factors such as sodicity, ionic strength, pH and cationic effects on the clay dispersibility, it has not clearly been shown what is the common factor of clay dispersion and how the forces involved in the electrical double layer change. The repulsive forces in the electrical double layer responsible for clay dispersion are affected mainly by the charge characteristics on clay surfaces. Soil clays are heterogeneous, and the association with organic molecules make it difficult to interpret the results of dispersion experiments. It is highly desirable to use pure clay systems and study how the net charge is altered under different conditions such as pH, ionic strength and cation type to show that net particle charge is the primary factor influencing clay dispersion.

The first objective of the study reported in this chapter was to compare the dispersive behaviour of three Na- and Ca- clay minerals viz. kaolinite, smectite and illite as influenced by pH and the associated changes in particle charge. The second objective was to examine the relationship between the zeta potential (ζ–potential) derived from electrophoretic mobility and the dispersive behaviour of these clays.

3.2 Materials and methods

3.2.1 Characteristics of Clays

The <2 µm fractions of Georgia kaolinite contained about 5% smectite, as shown by X-ray diffraction. The samples of Grundite illite (<2 µm) contained traces of quartz and about 2% kaolinite. No impurities could be detected by X-ray diffraction in Wyoming bentonite samples.

3.2.2 Clay preparation

Samples of Georgia kaolinite, Wyoming bentonite and Grundite illite were pre-treated to remove organic matter, free iron oxides and amorphous materials (Jackson 1974). The clays were fractionated by allowing larger particles to settle out of suspension and then collecting the <2 µm fraction. This fraction was used to prepare homoionic Na and Ca-clays by washing the clays with NaCl or $CaCl_2$ (1 mol dm^{-3}) solutions, respectively. Before use, samples were dialysed against distilled water until free from chloride. The salt-free clay samples were freeze-dried and stored at room temperature. The homoionic clays were resuspended at 10 g dm^{-3} in distilled water when ready for laboratory tests and adjusted to the desired pH values with dilute HCl or NaOH for Na-clays and $Ca(OH)_2$ for Ca-clays. After shaking for 24 hours, the suspension pH was measured and the proportion of clay remaining in suspension was determined turbidimetrically using an HACH turbidimeter

(Barzegar *et al.* 1994). A calibration curve was used to convert turbidity to amounts of dispersed clay. The sedimentation time was set for 16 hours for all measurements. This time was chosen to avoid the effect of time on the kinetics of coagulation (Hersterberg and Page 1990). Salt-free clay when suspended in water for 24 hours released small quantity of electrolytes, but the electrical conductivity of the suspension was always less than 0.01 dS m^{-1}.

3.2.3 *Flocculation of dispersed clay*

The Na-clay suspensions were used to determine the flocculation values (Rengasamy 1983) in NaCl solutions of different concentrations.

3.2.4 *Determination of electrical charge on pure clay minerals*

A 1% suspension of the clay (10 cm^3) was equilibrated with 0.1 mol dm^{-3} calcium chloride solution of known pH and converted to calcium clay by repeated washings with 0.1 mol dm^{-3} calcium chloride. The excess calcium chloride was removed by washing with 0.005 mol dm^{-3} calcium chloride once and then with A.R. methanol. The retained Ca^{2+} and Cl^- in the clay were exchanged with 0.1 mol dm^{-3} potassium nitrate solutions of the same pH. The negative charge was calculated on the basis of Ca^{2+} in potassium nitrate solutions, estimated by atomic adsorption spectrophotometry, and positive charge on the basis of Cl^- estimated by using an Orion chloride electrode (Model 94-17) in combination with a double junction reference electrode (Model 90-02).

3.2.5 *Scanning electron micrographs*

Scanning electron microscopy was used to examine individual and aggregated particles as affected by exchangeable cations. Each sample was coated with 40 nm of gold. Micrographs were taken to show aggregated particles and individual particles using an SEM Cambridge type stereoscan 250.

3.2.6 Zeta potential measurements

The theory of ζ–potential is related to the concept of the electrical double layer. When a chargedparticle is suspended in solution, ions of oppositecharge predominate near the surface of the particle and are tightly held in the Stern Layer. At some distance from the surface at the so-called shear plane (Hydrodynamic shear) the ions are no longer dragged along with a moving (or diffusing) particle, but remain in bulk solution, the potential at this distance is called the ζ–potential. The ζ–potential is often termed a "remote effect of surface charge". It is related to the thickness of the electrical double layer. When the ionic concentration of the suspending medium is increased, the double layer is compressed, resulting in a lower ζ–potential.

ζ–potential can most readily be measured by the technique of microelectrophoresis. Classically this technique involved measuring the velocity of individual particles in a suspension. The mobility is the velocity per unit electric field viz. by:

$$V=\mu e.\ E \qquad [3.1]$$

Where V is electrophoretic velocity, μe is electrophoretic mobility and E is applied electric field. The ζ–potential is related to the electrophoretic mobility of the particles by the Smoluchowski equation (Pashley 1985a):

$$\zeta = 4\pi\ \eta\ \mu e/D \qquad [3.2]$$

Where ζ is zeta potential (mV), $^{\mu}e$ is electrophoroetic mobility (μm Sec^{-1} V^{-1} cm-^{1}), η is the viscosity and D is dielectric constant. For aqueous media at 25°C, the relationship between mobility and zeta potential, is 12.85 mV per mobility unit.

The ζ–potential was measured using a Malvern Zetasizer model `Zetamaster particle electrophoresis analyser'. All ζ–potentials were measured at a constant 20°C and at a constant field strength of 80 V cm^{-1}. Measurements were conducted with a run time of 30 s and final values were averaged over ten runs. Suspensions containing 0.1 g l^{-1} of Na and Ca-clays were prepared in deionized water, sonified for 30 s and shaken for 2 hours in a Spex mixer mill. The ζ–potential was determined at different electrolyte concentrations of the appropriate cation (expressed as electrical conductivity, EC) and at constant pH for Na- and Ca-clays. The influence of different suspension pH on the ζ–potential of Na- and Ca-clays was also measured by the Zetamaster. The ζ–potentials measured in this study were negative in sign, because the clay particles moved towards the cathode.

3.3 Results and discussion

3.3.1 Na-clays

3.3.1.1 Influence of pH on the dispersibility of pure clay minerals

The percentage of dispersed clay remaining in suspension, as influenced by the pH is given for kaolinite, illite and smectite in Table 3.1. Adjustment of the pH resulted in the change in ionic strength, as shown by the different EC values. This change appeared greater at pH<4 and at pH >9. At high pHs the clay strongly dispersed, and the influence of electrolyte concentration (generated during addition of acid or alkali to change pH) was virtually nil. However, at pH <4, kaolinite and illite suspensions tended to flocculate. Despite the fact that the released electrolytes may have caused some flocculation, the major influence is believed to have been due to the charge reduction at lower pHs, and this is discussed in detail below. In smectite suspensions, even at pH 2.7, 86% of the clay remained dispersed in spite of the EC of 1.1 dS m^{-1}. When the electrolyte concentrations were kept as small as possible, the clays completely flocculated at the pH of 3.5 for kaolinite and 2.6 for illite. Smectite did not flocculate even when the pH was lowered to 1.5.

Smectite is unstable at this pH, forming a siliceous phase by incongruent dissolution (Churchman and Jackson 1976). However, on standing, the whole suspension gelatinized with time, possibly because of the protonation of the remaining, mainly silanol and aluminol groups resulting in positive charge and cross linking between positive edges and negative faces. Oster *et al.* (1980) reported that the edge-to-face attraction plays a dominant role in the gel formation of Na-smectite. The gel formation in smectite and flocculation by edge-to-face attraction in kaolinite may complicate the quantitative analysis of flocculation values.

Table 3.1. Effect of changing pH (with H^+ or OH^-) on dispersible clay

Na-Kaolinite			Na-Illite			Na- Smectite		
pH	EC^B dS m^{-1}	$Clay^C$ %	pH	EC^B dS m^{-1}	$Clay^C$ %	pH	EC^B dS m^{-1}	$Clay^C$ %
3.5^A	0.23	0	2.6^A	1.02	0	2.7	1.10	86
4.0	0.20	6	3.1	0.36	11	3.4	0.62	95
4.4	0.10	16	4.2	0.13	56	4.8	0.22	96
5.6	0.07	33	5.3	0.08	72	5.6	0.14	98
6.1	0.06	62	6.6	0.06	85	6.2	0.13	99
7.1	0.05	85	7.3	0.07	92	8.6	0.13	100
8.4	0.09	93	8.3	0.08	97	9.7	0.14	100
9.5	0.10	99						

^{A} pH at which clays flocculated without adding an electrolyte.
^{B} Without adding an electrolyte. ^{C} Proportion of dispersed clay.

The mechanisms proposed to account for the dispersion or flocculation of sodium clays at high and low pH are as follows;

1) Low pH:

At low pH, there is a replacement of adsorbed Na^+ by H^+ which has two effects: one is to increase the concentration of Na^+ in the solution and thus to increase the electrical conductivity of the suspension, and the other is to increase the concentration of H^+ on the surface. However, H^+ on the clay surface may slowly penetrate into the lattice (Shainberg 1973). This attack by protons causes the clay to decompose and releases cations such as Al^{3+} and Mg^{2+}. The presence of di- or trivalent cations in the electric double layer can decrease zeta potential by reducing net negative charge due to the inner sphere complexation of these ions with clay surfaces (Sposito 1989).

2) High pH:

At high pH, OH^- ions interact with the edges of the clay particles making them neutral or negatively charged. Laboratory studies have shown that the rate of dissolution of silicate minerals increases with increasing pH above 8 (Kohut and Dudas 1994). In spite of increasing EC at high pHs, the clays dispersed because of the development of strong negative charge.

When the pHs of the clay suspensions were at their natural values, the electrolyte concentration needed to flocculate the Na-clays (Table 3.2) was 1.25 and 4.54 dS m^{-1} respectively for kaolinite (pH ~6.8) and illite (pH ~ 5.6). For smectite, at pH ~ 5.5, the flocculation EC was 5.85 dS m^{-1}.

It would be less confusing if the results were obtained at different electrolyte concentrations and keeping pH constant so as to enable splitting the two effects, namely, flocculation and variable charge due to potential determining ions. But in practice this is difficult to achieve in clay systems. In the present study electrolyte concentration changed during pH changes.

Table 3.2. Effect of changing NaCl concentration on clay dispersion of pure clay minerals at natural pH

Na-Kaolinite			Na-Illite			Na-Smectite		
pH	EC dS m^{-1}	Clay^{B} %	pH	EC dS m^{-1}	Clay^{B} %	pH	EC dS m^{-1}	Clay^{B} %
7.1	0.05	85	6.3	0.06	84	6.2	0.13	99
7.0	0.23	64	5.9	0.65	61	5.9	1.21	94
6.9	0.43	49	5.8	1.25	47	5.8	1.92	91
6.9	0.92	26	5.8	2.65	27	5.7	2.52	89
6.8	1.05	10	5.7	3.98	12	5.7	3.14	81
6.8	1.25^{A}	0	5.6	4.55^{A}	0	5.6	4.26	60
						5.5	5.85^{A}	0

^{A} CCC values for flocculation system. ^{B} Proportion of dispersed clay.

3.3.1.2 Influence of pH on net particle charge and dispersibility

The changes in net negative charge as influenced by suspension pH are given for sodium forms of kaolinite, illite and smectite in Table 3.3. When the pH is changed from 2 to 9, the net negative charge on kaolinite particles increased from 62 to 94 mmol$_c$ kg^{-1}, on illite particles from 95 to 184 mmol$_c$ kg^{-1} and on smectite particles from 638 to 815 mmol$_c$ kg^{-1}. The kaolinite and illite had smaller net negative charge in this pH range, while smectite had values 6 to 8 times larger. This is clearly reflected in their flocculation values. For example, the flocculation value of smectite at pH 5.5 is 5.85 dS m^{-1}, and for illite at a comparable pH the flocculation EC is 4.54 dS m^{-1} (Table 3.2). However, many authors (e.g. Oster *et al.* 1980; Goldberg and Forster, 1990) have reported that smectite clays have smaller flocculation values than illites. It was found that the flocculation value at a given pH for smectite was always larger than that for kaolinite and illite, reflecting the strong net negative charge on smectite particles. In the absence of particle charge characterization, the reports in the literature are difficult to interpret, even though the size and shape of illite particles have been invoked by some authors to explain the difference. In variable charge systems, particularly charge characterization should also be done at different ECs to separate the effects of pH.

Table 3.3. Effect of pH on net negative charge of Na- clays

	Net negative charge (mmol$_c$ kg^{-1})		
pH	Na-Kaolinite	Na-Illite	Na- Smectite
2	62	95	638
2.5	64	95	656
3	67	102	683
3.5	69	-	-
4	73	120	711
5	78	130	771
6	81	143	782
7	85	156	797
8	89	173	802
9	94	184	815

In clay suspensions, regardless of the structure and shape of the particles, the charge (e.g. net negative or positive) gives rise to the electrostatic force responsible for particle repulsion. Charge density is used in the literature to account for the repulsive force but the reported flocculation values are generally not related to the calculated charge density of clay minerals. This is because of the surface heterogeneities due to non- uniform layer charge on clay particles and the variation of surface area from the conventionally measured N_2-adsorption values due to particle agglomeration. In the present study on pure clay minerals (Figure 3.1) highly significant correlations have been obtained between the percentage increase in net particle charge (based on the charge of flocculated clays at low pH; data from Table 3.3) and the percentage of dispersed clay for the three pure clay mineral systems; this confirms that

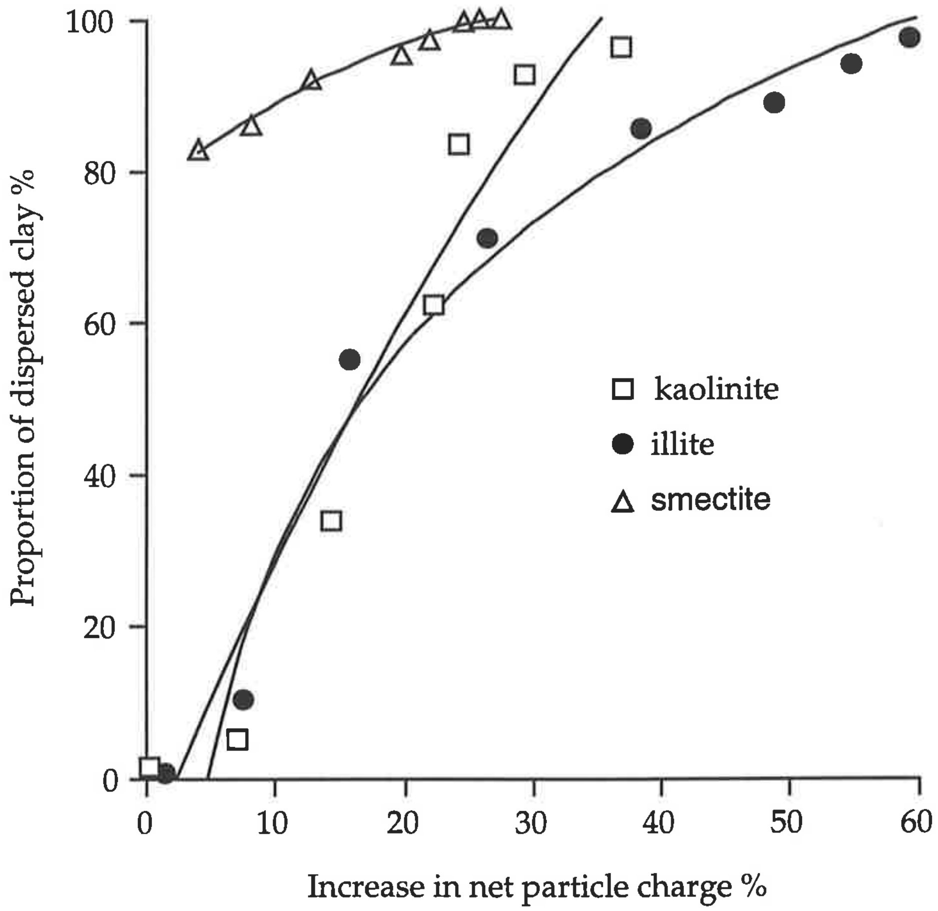


Fig. 3.1. Effect of increase in net particle charge(based on the charge at low pH) on dispersible clay of Na-clays

larger particle charge leads to more dispersion and hence larger flocculation values. The calculation of increase in net particle charge for Na-smectite was based on the gel formation rather than complete flocculation. Goldberg and Forster (1990) found that the flocculation values for reference clays were much less than those for soil clays, indicating that extrapolation from the results on reference-clays is not reliable, and that additional factors such as organic matter and Al- and Fe-oxide content influence the dispersion of soil clays.

The charge densities of Na-clay minerals are similar (Table 3.4) irrespective of the type of the clay mineral. However, the flocculation values are very much different for these three clays. Therefore, it has been suggested that total particle charge is more relevant in flocculation studies.

Table 3.4. Some characteristics of the clays used

	Na-clay			Mean diameter[C] µm	
Clay minerals	*A* [A] $m^2\ kg^{-1}$	CEC $mmol_c\ kg^{-1}$	Charge density [B] $mmol_c\ m^{-2}$	Na-clay	Ca-clay
Wyoming Bentonite	68×10^4	810	1.2×10^{-3}	0.20	2
Grundite Illite	11.5×10^4	175	1.5×10^{-3}	0.45	4
Georgia Kaolinite	4.1×10^4	69	1.7×10^{-3}	0.60	8

[A] Specific surface of sodium clays as determined by ethylene glycol method (Mortland and Kemper 1965), [B] Charge density= CEC / A

[C] Measured by sub micron particle sizer Nicomp Model 370 as the mean of an assumed Gaussian distribution

3.3.1.3 Zeta potential as a function of pH, EC, and dispersion

Figure 3.2 shows the variation of ζ–potential with the pH of the suspension, and Figure 3.2 shows that the ζ–potential of Na-clays increases as the pH is increased. In general, the relation between pH and ζ–potential for Na-clays was positive in the pH range 2.5 to 9. If the adsorbed Na is concentrated on the external surface of the clay we can explain the rapid increase in ζ–potential caused by the increase in the negative charge, which is affected by pH. These results are in good agreement with our data on dispersion, and they confirm that with increasing pH net negative charge (or ζ–potential) will increase.

The values of ζ–potential for Na-clay particles suspended in solutions of NaCl at different electrolyte concentrations but constant pH (~7) are shown in Figure 3.3, which also shows that the ζ–potential increases when the electrolyte

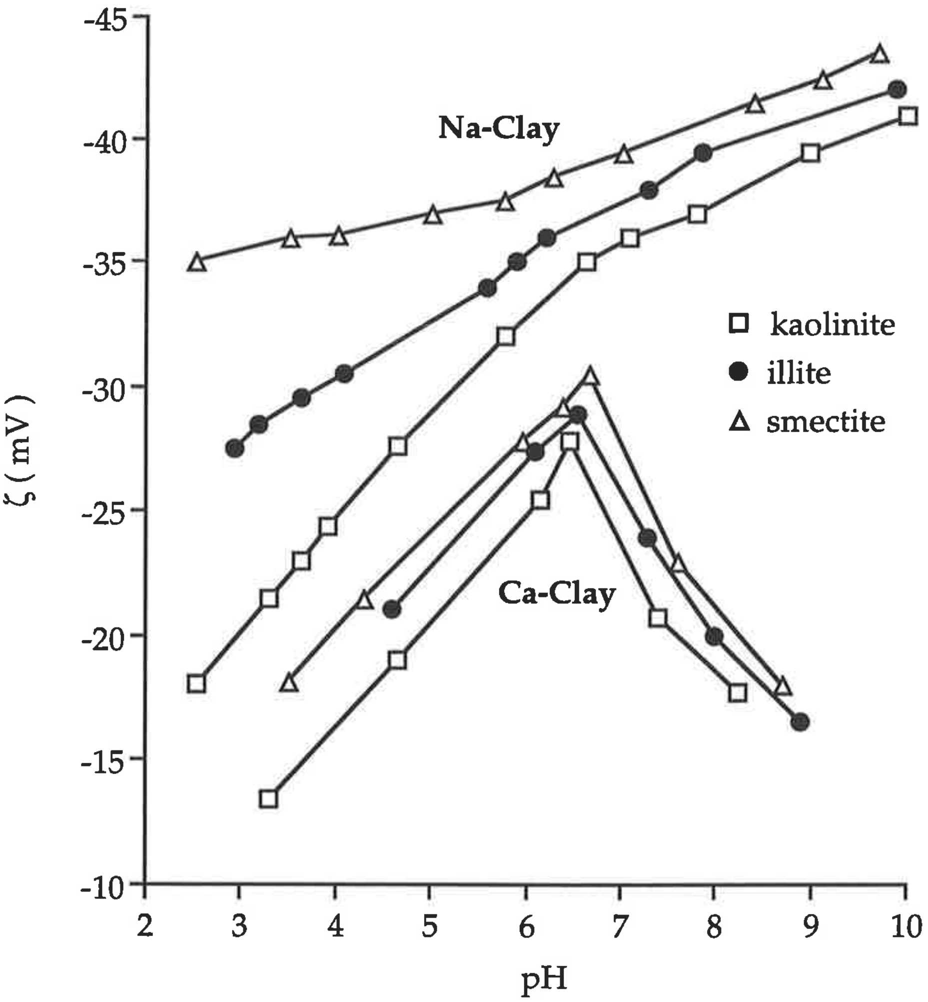


Fig. 3.2. Zeta potential of Na-clays and Ca-clays as a function of the pH of the suspension

concentration (expressed as electrical conductivity, EC) of NaCl is logarithmically increased. The mechanism of this reaction is related to the thickness of the electrical double layer. When the electrolyte concentration of the suspension is increased, the double layer is compressed, resulting in a smaller ζ–potential. Or, in other words, we can suggest that the flocculation due to the compression of the double layer is related to charge reduction in clay minerals as revealed by the diminished ζ–potential. But the increase in EC also has effects on the magnitude of the variable charge, and thus on the net particle charge. This also can have an effect on the ζ–potential, as shown by Lebron and Suarez (1992).

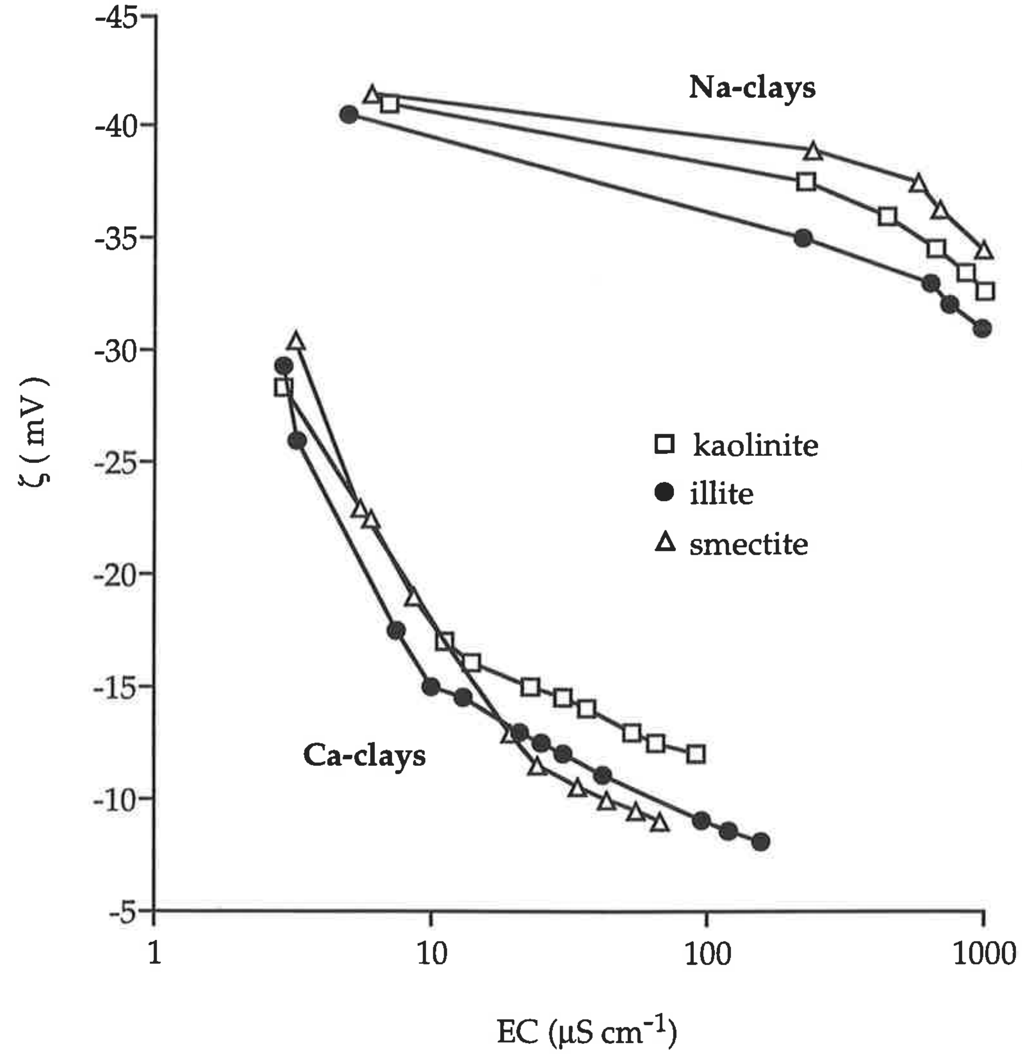


Fig. 3.3. Zeta potential of Na-clays and Ca-clays as a function of NaCl and $CaCl_2$ concentration at pH 7.0

There is a positive relation between ζ–potential and the percentage of dispersed clay (Figure 3.4). The change in ζ–potential has similar effects on the dispersion of Na-kaolinite and Na-illite. This observation agrees with previous data on the effect of pH on clay dispersion and confirms that by increasing the net particle charge (or ζ–potential), the percentage of dispersed clay increases.

3.3.2 *Ca-clays*

3.3.2.1 Influence of pH on the dispersibility of Ca-clay minerals

The pH of the resuspended Ca-clay minerals in distilled water was adjusted to the desired value by adding either HCl or $Ca(OH)_2$ and, after allowing 24 hours for equilibration the dispersible clay was determined. Figure 3.5 shows the percentage of dispersed clay, as influenced by the pH of the clay suspension. All Ca-clay minerals tended to disperse in the range of pH between 2 and 7, but, with increasing pH from 7 to 10, they tended to flocculate.

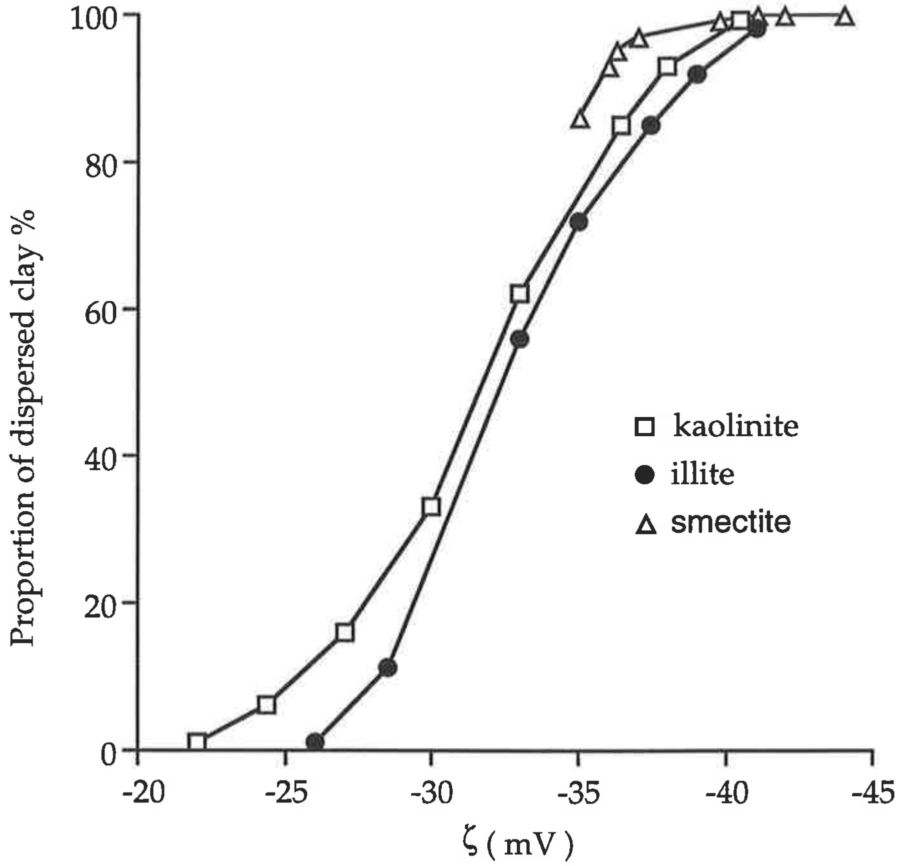


Fig. 3.4. Influence of zeta potential on dispersible clay of Na-clay minerals

At low pH, exchange of Ca^{2+} by H^+ releases Ca^{2+} into solution and at the same time net charge is also reduced due to the effect of pH on surface charge. As a result, the clay is flocculated. However, at pH above 7, by adding $Ca(OH)_2$ to Ca-clay suspension, $CaCO_3$ formed (Table 3.5). Rengasamy (1982) reported that strong aggregate formation in calcium clay is possible due to either flocculation by specific adsorption of hydroxy calcium at pH >10, as observed for iron polycations, or cementation by $CaCO_3$ precipitation. The results presented here suggest that $CaCO_3$ forms due to addition of $Ca(OH)_2$ in the presence of atmospheric CO_2, and that clay particles are flocculated by charge reduction due to cementation or coating by $CaCO_3$.

Table 3.5. The formation of $CaCO_3$ in Ca- clay system at high pH values

Ca-clay	pH	$CaCO_3$ mg g^{-1} clay
Kaolinite	8.2	5
	10.0	11
Illite	8.2	9
	10.1	19
Smectite	8.0	11
	9.8	22

3.3.2.2 Zeta potential as a function of pH and EC

Figure 3.2 shows the changes in ζ–potential of Ca-clay minerals as related to changes in pH. There is an increase in the particle mobility (more negative) when the pH increases from about 2 to 7 for all Ca-clay minerals. From pH 7 to 9, increasing pH caused decrease in ζ– potential of Ca-clay minerals. This results agree with the observations on flocculation. The data from this study suggest that $CaCO_3$ formation is responsible for the reduction in charge and lowering of ζ–potential.

The effect of electrolyte concentration on ζ–potential of Ca-clay minerals is shown in Figure 3.3. It is clear that the ζ–potential of Ca-clay minerals increases when the electrolyte concentration of $CaCl_2$ is logarithmically increased. In general, the electrolyte concentration (expressed as electrical conductivity, EC) needed to flocculate or increase the ζ–potential of Ca-clay

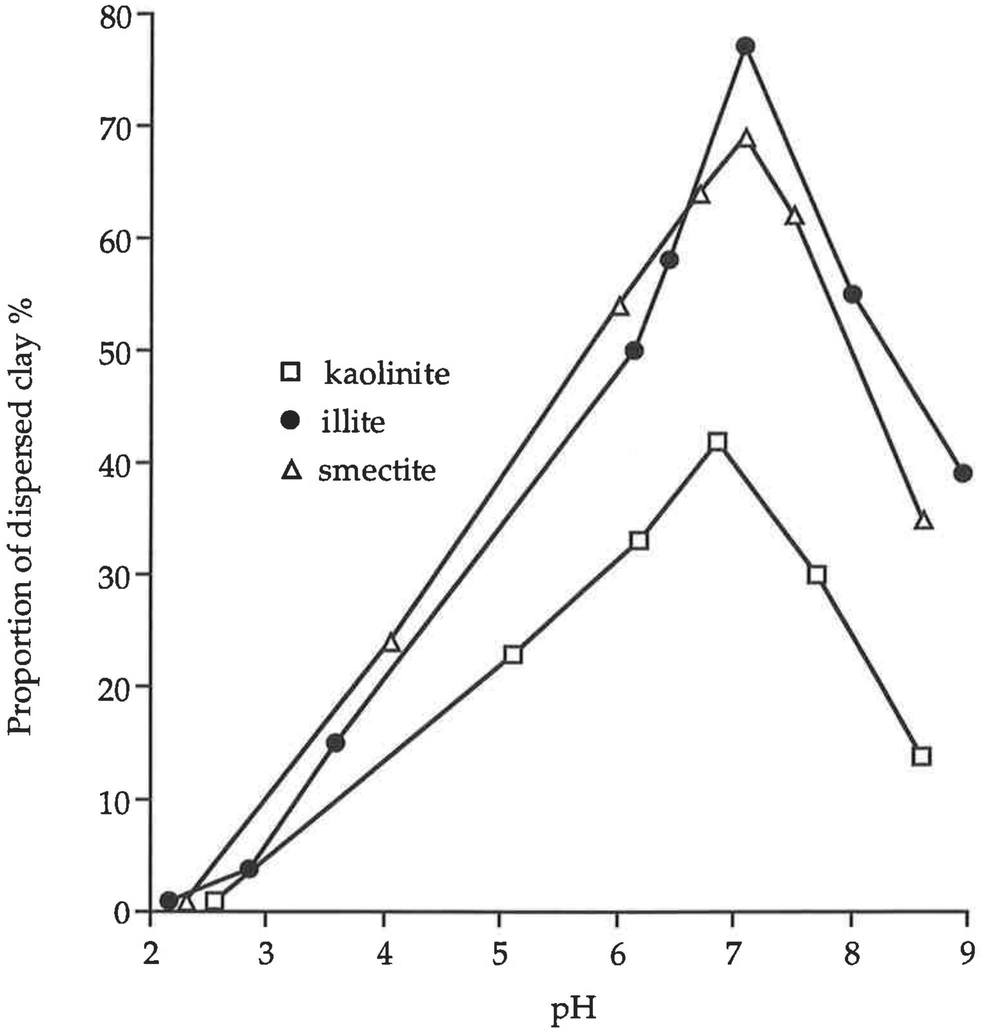


Fig. 3.5. Dispersible clay of Ca-clay minerals as a function of the pH of the suspension

minerals is much less than for Na-clay minerals. Although both Na^+ and Ca^{2+} ions tend to diminish the zeta potential as their concentration in solution increases, the action of Ca^{2+} is much more pronounced than that of Na^+, in accordance with the valency difference.

The mechanism responsible for restricted swelling of calcium clays in water and in aqueous salt solutions was explained by Kjellander *et al.* (1988). They reported that for divalent ions the double layer interaction is strongly attractive at fairly small surface separations, provided the density of surface charge is reasonably large. Sodium smectite in dilute suspensions exists largely as single platelets (van Olphen 1977). Norrish and Quirk (1954) reported that calcium smectite exists as packets (tactoids or quasi-crystals). The illites exist as quasi-crystals or aggregates of domains in the Ca-system (Rengasamy *et al.* 1984b). Therefore, the particle charge is screened by the inner-sphere complexation of Ca ions with clays, responsible for the formation of domains and quasi-crystals. The average particle size for Na- and Ca-clays (Table 3.4) supports this hypothesis.

Scanning electron microscopy of Na and Ca-clay minerals (Figure 3.6) also shows this variation of aggregation to be present and is related to the treatment given. The aggregation is greater for the Ca treated samples, as evident in the kaolinite sample where 10 μm size aggregates are present in micrograph (a), but are absent in micrograph (b) of the Na treated sample. This trend is also evident for the illite [micrographs (c), Ca treated and (d) Na treated], and the smectite specimens [micrographs (e) Ca treated, and (f) Na treated]. In micrograph (f) large surface undulations are present, but these are due to the shrinkage of the clay as it dried, and not due to aggregation.

The ζ–potential of the clays (kaolinite, illite and smectite) are similar when they are saturated by a given cation, Na or Ca (Table 3.6). They exhibit almost constant potential behaviour in the neutral solution. This is in agreement with the report by Horikawa *et al.* (1988). The ζ–potentials of Ca-clays are very much smaller than for Na-clays, confirming greater particle aggregation in the Ca-system.

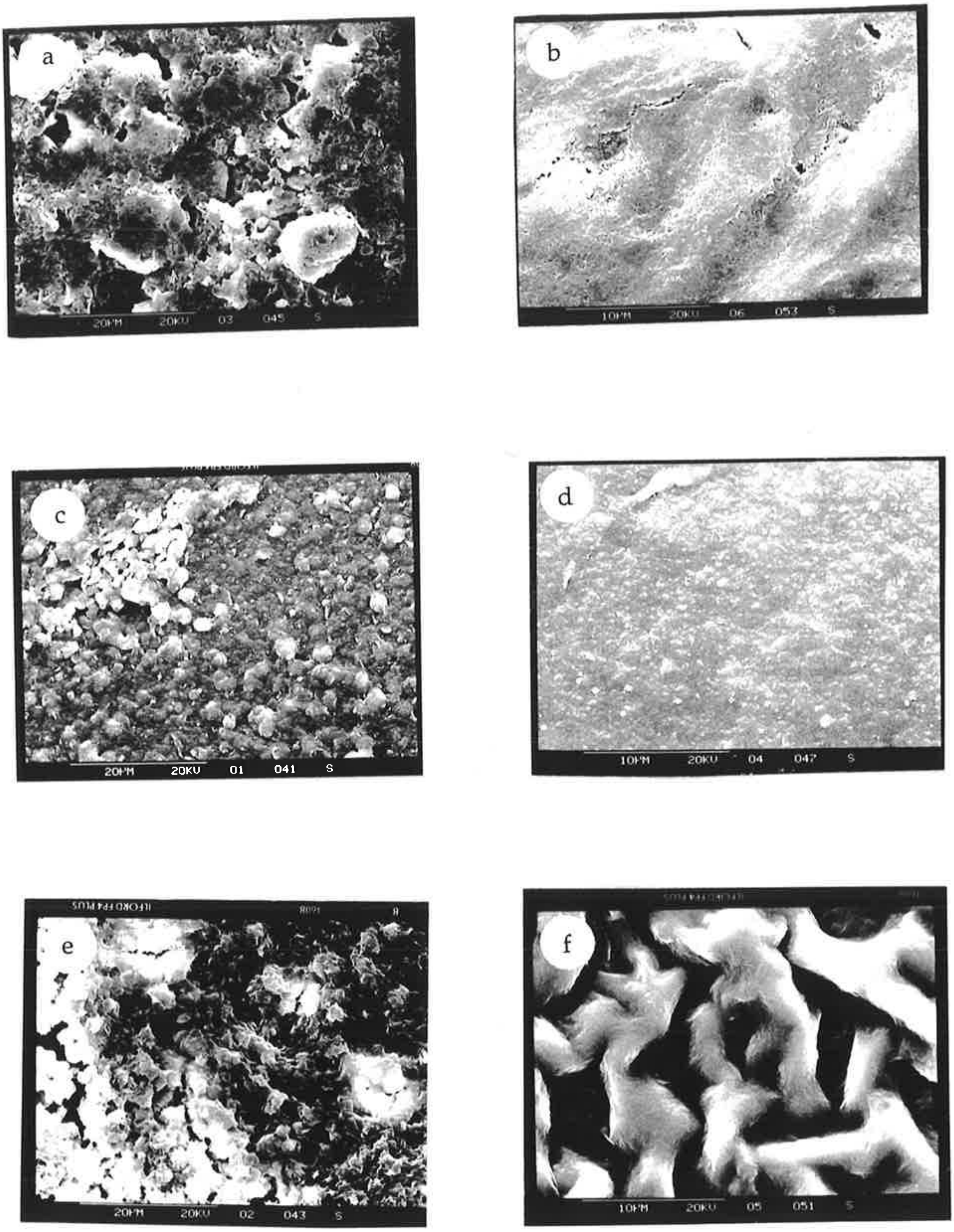


Fig. 3.6. Scanning electron micrographs of sodium and calcium clay minerals. (a) Ca-kaolinite, (b) Na-kaolinite, (c) Ca-illite, (d) Na-illite, (e) Ca-smectite and (f) Na-smectite.

Table 3.6. Constant ζ–potential of Na- and Ca-clays

Clay minerals	pH	EC dS m^{-1}	Dispersible clay %	Negative ζ–potential mV
Na- Kaolinite	7.1	0.050	85	40.5
Na- Illite	7.2	0.070	93	41.1
Na-Smectite	7.0	0.090	100	42.3
Ca- Kaolinite	6.6	0.010	39	27.3
Ca- Illite	6.7	0.015	78	28.2
Ca- Smectite	6.8	0.012	64	29.8

3.3.3 *Flocculation values of Na and Ca clay systems*

The flocculation values for Na-clays in near neutral NaCl solution were 1.25 dS m^{-1} for Na-kaolinite, 4.45 dS m^{-1} for Na-illite and 5.85 dS m^{-1} for Na-smectite (Table 3.2). The electrolyte concentration (expressed as, EC) needed to flocculate the Ca-clays in $CaCl_2$ solution in the neutral pH values were 0.025 and 0.11 dS m^{-1} respectively for Ca-kaolinite and Ca- illite. For Ca-smectite the flocculation EC was 0.072 dS m^{-1}. These values are different with the Schulze-Hardy valency rule of flocculation which predicts that the monovalent and divalent colloids coagulate at concentration ratio of $(1/2^6)$ or 1: 64. The ratio of flocculation values of sodium and calcium clays was 1: 50 for kaolinite, 1:42 for illite and 1: 80 for smectite. The different ratios for these clays are perhaps due to the difference in total charge of these clay minerals in suspension.

3.4 Conclusions

This study clearly shows that pH primarily affects dispersion of reference clays by changing the net negative charge on clay particles. The slopes of the positive relation between pH and the percentage of dispersible clay decreased in the order kaolinite > illite >> smectite when they are sodium saturated. The percentage increase in net negative charge with an increase in pH is in the order illite > kaolinite >smectite. However, the amount of clay dispersed and flocculation values were related to net negative charge on the clay particles. Thus, smectite with larger net charge at all pHs, always had larger flocculation values than illite and kaolinite.

In general, while the changes in pH increase the net negative charge and zeta potential, increasing electrolyte concentration at constant pH induces charge reduction and diminishes the zeta potential, probably because more cations enter the Stern layer. In Ca-clays, the trends were similar to the Na-clays up to pH 7. With further addition of $Ca(OH)_2$, the Ca-clays tended to flocculate, probably because of the formation of $CaCO_3$, and ζ–potential decreased. For Na-clays, the ζ–potential continued to increase. These results are reflected in the values of zeta potential at different pH. The present study has clearly demonstrated that net particle charge is the common factor affecting clay dispersion under different conditions of pH, ionic strength and cation type.

CHAPTER 4

Dispersion of soil clays as influenced by pH and net particle charge

4.1 Introduction

The threshold electrolyte concept has been used to define dispersive behaviour and for the management of sodic soils where the combined effects of sodium adsorption ratio (SAR) and electrolyte levels (as measured by electrical conductivity, EC) have been included (e.g. Quirk and Schofield 1955; Rengasamy *et al.* 1984a). These criteria have neglected the influence of soil pH on clay dispersion. Sodic soils all over the world vary widely in their pH values usually ranging from 4 to 10 (Szabolcs 1989).

The dispersive potential concept was proposed by Rengasamy and Olsson (1991) to combine the effects of SAR and EC on clay dispersion. This potential is calculated by measuring the flocculating concentration of electrolyte at the natural pH of a dispersive soil. Soil pH may be changed by management; these changes in soil pH can alter the behaviour of sodic soils. Therefore, the dispersive potential may not identify appropriate soil management strategies unless the pH effect is also included.

In the third chapter, the study on the effects of pH focussed on pure clay minerals. In soil clays, a number of clay minerals exist in association with oxides of iron and aluminium, either crystalline or amorphous, and a variety of organic compounds. Therefore, it is necessary to study soil clays in order to assess the mechanisms of the behaviour of soil systems.

The first aim of the work reported in this chapter was to compare the dispersive behaviour of three soil clays of mixed mineralogy as influenced by pH and the associated changes in particle charge. The second aim, on the basis of the mechanisms derived from this study, was to relate soil pH and CEC to the dispersive potential of a number of Alfisols, Oxisols, Vertisols and Aridisols (calcareous soils) collected from different parts of Australia.

4.2 Dispersive potential concept

On wetting an air-dry aggregate, the continued adsorption of water molecules on the exposed clay surfaces leads to the development of repulsive and attractive pressures which change in magnitude and direction as the distance between linked clay particles increases. In calcic systems the clay particles, at an interparticle distance of 2-5 nm, principally experience net attractive pressure (Quirk and Pashley 1991). However, in sodic system the interparticle distance continuously increases with continued wetting to beyond 7 nm. At separating distances greater than $2/\kappa$, where κ defines the double layer thickness in nm, electrical repulsive forces predominate. But, the osmotic pressure due to the electrolytes in the pore solutions oppose these repulsive pressures.

Swelling pressures between clay particles have been derived by using the Diffuse Double Layer (DDL) theory (Sposito 1984). These pressures consist of two components:

1- Physical swelling (Quirk and Pashley 1991) operating up to an interparticle distance of 2-5 nm and

2- Osmotic swelling (van Olphen 1977) mainly due to hydration of sodium ions leading to an interparticle distance >7 nm.

The latter phenomenon results in clay dispersion. Here, the dispersive region is defined as the interparticle distance > 7 nm and the dominant forces are the hydration forces causing repulsive pressure which is opposed by the attractive pressure due to ionic concentrations in the bulk solution.

When the ionic concentration in the bulk solution equals critical coagulation concentration (CCC), these two pressure components balance each other and the total potential energy per unit area of particle surface becomes zero and the interparticle distance is reduced to < 7nm (Rengasamy and Olsson 1991). The repulsive pressure, Pr, in the dispersive region is numerically equal to the osmotic pressure due to salt level at CCC. Thus,

$$P_r = (RT \sum_i C_i) \quad [4.1]$$

The calculated pressure at this distance using the DDL model agrees well with experimental values, but only in the case of monovalent ions. However, the stability of soil colloids has been related through an empirical relation to the CCC in the Schulze-Hardy rule. This empirical expression relates the coagulation concentration to the inverse 6th power of valance of the coagulation ions. This relation can also be derived from DLVO (Derjaguin, Landau, Verwey and Overbeek) theory (Sposito 1984).

Since clay flocculation is the resultant of interparticle forces altered by the electrolytes, the empirical Schulze-Hardy relation of must be used in combination with equation 4.1 to drive the repulsive pressure (P_r) in the dispersive region of soil clay systems especially in saline-sodic soils with mixed ionic species. If the electrolyte concentration is below CCC, the repulsive force which keeps the clay particles separated by a distance > 7 nm can be termed " Dispersive Potential ". Rengasamy and Olsson (1991) have defined this potential as the difference in osmotic pressure between the required concentration to flocculate (P_{ccc}) and the existing solution concentration (P_{sol}):

$$P_{dis} = P_{ccc} - P_{sol} \quad [4.2]$$

for $P_{sol} < P_{ccc}$. At CCC it is assumed that $P_r = P_{dis}$. The osmotic pressure due to individual ions, in kPa, can be calculated from:

$$P_{osm} = (\Sigma C_i Z_i) RT \qquad [4.3]$$

and using the valency factor for the divalent ions. Since the model for predicting accurately the CCC values in soil clay systems is not currently available, dispersive potential although a good index of dispersive soils, still remains empirical.

4.3 Materials and methods

4.3.1 Soil samples

A-horizons of the following three soils were used in this study: Evans (Rhodoxeralf), Meadows (Natrixeralf) and Claremont (Chromoxeret). The Evans soil was collected near Mintaro, approximately 130 km north of Adelaide in South Australia. The Claremont self-mulching black earth and Meadows fine sandy loam were taken from the Waite Agricultural Research Institute and Kuitpo in the Mount Lofty Ranges, respectively. These soils were chosen for differences in clay content and clay mineralogy. All samples were air-dried, crushed and passed through a 2-mm sieve.

4.3.2 Clay mineralogy

Clay mineralogy was determined by XRD analysis and XRF analysis on Mg-saturated and on Ba-saturated <2µm fractions respectively. The proportion of each clay mineral was determined using powder X-ray diffraction, XRF and supplementary XRD data (Riley 1993). The percentage of non-clay minerals (quartz, haematite, goethite, calcite and gibbsite) was identified by comparison with standard peaks. The difference between the percentage of non-clay minerals and 100% was attributed to kaolinite and illite in the ratio of twice that of the peak height of the 10Å illite signal to the peak height of 7Å kaolinite peak. The CEC due to kaolinite and illite were calculated using average values of 10 and 20 $\mathrm{cmol_c kg^{-1}}$, respectively. The CEC of clays was also measured experimentally by determination of Ba^{2+} on Ba-saturated clays using XRF. The calculated CEC was then subtracted from the CEC measured by XRF, and the remainder so obtained was allocated to expandable minerals (vermiculite, smectite and RIM) using 120, 100 and 80 $\mathrm{cmol_c kg^{-1}}$ for these minerals respectively (Churchman *et al.* 1994). The total percentage of these minerals plus the non-clay minerals was subtracted from 100%. The entire procedure was repeated five times using an iterative method and the difference from 100% was allocated in the ratio 2:1 to illite and kaolinite respectively (Riley 1993).

4.3.3 *Other measurements*

The particle size distribution was determined by sedimentation after sodium saturation followed by dispersion in deionized water (Gee and Bauder 1986). Electrical conductivity (EC) and pH of soils were measured (1:5 soil:water) after shaking overnight. The extraction of the exchangeable cations was carried out by shaking 5g of the soil with 30 ml of 1M NH_4Cl solution in a centrifuge tube overnight followed by centrifugation and collection of the supernatant solution. In two further subsequent extractions, the samples were centrifuged after 2 hours shaking. These extractions were combined and the cations, viz. lithium, sodium, potassium, magnesium, calcium and aluminium displaced by NH_4Cl were measured by inductively coupled plasma atomic emission spectrometry (ICPAES). The total negative charge (or CEC) of the soils were taken to be the sum of the charges on cations displaced by 1M NH_4Cl. Organic carbon was measured using Walkley and Black's rapid titration procedure. The physico-chemical properties of these soils are summarised in Table 4.1.

Table 4.1. Selected physical and chemical properties of the soils used

Soil	Particle- size distribution %			pH^A	Organic Carbon	EC^A	CEC	Clay mineralogy^B %			
	Clay	Silt	Sand		%	$dS.m^{-1}$	$mmol_c\ kg^{-1}$	I	K	RIM	Q
Evans	32	43	25	7.00	1.7	0.11	145	51	14	29	6
Meadows	13	32	55	6.70	2.8	0.19	65	16	25	36	23
Claremont	55	25	20	6.75	3.1	0.15	515	15	5	76	4

^{A} Determined on a 1:5 soil water extract.

^{B} Measured by X-ray diffractrometry and X-ray fluorescence. I=illite, K=kaolinite, RIM=randomly interstratified minerals, Q=quartz.

4.3.4 Experimental procedure

The soil samples(<2mm) were saturated with sodium by using 1M NaCl. Each soil suspension (20% w/v) was then dialysed until the external solution had an electrical conductivity less than 0.01 dS m^{-1}.

4.3.5 Determination of electrical charge on soils

Positive and negative charges on soil clay particles were determined by measuring the adsorption of Ca^{2+} and Cl^- as a function of pH. The method was essentially that described by Naidu *et al.* (1990). The homoionic Na-soils were suspended in distilled water and adjusted to various pH values using either NaOH or HCl (0.1M). After 24 hours shaking, the suspension pH was measured and the dispersible clay was measured turbidimetrically (Barzegar *et al.* 1994). The suspension was centrifuged and the supernatant was used to determine EC, Na^+, Ca^{2+}, Mg^{2+} and K^+.

4.2.6 *Soils used for correlation studies*

15 Oxisols, 30 Alfisols, 14 Aridisols and 15 Vertisols collected from different parts of Australia were used to measure dispersive potential, pH and CEC in order to obtain relationships between these factors. Oxisols were generally dominated by kaolinites and oxides of Fe and Al. Alfisols were dominated by illite and kaolinite. Vertisols were dominated by smectite and kaolinite. Aridisols had mixed mineralogy containing kaolinite, illite and randomly interstratified minerals. Bulk samples of each soil were air dried and gently crushed to pass a 2-mm sieve and then thoroughly mixed.

4.3.7 *Statistical analysis*

Statistical analyse of data were performed using the Genstat 5 Statistical package (Genstat 5 Committee 1987). These included simple and multiple linear regression and analysis of variance.

4.3.8 *Dispersive potential*

The dispersive potential of each soil was determined as described by Rengasamy *et al.* (1993). Soil samples and acid-washed sand were mixed in equal proportions and packed in perspex columns. Each column was wetted initially with a 0.5M chloride solution of appropriate SAR (Na, Ca only) and kept saturated. The SAR was selected according to the measured SAR for a particular soil. The columns were leached consecutively with solutions of constant SAR but decreasing concentration, between 0.05 and 0.001M, until steady effluent compositions were achieved. The electrolyte concentration at which the clay dispersed spontaneously and moved from the column was determined carefully. This minimum concentration when the clay starts dispersing is considered to be equal to the minimum electrolyte concentration (critical dispersion concentration, CDC) required to prevent clay dispersion from soil aggregates. Using the composition of the electrolyte in the effluent at this stage, dispersive potential is calculated (Rengasamy *et al.* 1993). The SAR values used in this experiment ranged between 6 and 30. The CDC values ranged between 1 and 4 $\text{mmol}_c\ L^{-1}$.

4.4 Results and discussion

4.4.1 Effect of pH on clay dispersion from three selected soils

As the pH decreases below 6, all three soils used in this study develop positive charge so that the net negative charge decreases. When the pH increases above 6, negative charge increases (Figure 4.1). Claremont soil is dominated by randomly interstratified minerals (RIM) and also has higher organic carbon. Therefore, the negative charge is higher, by a factor of three, for this soil compared to Evans and Meadows soils whose clay fractions are dominated by illite and kaolinite respectively. The change in the percentage of dispersible clay with change in pH (Figure 4.2) also reflects the trends in net negative charge of these soils as affected by pH. Thus, Claremont soil, dominated by RIM, has high net negative charge and hence high dispersible clay at high pH (>6.5).

The results for soil clays confirm that clay dispersion and flocculation is dependent on net particle charge and pH. The net negative charge on clay systems is influenced by pH. In general, we found that soil clays have higher flocculation values than the values reported for pure clay minerals at comparable pH values (Table 4.2); this agrees with observations reported by Rengasamy (1983); Goldberg and Forster (1990) and Heil and Sposito (1993). A comparison of net negative charge at similar pH values (Table 4.2) indicates that soil clays have more net negative charge (calculated on a clay basis) than

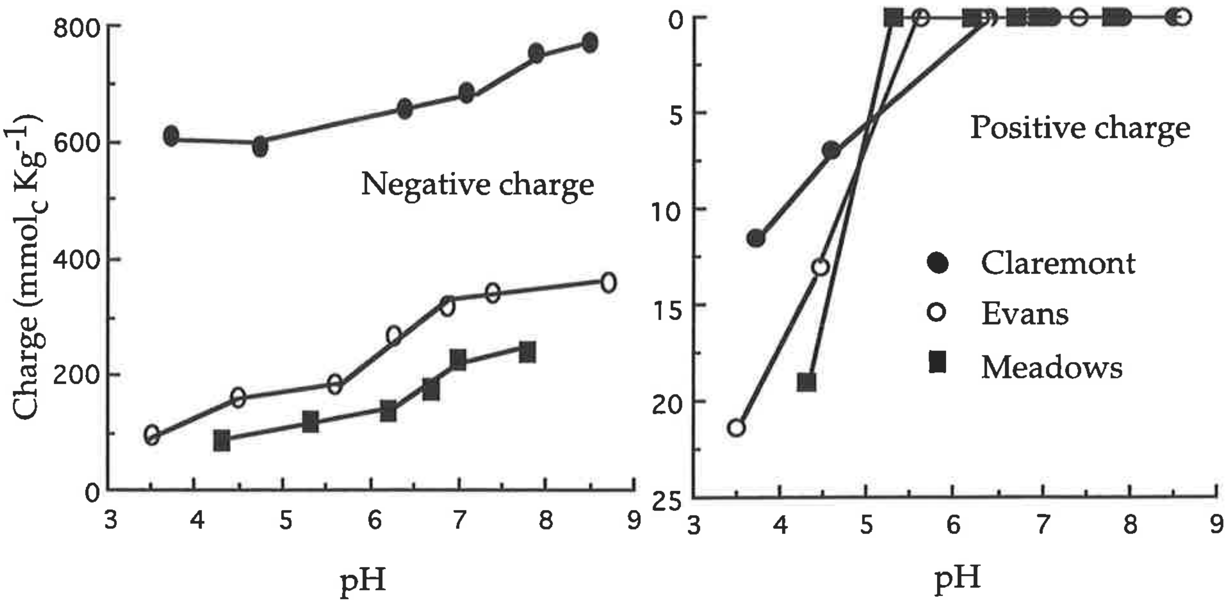


Fig. 4.1. Effect of pH on surface charge characteristics of the soils

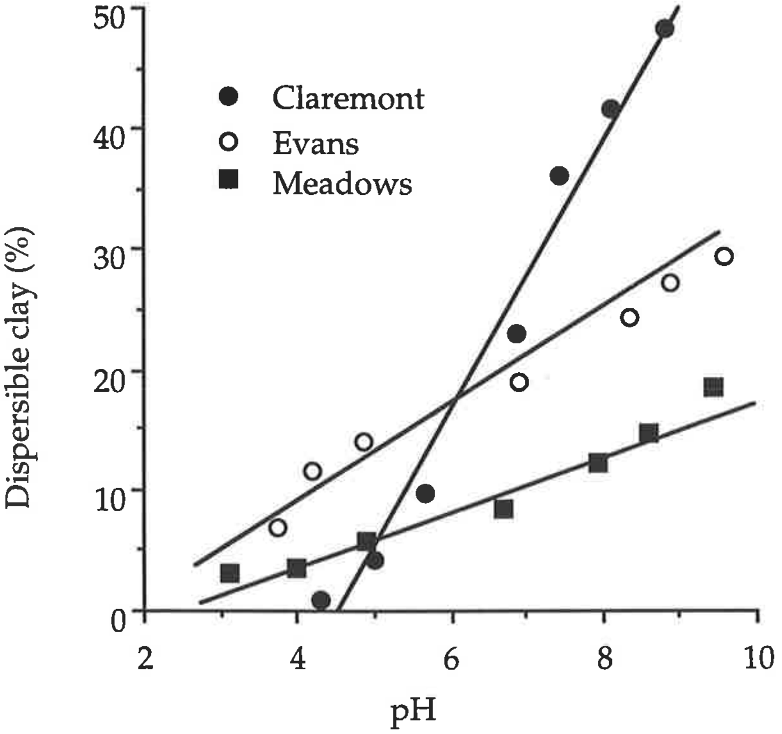


Fig. 4.2. Effect of pH on dispersible clay for three soils.

pure clays of similar mineralogy. Therefore, net negative charge on particles accounts for clay flocculation better than the dominant mineralogy of the soil clays. Soil clays have more net negative charge than those reported for pure clay minerals largely because of the association of organic matter and other components. If soil particles contain adsorbed organic matter, then organic functional groups also contribute to changes in particle charge. Dixit(1982); Oades (1984) and Goldberg *et al.* (1990) concluded that adsorption of organic matter onto clay particles increases their negative charge and hence, the dispersion of clay particles is promoted and the flocculation of clay particles is decreased. Heil and Sposito (1993) concluded that the amount of electrolyte required for flocculation of illitic soil clays, the effect of pH, and the relative effect of Ca vs. Mg all depended on soil organic matter content.

Table 4.2. Flocculation values and net negative charge for pure clays and soil clays at pH 7.0

Clay system	Flocculation values^A (mmol$_c$ L^{-1})	Net negative charge^B (mmol$_c$ kg^{-1})
Kaolinite	0 - 5	79
Meadows soil clay (kaolinitic)	120	720
Illite	9	166
Evans soil clay (illitic)	210	869
Montmorillonite	7- 20	783
Claremont soil clay (RIM))	100	1113

^{A} The flocculation values for pure clays are from Sumner (1993).^{B} The net negative charge values for the pure clays are from Rengasamy and Oades (1977).

When the pH of the clay suspensions are reduced below 6 by adding acid, mineral dissolution causes an increase in the electrolyte concentration, expressed as EC values in Table 4.3; this will also cause flocculation in addition to the effect of reduction in net negative charge at these pH values. This is particularly marked for the Claremont soil, which produces little dispersible clay at pH<6 (Figure 4.2) despite the high negative charge on this soil. As the pH is lowered, more dissolution of Fe and Al can occur and , depending on the extent of hydrolysis of these ions, flocculation of clay particles can be drastically altered. However, upon increasing the pH above 8 by adding alkali, mineral dissolution causes an increase in EC, but the corresponding increase in negative charge increases the clay dispersion.

4.4.2 Critical dispersion concentration for aggregates and the flocculation values of soil clays

The electrolyte concentrations at which clays dispersed spontaneously from soil aggregates (i.e. CDC) were below 4.0 $\mathrm{mmol_cL^{-1}}$ whereas the flocculation values for soil clays were very high and ranged between 100 and 210 $\mathrm{mmol_cL^{-1}}$. The clay fractions separated from soils have high negative charge (Table 4.2) and the increased charges due to exposure of surfaces generate high repulsive forces in the diffuse double layer and hence, high flocculation value. In soil aggregates, the clays are bonded to each other via organic polymers and exchangeable cations. Therefore, only a portion of the total negative charge (i.e. CEC) associated with the adsorbed sodium, interacts with water molecules, generating a low repulsive hydration force leading to clay dispersion. Hence, low levels of electrolyte are enough to oppose this repulsion. Rengasamy and Naidu (1995) reported that the charges involved in the repulsive hydration forces in sodic soil aggregates, as measured by methylene blue adsorption, were lower than the CEC estimated by the conventional ammonium chloride method.

Table 4.3. Effect of changing soil pH on mineral dissolution and clay dispersion

Added acld/alkali ml L^{-1}	Meadows soil			Evans soil			Claremont soil		
	pH	EC dS.m^{-1}	Dis. clay %	pH	EC dS.m^{-1}	Dis. clay %	pH	EC dS.m^{-1}	Dis. clay %
Control	6.7	0.11	9	7 .0	0.19	18	6.8	0.15	23
HCl (1M) added									
1	4.9	0.44	5	5.0	0.53	14	5.7	0.40	9
2	4.0	0.71	3	4.2	0.68	9	5.0	0.83	4
3	3.1	1.10	1	3.7	0.93	2	4.4	1.28	1
NaOH (1M) added									
0.2	8.0	0.25	10	8.4	0.40	24	7.4	0.23	37
0.5	8.7	0.32	11	8.9	0.62	26	8.1	0.29	41
1	9.4	0.49	14	9.5	0.74	29	8.9	0.31	46

4.4.3 Dispersive potential of Australian soils in relation to their pH and CEC

The results for three soil clays discussed above clearly indicate that soil pH is an important factor in altering dispersive behaviour. The basic mechanism of the pH influence is through its effect on the net negative charge on clay particles. Therefore, we wanted to establish a relationship between soil pH, negative charge, as measured by CEC, and the dispersive behaviour of soils. In order to balance the opposing effects due to sodicity (SAR) and electrolyte, we estimated the dispersive potential (P_{dis}) in pressure units (which is directly related to the dispersible clay as reported by Rengasamy and Olsson 1991) of a number of Australian soils belonging to Oxisols, Alfisols, Aridisols and Vertisols. These soils ranged from weakly to strongly sodic and were spontaneously dispersive. The mean and average values of pH, CEC, EC, SAR and P_{dis} of the soils are given in Table 4.4.

Table 4.4. General characteristics of soil groups used

Characteristics	Oxisols	Alfisols	Aridisols	Vertisols
Number of samples	15	30	14	15
pH^A				
Range	4.1- 5.0	5.8- 8.3	7.7- 10.0	5.6- 9.4
Mean	4.6	7.0	8.9	8.3
EC^A ($dS.m^{-1}$)				
Range	0.1- 0.4	0.1- 0.6	0.2- 0.6	0.1- 0.6
Mean	0.2	0.4	0.4	0.3
CEC ($mmol_c$ Kg^{-1})				
Range	6- 10	13- 129	140- 176	460- 686
Mean	8	82	161	583
SAR				
Range	9- 16	4- 30	6- 20	6- 19
Mean	8	16	11	10
$Pdis^B$ (kPa)				
Range	6.3- 21	37- 180	153- 311	156- 281
Mean	13	117	249	215
Clay mineralogy^C	K, O	K, I	K, I, RIM	S, I

^{A}Determined on a 1:5 soil water extract. ^{B} Dispersive potential
^{C} K= kaolinite, I= illite, S= smectite, O= oxides and RIM= randomly interstratified minerals.

Linear regressions between $P_{dis}(Y)$ and either soil pH (X_1) or soil CEC (X_2) for each soil group and also for all soils pooled together are presented in Table 4.5. When each soil group is considered, dispersive potential is significantly correlated with pH while the correlation between P_{dis} and CEC was significant in soils other than Oxisols. In all cases, R^2 values were lower for CEC relationships. When all soils were pooled together, P_{dis} was highly correlated with pH ($R^2 = 0.96$).

Table 4.5. Regression analyses of dispersive potential (Y) with either pH (X_1) or CEC (X_2) for different soil groups

Soil Group	Regression equations	R^2	No. of soils
Oxisols	$Y = -37.2 + 10.8X_1$	0.77	15
	$Y = 2.5 + 1.2X_2$	0.34	
Alfisols	$Y = -195.4 + 44.9X_1$	0.93	30
	$Y = 48.5 + 0.8X_2$	0.68	
Aridisols	$Y = -3.5 + 55.6X_1$	0.86	14
(calcareous)	$Y = -268.5 + 3.2X_2$	0.68	
Vertisols	$Y = 7.4 + 25.1X_1$	0.78	15
	$Y = 120.3 + 0.2X_2$	0.57	
All soils	$Y = -223.6 + 51.1X_1$	0.96	74
	$Y = 91.6 + 0.3X_2$	0.63	

Multiple linear regressions were carried out individually for each soil group. Equations relating dispersive potential (P_{dis}, Y) to soil pH (X_1) and soil CEC (X_2) were fitted. In each instance, it was found that CEC was not important when pH was included in the model. This indicates that dispersive potential depends significantly upon pH only. Because CEC was estimated using ammonium chloride at pH 8.5, it does not represent the actual negative charge which may occur at the pH of the soil in electrolyte-free water. The net charge at the pH of the soil in electrolyte free water is the major factor influencing dispersive potential.

These correlation studies clearly show the importance of pH in influencing clay dispersion in many diverse types of soils, even though the mineralogy of these soils varies widely. It was concluded that soil pH is an important factor to consider in the management of dispersive soils. The effect of increasing pH on clay dispersion is significantly higher in Alfisols and Aridisols than in Oxisols or Vertisols as seen from the slopes in Figure 4.3.

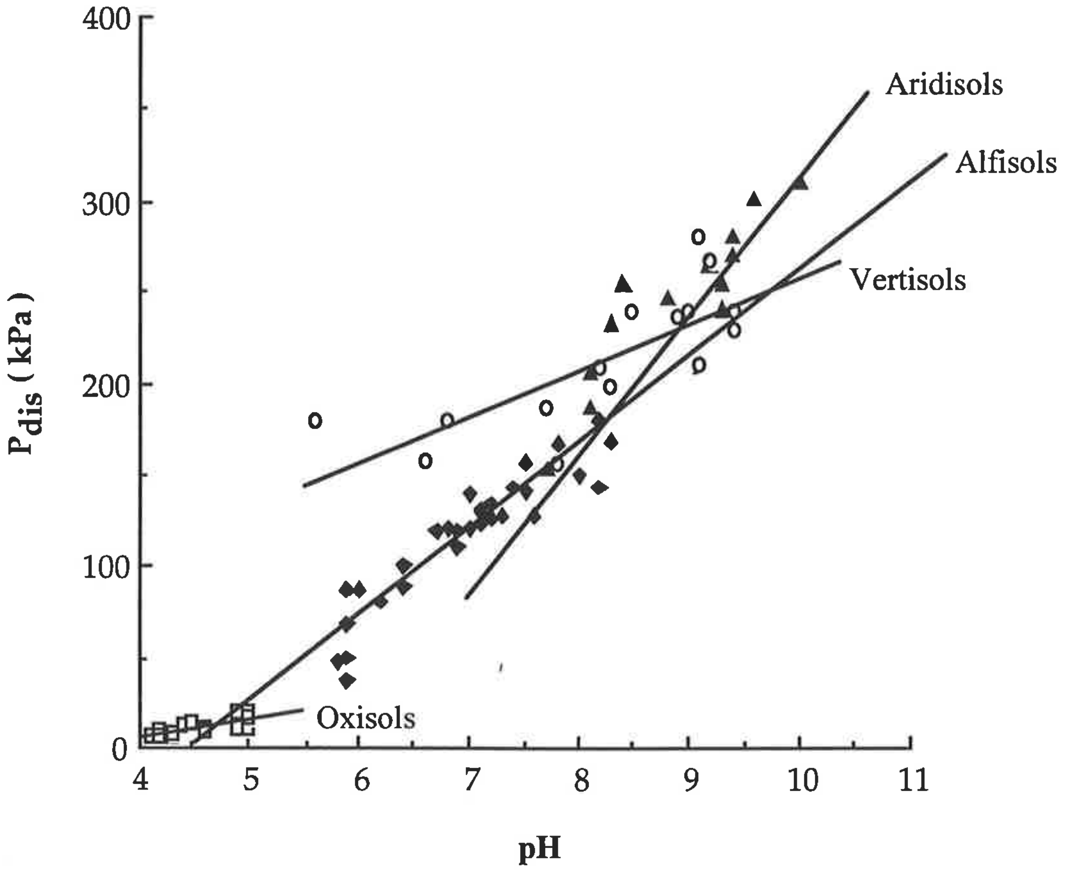


Fig. 4.3. The influence of increasing pH on dispersive potential of soils from different soil groups

4.5 Conclusions

This study clearly shows that pH affects clay dispersion from soils primarily by changing the net negative charge on clay particles. The results for soil clays showed that clay dispersion was dependent on net negative charge which increased with increasing pH. On comparing the reported values for pure clay minerals with the soil clays of similar mineralogy, soil clays always had higher flocculation values. The soil clays at comparable pH values had higher net negative charge probably because of the association of organic materials and other components.

The dispersive potential, P_{dis}, of a number of Alfisols, Oxisols, Aridisols (calcareous soils) and Vertisols was clearly related to soil pH and soil CEC individually. The correlation coefficient of P_{dis} with pH was higher than with CEC. Multiple regression analyses indicated that CEC was not important in relation to pH. This is probably because of the problem of estimating soil CEC using ammonium chloride of pH 8.5 instead of using the soil pH measured in electrolyte-free water.

For the management of dispersive soils under field conditions a knowledge of soil pH is an important factor. Soil pH and particle charge may fluctuate under field conditions due to management factors. While particle charge is difficult to determine routinely, soil pH can easily be measured and used to predict changes in the dispersive nature of field soils.

CHAPTER 5

Changing particle charge and altering clay behaviour

5.1 Introduction

The swelling and dispersion of clays in salt-free water are functions of exchangeable cations and layer silicate structure. These processes are governed by the balance between attractive and repulsive forces arising from intermolecular and electrostatic interactions between solution and solid phases in the suspension. Many workers have studied the relationship between clay swelling and clay crystallographic factors. It was shown in chapters 3 and 4 that net particle charge is the most important factor controlling clay dispersion for a range of pH and ionic strength values. In many studies (Glaeser and Mering 1968; Jenkins and Hartman 1982; Slade *et al.* 1991; Sato *et al.* 1992) investigating the effect of interlayer cations, net layer charge and charge location (octahedral or tetrahedral) on the expansion properties of smectites, the general conclusion was that the basal spacings of tetrahedrally-charged smectites were smaller than those of octahedrally-charged smectites under the same hydration and solvation conditions. On the other hand, Schultz (1969) suggested that the expansion properties did not depend on the charge location, but on the total net charge and the amounts of structural (OH).

The thermal treatment of smectites saturated with lithium has been shown to reduce their layer charge and also cause a decrease in exchangeable lithium (Hoffman and Klemen 1950; Lim and Jackson 1986; Jaynes and Bigham 1987). Similar reduction in charge has also been found when Mg^{2+} or Al^{3+} saturated montmorillonite clays were heated up to 300°C (Greene-Kelly 1955a; Glaeser and Mering 1968; Calvet and Prost 1971). The mechanism of charge reduction was argued to be the migration of these cations of small radius into vacant octahedral sites to reduce the octahedral charge. However, this hypothesis has been disputed by others including Tettenhorst (1962).

The effect of heating on the cation exchange capacity (CEC) of kaolinite saturated with Li, Na, Mg and Ca was studied by Green-Kelly (1955b); Cashen, (1959) and Pennell *et al.* (1991). A fixation of a portion of the Li ions within the kaolinite structure during the migration of Li ions into the structure was reported by Green-Kelly (1955b); Glaeser and Mering (1971) and Pennell *et al.* (1991). Green-Kelly (1955b) found Li ions to be non-exchangeable after the kaolinites are dried by heating to 200°C. Pennell *et al.* (1991) showed that the total charge of Li-kaolinite was reduced by approximately 50% after heating to 130°C, but the total charge of Ca-kaolinite remained essentially constant while that of Na-kaolinite decreased slightly. Thermal treatment not only reduced the total charge of the Li-kaolinite but also displaced Al and H^+ from the kaolinite structure, by Li ions. Infrared spectroscopy indicated that Li migrated into the kaolinite structure and replaced a portion of the Al from the octahedral sheet (Pennell *et al.* 1991). Sennett, (1990) studied the effect of heating at various temperatures on the physical properties of the kaolinites. He found, the brightness (% blue reflectance) and the soluble salts (%) decreased whereas, the mean particle size of the clays increased as the temperature of heating increased from 100 to 1000°C. There is no information available in literature related to the effect of heating on swelling and dispersion properties of illite saturated with different cations.

Some recent studies have suggested that hydration forces are more important in swelling than DLVO (Derjaguin-Landau-Verwey-Overbeek) forces (Low 1981; Pashley 1985b; Israelachvili and McGuiggan 1988). Hydration reactions during clay swelling and dispersion are controlled by electron-acceptor and electron-donor (EAED) interactions between water molecules, clay surfaces and exchangeable cations (Christenson and Horn 1985; van Oss *et al.*

1990). This is also referred to as acid-base (AB) reactions based on the principle of the Hard-Soft Acid-Base (HSAB) concept of R.G. Pearson (Huheey *et al.* 1993). Rengasamy and Sumner (1996) proposed that HSAB reactions lead to different types of bonding between clay surfaces and cations *viz.* covalent, polar covalent and ionic which control hydration, and hence the swelling and dispersive properties of soil clays.

5.2 Effect of heating on swelling and dispersion of different cationic forms of a smectite

Thermal treatment of clays can lead to changes in particle charge and thus alter clay behaviour. To understand the mechanisms of clay swelling and dispersion, clays were heated up to 400°C to provide variously charged minerals without significant change in their crystalline structures. Therefore, the study reported in this section was to investigate the effects of heating up to 400°C on charge reduction, swelling and dispersion of a smectite saturated with Li, K, Na, Mg, Ca, and Al . It was hypothesised that these properties are related to the type of bonding resulting from EAED interactions during heating.

5.2.1 Materials and methods

5.2.1.1 Clay preparation

A Wyoming bentonite sample was dispersed, fractionated and deferrated by conventional procedures (Jackson 1974); XRD revealed no crystalline impurities. Clays which were homoionic in Li, Na, K, Mg, Ca and Al were prepared by treating the clay fractions with 1 M chloride solutions, three times at 24 hours intervals. Afterwards, the clays were dialysed against distilled water until chloride free. Then, the salt-free clay samples were freeze-dried and stored at room temperature (25°C). Samples of the homoionic clays were heated for 6 hours at 100, 200, 300 and 400°C in a muffle furnace. The clays were cooled in a desiccator and placed in a sealed glass container kept at 25°C. Electrical conductivity (EC) and pH were determined using a 1:10 water extract.

5.2.1.2 *Exchangeable cations and cation exchange capacity*

The extraction of the exchangeable cations was carried out by shaking 20 mg of the homoionic clays with 10 ml of 1M NH_4Cl solution in a centrifuge tube overnight followed by centrifugation and collection of the supernatant solution. In the two subsequent extractions, the samples were centrifuged after 2 hours shaking. These extractions were combined and the cations, viz. Na, Li, K, Mg, Ca and Al displaced by NH_4Cl were measured by inductively coupled plasma atomic emission spectrometry (ICPAES). The total negative charge (or CEC) of the clays was taken to be the sum of the charges on cations displaced by 1M NH_4Cl.

5.2.1.3 *X-ray diffraction studies*

1 ml of a 1% suspension of each clay was pipetted onto a zero background silica wafers and step scanned at 40 kV and 30 mA over 3-33° (0.02° per sec.) in a Philips 1729 X-ray diffractometer with cobalt radiation fitted with a graphite monochrometer. Interlayer swelling was monitored by XRD patterns of the samples after glycerol solvation (Sato *et al.* 1992).

5.2.1.4 *Measurements of dispersible clay*

The amount of spontaneously dispersible clay was determined by the following method. 10 ml of distilled water was added to 20 mg of the clays and kept overnight without any disturbance. After 24 hours, the supernatant solution of this suspension was siphoned to measure the proportion of clay remaining in suspension.

The amount of mechanically dispersed clay was measured by the following method. A mixture of 20 mg of clay and 10 ml distilled water was shaken for 24 hours. After shaking, the sedimentation time was set for 16 hours for all measurements. Then the supernatant liquid was siphoned to estimate the mechanically dispersed clay. The proportions of total clay in both suspensions were determined turbidimetrically using an HACH turbidimeter. A calibration curve, different for each cationic clay, was used to convert turbidity to amounts of dispersed clay.

5.2.1.5 *Zeta potential measurements*

The zeta potential (ζ–potential) of clay particles was determined using a Malvern `Zetamaster particle electrophoresis analyser' as described in section 3.2.4. The ζ–potentials measured in this study were negative in sign, because the clay particles moved towards the cathode. The pH values were monitored and are presented in Table 5.2.1.

5.2.1.6 *Clay particle size*

Clay particle size in the suspension after mechanical dispersion was measured by sub micron particle sizer NICOMP model C370 using photon correlation spectroscopy as the mean of an assumed Gaussian distribution.

5.2.2 Results

5.2.2.1 *Chemical properties*

The effects of heating on the chemical properties of Wyoming bentonite saturated with Li, Na, K, Mg, Ca and Al are shown in Table 5.2.1. In general, pH values of the 1:10 suspension in distilled water depended upon the nature of the cation. Among monovalent cationic clays, Li and Na-clays had higher pH values than K-clays. Further, divalent cationic clays had higher pH values than Al-clays (Table 5.2.1). In the suspension of unheated clays (25°C), the dissociation of cations and subsequent hydrolysis reactions led to the changes in H^+ concentration. For Al^{3+}, even though the dissociated ions were very low, strong hydrolysis reactions release more H^+ ions and the pH was 4.87. On thermal treatment cations are strongly bond to the clay surfaces. The water extracts of thermally treated clays have lower amount of dissociated cations (Tables 5.2.1). Because, the dissociated cations are lower, the release of proton due to hydrolysis reactions is also less; thus the pH is higher than in unheated clays. Electrical conductivity (EC) values also reflected the same trend.

Thermal treatment of cationic clays reduced the total negative charge (CEC) and the amount of exchangeable cations as the temperature of heating increased (Table 5.2.1). However, the extent of this reduction depended on the nature of the cation and the temperature of heating. Thus in Li-clays the charge, after heating at 200°C, was drastically reduced from 94 to 24 $\mathrm{cmol_c\ kg^{-1}}$. After heating at 400°C, the charge fell to 8 $\mathrm{cmol_c\ kg^{-1}}$. However, in Na-clays the reduction was minimal compared to Li-clays. The reduction in K-clays was similar to Na-clays, even though the total charge was lower. Among divalent cations, the charge reduction in Mg-clays was similar to Li, with a huge reduction only after heating at 400°C. The Ca-clays were similar to K and Na-clays, with minimal charge reduction. The trend in Al-clays was similar to Li and Mg-clays. As the cations are strongly bound to surface -O or -OH, exchange by NH_4^+ becomes more difficult. As the valency of the cations increases, the bonding is stronger, and the total charge estimated by NH_4^+ exchange is reduced (Table 5.2.1).

Table 5.2.1. The effect of heating on pH, EC, the concentration of the saturating cation in 1:10 clay-water extract, exchangeable cation and total negative charge of homoionic Wyoming bentonite

Cation (M-clay)	Temperature of heating °C	pH	EC µS cm^{-1}	Dissociation cation mg L^{-1}	Exchangeable cation						CEC
					Li	Na	K	Mg	Ca	Al	
					<— cmol$_c$ kg^{-1} —>						
Li (0.68)^A	25	6.11	34	2.8	85	4	0	1	4	0	94
	200	6.62	7	0.3	18	2	0	1	2	0	24
	400	6.94	4	0.2	6	0	0	1	1	0	8
Na (0.97)^A	25	6.27	47	4.6	0	79	0	1	13	0	93
	200	6.35	15	3.9	0	72	0	2	11	0	88
	400	6.52	12	2.3	0	65	1	2	11	1	80
K (1.33)^A	25	5.47	54	19	0	5	78	1	1	0	86
	200	5.61	10	4.3	0	5	68	1	0	0	76
	400	5.83	8	2.0	0	3	60	2	0	1	66
Mg (0.66)^A	25	6.08	10	1.2	0	2	0	78	0	0	81
	200	6.54	6	0.6	0	2	1	69	0	1	73
	400	6.69	3	0.3	0	2	1	9	0	1	14
Ca (0.99)^A	25	6.43	9	1.8	0	2	0	1	77	0	80
	200	6.54	6	0.8	0	2	0	0	69	0	71
	400	6.83	6	0.2	0	2	0	0	58	0	60
Al (0.51)^A	25	4.87	8	0.2	0	2	0	3	1	71	77
	200	4.91	6	0.1	0	2	0	2	1	62	68
	400	5.12	4	0.1	0	2	0	2	1	13	18

^{A} Crystal ionic radii (Å)

5.2.2.2 *Physical properties*

5.2.2.2.1 Swelling

The swelling of smectites depends upon their structures, their chemical compositions and the type of exchangeable cation. The variation of XRD patterns of Li, Na, K, Mg, Ca and Al-Wyoming bentonite (Figures 5.2.1 and 5.2.2) before and after heating and re-expansion after glycerol solvation was studied. Table 5.2.3 shows the swelling obtained for dry and glycerol solvated samples. The d_{001} spacings of Li, K, Na-Wyoming bentonite prior to heating correspond to a hydrated structure where the cations are located in the interlayer space and solvated by water molecules adsorbed from the atmosphere.

Lithium saturation and heating caused the Wyoming bentonite to become dark and also develop hydrophobic character viz. floating in water. Li-clays collapsed and did not expand after being heated at 200-400°C (Table 5.2.2). The XRD patterns of Li-clay after heating between 200°C and 400°C exhibit a d_{001} reflection corresponding to 9.6Å, even after treatment by glycerol.

The high charge reduction for Li-clay from 94 to 8 $\text{cmol}_c\ \text{kg}^{-1}$ after heat treatments is in good agreement with previous work. Calvet and Prost (1971) showed that the clay did not swell with water when the amount of exchangeable cation was lower than 50 percent of original exchange capacity.

No differences were detected between XRD patterns of Na-clays heated at 100-400°C and 25°C (unheated). Even after thermal treatment (up to 400°C), the hydrated sodium ions remained in the interlayer as reflected by d_{001} spacings (Figure 5.2.1, Table 5.2.2). As a result of glycerol solvation, d_{001}

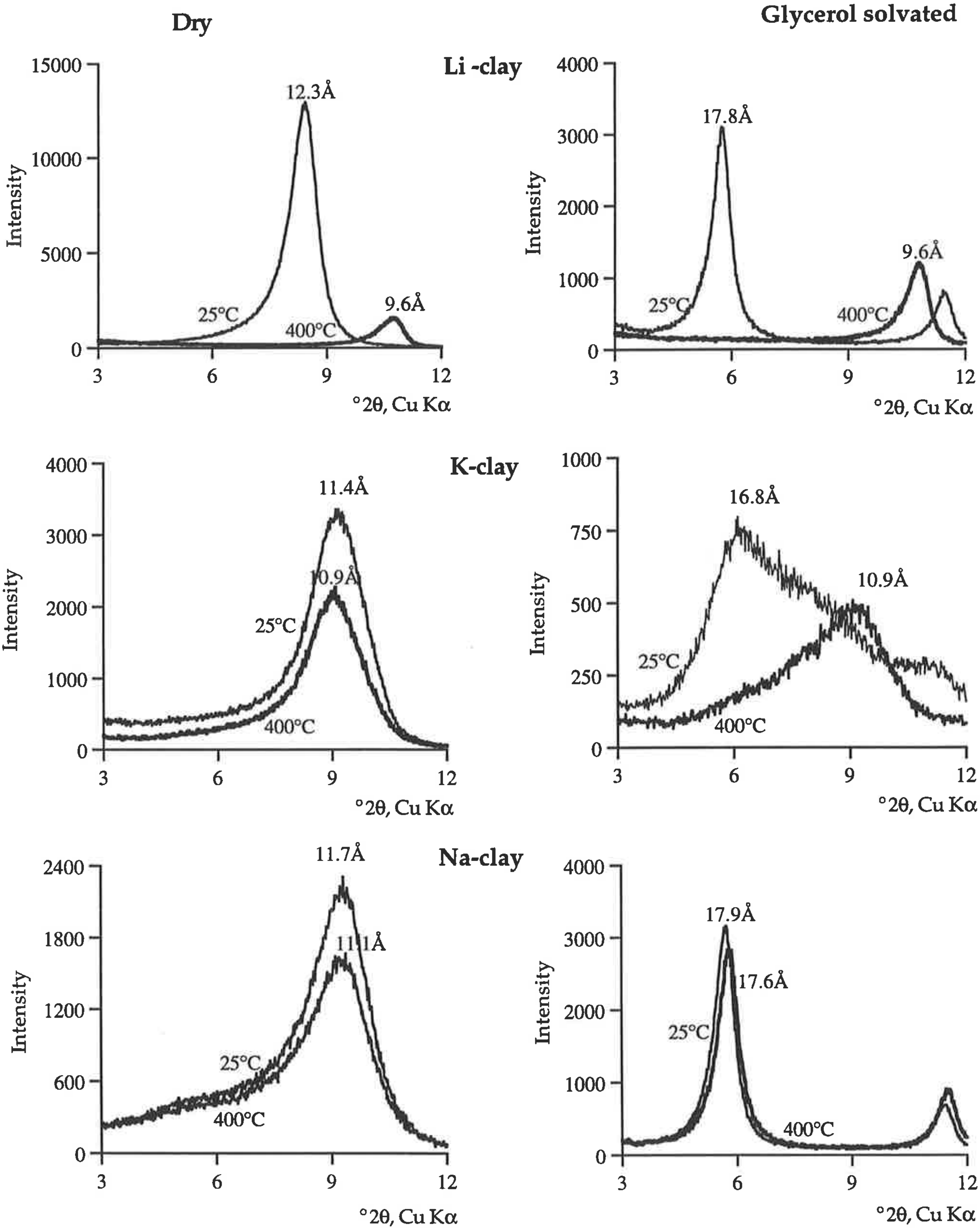


Fig. 5.2.1. XRD patterns of the Wyoming bentonite saturated with Li, K and Na at different temperatures.

spacings of treated clays increased to 17.6Å, indicating swelling even after heating up to 400°C. This behaviour, as for the charge characteristics, is opposite to that of Li-clays.

The d_{001} spacings of K-clays heated up to 300°C and after glycerol solvation were similar to those of Na-clays. The charge reduction of K-clays after heat treatment is small compared to the drastic reduction in Li-clays (Table 5.2.1). Expansion in d_{001} spacing after glycerol solvation is observed even after heating at 300°C or 400°C (Table 5.2.2). Thus it appears, K^+ migration into octahedral sites does not occur, part of the interlamellar K^+ remaining exchangeable (Table 5.2.1). Thus it appears, K^+ in the interlayer space is progressively fixed or strongly bonded to the surface -O or -OH groups by the increase in temperature of heating.

Among the divalent cations, d_{001} spacings of unheated (25°C) clays (Table 5.2.2) indicated that interlayer divalent cations were more hydrated than K^+. Spacings for Al-clays were also consistent with substantial cation hydration. Heating up to 300°C did not result in any substantial collapse of d_{001} spacing, which on glycerol solvation expanded with d_{001} spacings ranging from 16.7 to 18.2Å. However, on heating at 400°C, Mg and Al-clays collapsed to a d_{001} spacing of 9.6Å and on glycerol solvation did not expand (Figure 5.2.2). Thus it appears that migration of Mg and Al from the interlayer space to the vacant octahedral sites occurred. Calvet and Prost (1971) showed that when Mg-montmorillonite and Ca-montmorillonite were heated at 400°C, Mg^{2+} ions could migrate in the structure while Ca^{2+} ions could not. Alternatively, it can be suggested that these cations are strongly bonded to the clay surfaces while still remaining in the interlayers.

Table 5.2.2. The effect of heating on swelling, dispersion, ζ-potential and mean particle diameter (MD) of homoionic Wyoming bentonite

Cation M-clay	Temperature of heating°C	Swelling d_{001} Å dry glycerol	Dispersion (%) spontaneous	mechanical	pH	ζ-potential -mV	MD µm
Li							
	25	12.3 → 17.8	90	98	6.11	40.5	0.30
	100	12.2 → 17.8	70	72	6.34	36.1	0.75
	200	9.6 → 9.6	Nil	23	6.62	34.0	1.78
	300	9.6 → 9.6	Nil	6	6.73	33.6	2.42
	400	9.6 → 9.6	Nil	2	6.94	33.2	3.51
Na							
	25	11.7 → 17.9	80	98	6.27	39.1	0.33
	100	11.2 → 17.9	70	87	6.31	38.6	0.82
	200	11.1 → 17.6	22	82	6.35	38.4	1.04
	300	11.1 →17.6	Nil	78	6.42	38.2	1.46
	400	11.1 → 17.6	Nil	67	6.52	37.7	1.75
K							
	25	11.4 → 16.8	55	86	5.47	37.3	0.75
	100	11.3 → 16.8	15	55	5.51	36.8	1.41
	200	11.3 → 16.8	2	41	5.61	36.7	1.61
	300	11.1 → 16.7	Nil	32	5.76	36.2	1.75
	400	10.9 → 10.9	Nil	18	5.84	35.2	2.21
Mg							
	25	15.5 → 17.8	Nil	25	6.08	28.8	0.82
	100	15.5 → 17.8	Nil	14	6.26	26.3	0.94
	200	15.1 → 17.8	Nil	11	6.54	25.3	1.34
	300	13.2 → 17.8	Nil	10	6.62	25.2	2.81
	400	9.6 → 9.6	Nil	2	6.69	24.9	3.32
Ca							
	25	15.3 → 17.7	Nil	18	6.43	24.7	1.06
	100	15.2 → 17.6	Nil	8	6.52	21.8	1.25
	200	15.2 → 17.6	Nil	6	6.54	19.9	1.92
	300	15.2 → 17.6	Nil	5	6.67	19.7	2.15
	400	15 → 17.6	Nil	3	6.83	19.4	2.79
Al							
	25	15.3 → 18.2	Nil	5	4.87	20.1	1.44
	100	15.3 → 18.2	Nil	4	4.89	19.4	1.86
	200	14.5 → 18.1	Nil	4	4.91	18.4	2.78
	300	14.1 → 18.1	Nil	3	4.99	17.9	4.65
	400	9.6 → 9.6	Nil	2	5.12	16.8	5.66

In general, the intensity of the peaks reduced on heating as the temperature of heating increased (Figures 5.2.1 and 5.22). The extent of reduction in the intensity of peaks was similar to the charge reduction. In the case of Li, Mg and Al-clays, after heating at 400°C, the charge reduction was drastic and the intensity of d_{001} peaks was also very low.

5.2.2.2.2 Dispersion

The results for spontaneous dispersion are presented in Table 5.2.2. All the freeze-dried monovalent cationic clays exhibited spontaneous dispersion when placed in distilled water. Li-clay had partial spontaneous dispersion after heating at 100°C while no dispersion was observed after heating from 200°C to 400°C (Table 5.2.2). K-clay had lower dispersible clay after heating at 100 and 200°C and no spontaneous dispersion occurred after heating at 300°C and 400°C. Na-clay had spontaneous dispersion after heating up to 200°C while no spontaneous dispersion occurred after heating at 300 or 400°C. Di- and tri-valent cationic clays (before and after heating) did not exhibit spontaneous dispersion when placed in distilled water (Table 5.2.2).

The results for mechanical dispersion are given in Table 5.2.2. Compared with those treated at 25°C, for clays heated at 400°C, the dispersion of Li-clay particles decreased from 98 to 2 percent, Na-clay particles from 98 to 67 percent and K-clay particles from 86 to 18 percent. There was a greater reduction in mechanical dispersion for Li- and K-clays than for Na-clay after heating at >200°C. The changes correspond to the charge reductions at higher heating temperatures.

Mechanical dispersion of unheated divalent and Al-clays was much lower than of clays with monovalent ions (Table 5.2.2). When the temperature of heating increased from 25°C to 400°C the percentage of dispersed clay in Mg-, Ca- and Al-clays all decreased to 2-3 percent.

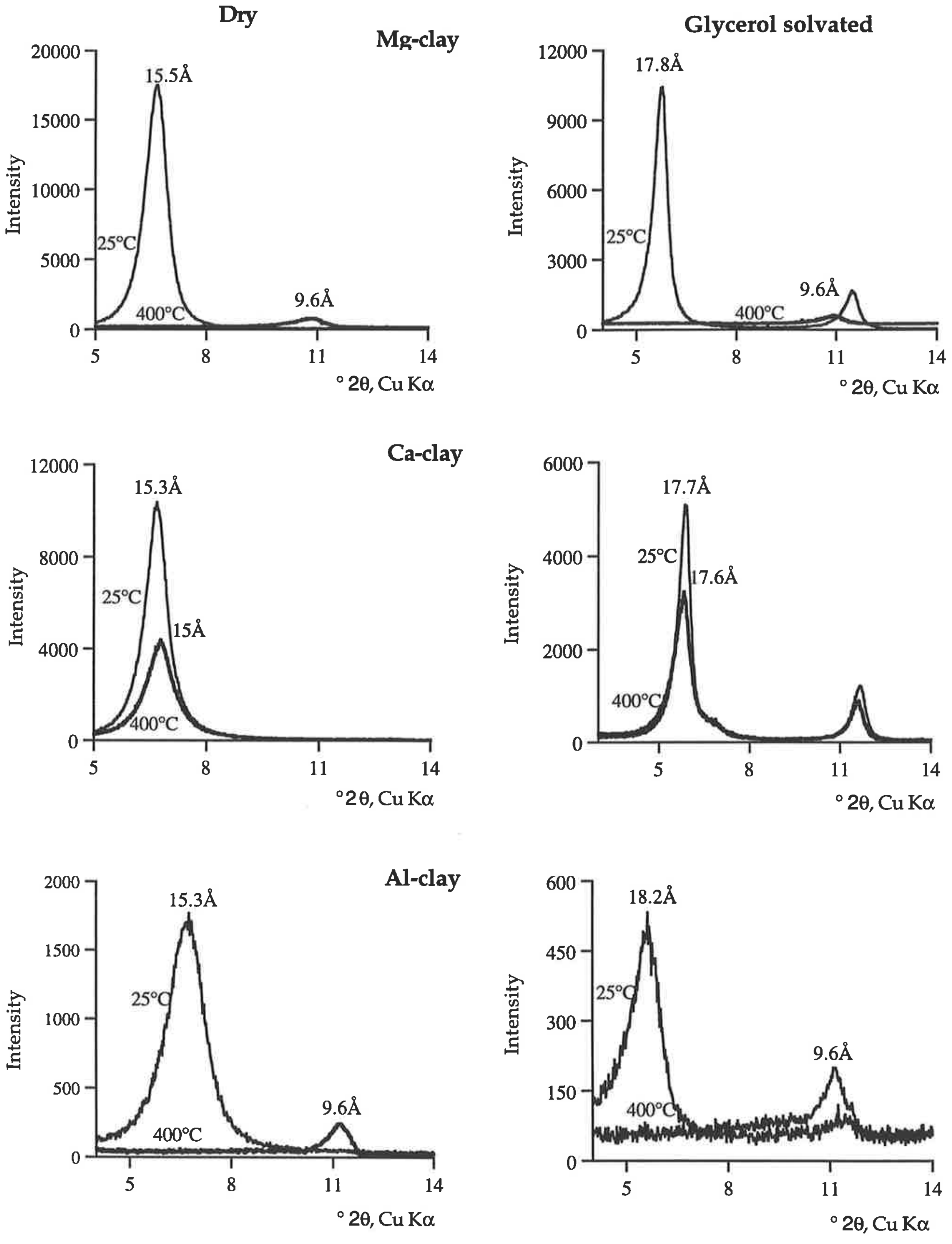


Fig. 5.2.2. XRD patterns of the Wyoming bentonite saturated with Mg, Ca and Al at different temperatures

5.2.2.2.3 Zeta potential and particle aggregation

Table 5.2.2 shows the changes in the ζ- potential as related to the temperature of heating. There is a decrease in the particle mobility (ζ- potential becomes less negative) when the temperature of heating increases from 25°C to 400°C. The decreases in ζ- potential suggest more aggregation of clay particles or the formation of large domains and correspond to reductions in charge. In general, the ζ- potential did not change as much as expected on heating because charge reduction was perhaps due to a decrease in the CEC caused by irreversible collapse of the layers upon heating.

Mean diameters of the clay particles saturated with Li, Na, K, Mg, Ca and Al (after mechanical dispersion) as measured by the sub micron particle sizer are given in Table 5.2.2. The diameters of particles are influenced by the nature of cations and heating temperature due to particles aggregation. Unheated clays (25°C) showed increases in their diameters in the following order: Li< Na< K< Mg< Ca<Al. However, on heating at 200°C, the particle size reflected the charge reduction. Thus Li, Mg and Al-clays, which showed greater charge reduction, had larger diameters compared to Na-, K- and Ca-clays. This indicates that stronger bonding and greater aggregation is responsible for the charge reduction.

5.2.3 Discussion

The data on swelling, dispersion, particle charge and particle size show the influence of the nature of bonding of cations to clay surfaces and indicate how this bonding is affected by thermal treatment. Even though the cations studied viz. Li. Na, K, Mg, Ca and Al are considered to form ionic bonds, any given hetero-nuclear bond formed in natural systems has a mixture of covalent and ionic character. The degree of covalency in a bond involving metal cations is characterised by a softness parameter derived from ionisation and ionic potentials (Misono *et al.* 1967). The Misono factor indicates the tendency of a metal cation to form a dative π-bond and the ability to enter into electron-acceptor and electron-donor (EAED) or Hard-Soft Acid-Base (HSAB) reactions. Based on these principles, Rengasamy and Sumner (1996) proposed the following factor:

$$\text{Flocculative power} = 100(I_Z / I_{Z+1})^2 \; Z^3 \qquad [5.2.1]$$

where I_Z and I_{Z+1} are z^{th} and $z+1^{th}$ ionization potentials, respectively, of the cation and Z is its valency. This factor determines the degree of covalent bonding between cations and clay surfaces and hence their flocculative power. This factor increases in the order: Li(0.5)< Na(1.2)< K(1.9)< Mg(28.2)< Ca(43.5)< Al(155.8).

The cationic effects on unheated clays follows the above order in terms of swelling (during glycerol solvation) and dispersion. As the degree of covalency in the bonding between cation and clay surface increases, hydration of cations becomes increasingly difficult. Thus, Li-, Na- and K-clays swell and disperse spontaneously whereas Mg-, Ca- and Al-clays only swell without any spontaneous dispersion. However, polar covalent bonds can be disrupted by mechanical agitation. The mechanically dispersed clay decreases as the degree of particle aggregation increases, as indicated by the mean diameter of the particles (Table 5.2.2).

Thermal treatment affects these bonds in different ways. The smaller cations (ionic radius <0.7Å) Li, Mg and Al apparently migrate to octahedral vacant sites (Calvet and Prost 1971), form covalent bonds after heating at 400°C and reduce the negative charge drastically. This process starts at 200°C for Li.

Covalent bonding and charge reduction in the clays prevents hydration and hence there is no swelling and reduced dispersion. At lower temperatures of heating (100-300°C) polar covalent bonding in Mg and Al-clays is increased, due to polarisation of atoms by thermal energy. Therefore, limited hydration results in swelling but not in spontaneous dispersion.

Larger cations (Na, K, Ca) apparently do not migrate to octahedral vacant sites on thermal treatment but there is an increase in the degree of covalency of the bonding between cations and clay surfaces due to thermal effects. Therefore, increase in the temperature of heating of these clays results in swelling with only limited hydration. Ca-clays have limited swelling even without heating; in the case of K, stronger fixation occurs at 400°C, without any swelling.

5.2.4 Conclusions

Swelling and dispersion of homoionic Wyoming bentonite after heating at various temperatures can be explained by the nature of bonding between clay particles and the cations. A degree of covalency exists in the bonds between the clay surface -O or -OH and the cations, resulting in a polar covalent bond. The degree of covalency increases, as indicated by the flocculative power, in the following order: Li< Na< K< Mg< Ca< Al. In unheated clays, the more ionic nature of the bonding in Li, Na and K-clays leads to extensive hydration and hence in swelling and spontaneous dispersion. Increased covalency and polar covalent bonding in Mg, Ca and Al-clays result in limited hydration and therefore, these clays only swell and do not disperse spontaneously.

Upon thermal treatment, the bonding characteristics change according to the size of the cations. Smaller cations (ionic radius < 0.7Å) Li, Mg and Al apparently migrate to the octahedral vacant sites and form covalent bonds after heating at 400°C. This results in severe charge reductions and the cation becomes non-exchangeable. This process occurred even at 200°C for Li-clays. After heating at 400°C, these clays neither swell nor disperse spontaneously.

Larger cations Na, K and Ca apparently do not migrate to the octahedral vacant sites on thermal treatment. However, on heating up to 400°C thermal energy leads to a higher degree of covalency in the polar covalent bond. The interlayer cations are still exchangeable at a reduced level resulting in limited hydration. Therefore, these clays swell but do not disperse spontaneously. However, K-clays after heating at 400°C do not swell, but interlayer K^+ remains exchangeable. The data on d_{001} spacing, dispersible clay, particle charge, ζ- potential, exchangeable cations and particle size confirm these conclusions.

5.3 Slaking and dispersion of different cationic forms of illite and kaolinite as influenced by heating

In the previous section (5.2) the results on a thermally treated smectite were presented. Swelling of a smectite can be inferred from XRD patterns. However, in the case of illite and kaolinite, XRD patterns cannot reveal the swelling properties. Therefore, slaking characteristics of these clays were used to infer the swelling phenomena. In this section (5.3) the results on Li, Na, K, Mg and Ca saturated kaolinite and illite are presented.

5.3.1 Materials and Methods

5.3.1.1 *Characteristics of Clays*

The samples of Grundite illite (<2 μm) contained traces of quartz and about 5% kaolinite, as shown by X-ray diffraction. The <2 μm fractions of Georgia kaolinite contained about 2% smectite. Samples of Georgia kaolinite and Grundite illite were pre-treated to remove organic matter, free iron oxides and amorphous materials (Jackson 1974). The clays were fractionated by allowing larger particles to settle out of suspension and then collecting the <2 μm fraction. The clays which were homoionic in Li, Na, K, Mg, and Ca were prepared as described in section 5.2.1.1.

5.3.1.2 *Other measurements*

Clay preparation, pH, EC, exchangeable cations and cation exchange capacity, X-ray diffraction studies, dispersible clay, zeta potential and clay particle size were determined as described in detail in section 5.2.2.

5.3.1.3 *Slaking test*

Samples of kaolinite and illite which had been heated at various temperatures were used. Clay flakes were remoulded after wetting and made into small aggregates of diameter 5 mm and dried at 40°C for 48 hours. 0.5g of these aggregates were placed in distilled water contained in a 50ml glass vials. After 24 hours, the percentage of < 2mm material was estimated after wet sieving.

5.3.2 Results and discussion

5.3.2.1 Chemical properties

The effect of heating on the chemical properties of Georgia kaolinite and Grundite illite saturated with Li, Na, K, Mg and Ca is shown in Tables 5.3.1, 2, 3 and 4. In general, pH values of the 1:10 suspension in distilled water depended upon the nature of cation. With increasing positive charge of the cation and with increasing ionic radius the proton release from cation-water interaction decreased. Among monovalent cationic clays, Na-kaolinites had higher pH values than Li and K-kaolinites whereas, the pH values of divalent cationic clays were almost similar (Table 5.3.1). In thermal treatment, the pH increased in all cationic clays, suggesting that the cations are strongly bonded to the clay surface because of cation interaction with silanol or aluminol groups; and reducing the release of protons from -OH groups. This is clearly shown in the decreased amounts of cations dissociated in water with increase in temperature of heating (Tables 5.3.1 and 5.3.3). Electrical conductivity (EC) values also reflected the same trend. These results were similar to that obtained with a smectite clay (see section 5.2). Even though the trends were similar in both kaolinite and illite samples, illitic samples always had a lower pH. Because of higher negative charge than kaolinite, illitic samples released more protons in water. Cations, particularly sodium, dissociated more from illite than kaolinite, reflecting the weaker bonding between cations and illite surfaces.

Table 5.3.1. The effect of heating on pH, EC and the concentration of the saturating cation on 1:10 clay-water extract of homoionic Georgia kaolinite

Cation (M-clay)	Temperature of heating °C	pH	EC µS cm^{-1}	Dissociation cation mg L^{-1}
Li (0.68)[A]				
	25	6.47	14	10
	200	6.59	4	3
	400	6.82	3	2
Na (0.97)[A]				
	25	7.22	61	30
	200	7.41	38	19
	400	7.61	19	10
K (1.33)[A]				
	25	6.11	9	6
	200	6.39	5	3
	400	6.81	4	2
Mg (0.66)[A]				
	25	6.37	6	4
	200	6.45	4	2
	400	6.66	4	2
Ca (0.99)[A]				
	25	6.11	6	5
	200	6.23	4	3
	400	6.69	4	2

[A] Crystal ionic radii (Å)

Thermal treatment of cationic kaolinite and illite has reduced the total charge and the exchangeable cations as the temperature of heating increased (Tables 5.3.2 and 5.3.4) and the extent of this reduction depended on the nature of cation and the temperature of heating. Thus, in Li-kaolinite, the charge reduced from 7 to 2 $cmol_c\ kg^{-1}$ after heating at 400°C. The reduction in Na- and K-kaolinites were similar to Li-clays. Among divalent cations, the charge reduction in Mg-clays was similar to monovalent-kaolinites, with same charge reduction after heating at 400°C whereas, the Ca-kaolinites had a lower charge reduction from 6 to 4 cmol$_c$ kg^{-1}. As the cations are strongly bonded to surface -O or -OH, they become difficult to exchange with NH_4^+. When the cationic bonding is stronger, the total charge estimated by NH_4^+ exchange is reduced (Table 5.3.2).

Table 5.3.2. The effect of heating on exchangeable cation and total negative charge of homoionic Georgia kaolinite

Cation type	Temperature of heating °C	Exchangeable cation						CEC
		Li	Na	K	Mg	Ca	Al	
		<———			cmol$_c$ kg^{-1}			———>
Li								
	25	5	1.2	1	0.2	0.5	1	7
	200	2.2	1.2	0.8	0.3	0.5	1	4
	400	0.3	1.5	0	0.1	0.4	1.7	1
Na								
	25	0	6.9	1.8	0.6	0.4	0.3	7
	200	0	5	1.2	0.8	0.3	0.7	5
	400	0	4.3	0.2	0.8	0	0.7	3
K								
	25	0	1.6	6	0.4	0.2	0.8	7
	200	0	1.2	3.4	0.4	0	1	5
	400	0	1.1	2.4	0.5	0	1	2
Mg								
	25	0	1.6	1	5.8	0.4	0.2	6
	400	0	1.4	0.2	2.4	0.2	0.8	2
Ca								
	25	0	1.6	0	0.2	6	0.2	6
	200	0	1.7	1	0.2	3.8	0.3	5
	400	0	1.8	1.5	0.3	1.8	0.6	4

A similar trend was observed in illite samples (Table 5.3.4). But the percentage of charge reduction in illite was slightly less than in kaolinite. Generally, on heating up to 400°C the charge was reduced from 26 to 15 $\mathrm{cmol_c\ kg^{-1}}$.

5.3.2.2 *Physical properties*

5.3.2.2.1 X-ray diffraction

The variation of XRD patterns of Li, Na, K, Mg and Ca- kaolinite and -illite before and after heating were studied. The d_{001} spacing of all treatments was the same (7.1Å for kaolinite and 10.1Å for illite); indicating that heating did not affect the integrity of structure of kaolinite and illite up to 400°C. In general the intensity of the XRD peaks of the clays reduced as the temperature of heating increased.

5.3.2.2.2 Slaking

Because XRD measurements could not reveal the swelling of kaolinite and illite samples, slaking test was done to see the effect of hydration on swelling of these samples. Even though entrapped air can also cause slaking of remoulded samples, hydration reactions have been considered to be the major cause (Rengasamy and Olsson 1991). All freeze-dried kaolinites and illites, irrespective of cation type, slaked in water, illite samples slaking more than kaolinite samples (Tables 5.3.5 and 5.3.6). After heating, the slaking progressively reduced as the temperature of heating increased. After heating at 400°C, slaking of kaolinite samples was very low.

Table 5.3.3. The effect of heating on pH, EC and the concentration of the saturating cation in 1:10 clay-water extract of homoionic Grundite iliite

Cation (M-clay)	Temperature of heating °C	pH	EC µS cm^{-1}	Dissociation cation mg L^{-1}
Li				
	25	5.84	16	12
	200	6.22	8	5
	400	6.37	7	3
Na				
	25	5.21	52	33
	200	5.72	42	27
	400	5.83	40	24
K				
	25	5.52	17	13
	200	6.06	9	6
	400	6.58	7	4
Mg				
	25	5.84	9	7
	200	6.21	7	5
	400	6.43	6	4
Ca				
	25	5.03	17	12
	200	5.75	12	9
	400	6.98	11	8

5.3.2.2.3 Dispersion

The results of spontaneous dispersion are presented in Tables 5.3.5 and 5.3.6. All the freeze-dried monovalent cationic clays spontaneously dispersed, the extent of dispersion being in the order Li> Na> K. Mg- and Ca-kaolinites and Ca-illite did not disperse spontaneously whereas Mg-illite dispersed slightly (3%). This rare observation of spontaneous dispersion of Mg-illite is in consistent with the observation of Emerson and Chi (1977). After heating at 100°C and above Ca- and Mg clays did not disperse spontaneously. Similarly, Li- and K-kaolinite didnot disperse after heating at 100°C, whereas Na-kaolinite didnot disperse only after heating at 300°C. In the case of illite Li, Na and K-clays had to be heated at 200°C to prevent spontaneous dispersion.

Table 5.3.4. The effect of heating on exchangeable cation and total negative charge of homoionic Grundite illite

Cation (M-clay)	Temperature of heating °C	Exchangeable cation						CEC
		Li	Na	K	Mg	Ca	Al	
		<— cmol$_c$ kg^{-1} —>						
Li								
	25	23.5	3.4	2	0.2	0.5	0.4	25
	200	15.3	3.8	3	0.4	0.5	0.7	19
	400	9	4.1	5.1	0.5	0.5	0.8	15
Na								
	25	0	23.2	2	1.8	3	1	26
	200	0	21.2	3	1.8	2	1	24
	400	0	17.4	7	1.6	2	1	23
K								
	25	0	3.8	24.5	0.2	0.2	0.3	24
	200	0	4	21	0.3	0.3	0.4	21
	400	0	4.4	19	0.5	0.4	0.7	20
Mg								
	25	0	2	3	22.5	0.3	0.2	23
	200	0	3	4	17.3	0.3	0.4	20
	400	0	3.5	7.7	11.5	0.5	0.8	19
Ca								
	25	0	2	3	0.6	23.2	0.2	24
	200	0	2	4	0.6	20	0.4	22
	400	0	3	7	0.6	15	0.4	21

The percentage of mechanically dispersed clay, remaining in suspension after shaking overnight, as influenced by heating is given for kaolinite saturated with Li, K, Na, Mg and Ca in Table 5.3.5 and for illite samples in Table 5.3.6. When the temperature was increased from 25°C to 400°C, the dispersion of Li-kaolinite decreased from 68 to 1 percent, Na-kaolinite from 85 to 2 percent and K-kaolinite from 39 to 6 percent. Mechanical dispersion of freeze-dried kaolinite samples saturated with divalent cations was lower than for clays saturated with monovalent cations (Table 5.3.5). The percentage of dispersed clay from Mg-kaolinite decreased from 23 to 6 percent and from Ca-kaolinite from 32 to 5 percent, when the heating temperature increased from 25°C to 400°C. Here again, the illite samples behaved similarly (Table 5.3.6). However, the percentage of mechanical dispersion of illite samples after heating was always higher compared to kaolinite samples.

5.3.2.2.4 Zeta potential and particle aggregation

Tables 5.3.5 and 5.3.6 show the changes in the ζ- potential of Li, K, Na, Mg and Ca-clays as related to the temperature of heating. There is a decrease in the particle mobility (less negative) when the temperature of heating increases from 25°C to 400°C. The ζ- potential decreases slightly as the valency of cations increases, indicating more aggregation of clay particles, formation of large domains and reduction in charge due to cationic bonding. In general, the ζ- potential did not change much by heating even though charge reduction and particle aggregation were comparatively greater. This is because the electrophoretic mobility measurements were made only on dispersed clay particles which only partially reflect particle aggregation.

Table 5.3.5. The effect of heating on swelling, dispersion, ζ-potential and mean particle diameter (MD) of homoionic Georgia kaolinite

Cation	Temperature	Slaking (%)	Dispersion (%)		ζ-potential	MD
type	of heating °C	<2mm	Spontaneous	mechanical	-mV	µm
Li						
	25	48	31	68	39.1	0.52
	100	nd[A]	Nil	23	36.0	0.82
	200	26	Nil	15	35.5	0.97
	300	nd	Nil	6	34.4	1.35
	400	3	Nil	1	34.2	2.21
Na						
	25	39	52	65	43.7	0.16
	100	nd	31	38	39.2	0.19
	200	25	16	24	38.1	0.24
	300	nd	Nil	4	37.1	0.38
	400	2	Nil	2	36.0	0.49
K						
	25	38	18	39	37.7	0.41
	100	nd	Nil	17	37.2	0.48
	200	23	Nil	10	36.7	0.53
	300	nd	Nil	9	36.2	0.66
	400	5	Nil	6	35.8	0.77
Mg						
	25	41	Nil	23	36.4	0.59
	100	nd	Nil	9	35.1	0.63
	200	21	Nil	8	34.9	0.86
	300	nd	Nil	8	33.2	1.18
	400	2	Nil	7	34.1	1.41
Ca						
	25	35	Nil	32	35.8	0.82
	100	nd	Nil	21	35.4	0.97
	200	15	Nil	6	33.5	1.05
	300	nd	Nil	5	33.2	1.23
	400	1	Nil	5	32.6	1.55

[A] Not determined

Mean diameters of the clay particles saturated with Li, Na, K, Mg and Ca as measured by a sub-micron particle sizer are given in Tables 5.3.5 and 5.3.6. The diameters of particles are influenced by the nature of cations. However, on heating at 200°C, the particle size reflected the charge reduction. Thus Li and Mg-kaolinites which had higher charge reduction, had higher diameters compared to Na-, K- and Ca-kaolintes. In comparison, K- and Mg-illite had higher mean diameter compared to Li, Na and Ca-samples. This indicates that stronger bonding and higher aggregation is responsible for the charge reduction.

In the present study, heating of kaolinite and illite samples, irrespective of cation type resulted in the loss of CEC but not as drastic as observed in Li-, Mg- and Al-smectite (section 5.2). The maximum reduction of CEC was <50% in kaolinite samples and <34% in illite samples. This reduction in CEC could be due to either increased polar covalency or covalent bonding. While in smectites, XRD information about interlayer swelling can reveal the hydration effects (ie. covalency effects), it is not possible to get this information for kaolinites and illites. However, slaking results may indicate the extent of hydration in these samples.

Increasing the temperature of heating resulted in reduced slaking of both kaolinite and illite samples indicating progressive increase in covalent bonding. Whether this covalent bonding of cations occurs on kaolinite and illite surfaces or in the vacant sites (isomorphous substitution sites) in the inner structure of these clays is not clear. Kaolinites have very low CEC, mostly arising from edge surfaces. The results presented here can only indicate that covalent bonding between cations and clay are formed thereby reducing cation hydration, as evidenced by reduced slaking.

Table 5.3.6. The effect of heating on swelling, dispersion, ζ-potential and mean particle diameter (MD) of homoionic Grundite illite

Cation (M-clay)	Temperature of heating°C	Slaking (%) <2mm	Dispersion (%) Spontaneous	Dispersion (%) mechanical	ζ-potential -mV	MD µm
Li						
	25	66	65	89	38.4	0.35
	100	nd[A]	28	53	36.9	0.38
	200	35	Nil	6	36.7	0.43
	300	nd	Nil	3	36.4	0.46
	400	13	Nil	0	36.2	0.56
Na						
	25	62	53	75	43.9	0.17
	100	nd	21	41	42.8	0.29
	200	46	Nil	13	42.1	0.33
	300	nd	Nil	5	41.1	0.44
	400	16	Nil	2	39.9	0.51
K						
	25	50	23	44	39.3	0.44
	100	nd	8	20	37.9	0.53
	200	36	Nil	17	37.6	0.71
	300	nd	Nil	15	37.4	0.95
	400	15	Nil	11	36.6	1.51
Mg						
	25	60	3	41	34.4	0.38
	100	nd	Nil	15	33.9	0.64
	200	44	Nil	7	33.2	0.97
	300	nd	Nil	5	32.8	1.12
	400	14	Nil	5	31.3	1.35
Ca						
	25	52	Nil	39	32.1	0.58
	100	nd	Nil	22	31.4	0.73
	200	38	Nil	18	30.2	0.88
	300	nd	Nil	17	29.6	1.12
	400	12	Nil	14	29.2	1.28

[A] Not determined

The results of spontaneous dispersion, mechanical dispersion and particle size measurements are all consistent with the hypothesis proposed on the nature of bonding between cations and clay surfaces. Thus in Li-, K- and Na-clays, heating up to 100°C reduces the ionicity of bonding and hence reduces spontaneous dispersion. Divalent ions form polar covalent bonds and hence these clays hydrate and slake, but do not disperse spontaneously. The only exception is freeze-dried Mg-illite which was observed to spontaneously disperse, though to a less degree (ie. 3%). On heating, the polar covalency of monovalent clays is increased and spontaneous dispersion stops completely. In Li-, Na- and K- clays, after heating at 200°C and above the spontaneous dispersion is prevented but for Na-kaolinite, heating up to 300°C is needed. The results of mechanical dispersion measurements after heating also reflect the increased covalent bonding between clays and cations; more covalent bonding produces less mechanical dispersion. Illite samples dispersed more compared to kaolinite, indicating illite-cation bonding is less covalent. Further, the increase in particle size after heating also indicates the aggregation of clay particles by covalent bonding, without hydration affecting the separation of clay particles.

5.3.3 Conclusions

Slaking and dispersion of Li, Na, K, Mg and Ca-kaolinite and illite after thermal treatment depended on both temperature of heating and the type of cation. Heating processes affect the nature of bonding between cations and clay surfaces by accelerating electron-acceptor and electron-donor (EAED) interactions and increase the polar covalency and covalency with the simultaneous decrease in ionicity.

In monovalent clays, progressive heating up to 200-300°C, reduces the ionicity of cation bonding and hence the spontaneous dispersion. Above these temperatures the bonding becomes increasingly polar covalent or covalent when spontaneous dispersion is completely prevented. In divalent clays where polar covalency is dominant, slaking due to hydration of cations occurs. On heating covalent bonding increases and hydration is reduced thereby reducing slaking. Covalent bonding is more in smaller cationic (Li and Mg) clays than in larger cationic (Na, K and Ca) clays. In general, covalent bonding is lower in illites compared to kaolinites.

5.4 Behaviour of alkaline sodic soils after heating

5.4.1 Introduction

Studies on soil heating at temperatures between 100 - 600°C as related to bush fire and stubble burning have concentrated on the enhanced release and availability of nutrients like nitrogen and phosphorus (eg. Chambers and Attiwill 1994), changes in organic carbon and microbial activity (eg. Blank *et al.* 1994), increased pH (eg. Bauhus *et al.* 1993) and reduced soil-borne pathogens due to the release of anti-fungal compounds (Gamliel and Stapleton 1993).

Shear strengths of foundation soils have been found to change significantly even by heating up to 90°C (Kuntiwattanakul *et al.* 1995). Clay weakening in foundation soils by the reduction of shear strength and elastic modulus of clay materials at higher temperatures has been reported by Mitchell (1964) and Murayama (1969). High temperatures induced lower shear strength, lower stiffness and higher volume change during shear on over-consolidated Pontida silty clay (Huckel and Baldi 1990). However, Housten *et al.* (1985) reported an increase in shear strength of illite and smectite- rich clays with increasing temperature. This apparent lack of agreement stems from the deficit in our knowledge without any systematic study relating changes in clay chemistry to increasing temperatures.

The studies, reported in sections 5.2 and 5.3, on heating various cationic forms of pure smectite, illite and kaolinite up to 400°C have shown that swelling and dispersion of these clays was reduced significantly after thermal treatments and the extent depended on the type of cation involved and the temperature of heating. The aim of the experiment in this section was to find out the effects of thermal treatment on two alkaline sodic soils containing a mixture of kaolinite, illite, RIM (randomly interstratified minerals) and quartz in their clay fractions.

5.4.2 Materials and methods

5.4.2.1 Soils

The soils used in the present study were located at Bordertown and Yelanna in South Australia. The soils were classified as Typic Natrixeralf, clayey. mixed (calcareous), thermic (Soil Survey Staff 1975). The soil samples were collected from sub-soils (20-40 cm) which were sodic.

5.4.2.2 Sample preparation

The soil samples were air-dried and sieved to collect aggregates of 2-4 mm size. Samples of the soil aggregates were heated for 6hr at 100, 200, 300 and 400°C in a muffle furnace. The aggregates were cooled in a desiccator and placed in a sealed glass container kept at 25°C.

5.4.2.3 Soil chemical analyses

The pH and electrical conductivity (EC) were determined using 1:5 water extracts. The suspension was centrifuged and the supernatant was used to determine, Na^+, K^+, Ca^{2+}, and Mg^{2+}. The exchangeable cation (Na^+, K^+, Mg^{2+} and Ca^{2+}) and cation exchange capasity (CEC) were determined by alcoholic 1 M ammonium chloride at pH 8.5, as described by Rayment and Higginson (1992). Organic carbon was measured by using Walkley and Black's rapid titration procedure (Allison *et al.* 1965). A volumetric calcimeter method was used for determination of carbonate in soils (Allison and Moodie 1965).

5.4.2.4 *Slaking measurement*

Samples of aggregates (2-4 mm) which were air-dried and heated at various temperatures were used. 20 g of these aggregates were placed in distilled water contained in 100 ml glass vials. After 24 hours, the percentage of <250 µm fractions was estimated by wet sieving.

5.4.2.5 *Saturated hydraulic conductivity measurements*

Duplicate 100 g samples of the aggregates (2-4 mm) were packed in perspex permeameters (5cm diameter, 18 cm high) to form a 7 cm high column. The aggregates were retained using a piece of nylon mesh supported by fine wire gauze at the bottom of the column, and a piece of filter paper (No. 42) was also placed on the soil surface to protect it from splash. All columns were slowly wet from below by capillary rise by placing the permeameter into a beaker of R.O. water (reverse osmosis water). The saturated hydraulic conductivity was determined by maintaining a constant head of water above the soil surface and water percolation was measured (Greene *et al.* 1988).

5.4.2.6 *Other measurments*

Clay mineralogy of the soil clays was determined as described in section 4.3.2. Spontaneously and mechanically dispersed clays were measured with the same procedure as explained in section 5.2.1.4 using 20 g of soil aggregates.

5.4.3 Results and discussion

5.4.3.1 *Characteristics of soils used*

Bordertown and Yelanna soils, chosen for this study, are alkaline with a pH (soil: water, 1:5) of 9.2 and 9.6 respectively as given in Table 5.4.1. These soils, in spite of having 6.2 and 4% $CaCO_3$ respectively, are sodic with low EC

(0.06 and 0.17dS m^{-1}) and high SAR (8.4 and 12.1). The clay mineralogy of the soils is a mixture of kaolinite, illite and randomly interstratified minerals (RIM). The Bordertown soil sample had higher CEC than Yelanna soil which may be due to more RIM (Table 5.4.1).

5.4.3.2 Chemical properties

Table 5.4.2 shows the pH values of the soils changed after thermal treatment. The pH decreased from 9.2 to 7.0 and from 9.6 to 8.2 for Bordertown and Yelanna soils respectively as the temperature of heating increased from air-dried to 400°C. The changes in pH due to the thermal treatment varied with the temperature of heating. The reasons for this reduction could be due to decomposition of carbonates such as $NaHCO_3$ and Na_2CO_3. After sodium carbonates have decomposed, the pH is lowered to 8.0. However, on heating up to 400°C, calcium carbonates also decompose and the pH of the heated soil is lowered to 7.0. In Yelanna soil $CaCO_3$ is not completely decomposed on thermal treatment and hence, the pH is not lowered below 8.2. The fixation of cations could also cause a reduction of pH when measured after rehydration. Electrical conductivity (EC) decreased from 1.7 and 1.3 dS m^{-1} to 0.3 and 0.2 dS m^{-1} for Bordertown and Yelanna soils, respectively, as the temperature of heating increased to 400°C. Reduction in the amounts of cations dissociated in water shows the same trend (Table 5.4.1). Thermal treatment of the soils reduced the total negative charge (CEC) and the amount of soluble cations as the temperature of heating increased. However, the extent of this reduction depended on the nature of soil minerals and the temperature of heating. Thus, in Bordertown soil, the CEC reduced after heating at 400°C from 22.6 to 9.3 $cmol_c\ kg^{-1}$ (60% reduction). A similar trend in CEC reduction for Yelanna soil was observed but the percentage of charge reduction was slightly less than Bordertown soil (50%). Following the charge reduction, the ESP of the soils decreased drastically as the temperature of heating increased (Table 5.4.2). It is

Table 5.4.1. Properties of Natrixeralfs used

Soil (20-40cm)	$pH_{1:5}$	$EC_{1:5}$ dS m^{-1}	$SAR_{1:5}$	CEC cmol$_c$ kg^{-1}	Organic Carbon %	$CaCO_3$ %	Clay Mineralogy^A %
Bordertown	9.2	0.06	8.4	22.6	0.29	6.2	K(30), I(40), Q(10), RIM(20)
Yelanna	9.6	0.17	12.1	18.2	0.58	4.0	K(37), I(40), Q(13) RIM(10)

^{A} Measured by X-ray diffractrometry and X-ray fluorescence. I= illite, K= kaolinte, Q= quartz, RIM= randomly interstratified minerals.

Table 5.4.2. Changes in soil chemical properties after thermal treatment

Soil	Temperature of heating °C	$pH_{1:5}$	$EC_{1:5}$ dS m^{-1}	CEC Cmol$_c$ kg^{-1}	Organic carbon %	Soluble cations				ESP
						Na	K	Ca	Mg	
						mmol$_c$ L^{-1}				
Bordertown										
	Air dried	9.2	1.7	22.6	0.29	2.9	1.2	5.6	6.9	16.2
	100	8.6	1.2	21.0	0.28	2.3	0.9	4.2	4.2	12.4
	200	8.0	1.1	16.8	0.43	2.1	1.2	4.1	4.1	8.1
	300	7.6	0.4	14.2	0.09	0.9	1.1	2.0	1.3	2.4
	400	7.0	0.3	9.3	0.01	0.2	1.0	1.1	1.0	1.0
Yelanna										
	Air dried	9.6	1.3	12.1	0.58	4.1	0.9	3.8	3.7	24.5
	100	9.5	1.2	11.9	0.58	3.9	0.9	3.8	3.4	19.6
	200	9.0	0.8	10.2	0.71	1.1	1.0	2.9	2.2	8.4
	300	8.9	0.3	9.8	0.82	0.6	0.8	0.6	1.2	1.4
	400	8.2	0.2	6.0	0.26	0.4	0.6	0.2	1.1	0.8

obvious, when the temperature of heating increased, the percentage of organic carbon in the soils reduced, because of decomposition.

5.4.3.3 *Physical properties*

Clay dispersion, either spontaneously or mechanically, reduced sharply as the heating increased from air-dried to 400°C (Table 5.4.3). In both soils no spontaneous dispersion occurred after heating at 300°C and 400°C. The trend for mechanical dispersion for the soils were similar at different temperatures. The slaking of soil samples progressively reduced as the temperature of heating increased and it was completely prevented at 400°C.

Saturated hydraulic conductivity (HC) increased more than 100 times after heating at 400°C (Table 5.4.3). This is similar to the reverse effect on mechanically dispersed clay. However, the drastic increase in HC with heating could be also due to particle aggregation, in addition to the prevention of swelling and dispersed clay blocking the pores.

Table 5.4.3. Changes in soil physical properties after thermal treatment

Soil	Temperature of heating °C	Clay dispersion[A] Spontaneous	Clay dispersion[A] Mechanical	Slaking % (< 250 μm)	H.C[B] cm hr^{-1}
Bordertown					
	Air dried	20	80	40	0.1
	100	12	80	36	0.6
	200	1	42	15	20.2
	300	Nil	16	12	30.8
	400	Nil	2	Nil	40.6
Yelanna					
	Air dried	26	76	32	0.4
	100	14	70	32	0.8
	200	4	60	20	16.2
	300	Nil	10	8	20.4
	400	Nil	2	Nil	46.2

[A] Percentage of total clay, [B] Hydraulic conductivity.

5.4.4 Conclusions

In sections 5.2 and 5.3, it was shown that types of bonding between clay surfaces and cations, *viz.* covalent, polar covalent and ionic, control hydration and hence swelling and dispersion properties of soil clays. The results obtained for soil clays heated up to 400°C are consistent with the results of pure clay minerals. Both sodic soils, after heating up to 200°C, do not disperse spontaneously, but on mechanical shaking clay dispersion still occurs. Similarly, aggregates heated up to 300°C slake. This indicates that cations, particularly exchangeable sodium ions are bound to the clay surfaces by polar covalent bond. Limited hydration of these cations lead to slaking as it was observed for illite and kaolinite minerals. After heating at 400°C, the cations formed covalent bonds with clay surfaces and hence no rehydration was possible. As a result, there was no slaking and dispersion. This was consistent with the reduction in CEC, ESP (exchangeable sodium percentage) and soluble cations.

5.5 Infrared spectra of heated clays

5.5.1 Introduction

Infrared spectroscopy can be a useful tool for studying the migration of interlayer cations into the structure of clays and the bonding of water molecules on clay surfaces after thermal treatment (Tettenhorst 1962; Calvet and Prost 1971; Bishop *et al.* 1994). The infrared absorption bands of phyllosilicates can generally be divided into three groups: 1) Hydroxyl stretching (between 3750 and 3400 cm^{-1}) and bending vibrations (between 950 and 600 cm^{-1}). 2) Si-O and Al-O-H stretching and bending lattice vibrations (between 1200 and 700 cm^{-1}), and 3) the bands due to adsorbed species (Farmer 1974; Kodama 1985; Nguyen *et al.* 1991). Infrared absorptions due to water in smectites were assigned by Russell and Farmer (1964) as follows: 3415 cm^{-1} to the H-O-H asymmetric stretching vibration of H_2O readily lost upon heating, 3610 cm^{-1} to the H-O-H asymmetric stretching vibration of firmly bonded H_2O, and 1630-1640 cm^{-1} to the H-O-H bending vibration. The lattice-bending mode absorbs between 700 and 950 cm^{-1} and shows the cation composition in the octahedral sheet (Farmer 1974).

Prost *et al.* (1989) found that all the kaolinite samples heated at 600°K had very similar IR spectra. Srasra *et al.* (1994) found that illite is less thermally stable than the smectites.

In sections 5.2 and 5.3, it was shown that swelling and dispersion of homoionic clays depended on the net particle charge and the nature of bonding between clay particles and the cations. It was also demonstrated that thermal treatment affects this bonding in different ways. The smaller cations (ionic radius <0.7Å) Li, Mg and Al after heating at 400°C formed covalent bonds probably due to migration to octahedral vacant sites and resulted in reducing the negative charge drastically. The larger cations (ionic radius ≥ 0.9Å) Na, K and Ca ions after heating up to 400°C still remained exchangeable and formed polar covalent bonds, presumably without migration of these ions to octahedral vacant sites. Therefore, infrared studies were carried out to understand the mechanism of charge reduction due to heating and to get direct evidence on the possible migration of cations into clay structure in the formation of covalent bonding.

5.5.2 Materials and methods

Characteristics of Wyoming bentonite, Georgia kaolinite and Grundite illite and preparation of the clays are explained in detail in sections 5.2.1.1 and 5.3.1.1. Diffuse reflectance infrared fourier transform (DRIFT) method as described by Nguyen *et al.* (1991) was used for infrared (IR) analysis. Nguyen *et al.* (1991) showed DRIFT can be useful for rapid identification and characterization of the clays saturated with different cations in terms of aqueous and heated systems. IR spectra were recorded for 400 cm^{-1} scans from 4000 to 500 cm^{-1} at 4 cm^{-1} intervals using a Digilab FTS 15E/90 spectrometer. The instrument contained a Model 396A Michelson rapid-scanning interferometer with a mirror velocity of 0.33 $cm\ s^{-1}$, a KBr beamsplitter, a high intensity water-cooled ceramic globar source and a deuterated triflycine-sulfate detector with a CsI window. The data files containing the spectral data points were translated into Spectra-Calc^{TM}, (Galactic, New Hampshire, format) for display.

5.5.3 Results and discussion

The migration of cations into the vacant octahedral sites is shown by the changes in the adsorption spectra either in the OH-stretching or OH-bending regions. When no migration occurs, one does not observe any change in the absorption spectra either in the OH-stretching or bending regions (Calvet and Prost 1971). In the following paragraphs, the results which are significant to OH- stretching or OH-bending regions in the infrared spectra of Li-, Mg-, Al-, Na-, K- and Ca- clays are discussed. Other frequencies are not discussed because they are not relevant to the migration of cations into the structure.

It is possible that by heating up to 400°C the small cations like Li, Mg, and Al migrate to octahedral vacant sites and form covalent bonds by either of the three different mechanisms: (1) replacing H^+ (proton) from Al-OH and forming Al-O-Li; (2) replacing Mg^{2+} or Fe^{2+} isomorphously substituted in the clay structure and forming Li-Al-OH or (3) the small cations move into the hexagonal hole and form covalent bond with surface -O or -OH(fixation). The changes in Al-OH stretching and bending region and Si-O stretching bands as well, may reflect any of these mechanisms.

5.5.3.1 Li-clays

IR spectra of Li-smectite samples heated at different temperatures are shown in Figure 5.5.1. The Al-Li-OH stretch was observed at 3695 cm^{-1} after heating to 400°C. This peak attributed to hydroxyl groups not observed at 25°C. There is a change in the perturbation of some OH groups was related to the cation migration into octahedral sites in the structure as also observed by Calvet and Prost (1971). The lattice Al,Mg-OH shifted from 3635 to 3640 cm^{-1} by heating to 400°C. The shifts were larger (30 and 12 cm^{-1}) for H_2O bending, being from 1639 to 1627 cm^{-1}. New peaks at 807 and 1727 cm^{-1} were observed at 400°C. As the temperature of heating increased from 25°C to 400°C, the frequency of the Si-O-Si stretch increased from 1250 to 1270 cm^{-1}, but the intensity decreased. The peak at 1110 cm^{-1} shifted upward to 1118 cm^{-1} with the appearance of another peak at 1185 cm^{-1}. The Al-OH bending region of Li-samples after heating at 400°C, shifted upward from 928, 888, 849 cm^{-1} to 934,

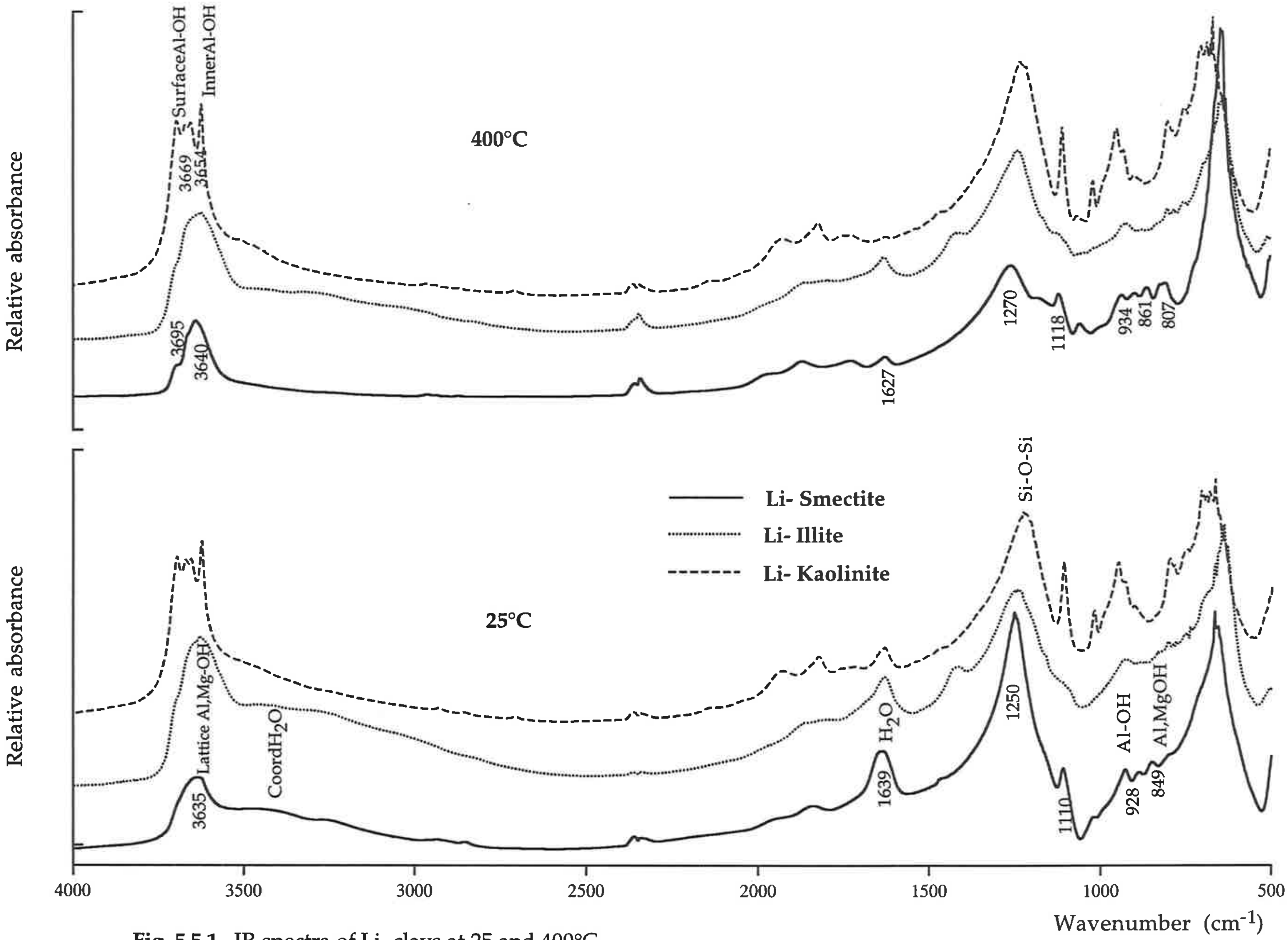


Fig. 5.5.1. IR spectra of Li- clays at 25 and 400°C

896 and 861cm^{-1}, respectively. These indicate changes in octahedral structure due to change in electron density (repulsion by cation) or splitting of the symmetrical degenerate frequencies as explained by Farmer (1974). These changes are consistent with the results reported by Calvet and Prost (1971) and confirm the migration of Li ions to the octahedral vacant sites in the smectite, viz. Wyoming bentonite, used in this study.

The H_2O bending mode for water adsorbed by the Li-kaolinite changed after heating to 400°C from 1631 cm^{-1} to 1625 cm^{-1} (Figure 5.5.1) obviously due to a stronger H-bond during dehydration. No significant change was observed for OH-stretching vibrations for Li-illite but the intensity of the peaks reduced as the temperature of heating increased from 25 to 400°C (Figure 5.5.1).

5.5.3.2 Mg-clays

The infrared spectra of the Mg-smectite samples before and after heating are presented in Figure 5.5.2. The 1638 cm^{-1} peak (H_2O bend) shifted to 1629 cm^{-1}at the higher temparature, corresponding to a shift of about 8. A new peak at 1734 cm^{-1} appeared at 400°C. The Si-O stretching bands, at 1247 and 1111cm^{-1} shifted to 1285 and 1120cm^{-1} respectively, but new peaks appeared at 1184 and 1054 cm^{-1} at 400°C. In the Al-OH bending range large shifts from 927 and 889 cm^{-1} were observed at 936 and 877 cm^{-1} respectively, and the 849 band split into two components at 822 and 806 cm^{-1}, indicating changes in octahedral structure. The Si-O stretching bands increased from 651 to 659 cm^{-1}. These observation confirm that Mg ions also migrate to the vacant octahedral position in the smectite.

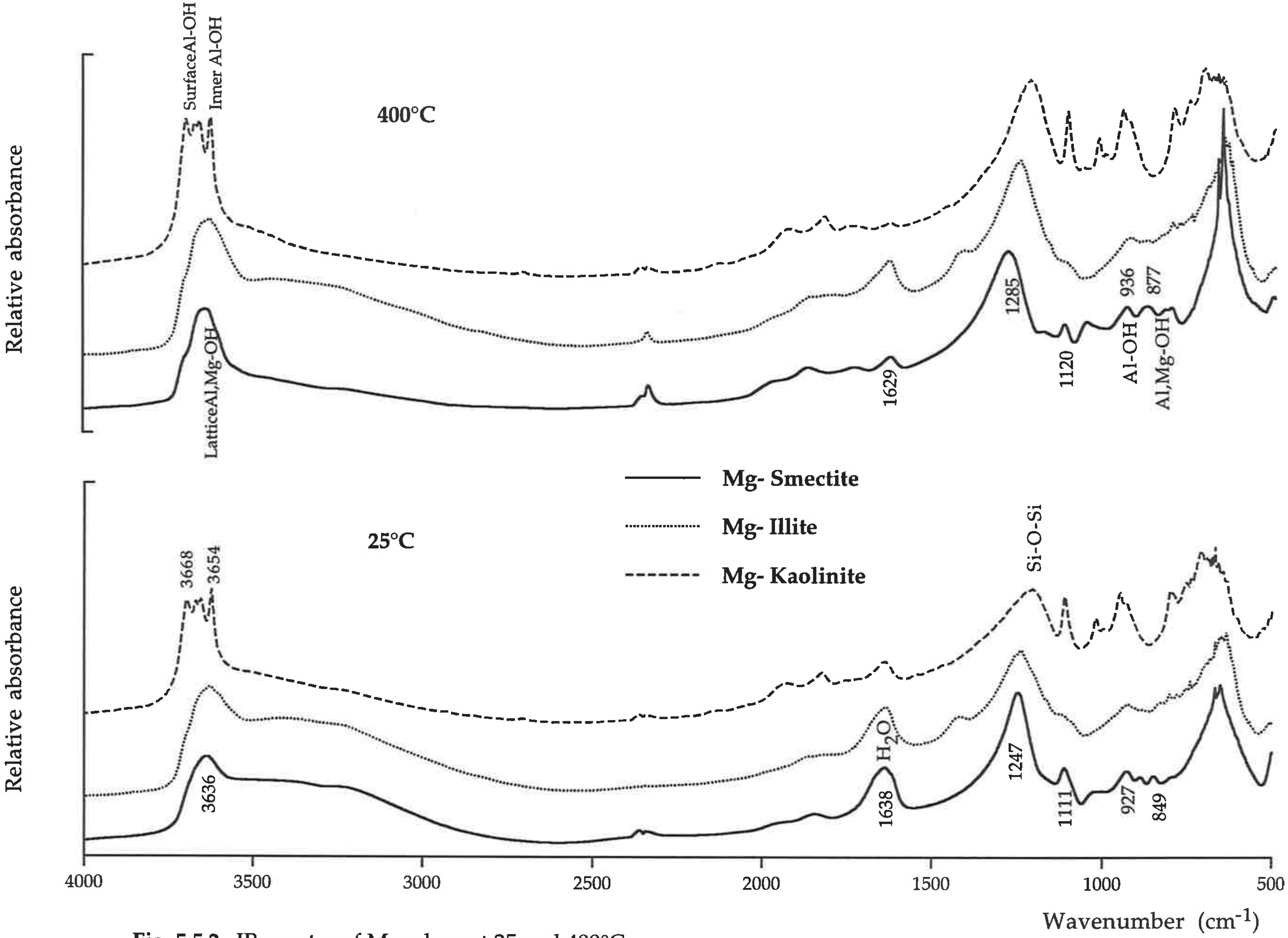


Fig. 5.5.2. IR spectra of Mg- clays at 25 and 400°C

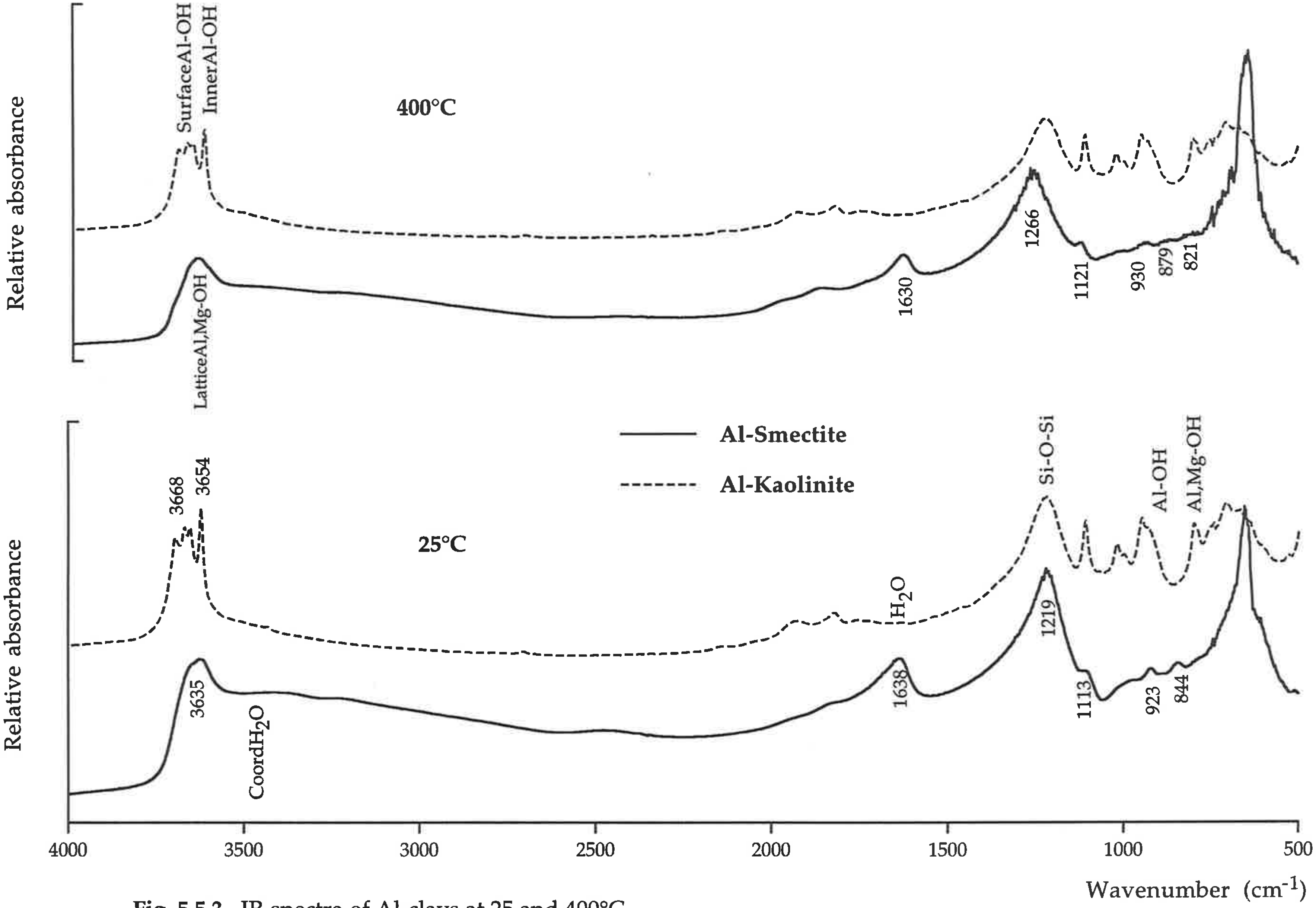


Fig. 5.5.3. IR spectra of Al-clays at 25 and 400°C

A large shift from 1639 to 1629 cm^{-1} was observed for the H_2O bending frequency of structural water in Mg-kaolinite indicating the dehydration effects. In general, the stretching vibrations of the clay lattice did not change significantly with temperature in both Mg saturated kaolinite and illite (Figure 5.5.2).

5.5.3.3 Al-clays

The IR spectra of Al-smectite showed that the OH-stretching mode had large shift from 3625 to 3639cm^{-1} and the intensity of the peaks decreased as the temperature of heating increased from 25°C to 400°C (Figure 5.5.3). The H_2O deformation shifted from 1638 to 1630cm^{-1} at 400°C. In the Si-O stretching in plane range the 1113cm^{-1} component shifted about 8cm^{-1} to 1121cm^{-1}, whereas the 1219cm^{-1} band split into three components at 1266, 1261 and 1255cm^{-1}. In the OH-bending range the 923cm^{-1} wavenumber shifted to 930cm^{-1} and new component appeared at 996cm^{-1} at high temperature of heating. The 844cm^{-1} band split into four components at 879, 867, 855 and 821cm^{-1} as the temperature of heating increased up to 400°C. Several new components such as 786, 746, 724, 711, 691 and 570 cm^{-1} were observed at high temperature which are not visible at 25°C. In the H_2O deformation region, the 1537 cm^{-1} shifted to 1557 cm^{-1} and also a new peak at 1858 cm^{-1} appeared after heating up to 400°C. These observation are similar to those observed in Li- and Mg-smectite and again, confirm the migration of Al ions into the clay stucture.

Figure 5.5.3 shows the IR spectrum of Al-kaolinite heated to 400°C. The OH-bending frequency of water at 1633 cm^{-1} shifted to 1622 cm^{-1}. In general, no significant differences were observed in the IR spectra of Al-kaolinite after heating which showed no changes in clay structure.

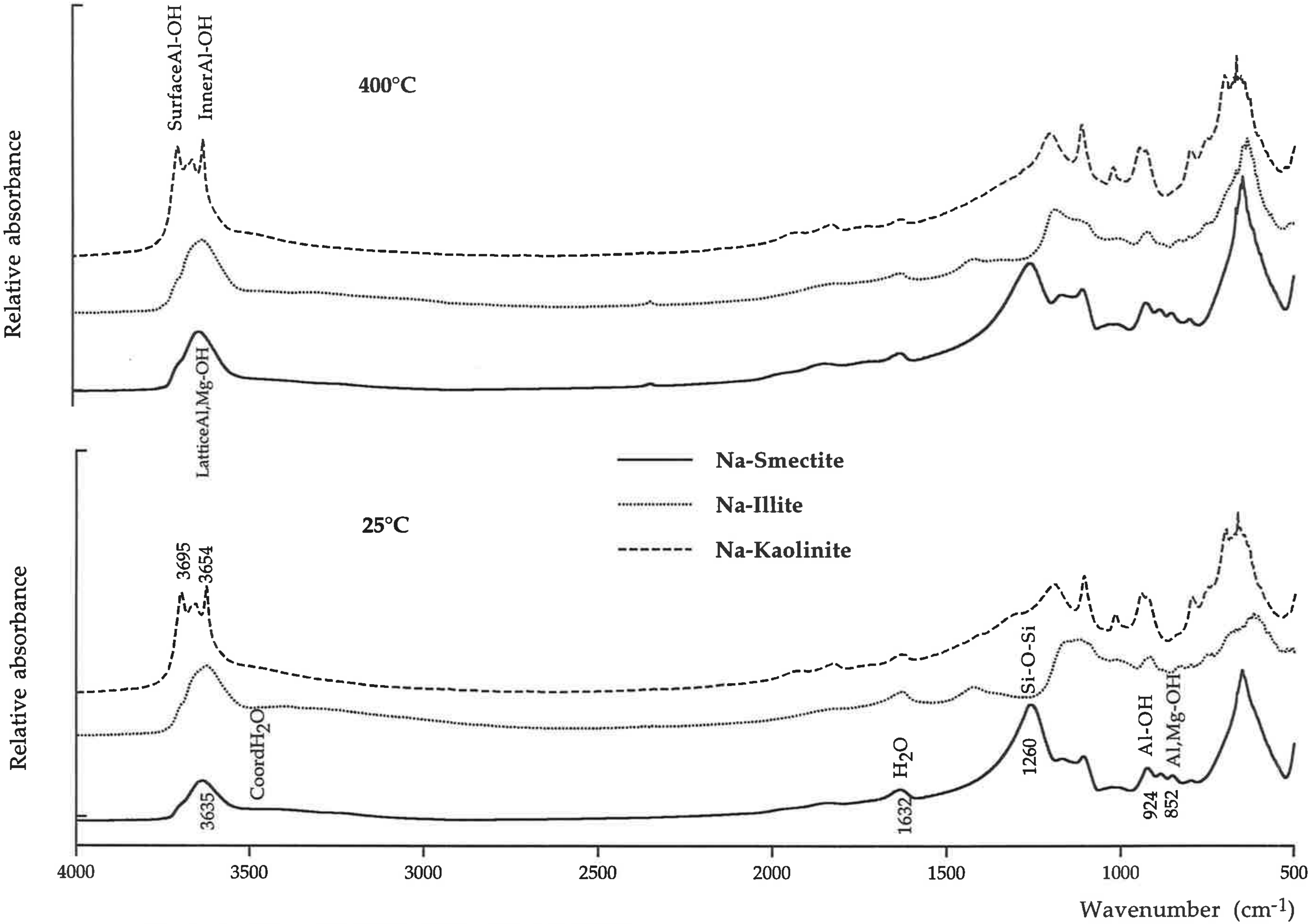


Fig. 5.5.4. IR spectra of Na-clays at 25 and 400°C

5.5.3.4 *Na-, K,- and Ca-clays*

The IR spectra of Na, K and Ca-smectite heated up to 400°C are shown in Figures 5.5.4, 5.5.5 and 5.5.6. Heating up to 400°C did not affect the OH-stretching vibrations and OH-bending of the samples. Together with a shift of OH- bending frequency of water from 1634 cm^{-1} to 1628 cm^{-1}, there were also shifts observed for the Si-O in-plane stretching from 1264 cm^{-1} to 1257 cm^{-1} with increasing temperature for K-smectite. A new peak was observed for Ca-smectite at 1734 cm^{-1} after heating to 400°C. The change was large for Si-O stretching bend from 1242 to 1253 at high temperature, corresponding to a shift of about 11 cm^{-1}.

No significant differences were observed in OH-stretching, OH-bending frequencies and Si-O bending range of Na-, K- and Ca-kaolinite or illite samples heated up to 400°C (Figures 5.5.4, 5.5.5 and 5.5.6).

Shifts in the IR spectra suggested that Li, Mg and Al ions migrated to the octahedral vacant sites after heating cationic smectite at 400°C. This phenomenon is consistent with changes in the swelling and dispersion properties of Li-, Mg- and Al-smectite samples heated to 400°C (section 5.2.2). The size of interlayer cations determines the extent to which they migrate into the inner structure. It seems that the extent of migration is affected little by the charge or polarizing power of the cation as observed by Tettenhorst (1962).

There are two reasons for the reduction in charge and strong bond between cations and the smectite surfaces after heating: 1) cations migrated to octahedral vacant sites are closer to the locus of the negative charge and consequently are more tightly held, and 2) the basal oxygen layers of adjacent units are closer, because the cations migrated from the interlayer positions. This would tend to seal off the avenues of exchange.

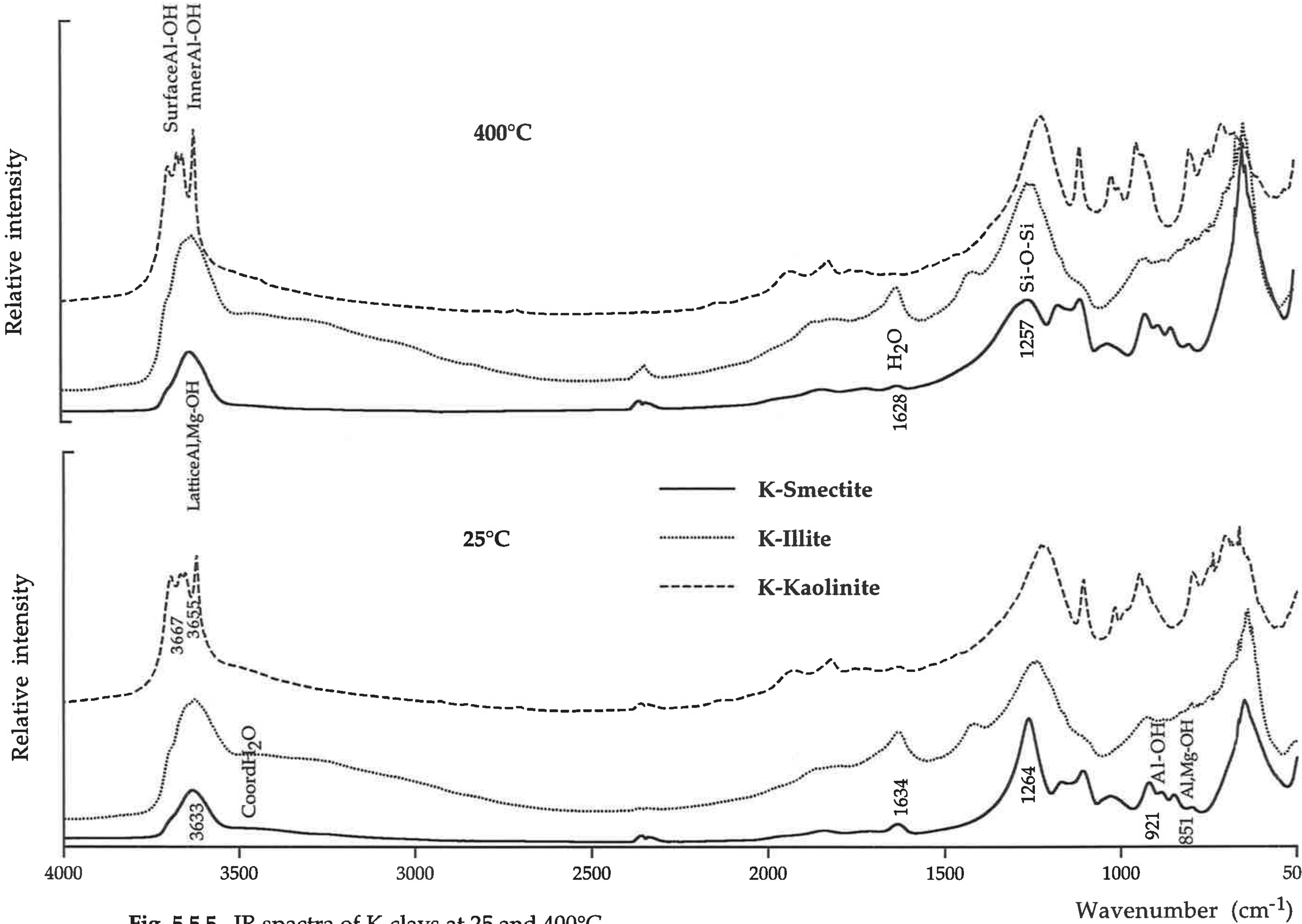


Fig. 5.5.5. IR spactra of K-clays at 25 and 400°C

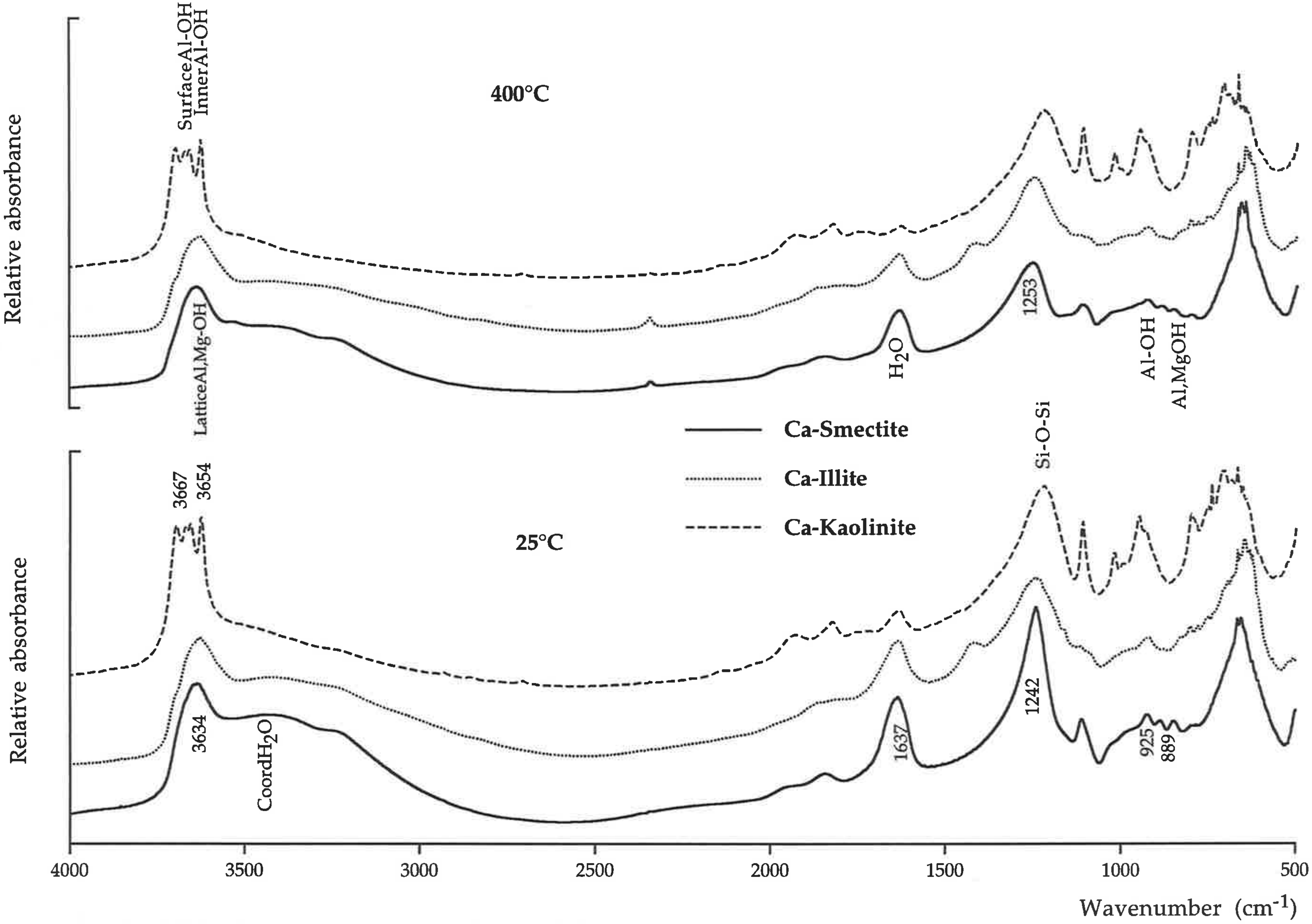


Fig. 5.5.6. IR spectra of Ca-clays at 25 and 400°C

The frequency of the external and internal OH groups of the kaolinite and illite samples did not shift significantly as the temperature of heating increased. Therefore, no changes occurred in the structure over the same temperature range.

5.5.4 Conclusions

The smaller cations Li, Mg and Al (ionic radius < 0.7Å) migrate to the vacant octahedral sites in smectite on heating at 400°C, as evidenced by IR spectra and form covalent bonds. IR spectra also show that larger cations such as Na and Ca (ionic radius > 0.9Å) do not migrate into the clay structure on thermal treatment. Therefore, they form polar covalent bonds close to the hexagonal holes. This is consistent with the swelling on rehydration of heated Na- and Ca samples (section 5.2)

Infrared spectra of kaolinite and illite do not show any significant change after thermal treatment and therefore the bond types could not be inferred.

CHAPTER 6

Influence of amendments on the behaviour of an alkaline sodic soil

6.1 Introduction

The presence of carbonate minerals exerts a major influence on the chemistry of a soil. Calcareous sodic soils maintain much higher pH values, alkalinity and alkaline earth cation concentrations than do non-calcareous soils. If carbonate minerals are present, prediction of soil pH requires consideration of carbonate equilibrium reactions. Soil pH is required for evaluation of many processes in soils, including micronutrient availability, heavy metal transport and Al toxicity. Under arid conditions calcium carbonate precipitation is a dominant process affecting solution chemistry and pedogenesis (Suarez 1995). Theoretical descriptions of the $CaCO_3$-H_2O-CO_2 system in soils and its control of pH and Ca^{2+}, HCO_3^- and CO_3^{2-} ions concentrations, including their interactions with other soluble and exchangeable ions are well defined (Ponnamperuma 1967; Robbins 1985). Alkaline sodic soils contain Ca^{2+} as $CaCO_3$ which is insoluble at high pH.

The presence of sodium increases the pH of calcareous soils by increasing the activity of carbonate and bicarbonate. Na_2CO_3 and $NaHCO_3$ are relatively soluble, and their removal by leaching can substantially reduce pH and ESP. In alkaline sodic soils, removal of Na^+, HCO_3^- and CO_3^{2-} by adding protons in the form of weak acids through microbial or biological reactions make it easier to lower pH and increase the solubility of $CaCO_3$. Thus, an important process for the amelioration of alkaline sodic soils is the reduction of soil pH when leaching processes are normal. Microbial decomposition of organic matter is also correlated with pH (Nelson and Oades 1996). Increased P_{CO_2} due to plant root respiration and decomposition of organic matter

(Robbins 1986; Gupta *et al.* 1989) decreases pH in soils. Excretion of protons from plant roots can be a major acidification mechanism. Robbins (1986) found that the most effective organic amendment in a calcareous sodic soil is the one which produces the highest P_{CO_2}. Adding Ca^{2+} with organic matter is much more beneficial than adding organic matter alone for remediation of sodic soils (Sadana and Bajwa 1985). Organic matter may have some beneficial effect on the structure of sodic soils; its effects are much greater following displacement of Na by Ca (Muneer and Oades 1989; Rengasamy and Olsson 1991).

Experiments on pure clays and soil clays detailed in chapters 3 and 4, have clearly shown that reduction of pH from alkaline to neutral levels would considerably reduce swelling and dispersion. It has also been shown that this effect is mainly because lowering pH results in the reduction of net negative charge. Similarly the experiments described in chapter 5 have shown that charge reduction in clay minerals, obtained by thermal treatment, also inhibits swelling and dispersion. By heating sodic soils at various temperature, it is possible to reduce or prevent clay dispersion (section 5.4). However, thermal treatment of alkaline sodic soils in the field, for agricultural purposes, may not be practical or even economical. Therefore, it is necessary to find out ways of altering particle charge preferably by agronomic practices.

Because alkaline sodic soils contain native lime, reduction in pH also helps, in addition to charge reduction, to dissolve $CaCO_3$, as discussed in previous paragraphs. Proton injection through plant roots, organic matter decomposition or biological reaction is a logical step in aiming for pH reduction. Hence, carbonate chemistry and pH are critical factors in the reclamation of alkaline sodic soils.

The study reported in this chapter evaluates the chemical and physical changes of an alkaline sodic soil (an Alfisol) as influenced by the changes in carbonate chemistry, pH and particle charge on the application of a few amendments *viz.* gypsum, green manure and glucose.

6.2 Materials and methods

6.2.1 Soil

The soil used in the present study was located at Two Wells, 25 km north of Adelaide, South Australia. The terrain is a flat coastal plain in a region which has a Mediterranean-type climate. The mean annual rainfall is 396 mm (winter maximum). The soil was classified as Typic Natrixeralf, clayey. mixed (calcareous), thermic (Soil Survey Staff 1975). The soil samples were collected from sub-soil (20-40 cm) which is sodic. Table 6.1 summarises some of the relevant physico-chemical properties of this soil.

6.2.2 Treatments and experimental design

The experimental design consisted of 4 different treatments (control, green manure, gypsum and green manure + gypsum), 4 gypsum levels, and 3 levels of green manure with 3 replicates, in a complete randomised design.

6.2.3 Gypsum trial

The sodic soil was passed through a 2-mm sieve and then placed in 2-kg plastic pots. The pots had holes at the base for passage of leachate. The soils were treated with 4 different amounts of dry gypsum ($CaSO_4.2H_2O$) viz. 0.5, 1.0 and 1.5% by weight of soil. All treatments were replicated thrice.

6.2.4 Green manure treatment

At the same time 4 different sets of replicates were used for green manure studies. Chopped alfalfa (*Medicago Sativa l.*) was applied and mixed with the soil. The treatments of green manure were 0.0, 1.0 and 3.0% (based on dry material) by weight of soil. Similarly, green manure was also added to the soils treated with four levels of gypsum to find out the combined effect of these treatments. All the pots were wetted with reverse osmosis water (R.O) up to field capacity (400 cm^3 kg^{-1} soil) every week for 12 weeks. The pots were incubated for 12 weeks with the same water treatments and kept at a constant temperature of 20°C± 1 in a glasshouse. At the end of experiment, all pots were air dried.

6.2.5 Glucose treatment

In a separate experiment, addition of glucose was tried to increase microbial activity to generate protons. The treatments of glucose were 0.0, 20, 40 and 60 g kg^{-1} of soil. Soils were thoroughly mixed with glucose at an air dry water content and then wetted up to the saturation point. The pots were kept at saturation with extra water (10 mm above soil) for 10 months in a glasshouse at constant temperature (20°C). All treatments were replicated thrice.

6.2.6 Soil chemical analyses

The soil samples in all the pots were sieved in order to separate 2-4 mm (for aggregate stability and hydraulic conductivity) and <2 mm fractions (for chemical analysis). The pH and electrical conductivity (EC) were determined using 1:5 water extracts. Exchangeable cations and Cation Exchange Capacity (CEC) were determined following the methods described by Heanes (1981). Exchangeable cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) were extracted with 1M NH4Cl in 60% V/V ethanol and water at pH 8.5. The cations, viz. sodium, potassium, calcium, and magnesium were measured by inductively coupled plasma atomic emission spectrometry (ICPAES). CEC was determined by dilution of the residual exchange cation extract with M/100 NH_4Cl, followed by extraction of the added forms of NH_4^+ and Cl^- with 1M KNO_3, 0.5 M $Ca(NO_3)_2$ and subsequent determination after steam distillation. Organic carbon and carbonate in soils were measured as described in section 5.4.2.3. Soluble CO_3^{2-} and HCO_3^- were determined by a titration method (Rayment and Higginson 1992). The amount of mechanically dispersed clay and zeta potential (ζ-potential) of the clay particles from different treated soils were determined according to the procedures outlined in section 3.2. The ζ-potentials measured in this study were negative in sign, because the clay particles moved towards the cathode.

6.2.7 Physical measurements

6.2.7.1 Wet aggregate stability

The samples of air-dried soils were sieved and 2-4 mm size aggregates were collected. Three replicates of 10 g aggregates were wet sieved for 3 minutes on a set of 3 sieves of 500µm, 250 µm and 53 µm diameter using the method of Kemper and Rosenau (1986). The material on each sieve and the fraction passing through were collected, dried at 105°C, and weighed. The amount of soil on each sieve was expressed as a percentage of the total sample weight. The aggregate stability results were expressed as mean weight diameter (MWD) which was calculated using the equation of (Kemper and Rosenau 1986) as follows:

$$\mathrm{MWD} = \sum_{n=1}^{i} X_i W_i \qquad [6.1]$$

where X_i is the mean weight diameter of each size fraction, W_i is the proportion of the total sample weight and n is number of the fractions.

6.2.7.2 Soil friability

The soil samples were wetted to a water content between the plastic and liquid limits and remoulded until they were as homogeneous as possible. Artificial aggregates were formed at various sizes between 4 and 20 mm diameter, then oven dried at 40°C. 20 aggregates of each size were selected for individual measurement of dry tensile strength using indirect tension (Brazilian core test) as described by Dexter and Kroesbergen (1985). Each aggregate was weighed and its diameter was recorded before crushing it between flat parallel plates in a loading frame. The soil friability constant, k, was calculated according to the analysis presented by Utomo and Dexter (1981), and represents the slope of the linear regression of the log-transformed values of aggregate tensile strength, s (kPa), on aggregate volume, V (m^3):

$$\log_{10} s = A + k \log_{10} V \tag{6.2}$$

The regression intercept, A, represents the extrapolated tensile strength of 1 m^3 samples of the bulk soil.

Saturated hydraulic conductivity was measured as described in detail in section 5.4.2.5.

6.2.8 NMR analyses

Prior to NMR analysis the soil was treated with HF to avoid the effect of iron (Skjemstad *et al.* 1994). Solid-state ^{13}C NMR spectra, with cross-polarization and magic-angle spinning (CP/MAS), of the whole soil was obtained at 50.3 MHz on a Varian Unity 200 Spectrometer as described by Golchin *et al.* (1994).

6.2.9 Biomass measurement

Microbial C was estimated on three replicate sub samples using the method described by Wu *et al.* (1990). Soils were moistened to 40% of their water holding capacities and kept for three days. Sub samples were fumigated with ethanol-free $CHCl_3$ for 21 days at 20°C in sealed desiccators.

Simultaneously, the non- fumigated soils were extracted by shaking for 30 min with 0.5M K_2SO_4. After 21 days, the fumigated soils were extracted similarly. Organic C was measured in these extracts by automated u.v.-persulphate oxidation. Biomass C was calculated from the following equation:

$$B_C = (A - B)/K_C \qquad [6.3]$$

where, B_C is biomass C (µg g^{-1} soil), A and B are CO_2-C evolved from fumigated and non-fumigated soil, respectively and K_C was taken as 0.45.

6.2.10 Methane measurement

Equal volumes of soil water (from glucose-treated, waterlogged soils) and atmospheric gas were shaken. The gas phase was used for methane analysis. Gas samples were analysed for CH_4 on a Perkin-Elmer "Autosystems" gas chromatograph, equipped with a Flame Ionisation Detector (Perkin- Elmer) and a Porapak Q 80/100 column. The carrier gas (ultra-high purity He) flow rate was 25 ml min^{-1}, the injector and oven temperatures were 60°C and detector temperature was 250°C. Dissolved CH_4 was calculated according to the following equation:

$$\frac{\text{Methane in headspace}}{1.401} = \mu g CH_4 / L \qquad [6.4]$$

6.3 Results

The soil chosen for this study is alkaline with a pH (soil:water, 1:5) of 9.38. The $CaCO_3$ content is 5% and the soluble Ca is low (0.5 $mmol_c$ L^{-1}); SAR is 13 (Table 6.1). The clay mineralogy is a mixture of kaolinite, illite and randomly interstratified minerals (RIM).

6.3.1 Gypsum and green manure effects

6.3.1.1 Chemical properties

The pH values after 12 weeks changed because of the treatments (Table 6.2). Gypsum treatment reduced the pH from 9.38 to 7.89, an increasing amount of applied gypsum resulting in a decreasing pH. Green manure alone reduced the pH from 9.38 to 8.68. The gypsum effect on pH is due to increase in electrolyte concentration and exchange of Na^+ whereas the green manure effect is due to CO_2 produced. However, the interaction of gypsum plus green manure has resulted in a greater reduction of pH than in the single treatments. The interactions were more significant at the 3% green manure level than at 1%. These results are consistent with the observation by Sadana and Bajwa (1985), who showed that addition of gypsum with green manure decreased soil pH more than gypsum alone in submerged sodic soils.

The changes in electrical conductivity (EC) due to the gypsum and green manure treatments varied with the rates of addition. The EC was maintained at a much higher level in soil which received gypsum than in the soil receiveing only green manure; this is obviously due to the increased level of soluble electrolyte. Green manure, by producing CO_2, increases the solubility of native $CaCO_3$. Application of gypsum plus green manure resulted in a higher EC value than for the control (Table 6.2). Changes in the EC values for gypsum and green manure alone were 0.82 and 0.35 dS m^{-1}, respectively. Synergistic effects of gypsum and green manure on EC were highly significant. Sadana and Bajwa (1986) observed that addition of green manure along with gypsum caused a greater increase in EC than gypsum alone.

The sodium adsorption ratios (SAR) of 1:5 soil:water extracts were determined to investigate the changes in soil sodicity after addition of gypsum and green manure. Although the SAR of the soil solution was affected

Table 6.1. **Physical and chemical properties of the soil used**

Soil	Particle-size distr. (%) Clay	Silt	Sand	pH[A]	EC[A] (dS m^{-1})	Org. C %	SAR[A]	CEC[B]	$CaCO_3$ (%)	Clay mineralogy[C] (%) I	K	RIM	Q	G/H
Two Wells 20-40 cm	51	24	25	9.4	0.35	0.45	13	290	5	35	20	35	4	10

[A] Determined on a 1:5 soil water extract. [B] Units ($mmol_c$ kg^{-1}). [C] Measured by X-ray diffractrometry and X-ray fluorescence. I, illite; K, kaolinite; RIM, randomly interstratified minerals; Q, quartz; G/H, Goethite/Haematite.

Table 6.2. **Changes in soil chemical properties of sodic soil after applying gypsum and green manure**

Gypsum Application g Kg^{-1}	Green Manure addition (%)																	
	0	1	3	0	1	3	0	1	3	0	1	3	0	1	3	0	1	3
	pH(1:5)			EC(dS m^{-1})			SAR			Exchangeable Ca[A]			Exchangeable Mg[A]			Carbonates[B]		
Control	9.38	8.91	8.68	0.37	0.57	0.72	11.6	9.50	7.52	111	132	149	145	130	119	129.16	57.01	34.63
5	8.47	8.32	8.17	0.65	0.79	0.88	3.95	3.12	2.45	189	195	203	126	112	108	20.66	14.77	10.74
10	8.14	8.04	7.98	0.91	1.08	1.30	1.94	1.63	1.31	218	228	230	102	95	92	8.43	7.62	6.97
15	7.89	7.77	7.67	1.19	1.30	1.59	1.20	1.02	0.91	238	248	261	80	71	66	5.95	4.21	3.89
l.s.d (P= 0.01)[C]	**0.13**			**0.11**			**0.52**			**13.6**			**8.6**			**10.42**		

[A] ($mmol_c$ kg^{-1}), [B] Soluble Na_2CO_3 and $NaHCO_3$ ($mmol_c$ L^{-1}), [C] Gypsum x Green manure interaction.

significantly by the applied gypsum and green manure treatments, gypsum had a greater effect on decreasing sodicity than green manure because of high levels of Ca^{2+} in soil solution. Use of both treatments together had a significant effect in reducing soil sodicity as indicated by the significant interaction term derived from the ANOVA analysis. The decrease in the SAR of the treatments was also a function of the changes noted in exchangeable Ca^{2+}.

Table 6.2 shows the negative relation between exchangeable calcium and exchangeable magnesium after addition of gypsum and green manure. Exchangeable calcium increased significantly at all levels of applied gypsum and green manure in both, alone or together, than that of the control, whereas exchangeable magnesium decreased in contrast with exchangeable calcium. The magnitude of the changes in exchangeable calcium of the gypsum-amended soil was greater than for the green manure treatments. Incorporation of gypsum and green manure together also significantly increased exchangeable calcium. The increase in Ca^{2+} concentration in soil solution is due to gypsum dissolution and pH reduction causing increase in $CaCO_3$ solubility. CO_2 from decomposition of green manure and enhancing microbial activity also increased the solubility of $CaCO_3$.

Soluble carbonate in the form of Na_2CO_3 and $NaHCO_3$ usually appears at high pH (>8.4) and enhances the effect of soil sodicity (see chapter 4). Therefore, lowering soluble carbonate and pH reduction can reduce sodicity hazards. The results of this study demonstrate that by incorporating gypsum and green manure, soluble carbonate concentration can be decreased. Addition of gypsum and green manure resulted in a lower soluble carbonate value than that of the control (Table 6.2). While differences between all green manure treatments were significant, addition of gypsum up to 10 g kg^{-1} greatly reduced soluble carbonate.

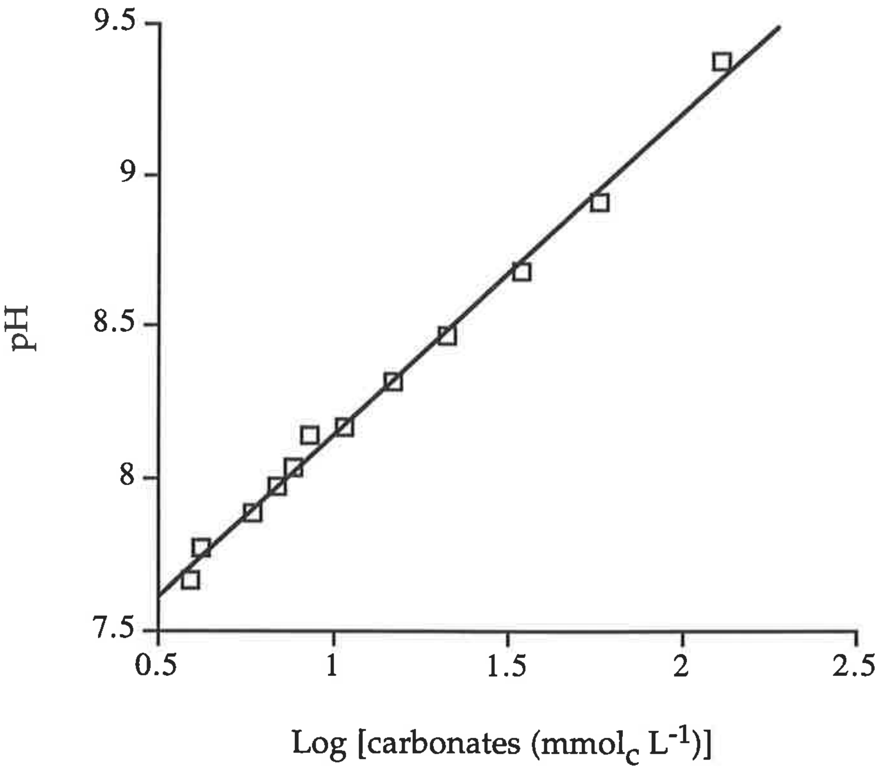


Fig. 6.1. The relationship between soluble carbonates and pH of the soil suspension

The logarithm of carbonate concentration in soil solutions from all treatments was highly correlated with the pH values measured (Figure 6.1) as follows:

$$Y = 1.062X + 7.085 \quad (R^2 = 0.995) \qquad [6.5]$$

where Y=pH and X= log [carbonates (mmol$_c$ L^{-1})]. Even though ionic strength and P_{CO_2} were not included in the regression, the relationship, being significant, indicates the importance of removing soluble carbonates to reduce soil pH.

6.3.1.2 Physical properties

Table 6.3 presents the ζ-potential of the soil clays in relation to the rates of gypsum and green manure addition. The decrease in ζ-potential of the gypsum-treated soils was much higher than green manure treatments. The mechanisms responsible for the reduction in ζ-potential with increasing rate of gypsum and green manure application are increase in electrolyte concentration of soil solution (EC), pH reduction and increase in the concentration of Ca^{2+}. All these are responsible for flocculation of soil clays and, particularly Ca^{2+}, for their aggregation. The ζ-potential decreases as the valency of cations increases, indicating more aggregation of clay particles, formation of large domains and reduction in charge on the clays due to cationic bonding (see chapter 3). The particle charge is reduced by the inner-sphere complexation of Ca^{2+} ions with clays, responsible for the formation of large particles of clay domains.

Table 6.3. Change in soil physical properties of sodic soil after applying gypsum and green manure

Gypsum application g /kg	Green manure addition (%)					
	0	1	3	0	1	3
	ζ-potential (-mV)			Dispersible Clay[A]		
Control	36.67	34.11	31.03	46.1	23.33	10.53
5	30.83	24.07	22.40	7.85	3.93	0.83
10	22.07	20.37	19.24	0.47	0.15	0.08
15	18.13	17.61	16.73	0.07	0.05	0.02
l.s.d ($p= 0.01$)[D]		**1.13**			**1.74**	
	MWD[B](mm)			HC[C] (cm hr^{-1})		
Control	0.51	0.88	1.17	0.07	23.73	69.67
5	1.04	1.19	1.37	26.02	43.03	78.17
10	1.09	1.22	1.48	37.57	58.21	86.77
15	1.14	1.31	1.62	40.07	66.17	97.67
l.s.d ($p= 0.01$)[D]		**0.09**			**3.52**	

[A] (% of total clay). [B] Mean weight diameter. [C] Hydraulic conductivity.
[D] Gypsum x Green manure interaction.

Mechanically dispersible clay contents were significantly reduced by the addition of both treatments, but the decrease induced by the addition of gypsum was much greater than that induced by the addition of green manure (Table 6.3). The results clearly show that the addition of a high rate of fresh organic material such as chopped alfalfa can reduce pH and dispersible clay. Because a threshold concentration of electrolyte (Rengasamy and Olsson 1991) is enough to prevent mechanical dispersion higher rates of gypsum (ie 10 and 15 g kg^{-1}) didnot produce significantly differentresults from lower rates. In the case of green manure the electrolyte generated was much lower than with gypsum and hence there was a smaller reduction in dispersible clay.

Water stable aggregates (expressed as mean weight diameter, MWD) were increased significantly by the addition of both gypsum and green manure (Table 6.3). However, green manure at the higher rate (ie 3%) increased MWD more than gypsum application. While the increased solubility of $CaCO_3$ from green manure addition enabled the stabilisation of clay domains, further aggregation into micro aggregates was facilitated by the products of organic matter from green manure. The gypsum effect was mainly due to the flocculation of clays resulting in the aggregation of clay particles into domains. Therefore, the combined effect of gypsum and green manure on MWD was highly significant, as observed by others (e.g. Muneer and Oades 1989).

Saturated hydraulic conductivities (HC) were significantly increased by both gypsum and green manure (Table 6.3). 3% green manure addition had a greater effect in increasing HC than gypsum, as shown in Table 6.3. The increase in HC by gypsum is mainly due to the increase in EC above threshold levels. As the threshold concentration is achieved at a low rate, a higher rate of gypsum application did not increase HC any further. This is similar to the effect on mechanically dispersed clay. However, the dramatic increase in HC with green manure is due to particle aggregation in addition to flocculation. As reflected by MWD values, green manure enhanced macroporosity and hence increased the HC.

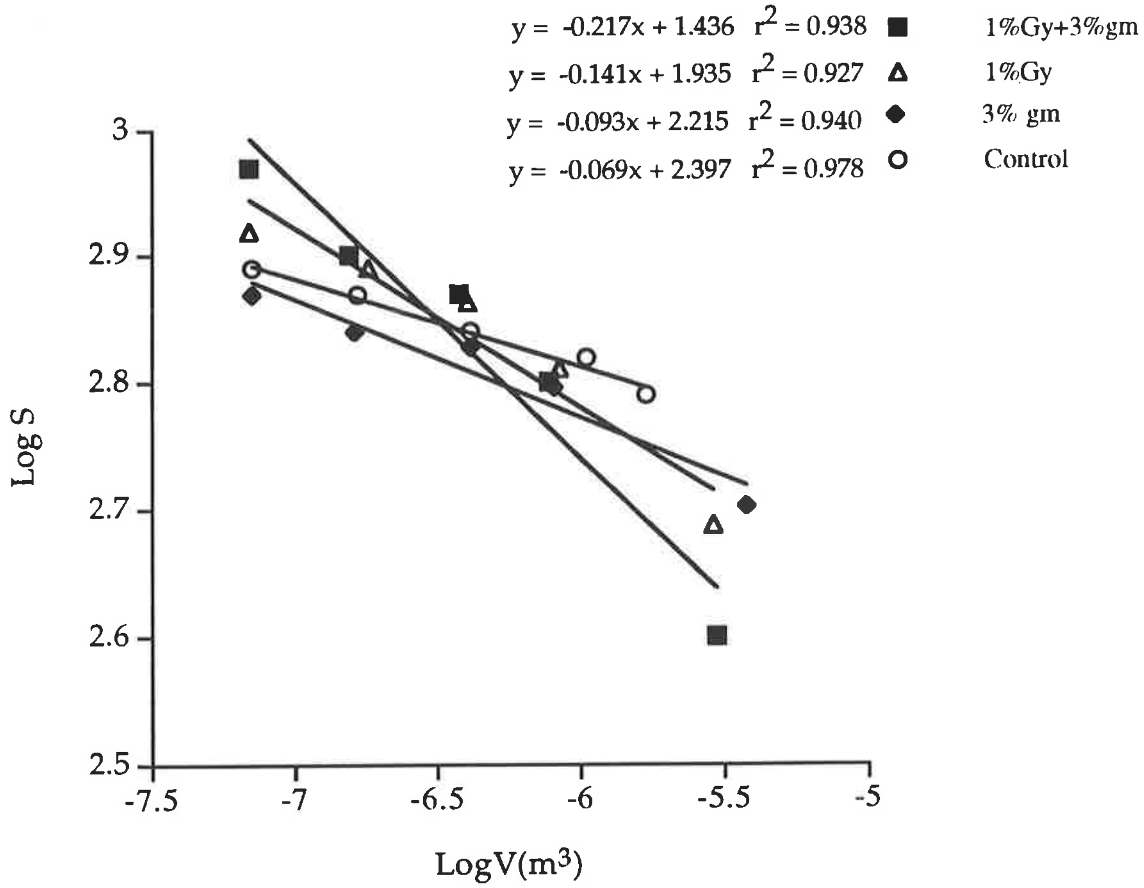


Fig. 6.2. Effect of Gypsum and green manure on soil friability

Figure 6.2 shows the effect of gypsum and green manure on soil friability. The friability of the soils was determined from remoulded soil aggregates. The soil friability increased in the order green manure+ gypsum > gypsum > green manure > control and corresponded to friabilities of 0.217 > 0.141 > 0.093 > 0.069, respectively. The friability is a measure of soil tilth (Utomo and Dexter 1981). These results indicate that gypsum plus organic matter, not only improve aggregation and hydraulic conductivity but also soil tilth.

The relative proportions of different types of carbon obtained by integration of the NMR spectra is shown in Figure 6.3. Golchin *et al.* (1994) showed that the O-alkyl to alkyl ratio in soil organic matter as determined by

NMR is a sensitive way of monitoring the extent of decomposition of organic materials in soils. According to this approach the ratio of O-alkyl to alkyl decreases as the extent of decomposition increases. The O-alkyl to alkyl ratio of soils as shown by NMR analysis was lower (1.25) in soil treated with 1% gypsum + 3% green manure than control (1.34), while this ratio was higher (1.57) in soil treated only with 3% green manure. The results indicate that the presence of gypsum in soil enhances the decomposition of organic carbon. This is consistent with the results of Golchin *et al.* (1996) who showed decomposition of glucose was greater in soils saturated with Ca compared with those saturated with Na and Al. The lower carbon content of soil treated with gypsum and

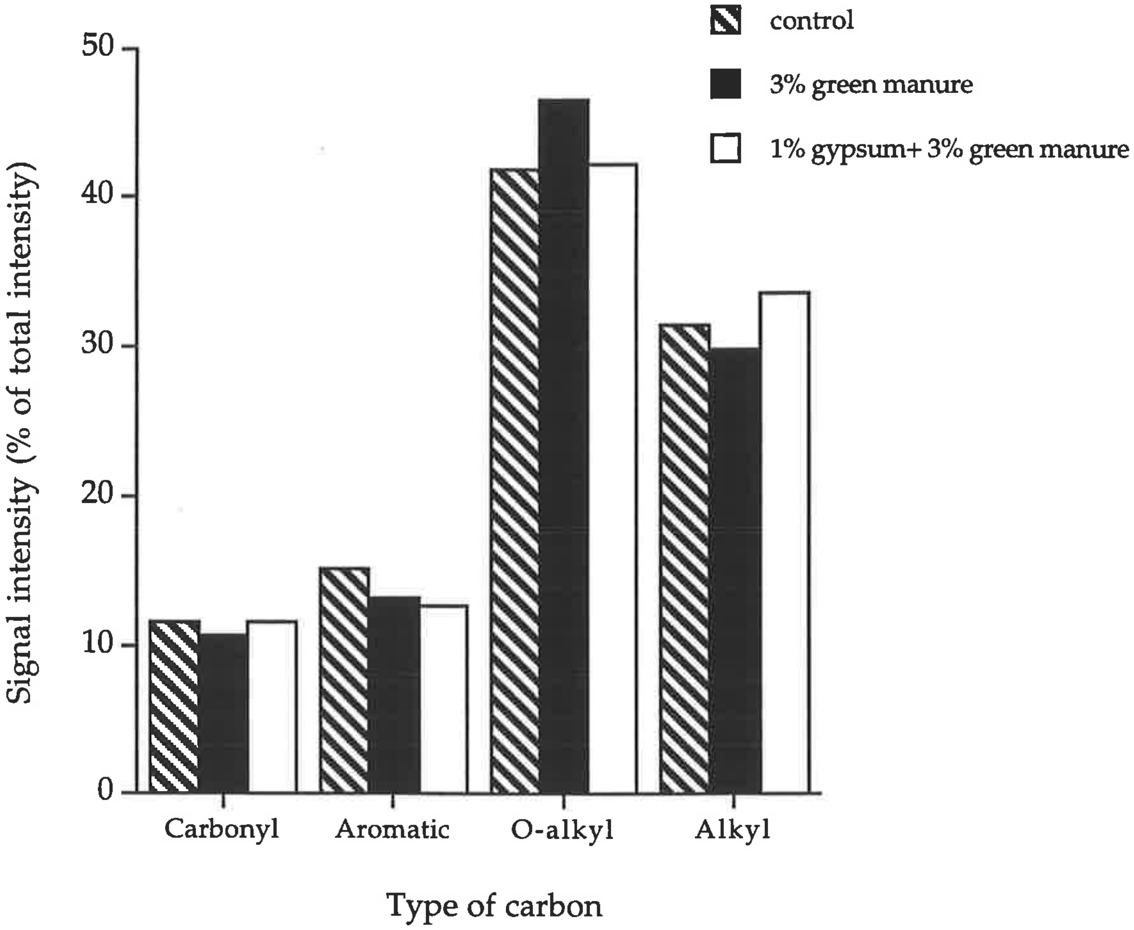


Fig. 6.3. Effect of gypsum and green manure on the proportion of different types of carbon

green manure together is in agreement with greater mineralisation of carbon from this soil and confirm the results obtained from NMR analysis (Figure 6.4).

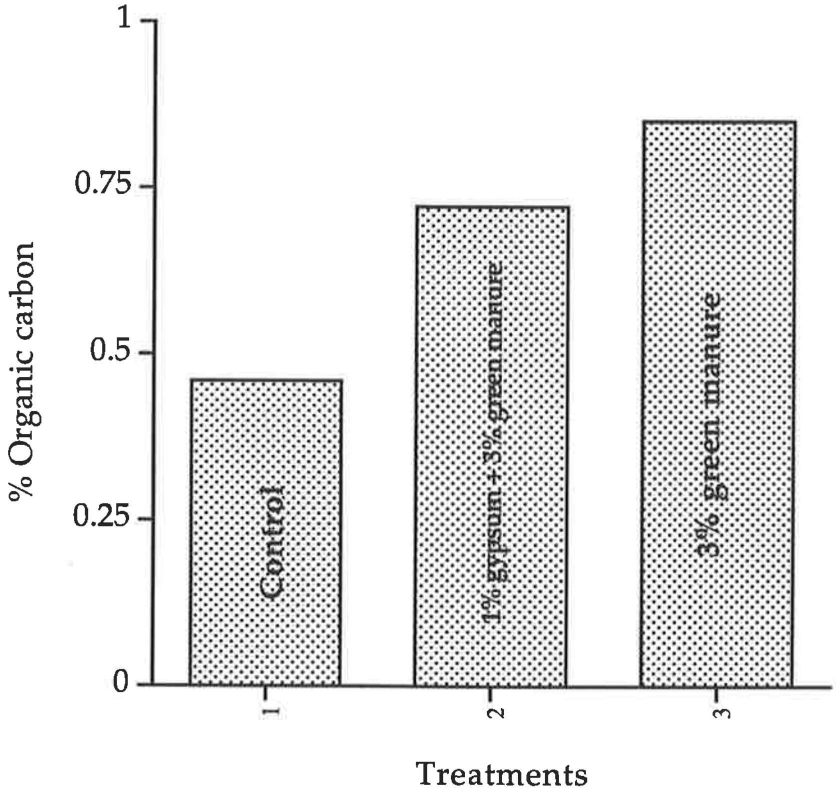


Fig. 6.4. Effect of interaction of gypsum and green manure on soil organic carbon

6.3.2 *Glucose experiment*

The glucose was added to increase the microbial activity within a short period. The amounts of glucose added was proportional to the organic matter additions ranging from 20 60 t ha^{-1}. The addition of glucose changed the chemical and physical properties of the sodic soil (Table 6.4) by enhancing microbial activity. The pH of soil suspensions decreased significantly with increase in the rates of glucose addition (Figure 6.5). Glucose addition decreased the pH from 9.38 to below 6.8 within 30 days. Once the microbial activity started to decline the pH of the soil suspension increased slightly. However, even after 320 days, the pH remained below 7.4. Table 6.4 shows the effects on soil properties of glucose additions. High solubility of $CaCO_3$ and other minerals due to addition of glucose increased EC of the soil. $SAR_{1:5}$ of the soil was decreased dramatically by the addition of glucose, as exchangeable Ca^{2+} increased and exchangeable Na^+ decreased. Soluble carbonates were reduced sharply by the addition of glucose; this was reflected by the larger pH reduction. The ζ-potential of the glucose-treated soils were much lower than those of the control as a result of the electrolyte effect and aggregation by Ca^{2+} (see chapter 3) mobilized by pH reduction. Mechanically dispersible clay decreased dramatically due to the electrolyte effect, pH and charge reduction.

Table 6.4. Changes in soil properties after adding glucose under anaerobic conditions

	Glucose addition			
	0%	2%	4%	6%
pH	8.65	7.37	6.67	5.95
EC (dS m^{-1})	0.96	5.59	6.15	6.51
$SAR_{1:5}$	8.75	3.86	3.56	2.38
Exchangeable Ca^A	113	130	156	160
Exchangeable Mg^A	126	108	80	76
Exchangeable Na^A	174	48	39	36
Soluble $carbonate^B$	34.7	2.93	0.58	0.12
Zeta potential (-mV)	31.1	15.1	14.9	14.3
Dispersible clay (%)	37.8	0.08	0.05	0.02
HC (cm hr^{-1})	0.5	12.4	27.8	52.3
MWD (mm)	0.75	1.32	1.47	1.61

^{A} Unites ($mmol_c$ kg^{-1}), ^{B} (mmol L^{-1})

Addition of glucose to the sodic soil increased its HC. The MWD of the soils from different glucose treatments, increased significantly with increase in the amount of glucose added and was higher than the control. The amount of microbial biomass-C was increased sharply in the soils by the addition of glucose. This is consistent with the results on MWD and HC.

Methane is another important product of acetate fermentation in water-saturated soil environments. The amount of dissolved methane measured under anaerobic conditions by treatment with different rates of glucose was not quantitatively reflected in microbial activity (Table 6.5). Adding 2% glucose to the soil decreased pH from 9.4 to 7.37, when methane production was high.

Table 6.5. Effect of glucose addition on pH and the amount of dissolved methane

Glucose addition (%)	pH	Dissolved methane $\mu g\ L^{-1}$	Biomass μgCg^{-1} soil
Control	8.55	24	2.2
2	7.37	135	36
4	6.67	55	43
6	5.95	37	59

6.4 Discussion

Alkaline sodic soils in Australia contain varying quantities of lime ($CaCO_3$) ranging from 10 to 2000 t ha^{-1} up to a depth of 1 metre. Because of the low solubility of $CaCO_3$ at pH values > 8.4, the native lime is not useful in providing Ca^{2+} in soil solution to combat sodicity. Therefore, a major strategy should aim at reducing pH of these soils below 8.4. The earlier experiments on soil clays and pure clays (see chapter 3 and 4) have clearly indicated that by reducing pH, behaviour of sodic clays can be improved significantly. The effect of pH on clay behaviour has been shown to occur via the reduction of charge on clay particles. The amendments chosen in this experiment have significantly reduced the soil pH, but through different mechanisms.

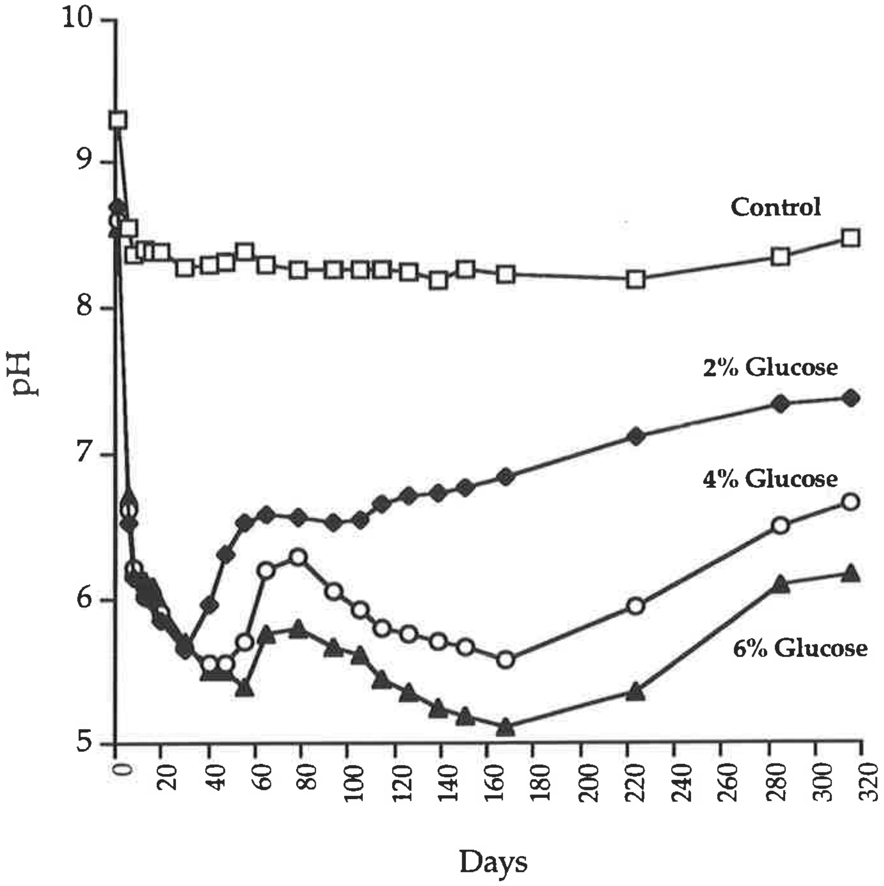


Fig. 6.5. Effect of glucose addition on soil pH under anaerobic condition

Gypsum is commonly used in reclaiming sodic soils. Under alkaline sodic conditions, gypsum increases the electrical conductivity of the soil solution immediately. Increased ionic strength leads to proton generation and reduction of soil pH. Even though this effect is temporary and will be lost as the gypsum is leached, the proton generation should help in dissolving native $CaCO_3$ and leach Na_2CO_3 and $NaHCO_3$.

Green manure reduces the pH by increasing P_{CO_2} and dissolving carbonates. This is confirmed by the increase of Ca^{2+} and carbonates in soil solution after addition of green manure. In addition to reducing the sodicity effects on soil clays, green manure also improves macro-aggregation.

Addition of green manure with gypsum has accelerated sodicity reclamation. Statistical analysis has shown the significant interaction effects of gypsum and green manure. In practice, initial addition of gypsum to sodic soils will help in producing green manure crops in the field and further reclamation of sodic soils by organic matter will be facilitated.

Glucose addition was aimed at increasing the microbial activity to produce protons via fatty acids. Dramatic reduction in pH which is linearly related to the rate of glucose addition confirms the effectiveness of microbial reclamation of alkaline sodic soils.

The present study has shown that pH reduction in alkaline sodic soils improves the soil physical properties when clay dispersion and swelling are also reduced. The particle charge as revealed by zeta potential is also significantly reduced at lower pH values.

In Australia, alkaline sodicity is generally present in the subsoils ie. below 20 cm from the surface. This poses a problem in the economical application of these amendments to the subsoil layers. However, about 30% of the alkaline sodic soils have pH > 8.4 in both surface and subsurface layers (R. H. Merry, personal communication). Use of green manure in these soils, at field level, is being trialed by some farmers. If green manure is not economical, use of legumes with deeper roots to reduce soil pH in subsurface layers may be of value.

6.5 Conclusions

Alkaline sodic soils in Australia contain significant amounts of $CaCO_3$in the profile but remain insoluble because of high pH. Therefore, reduction of soil pH will enable solubilisation of $CaCO_3$ and facilitate reclamation of sodicity. With this aim the amendments (viz gypsum, green manure and glucose) were added to an alkaline sodic soil from South Australia. All these amendments were effective in reducing soil pH and improving soil physical properties. However, the mechanisms involved in these reclamations were different.

Gypsum, because of the electrolyte effect and cation exchange reduced SAR and pH and increased soluble Ca^{2+}. The clay particles had lower charge as revealed by zeta potential. HC was much higher than the control. Green manure had similar effects on soil physical properties. Increased P_{CO_2} due to the decomposition of green manure resulted in more soluble Ca^{2+} and reduced pH. In addition to clay flocculation, macro aggregation resulted in high HC. The interactive effect of green manure and gypsum was highly significant in improving clay behaviour and soil physical properties.

Glucose addition resulted in increased microbial activity and fatty acid production. Drastic reduction in pH was achieved and this was linearly related to the amount of glucose added. Although pH increased slightly after the cessation of microbial activity, the pH remained well below the control even after 320 days. The present experiment has shown clearly that pH reduction by these amendments can improve soil physical properties and reclaim sodicity.

CHAPTER 7

GENERAL DISCUSSION

7.1 Introduction

This final chapter of the thesis discusses the findings of the whole research project. It attempts to integrate the conclusions drawn from each experiment and identify future research needs. Finally, some general conclusions are drawn from the work. The discussion will be presented in three main sections: the main factors related to clay dispersion, altering the clay behaviour by heating and improvement of alkaline sodic soils.

7.2 Dispersion, pH and particle charge

Sodic soils usually have poor physical and chemical properties particularly when soil electrolyte levels are inadequate to compensate for the effects of sodium. When sodic soils are wet, problems with slow water movement in the soil, poor aeration, trafficability and compaction commonly occur. In dryland agriculture, low infiltration rates often restrict water intake during rain; the consequent enhanced runoff on sloping land results in soil erosion.

Increasing crop production on sodic soils requires an understanding of the adverse impact of sodicity on soil properties. Swelling and dispersion are two processes responsible for the adverse physical behaviour of sodic soils. Research conducted since 1954 has documented that the tendency for swelling, aggregate failure and dispersion increases as salinity (EC) decreases and sodicity (ESP) increases. The extent of swelling and clay dispersion depend on the balance between EC and ESP. Alkaline sodic soils have pH greater than 8.4. In these soils pH, in addition to EC and ESP, has an influence on clay swelling and dispersion. Soil pH indirectly affects swelling and dispersion by altering the particle charge. Consequently, the nature and extent of the effect of pH and particle charge on sodicity related problems of pure clays and soil clays were the subjects of chapters 3 and 4.

The results of chapter 3 on pure clays (smectite, illite and kaolinite) clearly indicated that net particle charge was the common factor affecting clay dispersion under different conditions of pH, ionic strength and cation type. In sodium-saturated clays, there was a positive relation between pH and the percentage of dispersible clay, the effect decreasing in the order kaolinite > illite >> smectite. Also the percentage increase in net negative charge with an increase in pH was in the order illite > kaolinite > smectite. It was found that the flocculation value at a given pH for Na-smectite was always larger than that for kaolinite and illite, reflecting the strong net negative charge on smectite particles. In the absence of particle charge characterization, the reports in the literature are difficult to interpret, even though the size and shape of illite particles have been invoked by some authors to explain the difference. Particularly, in variable charge systems, charge characterization should also be done at different ECs to separate the effects of pH. Goldberg and Forster (1990) found that the flocculation values for reference clays were much less than those for soil clays, indicating that extrapolation from the results on reference-clays was not possible, and that additional factors such as organic matter and Al- and Fe-oxide content influenced the dispersion of soil clays.

The ζ–potentials of Ca-clays were very much smaller than for Na-clays, and particle size analysis confirm greater particle aggregation in the Ca-system. The particle charge is screened by the inner-sphere complexation of Ca ions with clays, leading to the formation of domains and quasi-crystals. The average particle size for Na- and Ca-clays (chapter 3) supports this hypothesis.

The flocculation values of different cationic clays reported in chapter 3, are different from those calculated using the Schulze-Hardy valency rule. The ratio of flocculation values of sodium and calcium clays was 1: 50 for kaolinite, 1:42 for illite and 1: 80 for smectite. The different ratios for these clays are perhaps due to the difference in total charge of these clay minerals in suspension.

The results on soil clays (chapter 4) confirm that clay dispersion and flocculation are dependent on net particle charge as influenced by pH. In general, it was found that soil clays had higher flocculation values than the values reported for pure clay minerals at comparable pH values. A comparison of net negative charge at similar pH values, indicated that soil clays had more net negative charge (calculated on a clay basis) than pure clays of similar mineralogy. Therefore, net negative charge on particles accounts for clay flocculation better than the dominant mineralogy of the soil clays. Higher negative charge of soil clays than those reported for pure clay minerals is largely because of the association of organic matter and oxide components. If soil particles contain adsorbed organic matter, organic functional groups also contribute to negative charge (Oades 1984; Goldberg *et al.* 1990) and hence, the dispersion of clay particles is promoted and the flocculation values increase.

The correlation studies (chapter 4) clearly showed the importance of pH in influencing clay dispersion in many diverse types of soils, the mineralogy of these soils varying widely. The effect of increasing pH on clay dispersion was significantly higher in Alfisols and Aridisols than in Oxisols or Vertisols. It was concluded that soil pH is an important factor to consider in the management of dispersive soils.

Further studies are needed to distinguish the effects due to charge from those of ionic concentration, both caused by pH changes. Models relating sodicity, pH and dispersibility of soils should be developed. This will help in applying amendments to ameliorate both sodicity and pH and to maintain soil clay particles in a flocculated state.

7.3 Altering particle charge and clay behaviour

Since particle charge has been established as a primary factor in clay dispersion, experiments in chapter 5 concentrated on artificially changing particle charge of pure clays and soil clays, and then relating the charge reduction to their swelling and dispersion properties. Thermal treatment up to 400°C of clays can lead to changes in particle charge and alter the clay behaviour without significant change in their crystalline structures .

Some recent studies have suggested that hydration forces are more important in swelling than DLVO (Derjaguin-Landau-Verwey-Overbeek) forces (Israelachvili and McGuiggan 1988). Further, Rengasamy and Sumner (1996) proposed that HSAB (Hard-Soft Acid-Base) reactions lead to different types of bonding between clay surfaces and cations viz. covalent, polar covalent and ionic which control hydration and hence swelling and dispersion properties of soil clays. In the present study (chapter 5) thermal treatment was used to understand the mechanisms of clay swelling and dispersion as well as the changes in the nature of bonding of cations to clay surfaces.

The results (chapter 5) clearly showed that the thermal treatment of smectites saturated with Li, Mg and Al reduced their layer charge and as well caused a decrease in exchangeable cations. This resulted in changes in the expansion properties of smectite. The extent of the charge reduction depended on the nature of cation and the temperature of heating.

Thermal treatment affects the bonds between clay surfaces and cations in different ways. The smaller cations (ionic radius < 0.7Å) like Li, Mg and Al, after heating at 400°C, apparently migrate to octahedral vacant sites, form covalent bonds and reduce the negative charge drastically. This process starts at 200°C for Li. Covalent bonding and charge reduction in the clays prevent hydration and hence reduce swelling and dispersion. At lower temperatures of heating (100-300°C), polar covalent bonding in Mg and Al-clays is increased, due to polarisation of atoms by thermal energy. Therefore, limited hydration results in swelling but not in spontaneous dispersion.

Larger cations Na, K, Ca (ionic radius > 0.9Å) apparently do not migrate to octahedral vacant sites on thermal treatment but there is an increase in the degree of covalency of the bonding between cations and clay surfaces due to thermal effects. Therefore, increase in the temperature of heating of these clays results in swelling with only limited hydration. Ca-clays have limited swelling even without heating. In the case of K, stronger fixation occurs at 400°C heating, without any swelling. Limited swelling indicates polar covalent bonds while absence of swelling indicates covalent bonding. These mechanisms are summarised diagrammatically in Figure 7.1.

In the present study, heating of kaolinite and illite samples, irrespective of cation type, resulted in the loss of CEC but not as drastic as observed in Li-, Mg- and Al-smectite (section 5.2). This reduction in CEC could be due to either increased polar covalency or covalent bonding. Increasing the temperature of heating resulted in reduced slaking of both kaolinite and illite samples indicating progressive increase in covalent bonding. Whether this covalent bonding of cations occurs on kaolinite and illite surfaces or in the vacant sites (isomorphous substitution sites) in the inner structure of these clays is not clear. The results presented in section 5.3 can only indicate that covalent bonding between cations and clay are formed thereby reducing cation hydration, as

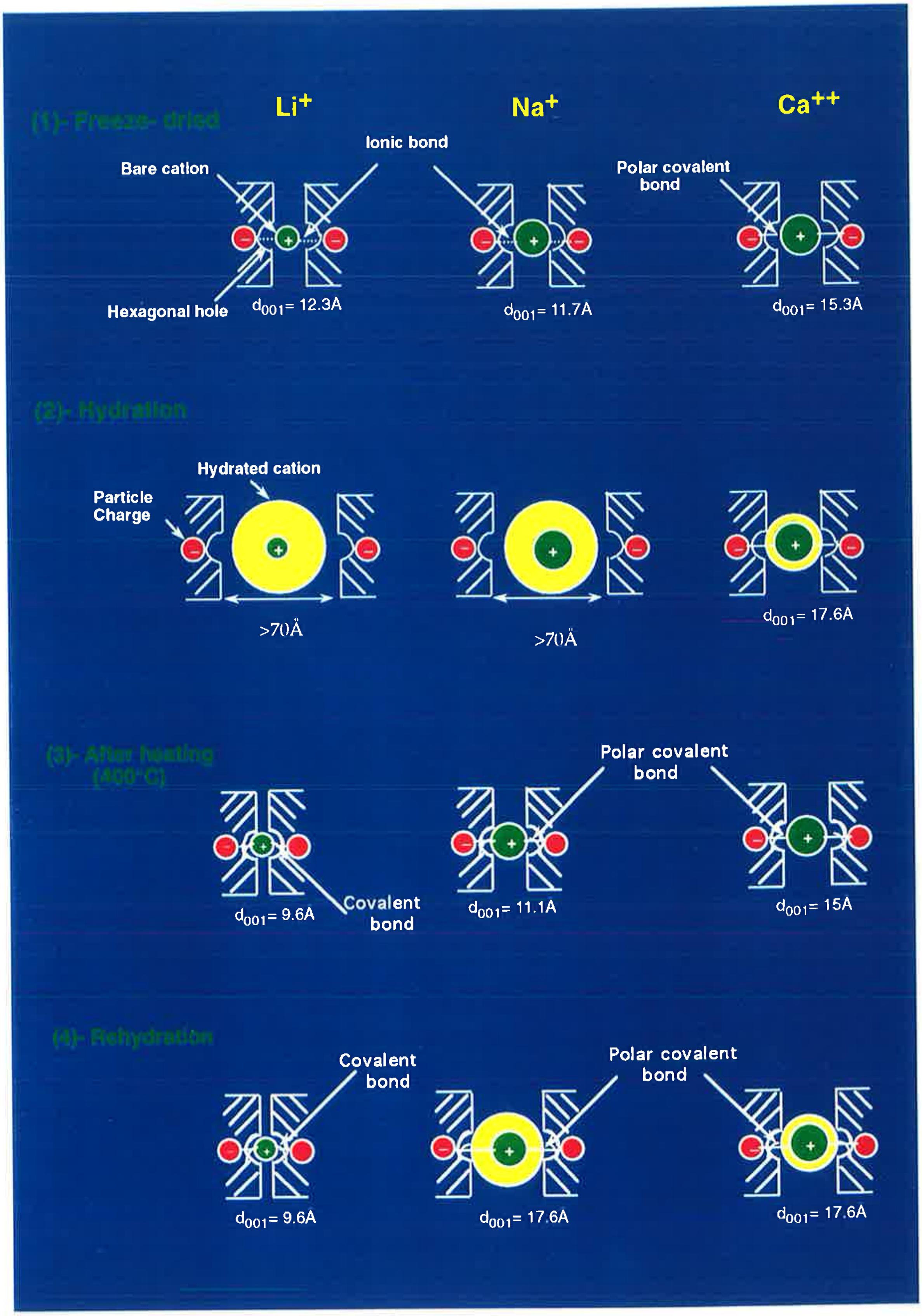


Fig. 7.1. Mechanisms of bonding of cations and clay particle before and after thermal treatment

evidenced by reduced slaking. Covalent bonding is more in clays bearing smaller cations (Li and Mg) than larger cations (Na, K and Ca). In general, covalent bonding is lower in illites compared to kaolinites.

The present study on kaolinite and illite has shown that the reduction in slaking (swelling) and dispersion of these clays on heating up to 400°C. These properties are important in agricultural soils dominated by these minerals where bush fires can heat the surface soils to more than 600°C. Further, stubble burning practised for weed control and soil heating to control soil borne-pathogens will increase the surface soil temperature to > 300°C. These practices will lead to changes in swelling and dispersion of these soils particularly when excess sodium is present. Heating clays lead to fixation of cations in the clay surfaces. This property will be useful in fixing heavy metal cations on clays to prevent mobilisation of these pollutants in the environment. Further research is needed to explore this application.

Infrared studies were carried out to understand the mechanism of charge reduction due to heating and to get direct evidence on the possible migration of cations into clay structure in the formation of covalent bonding. IR spectra of cationic clays showed that the smaller cations Li, Mg and Al (ionic radius < 0.7Å) migrated to the vacant octahedral sites in smectite on heating at 400°C, and formed covalent bonds. IR spectra also showed that larger cations such as Na and Ca (ionic radius > 0.9Å) did not migrate into smectite structure on thermal treatment. Therefore, they formed polar covalent bonds close to the hexagonal holes. This is consistent with the swelling on rehydration of heated Na- and Ca samples (section 5.2) Infrared spectra of kaolinite and illite did not show any significant change after thermal treatment and therefore the bond types could not be inferred.

The aim of the experiment in section 5.4 was to find out the effects of thermal treatment on two alkaline sodic soils containing a mixture of kaolinite, illite, RIM (randomly interstratified minerals) and quartz in their clay fractions. The results obtained for soil clays heated up to 400°C are consistent with the results for pure clay minerals. The results on both sodic soils show that, after heating at 400°C, the cations formed covalent bonds with clay surfaces and hence no rehydration was possible. As a result, there was no slaking and dispersion. This was consistent with the reduction in CEC, ESP (exchangeable sodium perecentage) and soluble cations. Thus, it seems that sodic clay behaviour can be improved by altering particle charge.

7.4 Amelioration of sodic soils

Accumulation of dispersive Na^+ in the solution and the exchange phase affect the soil physical properties such as soil structural stability. For sodic soils, reclamation generally proceeds by increasing Ca^{2+} ions on the absorbed phase at the expense of Na^+.

By heating sodic soils at various temperature, it is possible to reduce or prevent clay dispersion (section 5.4). However, thermal treatment of alkaline sodic soils in the field, for agricultural purposes, may not be practical or economical. Therefore, it is necessary to find out ways of altering particle charge preferably by agronomic practices.

The cheap source of Ca for replacing adsorbed Na may be the soil itself, involving the dissolution of Ca-containing minerals by producing acidity through organic matter and biological proton injection. The external sources such as gypsum or irrigation water containing Ca ions could be more expensive. The experiments in chapter 6 focussed on how chemical amendment (gypsum) and biological reactions (through green manure and glucose) can change the chemical and physical behaviour of an alkaline sodic soil (an Alfisol). Under alkaline sodic conditions, gypsum increases ionic strength, leads to limited proton generation and reduces soil pH. The protons generated should help in dissolving native $CaCO_3$ and leach Na_2CO_3 and $NaHCO_3$.

Green manure reduces the pH by increasing P_{CO_2} and dissolving carbonates. This is confirmed by the increase of Ca^{2+} and carbonates in soil solution after addition of green manure. In addition to reducing the sodicity effects on soil clays, green manure also improves macro-aggregation. Addition of green manure with gypsum has accelerated sodicity reclamation.

Glucose addition resulted in increased microbial activity and fatty acid production. Drastic reduction in pH was achieved which was linearly related to the amount of glucose added. The results in this part of study clearly showed that pH reduction by these amendments can improve soil physical properties and reclaim sodicity. Further research is needed to find out the ecological conditions under which organic residues in the field will accelerate the microbial activity necessary for pH reduction.

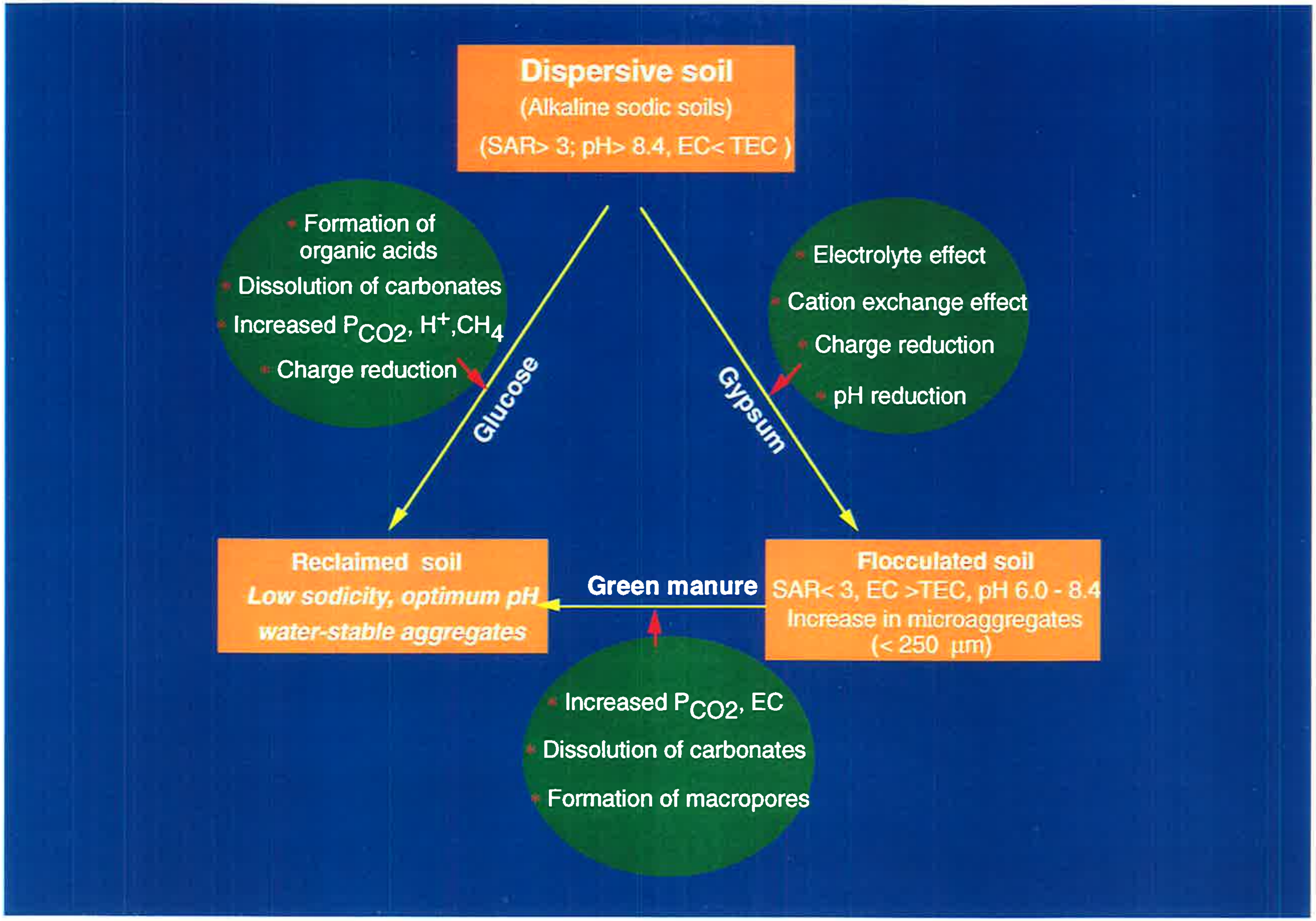
7.5 Perspectives

Sodic soils occur in about 30% of the total land area in Australia and 86% of these sodic soils are alkaline (pH> 8.4), particularly in dense clayey subsoils. Many of these alkaline soils also contain lime ($CaCO_3$) ranging from 10 to 2000 t ha^{-1} up to a metre depth. In spite of the presence of calcium compound, sodicity is highly prevalent and affects soil physical properties related to transport of air and water. High pH of these soils also interferes with nutrient availability. These constraints are considered to reduce the potential yields of crops to less than half.

The literature review has identified the soil pH as an important factor affecting these properties. Therefore, the mechanisms by which pH controls swelling and dispersion as well as how to reduce soil pH and solublise the native $CaCO_3$ were the foci of this thesis.

The particle charge emerges as the primary factor in controlling swelling and dispersion of soil clays in alkaline sodic soils. This study has shown that, under natural conditions, when these soils contain native lime, particle charge can be manipulated by aiming to reduce alkaline pH to values < 8.4.

The schematic diagram (Figure 7.2) describes different path-ways to achieve the reclamation of alkaline sodic soils. Inorganic amendments such as gypsum reclaim sodic soils by flocculating dispersive clays via an electrolyte effect and cation exchange. Green manure and glucose ameliorate sodicity by increasing microbial activity and dissolving native lime present in the soil. Further research should concentrate on the ecological condition in the field controlling the organic matter decomposition and microbial activity to facilitate reclamation of sodicity.



Dispersive soil
(Alkaline sodic soils)
(SAR> 3; pH> 8.4, EC< TEC)

- Formation of organic acids
- Dissolution of carbonates
- Increased P_{CO2}, H^+, CH_4
- Charge reduction

Glucose

- Electrolyte effect
- Cation exchange effect
- Charge reduction
- pH reduction

Gypsum

Reclaimed soil
Low sodicity, optimum pH
water-stable aggregates

Green manure

Flocculated soil
SAR< 3, EC >TEC, pH 6.0 - 8.4
Increase in microaggregates
(< 250 μm)

- Increased P_{CO2}, EC
- Dissolution of carbonates
- Formation of macropores

Fig. 7.2. Mechanisms and pathways involved in the improvement of alkaline sodic soils

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1. Chorom M., Rengasamy, P., and Murray, R. S. (1994). Clay dispersion as influenced by pH and net particle charge of sodic soils. *Australian Journal of Soil Research* **32**, 1243-52.

2. Chorom, M., and 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- 65.

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