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BARD

FINAL REPORT

PROJECT NO. US-2420-94

Improving Efficiency of Reclamation of Sodium-affected Soils

S. Miyamoto, R. Keren

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Publication Summary (numbers)

	Joint IS/US authorship	US Authors only	Israeli Authors only	Total
Refereed (published, in press, accepted) BARD support acknowledged				
Submitted, in review, in preparation	8			
Invited review papers				
Book chapters		1		
Books				
Master theses				
Ph.D. theses				
Abstracts				
Not refereed (proceedings, reports, etc.)		1		

Postdoctoral Training: List the names and social security/identity numbers of all postdocs who received more than 50% of their funding by the grant.

Cooperation Summary (numbers)

	From US to Israel	From Israel to US	Together, elsewhere	Total
Short Visits & Meetings		1		1
Longer Visits (Sabbaticals)		0		0

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Patent Summary (numbers)

	Israeli inventor only	US inventor only	Joint IS/US inventors	Total
Submitted				0
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ABSTRACT

Sodium-affected soils, along with salt-affected soils, are distributed widely in irrigated areas of the arid and semi-arid region of the world. Some of these soils can and must be reclaimed to meet the increasing demand for food, and existing irrigated lands must be managed to reduce salinization and alkalization associated with deteriorating irrigation water quality. This project was conducted for examining ways to reduce the use of chemical amendments and large quantities of leaching water for reclaiming sodic soils or for preventing soil sodification. We hypothesized that sodicity of calcareous soils irrigated with moderately sodic irrigation water can be controlled by maximizing dissolution of soil CaCO_3 . The work performed in Israel has shown that dissolution of CaCO_3 can be enhanced by elevating the CO_2 partial pressure in soils, and by increasing pore water velocity. The concentration of Ca in pore water was at an order of $1.5 \text{ mmol}_e \text{ L}^{-1}$ at a CO_2 partial pressure of 5 kPa, which is sufficient to maintain SAR below 4 at salinity of irrigation water of 0.5 dS m^{-1} or less. Incorporation of crop residue at a fresh weight of 100 Mg ha^{-1} reduced the exchangeable Na percentage from 19 to 5%, while it remained 14% without crop residue application. These findings indicate a possibility of preventing soil sodification with appropriate crop rotation and residue management without chemical amendments, provided that soils remain permeable. In the case of highly sodic soils, dissolution of CaCO_3 alone is usually insufficient to maintain soil permeability during initial leaching. We examined the effect of salinity and sodicity on water infiltration, then developed a way to estimate the amendments required on the basis of water infiltration and drainage characteristics, rather than the traditional idea of reducing the exchangeable Na percentage to a pre-fixed value. Initial indications from soil column and lysimeter study are that the proposed method provides realistic estimates of amendment requirements. We further hypothesized that cultivation of salt-tolerant plants with water of elevated salinity can enhance reclamation of severely Na-affected soils primarily through improved water infiltration and increased dissolution of CaCO_3 through respiration. An outdoor lysimeter experiment using two saline sodic Entisols sodded with saltgrass for two seasons did not necessarily support this hypothesis. While there was an evidence of increased removal of the exchangeable Na originally present in the soils, the final salinity and sodicity measured were lowest without sod, and highest when sodded. High transpiration rates, coupled with low permeability and/or inadequate leaching seemed to have offset the potential benefits of increased CaCO_3 dissolution and subsequent removal of exchangeable Na. Although vegetative means of reclaiming sodic soils had been reported to be effective in sandy soils with sufficient permeability, additional study is needed for its use in saline sodic soils under the high evaporative demand. The use of cool season grass after initial salt leaching with CaCl_2 should be explored. Results obtained from this project have several potential applications, which include the use of crop residues for maintaining sodium balance, the use of CaCl_2 for initial leaching of poorly permeable clayey sodic soils, and appraisal of sodicity effects, and appropriate rates and types of amendments required for reclamation

ACHIEVEMENTS

1. Significance of Scientific Accomplishments and Innovations

This project produced three main scientific accomplishments which are relevant not only to the practice of sodic soil reclamation, but also to the development of soil and water management strategy when irrigated lands are affected by sodium (Na). The accurate measurements of and formulation of factors affecting CaCO_3 dissolution rates, which were achieved through this project, provided a scientific basis for this project, and may contribute to the advancement of soil and environmental sciences in arid and semi-arid regions. The development of water infiltration equations applicable to saline and sodic conditions is another achievement which is likely to help advance research in soil and water management options in the arid and semi-arid regions. Water infiltration is a most fundamental process which affects analyses and management of soil and water systems. The results of the outdoor lysimeter experiment present an excellent picture of the soil and plant interaction, and provide the data needed for future modeling. The idea to utilize indigenous substances such as soil CaCO_3 , organic matter and vegetation, in place of or in combination with traditional chemical amendments may help improve sustainability of irrigated crop production under appropriate circumstances.

2. Potential Application of the Project Findings

Findings related to water quality impacts on water infiltration (Reports 4 and 6) as well as ways to modify infiltration rates (Report 5) have immediate applications to soil and water management under irrigation. Soil and water conditions have been in use in a large quantities in irrigated areas of the western US. Research findings should help improve appraisal and selection of appropriate type(s) and application rates of amendments. Findings are applicable to many irrigation projects in the west, as the soils used for experiment two dominant soil types in arid and semi-arid regions; Aridisols and Entisols.

Several research findings from this project may have short to mid-term applications. These include the use of crop residue for maintaining water infiltration and the salt and sodium balance when water of elevated salinity is used for irrigation. Additional study, especially of handling and placement of crop residue has to be made prior to practical uses. Another potential application is the use of

calcium chloride, instead of gypsum for improving leaching potential of clayey soils affected by Na. Additional study is needed to determine the method of CaCl_2 application to maximize its impact on water infiltration. Both techniques have a potential for extensive application.

The use of vegetation or crops for reclamation requires additional investigation, focusing on numerical modeling, then verification on a field scale. The lysimeter data obtained indicate that high transpiration rates of the salt-tolerant plant used, coupled with low soil permeability and/or inadequate leaching, essentially negated beneficial effects of respiration on CaCO_3 dissolution and Na replacement. It is probable that the use of cool season vegetation, following initial leaching involving CaCl_2 , may produce more favorable results. At present, the use of reclamation crops is most suited in nonsaline sodic soils with coarse texture under low to modest evaporative demands.

3. Potential Impacts

The latest assessment of soil degradation indicates that irrigated lands lost to salinization and/or sodification have reached 72 million ha worldwide. This amounts to 36% of the existing irrigated lands of the world, which produces 1/3 of the world food supply. The assessment also indicates that the rate of soil salinization and sodification is estimated at 1.5 million ha annually, which coincides with the current rate of irrigation development worldwide. Meantime, the world population, especially in developing countries, continues to grow. The project useful for developing efficient methods of reclaiming these lands, such as this project, have a significant social, economic and environmental impact worldwide.

The proportion of irrigated land lost to salinization and/or sodification in the US is currently about 8%, and in the case of the Rio Grande Project, 11%. This proportion is increasing. However, a greater concern now is to develop ways to sustain irrigated crop production with water of elevated salinity and/or sodicity, which includes reclaimed sewage water. This will allow the use of fresh water for municipal uses, which are expanding rapidly in irrigated areas of the western US as well as in Israel. Results of this project may have a positive impact on ways to manage soils irrigated with water of elevated salinity and sodicity in urbanizing areas of the world.

4. Spin-Offs

One unexpected spin-off of this project was a conceptual advancement in river modeling in

semi-arid regions. The outdoor lysimeter data indicate that salinity of soils under saltgrass sods can increase rapidly to high levels. Saltgrass has been used to stabilize river banks of many river systems, including the Rio Grande. Incorporation of salt storage in and release from river banks provided an answer to the puzzling question of time-lag in salt transport in the river system, and led to a recent research proposal designed to modify the existing river models with a greater emphasis on salt storage and release in riparian zone.

5. Cooperation

Shortly after the initiation of this project, Dr. Keren, Co-Investigator was appointed as the Director of the Volcani Center. This obviously has placed a severe time constraint and has limited cooperative activities. Nonetheless, Dr. Keren and his associate provided unique expertise on the study of CaCO_3 dissolution, which provided a foundation for this research. Principal Investigator, S. Miyamoto, provided his expertise on water infiltration and modeling to this project. The mode of cooperation was basically complimentary.

Communication, which may not have reached a level of cooperation, has turned out to be a critical element in advancing concepts. The idea to use vegetation for reclamation was developed during a trip of PI to India. This idea was transmitted to Dr. Keren, who then decided to study the impact of crop residues on CaCO_3 dissolution. His finding helped develop a study to examine the effect of crop residue on water infiltration in the US. This finding, along with the results of the lysimeter experiment using salt tolerant plants has been transmitted to several institutions in India, Japan and several former Soviet Union states, and new scientific dialogue is developing.,

In spite of the limited time we spent for cooperation, communication with Dr. Keren and his colleague in Israel has impacted on concept developments and research targeting, which has a strong element of mission orientation, while studying basic processes. This blend of science and application is the unique thrust of this program.

BODY OF THE REPORT

Background and research objectives

Irrigated land, estimated to be 211 million ha in 1980, accounts for 17% of the total cultivated land in the world, yet it provides about one-third of the world food supply (FAO, 1999). Due to the increasing costs, coupled with the competitive demands for water, irrigated land developments have declined in recent years to below 1.5 million ha annually (UNEP, 1992). What is important and relevant to this project is that existing irrigated lands are being lost to salinization and alkalization at a rate almost equal to the new development. This trend has to be considered significant, as the world population continues to grow (UN, 1989; Dudal and Purnell, 1986). Irrigated lands lost to salinization and alkalization have reportedly reached 76 million ha, which is equal to 36% of the existing irrigated lands worldwide (ISRIC, 1990). In order to meet the future demand for food, some of these salted lands have to be reclaimed, while minimizing salinization and sodification of existing irrigated lands.

In the case of the western US and Israel, irrigated lands which were lost to salinization and sodification are not as extensive as in some other countries. In the case of the Rio Grande Project for example, we estimate that about 100,000 ha of irrigated lands is now taken out of crop production, largely due to sodification and salinization (Miyamoto, 1996). This amounts to 11% of the original irrigated lands of the project area. However, the real future threat to irrigated crop production is the limited availability of water suitable for irrigation. The increasing demand for water from rapidly increasing municipalities is making it necessary for crop production to rely more on saline water or reclaimed water for irrigation. However, the use of water with poor quality has traditionally compounded the problem of soil salinization and sodification.

The traditional method of controlling sodicity involves frequent uses of chemical amendments, most commonly phospho-gypsum in Israel, and a dozen of products in the western US (Keren and Miyamoto, 1990; Miyamoto, 1998). The use of chemical water conditioners is especially popular in the Southwestern US, but it does add to production costs and to salinity of irrigation returnflow. When the soil to be reclaimed contains large quantities of exchangeable Na, the quantities of chemicals required, as estimated by the conventional theory of the cation exchange reaction, becomes impractically large (e.g., Keren and Miyamoto, 1990). Some workers advocated the use of highly

saline water for leaching, instead of using chemical amendments (E.G., Reeve and Bower, 1960). However, such a method yields large quantities of highly saline drainage water which must be disposed of. The use of large quantities of chemicals as well as the discharge of drainage water highly charged with salts are becoming less compatible with today's farming strategy as well as water quality control objectives of most irrigated basins (Miyamoto and Mueller, 1994).

This project was proposed mainly to explore ways to manage sodium-induced problems with minimal uses of chemical amendments, both in maintaining irrigated production and in reclaiming sodium-affected soils. Specific research objectives included: i) Determine soil factors and crop residue effects on dissolution of soil CaCO_3 , and soil permeability, ii) Estimate chemical amendments needed to maintain permeability during initial leaching of sodium-affected soils, and iii) Evaluate the potential for removing sodium with crop residue and salt tolerant reclamation crops. In addition, the review comments provided by the BARD office indicated a need to carry out an additional review of the topic prior to entering the research phase.

7. Methodology and Results

1. Review of Sodic Soil Reclamation and Alkali Water Conditioning

This review was a response to the reviewer recommendation, and has focused on acid and acidulants. The general principle and the use of gypsum for reclamation had been reviewed earlier (Keren and Miyamoto, 1990). Results of this review are documented in an attached article (Miyamoto, 1998). In brief, this review points out; i) the targeted reduction in the use of chemical amendments may be achieved through enhanced dissolution of soil CaCO_3 , ii) soil permeability plays a critical role in maintaining proper salt balance as well as in leaching Na from sodic soils, and the effects of water quality on permeability warrant additional study, especially at salinity levels exceeding 1 dS m^{-1} , and iii) there are many indications that the quantities of amendments required can be reduced in sodium-affected sandy soils, and iv) existing reports on vegetative means of reclaiming sodic soils are in conjuncture.

2. Calcite Dissolution and Sodium Removal

This research topic was approached through a series of laboratory experiments. The first experiment utilized crushed calcite (44 to 105 μm) placed in a batch of water slowly stirred at 25C. The pH of the solution was maintained at 7.0, and the CO_2 partial pressure at the atmospheric level. The samples of the solution were drawn periodically from the batch, and were analyzed for EC (electrical conductivity), Ca, Mg, Na, K, Cl and HCO_3 . Results have shown that the initial dissolution rate of the crushed calcite particles were in the order of $1 \times 10^{-6} \text{ mmol cm}^{-2} \text{ sec}^{-1}$, and was reduced to $2.4 \times 10^{-8} \text{ mmol cm}^{-2} \text{ sec}^{-1}$ in about 10 hrs. The rate of dissolution was theoretically shown to increase in proportion to CO_2 partial pressures. Additional details are given in attached Report 1.

The second experiment was conducted in columns filled with a mixture of the calcite particles and 0.1 - 0.5 mm quartz sand. The column extended 12 cm in length, and contained the calcite particles at 45 g kg^{-1} . Distilled water was applied to the top of the sand columns with a pump at the application rates ranging from 1 to 140 cm hr^{-1} on the basis of the column cross-sectional area. The leachate from the columns was guided through a pH measuring port, then was captured in a fraction collector and was analyzed as above. Results have shown that the rate of the calcite particle dissolution increases roughly in proportion to the flow rates tested, which were 1 to 140 cm hr^{-1} . A theoretical consideration indicates that the rate of calcite dissolution is likely to be controlled by the concentration gradients which exist between the surface of the calcite particles and the mobile portion of the liquid phase. If the liquid phase is not mobile, the dissolution process ceases as the concentration gradient approaches zero. The dissolved salt concentration in the leachate averaged $0.30 \text{ mmol}_e \text{ L}^{-1}$ at a flow rate of 1 cm hr^{-1} and $0.35 \text{ mmol}_e \text{ L}^{-1}$ at 14 cm hr^{-1} . Additional details are shown in Report 1.

The third experiment used loamy loess soil (*Calcic Haploxeralf*) containing soil CaCO_3 at 9.4% by weight. The soil samples, pre-treated to have different ESP levels, were packed in plastic pipes, and leached with water having different CO_2 partial pressures. The leachate was analyzed as before, and the soil column was sectional for ESP analysis. Results of this study have shown that the rate of CaCO_3 dissolution increased from $5 \times 10^{-10} \text{ mmol cm}^{-2} \text{ sec}^{-1}$ to 1.6×10^{-9} and $3.0 \times 10^{-9} \text{ mmol cm}^{-2} \text{ sec}^{-1}$ with increasing CO_2 partial pressure from the atmospheric level to 2.4 and 4.8 kPa at a flow rate of 20 cm hr^{-1} . At a flow rate of 1.7 cm hr^{-1} , observed dissolution rates were $0.5 \times 10^{-10} \text{ mmol cm}^{-2} \text{ sec}^{-1}$ at the atmospheric CO_2 partial pressure, and $1.2 \times 10^{-10} \text{ mmol cm}^{-2} \text{ sec}^{-1}$ at 5 kPa.

These results indicate that CO_2 partial pressures affect CaCO_3 dissolution at a high flow range more so than at a low flow range. When the soil was Na-affected (ESP of 12 and 19%), however, the dissolution rates of CaCO_3 increased, especially at low flow rates ($< 1.7 \text{ cm hr}^{-1}$), and the effect of water flow rates became less apparent. The cation exchange sites might have acted as a sink for Ca. The replacement of Na has occurred mostly during the leaching process involving about 20 pore volumes. The steady EC values ranged from the lowest value of 0.1 dS m^{-1} at the atmospheric CO_2 level to as high as 0.3 dS m^{-1} at 5 kPa under the flow rate of 1.8 cm hr^{-1} . Additional details are given in Report 2.

The CO_2 partial pressure reported in cropped soils ranges from 3.5 to 10 kPa (Buyanovsky and Wagner, 1983; Elliott and McCalla, 1972; Robbins, 1986), although some higher values are reported in flooded rice fields. Assuming a CO_2 partial pressure of 5 kPa, the steady concentration of Ca, according to the result of this study, is 0.75 mmol L^{-1} (or 1.5 meq L^{-1}). This level of Ca concentration can hold sodicity of water below 4.0 at an assumed salinity of 0.5 dS m^{-1} (5 meq L^{-1}). However, at salinity of 1 dS m^{-1} , sodicity will approach near 10 at this level of Ca. The quantity of Ca which can be dissolved from calcareous soils appears to be an order of 30 g m^{-3} or 300 kg per ha per water application depth of 1 m. This quantity of Ca, equivalent to 1290 kg of gypsum can potentially replace 345 kg of exchangeable Na. The extent of CaCO_3 dissolution obtained in these experiments are substantially larger than previously recognized. A greater quantity of Ca can be released if crop residues are incorporated into the soils.

The last experiment was conducted in the presence of crop residue

3. Soil Permeability as Affected by Salinity and Sodicity

The effects of sodicity on soil structural stability and permeability have been studied for several decades, especially when salinity is lower than 1 dS m^{-1} (e.g., Shainberg and Letey, 1986; Keren and Singer, 1988). In this project, we focused on sodicity effects on water infiltration at salinity greater than 1 dS m^{-1} . In the study reported in Report 4, we measured soil aggregate stability and water infiltration rates when two clay loam soils (Vertic Torrifluvent and Typic Calciorthid) were subjected to irrigation with saline water ($> 1 \text{ dS m}^{-1}$) having the sodium adsorption ratio (SAR) up to 37. Aggregated fractions of soil particles less than $20 \mu\text{m}$ decreased logarithmically with decreasing salinity, but dispersion into individual clay particles ($< 2\mu\text{m}$) did not occur to any significant degrees. The use of saline water for irrigation caused only a limited reduction (15 to 25%) in sorptivity following repeated irrigation events. When water of low salinity was used following the use of saline water, however, the reduction in infiltration was extensive, as much as 66% in Torrifluvent, and 35% in Calciorthid. The measurement of hydraulic gradients indicated that the resistant to flow appeared in a depth less than 3 cm in Vertic Torrifluvent, and 7 cm in Calciorthid.

The second experiment, reported in Report 5 addressed a practical question of improving infiltration of water into moderately Na-affected soils. The experimental materials and methods used were the same as those of the first experiment, except for using water treated with CaCl_2 , urea-acid blend, NH_4 -polysulfide, and polyacrylamide. In addition, chopped dry sorghum leaves were incorporated into the soils to a depth of 2.5 and 5.0 cm at two rates, 7 and 14 Mg ha^{-1} . Application of inorganic amendments at rates up to 600 kg ha^{-1} helped maintain infiltration rates, irrespective of the compounds tested, except for NH_4 -polysulfide which provided somewhat higher rates of infiltration into initially dry soils. Polyacrylamide applied at 5 to 10 kg ha^{-1} was just as effective as the inorganic compounds, and sorghum leaves incorporation gave the best result, especially in Torrifluvent.

4. Amendments Required for Initial Leaching of Sodic Soils

This topic was approached in three stages; the first stage was to develop equations needed to describe salinity and sodicity effects on water infiltration into and drainage from sodic soils.

Results are documented in Report 6. The second stage dealt with a conceptual development necessary for estimating amendment requirements based on water infiltration and drainage characteristics, instead of the traditional idea to lower the exchangeable Na to a prefixed value (Report 7). The third and final stage was to test the workability of the idea (Reports 7 and 8).

For describing salinity and sodicity effects on water infiltration under continuous ponding, we first tested applicability of two-term infiltration equations. Infiltration parameters used such as sorptivity and hydraulic conductivity were then equated with salinity and sodicity. The empirical equation developed was found to provide a good estimate of salinity and sodicity effects on infiltration under continuous ponding (Report 6). The analysis was then extended to the cases involving intermittent application of leaching water (Report 7).

The infiltration equation developed above was then used to estimate the ESP necessary to obtain the necessary water intake within a described time period. Once the target ESP was evaluated the quantities and the type of amendments required were estimated with a mass balance equation considering a solubility and cation exchange reaction as proposed earlier (Miyamoto et al., 1975). An application of high concentration CaCl_2 solutions was found far superior to gypsum in improving water infiltration into clayey soils affected by Na. The proposed method of estimating the amendment required offers an option to the traditional method, and was consistent with the observations made during the outdoor lysimeters experiment documented in Report 8.

5. Impact of Live Plants on Reclamation

This topic was approached through an outdoor lysimeter experiment. Two saline sodic Entisols differing in texture (silt loam and silty clay loam) were packed into lysimeter columns made of large PVC pipes to a depth of 1 m. Half of the lysimeters columns was sodded with saltgrass (*Dischilis spicata*), and received broadcast applications of gypsum, mulching and/or water-application of calcium chloride. They were irrigated at three levels of salinity; 10, 25 and 50 $\text{mmol}_e \text{L}^{-1}$ in irrigation water for two growing seasons. Transplanted saltgrass seedlings grew rapidly and established solid stands during the first season. Yet, it had only a limited impact on drainage rates and removal of exchangeable Na, especially in Saneli silty clay loam with low permeability. These findings coincided with several earlier reports (e.g., Overstreet et al., 1951; Stroehlein et al., 1978).

The dissolution of CaCO_3 , enhanced by respiration seems to have been offset by the increase in sodicity associated with transpirational losses of soil water. This led to the situation where sodicity of the soils measured at termination was actually greater in sodded cases. This problem is pronounced when saline water is used for irrigation, and the use of gypsum or water-application of CaCl_2 at low concentrations could not alleviate the increase in sodicity caused by water-uptake. In order to enhance Na removal through irrigated cultivation of reclamation crops, irrigation may have to be performed to assure leaching fractions no less than those attained without live plants. Although vegetative means of reclaiming sodic soils are likely to be effective in coarse-textured sodic soils with low salinity (e.g., Robbins, 1986), additional quantitative studies are needed for assessing its application in saline sodic soils.

3. Scientific Implications

1. Dissolution of Soil CaCO_3

There has been considerable uncertainty about the magnitude of CaCO_3 dissolution under diverse soil conditions. The study report in Reports 1, 2 and 3 provided the accurate data and appraisal of the rate of CaCO_3 dissolution in soils, which are useful not only for assessing its contribution to reclamation and soil management, but also to the advancement of soil and environmental sciences in arid and semi-arid regions.

2. Infiltration Equations for Saline-Sodic Soils

There have been several attempts to develop equations which can be used to describe the impacts of salinity and sodicity on hydraulic conductivity and water infiltration. The formulation proposed in Reports 4 and 6 is the most comprehensive of this type, and can be used not only for assessing reclamation strategy, but also for analyzing soil and water management issues in salt-affected areas.

3. Impact of Vegetation on Saline Soil Properties

The results of the outdoor lysimeters experiment present a comprehensive picture of the

multiple roles that live plants play in soil and water systems. These data are useful not only for assessing their role in reclamation, but also for improving modeling of the soil-water systems in arid and semi-arid regions.

4. Practical Relevance

The entire project activities conducted are relevant to soil and water management practices in saline areas of the arid and semi-arid regions. Some of the applications may include; i) potential uses of crop residue for maintaining permeability of moderately Na-affected soils, ii) Effective and improved application of chemical amendments for initial leaching of sodic soils, and iii) Selective and rationale uses of vegetation and water management for reclamation.

5. Selected References

6. List of Publications

APPENDICES

1. Published Paper

Miyamoto, S., 1998. Use of Acid and Acidulants on Alkali Soil and Water. In "Handbook of Soil Conditioners". Wallace and Terry (Eds). Marcel Dekker INC. New York, NY.

Miyamoto, S., 1997. Changing opportunities for soil and water conditioning in irrigated land management. Sulf. Inst. J. 20:21-26.

2. Manuscripts in Preparation

1. Kinetics of Calcite Dissolution as Affected by Water Flow Velocity
2. Dissolution of Soil CaCO_3 and Na Replacement in Moderately Na-affected Soil
3. Effects of Crop Residue Incorporation on CaCO_3 Dissolution and Na removal
4. Aggregate Stability and Water Infiltration into Clay Loam as Affected by Saline Water Quality
5. Comparative Effects of Chemical Amendments and Crop Residues on Infiltration of Moderately Saline Water into Silty Clay Loam
6. Predicting Salinity and Sodicity Effects on Water Infiltration under Ponding
7. Estimating Chemical Amendments Required for Leaching Saline Sodic Soils
8. Reclamation of Saline Sodic Soils Involving Salt-Tolerant Grasses and Chemical Amendments

ISRAEL

Research report 1

KINETICS OF CALCITE DISSOLUTION AS AFFECTED BY WATER FLOW VELOCITY

Abstract

Better understanding the role of CaCO_3 dissolution in reclamation process may greatly improve efficiency of sodic calcareous soil reclamation. The dissolution of native calcium carbonate mineral in soil can continuously replenish calcium ions to soil. In order to simulate calcite dissolution, a pH-stat experiment at pH 7 and a series of leaching experiments of calcite-sand mixtures were conducted under the range of water flow velocities from 9.3 to 1407.1 mm h^{-1} .

The experimental results demonstrated that the dissolution rate of calcite was about two orders of magnitude greater in the pH-stat experiment than in calcite-sand mixtures leached by distilled water at low velocity. Under the pH-stat conditions, surface chemical reaction dominated calcite dissolution at pH 7; but under leaching conditions for calcite-sand mixtures, the calcite dissolution was controlled by diffusion mechanism even at very high pH, and its rate linearly increased with the water flow velocity.

The dissolution rates of calcite under two extreme cases, i.e., either surface reaction-controlled or diffusion-controlled mechanisms, were analytically described according to the elementary chemical reactions involved. An empirical hydrodynamic model for calcite dissolution was developed and tested for a wide range of leaching water fluxes. The observed and calculated results indicated that the model could satisfactorily predict calcite dissolution rate under leaching condition, and the prediction error was acceptable.

Introduction

Calcite dissolution mechanism depends on the conditions under which the dissolution takes place: 1) Under acid conditions ($\text{pH} < 4$), the dissolution is transport-

controlled process (i.e., diffusion rate-limiting step), and the rate depends on the diffusion speed of hydrogen ion and reaction products to or from solid particles (Berner and Morse, 1974; Plummer et al., 1978; Rickard and Sjöberg, 1983; Sjöberg and Rickard, 1984); and 2) Under alkaline conditions, the dissolution is considered as a surface reaction-controlled process (Berner and Morse, 1974; Plummer et al., 1978; Sjöberg, 1976). At the intermediate pH range, the calcite dissolution is possibly controlled by a more complicated kinetics (Rickard and Sjöberg, 1983; Sjöberg and Rickard, 1984), but so far this mechanism is not well understood.

The existing models that describe mineral dissolution or weathering can be divided into three categories: 1) Empirical models that are derived from diffusion. The mineral dissolution rate is expressed as a function of concentration difference or relative saturation, which is the first-order or higher order reaction depending on the property of the mineral itself (Lerman, 1979; Plummer, 1976; Rickard and Sjöberg, 1983); 2) Semi-mechanism models. The models are based on empirical formulas in conjunction with some theoretical consideration (e.g., rate constant etc.), the ionic concentration difference or the activity difference is used as the driving force (Berner and Morse, 1974; Jurinak et al., 1977; Lasaga, 1981). However, the distinction between two aforesaid types of models is arbitrary; and 3) Models based on reaction mechanisms. The net reaction rate is taken as the difference between all forward and backward reaction rates, and the rate is considered to be proportional to the exposed surface area of the mineral (Plummer et al., 1978; Sverdrup and Warfvinge, 1988; Warfvinge and Sverdrup, 1989). Nevertheless, in this type of models, some parameters are difficult or impossible to acquire at present.

A practical model that reasonably describes the process of calcite dissolution within a broad pH range is not available yet. Moreover, the influence of solution percolation velocity on calcite dissolution, which simulates the dissolution of soil calcite under leaching of natural rainfall or irrigation, hasn't well been established yet.

It is well known that the calcite dissolution rate depends on the rates of heterogeneous reactions at mineral surface as well as the hydrodynamic conditions around calcite particles. Almost all published experimental results were based on a stirred calcite - liquid system that used either a pH-stat method or a pH free drift

technique. It has been observed, however, that the dissolution rate of calcite or other Ca-minerals depends on the stirring rate or the flow velocity of aqueous solutions (Plummer et al., 1979; Sjöberg and Rickard, 1983; Suarez, 1983). Because of the low diffusion ability of reaction products in porous media under low leaching velocity, it is plausible that at $\text{pH} > 7$, calcite dissolution in porous media may be controlled by diffusion process rather than by surface reaction under certain hydrodynamic conditions. This hypothesis was tested in the present study.

The objectives of these experiments were 1) to evaluate the effect of water percolation velocity on the dissolution rate of calcite mineral; and 2) to develop a calcite dissolution model under leaching condition and test its validity.

Theory

Two geometric regions can be distinguished around calcite particle immersed in aqueous solution: 1) an inner water layer adsorbed on the calcite surface (the adsorption layer); and 2) an outer stationary water layer (the subsurface layer). These two regions are presented schematically in Fig. 2.1.

Surface reactions take place in the adsorbed water layer associated directly with the solid surface. The thickness of adsorbed layer is of one or two water molecules, and can be neglected compared with the thickness of the outer stationary layer. The reacting sites on the calcite surface are supposed to occupy only a small fraction of the total surface area. The chemical property of water in the adsorbed layer is different from that of bulk water. The ions in the adsorbed layer generally have a lower mobility than that in the bulk solution (Berner and Morse, 1974; Plummer et al., 1978; Sposito, 1984).

The thickness of the outer stationary layer depends on the hydrodynamic conditions in the bulk solution. Stirring rate, percolated water velocity as well as factors that may change hydrodynamic conditions (e.g., temperature, rheological characteristic of solution etc.) will determine the thickness of subsurface layer (Akratanakul et al., 1983; Sjöberg and Rickard, 1983). It is assumed that the ion concentration at the interface of the inner and outer layers is equal to that of the adsorbed inner layer, and the ionic concentration at the interface of the outer layer -

bulk solution is equal to that in the bulk solution (Fig. 2.2). The water flow velocity at the interface of the inner - outer layers is zero, whereas it is equal to that in the bulk solution at the interface of outer layer - bulk solution. The outer layer is a region in which ions can move freely from the adsorbed layer to the bulk solution or vice versa. The ionic movement perpendicular to the particle surface in the outer layer is controlled by diffusion, which is governed by ionic activity gradient in this layer.

Several steps are involved in a chemical reaction on a solid surface (Castellan, 1983). From diffusion of reactants to the solid surface, its adsorption and reaction on the surface, and to desorption of products from the surface and diffusion into the bulk solution is a sequential process. The rate-limiting step of calcite mineral dissolution is either surface chemical reaction or diffusion process (Berner and Morse, 1974; Plummer et al., 1978, 1979; Sjöberg and Rickard, 1984). Theoretically, when the surface reaction rate is faster than the diffusion rate through the outer stationary layer, the diffusion process across the outer layer is a "bottle-neck" region of overall chemical reactions, this situation can be defined as a diffusion-controlled process (Fig. 2.2a). In the diffusion control, it is assumed that the concentrations of reaction products in the inner layer reach equilibrium with calcite, and they decrease linearly in the outer layer with distance from calcite particle surface. On the contrary, when the reaction rate at the solid surface is slower than the diffusion rate in the outer layer, the dissolution process can be defined as a surface reaction-controlled mechanism. Under such conditions, the reaction products in the inner layer can be easily diffused into bulk solution, their ionic concentrations in the subsurface layer are supposed to be equal to that in the bulk solution (Fig. 2.2b). Since the chemical reactions involving in calcite dissolution determine net surface reaction rate, and the activity gradient of reaction products in the outer layer controls the diffusion rate, both rates may be approximately equal under some hydrodynamic conditions. At this point, the calcite dissolution is thought to be controlled by both surface reaction and diffusion process - a mixed kinetics. Obviously, at some special conditions, the dissolution rate-limiting step can be shifted from surface control to diffusion and vice versa as environmental hydrodynamic conditions change.

Two factors determine the characteristics of surface layer: 1) the thickness of subsurface layer, and 2) the difference of ionic activities between the inner layer and the bulk solution. Thus, the ionic activity gradient across the outer layer determines ion diffusion rate through it, and the external hydrodynamic condition greatly change the dissolution rate of calcite mineral.

Generally, the ions in the outer layer and in the bulk solution without stirring move at relatively slow rate under diffusion-driving force. When an external hydrodynamic force, e.g., a stirring or leaching, is exerted, the thickness of outer stationary layer decreases and the diffusion rate enhances due to increasing of ion activity gradient across the outer layer. Therefore, the diffusion control mechanism may change into chemical reaction control mechanism under this situation.

It is supposed that all chemical reactions occur in the adsorbed layer, then the reaction products diffuse through the outer layer into the bulk solution. The suggested chemical reactions involved in calcite dissolution are as follows:

1) Hydrogen attack reaction under acidic condition:

This is a fast reaction.

2) Carbonic acid attack:

The aqueous $\text{CO}_2 (\text{aq})$ is involved in calcite dissolution.

3) Calcite hydrolysis reaction:

This reaction is slower than the reaction presenting in Eq. 2.

Let k_i and k'_i ($i = 1, 2, 3$) be the forward and the backward reaction rate coefficients, respectively, for the reactions described in Eqs. 1 to 3. Based on Eq. 1, the calcite dissolution rate can be expressed as:

$$\left\{ \frac{d(\text{Ca}^{2+})}{dt} \right\}_n = k_1(\text{H}^+) - k'_1(\text{Ca}^{2+})(\text{HCO}_3^-)$$

where subscript n represents the net reaction rate; t is reaction time; and parenthesis refers to the ionic activity in the adsorbed layer.

Assuming that the H₂O activity in Eq. 2 is unity in an infinitely dilute solution, the calcite dissolution rate under carbonic acid attack can be expressed as:

$$\left\{ \frac{d(Ca^{2+})}{dt} \right\}_n = k_2(CO_2)(aq) - k_2'(Ca^{2+})(HCO_3^-)^2$$

Similarly, for Eq. 3:

$$\left\{ \frac{d(Ca^{2+})}{dt} \right\}_n = k_3 - k_3'(Ca^{2+})(HCO_3^-)(OH^-)$$

Supposing that all these three dissolution reactions occur simultaneously, the overall net reaction rate of calcite dissolution can be described as:

$$\begin{aligned} \frac{d(Ca^{2+})}{dt} &= [k_1(H^+) - k_1'(Ca^{2+})(HCO_3^-)] + [k_2(CO_2)(aq) - k_2'(Ca^{2+})(HCO_3^-)^2] \\ &\quad + [k_3 - k_3'(Ca^{2+})(HCO_3^-)(OH^-)] \\ &= [k_1(H^+) + k_2(CO_2)(aq) + k_3] - k_b(Ca^{2+})(HCO_3^-) \end{aligned}$$

... ... (4)

in which $k_b = k_1' + k_2'(HCO_3^-) + k_3'(OH^-)$; and all ionic activities refer to that in the adsorbed layer.

Eq. 4 is a general rate formula for calcite dissolution that may be used under a wide range of conditions. It is similar to the rate equation of Plummer et al. (1978) except the total backward rate coefficient k_b . Eq. 4 predicts that the calcite dissolution rate is enhanced when hydrogen ion and aqueous CO₂ activities increase, and it decreases as reaction product concentrations increase. Therefore, when a sink for reaction products exists (such as leaching process or adsorption by clays), a higher dissolution rate of calcite will be maintained.

$$\text{Let } R_f = k_1(H^+) + k_2(CO_2)(aq) + k_3$$

and

$$R_b = k_b(Ca^{2+})(HCO_3^-), \text{ Eq. 4 can be rewritten as:}$$

$$\frac{d(Ca^{2+})}{dt} = R_f - R_b \quad \dots \dots (5)$$

where R_f and R_b are the forward and the backward reaction rates of calcite dissolution, respectively.

If $R_f > R_b$, calcite mineral will dissolve; if $R_f < R_b$, the suspension solution will precipitate as calcite; and if $R_f = R_b$, the reaction solution remains at equilibrium with calcite.

Surface reaction rate-limiting mechanism:

In neutral to alkaline environments, calcite dissolution usually is limited by surface reactions (Plummer et al., 1978; Sjöberg, 1976). Under this situation, the diffusion rate through the outer layer is much faster than the net rate of surface reactions. The reaction products easily enter into bulk solution, and their concentrations in the inner layer are far less than that obtained at equilibrium. So, under surface reaction control, the backward reaction rate in the adsorbed layer can be ignored, and the thickness of the outer layer does not have any influence on calcite dissolution. Assuming that the ionic concentrations of reactants in the inner layer are equal to those in the bulk solution because of their fast diffusion to the solid surface under this situation (Plummer and Wigley, 1976), Eq. 4 can be reduced to:

$$\frac{d(Ca^{2+})}{dt} = k_1(H^+)_w + k_2(CO_2)(aq)_w + k_3 \quad \dots \dots (6)$$

where subscript w refers to ionic activities in the bulk solution.

Eq. 6 indicates that when the surface reaction is the rate-limiting step, only the solution pH and the CO_2 partial pressure are the two variables in the calcite dissolution rate equation.

The surface reaction rate-limiting step appears at pH value above 5.5 (Berner and Morse, 1974; Plummer et al., 1978; Sjöberg and Rickard, 1984). At this pH range, the pH in the bulk solution is mainly determined by the CO_2 partial pressure. Therefore, the H^+ ion term in the rate equation can be ignored, and Eq. 6 is reduced further:

$$\frac{d(Ca^{2+})}{dt} = a * p_{CO_2} + b \quad \dots \dots (7)$$

in which, a and b are constant coefficients; P_{CO_2} is the partial pressure of CO_2 gas in equilibration with aqueous $(CO_2)_{aq}$.

Eq. 7 shows that the dissolution rate of calcite depends linearly on the CO_2 partial pressure when surface reaction-controlled condition prevails. Many

experimental results supported this dependence (Plummer et al., 1978; Sjöberg, 1976; Sjöberg and Rickard, 1984). The dissolution rate of calcite as a function of CO₂ partial pressure was calculated by using the experimental data of Plummer et al. (1978), and the values are given in Fig. 2.3. The calcite dissolution rate linearly increased with the CO₂ partial pressure at the solution pH ≥ 6 ($R^2 = 0.968^{***}$). These data (Fig. 2.3) support the validity of Eq. 7.

Diffusion rate-limiting mechanism:

Under diffusion rate-limiting condition, the net surface reaction rate in the adsorbed layer is faster than the diffusion rate of ions through the outer stationary layer. The diffusion of reaction products from solid particle surface becomes rate controlling under given environment conditions. Hereafter we just discuss the special case that the diffusion ability of reaction products controls the calcite dissolution rate.

When chemical reactions reach an equilibrium state in the inner layer, the forward and the backward reaction rates of all elementary reactions must be equal according to the principle of microscopic reversibility.

$$k_1(H^+) = k'_1(Ca^{2+})(HCO_3^-)$$

$$k_2(CO_2)(aq) = k'_2(Ca^{2+})(HCO_3^-)^2$$

$$k_3 = k'_3(Ca^{2+})(HCO_3^-)(OH^-)$$

Let K_1 , K_2 , K_{sp} and K_w are equilibrium constants for the reactions $H_2CO_3^* = H^+ + HCO_3^-$, $HCO_3^- = H^+ + CO_3^{2-}$, $CaCO_3 = Ca^{2+} + CO_3^{2-}$, and $H_2O = H^+ + OH^-$, respectively. Thus:

$$k'_1 = \frac{k_1 K_2}{K_{sp}}, \quad k'_2 = \frac{k_2 K_2}{K_1 K_{sp}}, \quad \text{and} \quad k'_3 = \frac{k_3 K_2}{K_w K_{sp}}$$

The backward reaction rate in Eq. 4 becomes:

$$\begin{aligned}
R_b &= k_b * (Ca^{2+})(HCO_3^-) \\
&= \frac{k_1 K_2}{K_{sp}} * (Ca^{2+})(HCO_3^-) + \frac{k_2 K_2}{K_1 K_{sp}} * (Ca^{2+})(HCO_3^-)^2 \\
&\quad + \frac{k_3 K_2}{K_w K_{sp}} * (Ca^{2+})(HCO_3^-)(OH^-) \\
&= k_1 (H^+) \frac{(Ca^{2+})(CO_3^{2-})}{K_{sp}} + k_2 (H_2CO_3^*) \frac{(Ca^{2+})(CO_3^{2-})}{K_{sp}} \\
&\quad + k_3 \frac{(Ca^{2+})(CO_3^{2-})}{K_{sp}} \\
&= [k_1 (H^+) + k_2 (H_2CO_3^*) + k_3] \frac{(Ca^{2+})(CO_3^{2-})}{K_{sp}}
\end{aligned}
\tag{8}$$

The saturation index, Ω , can be defined as

$$\Omega = IAP/K_{sp} \tag{9}$$

where IAP is the ionic activity product of calcite in solution. When $\Omega < 1$, calcite dissolves; when $\Omega > 1$, calcite precipitation occurs and at equilibrium, $\Omega = 1$.

Introducing Eqs. 8 and 9 into Eq. 4 yields:

$$\frac{d(Ca^{2+})}{dt} = [k_1 (H^+)_s + k_2 (CO_2)(aq)_s + k_3](1 - \Omega_s) \tag{10}$$

where the subscription s refers to the ionic activity in the inner layer; and $(1 - \Omega_s)$ is the saturation deficiency there.

Eq. 10 indicates that under diffusion rate-limiting mechanism, the dissolution rate of calcite depends not only on the forward reaction rate but also on the saturation deficiency of calcite in the adsorbed layer. The calcite dissolution rate approaches to zero when the ionic concentrations of reaction products in the bulk solution are saturated in respect to calcite.

Under diffusion control, the calcite dissolution rate depends on the activity gradient of reaction products through this layer. At a given hydrodynamic condition, the thickness of subsurface layer is steady, thus the ionic activities of reaction products in the bulk solution determine the gradient since the ion concentration at the interface between the adsorbed and the outer layers is constant. Therefore, the saturation

deficiency in the adsorbed layer can be approximately replaced by that in the bulk solution.

Eq. 10 can be rewritten as

$$\frac{d(Ca^{2+})}{dt} = a'[k_1(H^+)_s + k_2(CO_2)(aq)_s + k_3](1 - \Omega_w) \quad \dots \dots (11)$$

in which, a' is a coefficient; Ω_w refers to saturation in the bulk solution; and the other symbols have been defined above.

As mentioned previously, an equilibrium concentration with respect to calcite in the adsorbed layer is prevailed under diffusion rate-limiting mechanism at a given reaction condition, so the forward reaction rate should be a constant.

Thus, Eq. 11 can be further reduced into:

$$\frac{d(Ca^{2+})}{dt} = a''(1 - \Omega_w) \quad \dots \dots (12)$$

where a'' is a coefficient; and the other symbols have the same meanings as above.

Eq. 12 shows that under diffusion rate-limiting situation, the dissolution rate only depends on the saturation deficit of the ion activities of reaction products. Many experimental results have verified the validity of this equation (Berner and Morse, 1974; Plummer and Wigley, 1976; Rickard and Sjöberg, 1983; Sposito, 1994).

So far, the influence of calcite surface area is ignored. If the surface area of calcite per solution volume is lower than some critical value, its particle size and content in aqueous solution will affect the dissolution rate of calcite. Under this situation, the actual dissolution rate should be lower than the predicted value, and the reaction rate increases proportionally with the increase of calcite surface area. So, a factor that represents the influences of particle size and content of calcite should be included in the rate equation, Eqs. 4, 6 and 11 are modified, respectively, as:

$$\frac{d(Ca^{2+})}{dt} = c_0\{[k_1(H^+)_s + k_2(CO_2)(aq)_s + k_3] - k_b(Ca^{2+})_s(HCO_3^-)_s\} \quad \dots \dots (4a)$$

$$\frac{d(Ca^{2+})}{dt} = c_0[k_1(H^+)_w + k_2(CO_2)(aq)_w + k_3] \quad \dots \dots (6a)$$

$$\frac{d(Ca^{2+})}{dt} = c_0a'[k_1(H^+)_s + k_2(CO_2)(aq)_s + k_3](1 - \Omega_w) \quad \dots \dots (11a)$$

where c_0 is a coefficient representing the influence of surface area of solid particles in solution, and $c_0 \leq 1$. It is a function of the surface area of calcite per solution volume. Subscripts s and w refer to the adsorbed layer and the bulk solution, respectively.

An empirical rate formula for calcite dissolution:

When calcite dissolution is controlled by chemical reactions on solid particle surface, its dissolution rate is considered to be independent on hydrodynamic conditions. On the contrary, the influence of hydrodynamic conditions on dissolution rate should be taken into consideration when the dissolution is controlled by diffusion process. The rate of calcite dissolution in natural environments may be influenced by both transport and surface-reaction process (Plummer and Wigley, 1976). The rate-limiting step may change with reaction time, solution pH, and environmental hydrodynamic conditions. Usually it is difficult to, or even impossible to distinguish which mechanism controls the overall dissolution process at a given time and reaction condition.

When the surface reaction rate and the diffusion rate are equal, both processes are simultaneously equivalently important in determination of dissolution rate. Therefore, the rate equation of calcite dissolution under the mixed rate-limiting mechanism is approximately postulated as:

$$\frac{d(Ca^{2+})}{dt} = c_0 b' [k_1(H^+) + k_2(CO_2)(aq) + k_3](1 - \Omega) \quad \dots \dots (13)$$

where b' is a coefficient, and the all other symbols have been defined above. The ionic activities are referred to those in the bulk solution, and the subscript w is omitted for the sake of convenience.

This empirical equation is a combination of Eq. 6 and Eq. 12, which represents the forward reaction rate from chemical reaction-controlled mechanism and the saturation deficit term from diffusion-controlled mechanism, respectively.

Dissolution rate equation under leaching condition:

A leaching process not only affects the thickness of subsurface layer but also removes reaction products successively, therefore it increases the gradient of ionic activities in the subsurface layer and subsequently the diffusion ability of reaction products. Under high pH and low CO_2 partial pressure in stirring systems, the calcite

dissolution rate in the majority of published results is directly depended on the flow velocity of aqueous solution (Liu and Dreybrodt, 1997; Sjöberg and Rickard, 1983) rather than on the saturation deficit term $1 - \Omega$. Thus, under leaching condition, Eq. 13 can be changed into:

$$\frac{d(Ca^{2+})}{dt} = c_0 \alpha [k_1(H^+) + k_2(CO_2)(aq) + k_3] V^n$$

$V \neq 0 \quad \dots \dots (14)$

where α and n are coefficients; and V is water flow velocity. The other symbols have been defined above.

Eq. 14 indicates that when leaching process approaches steady state in respect to solution pH and aqueous CO_2 concentration, the dissolution rate of calcite is a power function of flow velocity with an exponent n .

Calcite dissolution rate under various hydrodynamic conditions:

The calcite dissolution is affected by both aqueous chemistry environments (such as solution pH and aqueous CO_2 concentration) and hydrodynamic conditions (such as the speed and placement of stirring impeller, and the hydrodynamic characteristics of reaction vessel etc. (Sjöberg and Rickard, 1983)). In order to describe the calcite dissolution process more reasonably and accurately, a rate equation for calcite dissolution is supposed to be composed of two parts: one part describes the calcite dissolution that is caused by molecular diffusion at the given aqueous chemistry environments; and the other one represents the dissolution that derives from convection under various hydrodynamic conditions. Thus, a general calcite dissolution rate equation under leaching condition can be suggested as:

$$\begin{aligned} \frac{d(Ca^{2+})}{dt} &= c_0 [k_1^0(H^+) + k_2^0(CO_2)(aq) + k_3^0](1 - \Omega) \\ &+ c_0 \alpha [k_1^v(H^+) + k_2^v(CO_2)(aq) + k_3^v] V^n \quad \dots \dots (15) \\ &= c_0 \{ R_0 + \alpha [k_1^v(H^+) + k_2^v(CO_2)(aq) + k_3^v] V^n \} \end{aligned}$$

in which, all ionic activities refer to the bulk solution; $R_0 = [k_1^0(H^+) + k_2^0(CO_2)(aq) + k_3^0](1 - \Omega)$, which represents the dissolution rate at a stationary condition; k_i^0 and k_i^v ($i = 1, 2$, and 3) refer to the forward reaction rate

coefficients at the water flow velocity of zero and V , respectively; and the other symbols have been defined above.

At present, all available data in literature for the forward reaction rate coefficients k_1 , k_2 and k_3 were determined at some stirring speed by using a magnetic stirrer. The investigators employed various stirring speeds and locations of impeller, which led to different rate coefficient values (Amrhein, 1984). These values only can be used to simulate the calcite dissolution under the same system conditions as which they were obtained in.

Materials and Methods

Crystal Iceland Spar (49E1600, Ward's Natural Science Establishment, Inc., NY) was used in this study. The Mg^{2+}/Ca^{2+} mole ratio in this mineral was about 0.005.

The calcite was crushed and sieved to obtain a particle size range of 44 - 105 μm , then they were washed with 0.01 M HCl solution under vigorous stirring. About 5% of the calcite mass were dissolved during the acid washing. This procedure was done in order to minimize the presence of highly reactive, finer particles of calcite in the sample. After that, the calcite particles were washed with distilled water to remove excessive acid and resultant salts. The washed particles were dried in an oven at 50°C and stored at room temperature. The specific surface area of Iceland Spar sample was evaluated from the particle size, and its geometric average value was 32.5 $m^2 kg^{-1}$.

Total 4 treatments, i.e., Treatments A, B, C and D were employed in pretreatment and their effects were compared. The Treatment C was adopted in this research and it was treated by 0.01 M HCl solution for about 5% dissolution of initial calcite mass. The Treatment A (control) was not disposed by acid solution and it only passed through a sieve of 44 - 105 μm and was washed by distilled water. The Treatment B was underdisposed by 0.01 M HCl only for about 2% dissolution of original calcite sample mass, and the Treatment D was overdisposed by 0.1 M concentrated HCl solution.

pH-stat experiment:

The pH-stat technique was used to study the dissolution rate of calcite at pH 7 under the CO₂ partial pressure of 0.035 kPa.

A reaction vessel was filled with 2 liters of distilled water and immersed in a water bath at constant temperature of 25°C. 1.5 grams of Iceland Spar sample were put into the reaction vessel. The suspension solution of calcite was gently stirred by a magnetic stirrer at a constant speed, and the grinding effect of the magnet could be ignored (Sjoberg, 1976). The solution pH in the reaction vessel was automatically adjusted at pH 7 by an auto-titration meter (TTA80 Titration Assembly, Denmark) using 0.1 M HCl. The reaction solution was bubbled throughout the experiment with a commercial CO₂-N₂ mixture gas whose CO₂ partial pressure was 0.035 kPa (100 kPa total pressure).

Solution samples of 8 mL each were taken at different time intervals, and the total volume of samples drawn from the reaction vessel was less than 5% of the initial solution volume. The electrical conductivity of the sample was determined by an EC meter (TH-2400, El-Hamma). The concentrations of Ca²⁺ and Mg²⁺ in the sample were analyzed by the atomic absorption spectrophotometry (Perkin-Elmer 460); the concentrations of Na⁺ and K⁺ were determined by a flame photometer (Corning 400); the Cl⁻ concentration was determined by an auto-digital chloridometer (Haake Buchler); and the HCO₃⁻ concentration was determined by the standard acid titration method.

The dissolution rate of calcite was calculated by following Ca²⁺ concentration in bulk solution, and it also was obtained from the amount of added HCl solution in the pH-stat experiment (Plummer et al., 1978).

Leaching of calcite-sand mixtures:

The preparation of calcite sample was the same as that for the pH-stat experiment. Quartz sand grains with a diameter range of 0.1 - 0.5 mm were successively washed by concentrated hydrochloric acid followed by distilled water until the leachate EC reached the value of distilled water.

The calcite-quartz sand mixtures were packed in a plexiglass column of 100 mm high and 52 mm in diameter at bulk density of 1.65 Mg m⁻³. Two calcite contents

of 45 and 90 g kg⁻¹ were studied. The total height of calcite-quartz sand mixtures in the column was 75 mm. A filter paper was placed respectively at the bottom and at the top of calcite-sand mixture.

The columns were immersed in a water bath at the constant temperature of 25°C. The calcite-sand mixtures were saturated with distilled water from the bottom of the column, and the flow direction was changed from the top to the bottom after saturation has been reached. The distilled water as a leaching solution was equilibrated with CO₂-N₂ mixed gas that had a constant CO₂ partial pressure of 0.035 kPa (100 kPa total pressure). Several water flow velocities in the range of 10 - 1400 mm h⁻¹ were tested by using a peristaltic pump.

The leachate pH was measured during leaching process before it was exposed to the atmosphere. The leachate was collected by a fraction collector in tubes, and the solution volume in each tube was measured. The EC and Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, and HCO₃⁻ concentrations in the leachate were determined as described above. All experimental treatments were in duplicate.

Results and Discussion

pH-stat experiment:

The calcite dissolution rates at pH 7, calculated respectively from the Ca²⁺ concentration in bulk solution and from the added HCl amount, are shown in Fig. 1.4 under the CO₂ partial pressure of 0.035 kPa and 25°C. The rates from both calculation methods were consistent. The dissolution rate decreased sharply during the first couple hours and reached to a steady value of about 3.87*10⁻⁷ mol m⁻² s⁻¹ after 5 hours. The fast drop of dissolution rate is probably due to the existence of highly reactive finer particles. A plot of Ca²⁺ concentration in solution against the square root of reaction time (data not shown) produced a straight line with a great correlative coefficient (R² = 0.984***), so the rate reduction with the reaction time follows the parabolic law (Lerman, 1979).

Supposing all involved experiments in this research have similar hydrodynamic conditions to that the reaction rate coefficients were measured, the following values of rate coefficients are applied to predict the dissolution rate of calcite: k₁ = 5.1*10⁻⁴ m s⁻¹

and $k_2 = 3.45 \times 10^{-7} \text{ m s}^{-1}$ (Plummer et al., 1978); $k_3 = 2.2 \times 10^{-10} \text{ m s}^{-1}$ (Amrhein, 1984). At solution pH 7 and CO_2 partial pressure 0.035 kPa, there was a good agreement between the observed and the predicted dissolution rates from Eq. 6 that is deduced from the surface chemical reaction rate-limiting mechanism (Fig. 1.4). The ratio of the predicted to the measured steady dissolution rates was equal to 1.43. Thus, Eq. 6 is valid to describe calcite dissolution at surface reaction rate-limiting step.

The calcite dissolution rate in the present study and those published in literature under similar conditions are listed in Tab. 2.1 at low CO_2 partial pressure, high solution pH and experiment temperature of about 25°C . Their predicted dissolution rates calculated by Eq. 13 (assuming $c_0 = 1$ and $b' = 1$) also are given in Table 1.1. A wide range of dissolution rates (10^{-5} - 10^{-9} orders of magnitude, $\text{mol m}^{-2} \text{ s}^{-1}$) existed among the measured values. It is evident that the agreement between the predicted and the observed dissolution rates was not very good (Tab. 1.1). The ratio of the predicted to the observed rates ranged from 0.03 to 34.2. Nevertheless, as compared with the wide difference among the observed dissolution rates themselves under similar dissolution conditions, the prediction accuracy of Eq. 13 is acceptable.

Leaching of calcite-sand mixtures:

1. Effluent pH:

When the Iceland Spar - sand mixtures were leached with distilled water equilibrated with the CO_2 partial pressure of 0.035 kPa, the effluent pH rapidly rose with the leaching volume at the beginning of the leaching process as a result of calcite hydrolysis (Fig. 1.5). The effluent pH increased more than 2 pH units during the whole leaching process. The exposed -Si-OH function group on silica surface can readily dissociate proton ions into solution in alkaline environment, and hence counteracts the further raise of solution pH. After the hydroxyl function group on the silica surface gets equilibrium with the solution pH, no more protons from silica surface are released into the solution, so the leachate pH reaches a steady value at about 10 pore volumes of effluent. A steady effluent pH as high as 9.5 - 10.2 is similar to the theoretical calculation value of 9.9 in a CaCO_3 - water system without CO_2 gas phase (Butler, 1982), which infers that except the initial stage of leaching process, there is no dissolved aqueous CO_2 involving in calcite dissolution at the bottom section of calcite -

sand columns, the leaching of the column is an approximately close system about CO_2 phase.

When the water flow velocity was very low, the leachate pH abruptly increased with it. Then it maintained a constant until the flow velocity up to 1407 mm h^{-1} (Fig. 1.6). The maximum increment of effluent pH in the tested range of water flow velocity is about 0.7 pH units. Under the diffusion rate-limiting mechanism of calcite dissolution in porous media which will be demonstrated below, diffusion ability increases as water flow velocity increases, hence calcite hydrolysis is augmented and in turn the effluent pH raises with the flow velocity (Fig. 1.6). The thickness of subsurface layer (Fig. 1.1) decreases along with the increase of water flow velocity, however it becomes more and more difficult to be thinned by the flow velocity because of the increased resistance near solid surfaces. So the effect of flow velocity is smaller and smaller on the diffusion ability and subsequently the leachate pH. Moreover, a slight increase of leachate pH with the further increasing of flow velocity probably is buffered by the function group on silica surface. Therefore, after the flow velocity is bigger than some threshold, the leachate pH will keep steady and is independent on water flow velocity. This threshold of water flow velocity didn't be exactly measured in this study, it probably is about $50 - 100 \text{ mm h}^{-1}$ inferred from present available observed data of effluent pH.

2. Saturation extent in leachate:

The solution pH is a result of overall chemical reactions. It determines the proportion of HCO_3^- to CO_3^{2-} in solution (Lindsay, 1979), which in turn affects the saturation index of leachate with respect to calcite in large extent and subsequently governs the backward reaction rate of CaCO_3 dissolution during calcite dissolution process.

The experimental data demonstrated that the saturation index of effluent with respect to calcite increased with the leaching volume (Fig. 1.7). At the initial stage of leaching, the activity product of Ca^{2+} and CO_3^{2-} in leachate was below the solubility product of calcite. It became supersaturated after about 10 PV and then gradually approached to a steady value. During the whole leaching process, the CO_3^{2-} concentration in solution increases more than 20 times with the rise of solution pH

(Fig. 1.5); whereas, at the same time, the calcium concentration in solution released from calcite dissolution reduces much less than this extent. So, the ionic activity product of leachate increases with leaching. After the solution pH gets steady, the saturation index of leachate finally tends to a steady value in respect to calcite under the flow velocities of $9.2 - 18.3 \text{ mm h}^{-1}$ and calcite contents of $49 - 91 \text{ g kg}^{-1}$.

The steady saturation index in leachate versus the water flow velocity is shown in Fig. 1.8 for calcite content of 91 g kg^{-1} . The saturation index increased with the water flow velocity, and the ionic activity product of calcite increased from 50% to 200% of solubility product as the flow velocity increased from 9.2 mm h^{-1} to 1407 mm h^{-1} . When the flow velocity is low, the saturation index in leachate increases rapidly with the flow velocity as a result of increased pH. After the flow velocity is above a critical value of about $50 - 100 \text{ mm h}^{-1}$, the saturation index continues to increase with water flow velocity but at very little gradient. These results suggest that $\Omega \rightarrow 1$ when water flow velocity approaches to zero (Fig. 1.8), that is, a saturated leachate maybe can be obtained at equilibrium status. The supersaturated leachate is probably due to the inhibition of calcite precipitation in moving solution with a short residence time.

By comparing Fig. 1.7 with Fig. 1.5 as well as Fig. 1.8 and Fig. 1.6, it can be concluded that the saturation index of leachate mainly is determined by the leachate pH because of their similar behaviour against the leaching volume and water flow velocity.

3. Effluent EC and solution concentration composition:

When calcite-sand mixtures were leached with distilled water, the effluent EC sharply decreased with the leaching volume at the beginning of the experiment due to the depletion of highly reactive finer calcite particles and the increasing of solution pH. It usually became steady within $5 - 10 \text{ PV}$.

The experimental results indicated that the EC in effluent almost did not change with the water flow velocity, and it was about 0.036 dS m^{-1} regardless of calcite content and water flow velocity. Therefore, the surface area of calcite and the residence time of elemental solution volume in the columns are enough to reach a steady electrolyte concentration. The total electrolyte concentration in leachate is determined by solubility property of dissolving mineral within the tested range of flow velocity in this research.

The $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentration and carbonate alkalinity $\text{HCO}_3^- + \text{CO}_3^{2-}$ were the two major ion groups in the leachate. The experimental data demonstrated that the electrostatic charge of $\text{HCO}_3^- + \text{CO}_3^{2-}$ was 45% higher than that of $\text{Ca}^{2+} + \text{Mg}^{2+}$ at the initial stage of leaching, then their difference declined to less than 10% after leaching of 40 pore volumes. This result suggests that among all possible chemical reactions involving in calcite dissolution under leaching of calcite-sand mixture leached by distilled water, the carbonic acid attack is probably the dominant one. Only under this situation, is the equivalent concentration of carbonate alkalinity equal to that of divalent cations. Before leaching solution enters the column of calcite-sand mixtures, the carbonate alkalinity in the leaching solution, which is dissolved from the atmospheric CO_2 gas, is $2.04 \times 10^{-3} \text{ mmol}_e \text{ L}^{-1}$. Its contribution to the carbonate alkalinity in leachate is very small and is less than 0.6% at calcite content of 91 g kg^{-1} , this can't explain the excessive alkalinity of about 10% - 45% over the concentration of divalent cations. The bigger concentration of carbonate alkalinity than Ca^{2+} in effluent in the present experiment perhaps is a result of the chemical reaction of aqueous CO_2 with hydroxyl ions at the high pH condition (Lasaga, 1981).

Magnesium content in the calcite used in this experiment was very low, and $\text{Mg}^{2+}/\text{Ca}^{2+}$ mole ratio was only 0.005. When a leaching process began, the Mg^{2+} to Ca^{2+} molar concentration ratio in the leachate was very high, and usually it was as high as 0.7 - 0.8. It gradually decreased to about 0.05 at the 80 PV, but it still is 10-fold of that found in stoichiometric composition of the calcite. This incongruent dissolution phenomenon also was reported by Bratter et al (1972) for magnesium calcite and dolomite dissolution. Although its reason is difficult to explain, this phenomenon is common in nature (Bohn et al., 1985).

The Na^+ , K^+ and Cl^- were minor ions in leachate, and their concentrations in leachate were rather low. The Na^+ concentration in the leachate usually was $0.02 \text{ mmol}_e \text{ L}^{-1}$, its charge equivalent fraction was less 0.03. All of them derive from trace impurities in calcite composition. Analysis about variation of ionic concentrations in leachate show both K^+ and Cl^- are from soluble salt of potassium chloride incorporated in mineral structure and they are easily released into effluent. Although K^+ content in calcite is rather low (the $\text{K}^+/\text{Ca}^{2+}$ mole ratio in the mineral composition is 0.035), the

extremely fast dissolution kinetics of KCl deserves to pay enough attention during experiment process.

4. Calcite dissolution kinetics:

The calculated results demonstrated that the dissolution rate of calcite decreased with the leaching volume (data not shown). Its variation tendency is similar to that of leachate EC during leaching process.

The steady dissolution rates of calcite, together with the prediction values from Eq. 14 under assuming $c_0 = 1$ and $\alpha = 0.515$, versus the water flow velocity are plotted in Fig. 1.9 at two calcite contents of 49 and 91 g kg⁻¹. Under the leaching of calcite-sand mixtures, the higher was the water flow velocity, the greater was the dissolution rate, which verifies the above theoretical analyses that the leaching process reduces the thickness of subsurface layer and thereby enhances calcite dissolution. Because the dissolution rate of calcite linearly increases with the leaching velocity ($R^2 = 0.9996^{***}$) (Fig. 1.9), the exponent n in Eq. 14 should be 1 under the present experimental conditions. That the n value is bigger than the theoretical value of 0.5 at diffusion condition (Sjoberg and Rickard, 1983) shows a greater dependence of calcite dissolution in porous media on flow velocity. It can be concluded from these calculated results that the calcite dissolution in porous media is governed by diffusion process under leaching situation rather than by surface chemical reaction although the solution pH is very high (9.5 - 10.2) (Fig. 1.6). When the leaching velocity increased from 18 mm h⁻¹ to 1407 mm h⁻¹, the dissolution rate increased approximately two orders of magnitude, which is nearer to that in pH-stat experiment at pH 7 (Tab. 1.1). Therefore, with the further increase of flow velocity, it is possible that the rate-limiting step of calcite dissolution in porous media may change to surface reaction from diffusion after the subsurface layer is thinned sufficiently.

An excellent agreement between the predicted and the measured values existed within the whole tested range of flow velocity (Fig. 1.9), which verifies the validity of Eq. 14. The ratio of the predicted to the observed values was among 0.55 to 1.37, and their discrepancy was slightly greater at low flow velocity than at high velocity (Tab. 1.1).

The dissolution rate of calcite at the flow velocity of 18 mm h^{-1} was about 2 orders of magnitude lower than that obtained by pH-stat experiment at $\text{pH} = 7$ (Tab. 1.1). Though a high solution pH (≈ 10) is a factor for so low a dissolution rate under leaching condition, it is too high to play any obvious role (that is, hydrogen ion attack) on calcite dissolution (Plummer et al., 1978; Sjöberg, 1976). The most possible reason maybe is due to different experimental methods. It was reported that the difference of calcite dissolution rates examined respectively by the pH-stat experiment and the free-drift experiment almost was two orders of magnitude at similar experimental conditions in near neutral aqueous solution (Plummer et al., 1978). Different experiment techniques and apparatus conditions will result in different dissolution environments. Besides the low contact area and short contact time between calcite particles and solution phase, the tortuous pore passage in calcite-sand mixtures should be responsible for such a low dissolution rate because of its unfavourable effect on diffusion of reaction products. A low diffusion ability of reaction products caused by longer diffusion passage and non-mobile water body in blocked pores possibly is a main factor for the formation of nonchemical rate-limiting mechanism.

Due to hydrodynamically poor-defined experimental conditions and the sparse solubility of calcite, considerable uncertainty is involved when calcite dissolution is studied whether in laboratory or under natural environment situation. This may result in great disagreement among the measured dissolution rates and a large discrepancy between the observed and predicted values. Although the influence of stirring speed on the dissolution rate of calcite is unnoticeable at high pH (≥ 5) in aqueous solution (Plummer et al., 1978), leaching velocity does play a significant role on calcite dissolution in porous media by improvement of diffusion ability. Hydrodynamic condition is an important environmental factor on calcite dissolution in some specific situations.

There are no available values about forward rate coefficients in Eq. 15 both at the stationary and the moving systems, so application of Eq. 15 seems to be impossible for the time being. However, it is certain that Eq. 15 is a more reasonable expression about calcite dissolution, and it is expected to improve the prediction precision of calcite dissolution. Therefore, a systematic investigation about values of rate

coefficients in Eq. 15 is imperative. The calcite dissolution rate R_0 under non-leaching situation was about $1.63 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ that is estimated from the present leaching experiment about calcite-sand mixtures when the water flow velocity approaches zero.

Conclusions

The dissolution rate of Iceland Spar at pH 7 followed the parabolic law along with the reaction time, and its steady rate was two orders of magnitude bigger than that from leaching of calcite-sand mixtures at the low flow velocity.

Under the leaching situation of calcite-sand mixtures, the dissolution rate of calcite was linearly directly proportional to the water flow velocity, and its rate-limiting step was diffusion-controlled rather than chemical reaction-controlled. The leachate pH kept steady in the great majority of tested velocity range except at very low flow velocity, where it increased rapidly. The leachate EC did not change with the leaching velocity, and it was about 0.036 dS m^{-1} under the atmospheric CO_2 partial pressure. Slightly supersaturated state of leachate with respect to calcite appeared in the whole tested range of flow velocities, which was mainly controlled by the leachate pH rather than the calcite dissolution rate. The inhibition of calcite precipitation in moving solution possibly was the main reason of supersaturation appearance in leachate.

A semi-empirical rate model, which came from an empirical combination of two extreme cases, that is, the chemical reaction-controlled mechanism and the diffusion-controlled mechanism, generally could describe the dissolution process of calcite. It had relative high prediction ability, and its prediction error was acceptable.

Under the leaching of calcite-sand mixtures, a hydrodynamic model about calcite dissolution was developed and tested. The results showed that it could satisfactorily explain and predict the dissolution process of calcite under leaching condition, and the prediction precision was excellent.

Table 1.1 Comparison about dissolution rates of calcite minerals at high solution pH, low CO₂ partial pressure and about 25°C

No.	pH	Pco ₂	Temper -ature	Mineral identity	Specific surface area	Measured rate	Predicted rate [†]	Rate ratio [‡]	References	Note
		kPa	°C		m ² kg ⁻¹	mol m ⁻² s ⁻¹	mol m ⁻² s ⁻¹			
1	7.0	0.035	25	Iceland Spar	32.5	3.87*10 ⁻⁷	5.53*10 ⁻⁷	1.43	This study	Ω [§] = 0.064, initial conc. of Iceland Spar was 0.75 g L ⁻¹
1a							1.41*10 ⁻⁶	3.64		
2	10.2	0.035	25	Iceland Spar	32.5	1.54*10 ⁻⁹	2.10*10 ⁻⁹	1.37	This study	Leaching of calcite-sand mixture with calcite content of 91 g kg ⁻¹ at water flow velocity of 18.3 mm h ⁻¹
3	10.2	0.035	25	Iceland Spar	32.5	1.64*10 ⁻⁷	1.61*10 ⁻⁷	0.98	This study	Leaching of calcite-sand mixture with calcite content of 91 g kg ⁻¹ at flow velocity of 1407 mm h ⁻¹
4	7.0	0	25	Iceland Spar	9.7	2.51*10 ⁻⁶	5.20*10 ⁻⁷	0.21	Plummer et al., 1978	Assuming Ω = 0.05, pH-stat experiment
5	7.0	3.05	25	Iceland Spar	9.7	5.01*10 ⁻⁸	9.06*10 ⁻⁸	1.81	Plummer et al., 1978	Assuming Ω = 0.9, free-drift experiment
6	7.4	0.25	25	Fisher reagent CaCO ₃	250	2.12*10 ⁻⁸	7.24*10 ⁻⁷	34.2	Berner and Morse, 1974	Ω = 0.52, phosphate concentration was 1.6 μmol L ⁻¹ , in sea water

Table 1.1 Comparison about dissolution rates of calcite minerals at high solution pH, low CO₂ partial pressure and about 25°C

(continued)

No.	PH	Pco ₂	Temper -ature	Mineral identity	Specific surface area	Measured rate	Predicted rate [†]	Rate ratio [‡]	References	Note
		kPa	°C		m ² kg ⁻¹	mol m ⁻² s ⁻¹	mol m ⁻² s ⁻¹			
7	7.3	0.3	25	--	--	2.51*10 ⁻⁸	5.77*10 ⁻⁷	23.0	Morse's data from Plummer et al., 1979	Ω = 0.62, in sea water
8	9.8	0	25	Iceland Spar	Powder	1.00*10 ⁻⁵	9.62*10 ⁻⁷	0.10	Rickard & Sjoberg, 1983	Ω = 0.34, in 0.7 M KCl solution
9	9.8	0	25	Iceland Spar	Powder	8.20*10 ⁻⁶	3.06*10 ⁻⁷	0.04	Rickard & Sjoberg, 1983	Ω = 0.79, in 0.1 M KCl solution
10	8.0 - 10.1	0	20	Reagent grade CaCO ₃	370	1.40*10 ⁻⁵	1.28*10 ⁻⁶	0.09	Sjoberg, 1976	Ω = 0.12, in 0.7 M KCl solution
11	6.6	0.035	22±1	Iceland Spar	9	9.07*10 ⁻⁶	6.29*10 ⁻⁷	0.07	Kachanoski et al., 1992	Ω = 1.3*10 ⁻⁵ , initial conc. of Iceland Spar was 0.3 g L ⁻¹
12	9.2	0.035	22±1	Iceland Spar	9	1.51*10 ⁻⁵	5.00*10 ⁻⁷	0.03	Kachanoski et al., 1992	Ω = 8.9*10 ⁻⁴ , initial conc. of Iceland Spar was 1 g L ⁻¹

Note: † predicted values using Eq. 13 except No. 1 (using Eq. 6), No. 2 and No. 3 (using Eq. 14); ‡ ratio of the predicted to the measured dissolution rates; § saturation index with respect to CaCO₃.

Fig. 1.1 Diagram of the inner water layer adsorbed on calcite particle surface, outer stationary water layer and bulk solution for calcite dissolution

Fig. 1.2 Schematic representation of ion concentrations in solution as a function of radial distance from the surface of calcite particle

(a. diffusion control; b. surface reaction control. C_{ad} , C_{eq} and C_w are surface concentration and equilibrium concentration of products in the inner water layer, and the concentration in the bulk solution, respectively)

Fig. 1.3 The dissolution rate of calcite versus the CO₂ partial pressure calculated from the pH-stat experiment of Plummer et al. (1978)

Fig. 1.4 The dissolution rate of calcite vs. time at pH 7 and 25°C under the atmospheric CO₂ partial pressure

Fig. 1.5 The pH variation along with the leachate volume when calcite-sand mixtures with two calcite contents were leached by distilled water at two flow velocities

Fig. 1.6 The pH in effluent versus the water flow velocity when calcite-sand mixtures were leached by distilled water

Fig. 1.7 Saturation index of leachate with respect to calcite along with leaching when Iceland Spar - sand mixtures at calcite content of 91 g kg^{-1} were leached by distilled water at flow velocity of 9.4 mm h^{-1}

Fig. 1.8 The saturation index Ω (IAP/K_{sp}) of leachate with respect to calcite vs. the water flow velocity when the calcite-sand mixtures at the calcite content of 91 g kg^{-1} were leached with distilled water

Fig. 1.9 The relationship of the dissolution rate of calcite with the water flow velocity

Research report 2

RECLAMATION OF SODIUM-AFFECTED SOILS BY NATIVE CALCIUM CARBONATE

Abstract

Sodic soil reclamation that takes environment protection into consideration is a basis of sustainable agriculture. A series of leaching experiments of sodic calcareous soil was conducted to investigate the effect of native soil CaCO_3 mineral as an amendment on moderate sodic soil reclamation under elevated CO_2 concentration. The ESP values of employed sodic soils were 0.6% - 19.6%, the water flow velocities ranged from 1.9 to 183 mm h^{-1} , and the CO_2 partial pressures were 0.035, 2.4 and 5.1 kPa at 100 kPa total pressure.

The experimental results indicated that under leaching condition, the soil CaCO_3 dissolution followed a fractional power function with leaching. Its dissolution process in porous media was controlled by diffusion, and the dissolution rate increased linearly with the water flow velocity.

The soil ESP level, the CO_2 partial pressure and the water percolation velocity all enhanced the dissolution rate of soil CaCO_3 mineral significantly; but the effect of elevated CO_2 partial pressure on native CaCO_3 mineral dissolution was significantly lower in sodic calcareous soil than in nonsodic calcareous soil. The total solution concentration of leachate within the initial 6.5 PV was equivalent to the critical flocculation value of moderate sodic calcareous soil. At the elevated CO_2 partial pressure of 5 kPa, the supply of soluble Ca^{2+} from soil CaCO_3 mineral dissolution was obviously improved in moderate sodic soil reclamation. An elevation of CO_2 concentration from 0.035 to 5 kPa increased the reclamation efficiency of moderate sodic soil by 1.8% - 4.1% after leaching of 6.5 PV. The moderate sodic soil was effectively reclaimed by native soil CaCO_3 mineral, 34% - 38% of the initial Na^+

adsorbed in soil clay was substituted and leached out of soil within the initial 6.5 PV at the CO₂ partial pressure of 5 kPa.

Introduction

Calcium carbonate minerals are abundant in soil of arid or semi-arid region. Usually they are composed of two parts: one part comes from pedogenic process; the other part derives from the precipitation of saline irrigation water or drainage water by evaporation (Jury et al., 1978, 1979; Levy, et al., 1995; Miyamoto and Pingitore, 1992).

The solubility product of soil carbonate mineral is generally assumed to be as CaCO₃ (Suarez and Rhoades, 1982). However, more and more evidences indicate that the calcareous materials in soil are more soluble than pure calcite (Doner and Pratt, 1968; Suarez, 1977). This supersaturation phenomenon in respect to calcite is common in the natural environments such as river water, seawater, groundwater, lake and soil solution (Amrhein and Suarez, 1987; Levy, 1981a; Reddy et al., 1990; Suarez, 1977, 1983). The extent of supersaturation in soil usually is 3 - 10 times the solubility product of calcite, some extreme values in calcareous soil as high as 40-fold the solubility product have been reported (Inskeep and Bloom, 1986a).

The solubility of calcareous mineral depends on both its immediate past history of precipitate formation (Inskeep and Bloom, 1986b; Levy et al., 1995; Plummer and Mackenzie, 1974) and the environmental factors of dissolution (Amrhein and Suarez, 1987; Reddy et al., 1990; Sekhon and Bajwa, 1993; Suarez, 1983). Reasons of supersaturation are not fully explained, but it has been attributed to the following aspects:

- 1) Fresh precipitated CaCO₃ minerals: the fresh precipitated calcium carbonate mineral from high saline irrigation and drainage water have a higher solubility (Levy et al., 1995; Miyamoto and Pingitore, 1992).

- 2) Defects during crystallization processes: the overgrowth of crystals during the formation process does take place in nature, and this phenomenon causes precipitation of more soluble mineral form (Katz, 1973).

3) Impurity in crystallization processes: the ions such as Mg^{2+} and SO_4^{2-} etc., organic matter molecules or clay minerals that are present in an original solution when calcium carbonate is precipitating will retard nucleation and growth of crystal, and form more soluble carbonate salts. Usually the greater the impurity concentration, the higher the solubility (Benjamin et al., 1977; Berner et al., 1978; Inskeep and Bloom, 1986b; Levy et al., 1995). On the other hand, the solubility of carbonate mineral will be enhanced in the presence of organic matter and some ions such as Mg^{2+} , SO_4^{2-} and orthophosphate anions in solution (Amrhein and Suarez, 1987; Moller and Parekh, 1975; Reddy et al., 1990; Sekhon and Bajwa, 1993).

4) The presence of more soluble Ca-containing silicate minerals in soil: more Ca^{2+} and HCO_3^- can be released from these minerals, so a greater ionic activity product of CaCO_3 is obtained (Levy, 1981b; Suarez and Rhoades, 1982).

5) Non-equilibrium state: the short residence time and the unavailability of reactive calcite seed in moving solution limit crystal growth and calcite precipitation (Suarez, 1983), and hence results in a higher ion activity product.

The net effect of above-mentioned internal and external reasons leads to supersaturation solution of calcium carbonate in nature.

Pure calcite is a sparsely soluble mineral. Even though native soil CaCO_3 mineral is slightly more soluble than calcite, its slow dissolution kinetics still is a restricted factor for practical application as a calcium source in sodic soil reclamation. Therefore, to increase dissolution rate of soil CaCO_3 mineral to a level that maintains soil solution above the critical flocculation concentration as well as to keep a sufficiently high Ca^{2+} concentration in solution for reducing sodic level significantly are two main practical problems that should be considered.

It is important to note that the dissolution of soil CaCO_3 mineral was investigated in "static state", i.e., in soil paste extracts with a range of soil:water ratio from 1:0.4 to 1:12.5 in most recent literature. There exists certain difference between the "static state" and the leaching situation where both the dissolution of native soil CaCO_3 mineral and the cation exchange between Ca^{2+} and Na^+ don't reach equilibrium. Up to now, there are only few studies that investigated the dissolution behaviour of

soil CaCO_3 mineral and its contribution to calcium ionic concentration in soil solution under leaching condition.

Keren and O'Connor (1982) studied the gypsum dissolution and sodic soil reclamation under leaching condition. They concluded that the increasing of water flow velocity would decrease the dissolution rate of gypsum; meanwhile, the lower the water flow velocity in soil, the higher the efficiency of replacing adsorbed Na^+ by soluble Ca^{2+} . Nadler et al. (1996) investigated the efficiency of naturally occurring CaCO_3 in reclaiming sodic loess soil. They found that when distilled water was used, the Ca^{2+} ion from the CaCO_3 dissolution was the main source (85%) in exchanging sodium by calcium. Moreover, a low water flow rate (11.5 mm h^{-1}) improved the reclamation efficiency by about 30% than that obtained at the high flow velocity of 50 mm h^{-1} . However, they did not systematically investigate the effects of many variables such as water flow velocity, soil ESP level and CO_2 partial pressure on soil CaCO_3 dissolution.

There are some controversial about the effectiveness of CO_2 on CaCO_3 dissolution at low concentration (Loveday, 1984). Plummer et al. (1978) suggested that the dissolution rate of calcite was independent on or had little relation with the CO_2 partial pressure when it was below 10 kPa. Although the improved reclamation efficiency of sodic calcareous soil often was attributed to the enhancing role of elevated CO_2 partial pressure on calcite dissolution in soil (Nadler et al., 1996; Robbins, 1986a; Sekhon and Bajwa, 1993), the effect of CO_2 at low partial pressure on soil CaCO_3 dissolution and reclamation efficiency of sodic soil was not investigated exactly.

The objectives of this study were: 1) to investigate the effects of water flow velocity, CO_2 partial pressure and exchangeable Na^+ level on the soil CaCO_3 mineral dissolution under leaching condition; and 2) to evaluate the reclamation efficiency of sodic soil due to the dissolution of native soil CaCO_3 mineral at various CO_2 partial pressures and water flow velocities.

Materials and Methods

The soil:

The studied soil was a loamy loess soil (Calcic Haploxeralf) from Nahal-Oz, Israel. Its mechanical composition was 190 g clay kg^{-1} , 310 g silt kg^{-1} and 500 g sand kg^{-1} . Montmorillonite was the dominant component of the clay fraction. The soil contained 120 g CaCO_3 kg^{-1} and 20 g organic matter kg^{-1} . The cation exchangeable capacity was 22 $\text{cmol}_c \text{kg}^{-1}$. Assuming the soil CaCO_3 particle is spheroidal and has a geometric mean diameter of 10 μm (Bui et al., 1990), its specific surface area is about 220 $\text{m}^2 \text{kg}^{-1}$.

Column study:

Soil from the upper 0.25 m of soil profile was collected, dried and carefully crushed. It was successively leached with different NaCl- CaCl_2 solution concentrations of 500, 100 and 10 $\text{mmol}_c \text{L}^{-1}$ at a designed SAR level. When the ionic composition of leachate reached a steady state, the concentration of leaching solution was changed to the next lower one with the same SAR. After the soil was washed with all these three solution concentrations, it was free drained overnight and dried in an oven at the temperature of 45 - 50°C for about one week.

The dry soil sample was evenly packed into a plexiglass column, which had a diameter of 52 mm, to a total height of 100 mm at a bulk density of 1.25 Mg m^{-3} . A filter paper was laid at the bottom and the top of soil sample, respectively. The soil column was saturated from its bottom, and then leached from its top with distilled water that was supplied by a peristaltic pump. The distilled water was equilibrated with a CO_2 - N_2 mixed gas at a given CO_2 partial pressure before and throughout the whole experiment.

Three CO_2 partial pressures of 0.035, 2.5 and 5 kPa under the total pressure of 100 kPa were employed in this research. The designed soil ESP levels were 0%, 12% and 20%, and the water flow velocities ranged from 2 to 190 mm h^{-1} .

Leachate samples were collected by a fraction collector. The leachate volume, the EC and clay content in leachate were measured, and the ionic concentrations in effluent also were analysed. The leachate pH was monitored by an automatic pH-meter

before the leachate was exposed to the atmosphere. The HCO_3^- concentration was measured as soon as possible in case it was affected by the different CO_2 partial pressures in the atmosphere. The leachate EC and the concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- and HCO_3^- in leachate were determined according to standard methods described in Ch. 2.

At the end of the leaching process, the soil in the column was freely drained for one day. Then, the soil was sectioned into 5 slices, each was 20 mm thick, and dried in an oven at 105°C for 10 hours. The adsorbed Na^+ and the ESP values for every slice were determined and calculated respectively.

During the experiment, the soil columns were immersed in a water bath at the constant temperature of 25°C . All experimental treatments were carried out in duplicate.

Results and Discussion

Leachate pH:

When nonsodic calcareous soil was leached at the flow velocity of 17.4 mm h^{-1} , the effluent pH was low and almost steady (Fig. 2.1, and it was among 7.7 - 8.2. However, when sodic calcareous soil was leached at the similar velocity, the leachate pH increased rapidly at the beginning of leaching, then it progressively decreased after reaching a maximum (Fig. 2.1). The maximum leachate pH from moderate sodic calcareous soil was about 9.9. Because the OH^- activity in soil solution was increased by hydrolyses of Na^+ -clay and soil CaCO_3 mineral, the leachate pH from sodic calcareous soil raised about 2 pH units from that generally found in nonsodic calcareous soil at equilibrium or under leaching condition.

Nevertheless, if the sodic calcareous soil (ESP 18.6%) was leached at a low flow velocity ($\approx 2 \text{ mm h}^{-1}$), the leachate pH did not rise and it was similar to that when nonsodic calcareous soil was leached at a high velocity ($\approx 18 \text{ mm h}^{-1}$) (Fig. 2.1). When sodic soil is leached at a high speed, hydrogen ions from soil colloids and organic matter can't be released fast enough to neutralize the hydroxyl ions in soil solution that derive from hydrolyses of sodium clay etc. in time. On the contrary, if the leaching velocity is very low, the increased hydroxyl ions in soil solution are well neutralized,

hence the rising of solution pH is oppressed, and the leachate pH is kept at a low level during the leaching process. In addition, a high electrolyte concentration at the low flow velocity also is beneficial to counteract the raise of leachate pH (Bache, 1979). Thus, a high leaching velocity elevates the leachate pH value and a low velocity prohibits its rising when sodic calcareous soil is leached.

The influence of CO₂ partial pressure on leachate pH is displayed in Fig. 2.2 under various ESP levels. Generally, the elevation of CO₂ partial pressure had little effect on leachate pH in nonsodic soil, but it indeed lowered it in sodic soil. When non-sodic calcareous soil was leached, the influence of elevated CO₂ partial pressure was buffered by soil very well, the effluent pH was about 7.7 - 8.5 at the CO₂ concentrations from 0.035 kPa to 5 kPa. However, when sodic calcareous soil was leached, the elevated CO₂ partial pressure lowered the leachate pH at different extents, and the decline extent of effluent pH value was dependent on leachate volume and soil ESP level.

Because a lot of dissolved CO₂ molecules in soil dissolution are consumed on CaCO₃ dissolution, the remained aqueous CO₂ concentration at the bottom part of soil column is too low to overcome the rising of solution pH in sodic soil. Therefore, within the first a few PV, the increased CO₂ partial pressure can not exert any distinct influence on solution pH in moderate sodic soil. Only after some Na⁺ adsorbed in soil clay are substituted and the Na⁺-clay hydrolysis attenuated, can the elevated CO₂ concentration play an obvious influence on the leachate pH.

The overall chemical reactions involved in the dissolution of calcium carbonate in soil solution in the presence of CO₂ should be:

and hydrolysis reaction of CaCO₃ mineral:

In Eq. 1, H₂CO₃^{*} mainly is the dissolved aqueous CO₂, only a small fraction exists as ionic status of H⁺ and HCO₃⁻, and the ratio of dissolved CO₂ to undissociated carbonic acid is about 386 (Lindsay, 1979). When the CO₂ partial pressure is increased, it is obvious from Eq. 1 that the solution pH value decreases. From theory,

the solution pH value decreases from 5.7 at the atmospheric CO_2 partial pressure to 4.6 at the CO_2 partial pressure of 5 kPa. Because of CaCO_3 hydrolysis (Eq. 3), the pH value in CaCO_3 - water system is higher than that in aqueous solution in the absence of calcite at the same CO_2 partial pressure. An elevated CO_2 concentration accelerates the forward reaction of Eq. 2; in the meantime, it also increases the backward reaction of Eq. 3 as a result of common ion effect. Therefore, when CO_2 partial pressure increases, the pH in calcite - water system decreases. Theoretical calculation shows that in an open system, the solution pH in CaCO_3 - water system is 8.25 in equilibrium with the atmospheric CO_2 partial pressure; whereas when the CO_2 partial pressure is elevated to 5 kPa, the solution pH decreases to 6.79 (Butler, 1982). Under leaching condition, soil solution system acts as a closed system consisting of the dissolved CO_2 , water plus calcite. Although the effect of elevated CO_2 concentration on solution pH is smaller in closed system as compared with that in an open system, especially under the existence of exchangeable Na^+ and soil buffer capacity, it seems to be undoubted that the elevated CO_2 partial pressure will lower the solution pH in CaCO_3 - water system. This theoretical prediction is verified by present experimental results (Fig. 2.2). In one word, the hydrolyses of Na^+ -clay and CaCO_3 , CO_2 concentration in solution and soil buffer capacity determine the leachate pH in sodic calcareous soil.

The leachate pH did not go up when nonsodic calcareous soil was leached but it did when Iceland Spar - sand mixture was leached; it also rose when sodic calcareous soil was leached (Fig. 2.3). As a result of calcite hydrolysis, the effluent pH from Iceland Spar - sand mixtures rises, but CaCO_3 hydrolysis could not cause leachate pH up in nonsodic soil due to soil buffer. The pH rise caused by hydrolysis of soil carbonate mineral is completely counteracted by the release of hydrogen ions from clay mineral and organic matter in soil, so the pH value from nonsodic calcareous soil is significantly lower than that from Iceland Spar - sand mixture. Their difference from both media is about 1.5 - 2 pH units. On the other hand, the effluent pH value from sodic calcareous soil is similar to that from Iceland Spar - sand mixtures, which means that the pH rising caused by Na^+ -clay hydrolysis in sodic calcareous soil can not be prevented by soil buffer capacity. The influence of Na^+ -clay hydrolysis on solution pH is obviously bigger than that of CaCO_3 mineral.

Soil CaCO₃ dissolution rate-limiting step:

Dissolution rate of native CaCO₃ mineral in nonsodic calcareous soil was calculated according to the Ca²⁺ concentration in leachate and the flow velocity of percolation water. The dissolution rate linearly increased with the water flow velocity within the velocity range of 17 - 183 mm h⁻¹ under the CO₂ partial pressures from 0.035 kPa up to 4.8 kPa (Fig. 2.4). When the water flow velocity was 17 mm h⁻¹, the dissolution rates of soil CaCO₃ mineral were 5.65*10⁻¹⁰, 1.09*10⁻⁹ and 1.37*10⁻⁹ mol m⁻² s⁻¹ respectively for the CO₂ partial pressure of 0.035, 2.4 and 4.8 kPa. However, when the water flow velocity increased to 170 mm h⁻¹, their values were 5*10⁻⁹, 1.4*10⁻⁸ and 2.2*10⁻⁸ mol m⁻² s⁻¹, respectively. Along with the increasing of CO₂ partial pressure, the effect of leaching velocity on soil CaCO₃ dissolution was enlarged and the gradient of the dissolution rate against the flow velocity obviously increased. Therefore, the leaching plays a more important role on soil CaCO₃ dissolution at high CO₂ partial pressure than at low one.

These results indicate that the dissolution of soil CaCO₃ in porous media is diffusion-controlled process under leaching situation. The leaching process not only removes the end products of chemical reactions and in turn lowers the saturation degree of effluent, but also decreases the thickness of diffusion layer, both of which enhance the dissolution of soil CaCO₃ mineral.

Dissolution kinetics of carbonate minerals:

The logarithm of the Ca²⁺ concentration in leachate against the logarithm of the pore volume of effluent is given in Fig. 2.5 when nonsodic calcareous soils, together with the Iceland Spar-sand mixture, were leached by distilled water at the velocity of 10 mm h⁻¹ under three CO₂ partial pressures. Due to the influence of initial residual salt in soil sample on mineral dissolution, only experiment data beyond the first pore volume of effluent are plotted in this figure.

In logarithm coordinate, the Ca²⁺ concentration in leachate against the leaching volume displayed two partitioned straight lines when native soil carbonate mineral was leached. All fitted straight lines in Fig. 2.5 were significant on 0.01 statistical level. The linearity in Fig. 2.5 manifests that the dissolution of carbonate mineral follows a fractional power function during leaching process.

Native soil carbonate mineral, no matter whether it is pedogenic or evaporitic from saline water, is formed in a rather complicated natural environment. Although their chemical compositions are similar, the dissolution kinetics of soil carbonate mineral is not necessary to be the same as that of pure Iceland Spar.

Because of the fresh precipitated mineral coating and the influence of environmental factors on mineral surface layer, the dissolution of native soil carbonate mineral is heterogeneous. Its dissolution follows two kinetic processes, and the dissolution rate is faster in the initial leaching stage than that in the second one. The dividing line for two dissolution stages usually is among 4.5 - 6.5 PV.

In general, the dissolution rate equation of calcium carbonate mineral in nonsodic calcareous soil during leaching process can be expressed as:

$$C_{Ca} = a * (PV)^b \quad \dots \dots (4)$$

where C_{Ca} is Ca^{2+} concentration ($mmol\ L^{-1}$) in leachate at a given leaching velocity; PV stands for the pore volumes of effluent; a and b are two coefficients.

The coefficient a stands for the magnitude of dissolution rate. Under the dissolution of native soil carbonate mineral, the coefficient a is greater in the first stage of dissolution than in the second one. The coefficient b represents the decline gradient of dissolution rate with the leaching volume, and it is negative for all experiment treatments. The bigger the decline gradient of dissolution rate along with the leaching volume, the smaller the coefficient b. The coefficient b is smaller in the first stage of dissolution than in the second one when soil carbonate mineral is leached.

Under the experimental conditions, $a = 3.6 - 6.1$, $b = -1.0 - -0.45$ for the first stage of dissolution, and $a = 1.6 - 2.4$, $b = -0.25 - -0.06$ for the second stage of native soil carbonate mineral dissolution.

However, when Iceland Spar-sand mixture was leached, the Ca^{2+} concentration in leachate versus the leaching volume in the logarithm coordinate system was a linear function over the whole observed range of leaching volume. The Iceland Spar is a well-crystallised carbonate mineral with high purity, and its solubility is homogeneous, so its dissolution rate could be described by a single fractional power equation during leaching process. $a = 0.4 - 0.7$, $b = -0.3 - -0.03$ for the dissolution of Iceland Spar mineral.

It can be found by comparison that the coefficient a of soil carbonate mineral at the second dissolution stage in all experimental treatments was bigger than that of Iceland Spar mineral, and it was about 2 - 6 times the latter value. The coefficient b in the second stage of soil carbonate mineral dissolution was close to that of Iceland Spar, which suggests that the dissolution characteristics of the inside part of soil carbonate mineral particles is similar to that of Iceland Spar along with the leaching although the soil carbonate mineral still has a greater dissolution rate.

Leachate EC and total solution concentration:

Leachate EC value decreased with the leaching volume during leaching process due to dilution by percolation water and the attenuation of exchange reaction, but it increased with the increase of soil ESP level (Fig. 2.6). At the atmospheric CO_2 partial pressure, the leachate EC values at the 10 PV were 0.1 and 0.3 dS m^{-1} respectively for calcareous soils with ESP of 0.8% and 19.6% at the leaching velocity of about 18 mm h^{-1} , the latter is 3 times the former, which is caused completely by the increased soil sodicity. The soluble Ca^{2+} in soil solution replaces the Na^+ in clay and are remained in the exchangeable phase, therefore as a sink of Ca^{2+} in solution, soil sodicity improves the dissolution of CaCO_3 mineral in soil and subsequently increases effluent EC. After depletion of Na^+ adsorbed in clay, the leachate EC values from sodic calcareous soils with different initial ESP levels are expected to be equal, and the promoting role of exchangeable Na^+ on CaCO_3 dissolution disappears.

A low leaching velocity led to a great leachate EC (Fig. 2.6). The difference of EC values at different flow velocities became smaller and smaller with leaching after majority of Na^+ adsorbed in clay were replaced, which indicates that the flow velocity functions on EC mainly by cation exchange. A low leaching velocity increases the residence time of solution in soil column and the contact area between mineral particles and unit solution volume. So, the diffusion time of exchangeable cations and subsequently their exchange amount increase, and in turn lead to more dissolution of soil CaCO_3 mineral and bigger leachate EC. On the other hand, a relative low solution pH at the low flow velocity (Fig. 2.1) also is conducive to CaCO_3 dissolution due to its small ionic activity product in solution. When soil ESP was about 19%, the effluent EC at the 10 PV increased by 30% from 0.3 to 0.39 dS m^{-1} if the leaching velocity declined

from 17.8 mm h^{-1} to 1.9 mm h^{-1} . Whereas at the 40 PV, the corresponding EC values respectively decreased to 0.14 and 0.17 dS m^{-1} , the latter was 21% higher than the former.

The leachate EC values at various CO_2 partial pressures are shown in Fig. 2.7 for various soil ESP levels. The leachate EC increased with the elevation of CO_2 partial pressure in soil (Fig. 2.7). The influence of CO_2 partial pressure on carbonate mineral dissolution was more significant in nonsodic soil than in sodic soil although the elevation of CO_2 partial pressure did not significantly affect leachate pH in nonsodic soil (Fig. 2.2). Due to the increased carbonic acid attack, an elevated CO_2 partial pressure promotes soil CaCO_3 mineral dissolution, and subsequently increases the electrolyte concentration and leachate EC in the nonsodic soil. This experiment result is not in agreement with the conclusion of Plummer et al. (1978) where they thought the CO_2 partial pressure less than 10 kPa could not increase the CaCO_3 dissolution in alkaline environment. However, in the sodic calcareous soil, the role of exchangeable Na^+ on CaCO_3 mineral dissolution is greater than that of the elevated CO_2 partial pressure, the effect of CO_2 on CaCO_3 dissolution is overshadowed by that of exchangeable Na^+ , and their effects are not additive. For example, when the CO_2 partial pressure was elevated from the atmospheric level to about 5 kPa, the leachate EC at the 10 PV increased by 120% for the nonsodic soil. However, at the same conditions, it increased only by 15% for the sodic soil with ESP of about 19.5%. It is believed that the CaCO_3 dissolution is mainly caused by carbonic acid attack in nonsodic calcareous soil, but it is dominantly resulted from the promotion function of exchangeable cation in sodic calcareous soil under leaching condition.

Because of the depletion of Na^+ adsorbed in soil clay, the initial soil ESP level did not affect the leachate EC value after about 45 PV at the CO_2 partial pressure of 5 kPa (Fig. 2.7). However, when the CO_2 partial pressure was 0.035 kPa, the Na^+ adsorbed in the exchangeable phase were not completely substituted. So the initial soil ESP level still remained a little influence on the leachate EC value at the 45 PV, where a high soil ESP level corresponded to a big effluent EC. The effluent EC at the 45 PV was about 0.2 dS m^{-1} at the CO_2 partial pressure of 5 kPa, 172% - 65% greater than those for soil ESP from 0.8% to 19.6% at the atmospheric CO_2 partial pressure.

The leachate EC from nonsodic calcareous soil had a little variation along with water flow velocity under the tested range of CO₂ partial pressures (Fig. 2.8). The EC slightly declined against the leaching velocity when the CO₂ partial pressure was 0.035 kPa, yet it increased a little with the increase of flow velocity after the CO₂ concentration was elevated. Under the experimental conditions, the EC variation caused by flow velocity was obviously smaller than that caused by the elevated CO₂ partial pressure.

The native soil carbonate mineral released more electrolytes than Iceland Spar did and its effluent EC always was greater than that of the latter mineral. At the atmospheric CO₂ concentration, the steady leachate EC from native carbonate mineral in nonsodic soil was 0.072 dS m⁻¹ and that from Iceland Spar was 0.037 dS m⁻¹ at the same flow velocity. The solubility of soil carbonate mineral is about 2 times that of Iceland Spar. Non-crystal morphology, impurity of chemical composition and organic matter in soil, together with fresh precipitated CaCO₃ mineral, increase the solubility of soil calcium carbonate minerals (Amrhein and Suarez, 1987; Kachanoski et al, 1992; Levy et al, 1995; Miyamoto and Pingitore, 1992). In addition, because of greater CO₃²⁻ activity fraction at high pH, a pH as high as 9.5 from Iceland Spar - sand mixtures (Fig. 2.3) maybe also is a reason for its low dissolution rate under leaching condition.

Similar to its influence on leachate EC, the elevation of CO₂ partial pressure didn't significantly increase the solution concentration of leachate from sodic calcareous soil, but it resulted in a great increase when nonsodic calcareous soil was leached (Tab. 2.1). When the CO₂ partial pressure up to 5 kPa was used, for example, the total solution concentration at the 6.5 PV from nonsodic soil reached 2.3 mmol_e L⁻¹ from 1.25 mmol_e L⁻¹ at the atmospheric CO₂ level. The experimental results showed that at the leaching velocity of 18 mm h⁻¹, the total solution concentrations in leachate from sodic calcareous soils were above 3 mmol_e L⁻¹ within the first 6.5 PV even at the atmospheric CO₂ partial pressure (Tab. 2.1), which is equivalent to the critical flocculation value of 3 - 5 mmol_e L⁻¹ for moderate sodic soil (ESP ≤ 20%) (Shainberg and Letey, 1984). Therefore, the electrolyte concentration of leachate from sodic calcareous soils is high enough to prevent soil structure destruction within the initial 6.5 PV.

Leachate composition:

When Ca-soil was leached, the Ca^{2+} concentration in the effluent was high, and it gradually decreased to a steady value after 5 PV (Fig. 2.9). An elevated CO_2 partial pressure greatly increased Ca^{2+} concentration in effluent (Fig. 2.10). When CO_2 partial pressure was 0.035 kPa, the steady Ca^{2+} concentration was $0.7 \text{ mmol}_e \text{ L}^{-1}$ at the leaching velocity of 17.4 mm h^{-1} ; but when the CO_2 partial pressure was elevated to 4.8 kPa, it was 2.5 times that at the atmospheric CO_2 level and got to $1.75 \text{ mmol}_e \text{ L}^{-1}$. Thus, leachate Ca^{2+} concentration increases with the elevation of CO_2 partial pressure in soil as a result of the improved soil CaCO_3 dissolution.

However, when sodic calcareous soil was leached, the Ca^{2+} concentration in leachate was much lower than that from nonsodic calcareous soil (Fig. 2.9 and Fig. 2.10). The Ca^{2+} concentration was decreasing with the leaching process because of exchange of adsorbed Na^+ by Ca^{2+} until a minimum value where the Ca^{2+} supply was inadequate for $\text{Ca}^{2+} - \text{Na}^+$ exchange. After majority of Na^+ in the exchangeable phase is substituted, cation exchange attenuates, so the Ca^{2+} concentration in effluent begins to increase after a depression period whose duration depends on the supply and consumption of Ca^{2+} . This moment, the Ca^{2+} supply may be considered to be enough. After the Na^+ in clay are exhausted, the effluent Ca^{2+} concentration gradually gets to the value that when nonsodic calcareous soil is leached at the same conditions.

From the experimental data, the smallest Ca^{2+} concentration in effluent was to appear at about 10 PV when sodic calcareous soil with ESP of 18.6% was leached at the flow velocity of 1.9 mm h^{-1} under the atmospheric CO_2 partial pressure (Fig. 2.9). Yet if the water flow velocity was up to 17.8 mm h^{-1} , the depression period of Ca^{2+} concentration in effluent extended beyond the 20 PV at the equal soil ESP level and CO_2 partial pressure. As discussed above, a low velocity of percolation water leads to a big effluent EC and subsequently a high Ca^{2+} concentration in leachate. Therefore, at the low water flow velocity, the exchange reaction can be satisfied more rapidly by the supply of Ca^{2+} from soil CaCO_3 dissolution than at the high flow velocity (Fig. 2.9).

When CO_2 partial pressure was 4.8 kPa, the minimum Ca^{2+} concentration in effluent appeared at about 8 PV for sodic soil with ESP of 12.5% at the water flow velocity of 18 mm h^{-1} , and then it increased rapidly (Fig. 2.10). If the CO_2 partial

pressure is lower or the soil ESP level is higher, the Ca^{2+} concentration in leachate from slow dissolution kinetics of carbonate mineral can not meet the exchange reaction with the adsorbed Na^+ , so the depression period of Ca^{2+} concentration in effluent will keep for a longer time. For example, when the soil ESP level was up to 19.3%, the Ca^{2+} concentration was to increase only after about 16 PV at the CO_2 partial pressure of 5.1 kPa. It is inferred from its long depression period that the Ca^{2+} concentration in effluent at the atmospheric CO_2 level is seriously insufficient for sodic soil reclamation at the flow velocity of 18 mm h^{-1} . The experiment data confirm that even though at the elevated CO_2 partial pressure of 2.4 - 5 kPa, the Ca^{2+} concentration from soil CaCO_3 dissolution still is not enough at the high ESP of 20% (Fig. 2.10), however its supply is significantly improved under the elevated CO_2 concentration. With the further increase of CO_2 partial pressure, it is possible that the soluble Ca^{2+} concentration in soil solution from soil CaCO_3 dissolution may satisfy cation exchange requirement in moderate sodic soil reclamation.

By comparing Fig. 2.10 with Fig. 2.2, it can be found that the effluent pH began to lower where the leachate Ca^{2+} concentration just began to increase. Although attenuation of Na^+ -clay hydrolysis is its main reason, the relative composition of Ca^{2+} and Na^+ in solution perhaps also affects solution pH. A big Ca^{2+} concentration in solution lowers pH via bicarbonate equilibrium in weak acid solution due to low dissolution ability of Ca^{2+} (Bache, 1979).

The experimental data indicated that the Na^+ concentration in effluent monotonously descended to a residual value with leaching (Fig. 2.11). The higher the soil ESP level or the smaller the flow velocity, the greater the Na^+ concentration in effluent. However, the influence of CO_2 partial pressure on Na^+ concentration was not obvious (Fig. 2.11). Although the dissolution rate of soil CaCO_3 mineral is small at low flow velocity, the electrolyte concentration in leachate is high and the unit solution volume supplies more soluble Ca^{2+} amounts to displace the Na^+ adsorbed in clay, so a low leaching velocity leads to a high Na^+ concentration. The Na^+ concentration in leachate depends on both the supply of Ca^{2+} from dissolution of soil CaCO_3 mineral and the amount of Na^+ adsorbed in soil clay. Because the elevated CO_2 partial pressure

doesn't enormously improve native CaCO_3 dissolution in sodic soil (Fig. 2.7), the Na^+ concentration in leachate has little dependence on CO_2 partial pressure.

Soil CaCO_3 dissolution and leaching velocity controlled carbonate alkalinity in leachate (data not shown). The alkalinity in leachate increased with the increase of soil ESP level or CO_2 partial pressure, meanwhile, it also became greater at a low leaching velocity. The variation of carbonate alkalinity in leachate with various variables was similar to that of leachate EC.

The Mg^{2+} and K^+ concentrations in effluent were very low, and usually they were below $0.05 \text{ mmol}_e \text{ L}^{-1}$ at the flow velocity of 18 mm h^{-1} . Both ions possibly come from the dissolution of soil CaCO_3 mineral that contains trace of these two elements. The Cl^- concentration in effluent got to a steady residual value of about $0.1 \text{ mmol}_e \text{ L}^{-1}$ within 1 - 2 PV. It derives from soluble salts and can be easily leached out of soil.

Sodicity in leachate:

The SAR is a useful and convenient criterion to check soil reclamation efficiency and possible impact of reclamation activity on soil structure stability during reclamation process. It is expressed as relative concentration of Na^+ to bivalent cations in effluent and determined mainly by the dissolution rate of carbonate mineral and soil ESP level. If there are sufficient exchangeable Na^+ in clay particles, an enhanced mineral dissolution just increases the substitution of adsorbed Na^+ and subsequently the Na^+ concentration in effluent, and the soluble Ca^{2+} concentration in effluent does not simultaneously increase or increases little. So, the SAR of effluent becomes great at this situation. On the contrary, if the Na^+ adsorbed in clay is a limited factor, the dissolution of carbonate mineral can supply enough soluble Ca^{2+} to substitute the adsorbed Na^+ , the Ca^{2+} concentration in effluent will increase when the dissolution rate of carbonate mineral is enhanced, hence the SAR in leachate declines. With the leaching, the first extreme case progressively transfers to the second one after lots of adsorbed Na^+ are substituted.

The calculated data demonstrates that SAR in effluent decreased with leaching process after a peak value that appeared during the depression period of soluble Ca^{2+} concentration in effluent (Fig. 2.12). The SAR increased with soil sodicity, yet water flow velocity didn't have significant influence on it as a result of simultaneous increases

of Ca^{2+} and Na^+ concentration in solution (Fig. 2.9 and Fig. 2.11). Similar to above conceptual inference, the elevation of CO_2 partial pressure increased leachate SAR value at the high soil ESP of 19.3% due to increased CaCO_3 mineral dissolution, but decreased it at the low ESP of 12.5% as a result of limitation of less Na^+ in soil clay. The maximum leachate SAR of $18 \text{ (mmol}_\text{c} \text{ L}^{-1})^{0.5}$ at soil ESP of 19.3% and CO_2 partial pressure of 5.1 kPa should be safe to soil structure stability because of its high solution concentration above $3 \text{ mmol}_\text{c} \text{ L}^{-1}$ within the initial 10 PV (Tab. 2.1) (Shainberg and Letey, 1984), but its sustaining high value beyond the 10 PV is disadvantageous to soil stability (Fig. 2.12).

Saturation index in leachate:

The ionic activity product of leachate in respect to calcite generally decreased with the leaching volume (Fig. 2.13). Both soil sodicity and water flow velocity increased saturation index in leachate at the atmospheric CO_2 partial pressure. The elevation of CO_2 partial pressure increased the saturation index in nonsodic calcareous soil but decreased it in sodic calcareous soil (Fig. 2.13).

The saturation index of leachate is determined by both calcium and carbonate ionic activities in solution. Because of short contact time between CaCO_3 particles with unit volume of moving solution under leaching condition, soil solution can not reach equilibrium with CaCO_3 mineral. The ionic activity product of Ca^{2+} and CO_3^{2-} in leachate is close related with mineral solubility and solution pH at a given leaching flux.

When sodic calcareous soil is leached at the atmospheric CO_2 partial pressure, existence of exchangeable Na^+ decreases effluent Ca^{2+} concentration at a relative small extent, but it greatly increases carbonate ionic concentration in solution by the enhanced dissolution and the rising of pH, which results in an increase of saturation with increase of soil sodicity.

However, elevation of CO_2 partial pressure increases effluent Ca^{2+} concentration and carbonate alkalinity, but its influence on CO_3^{2-} concentration depends on solution pH. The final solution saturation index is controlled by a balance between the increase of Ca^{2+} concentration and the decrease of CO_3^{2-} concentration. When nonsodic calcareous soil is leached, because of soil buffer on solution pH, the leachate saturation extent is dominated by mineral dissolution. A high CO_2

concentration brings about more dissolution of carbonate mineral; meanwhile, it does not result in an obvious decline of solution pH, so a big ionic activity product is gotten during leaching process. For example, when nonsodic soil was leached at the CO_2 partial pressure of 0.035 kPa, the ionic activity product in leachate at the 40 PV was only 15% of solubility product of calcite. If the CO_2 partial pressure was elevated to 4.8 kPa, it increased to 130%. However, when sodic calcareous soil is leached, the leachate pH is lowered significantly after a lot of adsorbed Na^+ are substituted. Even though Ca^{2+} concentration is increased a little at a high CO_2 partial pressure, the saturation index still declines. For example, when sodic soil with ESP of 19.6% was leached at the CO_2 partial pressure of 0.035 kPa, the ionic activity product of calcite at the 40 PV was 8 times the solubility product. At the same conditions, if the CO_2 concentration was elevated to 5.1 kPa, it was only 3 times. The influence of CO_2 partial pressure on ionic activity product is just opposite in the nonsodic and the sodic calcareous soils under experiment conditions.

Due to rather low leachate pH at low leaching velocity, the CO_3^{2-} concentration in solution is very small; comparatively, the Ca^{2+} concentration in solution is only slightly increased. Therefore, when sodic calcareous soil is leached at a low velocity, ionic activity product reduces greatly. On the contrary, if leaching velocity is high, a supersaturated phenomenon appears. For example, when sodic calcareous soil with ESP of 18.6% was leached by distilled water at 1.9 mm h^{-1} under the atmospheric CO_2 partial pressure, its ionic activity product was undersaturated after leaching of 5 PV (Fig. 2.13). If the leaching velocity was increased to 17.7 mm h^{-1} , its effluent became into supersaturated. The ionic activity product increased more than 20 times at the same soil ESP levels.

By comparison of Fig. 2.13 and Fig. 2.1 as well as Fig. 2.2, it can be concluded that the saturation of effluent mainly is controlled by effluent pH. A high pH generally leads to a greater saturation index and vice versa.

Clay dispersion:

Clay dispersion is a critical factor about sodic soil reclamation. It greatly affects the infiltration rate that sometimes determines success or failure of soil reclamation activity because too slow infiltration rate is impractical from viewpoint of engineering.

The experimental results demonstrated that the clay dispersion mainly depended on soil ESP level, and the higher was the soil ESP level, the bigger were the clay content and the total cumulative amount of dispersed clay in effluent (data not shown). The accumulative weight of the dispersed clay accounted for 0, 0.9% and 2.0% of total clay mass in soil samples (i.e., 0, 1.7 and 3.8 g clay kg⁻¹ soil) respectively for soil ESP of 0.8%, 12.5% and 19.6% under the CO₂ partial pressure of 0.035 kPa and the water flow velocity of 18 mm h⁻¹, which is within the threshold of 4 g clay kg⁻¹ soil on severe reduction of hydraulic conductivity (Yousaf et al., 1987). The variation tendency of the cumulative dispersed clay weight against the soil ESP level is similar to the result of Shainberg et al. (1981), but the amounts of dispersed clay at various soil ESP levels in present research are only about one tenth of their data because they employed a soil with more insoluble mineral. Native soil CaCO₃ mineral shows a great beneficial influence on prevention and inhibition of clay dispersion.

The total accumulative amount of dispersed clay in leachate didn't change with the flow velocity of percolation solution, but the clay content in effluent depended on it. A low flow velocity caused a gradual decrease of clay content in leachate; on the contrary, a high flow velocity led to great clay content at the beginning of leaching and then a fast decline of clay content during leaching process. So, in order to minimize the destruction of soil physical properties, a low flow velocity should be adopted when sodic calcareous soil is reclaimed.

The experiment data also showed that there was no significant dependence of clay dispersion on CO₂ partial pressure under experiment conditions. Because the solution concentration within the first 6.5 pore volumes of effluent is equivalent to the critical flocculation value in moderate sodic calcareous soil at the atmospheric CO₂ level (Tab. 2.1), clay dispersion has been effectively inhibited (Shainberg et al., 1981). Moreover, as discussed above, the elevation of CO₂ partial pressure does not increase

the electrolyte concentration of leachate in sodic soil a lot (Tab. 2.1), thus the elevated CO₂ concentration can't further decrease the clay dispersion obviously.

Reclamation efficiency and soil ESP profile after reclamation:

The soil ESP variation during leaching process was calculated from leachate Na⁺ concentration, soil sample weight and its cation exchange capacity. The calculated results demonstrate that the soil ESP level during reclamation process decreased with the leaching volume, and its decline rate was faster at low flow velocity than at high one (Fig. 2.14). If the reclamation efficiency of sodic soil is defined as $(ESP_i - ESP_f) / ESP_i * 100$, where ESP_i is initial soil ESP value and ESP_f is final averaged ESP value after a given leaching volume, the calculated reclamation efficiencies respectively at the 6.5 PV and 10 PV are listed in Tab. 2.1 for two soil sodicities and CO₂ partial pressures. At the 10 PV, the reclamation efficiency is 10.6% higher at the low velocity (1.9 mm h⁻¹) than that at the high velocity (18 mm h⁻¹) under the atmospheric CO₂ partial pressure.

Sodic soil reclamation is the aim of CaCO₃ dissolution research in this experiment. Reclamation efficiency is an important index about sodic soil reclamation from economic viewpoint, and it is represented by the reduction rate of exchangeable sodium percentage in soil during leaching process.

The release rate of Ca²⁺ from soil CaCO₃ dissolution determines the reclamation efficiency of sodic soil within the first 8 - 10 PV due to its shortage, the leaching velocity of percolation solution, soil ESP level and CO₂ partial pressure are three major factors. It is shown previously that the Na⁺ concentration in effluent is declining during leaching process (Fig. 2.11), so it is certain that the reclamation efficiency decreases with the leaching volume.

Although a high flow velocity increases the dissolution rate of soil CaCO₃ mineral (Fig. 2.4) and accelerates the removal of the end products of exchange reactions. However, the increased flow velocity not only decreases the leachate EC and subsequently available soluble Ca²⁺ concentration in effluent, but also cuts down the contact time and contact area among mineral particles - soil solution - clay particles. Under the high flow velocity, most of the percolation solution flows through the big pores in bulk soil. On the contrary, a major fraction of the leaching water passes

through the small pores and penetrates into soil aggregates under the low flow velocity, hence the contact time and contact area of percolating solution with mineral particles increase, and the diffusion distance of exchange cations is shortened. The declined contact time and contact area as well as the decreased Ca^{2+} concentration in solution under high flow velocity impose a detrimental effect on the exchange process between calcium and sodium ions. Therefore, a low flow velocity is beneficial to soil reclamation. This result is consistent with those of Keren and O'Connor (1982) as well as Nadler et al. (1996).

The calculated results also demonstrate that reclamation efficiency increased with the elevation of CO_2 partial pressure, and the higher the initial soil ESP level, the more obvious the effect of elevated CO_2 partial pressure (Fig. 2.14 and Tab. 2.1). At the 6.5 PV, the reclamation efficiency at the CO_2 partial pressure of 5 kPa increased by 1.8% - 4.1% over that at the CO_2 partial pressure of 0.035 kPa when leaching velocity was 18 mm h^{-1} (Tab. 2.1). This increment extent about reclamation efficiency of sodic soil is not so high as people imagine from the role of CO_2 on CaCO_3 dissolution in nonsodic soil. Although the soil with a high initial ESP level releases more Na^+ into effluent (Fig. 2.11), because of its more Na^+ in clay, the reclamation efficiency was lower at the high ESP level than that at the low level even though at an elevated CO_2 partial pressure of 5.1 kPa (Tab. 2.1). It is confirmed again that the reclamation efficiency still is retarded by the supply of soluble Ca^{2+} even at the CO_2 concentration of 5 kPa when initial soil ESP level is high.

It can be seen from Tab. 2.1 that within the first 6.5 PV, as high as 34% - 38% of initial adsorbed Na^+ was leached out of the reclaimed soil layer at the CO_2 partial pressure of 5 kPa. Although the supply of Ca^{2+} from native soil CaCO_3 dissolution is not fully sufficient, the Na^+ removal efficiency is significant under present experiment conditions, the native soil CaCO_3 mineral functions well as a soil amendment.

The experimental results showed that after reclamation, the soil ESP level was smaller at the upper part and bigger at the deep part of soil profile. The more the leaching water or the higher the CO_2 concentration, the lower the final soil ESP level in soil profile (data not shown). During reclamation process, the soluble Ca^{2+} in solution displaces the Na^+ adsorbed in clay until the soil ESP level reaches equilibrium with the

SAR of soil solution, so the soil ESP level at the upper part of soil profile was lowered firstly due to its low solution SAR value. Then, with the increase of Na^+ concentration in soil solution, the reduction extent of soil ESP level becomes smaller and smaller along with the depth of soil profile. Thus, together with the role of valence effect, more Na^+ ions at the upper part of soil profile are substituted and released into solution than that at the deep part of soil profile.

Summary and Conclusions

The dissolution of soil CaCO_3 mineral in porous media followed a fractional power function with leaching. The dissolution rate was controlled by diffusion process under leaching condition, and it was directly proportional to the water flow velocity.

The soil sodicity, CO_2 partial pressure and water flow velocity all affected soil CaCO_3 dissolution. A high soil ESP level significantly increased the soil carbonate mineral dissolution and the electrolyte concentration of effluent; meanwhile, it also led to a high effluent pH. The elevated CO_2 partial pressure lowered leachate pH value and enhanced the calcium carbonate mineral dissolution; however its effect was weaker in sodic calcareous soil than in nonsodic calcareous soil. In the nonsodic soil, carbonic acid attack was the main reason of soil CaCO_3 dissolution, but in the sodic soil the role of exchangeable Na^+ was dominant. A low flow velocity not only effectively inhibited the rising of solution pH value but also greatly increased the effluent EC and the reclamation efficiency of sodic calcareous soil.

The saturation extent of leachate mainly was controlled by its pH under present experimental conditions. Generally, a high solution pH led to supersaturation of effluent and a low pH caused an undersaturated state with respect to calcite.

Clay content in effluent depended on soil sodicity and water flow velocity. The higher the soil ESP value, the bigger the clay content. In addition, a low flow velocity caused a gradual decrease of clay content during leaching process, but a high flow velocity decreased it sharply. The accumulative weight of dispersed clay only depended on soil ESP level: a high soil ESP level resulted in a great cumulative clay weight and vice versa.

The total solution concentration within the initial 6.5 PV was equal to the critical flocculation concentration in sodic calcareous soil. Under the elevated CO₂ partial pressure of 5 kPa, the supply of soluble calcium ions from the dissolution of native soil CaCO₃ mineral was significantly improved during moderate sodic soil reclamation. The elevation of CO₂ concentration from 0.035 kPa to 5 kPa increased the reclamation efficiency of sodic soil by 1.8% - 4.1% after leaching of 6.5 PV. Soil ESP level was greatly lowered by native soil CaCO₃ mineral, 34% - 38% of initial Na⁺ amount adsorbed in soil clay was substituted within the first 6.5 PV at the CO₂ partial pressure of 5 kPa. The native soil CaCO₃ can be used as an amendment if suitable management means is adopted.

Tab. 2.1 The total solution concentrations in effluent and the reclamation efficiency (the reduction rate of soil ESP level in a given leaching water amount) respectively at the 6.5 PV and 10 PV when leaching velocity was 18 mm h⁻¹

Soil ESP level	CO ₂ partial pressure	Total solution concentration		Reclamation efficiency [†]	
		At 6.5 PV (mmol _c L ⁻¹)	At 10 PV (mmol _c L ⁻¹)	At 6.5 PV (%)	At 10 PV (%)
0.8	0.035	1.25	1.05	--	--
12.5	0.035	3.1	2.5	35.8	47.2
19.6	0.035	3.6	3.0	29.6	38.8
0.6	4.8	2.3	2.05	--	--
12.5	4.8	3.05	2.5	37.6	48.8
19.3	5.1	3.7	3.3	33.7	45.1

Note: † calculated from Na⁺ concentration in effluent.

Fig. 2.1 Leachate pH values against the leaching volume at various soil ESP levels and two water flow velocities under the atmospheric CO_2 concentration

Fig. 2.2 The leachate pH value versus the leaching volume under two CO_2 partial pressures and three soil ESP levels at the water flow velocity of 18 mm h^{-1}

Fig. 2.3 The leachate pH versus the leaching volume when sodic calcareous soils with two soil ESP levels and Iceland Spar-sand mixture were leached by distilled water at the velocity of 10 mm h^{-1} under the atmospheric CO_2 partial pressure

Fig. 2.4 The dissolution rate of calcium carbonate mineral in nonsodic calcareous soil as a function of the flow velocity of percolation solution

Fig. 2.5 The logarithm of the Ca^{2+} concentration (mmol L^{-1}) in leachate against the logarithm of the pore volumes of leachate when nonsodic calcareous soils, together with Iceland Spar - sand mixtures, were leached by distilled water at the velocity of 10 mm h^{-1} under three CO_2 concentrations

Fig. 2.6 The effluent EC from sodic calcareous soil against the leaching volume at various soil ESP levels and two water flow velocities under the atmospheric CO_2 partial pressure

Fig. 2.7 The leachate EC values against the leaching volume under two CO₂ partial pressures and three soil ESP levels at the water flow velocity of 18 mm h⁻¹

Fig. 2.8 The effluent EC at the 10 PV versus the water flow velocity when nonsodic calcareous soil was leached by distilled water under various CO₂ concentrations

Fig. 2.9 The calcium ionic concentration in leachate from sodic calcareous soils against the leaching volume at various soil ESP levels and two water flow velocities under the atmospheric CO_2 partial pressure

Fig. 2.10 The Ca^{2+} concentration in effluent against the leaching volume under two CO_2 partial pressures and three soil ESP levels at the water flow velocity of 18 mm h^{-1}

Fig. 2.11 The sodium ionic concentration in leachate from sodic calcareous soil against the leaching volume at various soil ESP levels and two water flow velocities under the atmospheric CO₂ partial pressure

Fig. 2.12 SAR (mmol_c L⁻¹) in effluent against the leaching volume at various soil ESP, CO₂ partial pressures and water flow velocities

Fig. 2.13 The saturation index of leachate in respect to calcite versus the leaching volume at three soil ESP levels, two water flow velocities and CO_2 partial pressures

Fig. 2.14 The soil ESP variation during the leaching process under two CO_2 partial pressures and water flow velocities

Research report 3a

DYNAMICS OF CO₂ PRODUCTION IN SODIC CALCAREOUS SOIL CONTAINING CROP MATERIALS

Abstract

The soil CO₂ partial pressure regulates the solution chemistry in sodic calcareous soil to a great extent. The dynamics of CO₂ production in sodic calcareous soil after mixing it with chopped corn materials (*Zea mays* L.) was investigated in this study. The concentrations of CO₂ and O₂ gases in soil were monitored during the incubation period of 30 - 60 days, and the production rate of CO₂ gas and its surface flux were calculated after corn materials at a rate range of 0 - 153 Mg ha⁻¹ were added to the sodic calcareous soils with ESP range of 0.4% - 19.4%.

The CO₂ in sodic calcareous soil after corn material application was obviously different from that in control treatments. After application of corn materials, an anaerobic decay took place at the majority of soil profile at the initial stage of incubation as a result of fast consumption of oxygen by microbial activity. The duration and the depth of anaerobic decay increased with the application rate of corn materials and the soil ESP level. The CO₂ partial pressure in soil profile declined with incubation time, but increased with the soil depth as well as the application rate of corn materials. The calculated data indicated that the surface flux and the production rate of CO₂ gas increased with the increasing application rate of crop materials.

The soil ESP level significantly increased the CO₂ partial pressure in soil, which possibly is caused by more suitable pH range for decomposition of applied crop materials and more clay dispersion. However, it did not have an obvious influence on the surface flux and the production rate of CO₂ gas.

Introduction

Carbon dioxide is an important component of carbon cycle in soil. It directly or indirectly regulates many properties of soil such as the pH of soil solution, the mineral dissolution, and the chemical element composition and nutrient absorption (Castelle and Galloway, 1990; Solomon and Cerling, 1987).

The atmospheric "greenhouse effect" causes an increase of CO₂ concentration in atmosphere, subsequently leads to more biomass production and bigger ratio of carbon to nitrogen (C/N) in plant tissue (Berntson and Bazzaz, 1996). It results in increasing of residual content within surface soil layer, and in turn accelerates the elevation of CO₂ partial pressure in soil (Johnson et al., 1994). In addition, the introduction and development of non-conventional conservation tillage technique also increases crop residue content in soil, and declines CO₂ diffusion rate out of soil due to high soil compactness (Reicosky et al., 1997), this also increases the CO₂ partial pressure in soil. An increased CO₂ partial pressure in soil due to both greenhouse effect and non-conventional tillage system results in some dynamic change of soil environment and in turn influences the balance of soil chemical system. Once a lot of crop materials are added into soil for some specific purpose, its impact should be more significant and cannot be ignored.

A high CO₂ concentration in soil can promote the weathering and dissolution of soil calcareous minerals (Solomon and Cerling, 1987; Taylor and Ashcroft, 1972). Any process that increases the available CO₂ in soil solution will play a similar role like this. Decay of organic matter in the presence of air or aerated water produces CO₂ gas a lot, and hence makes the CaCO₃ mineral in the vicinity more soluble, even though an anaerobic decay also often leads to an increased acidity (Krauskopf, 1976). So it can be assumed that adding crop materials into sodic calcareous soil will enhance soil CaCO₃ mineral dissolution, and improve reclamation efficiency of sodic calcareous soil, hence it can be employed as a practical, economical and sustainable method for sodic calcareous soil reclamation. As the first step for verification of this hypothesis, it is necessary to understand the role and effect of crop material application on the CO₂ production and its dynamic process of production in sodic calcareous soil.

The CO₂ concentration in soil can be increased by 10 or even by 1000 fold (0.3 - 30 kPa) above that in atmosphere (Singer and Munns, 1987). The CO₂ level in soil depends on its production rate and its diffusion rate out of soil. In the absence of active plant roots, the CO₂ production rate is controlled by the decay process of organic matter under microbial activity. It is related with the composition of organic matter (C/N ratio), its physical state (such as age and size of material, amount, type as well as decay stage), and the environmental factors (such as temperature, soil moisture, soil solution pH, salinity and mineral nutrient of soil, oxygen content (aeration) and cultivation). However, the diffusion rate of CO₂ is dominated by the soil moisture content and soil compactness.

Studies about plant material decomposition were conducted under various management practices (Douglas and Rickman, 1992; Ghidey and Alberts, 1993; Ghidey et al., 1985). The decomposition of crop material generally follows a first-order kinetic process. Of all factors, temperature and soil moisture are the two main environmental factors that affect this process. The release of CO₂ is proportional to the organic matter content in soil, and the carbon mineralization is most rapid in neutral to slightly alkaline soil (Alexander, 1977; Singer and Munns, 1987).

The distribution of CO₂ partial pressure and its seasonal change in soil was investigated in forest ecosystem (Castelle and Galloway, 1990; Edwards and Ross-Todd, 1983; Fernandez and Kosian, 1987; Fernandez et al., 1993), as well as on soil respiration and microbial activity (Buyanovsky and Wagner, 1983; Buyanovsky et al., 1986; De Jong et al., 1974; Solomon and Cerling, 1987). Although cropping or addition of plant residues into soil increases soil CO₂ partial pressure (Robbins, 1986b), the effects of the application rate of crop materials and the soil sodicity on soil CO₂ partial pressure are not investigated intensively. The CO₂ production dynamics in soil after application of crop material at a large amount is not fully understood yet, especially in sodic calcareous soil. Because the sodium ions adsorbed by soil clay dominantly regulate the soil pH, and increase the dissolution of soil CaCO₃ mineral and in turn the soil salinity, soil sodicity affects the production dynamics of CO₂ gas in sodic calcareous soil. This hypothesis will be tested in the present study.

Thus, the objectives of this research were: 1) to investigate the temporal and spatial distributions of CO₂ and O₂ partial pressures during incubation period; 2) to evaluate the influences of crop material application rate and soil ESP level on CO₂ partial pressure in sodic calcareous soil; and 3) to calculate the surface flux and production rate of CO₂ gas after crop materials were incorporated with sodic calcareous soil.

Materials and Methods

The soil and its sample preparation were described in research report 2.

Corn materials (*Zea mays* L.) were collected from farm field near Bet Dagan, Israel. They were air-dried, chopped into fine pieces ($\approx 20 \times 20 \times 5$ mm) and mixed thoroughly.

Plastic buckets with an internal diameter of 0.24 m and a height of 0.33 m were used as lysimeters. Five small holes of 0.05 m apart along the vertical direction of the lysimeter were drilled and connected with fine plastic tubes for sampling gas phase in the soil profile. These fine tubes with a diameter of 4 mm were inserted through the holes into the center of lysimeter. The inside ends of the tubes were left open, and the outside ends were plugged with clips. At the bottom of the lysimeter, another small hole was opened and a hard plastic tube was installed as an outlet for free-drainage. The plastic tubes were glued by epoxy adhesive to the lysimeter so as to prevent water or gas leaks.

Coarse quartz sand grains were successively washed by a concentrated hydrochloric acid and distilled water thoroughly until the electrical conductivity of the drained solution was as low as that of the distilled water. Then they were dried in an oven at 105°C. The clean coarse sand grains were packed on the bottom of lysimeter for a layer of 15 mm thick. A metal fine net was placed on the bottom tube to avoid sand discharge before adding the sand grains into the lysimeter.

The dry soil sample with a known ESP level was evenly mixed with the chopped corn materials at a designed rate, and packed in the lysimeter layer by layer to a total height of 0.3 m at bulk density of 1.2 Mg m⁻³.

The lysimeter was saturated from its bottom tube with distilled water at a slow velocity. After saturation, it was drained for about one days, then the first gas samples were collected.

Gas samples each with 0.01 L were collected by 0.02 L perspex syringes every other day during the first week of incubation and thereafter twice a week. The syringe needles were inserted into a piece of rubber, and the gas samples were analyzed for CO₂ and O₂ concentrations by the gas chromatography technique (HPGC).

During the incubation period, the soil in lysimeter was left open to the atmosphere. The water content in the lysimeter was maintained by spraying distilled water until the initial soil water content was restored (by weighting). The water capacity of the soil in the lysimeter was 0.35 (kg kg⁻¹). In order to reduce disturbance on the soil surface in lysimeter, a filter paper was covered on it during the whole incubation period.

The variables that were investigated in this experiment were as follows: soil ESP (0, 10% and 20%), application rates of corn materials (0 (control), 80 and 150 Mg ha⁻¹), and incubation time (30 and 60 days). All experiments were carried out in the constant temperature chamber of 25°C.

Results and Discussion

CO₂ and O₂ partial pressures in soil profile:

In the sodic calcareous soil without corn material application (control treatment), the CO₂ partial pressure in soil profile was low and steady with incubation time. It usually was within 1 - 4 kPa at the soil depth of 0.2 - 0.25 m in sodic soil with ESP below 20%, which agrees with result of Robbins' (1986b). However, the O₂ partial pressure in soil was high. In all control treatments, there existed an adequate oxygen supply of nearly 20 kPa except first few days of incubation, in which slightly low O₂ partial pressure of 10 - 18 kPa appeared at the soil depth of 0.25 m. Because the organic matter content in control soil is small and its easily decomposable parts have been decayed and depleted, the production of CO₂ gas and the consumption of O₂ gas don't greatly change with incubation time in control treatments.

After corn materials were added into sodic calcareous soil, the CO₂ partial pressure in soil diminished with incubation time (Fig. 3a.1a) but increased with soil depth (Fig. 3a.1b). The CO₂ partial pressure approximately followed an exponent attenuation process during the incubation period. At the first few days of incubation, the CO₂ partial pressure at the deep soil layers could be as high as 20 - 40 kPa. On the contrary, the O₂ partial pressure in soil increased with incubation time (Fig. 3a.2a) but decreased with soil depth (Fig. 3a.2b). The O₂ partial pressure usually maintained at a residual concentration of 1 - 2 kPa for a long time at the deep soil layers, which leads to an anaerobic decomposition environment. Its change tendency was temporally and spatially opposite to that of CO₂ partial pressure.

The dynamics of CO₂ production after application of corn materials is obviously different from that when no crop material is applied (control treatment). After corn materials are added into soil, easily decomposable compounds such as sugar and starch are promptly attacked by soil bacteria, carbon dioxide is produced and oxygen is consumed by microbial activity. After the easily decomposed organic matters are exhausted, microorganism numbers begin to decline. As a result, the release rate of carbon dioxide also simultaneously reduces.

The variation of CO₂ partial pressure with the incubation time generally is in agreement with the decay process of crop residues. At the initial stage of incubation, the CO₂ production rate is faster than its diffusion rate, the CO₂ gas diffusion at the surface soil layer and the accumulation at the deep soil profile result in its convex curve distribution along with the soil depth. Due to its fast diffusion into the atmosphere, the CO₂ partial pressure at the upper soil layer is obviously lower than that at the deep soil layers. The diffusion gradient of CO₂ partial pressure decreases with incubation time and soil depth, and the dominant diffusion layer moves down with incubation time. At the beginning of incubation, the thickness of diffusion layer was less than 0.1 m. Yet it was down to the whole soil profile that was being investigated at the 60th day of incubation (Fig. 3a.1b), which makes the CO₂ partial pressure in soil profile linear distribution against the soil depth.

The O₂ concentration in soil determines the type of decomposition reaction of organic matter and the CO₂ production rate. When adequate amounts of oxygen are

present in soil gas phase, aerobic reactions prevail; otherwise, anaerobic reactions predominate. Although carbon dioxide can be released from completely anaerobic environment through activities of obligate and facultative anaerobes, aeration invariably stimulates CO₂ production. Under a low oxygen concentration or anaerobic condition, decay of major crop constituents is depressed, and it takes place more slowly than when oxygen is in excess. It was reported that the soil respiration rate decreased to half of its maximum value when the O₂ concentration was below 2 kPa in the soil gas phase (Suarez and Simunek, 1993).

In an well-aerated soil, microbes consume O₂ about as fast as they release CO₂, the respiratory quotient is equal to 1 (Singer and Munns, 1987; White, 1997). The experimental results from control treatments follow this regulation because a constant sum of oxygen plus carbon dioxide partial pressures was obtained during the incubation process. It is believed that an aerobic decomposition of organic matter is maintained throughout the incubation period and the whole soil profile for the control experiments, and the CO₂ gas mainly is produced from aerobic reactions.

However, after corn materials are added into soil, a lot of O₂ consumption by microbial activity makes its concentration very low. At the shallow soil layer, the sum of oxygen and carbon dioxide partial pressures is a steady value of 20.51 kPa, which is comparable to the average value of 20.98 kPa in soil air (Taylor and Ashcroft, 1972). The respiratory quotient approximately is equal to 1, which manifests aerobic decomposition, throughout the incubation period, so aerobic reactions prevail at the upper part of soil profile. However, the sum of oxygen and carbon dioxide partial pressures at the deep soil layers is bigger than that at the shallow soil layer at the beginning of incubation, and then it tends to the same constant value as that at the shallow soil layer. Therefore, the respiratory quotient is greater than 1 at the initial stage of incubation, indicating anaerobic decomposition (White, 1997), and then approaches to 1 at the deep soil layers.

The calculated results indicate that the duration and the soil depth that suffer an anaerobic decomposition were changeable, and they depended on the application rate of corn materials and the soil ESP level. The bigger the application rate of corn

materials or the higher the soil ESP level, the longer the duration and the greater the soil depth that anaerobic decomposition persisted.

By comparing with the control treatments, it can be concluded that after corn material application, insufficiency of oxygen in the deep soil layers is caused by its fast consumption as a result of microbial respiration rather than by the poor-aeration from high soil wetness or soil compactness. The consumption rate of oxygen by microbial activity is too fast to be replenished in time from gas exchange with the atmosphere after application of corn materials.

CO₂ partial pressure as affected by corn material application and soil sodicity:

The CO₂ partial pressure in soil increased with the application of more corn materials (Fig. 3a.3). The relationship between the CO₂ partial pressure at the 30th day of incubation and the application rate of corn materials, and its correlative coefficient are listed in Tab. 3a.1 for two soil depths of 0.05 and 0.25 m. The intensity of microbe activity close depends on organic matter content in soil, the more the corn materials are applied, the greater the soil microorganism activity and the more they release CO₂. Statistical analyses show that the correlation coefficient between the CO₂ partial pressure and the application rate of corn materials is rather high (Tab. 3a.1). Due to fast CO₂ diffusion under a big gradient near the soil surface, the CO₂ partial pressure is less affected by the application rate of corn materials at the shallow soil layer than at the deep soil layer. Thus, their correlative coefficients at the deep soil layers are bigger than that at the shallow ones.

The experimental data showed a detectable influence of soil sodicity on soil CO₂ partial pressure within incubation of 30 and 60 days when the soil ESP ranged from 0.4% to 19.4% (Fig. 3a.3). The CO₂ partial pressure in soil increased with the increasing of soil ESP level at the application rate of corn materials less than 100 Mg ha⁻¹, which is consistent with the result of Laura's (1976). A high soil ESP level resulted in a big soil CO₂ partial pressure throughout the whole soil profile and incubation period (Fig. 3a.4), and its effect on CO₂ partial pressure was more pronounced at the deep soil layers than at the upper soil layer as a result of diffusion.

The mechanism that soil sodicity affects CO₂ accumulation in soil is not known at present. Two possible reasons maybe are responsible for this phenomenon. The first

one is soil solution pH. It was reported that the decomposition of organic matter was inhibited when solution pH was below 4.5 and above 9, and the optimum range of soil solution pH was near neutral to slightly alkaline (Brady and Weil, 1999; Singer and Munns, 1987). Hydrolyses of Na^+ -clay and CaCO_3 mineral in soil increase soil solution pH, the soil solution pH is expected to be higher than 6.4 in sodic calcareous soil after corn material application that is the theoretical pH value in calcium carbonate - water system at the CO_2 partial pressure of 20 kPa. The higher the soil sodicity, the greater the soil solution pH and subsequently it is nearer to the optimal pH range. A big pH value near neutral or slightly alkaline benefits the decomposition of organic matter, and hence increases production of CO_2 gas. It can be postulated that during incubation period, a big soil sodicity results in a higher solution pH, which is nearer to the optimal pH range, than a low soil sodicity does, and hence promotes the decomposition of added corn materials, especially at the initial stage of incubation where there is a higher CO_2 partial pressure and subsequently a lower solution pH.

Another possible reason is that the soil with a high ESP level is more susceptible to dispersion and swelling of clay particles. During the incubation period, when distilled water are added to the lysimeter to keep an steady soil water content, the swelling and dispersion of clay at the soil surface in the lysimeter is enhanced because of low electrolyte concentration in soil solution, which is below the critical flocculation value (Gupta et al., 1984b). Thus, seal and crust layer on soil surface is formed, diffusion passages of gas are blocked and passage radius are narrowed, consequently the gas diffusion in soil declines, which makes easier accumulation of CO_2 gas in soil.

The application of corn materials and the soil ESP level had an opposite influence on O_2 partial pressure as on CO_2 partial pressure in soil (data not shown). The O_2 partial pressure in soil decreased with the increases of the soil sodicity and the application rate of corn materials.

CO_2 evolution flux and its production rate:

The three main mechanisms of gas exchange are diffusion, convection and the dissolved gas movement with water. Usually the diffusion is far more important than another two mechanisms and is a dominant governing factor on gas evolution.

Under the assumptions that the upper boundary is the atmospheric CO₂ partial pressure of 0.035 kPa and the bottom boundary is zero flux, the CO₂ flux from soil surface to the atmosphere and its production rate were calculated from the observed CO₂ partial pressures in soil according to the procedure of De Jong and Schappert (1972). A diffusion coefficient of CO₂ gas in bulk air $1.8 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, an air-filled porosity 0.2 and an impedance factor 0.2 were employed to calculate the effective diffusion coefficient of CO₂ gas in the soil (White, 1997). The calculated surface fluxes on the 30th day of incubation versus the application rate of corn materials are shown in Fig. 4.5 for three soil ESP levels.

The CO₂ surface flux was close depended on the application rate of added organic matters, and the more the corn materials were applied, the higher the CO₂ surface flux. The fitted curve between the CO₂ surface flux at the 30th of incubation and the application rate of corn materials was statistically significant on 0.01 level in the whole tested range of soil sodicity. A distinct influence of soil sodicity on the CO₂ surface flux was not detected. Likewise, a similar relationship was found between the CO₂ surface flux and the CO₂ partial pressure at the soil depth of 0.25 m.

The CO₂ surface flux from sodic calcareous soil was greater after application of corn material than that from soil mixed with farmyard manure (Taylor and Ashcroft, 1972) (Fig. 3a.5), but both were at the same order of magnitude. The surface fluxes without organic matter application from both researches were similar, i.e., about $1.5 \times 10^{-4} \text{ g CO}_2 \text{ m}^{-2} \text{ s}^{-1}$, which is comparable to the reported data in normal forest soil, cropping soil or fallow soil at similar conditions (Buyanovsky et al., 1986; De Jong et al, 1974; Fernandez et al., 1993).

The calculated results demonstrate that the CO₂ production rate it decreased with the incubation time, but increased with the application rate of corn materials (data not shown). The influence of soil ESP level on CO₂ production rate was not obvious.

The CO₂ production rates versus the soil depth at different incubation time are depicted in Fig. 4.6 for sodic calcareous soil with ESP of 18.2% and corn materials of 142.5 Mg ha^{-1} . The maximum production rate of CO₂ gas appeared at the shallow soil layer at the beginning of experiment, and then its location lowered to the next deeper soil layer once the easily decomposable components of corn materials in this layer were

depleted. At the same time, the maximum production rate decreased with the incubation time until the peak value finally disappeared. After incubation of 60 days, a relative small production rate of CO₂ gas less than $1 \times 10^{-2} \text{ g CO}_2 \text{ m}^{-3} \text{ s}^{-1}$ was maintained over the whole soil profile. Comparatively, the maximum CO₂ production rate in the control treatments was in the order of magnitude of $10^{-3} \text{ g CO}_2 \text{ m}^{-3} \text{ s}^{-1}$. Therefore, most of the microbial activities associated with the added corn materials reaches to an end after 60 days.

Within the initial 40 days of incubation, the peak location of CO₂ production rate follows a power function relation with the incubation time. For the soil with ESP 18.2% and the corn material application rate of 142.5 Mg ha^{-1} , the depth of the maximum production rate can be estimated as:

$$D = 0.0233 * T^{0.5782} \quad \dots \dots (1)$$

$$R^2 = 0.966^{***} \quad n = 6$$

where D is the soil depth in which the maximum CO₂ production rate appears (m); T is the incubation time (day); R is the correlation coefficient and n the sample number.

The location of the peak value of CO₂ production rate (Fig. 4.6) is almost consistent with the depth of the point where the slope of the CO₂ distribution curve changes significantly (3a.1b). This depth actually is the thickness of diffusion layer of the CO₂ gas in soil. It also can be seen by comparing Fig. 3a.6 with Fig. 3a.2 that the maximum CO₂ production rate approximately appears at the soil depth where the O₂ partial pressure still is low but it is to increase. It can be inferred that although the O₂ concentration at the bottom of diffusion layer is low at the moment, a transition from anaerobic reactions to aerobic reactions has substantially improved the decomposition of organic matter and leads to a big production rate of CO₂ gas. Therefore, it is verified again that the main restriction factor for the decomposition of applied corn materials is deficiency of O₂ gas in sodic calcareous soil.

The decomposition process of added organic matter, which is described in Fig. 3a.6, was confirmed by corn material residues in the lysimeter after incubation. It can be found from collection of corn material residues after experiment that the decomposed extent of applied organic matter was greater at the upper soil layers than at the deep soil layers. At the upper part of soil profile, majority of added corn

materials were almost completely decomposed, it was difficult to pick up the residue samples of corn materials from the experimental soil after incubation of 30 or 60 days, and the colour of residues became black. However, at the deep part of soil profile, only parts of added corn materials were decayed, non-easily decomposable constituents of corn materials remained, and their color had little change after incubation of 30 - 60 days.

Conclusions

When a lot of crop materials were added into sodic calcareous soil, their decomposition was more complicated and obviously different from that of native organic matter in soil that generally was subjected to an aerobic decomposition at normal content. The O_2 concentration in soil was a restriction factor for the intense decomposition of applied organic matter due to its fast consumption. An anaerobic decomposition often appeared at the deep soil layers during most majority of incubation period after corn material application. The duration and the soil depth of anaerobic decay increased with the increases of the application rate of corn materials and the soil ESP level.

During incubation period, the CO_2 partial pressure in soil declined with the incubation time but increased with the soil depth, which was temporally and spatially opposite to the variation of O_2 partial pressure in soil. The CO_2 partial pressure in soil increased with the application rate of corn materials. The CO_2 surface flux and its production rate also increased with the application rate of corn materials.

The soil ESP level had a significant influence on the CO_2 partial pressure in sodic calcareous soil, and the higher the soil ESP level, the bigger the CO_2 partial pressure. Yet its effect on the surface flux and the production rate of CO_2 gas was not distinguishable.

Tab. 3a.1 Regression equations between the soil CO₂ partial pressure (Pco₂, kPa) on the 30th day of incubation and the application rate of corn materials (ARC, Mg ha⁻¹) and their correlative coefficients for three kinds of soil ESP levels

Soil depth		0.05		0.25	
(m)					
ESP (%)	Item	Equation	R ²	Equation	R ²
1		$P_{CO_2} = -2 \cdot 10^{-5} \cdot ARC^2$	0.698 ^{**}	$P_{CO_2} = -3 \cdot 10^{-4} \cdot ARC^2$	0.996 ^{***}
		$+0.0109 \cdot ARC + 0.7278$		$+0.1548 \cdot ARC + 1.218$	
11		$P_{CO_2} = -3 \cdot 10^{-5} \cdot ARC^2$	0.462	$P_{CO_2} = -8 \cdot 10^{-4} \cdot ARC^2$	0.964 ^{***}
		$+0.0149 \cdot ARC + 0.5597$		$+0.2321 \cdot ARC + 1.9692$	
18		$P_{CO_2} = -3 \cdot 10^{-4} \cdot ARC^2$	0.859 ^{***}	$P_{CO_2} = -1.5 \cdot 10^{-3} \cdot ARC^2$	0.962 ^{***}
		$+0.0701 \cdot ARC + 0.1841$		$+0.3375 \cdot ARC + 1.8777$	

Note: ** and *** stand for the statistical significance on 0.05 and 0.01 levels, respectively.

Fig. 3a.1a The distribution of CO₂ partial pressures at different soil depths along with the incubation time after corn materials of 142.5 Mg ha⁻¹ were applied into sodic soil with ESP of 18.2%

Fig. 3a.1b The spatial distribution of soil CO₂ partial pressures at different times during the incubation period after corn materials of 142.5 Mg ha⁻¹ were applied into sodic soil with ESP of 18.2%

Fig. 3a.2a The distribution of O₂ partial pressures at different soil layers with the incubation time after corn materials of 142.5 Mg ha⁻¹ were applied into sodic soil with ESP of 18.2%

Fig. 3a.2b Spatial distribution of O₂ partial pressures in soil at different times during incubation period after corn materials of 142.5 Mg ha⁻¹ were applied into sodic soil with ESP of 18.2%

Fig. 3a.3 The CO₂ partial pressures at soil depths of 0.05 m and 0.25 m versus the application rate of corn materials for three soil ESP levels on the 30th day of incubation

Fig. 3a.4a The CO₂ partial pressures at soil depths of 0.05 and 0.25 m against the incubation time for three soil ESP levels at similar application rates of corn materials (ARC) of 82 - 87 Mg ha⁻¹

Fig. 3a.4b The CO₂ partial pressures on the 20th, 40th and 60th days of incubation against the soil depth for three soil ESP levels at similar application rates of corn materials (ARC) with 82 - 87 Mg ha⁻¹

Fig. 3a.5 The surface CO₂ flux on the 30th day of incubation versus the application rate of corn materials for three soil ESP levels. The dot line and its data were from the added farmyard manure (Taylor and Ashcroft, 1972)

Fig. 3a.6 The CO₂ production rate during the incubation period versus the soil depth for sodic calcareous soil with ESP of 18.2% after application of corn materials at the rate of 142.5 Mg ha⁻¹

Research report 3b

IMPROVING EFFICIENCY OF SODIUM-AFFECTED SOIL RECLAMATION BY CROP MATERIALS

Abstract

In order to find a new sustainable method about sodic calcareous soil rehabilitation, an investigation about the improving role of corn materials (*Zea mays* L.) on native CaCO_3 mineral dissolution and on sodic soil reclamation efficiency was carried out.

The experimental results demonstrated that application of crop materials significantly lowered the leachate pH, increased the dissolution rate of native calcium carbonate mineral and the effluent EC, subsequently remarkably enhanced the reclamation efficiency of sodic calcareous soil. When corn materials were applied at the rate of 100 Mg ha^{-1} , total solution concentration of effluent at the 6.5 PV was among $2.75 - 4.25 \text{ mmol L}^{-1}$ for various soil ESP levels and incubation periods, which is approximately equivalent to the critical flocculation concentration of moderate sodic soil. The reclamation efficiency of sodic calcareous soil increased with the application rate of corn materials. When corn materials were added into moderate sodic soil at the rates of 87.5 and 142.5 Mg ha^{-1} , the soil ESP levels were respectively cut down 27.9% and 50.1% above the control treatments after incubation of 60 days and leaching of 6.5 pore volumes.

Incubation of corn materials with soil played a very significant role on sodic calcareous soil reclamation, and it greatly increased the reclamation efficiency. A short incubation period obviously caused a lower effluent pH, favoured the dissolution of calcium carbonate minerals, and increased electrolyte concentration in sodic calcareous soil after application of crop materials. Yet incubation time had little influences on these factors in nonsodic soil.

A high soil ESP level improved the dissolution of native calcium carbonate mineral in soil and increased the effluent EC. The exchangeable Na^+ played a dominant role on carbonate mineral dissolution in alkaline environment ($\text{pH} > 6 - 7.2$).

Introduction

Reclamation of sodium-affected soil is an old subject for agricultural sustainable development in the arid and semiarid regions. Many chemical and biochemical methods for sodic soil reclamation have been investigated according to specific local situations (Dubey and Mondal, 1993; Keren, 1996; Robbins, 1986a; Sekhon and Bajwa, 1993).

Generally speaking, amelioration of sodic soil seems to be simple, exchange and leaching are two necessary processes. Nevertheless, two primary problems obstruct success of sodic soil rehabilitation activity: low percolation rate and high economic and environmental cost. Therefore, where the required divalent cations come from, how high the solution concentration in drainage water is and how big the infiltration rate is during reclamation process are interested by many soil scientists because these factors determine the cost efficiency, and the applicability and suitability of employed method at given conditions.

With the promotion of awareness about environmental protection, the choice of available scenarios for sodic soil reclamation has been restricted because of inevitable adverse impact of high salt drainage water caused by chemical amendments on ecological environment. It is imperative to find a suitable and economical method about sodic soil rehabilitation.

In widespread sodic calcareous soils in the arid and semiarid regions, native calcium carbonate minerals that come from either pedogenic process or fresh precipitation of high saline irrigation or drainage water exist in a large amount, and it is a vast source of calcium if it can be properly utilized. However, how to use this Ca^{2+} source during sodic soil reclamation still remains a practical obstacle because of the low solubility of carbonate minerals if there is no application of acid compounds or acid-forming chemicals that are detrimental to ecological environment.

A high CO₂ concentration in soil lowers the pH value of soil solution, and subsequently increases the dissolution of native CaCO₃ mineral in soil and the Na⁺ replacement from the exchange sites (Cruz-Romero and Coleman, 1974). The CO₂ concentration in soil is about ten to one thousand times that in atmosphere (Lindsay, 1979), it mainly is produced from biological activities such as root respiration and microbial oxidation of organic matter etc. The soil CO₂ concentration depends on soil type, organic matter content and vegetation, temperature, and soil moisture and so on. Although it has a great temporal and spatial variation, the CO₂ concentration in soil usually maintains a relatively high value at high moisture content (Buyanovsky and Wagner, 1983; Elliott and McCalla, 1972). In normally irrigated cropping field, the CO₂ concentration is within about 3.5 - 10 kPa or higher (Buyanovsky et al., 1986; Elliott and McCalla, 1972; Lindsay, 1979; Solomon and Lerling, 1987).

Besides, a leaching process also improves the dissolution of native carbonate mineral (Ch. 3). Therefore, it is possible that the native calcium carbonate mineral in soil may become as a potential amendment for sodic soil reclamation if its dissolution can be enhanced by some means except acidic chemicals. The utilization of native calcium carbonate mineral as a Ca²⁺ supplier not only can reduce the cost of soil reclamation but also cuts down the heavy load of high saline drainage water to surface water system and groundwater resource, and hence prevents the pollution of natural environment during reclamation process. By application and incubation of crop materials whose decomposition can release a lot of CO₂ gas into soil (Ch. 4), this hypothesis will be verified in present research.

Chhabra and Abrol (1977) found that the increased hydrolysis and CO₂ concentration liberated by plant roots were important on the dissolution of native CaCO₃ mineral. The results of Robbins' (1986) as well as Sekhon and Bajwa's (1993) confirmed that regardless of CO₂ source, one fact was that the soil CO₂ concentration was elevated, the solution pH value was lowered, the calcareous mineral was dissolved, and the Ca²⁺ concentration in solution was increased in cropping field. However, McNeal et al. (1966) thought no any enhanced solubility of CaCO₃ in the presence of CO₂ given off by rice roots could be found, and the observed beneficial effects of plant growth on sodic soil reclamation resulted largely from the physical

action of plant roots in improving soil permeability and leaching rather than from the production of CO_2 .

These research results greatly improve our understanding about CO_2 production and its role on the sodic calcareous soil rehabilitation in cropping field. Nevertheless, the CO_2 role on the CaCO_3 dissolution isn't built well under low concentration situation, the contribution of the increased CO_2 concentration to the native CaCO_3 mineral dissolution and sodic soil reclamation is not distinguished clearly from other factors such as the exchangeable cation and the physical role of plant roots etc. The beneficial effect of CO_2 gas produced from normal cropping soil on the practical reclamation engineering of sodic soil deserves to doubt because of its low concentration and weak influence.

Our previous experiments have verified that the native carbonate mineral dissolution was obviously improved by the leaching of CO_2 -enriched distilled water (Ch. 3) and that the application of crop materials into sodic calcareous soil significantly elevated CO_2 concentration in soil (Ch. 4). Thus, it is expected that the application of crop materials can improve the availability of soluble calcium ions so as to accomplish sodic calcareous soil reclamation faster and more economically than in the past, thereby to explore a new amelioration method about sodic calcareous soil.

The objectives of this study were: 1) to investigate the dissolution kinetics of native CaCO_3 mineral; 2) to observe the dynamic variation of chemical components in effluent; and 3) to evaluate the reclamation efficiency of moderate sodic calcareous soil after application of crop materials.

Materials and Methods

The soil collection and sample preparation has been described in Ch. 3 in detail.

The crop material (*Zea mays* L.) collection and its pre-treatment were the same as described in Ch. 4. The chemical element contents of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , P-phosphate, and N-NH_4^+ in corn materials were analysed by standard methods before the corn materials were applied.

The lysimeter preparation and operation in the incubation period was the same as that described in Research report 3a.

After incubation in a constant temperature chamber of 25°C for the designated time, the lysimeter was leached with distilled water, which was supplied by a peristaltic pump, at the pressure of 10 - 20 mm water head under the atmospheric CO₂ concentration.

The leachate pH was monitored by an automatic pH-meter before the effluent was exposed to the atmosphere. Effluent samples were collected by a fraction collector for the EC measurement, solid content observation, and chemical analyses. The concentrations of Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, SO₄²⁻, and P-phosphate ion in effluent were measured.

All chemical analyses were conducted according to routine procedures: the Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻ and HCO₃⁻ concentrations were respectively determined by the methods described in Ch. 2. The concentrations of N-NH₄⁺, SO₄²⁻ and P-phosphate by the spectrophotometry (Quikchem 800, Lachat).

After the leaching, the lysimeter was freely drained for one day. Then, the soil samples and corn material residues were respectively collected at seven different locations, that is, at every 50 mm interval along the vertical direction of the lysimeter, the soil surface and the bottom of soil profile. The soil samples were dried in an oven at 105°C for 12 hours, and their ESP values were determined. The crop residual samples were carefully washed with distilled water, and dried in an oven of 45°C for about one week, then they were analyzed for chemical elements that were the same as those before incubation.

The designed soil ESP levels were 0, 10% and 20%, the application rates of corn materials were 0 (control), 80 and 150 Mg ha⁻¹, and the incubation periods were 30 and 60 days, respectively. The leaching velocity was kept at 10 mm h⁻¹ in this study.

Results and Discussion

Leachate pH:

When nonsodic calcareous soil without application of corn materials (control treatment) was leached, the leachate pH was steady during the whole leaching process and kept at 8.1 (Fig. 3b.1), which is within the normal range of 7.5 to 8.5 found in calcareous soil (Loeppert and Suarez, 1996). The leachate pH is buffered by soil very

well. However, after corn materials were applied, the leachate pH was much smaller than that without application of corn materials, but it slightly increased with the leaching volume.

The leachate pH at the 6.5 PV linearly decreased with the application rate of corn materials, and it almost was independent on incubation duration in nonsodic calcareous soil (Fig. 3b.2). Because a lot of CO_2 gas is produced from organic matter decomposition and is dissolved in soil solution, the pH in leachate always is lower after application of corn materials than that without application of corn materials, and the more the corn material application, the lower the leachate pH.

When sodic calcareous soil was leached, if no corn material was added into soil, the effluent pH rapidly increased with the leaching volume because of the hydrolysis of Na^+ -clay particles (Fig. 3b.1). It reached as high as 9.7 at the 6.5 PV for soil with ESP of 16.2% no matter how long the incubation took. However, after some corn materials were applied, the pH in effluent was significantly cut down, and this effect remained during the whole tested leaching process. For example, when application rate of corn materials was 100 Mg ha^{-1} , the leachate pH from sodic calcareous soil with ESP of 16.2% - 19.4% was about 2 pH units lower during the whole leaching process than that without application of corn materials.

Similar to that in nonsodic soil, the effluent pH at the 6.5 PV from sodic calcareous soil decreased with the application rate of corn materials, but its reduction gradient was significantly greater than that in nonsodic soil (Fig. 3b.2). The rapid decline tendency of leachate pH with the increase of application rate stopped after the application rate was greater than 100 Mg ha^{-1} . Hereafter, the effluent pH maintained a steady value, and the increase of application rate no longer distinctly affected the effluent pH. Owing to a great influence of CO_2 concentration on solution pH, the CO_2 gas in soil produced from corn material decomposition obviously changes the dissolution environment of native CaCO_3 mineral after corn material application.

A short incubation period of 30 days resulted in a lower leachate pH than a long incubation period of 60 days did after corn materials were applied (Fig. 3b.2). Owing to its continuous decline during incubation period (Research report 3a), the CO_2 partial pressure in soil is obviously higher after a short incubation period than after

a long incubation period after corn material application. A high CO₂ partial pressure in soil leads to a low solution pH; on the contrary, a low CO₂ partial pressure is responsible to a high pH of soil solution. Although CO₂ gas can be produced from anaerobic reactions during leaching process, its production rate should be much smaller than that in incubation period. The CO₂ partial pressure and its dissolution in soil solution during incubation period have a dominant influence on leachate pH during leaching process. Therefore, the higher the CO₂ partial pressure in soil when a leaching process is to begin, the lower the effluent pH during the leaching process.

The effluent pH increased with the soil ESP level (Fig. 3b.2). The higher the soil sodicity, the greater the intensity of Na⁺-clay hydrolysis, so the higher the solution pH. If there is no application of corn materials, this pattern is very clear (Fig. 3b.2). After corn materials are used, a few exceptions exist. When the application rate of corn materials was bigger than 60 Mg ha⁻¹, the effluent pH from nonsodic soil even was higher than that from sodic soil with ESP of 11% after incubation of 30 days, which probably is the result of higher CO₂ concentration in sodic calcareous soil as compared with nonsodic calcareous soil (Research report 3a).

Generally, after corn materials were applied and incubated, the effluent pH was lowered at different extents, which mainly depends on the application rate of corn materials, soil sodicity, and incubation time. In comparison with the control treatments, the decline extent of effluent pH usually reached 0.8 - 2.2 pH units at the 6.5 PV after corn materials of 100 Mg ha⁻¹ were applied.

Moreover, the corn material application lowered the leachate pH more significantly than the elevated external CO₂ partial pressure did (Fig. 3b.3). After corn materials were applied, the effluent pH was greatly cut down no matter whether calcareous soil was sodic or nonsodic (Fig. 3b.2). However, though an elevated external CO₂ concentration also could decrease the effluent pH, its effect was not obvious within the first 10 PV even though the CO₂ partial pressure was up to 5 kPa owing to stronger influences of soil sodicity and its buffer capability (Fig. 2.2).

Leachate EC:

The leachate EC declined along with leaching, and its decrement gradient became smaller and smaller with the leaching process (Fig. 3b.4). The corn material

application increased leachate EC during the whole leaching process, but its influence on leachate EC was more significantly in nonsodic soil than in sodic soil. Meanwhile, due to incubation role, the leachate EC increased substantially within the first one to two pore volumes after application of corn materials.

The leachate EC value at the 6.5 PV increased with the application rate of corn materials, and the increase gradient versus the application rate depended on soil sodicity (Fig. 3b.5). In normal soils without application of corn materials (control treatments), the leachate EC was smaller from nonsodic calcareous soil than that from sodic calcareous soil, and their difference was about 0.1 dS m^{-1} . After corn materials were applied, the leachate EC increased because of the increased CaCO_3 mineral dissolution by more carbonic acid attacks and the decline of solution pH. Due to stronger influence of exchangeable cation on native CaCO_3 dissolution in sodic soil, the role of increased CO_2 partial pressure on CaCO_3 dissolution is overshadowed in sodic calcareous soil, so the increment gradient of EC against the application rate is much greater in nonsodic soil than in sodic soil. With the increase of application rate, the difference of effluent EC values between sodic and nonsodic soils became smaller and smaller. When application rate of corn materials reached about 70 Mg ha^{-1} , the leachate EC values from both soils were similar. This moment, the effect from crop material application in nonsodic calcareous soil and that from exchangeable cation together with corn material application in sodic calcareous soil are approximately equivalent on CaCO_3 dissolution.

The effluent EC values from sodic calcareous soils with different initial ESP levels were similar after leaching of 6.5 PV (Fig. 3b.5). It can be postulated that after application and incubation of corn materials, the difference of soil sodicities with different initial ESP values tends to be narrowed because of more CaCO_3 dissolution and cation exchange at the high soil ESP level during the incubation period. Assuming that the soil solution pH is 7.5 during the incubation period, a Ca^{2+} concentration of about $10 - 18 \text{ mmol L}^{-1}$ is available after equilibrium of CaCO_3 - water solution at the atmospheric CO_2 partial pressure (Butler, 1981; Lindsay, 1979). These soluble calcium ions may decrease the soil ESP from initial value of 20% to 13.7% - 16.9% according to theoretical calculation. If the improving role of exchangeable Na^+ on calcite

dissolution is taken into consideration, the reduction extent of soil sodicity during the incubation period will be much bigger and the different initial soil ESP levels approach to be more consistent. Therefore, the leachate EC at the 6.5 PV from different initial ESP values of 11% and 18% are not significantly different in present experimental treatments.

Fig. 3b.6 shows that the influence of incubation on soil CaCO_3 dissolution was significant. The application and incubation of corn materials at the rate of 111 Mg ha^{-1} made the effluent EC from nonsodic soil up to 0.34 dS m^{-1} at the 6.5 PV. This value is bigger than that under an elevated external CO_2 concentration of 4.8 kPa, whose EC is only 0.22 dS m^{-1} . However, because of the significant reduction of soil ESP level during the incubation period, although corn materials at the rate of 100 Mg ha^{-1} are applied and incubated in sodic calcareous soil with ESP of 19.4%, the leachate EC still is slightly lower than that of soil ESP of 19.3% at the CO_2 partial pressure of 0.035 - 5.1 kPa except the first pore volume, which demonstrates an importance of exchangeable cation on native CaCO_3 dissolution. The big EC in leachate within the first pore volume is a result of incubation.

However, the influence of incubation time on leachate EC was weak although it was distinguishable. A long incubation period of 60 days generally led to a low leachate EC and vice versa (Fig. 3b.5). During incubation period, carbonic acid attack is weakening and solution pH is rising, which possibly causes CaCO_3 to precipitate. So if incubation period is long, the dissolution of soil carbonate mineral is depressed. On the contrary, if a short incubation period is used, a big effluent EC can be obtained. Because of different mechanisms of soil carbonate mineral dissolution in sodic soil and in nonsodic soil, the effect of incubation time on leachate EC also is different. In nonsodic calcareous soil, incubation time almost doesn't affect soil solution pH owing to soil buffer (Fig. 3b.2), hence it affects leachate EC only by the intensity variation of carbonic acid attack. Although incubation time can obviously decreases effluent pH in sodic calcareous soil, its influence on leachate EC is cut down by stronger improving effect of exchangeable cation on carbonate dissolution, and the higher the soil ESP level, the weaker the influence of incubation time. This inference is verified by our experiment data (Fig. 3b.5).

Two fitted equations between the effluent EC at the 6.5 PV and the application rate of corn materials are built up regardless of incubation period, they are:

For nonsodic calcareous soil:

$$EC = 0.0018 * ARC + 0.1353 \quad \dots \dots (1)$$

$$R^2 = 0.936^{***} \quad n = 6$$

For sodic calcareous soils with ESP of 11% - 18%:

$$EC = -3.5 * 10^{-6} * ARC^2 + 9.48 * 10^{-4} * ARC + 0.239 \quad \dots \dots (2)$$

$$R^2 = 0.457 \quad n = 12$$

where EC is electrical conductivity in effluent (dS m^{-1}); ARC is application rate of corn materials (Mg ha^{-1}); R is correlative coefficient and n sample number.

It can be found by comparing Fig. 3b.5 with Fig. 3b.2 that the leachate EC generally was opposite to the effluent pH value against the application rate of corn materials. A low pH value brought about a big EC value in effluent and vice versa. The solution pH affects carbonate mineral dissolution possibly by carbonic acid attack and solution saturation extent other than by hydrogen ion attack in sodic calcareous soil. Hydrogen ion attack doesn't have any obvious effect on CaCO_3 dissolution at solution pH higher than 7, it can not explain this correlation relationship between the effluent EC and pH at all at so high pH range of 7 - 9.7. The carbonic acid attack is the main mechanism of CaCO_3 mineral dissolution in alkaline environments when CO_2 partial pressure is bigger than 10 kPa (Plummer, et al., 1978), it should be valid in the present experiment conditions. Furthermore, the soil CaCO_3 dissolution in a nonequilibrium solution under leaching situation is related with its saturation extent. CO_3^{2-} activity in solution is greatly affected by solution pH: a low pH causes a low carbonate ionic activity and subsequently a small ionic activity product of calcite, which results in more dissolution of native soil CaCO_3 mineral.

The relationship between EC and pH of effluent in sodic calcareous soil was apparently different from that in nonsodic calcareous soil (data not shown). When the effluent pH was above 7.2, the leachate EC was remarkably smaller in nonsodic soil than in sodic soil at the equal pH value. Therefore, the contribution of exchange-induced carbonate mineral dissolution to leachate EC is more important in alkaline environment. Yet, the gradient of the EC versus pH was smaller in sodic soil than in

nonsodic soil. When the effluent pH was below 7.2, the relations between EC and pH of effluent from both soils were similar. The solution pH will play a dominant role on carbonate mineral dissolution in acid solution. Therefore, the improved dissolution of carbonate mineral by exchangeable cations should not be neglected when we consider calcium carbonate dissolution under the leaching of sodic calcareous soil.

After corn materials were applied, effluent EC value declined sharply with the increase of water flow velocity possibly due to shortage of reaction time for biological activity in lysimeter (data not shown). The more the corn materials were applied, the faster the effluent EC declined with the flow velocity. The leachate EC value after corn material application is seriously affected by water flow velocity, so a low leaching velocity should be kept so as to obtain a high soil electrolyte concentration after crop materials are applied, which is beneficial to reclamation activity.

Dissolution rate of native calcium carbonate mineral:

By assuming a stoichiometrical exchange between Ca^{2+} and Na^+ , the release rate of Ca^{2+} , i.e., the dissolution rate of soil CaCO_3 mineral in mole per second was calculated under various application rates of corn materials.

The release rate of Ca^{2+} at the 6.5 PV from soil calcium carbonate mineral generally increased with the application rate of corn materials (Fig. 3b.7). The release rate was linearly related with the application rate of corn materials in nonsodic calcareous soil; but it had a decline tendency in sodic calcareous soil when the application rate was more than 80 - 90 Mg ha^{-1} because of the increased soil porosity. After more corn materials are added into soil, soil porosity increases, so more and more percolation water passes through big pore passages, and subsequently the ionic diffusion distance increases and the water flow velocity becomes small at a given infiltration flux. As a result, the concentrations of reaction products increase and the dissolution of calcium carbonate mineral declines. In addition, the increased porosity also leads to a decline of CO_2 partial pressure in soil and in turn a decline of carbonic acid attack and a raising of solution pH. This maybe also is a reason for the decrease of CaCO_3 dissolution rate in sodic calcareous soil after corn material more than some critical amount is applied.

Moreover, it can be found by comparison of Fig. 3b.7 and Fig. 3b.5 that CaCO_3 mineral dissolution rate is more sensitive to the increase of soil porosity caused by application of more corn materials than the leachate EC is.

The release rate of Ca^{2+} from nonsodic calcareous soil always was smaller than that from sodic calcareous soil owing to the enhanced dissolution of calcium carbonate mineral caused by exchange reaction in sodic calcareous soil. Yet its increment gradient against the application rate of corn materials was greater in nonsodic calcareous soil than in sodic calcareous soil (Fig. 3b.7). Similar to the effluent EC, the initial soil ESP level didn't obviously affect the release rate of Ca^{2+} at the 6.5 PV in sodic soils with ESP range of 11% - 18%, and their release rates were similar.

The incubation duration had a significant effect on the release rate of Ca^{2+} (Fig. 3b.7). For the nonsodic calcareous soil, a long incubation period of 60 days responded to a slightly greater release rate, which suggests that a long incubation time is advantageous to the dissolution of soil carbonate mineral under the similar pH conditions (Fig. 3b.2). However, for the sodic soil, a long incubation time brought about a low release rate of Ca^{2+} , which is caused by the same reason as that on the leachate EC.

The relationship between the release rate of Ca^{2+} and the effluent pH was similar to that between the leachate EC and pH at the 6.5 PV (data not shown). At the equal pH, the release rate of Ca^{2+} from sodic calcareous soil was obviously bigger than that from nonsodic calcareous soil. Both release rates from nonsodic and sodic soils are expected to be equal in an acid solution where a pH approximates to 6, which is lower than that when the effluent EC values from both soils are equal, i.e., pH = 7.2. Below this pH level, the influence of exchangeable Na^+ on the release rate of Ca^{2+} disappeared. Therefore, it can be concluded that if the solution pH is lower than 6 - 7.2, the effect of exchangeable cations on the dissolution of soil carbonate mineral can be neglected; otherwise, its role is significant. The solution pH always is higher than 7 under the leaching of sodic calcareous soil even after application of crop materials at a large amount (Fig. 3b.2), thus the contribution from exchangeable cations to soil carbonate mineral dissolution is dominant in sodic calcareous soil reclamation.

It can be seen from Fig. 3b.8 that the leachate EC at the 6.5 PV increased with the enhancement of carbonate mineral dissolution. The leachate EC linearly depended on the Ca^{2+} release rate respectively in the nonsodic and the sodic calcareous soils, yet it was close but not linearly correlated with the dissolution rate of calcium carbonate mineral when all tested soil ESP levels were taken as a whole. All above statistical relationships are significant on 0.01 level, so the effluent EC can be used as an approximate index to express the dissolution rate of calcium carbonate mineral in soil.

The regressive equation between the leachate EC and the dissolution rate for all observed soil ESP levels is as follows:

$$EC = 8.65 * 10^3 * RATE^{0.66} \quad \dots \dots (3)$$

$$R^2 = 0.634^{***} \quad n = 18$$

in which, RATE is the release rate of Ca^{2+} from dissolution of native calcium carbonate mineral (mol s^{-1}); the other symbols have the same meanings as above.

It also can be found from Fig. 3b.8 that the EC gradient against the release rate from nonsodic calcareous soil was obviously greater than that from sodic calcareous soil. If solution composition does not affect the leachate EC, the leachate EC should have a linear function relation with the dissolution rate of carbonate mineral no matter whether soil is sodic or nonsodic. This deviation between the sodic soil and the nonsodic soil displays that the exchange reaction between the soluble Ca^{2+} in solution and the Na^+ adsorbed in clay complexes lowers the effluent EC due to a smaller ionic equivalent conductance of Na^+ than that of Ca^{2+} (Weast and Astle, 1982).

Dynamics of chemical element composition in effluent:

1. Variation of ionic concentrations:

The concentrations of chemical elements in effluent were changing along with the leaching volume, application rate of crop materials, soil ESP level and incubation duration. All ionic concentrations in leachate were decreasing with the leaching volume (Fig. 3b.9) except sulfate and phosphate ions, whose concentrations were steady during leaching process.

In nonsodic calcareous soil, the ions in effluent could be divided into two groups: one was major ion group including $\text{HCO}_3^- + \text{CO}_3^{2-}$ and Ca^{2+} , their ionic concentrations were relative big. Another was minor ion group, Mg^{2+} , K^+ , Na^+ , P-

phosphate and SO_4^{2-} belonged to this group, and their concentrations were low. The Cl^- was a special ion, it transferred from the major ion group into the minor one within 2 - 3 PV. When sodic calcareous soil was leached, Ca^{2+} and Na^+ exchanged their groups due to exchange reactions between the soluble Ca^{2+} in solution and the Na^+ adsorbed in clay particles, and the Na^+ concentration was big and Ca^{2+} concentration was small in solution. These two cations are mutual complementary in effluent, they can not simultaneously stay at the same group when sodic calcareous soil is leached by distilled water.

The separation of two ion groups was obvious. Their relative positions in all experiment treatments were steady during leaching process though their concentrations in effluent were highly variable. The ionic concentrations in the major ion group usually were several to dozen times that in minor ion group, hence the influence of ions in the minor ion group on carbonate mineral dissolution and sodic soil reclamation can be safely discounted due to their rather low concentrations.

Concentrations of all ions in effluent were increased after application of corn materials (Fig. 3b.9). The influence of corn material application was especially evident at initial leaching stage as a result of incubation, yet it gradually decreased with leaching.

Fig. 3b.10 demonstrated that the corn material application at the rate of 111 Mg ha^{-1} played a similar role to the application of external CO_2 partial pressure of 4.8 kPa on carbonate mineral dissolution in nonsodic calcareous soil during leaching process. Their Ca^{2+} concentration was about $2 \text{ mmol}_e \text{ L}^{-1}$ at the 6.5 PV except the first 2 PV. When no crop material was applied, the Ca^{2+} concentration in effluent from nonsodic calcareous soil after incubation of 30 days was equal to that when an external CO_2 partial pressure of 0.035 kPa was applied, and they was $1 \text{ mmol}_e \text{ L}^{-1}$ at the 6.5 PV. The incubation of nonsodic calcareous soil without corn material application didn't show any obvious influence on carbonate mineral dissolution. Yet the incubation of corn materials resulted in a greater peak of Ca^{2+} concentration to $10.5 \text{ mmol}_e \text{ L}^{-1}$ after application of corn material at the rate of 111 Mg ha^{-1} in contrast with a peak concentration of $7.2 \text{ mmol}_e \text{ L}^{-1}$ at the CO_2 concentration of 4.8 kPa. It is postulated

that it is this part of soluble Ca^{2+} ions dissolved in the incubation period that exchanges the majority of all removed Na^+ ions from clay complexes.

As compared with the leachate EC from nonsodic calcareous soil (Fig. 3b.6), it is believed that the effluent EC value is greater after corn material application at the rate of 111 Mg ha^{-1} than that after application of elevated CO_2 concentration of 4.8 kPa possibly is caused by the release of Cl^- and K^+ from crop material decomposition.

Soil sodicity increased the concentrations of HCO_3^- and Na^+ , but decreased those of Ca^{2+} , Mg^{2+} and K^+ in effluent, and the Cl^- concentration almost was independent on soil ESP level (Fig. 3b.11). When soil ESP level increases, Ca^{2+} concentration in leachate is depressed because of its exchange with the Na^+ adsorbed in the exchangeable phase. The Na^+ is released into solution and the Ca^{2+} is adsorbed in clay complexes, thus the Na^+ concentration in effluent becomes greater. The concentration of carbonate alkalinity increases with the raising of soil sodicity as a result of improved carbonate mineral dissolution. However, the Mg^{2+} and K^+ concentrations in leachate decline with the increase of soil ESP level, both ions possibly involve in ion exchange with the adsorbed Na^+ , but their concentrations in solution usually are very low.

Influence of incubation period on ionic concentrations was weak and complicated; meanwhile, its uncertainty was high.

Like the effluent EC, total electrolyte concentration in effluent decreased with the leaching volume, but increased with the application rate of corn materials. The ionic concentrations and total solution concentration at the 6.5 PV are listed in the Tab. 3b.1 for various experiment treatments. After leaching of 6.5 pore volumes, the total solution concentration was about $1.4 - 2.7 \text{ mmol}_e \text{ L}^{-1}$ if no corn material was used (Tab. 5.1). When corn materials of 100 Mg ha^{-1} were applied, it got to about $2.75 - 4.25 \text{ mmol}_e \text{ L}^{-1}$, which is approximately equivalent to the critical flocculation concentration of $3 - 5 \text{ mmol}_e \text{ L}^{-1}$ for moderate sodic soil with ESP below 20% (Shainberg and Letey, 1984). Therefore, it is expected that serious clay dispersion and in turn the destruction of soil stability is impossible to happen during reclamation process if corn materials of 100 Mg ha^{-1} are applied.

The regressive equation between the total solution concentration at the 6.5 PV and the application rate of corn materials is:

For nonsodic calcareous soil:

$$TSC = 0.0162 * ARC + 1.4739 \quad \dots \dots (4)$$

$$R^2 = 0.949^{***} \quad n = 6$$

For sodic calcareous soils with ESP of 11% - 18%:

$$TSC = -1.08 * 10^{-4} * ARC^2 + 0.0212 * ARC + 2.58 \quad \dots \dots (5)$$

$$R^2 = 0.499^* \quad n = 12$$

where TSC is total solution concentration in effluent ($\text{mmol}_e \text{ L}^{-1}$); the other symbols have the same meanings as above.

2. Relative ionic composition:

The experiment result demonstrated that at the initial stage of leaching, the charge equivalent concentration of $\text{HCO}_3^- + \text{CO}_3^{2-}$ in leachate was much smaller than the Ca^{2+} concentration for nonsodic soil or the $\text{Ca}^{2+} + \text{Na}^+$ concentration for sodic soil as a result of residual calcium salt from soil sample preparation. Then carbonate alkalinity approached to be equal to or was slightly greater than the charge equivalent concentration of $\text{Ca}^{2+} + \text{Na}^+$ with the leaching (Fig. 3b.11), which depends on the application rate of corn material, soil sodicity and incubation period. If no corn material was applied, both concentrations were similar after leaching of 2 - 3 PV, and their difference was within 10%. After application of corn material, some CO_2 from decomposition of organic matter dissolved in the solution during incubation and leaching processes, the carbonate alkalinity at the 6.5 PV became about 30% higher than $\text{Ca}^{2+} + \text{Na}^+$ concentration for nonsodic soil, but this difference was only about 10% for sodic soil. These data demonstrate that the carbonate acid attack is the main mechanism of soil CaCO_3 dissolution in this study and the carbonate alkalinity mainly comes from the dissolution of native carbonate minerals.

When nonsodic calcareous soil was leached, the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio in effluent almost was a steady value of about 0.06 if no corn material was used; but it increased in sodic calcareous soil or after application of corn materials. The Mg^{2+} and Ca^{2+} maybe derive from a same source, that is, a congruent dissolution of calcium carbonate mineral that contains trace of Mg^{2+} in the nonsodic calcareous soil without application

of corn material. However, because of their different exchange preferences for the adsorbed Na^+ and possibly incongruent dissolution of native CaCO_3 mineral under the enhanced dissolution situation, this ratio becomes bigger after sodic calcareous soil and corn materials are employed.

During leaching process, the charge equivalent fractions of $\text{Ca}^{2+}+\text{Na}^+$, Mg^{2+} and K^+ to total solution concentration were almost steady, those of Ca^{2+} and Cl^- decreased, and those of Na^+ and carbonate alkalinity increased (Fig. 3b.12). After a lot of Na^+ in clay are substituted, the equivalent fraction of Ca^{2+} in effluent has an increase tendency, conversely, that of Na^+ tends to decline due to the attenuation of exchange reaction. Among all cations in effluent, the $\text{Ca}^{2+}+\text{Na}^+$ contributed about 92% of total cation concentration and both Mg^{2+} and K^+ ionic concentrations together accounted for less than 10%. Of all anions in leachate, the carbonate alkalinity was the only dominant anion except Cl^- at the initial stage of leaching, and it reached 95% of total anion concentration in the experimental conditions.

Some ions may be released into soil solution from decay of crop materials during incubation period (Rowell, 1994). The experimental results exhibited that the Cl^- concentration largely depended on the application rate of corn materials at the initial stage of leaching (Fig. 3b.9), so it is highly possible that a lot of soluble Cl^- are released into soil solution when corn materials are decomposing. The measured data about element composition in corn material before and after experiment indicated that some K^+ in plant materials also were significantly released into soil solution (data not shown), but its absolute concentration in effluent was rather low as compared with other elements (Fig. 3b.9 and Fig. 3b.12). The Ca^{2+} , Mg^{2+} , and Na^+ in plant materials were not released into soil solution during incubation period of 30 - 60 days and leaching process due to their relative high contents in soil. Therefore, the influence of ions from decomposition of added corn materials on sodic calcareous soil reclamation could be safely neglected.

3. Leachate sodicity:

The SAR values of effluent generally decreased with the leaching volume. Furthermore, it increased with soil sodicity, but greatly decreased with corn material application rate (Fig. 3b.13). When no corn material was applied, the decrement of

SAR value along with the leaching was small, and the leachate SAR value approached steady after 3 PV, which shows a low removal efficiency of adsorbed Na^+ . After corn materials were applied, as a result of improved mineral dissolution, the leachate SAR substantially declined along with the leaching volume. If the applied corn materials were sufficient, the leachate SAR even was significantly cut down at the beginning of leaching process.

Incubation of 60 days led to a lower SAR value than that of 30 days did at the soil ESP of about 16.5% if no corn material was used (Fig. 3b.13). Both SAR curves against the leaching volume almost were parallel for two different incubation periods, which indicates that a beneficial effect of long incubation time on displacement of adsorbed Na^+ happens only during the incubation period.

During reclamation process of sodic soil, physical degradation of soil structure is a critical problem that merits close attention. High sodicity of percolation solution under low electrolyte concentration will lead to deterioration of poor physical structure of sodic soil.

Under no application of corn materials, the steady SAR value of leachate was about $11 (\text{mmol}_\text{c} \text{ L}^{-1})^{0.5}$ from soil with ESP of 16.2% and incubation of 30 days, which is safe to soil structure stability because of its relative high solution concentration of $2.7 \text{ mol}_\text{c} \text{ L}^{-1}$ (Shainberg and Letey, 1984). This SAR value is expected to be the maximum in all present experiment treatments because of its most disadvantageous experimental conditions for SAR. When soil ESP level is lower, the adsorbed Na^+ is more difficult to be displaced (Amrhein and Suarez, 1991; Gupta et al., 1984a), hence the Na^+ concentration in leachate becomes less and the residual Ca^{2+} concentration in effluent increases, which leads to a smaller SAR value.

As compared with the application of elevated CO_2 concentration up to 5.1 kPa, the application of corn materials at 100 Mg ha^{-1} significantly cut down the leachate sodicity (Fig. 3b.14). It can be concluded that the application and incubation of crop materials is conducive to the stability of soil aggregates during leaching process because of its favourable effect on reduction of leachate sodicity (Barzegar et al., 1997; Gupta et al., 1984b). However, an overall investigation about influence of corn

material application on soil structure stability should be conducted due to the dissolution of added organic matter, which is detrimental to water permeability in soil.

4. Saturation index of effluent:

The calculated results demonstrated that during leaching process, the ionic activity products of CaCO_3 in effluent gradually declined (Fig. 3b.15). If no corn material was applied, the ionic activity product in leachate from nonsodic calcareous soil basically was at equilibrium with calcite after 3 PV. However, when sodic calcareous soil was leached, the leachate concentration always was supersaturated about CaCO_3 , and its ionic activity product was 1.6 - 3 times the solubility product at the 6.5 PV (Tab. 3b.1).

After application of corn materials, the ionic activity product of CaCO_3 in effluent transformed into an undersaturation state within two PV for all experimental treatments except that in nonsodic calcareous soil, which had a little dependence on corn material application. The more the corn materials were applied, the greater the undersaturation extent. The ionic activity product usually was only 20% - 85% of CaCO_3 solubility product at the 6.5 PV (Tab. 3b.1). So, it can be concluded that the application of corn materials significantly lowers the saturation extent of carbonate minerals, and improves dissolution environment of soil carbonate mineral.

The ionic activity product of Ca^{2+} and CO_3^{2-} in leachate depends on mineral dissolution and solution pH. The CO_3^{2-} activity decreases 10-fold for every unit decline of solution pH in a close system (Butler, 1982), whereas calcite dissolution almost is independent on the solution pH (i.e., hydrogen ion attack) when solution is neutral or alkaline (Plummer et al., 1978). Because of the inhibition of CaCO_3 precipitation in moving soil solution, the soil solution is difficult or impossible to get equilibrium with solid CaCO_3 mineral within short residence time in lysimeter under experiment conditions. The increase of Ca^{2+} concentration in effluent is far less than the decrease of CO_3^{2-} activity that are caused by pH decline after corn material application in present experimental conditions, thus the variation of CO_3^{2-} activity is much more important on ionic activity product than that of Ca^{2+} activity. Therefore, it can be concluded that solution pH level controls the saturation extent of effluent with respect to CaCO_3 in present experiment conditions.

Besides, soil sodicity increased saturation degree of leachate by the elevated solution pH and the increased dissolution of carbonate mineral when no corn material was applied (Fig. 3b.15). On the contrast, incubation time had opposite roles on Ca^{2+} and CO_3^{2-} concentrations in effluent by CO_2 regulation, so its influence was vague on saturation index of effluent with respect to calcite.

The saturation degree of leachate was much lower after application of crop materials than the elevated external CO_2 partial pressure (Fig. 3b.16) because soil solution pH was significantly lowered in the former case. The lack of equilibrium with calcite particles in moving solution should be responsible to this result.

Solid content in leachate:

Application of corn material and its incubation with soil may cause some obvious impacts on soil aggregate stability (Barzegar et al, 1997). When it is present in soil in small amount, organic matter increases dispersion of clay particle in sodic soil while suppressing its swelling. However, it may not even have a positive effect on aggregation under certain circumstance (Churchman et al., 1993; Goldberg et al., 1990; Gupta, et al., 1984b). Usually, plugging of pores by the dissolved organic matter and dispersed clay particles is the main reason of reduced hydraulic conductivity (Kosmas and Moustakas, 1990). Therefore, the solid content in effluent is an important index about permeability stability after corn materials are applied.

Our experimental results showed that the solid content of dispersed clay particle and dissolved organic matter in effluent gradually decreased during the leaching process. The solid content in effluent was independent on soil ESP level and incubation period, but the accumulative solid weight was obviously dependent on the incubation period at control treatments or on the application rate of corn materials after corn material application (data not shown).

When there was no application of corn materials, the maximum value of solid content in effluent on the average was less than 0.75 g L^{-1} and the average steady content was below 0.2 g L^{-1} for all experimental treatments. These data generally are similar to those at the low soil ESP level when an external CO_2 partial pressure from 0.035 kPa up to 5 kPa is used (Research report 2), which maybe also hints that the soil ESP level has been lowered during the incubation period. The total accumulative

amount of solid within 6.5 PV respectively was 10.8 g for incubation of 30 days and 7.5 g for incubation of 60 days at soil ESP of 1% - 18%, the former is 44% higher than the latter, which indicates a positive effect of incubation on the decrease of clay dispersion in sodic calcareous soil. The dispersed clay accounts for about 3‰ - 4.5‰ of total clay weight in lysimeter, that is, 0.6 - 0.9 g clay kg⁻¹ soil.

After corn materials are applied, the dissolved organic matter is the major component of total solid in effluent and also the main reason for decrease of hydraulic conductivity. Experiment data showed that the peak value of solid content in leachate usually went up to 2 - 3 times of that in control treatments. When the application rate of corn materials was 100 Mg ha⁻¹, the accumulative solid mass in effluent within the initial 6.5 PV was about 1.2 - 2.9 g kg⁻¹ soil. The accumulative amount of total solid within the first 6.5 PV against the application rate is significant on 0.01 statistical level regardless of soil ESP level and incubation period. Their regressive equation is as follows:

$$ATS = 9.304 * e^{7.645 * 10^{-3} * ARC} \quad \dots \dots (6)$$

$$R^2 = 0.655^{***} \quad n = 17$$

where ATS is the accumulative amount (g) of the dispersed clay particles and dissolved organic matter within the initial 6.5 PV; the other symbols have been defined above.

Reclamation efficiency:

The experimental data indicated that the soil ESP level was significantly cut down in the whole-reclaimed soil profile after application of corn materials (Fig. 3b.17). After incubation of 60 days and leaching of 6.5 pore volumes, the soil ESP levels dropped respectively from their initial values of 17%, 18.8% and 18.2% to averaged 12.2%, 8.3% and 4.0% when the application rates of corn materials were 0 (control treatment), 87.5 and 142.5 Mg ha⁻¹, the reclamation efficiency after leaching of 6.5 PV respectively were 28%, 55.9% and 78.1%. If the influences of the incubation and the leaching process, that is, the effect of check treatment was subtracted, the initial soil ESP values after reclamation were lowered respectively by 27.9% and 50.1% when corn materials of 87.5 and 142.5 Mg ha⁻¹ were applied.

As discussed above, after crop materials are applied, the dissolution rate of soil CaCO₃ mineral and leachate EC obviously increases. So, the removal efficiency of Na⁺

adsorbed in clay micellae is necessary to increase. The above experiment data indicate that the contribution from application of corn materials to the reclamation efficiency of sodic calcareous soil is significant. Although control treatments, i.e., the cases without application of corn materials also cut down soil sodicity due to hydrolysis of native calcium carbonate mineral and valence effect, the application of corn materials significantly increases total electrolyte concentration and available soluble Ca^{2+} , and subsequently the reclamation efficiency of sodic soil.

The soil ESP level after reclamation commonly was lower both at the surface soil owing to low SAR of percolation water and valence effect and at the deep part of soil profile as a result of high CO_2 concentration (Research report 3a). This distribution pattern of soil ESP level is obviously different from that when a CO_2 -enriched water is employed to assist reclamation of sodic calcareous soil, where the soil ESP level is lower at the upper part and higher at the deep part of soil profile after reclamation (Research report 2).

The reclamation efficiency increased with the increase of application rate of corn materials, and its gradient versus the application rate was greater for high soil ESP level than that for low soil ESP level (Fig. 3b.18). When corn materials are used in small amount, a high initial soil ESP level brings about low reclamation efficiency because the reclamation efficiency is confined by insufficient soluble Ca^{2+} . If corn materials are applied in large amount, the reclamation efficiency at high soil ESP level is higher than that at low soil ESP level as a result of enhancement role of corn materials on carbonate mineral dissolution and subsequently more available Ca^{2+} in solution.

A long incubation time obviously promoted reclamation efficiency of sodic calcareous soil when soil ESP was 11%, however its role was vague as soil ESP was up to 18% (Fig. 3b.18). This result seems contradicting with above discussion about carbonate mineral dissolution, but it maybe is reasonable and correct. From theory, ion exchange can finish instantaneously, yet the whole exchange process from obtainment of available soluble Ca^{2+} to diffusion into exchange sites and then back to solution needs time to accomplish, so a long incubation period necessarily is of benefit to the substitution of Na^+ and finally the soil reclamation efficiency.

When soil ESP is about 18%, the soil reclamation efficiency, i.e., the relative percentage of ESP reduction statistically correlates with the application rate of corn materials on 0.01 significance level after the incubation of 30 or 60 days and the leaching of 6.5 pore volumes. When the application rate of corn materials is less than 150 Mg ha⁻¹, their regressive equation is:

$$RE = 0.3725 * ARC + 22.802 \quad \dots \dots (7)$$

$$R^2 = 0.923^{***} \quad n = 6$$

where RE is soil reclamation efficiency (%) after a given leaching water amount; the other symbols have been defined above.

The soil ESP level declined faster with the leaching volume after application and incubation of corn materials than that after application of elevated CO₂ partial pressure at the experimental conditions (Fig. 3b.19). For example, within the first 6.5 pore volumes of leachate, the soil ESP value was lowered to 8.8% from the initial 19.4% after corn materials were applied at the rate of 100 Mg ha⁻¹ and incubated for 30 days. However, if an external CO₂ gas at a partial pressure of 5.1 kPa was applied, the soil ESP value only was reduced to 13.3% from the original 19.3% at the equal amount of percolation water. The efficiency of soil reclamation is 77% higher in the former case than that in the latter one.

The incubation of corn materials with soil improves the dissolution of soil carbonate mineral and subsequently the reclamation efficiency as a result of higher CO₂ partial pressure and exchange efficiency of cations during the incubation period. Experimental data displayed that after the sodic calcareous soil with ESP of 19.4% was mixed with corn materials of 100 Mg ha⁻¹ and incubated for 30 days, the maximum EC of effluent within the first pore volume was more than 3 times that when nonsodic calcareous soil was leached after incubation of 30 days without application of corn materials (Fig. 3b.4). More available soluble Ca²⁺ ions that are produced during the incubation period accelerate the substitution of Na⁺ adsorbed in clay, and hence improve the reclamation efficiency of sodic soil. Besides, a long residence time during incubation period also increases reclamation efficiency by the increased diffusion time of exchange cations. Only after the first two PV, was the soil ESP value lowered to 13% from its initial 19.4% if corn materials of 100 Mg ha⁻¹ were applied and incubated

for 30 days, which is achieved in fact as a result of incubation. However, if this soil is leached by CO₂-enriched distilled water with partial pressure up to 5.1 kPa, an equivalent effect can be obtained at least after leaching of seven pore volumes (Fig. 2.14). Because the supply of soluble Ca²⁺ from CaCO₃ dissolution under both cases are similar during the leaching process except the first two pore volumes (Fig. 3b.10), it is believed that it is this role of incubation that makes the application of crop materials more effective on sodic calcareous soil reclamation.

Furthermore, the different CO₂ sources in both experiment systems maybe are another reason for the low reclamation efficiency when CO₂-enriched water is applied. When an external CO₂ source is used, the aqueous CO₂ concentration in soil solution is high at the upper part and low or short at the deep part of soil column because of its consumption with calcite reactions during leaching process. Whereas in the lysimeter experiments where the CO₂ comes from decay of added organic matter throughout the soil, the aqueous CO₂ concentration is more even in the whole soil profile, which is favourable to the lowering of solution pH and the mineral dissolution, so the reclamation efficiency increases.

As demonstrated in Fig. 3b.4, the effluent EC maintains above 0.3 dS m⁻¹ within the initial 6.5 PV when soil ESP level is high or corn materials more than 100 Mg ha⁻¹ are applied. When soil sodicity is moderate, it is enough to prevent serious destruction of soil structure stability by clay dispersion (Shainberg and Letey, 1984). In the meantime, it is within this period that a large amount of adsorbed Na⁺ is displaced by soluble Ca²⁺. For example, when corn materials are used at the rate of 100 Mg ha⁻¹, initial soil ESP of 11 - 18% generally can be cut down 42% - 68% after leaching of 6.5 PV (Fig. 3b.18). Therefore, a leaching water amount of 6.5 PV, that is, about 3.5 times of the reclaimed soil depth can be recommended as maximum leaching water amount for sodic calcareous soil reclamation. Within this range of leaching water amount, the reclamation activity is most reasonable and feasible.

According to present experimental data, in an arid or semiarid region where annual rainfall is about 350 - 400 mm, if crop materials of 100 Mg ha⁻¹ are thoroughly incorporated with a moderate sodic calcareous soil with ESP of 20%, this soil with a depth of 0.5 m can be reclaimed to a slightly sodic soil with ESP of 9% after 4 - 5

years under the leaching of natural rainfall. The soil ESP value is decreased at an average rate of about 2.5% per year only by application of enough crop materials. Moreover, the application of crop materials increases organic matter content in soil and hence benefits to agricultural production. In one word, the application of crop materials is an effective and economical method on improving of sodic calcareous soil reclamation.

Conclusions

Application of corn materials significantly lowered the effluent pH, enhanced the dissolution of soil calcium carbonate mineral and increased the effluent EC. The more the corn material was applied, the lower the pH in leachate and the more the calcium carbonate mineral was dissolved. However, the role of corn material application on carbonate mineral dissolution was significantly weaker in sodic calcareous soil than in nonsodic calcareous soil.

Soil ESP level was strikingly cut down after application and incubation of corn materials, the more the crop materials were used, the more the Na^+ adsorbed in clay particles were removed. When corn materials were applied at the rate of 100 Mg ha^{-1} , the total electrolyte concentration in effluent was greater than the critical flocculation value of moderate sodic soil within the former 6.5 PV. The soil ESP level averagely was lowered about 63% from initial soil ESP of 18% after leaching of 6.5 pore volumes.

Incubation of corn materials with soil played a very significant role on improving of sodic calcareous soil reclamation. After corn materials were applied, a short incubation period resulted in a lower effluent pH, and more CaCO_3 dissolution and bigger leachate EC in sodic calcareous soil. However, the incubation time had little effect on leachate pH and CaCO_3 dissolution in nonsodic calcareous soil no matter whether corn materials were applied or not.

A high soil sodicity improved the dissolution of soil carbonate mineral and increased the leachate EC, the exchangeable Na^+ played a dominant role on carbonate mineral dissolution in alkaline pH range ($> 6 - 7.2$). The saturation extent of effluent

was dominated by the leachate pH value because of the lack of equilibrium between soil solution and calcite particles.

Tab. 3b.1 The ionic concentrations and saturation indexes of effluent at the 6.5 PV

ID	ESP	ARC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	c
Day	%	Mg ha ⁻¹	mmol _e L ⁻¹						
30	0.6	0	1.04	0.07	0.07	0.07	1.30	0.28	
	1.4	31.1	1.51	0.18	0.06	0.36	2.09	0.32	
	0.4	111.4	2.10	0.26	0.14	0.45	3.20	0.17	
60	0.6	0	1.27	0.08	0.08	0.06	1.31	0.11	
	1.4	86.9	1.83	0.29	0.08	0.43	1.94	0.59	
	1.4	134.8	2.28	0.50	0.12	0.73	3.38	0.79	
30	11.5	0	0.17	0.01	2.35	0.03	2.68	0.14	
	12.6	82.7	1.10	0.27	2.71	0.25	3.79	0.38	
	9.9	108.6	1.61	0.43	1.99	0.33	3.88	0.15	
60	12.1	0	0.17	0.02	2.33	0.03	2.42	0.14	
	11.0	82.3	0.38	0.06	2.17	0.11	2.55	0.22	
	8.1	153.4	0.86	0.30	1.21	0.33	2.77	0.31	
30	16.2	0	0.11	0.01	2.63	0.02	2.51	0.10	
	19.4	100.0	0.51	0.10	2.61	0.17	3.58	0.13	
	18.6	149.0	0.65	0.13	2.85	0.24	4.05	0.22	
60	17.0	0	0.10	0.02	2.24	0.02	2.30	0.20	
	18.8	87.5	0.35	0.08	2.86	0.12	3.11	0.40	
	18.2	142.5	0.48	0.09	2.20	0.20	2.82	0.12	

Note: all symbols in this table have the same meanings as in context.

Fig. 3b.1 Leachate pH versus the leaching volume when sodic calcareous soils with two ESP levels were leached by distilled water at the velocity of 10 mm h^{-1} after incubation of 30 days with or without application of corn materials

Fig. 3b.2 The effluent pH at the 6.5 PV versus the application rate of corn materials for three soil ESP levels and two incubation periods (ID)

Fig. 3b.3 The leachate pH versus the leaching volume when sodic calcareous soils with two ESP levels were leached by distilled water at the velocity of 10 mm h^{-1} under the CO_2 partial pressure of about 5 kPa or the application rates of corn materials from $100 - 111 \text{ Mg ha}^{-1}$

Fig. 3b.4 The effluent EC versus the leaching volume when sodic calcareous soils with two ESP levels were leached by distilled water at the velocity of 10 mm h^{-1} after incubation of 30 days with or without application of corn materials

Fig. 3b.5 The leachate EC value at the 6.5 PV versus the application rate of corn materials at three soil ESP levels and two incubation periods (ID)

Fig. 3b.6 The effluent EC versus the leaching volume when sodic calcareous soils with two ESP levels were leached by distilled water at the velocity of 10 mm h^{-1} under the CO_2 partial pressure of about 5 kPa or the application rates of corn materials from $100 - 111 \text{ Mg ha}^{-1}$

Fig. 3b.7 The release rate of Ca^{2+} (mol s^{-1}) at the 6.5 PV from soil carbonate mineral dissolution against the application rate of corn materials at three soil ESP levels and two incubation periods (ID)

Fig. 3b.8 The effluent EC versus the release rate of Ca^{2+} at the 6.5 PV from soil carbonate dissolution under three soil ESP levels and two incubation periods (ID)

Fig. 3b.9 Leachate ionic concentrations versus the pore volume of effluent when sodic calcareous soil with ESP of 18% was leached at two application rates of corn materials (0 and 87.5 Mg ha⁻¹) after incubation of 60 days

Fig. 3b.10 Calcium ionic concentration in effluent versus the leaching volume when nonsodic calcareous soil were leached by distilled water at the velocity of 10 mm h⁻¹ under two CO₂ concentrations and application rates of corn materials

Fig. 3b.11 The effect of soil ESP level on the ionic concentrations of leachate during the leaching process when sodic calcareous soils with ESP of 0.6% and 16.2% were leached by distilled water after incubation of 30 days without application of corn materials

Fig. 3b.12 The charge equivalent fractions of all observed ion species in effluent versus the leaching volume when sodic soil with ESP of 18.2% was leached after application of corn material at 142.5 Mg ha⁻¹ and incubation of 60 days

Fig. 3b.13 The SAR values ((mmol_e L⁻¹)^{0.5}) of leachate versus the leaching volume under two soil ESP levels, three application rates of corn materials (ARC) and two incubation periods (ID)

Fig. 3b.14 The leachate SAR variation with leaching when sodic calcareous soils with two ESP levels were leached by distilled water at the velocity of 10 mm h⁻¹ under the CO₂ partial pressures of about 5 kPa or the corn material applications of 83 - 100 Mg ha⁻¹

Fig. 3b.15 The variation of the saturation index in respect to calcite along with the pore volume of leachate when sodic calcareous soils at various ESP levels were leached by distilled water at the velocity of 10 mm h^{-1} after different corn material applications and the incubation of 30 days

Fig. 3b.16 The variation of the saturation index in respect to calcite along with the pore volume of leachate when sodic calcareous soils with two ESP levels were leached by distilled water at the velocity of 10 mm h^{-1} under the CO_2 partial pressure of about 5 kPa or the corn material application of 100 - 111 Mg ha^{-1}

Fig. 3b.17 The distribution of soil ESP level after incubation of 60 days and leaching of 6.5 pore volumes when corn materials at various rates (ARC) were added into sodic calcareous soils with initial ESP of about 18%

Fig. 3b.18 The influence of corn material application on the removal efficiency of Na^+ adsorbed in the exchangeable phase after incubation (ID) of 30 or 60 days and leaching of 6.5 pore volumes

Fig. 3b.19 The soil ESP level during the leaching process calculated from Na^+ concentration in effluent when sodic calcareous soils were leached by distilled water at the flow velocity of 10 mm h^{-1} under the CO_2 partial pressure of about 5 kPa or the corn material application of $83 - 100 \text{ Mg ha}^{-1}$

CONCLUSIONS

The dissolution kinetics of carbonate mineral as well as its influence variables (such as CO_2 partial pressure, soil sodicity, water flow velocity and crop material application), and the role of the application and incubation of crop materials on sodium-affected calcareous soil reclamation have been extensively and intensively investigated in this research.

The dissolution rate of Iceland Spar mineral followed a fractional power function with the leaching volume. It linearly increased with the leaching velocity. The dissolution of Iceland Spar in porous media under leaching condition could be predicted very well by the hydrodynamic model that was developed in this study. The

dissolution of native soil carbonate mineral followed a two-partitioned fractional power function with leaching. Its dissolution rate also linearly increased with the water flow velocity. The solubility of native soil carbonate mineral was 2 times that of Iceland Spar mineral. The dissolution process of both minerals in porous media was controlled by diffusion under leaching situation. A low leaching velocity inhibited the rising of solution pH, and got greater solution EC and total electrolyte concentration, in sodic calcareous soil, especially after application of corn materials; meanwhile, it also improved cation exchange efficiency and hence obtained higher reclamation efficiency.

The application and incubation of crop material significantly elevated soil CO_2 concentration and subsequently lowered pH and sodicity of effluent, increased dissolution rate of native soil carbonate minerals, and obviously increased reclamation efficiency of sodic calcareous soil. The incubation of crop materials with soil played a very important role on improvement of reclamation efficiency.

Although an elevated external CO_2 partial pressure also could decrease the leachate pH value, increase native soil CaCO_3 mineral dissolution and improve sodic calcareous soil reclamation, its effect was much smaller as compared with the application of crop materials. The existence of exchangeable Na^+ in soil greatly overshadowed the effect of CO_2 partial pressure on CaCO_3 dissolution no matter whether the CO_2 came from an external source or the decomposition of applied organic matter. The CaCO_3 mineral dissolution in neutral or alkaline pH range dominantly derived from the $\text{Na}^+ - \text{Ca}^{2+}$ exchange rather than solution pH (hydrogen ion attack), hence the exchange-induced improved dissolution of native CaCO_3 mineral should take into account during sodic calcareous soil reclamation.

The native soil CaCO_3 mineral released a large amount of calcium ions and appropriate electrolyte concentration under the presence of crop materials. The moderate sodic calcareous soil could be successfully reclaimed at a high efficiency and rate after application of crop materials. So, crop materials can be used as a subsidiary means to improve reclamation efficiency in sodic calcareous soil reclamation, and the native soil CaCO_3 mineral can serve as an amendment under no application of chemical substances.

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USA

RESEARCH REPORT 4

AGGREGATE STABILITY AND WATER INFILTRATION INTO CLAY LOAM AS AFFECTED BY SALINE WATER QUALITY

ABSTRACT

The extent of water infiltration reduction caused by irrigation with sodic water having elevated salinity ($>1 \text{ dS m}^{-1}$) is poorly known. This study examined the effect of five simulated irrigation water sources having salinity of 1.1 to 4.2 dS m^{-1} , and the sodium adsorption ratio of 3.5 to 37 on stability of microaggregates, and water infiltration into two calcareous silty clay loam soils; Saneli (montmorillonetic, Vertic Torrifluent, Entisol) and Hoban (micaceous, Typic Calciorthid, Aridisol). Aggregated fractions of soil particles less than 20 and $2 \mu\text{m}$ were determined with a pipette method after submerging dry soils into various saline solutions. Water infiltration and hydraulic gradients were measured in soil columns following water application of 10 cm each during five irrigation events. In addition, an empirical equation was developed for describing salinity and sodicity effects on the relative depth of infiltration. Aggregate measurements indicated that aggregated fractions of the soil particles less than $20 \mu\text{m}$ decreased with decreasing salinity, and increasing sodicity more so in Saneli soil than in Hoban soil. However, dispersion into clay particles ($<2 \mu\text{m}$) occurred to a minimal degree. The hydraulic gradient data indicate that soil particles detached from microaggregates might have translocated through the soils to a depth of approximately 3 cm in Saneli soil, and approximately 7 cm in Hoban soil, thus causing a reduction in water infiltration. The use of saline water alone caused limited reductions (15 ~ 20%) in infiltration rate, even though sodicity of the water was fairly high, ranging from 15 to 37. However, when water of low salinity was applied following saline sodic water, the reduction in infiltration depth reached 66% in Saneli and 35% in Hoban soil. An empirical equation proposed provided a reasonable estimate of salinity and sodicity effects on water infiltration into these soils, and could be used for descriptive or interpretive purposes.

INTRODUCTION

Water containing dissolved salt concentrations between 1000 to 3500 mg L⁻¹ (or 1.5 to 5.0 dS m⁻¹) has been or beginning to be used for irrigation in the western US. When soil texture transcends from loam to silty clay loam or clay loam, however, our experience in west Texas shows that salts tend to accumulate in the soil, due to inadequate soil permeability to maintain salt leaching. A traditional method of dealing with this problem is the use of physical implements such as chiseling, subsoiling or deep plowing, besides ordinary plowing and disking (e.g., Helmers and Miyamoto, 1990). However, field reports indicate that water penetration, even after such physical soil structural modification, often declines with repeated irrigations to the level that some crops suffer from both salt and water stress. Although existing literature generally indicates that high salt levels can substantially moderate dispersive effects of Na (e.g., Shainberg and Letey, 1984), recent reports seem to indicate that high sodicity may still be a factor of reducing water infiltration due to disaggregation (or slaking of microaggregates), instead of dispersion into individual clay particles (Abu-Sharar et al., 1987a; 1987b). Dispersion as well as clay swelling are pronounced under low salinity, typically < 1 dS m⁻¹ at an ordinary range of sodicity, such as the exchangeable Na percentage (ESP) below 20, although the threshold values vary considerably with soil types and other factors (McNeal et al., 1966; Shainburg et al., 1971; Emesson and Chi, 1977; Ali et al., 1987; Abu-Sharar et al., 1987b; Yousaf et al., 1987). The first objective of this study was to determine the extent of disaggregation when dry soil aggregates are brought in contact with saline solutions with salinity greater than 1 dS m⁻¹.

Assuming that disaggregation is associated with quality of saline water, a practical question which must be addressed is its impact on water infiltration. Several empirical equations are available, which describe salinity and sodicity effects on saturated hydraulic conductivity when clay swelling is considered to be a dominant factor (e.g., McNeal, 1968; Jayawardene, 1979; Cass and Sumner, 1982a/1982b). Equations which are suitable for estimating salinity and sodicity effects on infiltration impaired by disaggregation are yet to be developed. Occasional rain and conjunctive use with low salt water can complicate the formulation of the process (e.g., Minhas and Sharma, 1986). The

second objective of this study was to provide a simple equation which can be used for estimating salinity and sodicity effects on the relative depth of water infiltration.

MATERIALS AND METHODS

Two calcareous silty clay loam soils were used; Saneli silty clay loam (montmorillonetic, thermic, Vertic Torrifluent, Entisol), and Hoban silty clay loam (micaceous, Typic Calciorthid, Aridisol). Soil samples were collected from the Ap horizon in irrigated fields in El Paso and Pecos, Texas, and were air-dried, crushed and passed through a 2 mm screen. Some properties of the soil samples are shown in Table 1.

Aggregate Stability Measurements: Soil samples, 50 grams each, were placed on filtration flasks and were leached with high saline solutions ($300 \text{ mmol}_e \text{ L}^{-1}$) having three levels of the sodium adsorption ratio (SAR): 1.0, 15, and 30. The high saline solutions, prepared by adding analytical grade NaCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg Cl}_2 \cdot 7\text{H}_2\text{O}$, was applied in an amount of 250 ml per 50 gr (or equivalent to 10 pore volumes). The molar ratio of Ca to Mg was kept at unity. A preliminary study has shown that application of such a quantity of highly saline solutions is sufficient to complete the cation exchange reaction. These pretreated samples were then leached with 75 ml of saline solutions having the same SAR levels, but with lower salt levels; 300, 50, and $5 \text{ mmol}_e \text{ L}^{-1}$. The electrical conductivities of these solutions were 27, 4.8, and 0.5 dS m^{-1} , respectively. These samples were gently transferred to 1 liter cylinders, and were left overnight. Prior to aggregate analyses, the cylinders were inverted 30 times in 1 min, then the size fractions less than 20 and $2\mu\text{m}$ were measured with a pipette method (Day, 1965). In addition, the soil samples which had been dispersed using hydrogen peroxide and Na metaphosphate were subject to the same analyses. The above measurements were replicated three times. The percentage of soil particles less than $20\mu\text{m}$ which are held at the state of aggregates was then computed as:

$$\text{Aggregated fraction} = \left(\frac{Q_p - Q}{Q_p} \right) \times 100 \quad (1)$$

where Q_p is the quantities of soil particles less than 20 or $2\mu\text{m}$ after the dispersion treatment, and Q the quantities observed without the dispersion treatment. Aggregated fractions were measured in triplicate at a room temperature.

Water Infiltration and Hydraulic Gradient Measurements: This set of the experiments was to observe water infiltration responses when the five different saline water sources (Table 2) were applied. In addition, a CaCl_2 solution (38 meq L^{-1}) was used as a reference. The soil samples were packed into PVC pipes (3 cm ID and 75 cm long) at a bulk density of 1.43 kg L^{-1} with a soil packing vibrator to a depth of 65 cm. The low-end of the soil columns contained a layer of medium sand to allow unrestricted drainage. Soil columns which were to receive Sodic water, Well 1 and Well 3 waters, and the CaCl_2 solution were equipped with piezometers placed at 1, 2, 3, 5, 7.5, 10, 15 and 20 cm. The irrigation water was added to a depth of 10 cm, while protecting the soil surface with two layers of fiberglass screens, then the depth of water infiltrated and the hydraulic heads were monitored until the CaCl_2 solution disappeared from the soil surface. Evaporation of the ponded water was minimized by covering the columns with aluminum foil. During the 4th irrigation, all columns, except for the CaCl_2 solution, received 10 cm of the simulated Rio Grande water, and for the 5th irrigation, the soil columns were irrigated again with the designated saline solutions (Table 3). Soil columns were left to drain and to dry through circulation of forced air between these irrigations until the soil water depletion reached 3.0 cm for the first four irrigations, and 4.0 cm prior to the 5th irrigation. Irrigation intervals ranged from 12 to 15 days. The experiment was replicated 5 times with a completely randomized design.

Calculation of Hydraulic Gradients: Piezometer readings were used to compute the hydraulic gradients at different depths of the soil columns with the following formula.

$$\text{HG} = (H_1 - H_2)/L \quad (2)$$

where HG is the hydraulic gradient, H_1 and H_2 the hydraulic heads, and L the length between the two piezometers. Additional details can be found in Frenkel et al. (1978) and Miyamoto and Enriquez,

(1990).

Processing of Infiltration Data: The cumulative depth of water infiltration was fitted to the following equation.

$$D = St^P + fKt \quad (3)$$

where D is the cumulative depth of water infiltration, t the infiltration time, K hydraulic conductivity with an adjustment factor, f , and S and P are empirical coefficients. Note that Eq(3) is a modification of the Kostiakov equation, and details are given in Report 6. When P is equal to $1/2$, Eq (3) is the same as the two-term Philip equation for the vertical infiltration, except for the use of the adjustment factor, f .

Quality of water used for irrigation affects these infiltration parameters as discussed in Report 6. In this report, water quality effects on water infiltration were evaluated for simplicity by comparing the depth of water infiltration when the infiltration depth of the CaCl_2 solution reached 10 cm for each irrigation event.

$$R = D/D_c \quad (4)$$

where D_c is the infiltration depth of the CaCl_2 solution used as a reference, and D is the infiltration depth of water when D_c reached 10 cm. The ratio, R , will be referred to as the relative infiltration depth. The relative infiltration depth is approximately equal to the relative sorptivity at $t = 1$ day.

Once the relative infiltration depth was determined experimentally it was subjected to an analysis of salinity and sodicity effects as shown in Appendix. The resulting equation is:

$$R = 100 - b \text{ ESP}^n \log C_e/C + [(R_c - 100)/\log C_c + b \text{ ESP}^n] \log C \quad (5)$$

where R is the relative infiltration depth expressed in percentage, ESP the exchangeable Na percentage, C the salinity of irrigation water expressed in $\text{mmol}_e \text{L}^{-1}$ (or meq L^{-1}), R_c the relative infiltration depth at $C = C_c$ above which salinity has no impact on R , and b and n are empirical coefficients.

When R_c is close to 100%, or C_c is large as compared to $R - 100$, Eq (5) is reduced to

$$R = 100 - b ESP^n \log C_c/C \quad (6)$$

RESULTS

Aggregate Stability

Aggregated fractions of the soil particles less than $20 \mu\text{m}$ decreased with reducing salinity of the suspension solutions (Table 4). Sodidity also had a significant impact on aggregate stability. Dispersion of soil aggregates into the clay size ($2 \mu\text{m}$) has occurred only at the lowest salinity level, $5 \text{ mmol}_e \text{L}^{-1}$ to a limited extent ($<10\%$). Aggregated fractions of the soil particles less than $20 \mu\text{m}$ increased almost logarithmically with increasing salinity (Fig. 1). Disaggregation took place more extensively in Saneli soil than in Hoban soil. The presence of suspended solids of less than $2 \mu\text{m}$ was visible only in the suspension solution containing $5 \text{ mmol}_e \text{L}^{-1}$ of dissolved salts at a SAR of 30.

Water Infiltration

Cumulative Infiltration Depth: The depths of water infiltrated into Saneli soil during the 3rd through 5th irrigation are shown in Fig. 2A. Water infiltration during the first and the second irrigations had completed in less than half of the time duration required for the 3rd irrigation with no significant difference among the different water sources. The rate of water infiltration decreased with time and repeated irrigations with a significant reduction occurring starting at the 3rd irrigation. By this time, the wetting front had reached the full length of the soil columns. Water infiltration became even slower during the 4th irrigation using the simulated Rio Grande water having comparatively low

salinity (1.1 dS m^{-1}), but it has mostly recovered during the 5th irrigation with the saline water sources. Differences in infiltration rates among the water sources were most pronounced during the 4th irrigation when the simulated Rio Grande water was applied to all columns, except for the columns designated for the CaCl_2 reference solution.

The pattern of infiltration observed in Saneli soil were largely repeated in Hoban soil (Fig. 2B). However, the infiltration of two low salt water sources (the simulated Rio Grande and Sodic water) decreased from the 1st irrigation, and became significantly lower during the 2nd irrigation. Recall that Hoban soil initially had elevated sodicity (Table 1). Also, the reduction in infiltration during the 4th irrigation with the simulated Rio Grande water was not as extensive as those observed in Saneli soil. During the 5th irrigation using the saline solutions, water infiltration has improved over the 4th irrigation, but not to the same level as that of the third irrigation.

The infiltration parameters of Eq (3), determined for each irrigation event, are shown in Table 5. The hydraulic conductivity K , determined toward the end of each irrigation event, decreased with repeated irrigations, and so did the sorptivity, S , determined for the initial phase of infiltration. The coefficient P ranged from 0.3 to 0.6. The adjustment factor, f , was mostly in the range of 0.5 to 0.8, except in two cases involving infiltration of Rio Grande water into Saneli soil which had been irrigated with sodic water and Well 3 water prior to the 4th irrigation. The negative value of f indicates the situation of approaching the complete seal.

Relative Infiltration Depth: The relative infiltration depth estimated by Eq (4), is plotted in Fig. 3. The data points along the salinity of $11 \text{ mmol}_e \text{ L}^{-1}$ came from the 4th irrigation using simulated Rio Grande water, and other data points from the 3rd irrigation. The reduction in water infiltration is most evident in Saneli soil when irrigation was made with water of lower salinity following the prior irrigation with water of high salinity and sodicity (Well 3). In other cases, the reduction in infiltration depth was limited to less than 30%. The plots shown in Fig. 3 also indicate that the slope of the line increases with increasing sodicity, probably in a fashion which can be described by a curve-linear function. The plots also seem to show that the lines describing the relationship between the relative

infiltration depth and salinity might converge at a certain point above which salinity will no longer affect infiltration. These observations appear to satisfy the key assumptions made for developing Eq. (5).

The empirical coefficients of Eq (5) were determined by using the plots shown in Fig. 3. Two lines were drawn by using the data set from Well 3 water (having the largest SAR), and another set from Well 1 water (having the lowest SAR with at least two separate data points). The two coefficients (R_c and C_c) of Eq (5) were determined graphically at the conversion point for each soil. The two other coefficients (b and n) of Eq (5) were then calculated by using the relative infiltration depths of Well 1 and 3 water during the 3rd irrigation, and results are shown in Fig. 3 and in Table 6.

The relative infiltration depths of other water sources during the 3rd and 4th irrigations were estimated by Eq (5) using the empirical coefficients determined above. The results (Table 6) were in good agreement with the observed in Saneli soil, but not in Hoban soil where the observed values for the simulated Rio Grande water and Sodic water were markedly lower than the estimates. The relative infiltration depth of the simulated Rio Grande was then recalculated with the assumption that the high ESP of Hoban soil has caused soil structural degradation when irrigated with the low salt water. The results using the initial ESP of the soil (shown in parenthesis) were closer to the observed. The same procedure was applied to Sodic water, but did not make a substantive difference as the ESP was similar to the SAR of sodic water.

The relative infiltration depths observed during the 5th irrigation were lower than those observed during the 3rd irrigation (Table 5), presumably due to the continuing structural degradation. Therefore, the coefficients b and n were recalculated using the data set from the columns which have received Well 1 and 3 water. The ESP of the soils was assumed to be equal to the SAR of different water sources applied during the 4th irrigation. The results for Saneli soil have shown no change in n value, but a slight increase in b value. In Hoban soil, the value for n has increased due to the decline in the relative infiltration depth of Well 3 water (Table 6). The estimated relative infiltration

depths were in agreement with the observed in most cases.

Hydraulic Gradients: The hydraulic gradients computed from piezometer readings are shown in Fig. 4. During the 2nd irrigation of Saneli soil, the hydraulic gradients increased with depth, then the hydraulic head readings became negative at depths below the top 2 to 3 cm. The hydraulic gradient patterns during the 3rd irrigation were similar to those of the 2nd irrigation, thus they are not shown. During the 4th irrigation with the simulated Rio Grande water, the hydraulic gradients have increased near the soil surface, and the hydraulic head below 3 cm remained negative, except when the CaCl_2 solution was used. It appeared that the resistance to the flow was confined to the top 3 cm, except for the cases involving the CaCl_2 solution. In Hoban soils, the hydraulic gradient distribution of the CaCl_2 solution was centered around the unit gradient as it should be in homogenous stable soils. The use of sodic water as well as the Rio Grande water provided the peak resistance at the surface. The gradient distribution of well water 3 (saline sodic) provided the peak at 4 cm below the surface. These patterns were carried into the 3rd irrigation, and upon the 4th irrigation with the Rio Grande water, the peak gradient has shifted down to about 7 cm.

DISCUSSION

The aggregate analyses performed have shown that disaggregation was greater in Saneli soil than in Hoban soil (Fig. 1). Saneli soil is an Entisol developed from young sediments of the Rio Grande Flood plain, whereas Hoban soil (Aridisol) developed in upland contains large quantities (15 to 20%) of CaCO_3 which act as a cementing agent. In both soils, dispersion into clay particles ($<2 \mu\text{m}$) was, however, minimal, and this finding is consistent with some of the earlier reports (e.g., Abu-Sharar et al., 1987a). In the case of Saneli soil, clay swelling might have occurred, especially when irrigated with the simulated Rio Grande water. Measurable degrees of swelling of soils containing expandable clay is reported by several workers (e.g., McNeal et al., 1966). In the present study, a rise of the soil surface was as much as 3 mm in Saneli soil. Clay swelling has to be ruled out as the cause of reduced infiltration in Hoban soil consisting of mica

Soil particles detached from microaggregates of Saneli soil were probably washed into a few cm, thus having to develop the resistance to the flow at the depth (Fig. 4). Disaggregation usually occurs at the soil surface where soil aggregates are saturated with water (Emerson, 1984). The use of low salt water during the 4th irrigation seemed to have created the surface seal layer in Saneli soil, perhaps through clay swelling as indicated by the sharp increase in hydraulic gradient at the soil surface (Fig. 4). In Hoban soil, the use of sodic water developed the resistance to flow near the surface in the 2nd irrigation, whereas this did not occur in Saneli soil (Fig. 4). Recall that the exchangeable Na percentage of Hoban soil was high initially and disaggregation might have resulted when irrigated with water of low salinity. The high hydraulic gradient observed at a depth of approximately 7 cm during the 4th irrigation was probably caused by deposition of soil particles detached from micro-aggregates. This process appears to be similar to the translocation of dispersed clay particles reported by Frenkel et al (1978). The fact that the infiltration rates have largely recovered during the 5th irrigation from the low rates observed during the 4th irrigation with low salt water may suggest that pore plugging was partially alleviated through soil drying or new water conductive spaces had developed upon drying.

If the reduction in infiltration depth is to be directly proportional to the disaggregated fraction of less than 20 μm size, the two lines shown in Fig. 3 should not converge at salinity of 110 or 120 $\text{mmol}_\text{c} \text{L}^{-1}$. Instead, it should have converged, judging from the data shown in Fig. 1 somewhere at above 300 $\text{mmol}_\text{c} \text{L}^{-1}$. The primary factor which causes this apparent discrepancy is the salinity of the reference solution used for the infiltration experiment, which was 38 $\text{mmol}_\text{c} \text{L}^{-1}$, but not 300 $\text{mmol}_\text{c} \text{L}^{-1}$ as used in the aggregate stability measurement. If a solution of 300 $\text{mmol}_\text{c} \text{L}^{-1}$ were used, the reduction in infiltration could have been larger. Additionally, it is possible that soil particles with considerably smaller sizes than 20 μm are likely to be involved in translocation and pore plugging.

The flow process observed was certainly not at steady state, but a transient state. This is evident from both the infiltration data shown in Fig. 2A and 2B, Table 5, and the hydraulic gradient data given in Fig. 4. The values of S and K determined during the first and the second irrigation events were larger than those shown in Table 5 for subsequent irrigation events. The reduction in

S observed during the initial irrigation events includes the effect of increasing soil water storage prior to irrigation, in addition to soil structural degradation. Starting at the 3rd irrigation, however, all the soil columns were basically wet, except at the surface, and the reduction in S and K values should be considered as a direct result of soil structural degradation and the difference in soil water contents prior to irrigation. Infiltration rates are likely to decrease with additional irrigation events, especially in Saneli soils having weak soil structure. Furrow irrigation of field crops, mainly cotton and sorghum, is usually made 5 to 6 times per growing season, then the ground is reworked. Therefore, the use of transitional values may actually make a better sense than so-called steady-state values. At the same time, the listed data should not be considered as an indication for long-term effects. In the case of Hoban soil, the soil sample was collected from a field irrigated for many years with Well Water 2, and the infiltration data obtained from the water are likely to be indicative of long-term effects. The reduction in relative sorptivity or relative infiltration depth by 10% can be significant for sustaining salt leaching, but it is a comparatively small factor when considering inherent variation in infiltration rates.

A significant reduction in infiltration rate is likely to occur if water of low salinity is applied following the use of saline water with elevated salinity. This type of situation is common in irrigation districts where saline irrigation return flow is used for winter irrigation, then followed by the use of fresh water in the spring. The proposed equation can be useful for assessing the impact of such water management strategies on water infiltration. In using Eq (5), it should be noted that the relative infiltration is controlled by the ESP of the soil prior to irrigation, and salinity of, but not necessarily sodicity of water during irrigation. The estimates made with this stipulation agreed well with the observed, even in Hoban soils with initially high sodicity. The proposed equation is useful for descriptive or interpretive purposes, and perhaps for appraisal, once the empirical values become known for other soils.

Appendix

According to the plots shown in Fig. 3, the relative depth of infiltration R may increase in a logarithmic fashion in the salinity range of the present study (10 to 50 meq L^{-1}).

$$R = R_0 + S \log C \quad (1)$$

where C is the salinity of irrigation water in meq L^{-1} , S the slope of the increase in R with increasing $\log C$, and R_0 the relative infiltration depth at $C = 1.0$ meq L^{-1} . Both R and R_0 are expressed in percentage. This equation is analogous to the equation used by Cass and Sumner (1982) for expressing the effect of salinity on hydraulic conductivity.

The slope was then assumed to be related to the sodium adsorption ratio (SAR) of the irrigation water or the exchangeable Na percentage of the soils (ESP) at or near the soil surface.

$$S = a + b \text{ ESP}^n \quad (2)$$

where b and n are empirical coefficients, and a is the slope at $\text{ESP} = 0$. For simplicity, we assume that $\text{ESP} = \text{SAR}$, although this can be modified if the exchange constant is known.

In order to equate a and R_0 to salinity and sodicity, we further assumed that the relationship between R and C converges at a fixed point characterized by R_C and C_C as shown in Fig. 3. By definition,

$$S = (R_C - R_0) / \log C_C \quad (3)$$

and

$$a = (R_C - 100) / \log C_C \quad (4)$$

where R_0 is the relative infiltration depth at ESP . (or SAR) = 0, and is assigned to be 100% at C

= 1.0 meq L⁻¹ , although this can be modified to have $R_o = 100\%$ at a higher level of salinity, C_o .
 If so, the term, $\log C_c$ should be modified to $\log (C_c - C_o)$.

Substituting Eqs (3) and (4) into Eq (2) and solving for R_o ,

$$R_o = 100 - b \text{ ESP}^n \log C_c \quad (5)$$

Substituting Eq (4) into (2), then Eqs (2) and Eq (5) into Eq (1) yields

$$\begin{aligned} R &= 100 - b \text{ ESP}^n \log C_c + [(R_c - 100)/\log C_c + b \text{ ESP}^n] \log C \\ \text{or} \quad &= 100 + (R_c - 100) \log C / \log C_c + b \text{ ESP}^n \log C / C_c \end{aligned} \quad (6)$$

When C is equal to 1 meq L⁻¹, Eq (6) is reduced to the same form as Eq (5), indicating that relative infiltration of low salt water is controlled by ESP^n and $b \log C_c$. If there is no structural degradation, b and/or n are zero, thus Eq (5) is reduced to $R = 100\%$.

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Table 1. Some properties of the saturation extract of the initial soil samples.

Soil Type (subgroup)	pH	EC	SAR ^{1]}	Na	Ca	Mg	Satur. Water
		dSm ⁻¹		-----mmol (+) L ⁻¹ -----			kg kg ⁻¹
Saneli silty clay loam (Vertic Torrifuvent)	8.5	1.0	3.0	5.1	4.1	1.6	0.38
Hoban silty clay loam (Typic Calciorthid)	8.1	8.6	15.3	65.4	27.2	9.3	0.32

^{1]}SAR: the sodium adsorption ratio

Table 2. Quality of irrigation water used for the experiments.

Sources	pH	EC	TC ^{1]}	SAR ^{2]}	SAR/EC	Na	Ca	Mg	HCO ₃	Cl	SO ₄
		dSm ⁻¹	mmol (+) L ⁻¹			mmol (+) L ⁻¹			mmol (-)L ⁻¹		
El Paso, TX											
Rio Grande	8.3	1.1	12	3.5	3.2	6.0	4.5	1.3	3.8	6.0	5.0
Sodic water	8.2	1.7	17	15.0	8.5	15.0	1.28	0.72	3.4	10.0	3.6
Well 1	8.1	3.6	36	9.0	2.5	23.0	9.8	3.2	4.2	19.0	12.8
Pecos, TX											
Well 2	7.9	4.0	42	14.2	3.5	31.8	7.2	2.8	3.4	20.6	17.8
Well 3	8.2	4.2	43	37.3	8.9	40.9	1.6	0.8	3.9	19.4	20.0
CaCl ₂ soln.	8.5	4.0	38	0	0	0.0	38.0	0	0	38.0	0

^{1]}TC: total cation concentrations, ^{2]}SAR: the sodium adsorption ratio.

Table 3. The sequence and depths of water application used in the infiltration experiment.

Experiment	Irrigation Sequences				
	1st	2nd	3rd	4th	5 th
Types of Water used					
Rio Grande (Rio)	Rio	Rio	Rio	Rio	Rio
CaCl ₂ solution (CA)	CA	CA	CA	CA	CA
Other treat. solns (Tr)	Tr	Tr	Tr	Rio	Tr
Depths of water (cm)	10	10	10	10	10

Table 4. Aggregated fractions of soil particles less than 20 and 2 μm as affected by salinity and sodicity of the suspension solutions.

Sodicity of the suspension solutions.						
Size Fraction	Less than 20 μm			Less than 20 μm		
Sodium Adsorption Ratio	1	15	30	1	15	30
	-----%-----			-----%-----		
<hr/>						
Saneli Soil	(58% of the mass)			(44% of the mass)		
Salinity dS m ⁻¹	----- Aggregated Fraction (%) -----					
5	43	37	27	98.2	98.1	91.9
50	51	43	35	100	99.1	98.7
300	65	57	53	100	100	100
<hr/>						
Hoban Soil	(58% of the mass)			(32% of the mass)		
Salinity dS m ⁻¹	----- Aggregated Fraction (%) -----					
5	55	50	41	98.3	97.5	97.1
50	58	55	49	100	99.5	98.8
300	74	69	65	100	100	100

Table 5. Empirical coefficients of Eq (5) during five irrigation events.

Soils		Infiltration Depth					
Water sources		CaCl ₂	R. Grande	Well 1	Well 2	Sodic water	Well 3
Saneli							
K (<u>cm hr⁻¹</u>)							
3 rd		0.25	0.18	0.20	0.17	0.16	0.19
4 th		0.12	0.10	0.10	0.09	0.09	0.02
5 th		0.14	0.12	0.12	0.11	0.10	0.08
P							
3 rd		0.41	0.38	0.39	0.48	0.41	0.36
4 th		0.47	0.32	0.47	0.48	0.59	0.53
5 th		0.41	0.34	0.30	0.32	0.47	0.51
f							
3 rd		0.53	0.73	0.76	0.53	0.60	0.75
4 th		0.55	0.93	0.63	0.70	0.23	-0.70
5 th		0.50	0.80	0.85	0.95	0.52	0.23
S							
3 rd		1.61	1.60	1.38	1.32	1.36	1.07
4 th		0.89	0.79	0.56	0.55	0.48	0.48
5 th		1.54	1.32	1.44	1.21	0.87	0.90
Hoban							
K (<u>cm hr⁻¹</u>)							
3 rd		0.26	0.27	0.24	0.33	0.28	0.31
4 th		0.14	0.10	0.13	0.12	0.09	0.12
5 th		0.13	0.17	0.20	0.15	0.17	0.16
P							
3 rd		0.32	0.23	0.34	0.35	0.23	0.35
4 th		0.34	0.25	0.43	0.32	0.28	0.24
5 th		0.25	0.28	0.19	0.26	0.24	0.25
f							
3 rd		0.80	0.71	0.40	0.45	0.73	0.60
4 th		0.56	0.88	0.55	0.80	0.60	0.82
5 th		0.95	0.70	0.85	0.87	0.77	0.55
S							
3 rd		2.48	2.10	2.82	2.08	1.98	1.82
4 th		1.37	0.87	0.85	0.85	1.27	0.88
5 th		3.08	2.35	2.52	1.80	1.80	2.18

Table 6. Depths of water infiltration of various water sources when the reference CaCl_2 solution infiltrated 10 cm during the 3rd through the 5th irrigations.

Soils	Infiltration Depth					
	3rd		4th		5th	
	Obs.	Est.	Obs.	Est.	Obs.	Est.
Irrigation No						
Water sources	cm	%	cm	%	cm	%
Saneli (Coeff. b, n) ^{1]}	(4.7,	0.74)	(4.7,	0.74)	(5.9,	0.74)
CaCl ₂ Soln.	10.0	100	10.0	100	10.0	100
Rio Grande	9.1	90	8.5	90	8.7	87
Well 1	9.0	90	7.8	78	8.7	87
Well 2	8.9	88	7.5	69	8.1	84
Sodic water	7.9	73	6.9	68	7.3	66
Well 3	7.4	74	3.3	35	6.7	67
Significance						
Std. Error						
Hoban (Coeff. b, n) ^{1]}	(3.0,	0.66)	(3.0	0.66)	(3.3,	0.79)
CaCl ₂ Soln.	10.0	100	10.0	100	10.0	100
Rio Grande	7.8	94(82)	6.9	94(82)	9.0	92
Well 1	9.4	94	8.7	88	9.1	91
Well 2	8.9	93	8.0	83	8.0	88
Sodic Water	8.0	85	6.8	82	7.4	76
Well 3	8.6	86	6.5	68	7.5	75
Significance						
Std. Error						

^{1]} The coefficients b and n of Eq (6) of Appendix, and the values for other coefficients were; $R_C = 102\%$ and $C_C = 110 \text{ meq L}^{-1}$ for Saneli soil, and $R_C = 101\%$ and $C_C = 120 \text{ Meq L}^{-1}$ for Hoban soil.

Figure Legend

- Fig. 1. Aggregated fractions of soil particles less than 20 μm as affected by salinity and sodicity of the suspensions.
- Fig. 2. Depths of water infiltration observed in Saneli (Fig. 2A) and Hoban (Fig. 2B) soils during the 3rd through the 5th irrigation with various sources of water. The 4th irrigation was made with the simulated Rio Grande water, except for the CaCl_2 reference solution, and other irrigations with the treatment water.
- Fig. 3. The relative sorptivity during the 3rd and 4th irrigations as related to salinity of the water sources used. The salinity of the irrigating solution during the 4th irrigation was 12 mmol (+) L^{-1} , the salinity of the simulated Rio Grande water.
- Fig. 4. The hydraulic gradient observed at different soil depths when the infiltration of various water sources approached 10 cm in depth.

Fig. 1

Fig. 2A

Fig. 2B

Fig. 3

Fig. 4

RESEARCH REPORT 5

COMPARATIVE EFFECTS OF CHEMICAL AMENDMENTS AND CROP RESIDUES ON INFILTRATION OF MODERATELY SALINE WATER INTO SILTY CLAY LOAM

ABSTRACT

Chemical amendments are commonly used for improving water infiltration into irrigated soils in the western states. However, their effectiveness has not been adequately evaluated when irrigation water has elevated salinity, e.g., $> 10 \text{ mmol}_e \text{ L}^{-1}$. This study examined in laboratory soil column the effects of five chemical compounds (Ca chloride, urea-sulfuric acid blend, NH_4 -acid blend, NH_4 -polysulfide and nonionic polyacrylamide) and chopped sorghum leaves on water infiltration into two calcareous clay loam soils; Saneli (montmorillonetic, Vertic Torrifluvent) and Hoban (micaceous, Typic Calciorthid). The chemical amendments were applied to three types of water having salinity of 17, 36 and $43 \text{ mmol}_e \text{ L}^{-1}$ with the corresponding sodium adsorption ratio of 15, 9, and 37. Chopped sorghum leaves were incorporated into the soils to a depth of 2.5 and 5.0 cm as additional treatments. Water infiltration was measured following 10 cm of water application up to 5 irrigation events. In addition, a CaCl_2 solution ($3.8 \text{ mmol}_e \text{ L}^{-1}$) was used as a reference solution. The use of these water sources caused water infiltration reductions by 10 to 25% when compared to that of the reference solution. Applications of inorganic chemical amendments at rates ranging from 1.9 to 7.6 meq L^{-1} did help minimize the reduction in infiltration rates. No significant difference in infiltration rates was observed among the compounds tested at chemically equivalent rates. However, NH_4^+ polysulfides provided somewhat higher rates of infiltration into initially dry or moist soils. Polyacrylamide treatments at rates as low as 2.5 to 5.0 mg L^{-1} provided infiltration rates equal to those attained from treatments with inorganic compounds. Soil application of sorghum clipping at a rate of 0.7 and 1.4 kg m^{-2} (or equivalent to 7 to 14 Mg ha^{-1}) was just as effective as water application of chemical amendments, if not more, especially in Saneli soil.

INTRODUCTION

Chemical amendments have been used with varying degrees of success to minimize a reduction in soil permeability, especially when salinity of water used for irrigation is low, e.g., $1 < \text{dS m}^{-1}$ (e.g., Gumaa et al., 1976; Wildman et al., 1988; Mohammed, 1972). These include gypsum, calcium chloride, sulfuric acid, urea-sulfuric acid blends, and polysulfides (e.g., Stromberg and Tisdale, 1979; Miyamoto, 1998). These compounds can counter against the dispersive effect of Na directly or by solubilizing Ca from calcareous soils. Recently, polyacrylamide (PAM) has also been shown to improve water infiltration through improving aggregation or particle flocculation (e.g., Azzam, 1980; Wallace et al., 1986; Shaviv et al., 1987; Saleh et al., 1990). The effectiveness of chemical treatments of irrigation water, however, has not been adequately evaluated when salinity of irrigation water is high. A laboratory soil column study indicates that application of sulfuric acid to various simulated irrigation water sources with salinity greater than 1 dS m^{-1} resulted in significant improvement in hydraulic conductivity in some, but not all soils tested only when the SAR of the irrigation solutions exceeded about 7 (Gumaa et al., 1976). A field water infiltration study conducted in the Imperial Valley, California, however, has shown that application of Ca-polysulfide and sulfuric acid to the Coronado River water having salinity greater than 1 dS m^{-1} and the SAR of 3 to 5 resulted in some measurable infiltration responses, and that NH_4 -polysulfide applied at a chemical equivalent rate provided highly significant improvements in water infiltration (Robinson, et al, 1976). The work of Wallace et al (1986) shows a consistently positive infiltration response to polyacrylamide (PAM), yet a field study conducted by Mitchell (1986) shows that PAM applications had limited infiltration responses. Obviously, there is a need to improve the guidelines for chemical treatments for improving infiltration of water with elevated salinity. The first objective of this study was to evaluate the effects of calcium chloride, urea-sulfuric acid blend, NH_4 -sulfuric acid blend, NH_4 -polysulfide, and nonionic polyacrylamide on infiltration of water with salinity greater than 1 dS m^{-1} .

A number of reports also indicates that soil application of organic matter can improve soil aggregation owing to increased fungal hyphae (Roldan and Albaladejo, 1966; Tisdall and Oades, 1982; Metzger, et al., 1987), and the cation bridging between organic matter and colloids (Oades, 1984). In calcareous soils, Ca solubilized by CO_2 released during decomposition of organic matter or respiration from roots can help stabilize soil structure (Robbins, 1986 and Report 3). Several reports also indicate improved soil aggregation and water infiltration when manure, municipal refuse, and sewage sludge were applied to soils (Sekhon and Bajwa, 1993; Lax et al., 1994; Albaladejo, 1996). Little is, however, known about their effectiveness as compared to chemical amendments. The second objective of this study was to compare the effect of soil application of sorghum clipping with the chemical amendments

applied to irrigation water with elevated salinity.

Materials and Methods

Two calcareous silty clay loam soils were used; Saneli silty clay loam (montmorillonetic, Vertic Torrifluvent, Entisol), and Hoban silty clay loam (micaceous, Typic Calciorthid, Aridisol). Soil samples were collected from the Ap horizon in irrigated fields in El Paso and Pecos, Texas, and were air-dried, crushed and passed through a 2 mm screen. Some properties of the soil samples are shown in Table 1.

Three different sources of water available in the sampled areas (Table 2) were simulated by adding salts to deionized (DI) water. In addition, a CaCl_2 solution (38 meq L^{-1}) was used as a reference. Sodic Water represents a typical composition of secondary effluent contaminated with perched saline water in the Rio Grande basin, Well 1 water, a typical composition of irrigation return-flow of the El Paso Valley; and Well 3 water, a saline ground water resource used for irrigation in the Pecos Valley.

Five compounds were selected for testing (Table 3). Calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) is usually applied to water as a saturated solution. Ammonia/acid mixtures are made through simultaneous injection of NH_3 and H_2SO_4 into irrigation water at acid rates usually twice that of NH_3 in chemical equivalent (Miyamoto and Ryan, 1976). This permits neutralization of NH_3 as well as a partial removal of HCO_3^- from water. Urea/acid mixtures are marketed at several mixing ratios with N percentages ranging from 10 to 20%. Nitrosol (NH_4Sx), made by injecting NH_3 (gas) into colloidal sulfur roughly at an equal molar ratio, is usually dripped into irrigation water. Polyacrylamide is also applied to irrigation water using a granule hopper feeder or a gel injector. Sorghum leaves were dried at 75°C and were chopped to a size of several mm.

The two soil samples (air-dried, $< 2\text{mm}$) were packed into PVC pipes (3 cm ID and 70 cm long) to a depth of 75 cm at a bulk density of 1.43 kg L^{-1} using a soil packing vibrator. Piezometers were placed at depths of 1, 2, 3, 5, 7.5, 10, 15 and 20 cm for measuring hydraulic heads during the infiltration process. Dry sorghum leaves chopped to a size of several mm were incorporated into the top 2.5 or 5.0 cm at two rates, 0.7 and 1.4 kg m^{-2} (or 7 and 14 Mg ha^{-1}) on the basis of dry weight. The soil below the surface layer was packed in the same manner as those which received chemical amendments.

The five chemical compounds were added to the experimental waters during the 2nd and the 4th irrigations at the rates shown in Table 3. The high rate of application in the sodic water was approximately equal to the equivalent concentration of HCO_3^- , whereas in the well water 1 and 3, the highest rate was approximately twice the equivalent concentration of HCO_3^- . The rates of PAM

application were based on distributor's guidelines. The application rate in grams per one m³ of water (or equal to kg of the materials applied to the water depth of 10 cm covering 1 ha) for (NH₄)₂S₈, ammonia/acid mix, and urea/acid was estimated based on potential Ca release by S or H₂SO₄, ignoring the potential contribution of N oxidation or Ca precipitation caused by addition of NH₃.

During the first water application, all columns received the prepared saline solutions containing no chemical amendment to a depth of 10 cm in the case of Sodic Water, and 15 cm in simulated Well 1 and 3 water (Table 4). The depth of water infiltrated was measured over time, and soil columns were then rearranged into four groups having high to low ranges of water infiltration. This procedure was used to reduce the effect of soil packing variability on subsequent infiltration measurements. During the 2nd and the 4th irrigation, the five chemicals (shown in Table 4) were added to each water in a block design with 4 replicates. The 3rd irrigation was made with the saline solutions containing no chemical amendment, using 10 cm (as of the 2nd and 4th irrigations). The 5th irrigation was made with distilled water at an application depth of 5 cm. The depth of water infiltrated was monitored in all columns, and the hydraulic heads only in the columns with high rates of chemical applications.

Data Processing

The depths of water infiltrated were averaged for each treatment, and the standard deviation and/or the coefficient of variability computed. The depths of water infiltrated were also normalized by the infiltration depth of the CaCl₂ solution, and the normalized depths will be referred to as relative infiltration depths. The significance of treatment effects was tested by the analysis of variance (ANOVA) of the relative infiltration depths toward the end of infiltration processes, using a block design (Little and Hills, 1975). The mean separation among the treatments was made with the Duncan's Multiple Range (DMR) test at a 5% level of significance.

The effects of salinity and sodicity of irrigation solutions on relative infiltration depths were assessed quantitatively by using the following equations described in an earlier report (Report 4).

$$R = 100 - b \text{ ESP}^n \log C_c/C + [(R_c - 100)/\log C_c + b \text{ ESP}^n] \log C \quad (1)$$

where R is the relative infiltration depth expressed in percentage, ESP the exchangeable Na percentage, C the salinity of irrigation water expressed in mmol_c L⁻¹ (or meq L⁻¹), R_c the relative infiltration depth at C = C_c above which salinity has no impact on R, and b and n are empirical coefficients.

When R_e is close to 100%, or C_e is large as compared to $R - 100$, Eq (1) is reduced to

$$R = 100 - b \text{ ESP}^n \log C_e/C \quad (2)$$

When salinity is low, e.g., $C = 1.0$, Eq (1) is further reduced to

$$R = 100 - b \text{ ESP}^n \log C_e \quad (3)$$

In using these equations, the empirical constants R_e and C_e were first determined using the relative infiltration depths observed during the 3rd and 4th irrigations, using two data sets; Well 3 and Well 1 water. Additional details of this procedure are shown in Report 4, and the result section of this paper. The two other coefficients, b and n , of Eq (1) or (2) were then calculated by using the data from Well 1 and Well 3 water. In using the above procedures, it was assumed that the ESP of the soil during the 3rd and 4th irrigation was equal to the SAR of the irrigation water sources applied. In addition, infiltration was assumed to be controlled by the ESP of the soil prior to irrigation, and salinity of the irrigation water during the irrigation.

In using Eq (1) or Eq (2) in chemically treated water, the empirical constants R_e , C_e and n were assumed to remain the same, but the coefficient b was recalibrated against the infiltration data of untreated water. In the case of the 5th irrigation involving deionized water, both b and n were recomputed using the data from untreated water and one of the chemically treated cases. The relative infiltration depths of other chemically treated water were then estimated with the following assumptions; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ dissolves completely into irrigation water; sulfuric acid removes HCO_3 and releases equivalent amounts of Ca from CaCO_3 present in the calcareous soils, and ammonium polysulfide dissociates to NH_4^+ and colloidal S which may be oxidized prior to subsequent irrigations. Ammonium ions in polysulfide as well in the NH_4 -acid blend were considered to lower SAR of irrigation water.

Piezometer readings were used to compute the hydraulic gradients at different depths of the soil columns (Miyamoto and Enriquez, 1990). The hydraulic gradient, estimated as the hydraulic head difference divided by the applicable thickness of the soil column segments, changed somewhat with time. The gradients measured when about half of the ponded water had infiltrated were used to represent the gradient for each irrigation cycle.

Results

Water Infiltration

Sodic Water: The depths of water infiltrated into Saneli soil during the 2nd, 3rd and 4th irrigation are shown in Fig. 1A. Water infiltration during the first and the second irrigations had completed in less than half of the time duration required for the 3rd irrigation with no significant effect of any of the chemical amendments tested. The rate of water infiltration decreased with time and repeated irrigations with a significant reduction occurring starting at the 3rd irrigation. By this time, the wetting front had reached the full length of the soil columns. The effect of chemicals applied became evident during the 4th and 5th irrigation, whereas sorghum leaves incorporated to a depth of 5 cm at 14 Mg ha⁻¹ provided a significantly higher rate of infiltration from the first irrigation.

The above pattern of infiltration was also observed in Hoban soil (Fig.1B). However, in the soil, which is initially affected by Na, the infiltration of Sodic Water decreased from the 1st irrigation below that of the CaCl₂ solution. The effects of chemical amendments applied to the 2nd and the 4th irrigation were evident in the 3rd and the 5th irrigation as well. Incorporation of chopped sorghum leaves also improved water infiltration, but not as extensively as observed in Saneli soil. During the 4th irrigation, sorghum leaves incorporated had little impact on infiltration.

Among the chemicals tested, NH₄-polysulfide provided somewhat higher infiltration than others during the 2nd and 3rd irrigations both in Saneli and Hoban soils, but not necessarily during the 4th irrigation (Table 5). Polyacrylamide treatments performed equally to others and have provided a persisting effect on water infiltration in Saneli soil, but not in Hoban soils (Table 5). The performance of other chemicals tested was not significantly different from each other. The mean relative infiltration depth from the higher rate (3.8 meq L⁻¹) of inorganic amendments was significantly higher than the mean of the low rate of application (1.9 meq L⁻¹), especially in the 4th and the 5th irrigations. The rates or the depth of sorghum leaf application did not significantly affect water infiltration in Saneli soil. This was also true in Hoban soil for the 2nd and the 3rd irrigation. During the 4th irrigation, however, the rate of water infiltration was somewhat higher at the low rate of application.

Table 5 also contains the estimated relative infiltration depths using Eq (1) or Eq (2). The empirical coefficient, *b*, of Saneli soil for the 2nd through 4th irrigations was computed by using the relative infiltration depth of Sodic Water without chemical treatments. In Hoban soil, both *b* and *n* were estimated using the infiltration depth of Well 1 water, since the data from Sodic Water in this soil were affected by the high soil sodicity (Report 4). During the 2nd irrigation, the observed (Obs.) and

the estimated (Est.) relative infiltration depths were in good agreement in Saneli soil, but not always in Hoban soil, especially in polysulfide treated cases (Table 5). During the 3rd irrigation, the observed values were not far off from the values estimated with an assumption that the ESP of the soil at the onset of the 3rd irrigation is the same as the SAR of the water applied during the 2nd irrigation. In the case of polysulfide treatments, the ESP was also computed by incorporating NH_4^+ and S oxidation (shown in parenthesis), and this had provided the estimates closer to the observed. During the 5th irrigation with deionized water, the observed relative infiltration depths were not far off from the estimates by Eq (3) which was derived with an assumption that salinity of deionized water may reach 1 meq L^{-1} upon application to the soils, mainly due to dissolution of CaCO_3 .

Saline Well Water: The improvement in infiltration by chemical conditioning of Well 1 water in Saneli soil was limited (Table 6), owing to the limited infiltration reduction induced by the use of this water source. Nonetheless, polysulfide treatments, as the case of Sodic water, provided consistently higher rates of infiltration as compared to other inorganic amendments, even though the differences were not always statistically significant. Polyacrylamide also performed well, and has shown notable residual effects. Soil incorporation of sorghum leaves did not affect water infiltration in Saneli soil irrigated with Well 1 water. The observed relative infiltration depths resulting from application of inorganic amendments were not far from the estimated (Table 6). Chemical conditioning of Well 3 water in Hoban soil produced infiltration response similar to those observed with Well 1 water on Saneli soil, but with a greater degree of improvements (Table 6). This included good performance of polysulfide and polyacrylamide, especially in the 2nd and 3rd irrigations. Incorporation of sorghum leaves did not affect water infiltration to any significant degree, when Well 3 water having high salinity was used.

Hydraulic Gradient

Chemical conditioning of Sodic Water applied to Saneli soil did not significantly alter the hydraulic gradient distribution, except for the sorghum leaf incorporation which provided lower gradients at and near the soil surface (Fig. 2). The hydraulic gradient distributions of urea-acid and NH_4 -acid blend were nearly identical to that observed with the CaCl_2 treatment, thus the data are not shown. The hydraulic gradient distribution of chemically treated Sodic Water during the 2nd irrigation was highest at the depth of 1 to 2 cm below the surface. By the 4th irrigation, the gradient at the soil surface has also increased except in the soil columns treated with sorghum leaves. Incorporation of sorghum leaves caused the gradient distribution to shift deeper into the soil profile.

The gradient distribution during the 5th irrigation with deionized water reverted back to a pattern similar to that of Sodic Water during the 2nd irrigation, but with positive hydraulic head readings extending below 5 cm in all treatments.

The hydraulic gradient in Hoban soil during the 2nd irrigation with Well 3 water was mostly less than one in the depth less than 3 cm, then increased sharply with depth. Application of chemical amendments caused the gradient distribution to shift to lower values at the surface as well as at a depth of 4 cm (Fig. 2). The shift was pronounced in the Ca chloride treatment as well as in the acid blends. The gradient distribution further shifted downward during the 4th irrigation except for the polyacrylamide treatment. Incorporation of sorghum leaves caused the hydraulic gradient to decrease below unity in the application depth, but created a high gradient, comparable to that from the control, at the depth immediately below. The gradient distribution during the 5th irrigation shifted back to the pattern similar to the control with no positive hydraulic head readings below 5 cm, except for the polyacrylamide treatment.

DISCUSSION

The previous report (Report 4) indicates that the principle process which causes a reduction in infiltration rate under repeated irrigations with water of elevated salinity is the breakdown of soil aggregates, besides the reduction in hydraulic gradient associated with increasing soil moisture contents. The soil particles detached can be transported and cause pore plugging as shown by the hydraulic gradient distribution in Hoban soil (Fig. 2). In the case of Saneli soil containing expandable clay minerals, swelling of the clay particles can cause the phenomenon known as the surface seal, as shown by the high hydraulic gradient at the soil surface (Fig. 2).

Chemical amendments are supposed to counter against disaggregation. The mode of action appeared to vary with the compounds used. The first type is to provide Ca ions either directly or through solubilizing CaCO_3 present in calcareous soils, and include Ca-chloride, urea-acid, and NH_4 -acid blends. There was no significant difference in infiltration rate among these compounds when applied to sodic water with elevated salinity. However, it should be noted that the rate of sulfuric acid applied in NH_4 -acid blends was half of that used in urea-acid blend or the rate which may produce half of the Ca concentration when compared to the Ca chloride treatments. It seems that NH_4^+ ions acted similarly to Ca^{++} in reducing sodicity and increasing salinity, even though some earlier work reported that NH_4 is not nearly as effective as Ca in improving hydraulic conductivity (e.g., Martin and Richards, 1959). The present finding implies that acid rates can be reduced when combined with N

fertilization using NH_4 forms, but not with urea. Urea is a neutral compound and passes through the flow limiting surface layer with water percolation. In any case, the effectiveness of these water-soluble inorganic compounds decreases with increasing salinity of water used for irrigation, as projected by the equation proposed in Report 4.

The effects of chemical conditioning of irrigation water, especially that of NH_4 -polysulfide have been a matter of conjecture. In this study, polysulfide treatments at chemically equivalent rates provided infiltration somewhat greater than that from other treatments in the 2nd irrigation, but not in the 4th irrigation. The level of the improvement was, however, not nearly as great as those reported earlier in a field test conducted by Robinson et. al (1976) where polysulfide treatments were applied to initially dry soils irrigated with a furrow method. The improvement in infiltration with this compound appeared primarily during the initial stage of infiltration (e.g., Fig. 2), and did not necessarily provide the hydraulic gradient distribution favorable for water infiltration (Fig. 2). Polysulfide treatments seem to improve sorptivity prior to the oxidation of S or NH_4 . The observed improvement in infiltration is likely to be a combination of improved wettability and to a lesser extent, Na replacement by NH_4 . This compound is a strong reducing agent, and is capable of bleaching organic coating of soil particles.

Polyacrylamide treatments were effective, especially when considering the low application rates used. Judging from the hydraulic gradient distribution pattern (Fig. 2), it seems that this compound has helped reduce aggregate slaking during the 2nd irrigation. Polyacrylamides are known to promote soil aggregation (Raviv et al., 1987). This effect might have persisted during the 3rd irrigation (Table 5 and 6). Polyacrylamide applications seem to be more effective when applied to saline well water sources (Table 6), and this tendency is consistent with the finding of Shainberg et. al, (1990). However, the hydraulic gradient distribution patterns during the 4th irrigation indicated that this compound was not very effective in reducing the resistant to flow at and near the soil surface (Fig. 2). The fact that infiltration depths decreased with increasing rates of this compound in Hoban soil (Table 6 and 7), coupled with the above gradient distribution characteristics, may suggest that the application of this compound has formed some type of film over the soil surface. It is, however, uncertain if this phenomenon occurs in field soils with greater roughness, and requires additional observation, especially in highly sodic conditions. The problem of film formation was noted earlier, and was reportedly minimal with anionic polymers (Saleh, et al., 1990).

Incorporation of chopped sorghum leaves was effective in improving water infiltration, presumably through increasing pore spaces and dissolution of Ca (soil tests are currently pending for assessing the impact of Ca dissolution on the exchangeable Na percentage). This treatment was more

effective in Saneli soil than in Hoban soil. This finding is consistent with the hydraulic gradient distribution shown in Fig. 2. Note that the gradient in Saneli soil was reduced more than in Hoban soil. In the present study, the depth of application was shallow (2.5 to 5.0 cm), and this has created high gradients right below the depth of application (Fig. 2). One may expect that incorporation to a deeper depth can possibly provide more desirable infiltration characteristics. The present study, however, indicate that there is no great deal of differences in infiltration rate between the tested depths, owing to the flow resistance developed below the depth of application.

The extent of water infiltration improvement observed in the present experiments were in the range of 10 to 25%, which may be considered small as compared to the wide-variation existing among different soils. At the same time, the increase in leaching fraction at the magnitude can cause a major difference in salinity of subsoils. If the water used for irrigation is sodic enough to cause substantial infiltration reductions, and subsoil salinity is high enough to cause growth reduction, chemical treatments or crop residue application may prove to be beneficial. The cost-effectiveness may be enhanced by combining with water-run application of NH_4 and incorporation of crop residues. However, if the source of water is not sodic enough to cause a significant reduction in infiltration rate, or subsoil salinity is not high enough to cause growth reductions, the use of amendments may prove to be little value. Field experiments are warranted to evaluate these scenarios.

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Table 1. Some properties of the saturation extract of the initial soil samples.

Soil Type (subgroup)	pH	EC _e dSm ⁻¹	SAR _e ^{1]}	Na	Ca	Mg	Satur. Water kg kg ⁻¹
				-----mmol (+) L ⁻¹ -----			
Saneli silty clay loam (Vertic Torrifluvent)	8.5	1.0	3.0	5.1	4.1	1.6	0.38
Hoban silty clay loam (Typic Calciorthid)	8.1	8.6	15.3	65.4	27.2	9.3	0.32

^{1]}SAR_e: the sodium adsorption ratio of the saturation extract.

Table 2. Quality of irrigation water used for the experiments.

Sources	pH	EC dSm ⁻¹	TC ^{1]} mmol (+) L ⁻¹	SAR ^{2]}	SAR/EC	Na	Ca	Mg	HCO ₃	Cl	SO ₄
						mmol (+) L ⁻¹			mmol (-)L ⁻¹		
El Paso, TX											
Sodic water	8.2	1.7	17	15.0	8.5	15.0	1.28	0.72	3.4	10.0	3.6
Well 1	8.1	3.6	36	9.0	2.5	23.0	9.8	3.2	4.2	19.0	12.8
Pecos, TX											
Well 3	8.2	4.2	43	37.3	8.9	40.9	1.6	0.8	3.9	19.4	20.0
CaCl ₂ soln.	8.5	4.0	38	0	0	0.0	38.0	0	0	38.0	0

^{1]}TC: total cation concentrations, ^{2]}SAR: the sodium adsorption ratio.

Table 3. Types and rates of chemicals applied to selected water samples during the 2nd and 4th irrigations and chopped sorghum leaves applied initially to the soils.

Chemicals Molecular wt. (Ingrient %)	Water sources	Application Rates		
		meq L ⁻¹	mg L ⁻¹	kg ha ⁻¹
Calcium Chloride (CaCl ₂ • 2H ₂ O) 147 (100)	Sodic water	1.9	139	280
	Sodic, Well 1 & 3	3.8	279	560
	Well 1 and 3	7.6	558	1120
Ammonium/Acid ^{1]} (NH ₄) ₂ SO ₄ + H ₂ SO ₄ 132 + 98 (100, 93)	Sodic water	1.9 ^{1]}	110	220
	Sodic Well 1 & 3	3.8	220	440
	Well 1 and 3	7.6	440	880
Ammon-polysulfide ^{2]} (NH ₄) S 52 (66)	Sodic water	1.9	75	150
	Sodic, Well 1 & 3	3.8	150	300
	Well 1 and 3	7.6	300	600
Urea/acid ^{3]} CO (NH ₂) ₂ H ₂ SO ₄ 60 + 98 (100, 93)	Sodic Water	1.9 ^{3]}	146	290
	Sodic Well 1 & 3	3.8	292	580
Polyacrylamide ^{4]} (n C-CH ₂ CONHOCH ₂) 100-200K (90)	Sodic Water	-	2.5	5
	Sodic, Well 1 & 3	-	5.0	10
	Well 1 & 3	-	10.0	20
Chopped Sorghum Leaves				
Incorporated to 2.5 cm	Sodic Water	-	-	7
2.5 cm	Sodic, Well 1 & 3	-	-	14
5.0 cm	Well 1 & 3	-	-	14

^{1]}This mixture contained a 1:1 molar ratio and the application rates reflect the mixture.

^{2]}This product is marketed as 20-0-0--40(s).

^{3]}This product contained a 1:1 molar ratio and the application rates reflect the acid rate

^{4]}Nonionic Linear copolymer of acrylamide and Na acrylate. The application rates of this product were not adjusted to purity.

Table 4. The sequence and depths of water application used in the infiltration experiments.

Experiment	Irrigation Sequences				
	1st	2nd	3rd	4th	5th
Types of water used					
Sodic water (SD)	SD	SD ^c	SD	SD ^c	DI ^{1j}
CaCl ₂ Soln (CA)	SD	CA	CA	CA	DI ^{1j}
Depths of water applied (cm)	10	10	10	10	10
Types of water used					
Well water 1&3 (W)	W	W ^c	W	W ^c	DI ^{1j}
CaCl ₂ Soln (CA)	W	CA	CA	CA	DI ^{1j}
Depths of water applied (cm)	15	10	10	10	5

^{1j}DI: Deionized water

^c: Chemicals were applied to the 2nd & 4th irrigations.

Table 5. Relative infiltration depths of sodic water during the 2nd through 4th irrigation and those of deionized water during the 5th irrigation.

Soils	Chemicals	Appl. rate -----meq L ⁻¹ -----	Total cations	SAR	Relative Infiltration Depths								
					2nd		3rd		4th		5th		
					Obs. cm	Est. %	Obs. cm	Est. %	Obs. cm	Est. %	Obs. cm	Est. %	%
Saneli (Coeff. b, n)					(2.2, 0.74)		(3.2, 0.74)		(4.5, 0.74)		(6.5, 1.30)		
	Sodic water	0	17	15	8.8	88	8.2	82	7.4	74	2.7	55	55
	urea-acid	1.9	17	11	9.0	90	8.7	86	7.7	80	3.3	66	70
	Amm-acid	1.9	18	11	9.0	91	8.8	86	8.2	80	3.4	68	70
	Ca-chloride	1.9	19	11	9.1	91	8.9	86	8.2	81	3.2	63	70
	Polysulfide	1.9	18	12(9.7) ^{1]}	9.3	90	8.9	(87)	8.2	80	3.6	71	(74)
	Urea-acid	3.8	17	8.8	9.0	92	8.7	88	8.3	83	3.9	79	78
	Amm-acid	3.8	19	8.8	9.2	92	8.8	88	8.4	83	4.1	83	78
	Ca-chloride	3.8	21	8.8	9.2	93	8.9	88	8.4	85	3.9	78	78
	Polysulfide	3.8	19	11.0(7.6) ^{1]}	9.6	91	9.4	(89)	8.3	80	4.1	81	(81)
	PAM (ppm)	(2.5) ^{2]}	17	15	9.3	-	9.2	-	8.0	-	3.8	76	-
	(ppm)	(5.0)	17	15	9.1	-	9.1	-	8.2	-	3.8	77	-
	(ppm)	(10.0)	17	15	8.8	-	9.1	-	8.6	-	4.0	81	-
	Sorghum	(7) ^{3]}	17	15	10.7	-	10.3	-	10.2	-			
	2.5 cm	(14)	17	15	9.6	-	10.0	-	10.0	-			
	5.0 cm	(14)	17	15	11.3*	-	10.3	-	10.2	-			
	CaCl ₂ soln	38.0	38	0	10.0	100	10.0	100	10.0	100	5.0	100	100
Significance													
Std. Error													
Hoban (Coeff. b, n)					(0.60, 1.31)		(0.65, 1.31)		(96, 1.31)		(3.6, 0.66)		
	Sodic water	1.9	17	15	8.3	83	8.1	81	7.2	72	2.8	56	56
	Urea-acid	1.9	17	11	8.7	89	8.6	87	7.6	81	3.1	63	64
	Amm-Acid	1.9	18	11	8.6	89	8.6	87	7.6	82	3.1	63	64
	Ca-chloride	1.9	19	11	8.9	90	8.4	87	8.0	81	3.1	62	64
	Polysulfide	1.9	18	12(9.7) ^{1]}	9.4	89	9.1	(90)	9.0	82	3.9	78	(66)
	Urea-acid	3.8	17	8.8	9.3	92	8.9	91	8.7	86	3.4	69	69
	Amm-acid	3.8	19	8.8	9.6	92	9.5	91	9.3	87	3.8	77	69
	Ca-chloride	3.8	21	8.8	9.5	93	9.2	91	8.4	88	3.4	69	69
	Polysulfide	3.8	19	11.0(7.6)	9.7	89	9.4	(93)	9.3	82	3.8	77	(72)
	PAM (ppm)	(2.5) ^{2]}	17	15	8.2	-	8.4	-	8.1	-	3.8	69	-
	(ppm)	(5.0)	17	15	8.3	-	8.4	-	7.4	-	3.1	62	-
	(ppm)	(10.0)	17	15	8.4	-	9.4	-	6.5	-	3.3	67	-
	Sorghum	(7) ^{3]}	17	15	10.2	-	9.8	-	8.2	-			
	2.5 cm	(14)	17	15	9.0	-	9.0	-	7.3	-			
	5.0 cm	(14)	17	15	10.2	-	9.0	-	7.2	-			
	CaCl ₂ Soln		38	0	10.0	100	10.0	100	10.0	100	5.0	100	100
Significance													
Std. Error													

^{1]}SAR of water assuming NH₄ and S oxidation. ^{2]}Unit in mg L⁻¹. ^{3]}Unit in Mg ha⁻¹

Table 6. Relative infiltration depths of simulated well water sources during the 2nd through 4th irrigations and those of deionized water during the 5th irrigation.

Soils	Chemicals	Appl. rate	Total cations	SAR	Relative Infiltration Depths								
					2nd		3rd		4th		5th		
					Obs.	Est.	Obs.	Est.	Obs.	Est.	Obs.	Est.	%
-----meq L ⁻¹ -----					cm	%	cm	%	cm	%	cm	%	%
Saneli (Coeff. b, n)					(2.9, 0.74)		(4.2, 0.74)		(4.9, 0.74)		(.62, 1.4)		
Well water	0.0	36	9.0		9.4	94	9.1	91	8.9	89	3.6	73	73
urea-acid	3.8	36	7.9		9.6	95	9.2	92	9.3	91	4.1	81	77
Amm-acid	3.8	38	7.9		9.6	95	9.5	93	9.5	91	4.1	82	77
Ca-chloride	3.8	40	7.9		9.5	96	9.0	93	8.6	92	3.8	77	77
Polysulfide	3.8	38	8.7(7.5) ^{1]}		9.6	95	9.4	(93)	8.8	91	3.4	79	(79)
PAM (ppm)	(2.5)	36	9.0		9.7	-	9.3	-	9.6	-	4.2	84	-
(ppm)	(5.0)	36	9.0		9.5	-	9.7	-	9.6	-	4.3	87	-
(ppm)	(10.0)	36	9.0		9.7	-	9.7	-	9.7	-	4.4	88	-
Sorghum	(7)	36	9.0		9.8	-	9.0	-	9.1	-			
2.5 cm	(14)	36	9.0		9.9	-	8.9	-	8.9	-			
CaCl ₂ soln.	38	0.0	10.0	100	10.0	100	10.0	100	5.0	100			
Significance													
Std. Error													
Hoban (Coeff. b, n)				(2.9, 0.66)	(3.8, 0.66)	(4.5, 0.66)	(0.76, 0.84)						
Well 3 water	0.0	43	37		8.7	87	8.2	82	7.9	79	3.3	67	67
Urea-acid	3.8	43	23		9.3	91	8.5	87	8.9	85	3.7	74	78
Amm-Acid	3.8	45	23		9.3	91	8.7	88	8.5	85	3.6	72	78
Ca-chloride	3.8	47	23		8.7	91	7.9	89	7.9	85	3.3	67	(80)
Polysulfide	3.8	45	23(20) ^{1]}		9.5	91	8.5	(89)	8.9	85	4.0	80	82
Amm-acid	7.6	47	18		9.3	93	9.2	90	9.0	88	4.1	82	82
Ca-chloride	7.6	50	18		9.5	93	9.0	91	8.0	88	3.7	74	82
Polysulfide	7.6	47	23(16) ^{1]}		10.0	93	9.0	(91)	9.3	85	4.1	82	(84)
PAM (ppm)	(2.5)	43	37		8.9	-	9.0	-	8.5	-	4.2	84	-
(ppm)	(5.0)	43	37		8.9	-	9.2	-	8.1	-	4.0	80	-
(ppm)	(10.0)	43	37		9.3	-	9.9	-	8.1	-	4.2	84	-
Sorghum	(7)	43	37		8.7	-	8.2	-	8.3	-			
2.5 cm	(14)	43	37		8.0	-	7.8	-	7.8	-			
CaCl ₂ Soln	38	0	10.0	100	10.0		-		10.0	100	5.0	100	100
Significance													
Std. Error													

^{1]}SAR of water assuming NH₄ and S oxidation, ^{2]}Unit in mg L⁻¹, ^{3]}Unit in Mg ha⁻¹

Figure Legend

- Fig. 1A** The depth of water infiltration as affected by chemical amendments (high rates, Table 3) and chopped sorghum leaf incorporation (17 Mg ha^{-1}) into Saneli silty clay loam.
- Fig. 1B** The depth of water infiltration as affected by chemical amendments (high rates, Table 3) and chopped sorghum leaf incorporation (17 Mg ha^{-1}) into Hoban silty clay loam.
- Fig. 2** The hydraulic gradient distribution during the 2nd and the 4th irrigation into Saneli and Hoban soils as affected by chemical amendments (high rates, Table 3) and chopped sorghum leaf incorporation (17 Mg ha^{-1}).

Fig. 1A

Fig. 1B

Fig. 2

RESEARCH REPORT 6

ESTIMATING SALINITY AND SODICITY EFFECTS ON WATER INFILTRATION UNDER PONDING

ABSTRACT

Sodicity and salinity affect water infiltration, a process highly relevant to soil and water management. This study was conducted for evaluating suitability of various infiltration equations for describing intake of saline water into dry salt and/or sodium-affected soils. Water infiltration was measured under shallow continuous ponding, using three soils; Harkey loam (Typic Torrifluvent, Entisol), Hoban silty clay loam (Typic Caciorthid, Aridisol), and Saneli silty clay loam (Vertic Torrifluvent, Entisol). Air-dry soil samples were passed through a 2 mm screen, and were placed in soil columns. Saline solutions used contained dissolved salt concentrations of 10 to 300 mmol L⁻¹, and had the sodium adsorption ratio (SAR) of 1 to 70. Water infiltration progressively decreased with increasing SAR and with reducing salinity. The relationship between the depth of infiltration and time was best described by a modified two-term Kostiakov equation with a simple adjustment factor applied to the gravity term. The adjustment factor used accounted for a reduction in hydraulic conductivity with time and, at a low SAR range, the effect of soil layering. Empirical equations were then developed, which describe the relationship between the infiltration parameters (principally the infiltration coefficients in the Kostiakov equation and the hydraulic conductivity) and sodicity and salinity of infiltrating water. The use of these empirical relationships in the modified Kostiakov equation provided realistic estimates of sodicity and salinity effects on water infiltration in all three soils tested. For estimating the initial water infiltration into dry soils, however, the Kostiakov or the Philip equation without the gravity term offers a simpler option.

High sodicity usually lowers infiltration rates, especially when salinity of leaching water is low (e.g., Shainberg and Letey, 1984). Several studies have shown that such effects on saturated hydraulic conductivity can be described quantitatively in some soils (McNeal, 1968; Cass and Sumner, 1982; Jaywardance and Blackwell, 1991). If similar relationships can be found for describing the effect on sorptivity, it may be possible to estimate salinity and sodicity effects on water infiltration, provided that the process can be described by using sorptivity and hydraulic conductivity.

In structurally stable soils, Philip (1957) has shown that the initial horizontal infiltration is proportional to the square root of infiltration time with the slope designated as the sorptivity (Table 1). In Na-affected soils or soils with weak aggregates, however, soil aggregates undergo rapid disintegration upon the contact with water, thus leading to an accelerated reduction in infiltration rate. The water infiltration process of this type is analogous to water infiltration into a layered soil or a situation commonly referred to as water infiltration into crusted soils (e.g., Ahuja and Romkens, 1974; Morel-Seytoux, 1983). In the work of Ahuja and Romkens (1974), the hydraulic conductivity of a crust layer was found to decrease with a power function of time through curve fitting to the data reported by McIntyre (1958) and Edwards and Larson (1969). This empirical function was then used to solve the horizontal water infiltration equation. After some simplification, they have shown that the initial infiltration into crusted soils is no longer proportional to the square root of time, but a power function of time, as shown by Eq (3) of Table 1. Note that this equation is essentially the same as the empirical equation proposed by Kostiaikov (1932) where the coefficients are considered purely empirical.

For vertical infiltration, the gravity component Kt is usually added as shown by Eq (2) and Eq (4). This formulation originates from the observation that in structurally stable soils, the final or long-term infiltration rate approaches the steady-state hydraulic conductivity, K . However, observations of water infiltration into sodium-affected soils indicate that K does not always remain constant, but tends to decrease with time. In such cases, it would be more versatile if an adjustment factor is applied to Kt as shown in Eq (5), although it is uncertain how well such a simple procedure may work. In the field infiltration experiment report by Talsma (1969), for example, the factor f was found to be approximately $1/3$ when the two-term Philip equation or Eq (2) was used for describing water infiltration processes. An alternative approach would be to define K as a function of time, as

shown, for example, by Moore (1981) for describing the time-dependent formation of soil crust during infiltration.

The first objective of this study was to evaluate the applicability of some of these equations for describing water infiltration into sodic soils during ponded leaching. The second objective was to examine or develop empirical equations which describe salinity and sodicity effects on infiltration parameters. Once such relationships are determined, it should be possible to estimate the effect of any combinations of salinity and sodicity on water infiltration into similar soils.

MATERIALS AND METHODS

Three soil samples collected from irrigated fields were used: Harkey loam (calcareous, Typic Torrifluvent, Entisol), Hoban silty clay loam (calcareous, micaceous, Typic Caciorthid, Aridisol), and Saneli silty clay loam (calcareous, montmorillonetic, Vertic Torrifluvent, Entisol). Bulk samples of Harkey and Saneli soils were collected from the A-horizon of disked fields in the El Paso Valley, and that of Hoban from the Pecos Valley, TX. They were passed through a 4 mm screen, and were placed in five filtration tanks for pretreatment. The pretreatment solutions were prepared by adding NaCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 7\text{H}_2\text{O}$ to distilled water so as to provide the sodium adsorption ratio (SAR) of 1, 12, 25, 50 and 70 at a constant high salinity of 300 meq L^{-1} . The molar concentrations of Ca and Mg were equal. These solutions were applied to the five filtration tanks in an amount equal to 20 pore volumes. The pre-treated soils were drained, air-dried, crushed, passed through a 2 mm screen, and subsamples were analyzed for Na, Ca and Mg concentrations in the saturation extract. This analysis provided a confirmation that the SAR of the saturation extract was nearly equal to or somewhat greater than those of the leaching solutions.

For measuring water infiltration, the pretreated soil samples were packed into PVC pipes (3 cm ID, and 72 cm long) to a depth of 60 cm with a vibrator to a bulk density of 1.39, 1.42 and 1.43, kg L^{-1} in Harkey, Hoban, and Saneli soil, respectively. A layer of coarse sand (2.5 cm thick) was placed below the soil for free drainage. Two sheets of fiberglass screen were placed on the surface of the packed soils to minimize disturbance during water application. Piezometers were placed at 1, 2, 3, 5, 7.5, 10, 15 and 20 cm below the soil surface in order to determine the hydraulic head. The

salt solutions having different salinity levels, but with the SAR values similar to those of the pretreated soils were prepared by adding NaCl, and equivalent amounts of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 7\text{H}_2\text{O}$ to distilled water (Table 2). These saline solutions were added to the soil columns under a constant ponding depth of 4 cm, and the quantity of water infiltrated and the hydraulic head measured periodically. All the columns were covered individually with a parafilm with a pin-hole to eliminate water evaporation. The experiments continued for approximately 4 to 6 weeks. All the experiments were replicated 4 times.

The cumulative depths of water infiltration measured in four replicates were averaged, and the standard deviation or the coefficient of variability computed. The cumulative infiltration depth measured was then used to test the applicability of Eq (1) of Table 1, then Eq (3). Subsequently, the hydraulic conductivity, K , was estimated from the slope of infiltration curves toward the end of the infiltration process. The applicability of Eq (2) and Eq (4) was tested by examining the linearity of the full-log plots between $D/kt - 1$ and t . The coefficient p of Eq (4) was determined by using the linear portion of the plot applicable to the initial phase of infiltration. Finally, the adjustment factor, f , of Eq (5) was determined as the value which provides the highest degree of linearity of the above plots.

Once these hydraulic parameters (K , p , S , and f) were determined, they were correlated to salinity and sodicity of the irrigation solutions, first using the form proposed by Cass and Sumner (1982) for describing the relative hydraulic conductivity, which is described by Eq (7) of Table 1. This form of expression was also used by McNeal (1968) for describing clay swelling effects on saturated hydraulic conductivity. The applicability of Eq (7) was evaluated by plotting $(1 - R_K)/R_K$ against TDS on a full-log scale. Note that R_K denotes the hydraulic conductivity normalized by the maximum value.

The second approach used the concept of "equivalent salt solutions" originally defined by Jayawardane (1973) as solutions with the combination of sodium adsorption ratio (SAR) and salinity (TDS), which produce the same extent of clay swelling. We defined this term as salt solutions which yield the same hydraulic conductivity or other hydraulic parameters, and used the formulation shown by Eq (8) and (9) of Table 1. The equivalent constant n was determined by solving Eq (8) for n when two or more solutions (characterized by SAR and TDS) were found to yield the same hydraulic

conductivity or other hydraulic parameters of Eq (5). The regression and infiltration equations were then used to reconstruct infiltration curves for randomly selected cases, and the standard error of the estimate computed.

RESULTS

Water Infiltration

The cumulative infiltration depths measured are shown for randomly selected saline solutions in Fig. 1 for the three soils tested. Water infiltration significantly decreased with increasing sodicity and/or decreasing salinity. The differences in infiltration depth observed among the different water sources were far greater than the standard deviation of the replicates as shown in the figure.

Examples of the cumulative water infiltration plotted against the square root of time are shown in Fig. 2 for the three soils tested. The infiltration of high saline solutions into Harkey soil conformed to a typical plot common to structurally stable soils, e.g., the linear relationship during the initial stage of water infiltration, followed by the upward deviation caused by the gravity term involving the steady-state hydraulic conductivity. However, the slope of the plots or the sorptivity decreased as soon as the SAR of infiltrating solutions was elevated to 12. The deviation from the linear relationship became apparent after the cumulative infiltration became greater than about 25 cm. At this point, the wetting front has reached at the end of the soil columns. In Hoban and Saneli soils, we did not observe the typical pattern applicable to water infiltration into structurally stable soils. Instead, the plots for low SAR solutions ($SAR < 12$) deviated from the linearity after the cumulative infiltration depth reached 20 to 30 cm. The loss of capillary suction as well as the steady decline in hydraulic conductivity may have contributed to the downward deviation. When the SAR of infiltrating solutions exceed about 25, the plots generally deviated upward from linearly after varying periods of slow initial infiltration associated with low sorptivity. It is evident that Eq (1) applies only to the initial stage of water infiltration, usually not exceeding 20 cm or less in infiltration depth. The sorptivity given by Eq (1) was determined from the slope of the plot applicable to the initial infiltration occurred up to 1 to 5 day, and is listed in Table 3.

Examples of the cumulative depth of water infiltration with time, plotted on the full-log scale

to test the applicability of the Kostiakov equation or the equation proposed by Ahuja and Remkens (Eq. 3 of Table 1) are shown in Fig. 3A and 3B for Harkey and Hoban soil, respectively. The plots for Saneli soil were similar in pattern to those of Hoban soil, thus are not shown. In Harkey loam, the plots for low SAR solutions ($\text{SAR} < 12$) were mostly linear, but at higher SAR, the plots deviated upward from the initial linear relationship. In Hoban and Saneli silty clay loam, the plots did not conform to linearity in any consistent manners.

The data analyses were then directed to examine the applicability of Eq (2) and Eq (4), both of which include the gravity term. The term, $D/Kt - 1$, was computed by using the hydraulic conductivity evaluated at 25 days for Harkey, and 30 days for Hoban and Saneli. The hydraulic conductivity values (K) obtained are shown in Table 3. In Harkey loam, the plots appeared to be linear, but a close examination indicates that the slope has increased somewhat toward the end of infiltration process, thus presenting slightly curve-linear relationships with a downward shift. This pattern became more obvious in Hoban and Saneli soils, especially after the soil columns were saturated. We then examined if the curve-linear pattern could be affected by the time-selection made for determining the hydraulic conductivity. The conductivity was determined at both shorter and longer time periods than the originally used. This affected the positioning of these plots, but did not correct the curve-linear pattern.

An additional difficulty was encountered in estimating the parameters in Hoban soil when the SAR of the solutions was greater than 50 and/or the TDS less than 25. Such an example is shown in the case involving Hoban silty clay loam irrigated with a SAR of 75 and TDS of 25 mmol L^{-1} solution (Fig 3B). In these cases, the infiltration parameters were determined for the initial phase by using Eq (3). These are marked in parenthesis in Table 3. It should also be noted that the procedures used involve D/Kt term, thus do not apply to the case where the hydraulic conductivity is near zero. However, the one-term equation, or Eq (3), can be used in such cases.

We then proceed to examine the applicability of Eq (5). The coefficient p , determined from the slope of the pots for the initial phase of infiltration (usually t less than 1 day) ranged from 0.3 to 0.55 (Table 3). The adjustment factor f was estimated by evaluating the upswing or downswing necessary to make the plots linear toward the later stage of water infiltration through extrapolation of the lines from the earlier stage. The values of f so determined ranged widely (Table 3). The

negative values reflect the observation that water infiltration rate suddenly decreased after the soil columns became saturated (e.g., Fig. 2). The values for S were then determined by using Eq (3) or Eq 5) at $t = 1$ day. The results are listed in Table 3. The adjusted plots are shown in the far-right hand side of Figs. 3A and 3B. Since these plots provided satisfactory results, no further attempt was made to improve curve-fitting.

Relationships between Infiltration Parameters and Sodicty-Salinity

The full-log plots of $(1 - R_K)/R_K$ vs C did not yield straight lines for the tested range of salinity in any of the soils tested. Note that R_K designate the relative hydraulic conductivity. Therefore, Eq (7) of Table 1 was excluded from further consideration. The use of "equivalent salt solution" concept was found to be workable. In Hoban soil, for example, the salt solution having SAR of 25 and TDS of $25 \text{ mmol}_e \text{ L}^{-1}$ was found to yield the same sorptivity as another solution having SAR of 50 and TDS of $100 \text{ mmol}_e \text{ L}^{-1}$ (Table 3). The equivalent constant n of Eq (8) for this case is 2.0. The curve fitting of infiltration parameters using Eq (9) resulted in a high degree of correlation for coefficient p (Fig. 4), sorptivity S (Fig. 6), and conductivity K (Fig. 7). In the case of hydraulic conductivity, however, the data points from the SAR of 1 series lined along the vertical axis, and these points were excluded from curve-fitting, (Fig. 7). Note that, when $\text{SAR} = 1.0$, the SAR term becomes unity, regardless of n values. The use of an alternative equation, $x = \text{SAR}^n/\text{TDS}^m$, helped achieve a spread of these data points along the horizontal axis, and provided somewhat improved curve-fitting (the last row of Table 4). The adjustment factor, f , however, did not follow the same function, but was approximately linear (Fig. 5). The negative values prevailed in the silty clay loam, especially in solutions with SAR of less than 25, or more precisely SAR^n/TDS of 0.75 (Fig. 5) for the reasons stated earlier. In Harkey loam, the values of f were rarely negative, probably due to lower layering effects on water infiltration in coarse-textured soils (Aylor and Parlange, 1973).

DISCUSSION

The first objective of this study was to evaluate suitability of several simple infiltration

equations for describing water infiltration into dry sodic soils. It had been known that Philip equation without the gravity term is applicable mainly during the initial phase of infiltration into dry soils where sorption is the dominant factor. This study indicates that the applicability of this equation extends for a duration up to a few days or 20 to 30 cm in cumulative infiltration depth when sodicity is lower than about 25 in SAR (Fig. 2). However, in sodic soils having higher sodicity, its use can be extended to weeks, even though the accuracy may be reduced considerably.

The Kostiakov equation, Eq (3) of Table 1, provides flexibility in curve-fitting, since the coefficient p is not fixed as being 0.50. This equation was tested satisfactorily in sodic soils for a shorter duration by Yahia et al., (1975). In this study, the coefficient p decreased with increasing the parameter, SAR/TDSⁿ (Fig. 4). This observation is consistent with the earlier analyses by Ahuja and Romkens (1974) for water infiltration into crusted soils. The full-log plots was not always linear (e.g., Fig. 3A and 3B), and this problem was accentuated by the log-scale applicable to infiltration depths of less than 5 or 10 cm. Although the accuracy of representing the later process may be compromised somewhat, this equation is certainly a practical option. The applicability should be high under the condition which yields $f = 0$ or when SAR/TDS ratios are near unity in silty clay loam, and less than 1.0 in loam (Fig. 5).

The agreement between the measured and the back-calculated (or fitted) infiltration depth using Eq (5) was good (Fig. 8), except for one or two instances. The deviation experienced in Saneli soil irrigated at SAR of 12 and TDS of 25 mmol_e L⁻¹ is an example. In this case, the water infiltration rate decreased too abruptly upon saturation to use Eq (5). Another case involved poor fit at high SAR (e.g., 50 and 70), where the plots between $\log(D/Kt - f)$ and $\log t$ were not linear. In these cases, the use of Eq (3) or the full-log plots between D and t provided a workable alternative.

In predicting the cumulative water infiltration for water of different salinity and sodicity values, additional errors are introduced in the process of estimating the infiltration parameters, using the empirical equations proposed in Table 4. This problem appeared, for example, in estimating the infiltration depth of Harkey loam when irrigated with the solution with the SAR of 25 and the TDS of 50. In this case, the coefficient p estimated was 11% greater than the observed (Table 5). The error involved in estimating the coefficient p and the sorptivity S has a far greater impact on the infiltration estimate than do f , and K , since the cumulative water infiltration into dry soils is

dominated by the first term as exemplified in Table 5. This fact, however, helped minimize the estimation error for the SAR of 1 series where the proposed equation did not adequately simulate K .

Since the estimate of cumulative depths of infiltration is influenced sensitively by p and S , it is essential to be able to estimate these parameters with a high degree of accuracy. The proposed equation, Eq (9) of Table 1, seems to provide an excellent projection for S , but somewhat less for p . Some of the data for p deviated rather widely from the prevailing pattern (Fig. 4), and were often associated with the difficulties of determining the slope of D/Kt and t plots especially at low TDS under the high to medium range of SAR (Fig. 3). The use of one-term Kostiakov equation helped resolve this difficulty, but not completely.

The prediction of hydraulic conductivity was most difficult with the SAR of 1 series, even though this problem was largely alleviated by the use of the alternative expression for x . There are, however, some questions about the exceptionally high K values obtained through the use of low SAR solution, mainly because the time duration used for evaluating K was much shorter in these cases, as water infiltration proceeded much faster (e.g., Fig. 1). If the infiltration measurements continued for this series for the duration comparable to the prevalent cases, it is entirely possible that the measured K values would have been lower. There were also some difficulties of fitting the conductivity data of high SAR series, especially with Saneli soil (Fig. 7). If the infiltration measurements were taken for a longer duration, these data points would have reached zero. Overall we consider that the proposed equation provides realistic estimates of hydraulic properties of some Entisols and Aridisols, which are usually quite variable in time and space.

It should be kept in mind that all the data used were obtained in soil columns with air-dry soils passed through a 2 mm screen and were irrigated with salt solutions having the SAR values similar to the exchangeable Na percentage (ESP). The experimental condition may or may not represent water infiltration into deep plowed and disked fields under ponded leaching. The effects of initial soil moisture, soil compaction as well as the ESP levels substantially different from the SAR of leaching water on water infiltration processes are yet to be studied.

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Table 1. Various infiltration equations and regression equations tested: D: t: infiltration time,

Philip (1957)		Eq No	
Horizontal	$D = S t^{1/2}$	(1)	D: cumulative depth of water infiltrated
Vertical	$D = S t^{1/2} + Kt$	(2)	t: infiltration time K: Hyd. Conductivity
Ahuja & Romkens (1974) or Kostiaikov (1932)			
Horizontal	$D = St^p$	(3)	p: Empirical Coeff.
Vertical	$D = St^p + Kt$	(4)	
or	$D/Kt = (S/K)t^{p-1} + 1$		
Alternative Empirical Equation			
	$D = St^p + fKt$	(5)	f: Adjustment factor
or	$D/Kt = (S/K)t^{p-1} + f$		
	$D = St^p + K(t) t$	(6)	
Cass and Sumner (1982)	$\frac{1 - R_K}{R_K} = -a TDS^{-b}$	(7)	R_K : Relative hydraulic conductivity a, b: Empirical constants
Jayawardane (1973)	$\frac{SAR_1^n}{TDS_1} = \frac{SAR_2^n}{TDS_2}$	(8)	n: Empirical constant 1, 2: Designate solutions 1 and 2
Proposed	$Y = -aLn (SAR^n/TDS+1) + Y_0$	(9)	Y: Hydraulic parameters of Eq (5) $Y_0=Y$ at $x=0$ n:Equivalent constant

Table 2. Salinity and sodicity of saline solutions^{1]} used for the laboratory infiltration experiment.

SAR	Salinity ----- meq L ⁻¹ -----				
1	10	-	50	-	300
12	10	25	50	-	-
25	10	25	50	100	-
50	10	25	50	100	-
70	-	25	50	100	300

^{1]} Saline solutions containing NaCl, CaCl₂, 2H₂O and MgCl₂•7H₂O with equal molar concentrations of Ca and Mg in chemical equivalent.

Table 3. Infiltration parameters determined for the three soils at different salinity and sodicity.

Soils	Salinity (meq L ⁻¹)	Harkey Loam					Hoban S.C. Loam					Saneli S.C. Loam				
		10	25	50	100	300	10	25	50	100	300	10	25	50	100	300
SAR																
1	S of Eq (1), cm d ^{1/2}	20.80		21.20		22.50	17.00		17.20		17.50	15.20		16.70		17.00
	p of Eq (5)	0.50		0.51		0.54	0.51		0.54		0.58	0.50		0.50		0.53
	f of Eq (5)	0.00		0.10		0.30	-1.00		-0.80		-0.80	-0.70		-0.50		-0.40
	K of Eq (5), cm d ^{1/2}	2.91		3.23		3.75	1.61		1.94		2.00	1.22		1.54		1.55
	S of Eq (5)	20.84		20.47		22.08	17.65		18.11		17.62	15.01		16.89		15.90
12	S of Eq (1), cm d ^{1/2}	17.60	19.10	20.00			10.00	13.30	14.70			6.50	12.00	14.00		
	p of Eq (5)	0.48	0.48	0.48			0.40	0.43	0.49			0.45	0.45	0.48		
	f of Eq (5)	-0.20	0.05	0.10			0.20	-0.20	-0.60			0.20	-0.70	-0.70		
	K of Eq (5), cm d ⁻¹	1.50	1.80	1.90			0.65	0.86	1.08			0.35	0.62	0.93		
	S of Eq (5)	18.37	18.43	18.91			11.83	13.63	14.57			6.66	11.98	14.08		
25	S of Eq (1), cm d ^{1/2}	8.00	15.50	16.50	18.00		8.00	12.00	13.30	14.90		2.20	3.70	8.30	13.00	
	p of Eq (5)	0.35	0.36	0.37	0.45		0.41	0.43	0.51	0.51		0.43	0.49	0.44	0.45	
	f of Eq (5)	0.90	0.40	0.20	-0.10		0.80	0.00	-0.70	-0.70		1.00	0.20	-0.40	-1.00	
	K of Eq (5), cm d ⁻¹	0.55	0.82	1.10	1.50		0.45	0.70	0.86	1.10		0.10	0.20	0.36	0.54	
	S of Eq (5)	7.27	10.83	13.69	17.91		8.00	11.62	12.72	14.50		2.40	4.41	8.30	12.63	
50	S of Eq (1), cm d ^{1/2}	2.50	6.30	7.40	12.80		3.00	4.70	7.00	11.00		1.20	1.60	3.20	6.20	
	p of Eq (5)	(0.506)	0.31	0.31	0.36		(0.66)	(0.66)	0.48	0.53		0.34	0.37	0.44	0.41	
	f of Eq (5)		0.60	0.60	0.25				0.20	-0.40		0.07	-0.40	0.00	-0.20	
	K of Eq (5), cm d ⁻¹		0.40	0.62	0.90				0.70	1.00		0.07	0.11	0.21	0.45	
	S of Eq (5)	(2.29)	5.78	6.52	10.38		(3.802)	(4.365)	8.04	10.96		1.41	1.82	3.15	6.58	
70	S of Eq (1), cm d ^{1/2}		3.50	5.00	12.00	14.00										
	p of Eq (5)		0.29	0.35	0.31	0.38		2.50	4.00	6.00	10.00		1.10	2.00	5.20	12.50
	f of Eq (5)		1.00	0.70	0.25	0.10		(0.736)	(0.546)	0.52	0.53		0.29	0.39	0.43	0.47
	K of Eq (5), cm d ⁻¹		0.20	0.33	0.75	1.30				-0.50	-1.00		0.08	0.00	-0.30	-0.60
	S of Eq (5)		3.75	4.91	8.59	13.40		(3.120)	(6.607)	0.65	1.00		0.08	0.15	0.40	0.95
										10.79	14.45		1.56	2.10	5.25	12.24

1] The numbers in parenthesis were determined by Eq (3).

Table 4. Regression for describing the effects of salinity and sodicity on infiltration parameters of Eq (5) in three soils.

Infiltration Parameters	Equation Parameters		
	Harkey Loam	Hoban SC Loam	Saneli SC Loam
Coefficient P	$p = -0.04 \ln(x+1) + 0.52$	$p = -1.0 \ln(x+1) + 0.55$	$p = -0.04 \ln(x+1) + 0.49$
x	$\text{SAR}^{2.0}/\text{TDS}$	$\text{SAR}^{0.25}/\text{TDS}$	$\text{SAR}^{1.5}/\text{TDS}$
Range	$x < 250$	$x < 0.2$	$x < 38$
r^2	0.87*	0.78*	0.82*
Factor f	$f = 0.20x + 0.02$	$f = 1.09x - 0.75$	$f = 0.94x - 0.74$
x	$\text{SAR}^{1.15}/\text{TDS}$	$\text{SAR}^{0.85}/\text{TDS}$	$\text{SAR}^{0.9}/\text{TDS}$
Range	$0 < x < 5$	$0 < x < 1.6$	$0 < x < 1.8$
r^2	0.90*	0.88*	0.91*
Sorptivity S	$S = -3.54 \ln(x+1) + 22$	$S = -3.64 \ln(x+1) + 17$	$S = -6.4 \ln(x+1) + 15.5$
x	$\text{SAR}^{2.0}/\text{TDS}$	$\text{SAR}^{1.45}/\text{TDS}$	$\text{SAR}^{1.4}/\text{TDS}$
Range	$x < 250$	$x < 11$	$x < 8$
r^2	0.94*	0.93*	0.95*
Conductivity K	$K = -0.36 \ln(x+1) + 2.0$	$K = -0.48 \ln(x+1) + 1.3$	$K = -0.50 \ln(x+1) + 1.0$
x	$\text{SAR}^{1.9}/\text{TDS}$	$\text{SAR}^{1.3}/\text{TDS}$	$\text{SAR}^{1.3}/\text{TDS}$
Range	$x < 175$	$x < 11$	$x < 5$
r^2	0.90*	0.92*	0.71*
Alternatively,			
Conductivity K	$K = -1.07 \ln(x+1) + 2.8$	$K = -0.90 \ln(x+1) + 1.7$	$K = -\ln(x+1) + 1.3$
x	$\text{SAR}/\text{TDS}^{0.55}$	$\text{SAR}/\text{TDS}^{0.75}$	$\text{SAR}/\text{TDS}^{0.80}$
Range	$x < 10$	$x < 4$	$x < 3$
r^2	0.93*	0.83*	0.82*

* Significant at 1% level.

Table 5. Estimating the cumulative infiltration using a modified Kostiakov equation (or Eq. 5).

Soil Types		P		f		S		K		Predicted Inf. Depth			
SAR	TDS	mes	cal	mes	cal	mes	cal	mes	cal	Terms		Terms	
meq L ⁻¹										1 st	2 nd	1 st	2 nd
Harkey loam													
1	50	0.51	0.52	0.10	0.00	20.5	21.1	3.2	2.0	49	0	70.0	0
12	25	0.48	0.47	0.05	0.17	18.4	17.0	1.8	1.4	37	1	49.1	2.5
25	50	0.37	.41	0.20	0.19	13.7	13.9	1.1	1.2	27	1	17.5	5.2
25	10	0.35	.38	0.90	0.87	7.3	7.5	0.55	0.60	13	2	35.5	2.3
50	10	0.30	.30	1.00	1.00	3.2	2.0	0.21	0.14	3	1	4.0	1.4
70	50	0.35	.35	0.70	0.11	4.9	5.7	0.33	0.50	10	1	11.6	2.9
Hoban silty clay loam													
1	50	0.54	0.53	-0.80	-0.74	18.1	17.8	1.9	1.3	60.3	-9.6	87.1	-19.2
12	10	.40	.42	.20	.05	11.8	11.0	.65	.69	29.1	0.4	39.1	0.8
25	10	.41	.40	.80	.93	8.0	8.1	.45	.47	20.3	4.3	26.8	8.6
25	50	0.51	.50	-.70	-.42	12.7	12.5	.86	.84	39.5	-3.5	55.8	-7.0
50	25	(0.66)	0.44	-	0.59	(4.4)	8.0	0.4	0.47	21.8	2.7	29.5	5.5
70	25	(0.74)	0.43	-	1.0	(3.1)	8.0	0.2	0.40	21.3	4.0	28.6	8.0
Saneli silty clay loam													
1	50	0.50	0.49	-0.50	-0.69	16.9	16.0	1.54	1.0	49.4	-6.9	69.4	-13.8
12	25	.45	.46	-.70	-.40	11.9	11.2	.62	.57	32.7	-2.3	45.1	-4.5
25	25	.49	.43	-	-.08	4.4	5.7	.20	.36	15.5	-0.3	20.9	-0.6
25	50	.44	.45	-.40	-.41	8.3	8.9	.36	.51	25.1	-2.1	34.2	-4.2
50	50	.44	.41	.00	-0.12	3.1	3.8	.21	.32	9.9	-0.4	13.2	-0.8
70	50	.39	.39	.00	.11	1.5	1.5	.08	.07	3.7	0.3	4.8	0.5

Figures

- Fig. 1. Cumulative depth of infiltration of selected saline solutions into three soil types.
- Fig. 2. Cumulative depth of infiltration plotted against the square root of time in three soil types.
- Fig. 3A. Infiltration depths of selected saline solutions (D), depths normalized by the product of hydraulic conductivity (K) and infiltration time (t) with or without correction factor (f) as a function of time: Harkey loam.
- Fig. 3B. Infiltration depths of selected saline solutions (D), depths normalized by the product of hydraulic conductivity (K) and infiltration time (t) with or without correction factor (f) as a function of time: Hoban-silty clay loam
- Fig. 3C. Infiltration depths of selected saline solutions (D), depths normalized by the product of hydraulic conductivity (K) and infiltration time (t) with or without correction factor (f) as a function of time: Saneli-silty clay loam
- Fig. 4. The empirical coefficient p plotted against the parameter computed as the n^{th} power of the sodium adsorption ratio (SAR) divided by the total salt concentration (TDS) in $\text{mmol}_e \text{L}^{-1}$.
- Fig. 5. The adjustment factor, f , as related to the n^{th} power of the sodium adsorption ratio (SAR) divided by the total dissolved salt concentration (TDS) in $\text{mmol}_e \text{L}^{-1}$.
- Fig. 6. The sorptivity, S , determined by Eq (5) as related to the n^{th} power of the sodium adsorption ratio (SAR) divided by the total salt concentration (TDS) in $\text{mmol}_e \text{L}^{-1}$.
- Fig. 7. The hydraulic conductivity, K , as related to the n^{th} power of the sodium adsorption ratio (SAR) divided by the total salt concentration (TDS) $\text{mmol}_e \text{L}^{-1}$.
- Fig. 8. The estimated and the measured infiltration depth of selected saline solutions into three soil types.

Fig. 1

Fig. 2

Fig. 3A

Fig. 3B

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

RESEARCH REPORT 7

ESTIMATING CHEMICAL AMENDMENTS REQUIRED FOR LEACHING SODIC SOILS

ABSTRACT

The quantities of chemical amendments required for reclaiming sodic soils are currently estimated based on the idea to reduce the exchangeable Na percentage (ESP) to a prefixed value, irrespective of soil types. Yet, reclamation practices involve leaching of salts and Na, which is highly dependent of soil types, especially permeability. The study reported here was conducted to develop an alternative method of estimating the amendment required by considering water infiltration and percolation characteristics of Na-affected soils. The alternative method utilizes water infiltration and percolation equations which incorporate salinity and sodicity effects. Once the equations are calibrated for given soil, the ESP needed to achieve the necessary depths of water infiltration within a desired time duration is calculated for given salinity of water used for leaching. The quantities of chemical amendments required for the initial leaching are then calculated using the Gapon equation. Laboratory soil column study conducted with two saline sodic soils; Harkey loam (Typic Torrifluvent) and Saneli silty clay loam (Vertic Torrifluvent) indicates that the proposed equation provides a good estimate of water infiltration as affected by salinity and sodicity of leaching water as well as application of chemical amendments. The soil column study also indicates that the quantities of amendment estimated by the proposed method are smaller in sandy soils than the conventional estimates, but not necessarily so in clayey soils which require highly soluble compounds such as $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ for initial leaching. The fastest reclamation is likely to be obtained through soil application of calcium chloride followed by continuous, but not intermittent ponding.

Reclamation of saline sodic soils involves leaching irrigation to reduce soil salinity and sodicity to a level compatible with salt and waterlogging tolerance of target crops. When the soils are affected by elevated levels of exchangeable Na, however, water infiltration, consequently salt and Na leaching are usually curtailed. In order to counter dispersive effects of Na, the use of high salt water comparable to seawater for leaching was suggested (Reeve and Bower, 1960; Reeve and Doering, 1966). The successful use of the method is, however, highly site-dependent. A more common approach is to use chemical amendments and irrigation water with a moderate level of salinity for leaching. However, the use of chemical amendments is considered mostly to reduce soil sodicity, but not necessarily to improve water infiltration during leaching. The quantities of amendments to be added are thus estimated based on the idea to reduce the exchangeable Na percentage of the main root zone to a fixed level, e.g., down to 15%, irrespective of soil types (USSL, 1954). When the soil is severely Na-affected, the quantities estimated often become impractically large, yet several reports indicate successful reclamation in sandy soils at lower rates of chemical applications (e.g., Overstreet et al., 1951). One of the reasons for the apparent success is related to the fact that leaching irrigation with water of low sodicity itself reduces exchangeable Na (e.g., Jury et al., 1979). In addition, dissolution of CaCO_3 with CO_2 released through respiration from plant roots helps lower exchangeable Na (Robbins, 1986). In clayey soils, however, field reports (e.g. Stroehlein et al., 1978) indicate that these benefits are masked by limited permeability, and it is necessary to use chemical amendments, at least, for initial leaching. Therefore, it seems to be appropriate to determine the quantities of amendments required on the basis of maintaining water infiltration and percolation during leaching irrigation, rather than as the quantity needed to replace the exchangeable Na to a certain prefixed value.

If this approach is to be used, it is necessary to develop a practical means of assessing the effects of amendment application and leaching water quality on water infiltration into and drainage from sodic soils. Such an objective can be achieved by making the use of the empirical equations describing salinity and sodicity effects on sorptivity and hydraulic conductivity (Report 6). The sorptivity is a parameter useful for describing water infiltration into unsaturated soils, and the hydraulic conductivity is relevant for assessing drainage. The types of amendments suitable as well

as the appropriate methods of application can be assessed by a mixing cell model, coupled with the equations describing gypsum dissolution and cation exchange reactions (e.g., Miyamoto et al., 1975). This study was conducted mainly to develop an alternative method of estimating the amendment requirements considering water infiltration and percolation characteristics of sodium-affected Entisols.

THEORY

The depth of soils to be reclaimed was assumed to be determined by the prevailing rooting depths of target crops. The depth of leaching water needed can then be estimated by multiplying the water holding capacity and, in salt-affected cases, by the pore volumes (or the displacement volume) needed for the initial leaching (Table 1). The pore volume figures listed in Table 1 are from soil column studies (e.g., Miyamoto and Enriquez, 1990), and were sufficient to remove approximately 90% of the soluble salts initially present. The pore volumes required for salt leaching in field soils with large pore spaces are usually greater, and are close to two-pore volumes (e.g., Hoffman, 1980).

The quantities of water required for removing exchangeable Na are greater than those for leaching soluble salts. Nonetheless, the depth of leaching water required is proposed to be estimated on the basis of leaching soluble salts for several reasons. First, the flow-limiting layer during the initial leaching is usually in the top 15 cm (Miyamoto and Enriquez, 1990) where a greater number of pore volume replacement occurs. Secondly, any deficiencies in leaching water quantity can be supplemented during the cropping phase with a reduced chance of inducing drainage problems associated with insufficient salinity of pore water in subsoil. Cropping is known to increase salinity of drainage water, as discussed in Report 8.

Assessing Water Infiltration and Drainage

The primary feature for assessing reclamation potentials is the rate of water intake into sodic soils. The following two-term equation was used to describe the cumulative depth of water

infiltration, D

$$D = S t^p + fKt \quad (1)$$

where t is the infiltration time, S the sorptivity, K the hydraulic conductivity, and p and f are empirical coefficients. The methods of evaluating these parameters are shown in Report 6.

During the initial phase of water infiltration into dry soils, the depth of water infiltration is largely controlled by the first term of Eq (1). In addition, the previous study (Report 6) indicates that the impacts of salinity and sodicity on infiltration can be expressed as

$$D = S t^p \quad (2)$$

and
$$S = S_0 - a \ln(x + 1) \quad (2a)$$

$$p = p_0 - a \ln(x + 1) \quad (2b)$$

$$x = ESP^n / TDS \quad (2c)$$

where S_0 and p_0 are the sorptivity and the coefficient p at $x = 0$, ESP the exchangeable Na percentage, TDS the total dissolved cation or anion concentrations expressed in $\text{mmol}_e \text{L}^{-1}$, and a and n are empirical coefficients. The actual values of a and n differ, depending on the parameter of concern, either S or p .

The determination of the above infiltration parameters and coefficients can be made through water infiltration measurements made at two different TDS , but with the same ESP (Fig. 1). Rearranging Eq (2a) and substituting Eq (2c), we obtain.

$$\begin{aligned}
a &= (S_1 - S_2)/\ln [(x_1 + 1)/(x_2 + 1)] \\
&= (S_1 - S_2) \ln \left[\left(\frac{TDS_2}{TDS_1} \right) \left(\frac{1 + TDS_1/ESP^n}{1 + TDS_2/ESP^n} \right) \right]
\end{aligned} \tag{3}$$

where S_1 and S_2 are the sorptivity determined at salt levels of TDS_1 and TDS_2 , The unknown constant a can be approximated, first by ignoring TDS/ESP^n , as this term in sodic soil usually small as compared to 1.0.

Once the coefficient a is approximated, the coefficient n of Eq (2c) can be evaluated as

$$n = \ln[TDS \text{ Exp } [(S_o - S)/a]]/\ln ESP \tag{4}$$

The estimated n can then be used to recalculate a by Eq (3), until a satisfactory agreement is achieved. The above procedures can also be used for evaluating salinity effects on p .

Alternatively, leaching can be made under intermittent ponding.

$$D = \sum (D_i - E_i) \tag{5}$$

where D_i and E_i are, respectively, the depth of water intake and of evaporation at the end of the i -th irrigation. The cumulative infiltration depth corrected for evaporation losses can then be fit to Eq (2) by connecting the end point of each infiltration event as illustrated in Fig. 1.

The rate of drainage was considered to be governed by the hydraulic conductivity and the hydraulic gradient.

$$\Delta D/t = K\Delta H/Z \tag{6}$$

$$K = K_o - a \ln (x + 1) \tag{6a}$$

$$x = \text{ESP}^m / \text{TDS} \quad (6b)$$

where ΔD is the depth of water drained in a time period of t , ΔH the hydraulic gradient difference over the distance of Z , and m an empirical coefficient. The procedures described for determining n of Eq (2c) can be used to evaluate m .

The assessment of drainage rate requires the prediction of subsoil **ESP** and **TDS** (used in Eq. 6b). During the initial leaching of soluble salts from dry soils, **TDS** may be high enough to offset adverse effects of **ESP**. Once the soluble salts are leached, however, subsoil permeability can become flow limiting, especially when subsoil **ESP** is increased due to the transport of **Na** from the surface layer, or when subsoil consists of fine-textured soils. A procedure to estimate subsoil **ESP** is discussed elsewhere (Miyamoto et al., 1975).

Estimating Amendment Requirements

Once the infiltration parameters and coefficients are determined for given soil, leachability can be assessed for the depth of leaching water desired (e.g., Table 1). The leaching time required t_L can be determined as an intercept to the desired depth of leaching water application, D_L (Fig. 1). If the estimated t_L is greater than an acceptable time limit, or the rate of water infiltration is low relative to evaporation rates, chemical amendments may have to be considered.

The conventional method of estimating the chemical amendment required (**AR**) is based on the following formula (e.g., Keren and Miyamoto, 1990).

$$\text{AR} = \alpha \rho D_s (\text{CEC}) (\text{ESP} - \text{ESP}_d) \quad (7)$$

where **CEC** is the cation exchange capacity, **ESP** the exchangeable **Na** percentage, ESP_d the desired **ESP**, ρ the bulk density of the soils, D_s the depth of soils to be treated, and α a conversion factor,

and is 100 when **AR**, **ESP**, **CEC**, ρ and D_s are expressed in $\text{mol}_c \text{ ha}^{-1}$, %, $\text{mol}_c \text{ kg}^{-1}$, kg m^{-3} and m, respectively. The amendment required is usually estimated for the D_s of 0.3 m at an ESP_c of 15% (Keren and Miyamoto, 1990).

The target **ESP** of Eq (7) may be modified by considering the infiltration and drainage characteristics discussed earlier. A desired infiltration pattern can be selected from the plots such as shown in Fig. 1, by considering the leaching duration. Once the value for x is evaluated, the **ESP** necessary to achieve the infiltration characteristics can be estimated by Eq (2c). The **ESP** necessary to maintain subsurface drainage at a desired level can be estimated by Eq (6), assuming the unit hydraulic gradient. The target **ESP** estimated above is usually higher in sandy soils than in clayey soils.

The second factor which affects the estimate of **AR** is the depth of soils to be treated. As indicated earlier, the primary resistance to the flow usually develops in the top 15 cm of packed soils. In addition, applications of chemical amendments cause a reduction in **ESP** to a depth usually less than 30 cm (Robbins, 1986; Miyamoto, 1998). Under such circumstances, the target treatment depth can be reduced from the traditional depth of 0.30 m to a lesser depth.

The third factor which affects the estimate of **AR** is subsoil permeability when salinity of drainage water approaches salinity of the leaching water toward the end of the initial leaching process. At the point, the **ESP** of the subsoil is likely to be higher than the original value due to downward movement of Na replaced from the exchange site. Calcium compounds can be added to water to elevate salinity, and to reduce sodicity. The quantities of Ca required to elevate salinity through water-run application to a level necessary to maintain **K** can be estimated by Eq (6b). Alternatively, it can be estimated by the following equation where **ESP** is assumed to remain constant.

$$\text{AR} = \alpha D(\text{TDS} - \text{TDS}_0) \quad (8)$$

where **D** is the depth of irrigation, **TDS** the dissolved salts required to maintain **K**, **TDS₀** is the TDS of leaching water prior to amendment application, and α a unit conversion factor, and is 0.01 when **AR**, **D**, and **TDS** are expressed in Mg ha⁻¹, m and g m⁻³ (or mg L⁻¹).

Exchangeable Na upon an application of amendment is assumed to be estimated by the Gapon equation (1984).

$$\frac{100(\text{NaX} - Q)}{\text{CEC}} = \frac{\text{Na} + \beta Q}{(\text{Ca} - \beta Q + \text{Mg})^{1/2}} \quad (9)$$

where **Q** is the quantities of exchangeable Na removed, **NaX** the initial exchangeable Na in mmol_c kg⁻¹, and dissolved cation concentrations are in mmol_c L⁻¹. The initial concentration of **Ca** includes those which are added to meet **AR**, and β is a conversion factor from soil to a solution phase. Eq (9) can be used in sequence to account for the number of pore volume displacement involved. Additional details are described in Miyamoto et al.(1975).

The following experiment was conducted to evaluate the reliability of estimating the depth of water infiltration, and the soundness of several assumptions made in determining the quantities of amendment required on the basis of water infiltration and percolation characteristics.

MATERIALS AND METHODS

Two alluvial soils collected from the Rio Grande project area were used for this study: Harkey loam (calcareous, Typic Torrifluvent), and Saneli silty clay loam (calcareous, Vertic Torrifluvent). Samples were collected from the A-horizon of salted ground used for bermudagrass pasture. The silty clay layer of Saneli soil series usually extends 90 to 100 cm in depth over subsoil which consists of medium to fine sand. Soil clods obtained were crushed manually, air-dried, and passed through a 2 mm screen. Some of their properties are shown in Table 2.

Six different saline solutions were prepared by adding salts to distilled water (Table 3). The first four solution (1a and 1b for Harkey, and 2a and 2b for Saneli loam) were to determine the extent of infiltration reduction, while sodicity of leaching water was equal to soil sodicity. Solutions 3, 4, and 5 represent salinity and sodicity of some irrigation and drainage water used in our areas. Solution 6, having a CaCl_2 concentration of $300 \text{ mmol}_e \text{ L}^{-1}$, was used to determine the potentially maximum water infiltration rate.

Soil samples were packed into PVC pipes (7.02 cm^2 , 112 cm long) with a soil packing vibrator to a length of 95 cm at a bulk density of 1.39 kg L^{-1} for Harkey, and 1.42 kg L^{-1} for Saneli soil. The soil columns had a 2 cm layer of medium sand at the bottom for free drainage, and two sheets of fiberglass screens at the top to reduce soil surface disturbance during water application. Piezometers were inserted at 5, 10, 20, 40, 60, and 80 cm in selected columns. All soil columns were preirrigated with 10 cm of solution 1a or 2a, which has the same salinity and sodicity as those of the saturation extract. Based on the infiltration rate determined during the pre-irrigation, soil columns were rearranged to form a block design.

Water infiltration experiments were performed with the treatments outlined in Table 4. The first set was conducted under both continuous and intermittent ponding. The specified solutions were ponded at a water depth of 5 cm. For the intermittent ponding, the specified solutions were applied to a depth of 10 cm initially, and the intake was monitored periodically until the 10 cm of the solutions infiltrated. The soil columns were then allowed to dry until the evaporation reached 3 to 4 cm. The process was repeated four irrigation events. When applicable, gypsum (technical grade powder) was incorporated into the top 0.5 cm of the soils at a rate of 5.2 Mg ha^{-1} for Harkey loam, 7.5 Mg ha^{-1} for Saneli silty clay loam prior to the first irrigation. These rates are equal to the quantities which can be dissolved into 20 and 30 cm of water, respectively, and can be compared with the gypsum requirements estimated by the conventional method for the top 30 cm of the soil; 12.0 and 7.6 Mg ha^{-1} for Harkey and Saneli soils, respectively, at an assumed bulk density of 1.30 kg L^{-1} . In addition, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was applied as a solution of $300 \text{ mmol}_e \text{ L}^{-1}$.

The second set of the experiment utilized four saline solutions for leaching, and the third set involved soil application of chemical amendments. In treatment 7, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was applied to solution 5 at $10 \text{ mmol}_e \text{ L}^{-1}$ when the leaching water depth reaches 30 cm. The quantity applied reached $2.2 \text{ Mg CaCl}_2 \cdot 2\text{H}_2\text{O ha}^{-1}$ (or 2.9 Mg ha^{-1} for a water depth of 40 cm). In treatments 8 through 11, gypsum and/or calcium chloride were applied to soils at the rates shown in Table 4.

Soil columns were covered with a sheet of parafilm with pin holes during ponding to eliminate water evaporation. Upon the completion of irrigation needed to wet the entire length of soil columns, two of the four soil columns were sectioned every 10 cm, and analyzed for salinity and sodicity of the saturation extract. The remaining columns were monitored for percolation rates.

All the experiments mentioned above were conducted in four replicates at 23C. The analysis of variance was performed with a block design.

DATA ANALYSES

Water infiltration data obtained from continuous ponding of Set 1 solutions (shown in Table 4) were plotted on a full-log scale to evaluate p from the slope, and S at $t = 1$ day. Once S and p were determined, the data were used to evaluate the coefficients a and n , using Eq (3) and Eq (4). The S and p determined for the $300 \text{ mmol}_e \text{ L}^{-1} \text{ CaCl}_2$ solution were used as S_0 and p_0 .

Water infiltration data from intermittent ponding of Set 1 solutions were first used to determine the time duration needed for the 10 cm of water to infiltrate at each irrigation event. The cumulative infiltration depth was then adjusted to evaporative losses between irrigation events by Eq (5), and the adjusted depth was used for evaluating the empirical coefficients of Eq (2) as shown earlier in Fig. 1.

Once the infiltration parameters and coefficients are evaluated, they were used to estimate infiltration depths for the cases involving Set 2 and Set 3 of Table 4. In these cases, the SAR of

leaching water was significantly lower than the **ESP** of the soils. In the case of Set 2, the initial **ESP** of the soils was assumed to remain, whereas in Set 3, the **ESP** was assumed to decrease with the amendment application following Eq (9), up to 4 displacement volumes for the top 30 cm, and 8 for the top 15 cm. In the case of gypsum, a fixed solubility value of $28 \text{ mmol}_e \text{ L}^{-1}$ was used for simplicity.

The hydraulic conductivity toward the end of the leaching process was determined from the slope of the infiltration curves such as shown in Figs. 4 and 5. The hydraulic conductivity observed with the CaCl_2 solution was then used as K_0 of Eq (6a), and the coefficients **a** and **m** were estimated in a manner used for Eqs (2b) and (2c).

The hydraulic gradients for the earlier stage of water infiltration was computed as

$$G = (H_1 - H_2)/L \quad (10)$$

where **G** is the hydraulic gradient, H_1 and H_2 are hydraulic heads at positions 1 and 2, and **L** the length between the positions 1 and 2.

RESULTS

Water Infiltration

The cumulative depth of infiltration obtained under continuous ponding is shown on a log scale in Fig. 2 along the lines fitted to Eq (2). The sorptivity (**S**), and the coefficient **p** obtained for these cases are given in Fig. 2, when **D** and **t** are expressed in cm and day, respectively. Eq (2) provided a good approximation of infiltration process in Saneli soil. In Harkey soil, the first set of infiltration depth measurements taken less than a day did not follow the linear relationship. The best fit lines were drawn by ignoring these data points (obtained less than 1 day). The empirical constants **a** and **n** (which describe the impact of water quality) determined from these data sets are listed in

Table 5.

Water infiltration data obtained from intermittent ponding of Set 1 solutions are shown in Fig. 3 along with the curves fitted with Eq (2). Included in the figure are the fitted lines for the continuous ponding from Fig. 2 for comparison. Note that the actual quantities of water infiltrated (or the infiltration depth adjusted to evaporative losses) under intermittent ponding have actually lagged behind those under continuous ponding, especially when water of ordinary salt levels was used, presumably due to a greater degree of soil structural degradation caused by a prolonged period of wet and dry cycles. No further analysis was thus made with the data from intermittent ponding.

Water infiltration data obtained from continuous ponding of Set 2 solutions (Table 4) are shown in Fig. 4, along with the curves (dotted lines) predicted by Eq (2). The parameters S and p of Eq (2) were calculated using Eqs (2a) through (2c) and empirical constants a and n as determined from Set 1 solutions earlier. Since salinity of leaching water were significantly lower in all cases than salinity of the extract, the initial **ESP** were used in Eq (2c); 36 and 25 for Harkey and Saneli soils, respectively. The predicted infiltration curves shown by dotted lines and the measured infiltration data agreed within a range of experimental errors designated by the vertical bars. The bars indicate the mean standard deviation towards the end of the experiment.

Set 3 consisted of two (8 and 11) treatments for Harkey and four treatments (8 through 11) for Saneli soil (Table 4). The observed infiltration data for Set 3 along with the predicted are shown in Fig. 5. In estimating the infiltration depth for treatment 8, we first assumed that the gypsum applied had no effect on ESP but increased salinity by $28 \text{ mmol}_e \text{ L}^{-1}$ (solubility of gypsum). Then, upon dissolution of gypsum, ESP was assumed to decrease to 18 for Harkey and to 15 for Saneli soil. The measured data for treatment 8 was close to those of treatment 6 indicating that gypsum application had insignificant effects. The predicted infiltration depth was greater than the measured, but not significantly due to the large variability among the replicated measurements. In the second case, we assumed that the exchangeable Na was replaced by the gypsum applied in a fashion described by the Gapon equation (Miyamoto et al., 1975). In Harkey, the estimated ESP of the top

15 cm soil decreased to 22 and 16 when 20 and 34 cm of the leaching water was assumed to have infiltrated. In Saneli, the estimated ESP of the top 15 cm soil decreased to 16 and 13 when 21 and 35 cm of the leaching water was assumed to have infiltrated. The use of these lower ESP values did not improve the agreement with the measured.

In estimating the infiltration depth for treatment 11, we used the Gapon equation to calculate the amount of exchangeable Na replaced by the CaCl_2 and gypsum. In Harkey, the estimated ESP of the top 15 cm soil decreased from 36 to 10 when 10 cm of the leaching water was assumed to have infiltrated. In Saneli, the corresponding estimated ESP of the top 15 cm soil decreased to 8. The predicated infiltration curves using these ESP values are indicated by the solid lines in Fig. 5. Salinity of the infiltrating water was taken as $300 \text{ mmol}_c \text{ L}^{-1}$ for the first 10 cm, then $78 \text{ mmol}_c \text{ L}^{-1}$ for the next 20 and 30 cm for Harkey and Saneli soils, respectively. For the remaining infiltration process, salinity was taken as $50 \text{ mmol}_c \text{ L}^{-1}$. The agreement between the observed data from treatment 11 and the predicted infiltration curves with the computed ESP was found to be within the standard deviation.

The hydraulic gradients measured along the depth of columns when water infiltration reached 15 and 35 cm are shown for treatments 1, 5 and 8 in Fig. 6. When water infiltration was less than 10 cm, most piezometers placed below 10 cm did not register positive head readings, indicating that the resistance to flow was confined at the top 10 cm. The gradient distribution at water infiltration of 15 cm indicates that the resistance to flow has occurred mostly in the top 20 cm. At a later state, the gradient in the top 20 cm of Harkey soil has declined and the peak gradient appeared as deep as 30 cm, whereas in Saneli soil, the gradient distribution remained at a depth less than 30 cm.

The hydraulic conductivity determined from the infiltration curves of set 1 solutions toward the end of leaching process was used to estimate **a** and **m** (Table 5). These coefficients were then used to estimate **K** of different solutions (Table 5). The results show low **K** values, especially in Saneli.

Soil salinity measured at different depths upon the infiltration of 35 cm of designated solutions are shown in Fig. 7. Salt leaching pattern was found to be independent of the treatments used in Harkey. In Saneli soil, salt leaching from the depth increment of 60 to 70 cm was greater in Treatment 11 than Treatments 6 or 8, presumably due to greater water penetration. Salinity in the top 60 cm of the soil profile are reduced by 60% and 50% in Harkey and Saneli soils, respectively. Note that the solution infiltrated was equal to 1.3 pore volumes. When salinity of the water used for leaching (4.7 dS m^{-1}) was subtracted from the measured soil salinity readings, the reduction in soil salinity amounted to 85 and 80% of the initial salinity in Harkey and Saneli soils, respectively.

The vertical distribution of ESP is shown for three different treatments in Fig. 8. Application of gypsum (Treatment 8) provided lower ESP at soil depths less than 50 cm in Harkey soil, but no significant effect on ESP in Saneli soil. Application of both gypsum and CaCl_2 provided a significantly lower ESP in both soils. The ESP of the top 30 cm of Harkey soil was reduced to 12% in Treatments 6 and 8, and to 7% in Treatment 11. The corresponding ESP values in Saneli soil were 20 and 12% respectively.

The ESP estimated with the assumption that Ca added to the soils removes exchangeable Na in a quantitative manner did not agree with the observed (Table 6). The observed ESP was generally greater than the estimated ESP, except when no gypsum was added or when a comparatively small quantity of gypsum was applied to Harkey soil. When Ca present in the leaching water was included in the amount added, it did not improve the agreement except for treatment 6. The use of Gapon equation improved the estimate of ESP.

DISCUSSION

According to the conventional formula, Eq (7), the quantities of Ca required to lower the exchangeable Na percentage (ESP) to 15% in the top 30 cm depth of Harkey loam and Saneli silty clay loam are 150 and $97 \times 10^3 \text{ mol}_e \text{ ha}^{-1}$, respectively. These requirements correspond to the bulk densities of packed soils which were somewhat greater than the bulk density of 1.30 kg L^{-1} as initially assumed. If gypsum is to be used, these requirements equal 13 and 8.3 Mg ha^{-1} . According

to Eq (7), Harkey loam requires a greater quantity, mainly because the quantity of exchangeable Na present is greater.

At the onset, we proposed to incorporate water infiltration characteristics into the estimate of amendment requirements as the rate of water infiltration controls the rate and feasibility of salt and Na leaching from sodic soils. The depth of water required for leaching was assumed to be somewhat greater than the displacement volume of the projected main root zone (Table 1). Salinity distribution data shown in Fig. 7 indeed indicate that application of leaching water at 35 cm has leached 80 to 85 % of the soluble salts initially present. The water infiltration data shown in Fig. 2 indicate that the depth of water needed for initial leaching can infiltrate into Harkey soil in a matter of a week or 10 days, as long as salinity of leaching water is kept above 25 mmol_c L⁻¹ with or without chemical amendments. In the case of Saneli soil, however, the rate of water infiltration is so slow that leaching can not be achieved without the use of chemical amendments. Note that the water intake rate of this soil after the initial flow week is lower than the prevailing water evaporation rates in arid regions.

We applied gypsum to Harkey soil at a rate of 5.2 Mg ha⁻¹, instead of 12 to 13 Mg ha⁻¹, the requirement estimated by Eq (7), with an idea to provide elevated salinity during leaching and to reduce the ESP of the top 15 cm below 15% upon the completion of initial leaching. Note that this quantity of gypsum can dissolve into 20 to 30 cm-ha of water. This treatment resulted in a limited or insignificant improvement in water infiltration (Fig. 5). The limited impact of gypsum application on water infiltration can be expected from the infiltration data shown in Fig. 4, although the results could have been different if water of low salinity such as used in treatment 4 were used for leaching. Results of an outdoor lysimeter experiment (Report 8) indicate that this type of permeable soils can be reclaimed with the use of moderately saline water for leaching without amendment application.

In the case of Saneli soil with low water intake, we applied 7.5 Mg ha⁻¹, a rate comparable to the requirement estimated by Eq (7). This quantity of gypsum can be dissolved into 30 to 40 cm of water, and application at a higher rate would not likely to provide higher Ca concentrations into

leaching water during initial leaching. This treatment also provided only a slight increase in water infiltration (Fig. 5) as can be expected from the infiltration data shown in Fig. 4, although gypsum application is likely to cause a significant response if water used for leaching is low in salinity. The most significant improvement in infiltration requires application of highly soluble amendment such as $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Fig. 5), but at the rates much greater than the quantities estimated by Eq (7). Since the Gapon equation provided a reasonable estimate of ESP (Table 6), it would be possible to determine the quantity needed to achieve a desired or required rate of water infiltration using Eq (2), provided that infiltration parameters ('a' and 'n') had been predetermined.

The experimental data obtained here were short of addressing drainage rates. However, the hydraulic conductivity determined toward the end of the leaching process indicates that drainage rates became too slow to continue ponded leaching especially in Saneli soil (Table 5, Figs. 3, 4, and 5). In other words, evaporation from ponded water is likely to exceed the rate of drainage. At that stage, the resistance to flow has shifted down to a depth of about 30 cm in Harkey loam, and there was an indication of developing the resistance to flow at a deeper depth where salinity of soil solutions is being lowered more so than soil sodicity (Figs. 2 and 8). If ponded leaching were to be continued in this type of soils, lowering of soil solution salinity can induce subsoil drainage problems. Application of highly soluble compounds into leaching water did improve water percolation (Fig. 4), thus offering an option. Cropping of sodic soils after the initial leaching may prove to be another option in maintaining subsoil drainage through increasing salinity of drainage water and increasing CaCO_3 dissolution.

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Table 1. The depth of water required for initial leaching and the estimated pore volume passage through the top 15 cm of typical silt loam, clay loam and silty clay loam.

	Silt Loam		Clay Loam		Silty Clay	
	Nonsaline	Saline	Nonsaline	Saline	Nonsaline	Saline
Target soil depth (m)	0.60	0.60	0.50	0.50	0.45	0.45
Water holding ($\text{m}^3 \text{ m}^{-3}$)	0.40	0.40	0.45	0.45	0.50	0.50
Leaching pore volume ^{1]}	1.0	1.8	1.0	1.3	1.0	1.3
Salt Leaching Water (m)	-	0.36	-	0.30	-	0.30
Water Storage in 15 cm (m)	0.06	0.06	0.05	0.05	0.05	0.05
Leaching pore volume ^{2]}	4.0	6.0	3.0 ~ 4.6	3.9 ~ 6.0	3.0 ~ 4.6	3.9 ~ 6.0

^{1]}The ratio of the volume of water to the volume of soil pores present in the soil depths specified in the first row.

^{2]}The leaching water to the soil pore volume ratio for the top 15 cm of the soils.

Table 2. Some properties of the soil samples used for the infiltration experiment.

	Saturation water	Saturation Extract			CEC	Gypsum content
		EC	SAR	pH		
	g kg ⁻¹	dS m ⁻¹			mmol _c kg ⁻¹	
Harkey loam	455	19.6	36.2	8.2	171	0.00
Saneli silty clay loam	560	15.1	24.6	7.9	237	0.01

Table 3. Composition of water used for the experiment.

	EC	TDS	SAR	Na	Ca	Mg	HCO ₃	Cl	SO ₄
	dS m ⁻¹	mmol _c L ⁻¹		-----mmol(±) L ⁻¹ -----					
1a	24.6	280	36	211.00	39.50	28.90	2.4	184.7	92.3
1b	2.4	25	36	24.10	0.44	0.44	2.4	15.1	7.50
2a	18.3	206	25	141.00	49.90	15.90	2.4	136.3	68.10
2B	2.4	25	25	23.22	0.89	0.89	2.4	15.1	7.50
3	1.0	10	10	8.54	1.06	0.40	2.4	4.2	3.40
4	2.5	25	10	18.30	4.46	2.24	2.4	14.2	8.40
5	4.7	50	10	31.00	12.60	6.40	2.4	31.0	16.60
6	27.0	300	0	0.00	300.00	0.00	0.0	300.00	0.00

Table 4. The outline of the treatments used for the soil column experiment.

Amendment		Harkey				Saneli			
Applied		Rate	Soln	TDS	SAR	Rate	Soln	TDS	SAR
		Mg ha ⁻¹	#	mmol _c L ⁻¹		Mg ha ⁻¹	#	mmol _c L ⁻¹	
Set 1									
1	CaCl ₂ .2H ₂ O	0	6	300	0	0	6	300	0
2	none	0	1a	280	36	0	2a	206	25
3	none	0	1b	25	36	0	2b	25	25
Set 2									
4	none	0	3	10	10	0	3	10	10
5	none	0	4	25	10	0	4	25	10
6	none	0	5	50	10	0	5	50	10
7	CaCl ₂ .2H ₂ O	3.0	5	60	8.1	3.0	5	60	8.1
Set 3									
8	gypsum	5.2	5	50	10	7.5	5	50	10
9	CaCl ₂ .2H ₂ O	-	-	-	-	11.0	(6)5	300	0
10	CaCl ₂ .2H ₂ O	-	-	-	-	11.0	(6)	300	0
	+gypsum	-	-	-	-	7.5	5	50	10
11	CaCl ₂ .2H ₂ O	22.0	(6)	300	0	22.0	(6)	300	0
	+gypsum	5.2	5	50	10	7.5	5	50	10

Table 5 Infiltration and percolation parameters and coefficients determined for two salt and sodium affected soils.

Soil	Harkey Loam			Saneli SC Loam		
Empirical parameters ‘a’ and ‘n’ for sorptivity S (cm day ^p)						
Continuous	S ₀ =12.5	a=0.479	n=2.12	S ₀ =5.5	a=0.166	n=1.93
Intermittent	S ₀ =10.1	a=0.897	n=1.18	S ₀ =7.0	a=0.242	n=2.55
Empirical parameters ‘a’ and ‘n’ for coefficient p						
Continuous	p ₀ =0.54	a=0.008	n=2.55	p ₀ =0.56	a=0.031	n=1.82
Intermittent	p ₀ =0.47	a=0.360	n=0.57	p ₀ =0.38	a=0.028	n=1.92
Empirical parameters ‘a’ and ‘m’ for conductivity K (cm day ⁻¹)						
Continuous	K ₀ =2.69	a=0.99	m=1.11	K ₀ =1.20	a=0.214	m=2.11
Infiltration Parameters ^{1]}	S	p	K	S	p	K
	cm day ^{-p}		cm day ⁻¹	cm day ^{-p}		cm day ⁻¹
Treatment 1	12.5	0.54	2.69	5.5	0.56	1.20
Treatment 2	11.5	0.52	2.51	5.3	0.53	0.85
Treatment 3	10.4	0.50	1.55	5.0	0.48	0.43
Treatment 4	10.0	0.49	0.86	4.9	0.45	0.07
Treatment 5	10.4	0.50	1.56	5.0	0.48	0.27
Treatment 6	10.7	0.50	1.97	5.1	0.50	0.41
Treatment 7	10.8	0.50	2.06	5.1	0.51	0.45
Treatment 8 (<20 or 30 cm) ^{2]}	10.9	0.51	2.17	5.2	0.51	0.67
Treatment 8 (> 20 or 30 cm)	11.4	0.52	2.29	5.2	0.52	0.78
Treatment 11 (<10cm)	12.3	0.54	2.65	5.5	0.56	1.15
Treatment 11 (>10 and < 30 or 40 cm)	12.0	0.53	2.54	5.4	0.55	1.05
Treatment 11 (>30 or 40 cm)	11.9	0.53	2.46	5.4	0.55	1.00

^{1]} Infiltration parameters for Treatments 1 through 3 are determined based on the experimental data while infiltration parameters for remaining treatments are estimated using Eqs (2a) through (2c)

^{2]} Infiltration Depth

Table 6 Observed and estimated exchangeable Na percentage (ESP) of Harkey and Saneli soils after gypsum application and gypsum plus calcium chloride application then leached at 35 cm of water.

Soil	Harkey loam			Saneli SC loam		
	6	8	11	6	8	11
Treatments						
Gypsum (Mg ha^{-1})	0	5.2	5.2	0	7.5	7.5
Calcium Chloride (Mg ha^{-1})	0	0	22	0	0	22
Observed ESP ^{1]}						
0- 15 cm	>10	>10	>6	>11	>11	>6
0 - 30 cm	12	12	7	20	19	12
Estimated by the quantitative replacement						
0 - 15 cm	36	19	0	25	7	0
0 - 30 cm	36	28	0	25	16	0
Estimated as above but including Ca in water						
0 - 15 cm	24	7	0	16	0	0
0 - 30 cm	30	22	0	20	12	0
Estimated by the Gapon Equation						
0 - 15 cm	14	10	6	13	9	6
0 - 30 cm	22	18	9	17	15	9

^{1]} The actual ESP at 0 - 15 cm can be higher than the listed values which were obtained from a depth of 0 to 10 cm

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

RESEARCH REPORT 8

RECLAMATION OF SALINE-SODIC SOILS INVOLVING SALT-TOLERANT GRASS AND CHEMICAL AMENDMENTS

ABSTRACT

Cultivation of salt tolerant plants with water of elevated salinity may help promote reclamation of sodic soils, as high salinity can help maintain soil permeability, and respiration from live roots is known to increase dissolution of CaCO_3 , thus the removal of exchangeable Na. This lysimeter study was conducted to test the above hypothesis, using two calcareous saline-sodic Entisols, Harkey silt loam ($\text{EC}_e = 19 \text{ dS m}^{-1}$ with ESP of 36%, Typic Torrifluvent) and Saneli silty clay loam ($\text{EC}_e = 15 \text{ dS m}^{-1}$ with ESP of 36%, Vertic Torrifluvent). Half of the lysimeters was sodded with saltgrass (*Dischilis spicata*), and received broadcast applications of gypsum, mulching and/or water-application of calcium chloride. They were irrigated at three levels of salinity; 10, 25 and $50 \text{ mmol}_e \text{ L}^{-1}$ in irrigation water for two growing seasons. Transplanted saltgrass seedlings grew rapidly and established solid stands during the first season. Yet, it had only a limited impact on water infiltration and removal of exchangeable Na, especially in Saneli silty clay loam with low permeability. The dissolution of CaCO_3 enhanced by respiration seems to have been offset by the increase in sodicity associated with transpirational losses of soil water. This led to the situation where sodicity of the soils measured at termination was actually greater in sodded cases. This problem is pronounced when saline water is used for irrigation, and the use of gypsum or water-application of CaCl_2 at low concentrations could not alleviate the increase in sodicity caused by water-uptake. In order to enhance Na removal through irrigated cultivation of reclamation crops, irrigation may have to be performed to assure leaching fractions no less than those attained without live plants. Although vegetative means of reclaiming sodic soils are likely to be effective in coarse-textured soils with low salinity, additional quantitative studies are needed for assessing its application in saline sodic soils.

The idea to utilize salt and/or waterlogging tolerant plants for reclamation of salt and Na affected soils is not new. The plant species which had been tried range from rice, forage grasses to salt tolerant trees (e.g., Gupta and Abrol, 1990). It is, however, rather recent that applicable processes became a subject of research. Robbins (1986), for example, demonstrated through a greenhouse lysimeter experiment that reclamation of Freedom silt loam with an exchangeable Na percentage as high as 68% was greatly enhanced by planting sorghum (*Sorghum bicolor*) and several other crops, because of enhanced dissolution of soil CaCO_3 by CO_2 generated from live roots. A recent field plot study conducted by Qadir et al. (1996) has also shown that cropping sandy clay loam having an exchangeable Na percentage (ESP) of 52 to 72% with salt tolerant grass species helped reduced ESP, presumably for the same reason. The extent of the ESP reduction observed was comparable to or greater than those resulting from gypsum applications. These findings led the authors to conclude that cropping itself is an effective option for reclaiming Na-affected calcareous soils. However, these findings are in apparent contradiction with several other field reports. Overstreet et al. (1951), for example, have shown that forage species planted on sodium-saturated Fresno silt loam with soil salinity of 7 to 23 dS m^{-1} produced dismal results, both in biomass production and reducing ESP, unless gypsum or sulfuric acid was applied. Likewise, a field report by Stroehlein et al (1978) indicates that sorghum planted in Gothard clay loam with an ESP as low as 17% resulted in dismal growth, unless gypsum or sulfuric acid was applied. These apparent contradictions must be resolved before vegetative means of reclaiming Na-affected calcareous soils can be recommended with a greater degree of certainty.

One important factor which affects reclamation is soil permeability. Poor water infiltration and drainage not only affect soil water supply to crops, but also limit salt and Na leaching and, at times, can lead to waterlogging and crop failure. This problem is usually pronounced in soils with high clay contents and/or with high ESP. The application of soil amendments is a common method to improve water infiltration and salt leaching, but the quantities of chemical amendments required (as estimated by the conventional method) usually become impractically large in soils with large quantities of exchangeable Na (e.g., Keren and Miyamoto, 1990). An alternative is to use water of elevated salinity during the initial leaching so as to counter against dispersive effects of exchangeable

Na. In fact, the use of highly saline water with salinity comparable to that of sea water has been suggested for initial leaching (e.g., Reeve and Bower, 1960). However, high salt dilution methods require site conditions suitable for disposing of large quantities of saline drainage water, as compared to the use of chemical amendments. As reported earlier (Report 4), the use of water with elevated salinity such as agricultural drainage water or saline ground water helps minimize breakdown of soil aggregates and a reduction in infiltration rates during leaching. The presence of live plants, as noted earlier, is known to help maintain water infiltration (Gupta and Abrah, 1990; Ali and Swartzendruber, 1994) and reduces the exchangeable Na by increasing Ca dissolution (e.g., Robbins, 1986). It was thus hypothesized that cultivation of salt tolerant plants with water of elevated salinity can lead to faster rates of reclamation, and can reduce quantities of chemical amendments and leaching water required for reclamation. The study reported here was conducted to evaluate these possibilities using two calcareous saline sodic Entisols differing in soil texture.

MATERIALS AND METHODS

Two calcareous saline sodic soils; Harkey silt loam (coarse loamy, Typic Torrifluent, Entisol), and Saneli silty clay loam (montmorillonetic, Vertic Torrifluent, Entisol) were collected from the A-horizon of salted fields used for common bermudagrass pasture. The soil samples were air-dried, crushed, and passed through a 4 mm screen. Subsamples were analyzed for selected properties (Table 1).

Saline solutions simulating a broad range of irrigation and drainage water quality were prepared by adding technical grade salts to deionized water (Table 2). In addition, calcium chloride was applied to solution 2 at a rate of $5 \text{ mmol}_e \text{ L}^{-1}$ and to solution 3 at $10 \text{ mmol}_e \text{ L}^{-1}$. These solutions are designated as 2Ca and 3Ca, respectively. In addition, ammonium nitrate was added to these water sources at a rate of 30 mg N L^{-1} .

The soil samples were packed into large PVC pipes (500 cm^2 in cross-section) to a depth of 100 cm at a bulk density of 1.36 kg L^{-1} in Harkey, 1.43 kg L^{-1} in Saneli soil. The low-end of the PVC

pipe was plated with a fiberglass disk, and contained a 2.5 cm layer of medium sand, and another 5 cm layer of crushed gravel in which a drain tube was inserted for free drainage. The inner wall of the PVC pipes, hereafter referred to as lysimeter columns, contained a strip of flexible weathering tape (1.25 cm thick and 1.25 cm wide) at a depth of 5 cm from the soil surface, and was coated by amber wax to reduce the boundary flow. The PVC pipes, packed tight along the pipe wall with the soils, were placed on individual platforms for weighing with a strain gauge (accuracy of 10 grams or 0.2 mm in water depth). Some of the columns have received a broadcast application of gypsum (technical grade powder) at a rate of 5.2 Mg ha⁻¹ in Harkey, and 7.5 Mg ha⁻¹ in Saneli soil (Table 3). These rates correspond to the quantities of gypsum which can be dissolved in a water depth of 20 and 30 cm, respectively.

Preplanting irrigation of the lysimeter columns began on June 10, 1998, using 7.5 cm of solutions 3 and 3Ca shown in Table 2. The time required for the 7.5 cm of the solutions to infiltrate was measured. As soon as the 7.5 cm of the solutions was infiltrated, an additional 7.5 cm of the same solutions was applied, and the infiltration time measured. The lysimeter columns were numbered to form a block design based on the infiltration time determined during the preplanting irrigation.

Saltgrass (*Dischalis spicata*) seedlings grown in seedling trays for 2 months were transplanted into the lysimeter columns 1 week after the preplant irrigations, and wheatgrass (*Agropyron sp*) seedlings 2 weeks later on July 1 (which coincide with the beginning of the summer shower season in this area). Mulch consisting of a mixture of saltgrass and wheatgrass clipping was applied to selected columns (Table 3) at a dry weight of 50 grams per lysimeter, which provided a thickness of about 1 cm. This rate of application equals 1 kg m⁻² or 10 Mg ha⁻¹. Meantime, weekly irrigation with solutions 3 and 3 Ca continued until July 7. The cumulative depths of irrigation amounted to 45 cm, which include the 15 cm applied as preplanting irrigation (Table 4). No drainage has occurred during this period. Meantime, three extra soil columns were left to dry for 2, 3 and 4 weeks. Irrigation water was applied, then, water infiltration and Na concentrations of drainage water measured. The Na concentrations of drainage water from the 4 weeks of drying were at times lower

than other cases. This set of data was used to access the upper-limit of drying for minimizing the boundary flow.

Starting on July 14, 1998, or approximately 1 month after the preplanting irrigation, the sources of the irrigation water were changed to those listed in the column designated as Period II in Table 3. Prior to the irrigation, the second application of gypsum was made on treatments 3 and 4, in Harkey and treatments 4 and 5 in Saneli soils. The irrigation depth and interval for Harkey were kept the same as before, 7.5 cm per week for the next 5 weeks, and for Saneli, the irrigation depth was reduced to 3.8 cm per application for reducing waterlogging (Table 4). The third application of gypsum was made on August 13, 1998. Starting at September, 1998, irrigation depths were adjusted so as to obtain approximately the same quantity of drainage from sodded and unsodded lysimeters, while maintaining weekly irrigation intervals. The infiltration time was monitored as before, and drainage was collected and analyzed for volume, the electrical conductivity, pH, and the concentrations of Na, Ca, and Mg with an Inductively Coupled Plasma unit. Saltgrass was clip-harvested 10 cm above the ground on October 20, 1998, dried at 60C and weighed. The clipped plants were then used for mulch in treatments 3, 5, 7 and 9, 50 gram each, in the spring (March) of the second growing season.

Upon the harvest of the first year growth, irrigation intervals were extended to several weeks (Table 4). Starting at the end of April, the rate of grass growth increased sharply, and irrigation was made more or less bi-weekly in excess of 15 cm per application. The grass was clip-harvested again on August 13, and dry weights determined. Soil samples were then taken from lysimeter columns at 10 cm intervals, and were analyzed for salinity and the sodium adsorption ratio (SAR) of the saturation extract. The duration of the experiment lasted for 14 months, covering two growing seasons.

The above experiments were conducted in triplicates. The analysis of variance was performed using a split plot with sodding and nonsodding as the main plot, and chemical treatments as subplot. An exception was the analysis of infiltration time during the irrigation for transplant establishment.

These cases were analyzed by a block design.

RESULTS

Plant Growth

Transplanted saltgrass grew rapidly through the hot summer months, and reached 40 cm in height in Harkey, and 30 cm in Saneli soil by the end of September, irrespective of the treatments (Fig. 1). Regrowth from the clipped plants reached 55 cm in Harkey, and 45 cm in Saneli by the time of the second harvest. The analysis of variance did not indicate a significant effect of any of the treatments on plant heights.

Top dry matter production averaged 2 kg ha⁻¹ (or 20 Mg ha⁻¹) in Harkey soil, and 1.0 to 1.2 kg ha⁻¹ in Saneli soil at the first year harvest (Table 5). During the second season, biomass production in Saneli soil exceeded that in Harkey. Mulching suppressed growth during the first year, while gypsum application did not help promote growth. Waterlogging was aggravated by mulching, and appeared to be the source of reduced biomass production in the mulched treatment. The treatment effect on dry matter production was significant.

Wheatgrass transplants, mixed planted with saltgrass, did not survive waterlogging occurred in Saneli soil. In Harkey soil, they were dominated by saltgrass, but a few plants survived through the summer, and grew some during the fall and spring. Wheatgrass accounted for about 10% of the biomass produced in Harkey soil.

Water Balance

Irrigation water applied to the lysimeters with Harkey soil averaged 220 cm with sods and 93 cm without sods during the first year, excluding the initial irrigation of 45 cm (Table 6). Evapotranspirational losses averaged 35 cm without sods and approximately 150 cm with sods.

Corresponding leaching fractions were 62% without sods, and about 30% with sods. This water use pattern repeated itself during the second growing season, except for greater evapotranspiration losses and lower leaching fractions than those experienced during the first season. (Evapotranspiration losses are expressed by the volume per unit cross-sectional areas of the lysimeter columns, but not by the canopy area.) Leaching fractions and drainage increased with increasing salinity of irrigation water, but were not affected significantly by gypsum applications.

The water balance in lysimeters with Saneli soil followed the general patterns observed with Harkey, but with some notable exceptions. Evaporative losses from lysimeters without sods, for example, were considerably larger, especially when no mulch was placed. Drainage from mulched Saneli soil without sods (treatments 3 and 5) was significantly greater than non mulched treatments, whereas drainage from gypsum-treated lysimeters was not significantly greater. Lastly, the leaching fraction during the second growing season has decreased to 5% in sodded lysimeter, and approximately 15 to 25% in nonsodded lysimeters, depending on the presence or absence of the mulch.

The cumulative irrigation depth averaged for sodded and nonsodded cases is shown in Fig. 2, along with the cumulative drainage. The depths of water applied to sodded and unsodded lysimeters began to separate by August of the first growing season. The drainage from lysimeters with Harkey soil without sods exceeded that from sodded lysimeters for a month or two during the first growing season. The drainage from sodded and nonsodded lysimeters with Saneli soil was, as intended, about equal throughout the experimental period.

Water Infiltration

During the preplanting irrigations, water infiltration into Harkey soil was not affected by the surface broadcast application of gypsum (Table 7). However, in Saneli soil, the gypsum treatment had a significant positive effect on infiltration of solution 3 (Table 7). The positive effect of gypsum treatments persisted for subsequent irrigations in Saneli soil. In Harkey soil, a significant effect of

gypsum treatment appeared during the 5th and 6th irrigations (Table 7). By the time, most of the gypsum previously applied had been dissolved, except in some scattered areas. Water-run application of CaCl_2 at a concentration of $10 \text{ mmol}_e \text{ L}^{-1}$ (or 55.5 mg L^{-1}) to the leaching water (solution 3 of Table 2) did not affect water infiltration in either of the soils used. The quantity of CaCl_2 applied for the four irrigation events amounted to 1.66 Mg ha^{-1} in total (or 2.2 Mg ha^{-1} of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) on a cumulative water depth of 30 cm.

Water infiltration after these initial leaching irrigation events was increasingly affected by transpiration losses, and it was constantly higher in sodded soils due to lower soil moisture prior to irrigation. Such examples are shown in Table 7, using the 14th irrigation. Note that the time required for infiltration of 11.3 cm of water was an order of 2 hours, whereas it took 4 to as long as 13 hours for 7.5 cm of water to infiltrate into nonsodded Harkey soil. In Saneli soil, it took a day and a half for 11.3 cm of water to infiltrate into sodded lysimeters, whereas it took at least 2 days for 7.5 cm of water to infiltrate into nonsodded lysimeters. The enhanced infiltration in sodded cases was caused by the rapid intake into dry soils during the first 10 min. of water application.

The rate of evaporative water losses during winter months became about the same between sodded and nonsodded lysimeters. This provided an opportunity to test the effect of sodding on water infiltration when initial soil moisture levels were approximately equal. In the case of Harkey soil, water infiltration into sodded lysimeter soil was initially slower than that into nonsodded cases, but the rate of infiltration remained higher than nonsodded cases (Fig. 3). There was a significant difference in water intake between sodded and nonsodded cases, but not among the subplot treatments. In the case of Saneli soil, there was little difference in infiltration between sodded and nonsodded cases, as well as among the subplot treatments.

Salinity and Sodicity of Drainage Water

Salinity of drainage water was initially as high as 100 dS m^{-1} in Harkey soil, and in excess of 150 dS m^{-1} in Saneli soil (Fig. 4). Salinity of drainage water from Harkey soil decreased below

20 dS m⁻¹ when drainage depths reached 18 to 55 cm, depending on the treatments. Salinity of drainage water from sodded cases was significantly higher than that from nonsodded cases. The use of water with elevated salinity (solution 3) resulted in higher salinity of drainage water in sodded cases, but not necessarily in nonsodded cases. Any other treatments examined, including gypsum treatments, did not significantly affect salinity of drainage water.

Salinity of drainage water from Saneli soil decreased below 30 dS m⁻¹ when the drainage depths reached 10 to 20 cm, depending on the treatments (Fig. 4). Thereafter, it remained in a range of 20 to 30 dS m⁻¹, even when drainage depths were doubled. Sodded lysimeters produced higher salinity. Mulching of nonsodded lysimeters caused a significant reduction in salinity of drainage water during the initial phase of leaching. No other treatment caused significant effects on salinity of drainage water.

Sodicity of drainage water expressed by the sodium adsorption ratio (SAR) was in excess of 100 in Harkey soil, and decreased below 20 when the cumulative drainage depth reached 40 to 70 cm, depending on the treatments (Fig. 5). Sodicity of drainage water was higher in sodded cases than in nonsodded cases. The use of saline water (solution 3) produced significantly higher sodicity only during the late stage of leaching of sodded soils. No other treatments, including gypsum treatments, caused a significant effect on sodicity of drainage water. Sodicity of drainage water from Saneli soil was initially about 60 in SAR, and decreased by about 20% during the subsequent leaching process. Unlike the case of Harkey, no consistent trend was noted in regard to the effect of sodding or mulching on sodicity of drainage water from this soil.

Sodium concentrations of drainage water from Harkey soil were as high as 1.5 mol_e L⁻¹ initially (Fig. 6), then decreased exponentially with increasing drainage to an order of 100 mmol_e L⁻¹. Sodium concentrations from sodded lysimeters were significantly higher than those from nonsodded lysimeters, especially during the initial phase of leaching with the drainage depth less than 50 cm. Sodium concentrations of drainage water from Saneli soil also started at 1.5 mol_e L⁻¹, but did not decrease below 200 mmol_e L⁻¹ with no significant effect of any of the treatments, except for sodding.

Calcium concentrations of drainage water from Harkey soil were initially as high as 200 mmol_e L⁻¹, then decreased to about 30 mmol_e L⁻¹ in sodded cases, and below 20 mmol_e L⁻¹ in nonsodded cases when the cumulative drainage depth reached 10 to 25 cm (Fig. 7). Thereafter, Ca concentrations fluctuated, but usually with higher concentrations from sodded cases. Calcium concentrations of drainage water from Saneli soil was as high as 400 mmol_e L⁻¹ initially, then decreased to around 20 mmol_e L⁻¹ when drainage depths reached 10 to 15 cm (Fig. 7). Calcium concentrations were higher in sodded cases than in nonsodded cases. There was no significant effect of other treatments on Ca concentrations of drainage water.

Magnesium concentrations of drainage water from Harkey soil were as high as 250 mmol_e L⁻¹, and decreased to 40 mmol_e L⁻¹ when drainage depths reached 40 cm. The concentrations from Saneli soil was about 400 mmol_e L⁻¹ initially, then decreased to 20 mmol_e L⁻¹ when the cumulative drainage depth reached 10 to 20 cm. Magnesium concentrations then stayed essentially unchanged with increasing drainage. The pattern of reduction in Mg concentration was similar to that of Na, thus the data are not shown.

Sodium Removal

The quantities of Na removed (estimated as the quantities drained minus the added through irrigation) ranged from 150 to 200 mol_e m⁻² in Harkey soil. The largest removal occurred with the sodded treatments using low salt water, followed by sodded treatments using saline water. The least quantity of Na was removed from nonsodded lysimeters irrigated with saline water. The quantities of Na removed were reduced when the cumulative drainage depth reached about 75 cm in sodded lysimeters, due to the reduction in drainage during the peak growth period of the second growing season.

The Na removed from Saneli soil was initially negative in quantity, due to the prolonged period of no drainage. Thereafter, the quantity removed increased sharply until the cumulative drainage reached about 8 cm, then at a slower rate for the remaining period. The quantities removed

from sodded lysimeters were further reduced due to insufficient drainage. Additional details on the quantities of Na removed are given in Table 8 for each of the treatments.

When plotted against the cumulative irrigation depth, the quantities of Na removed at a given depth of water applied were greatly larger in nonsodded lysimeters in Harkey soil than in sodded lysimeters (Fig. 9). In addition, the effect of gypsum application on Na removal during the initial phase of leaching became evident, along with the effect of saline water on Na removal. In the case of Saneli soil, the quantities of Na removed were also greater in nonsodded lysimeters than in sodded lysimeters, except for treatment 9 where mulch and gypsum were applied. Starting at the 2nd irrigation season, the Na removed became stationary, then negative in quantity due to inadequate drainage.

Salinity and Sodicity of the Soils

Salinity of the saturation extract measured in Harkey soil at the end of the experiment ranged from 8 to 20 dS m⁻¹, which is less than or equal to the initial salinity of 19.6 dS m⁻¹ (Fig. 10). The lowest salinity reading was obtained from nonsodded lysimeters irrigated with low salt water, followed by nonsodded lysimeters irrigated with saline water. The highest salinity was obtained from sodded lysimeters irrigated with saline water. Salinity of the saturation extract measured in Saneli soil was lowest in nonsodded lysimeters with mulch, followed by nonsodded lysimeters which received CaCl₂ or gypsum (Fig. 10). In sodded cases, salinity of the saturation extract was unaffected by mulching or chemical applications.

Sodicity of the saturation extract measured in Harkey soil ranged from 8 to 35 in SAR (Fig. 11), which is less than the initial value of 38. As in the case of salinity, the lowest sodicity value was obtained from nonsodded lysimeters irrigated with low salt water, and the high value from sodded lysimeters irrigated with saline water. Sodicity of the saturation extract from Saneli soil followed the pattern of salinity distribution mentioned earlier.

DISCUSSION

It was hypothesized at the onset that cultivation of salt tolerant plants with water of elevated salinity can improve reclamation of sodic soils. This study demonstrated that salt tolerant grass can be grown on saline soils with EC_e as high as 20 dS m^{-1} with water having salinity of $50 \text{ mmol}_e \text{ L}^{-1}$ or 6 dS m^{-1} after the preplant irrigation of 15 cm. The top dry matter obtained (Table 5) is comparable to those of grass species grown in nonsaline soils. This set of the results indicates that the proposed scheme is logistically feasible, but its impact on reclamation is uncertain.

One of the reasons why such a practice may help reclamation is potential improvements in water infiltration necessary for leaching. In the case of Harkey silt loam, application of gypsum did not improve water infiltration greatly during the initial leaching period, presumably because saline water was used for leaching. Laboratory infiltration data reported earlier (Report 7) indeed support this interpretation. During the summer irrigation season, infiltration of solution 2 into nonsodded soil was slow (Table 7), and water infiltration was faster in sodded cases, mainly because of lower soil moisture contents prior to irrigation. Improved water infiltration, however, affected neither plant growth nor drainage (Tables 5 and 6). Judging from the infiltration rates and the extent of drainage achieved, it appears that the use of water with elevated salinity alone can facilitate leaching of saline sodic soils with coarse texture. Water infiltration into Saneli silty clay loam was, however, slow, even when saline water was used for leaching. Unfortunately, neither chemical amendments at the tested rates nor sodding per se made sufficient improvements in infiltration.

An additional reason why sodding can improve drainage is related to increases in salinity of drainage water. Salinity of drainage water from sodded cases were indeed greater than those from nonsodded cases (Fig. 4). High salinity is known to counter against dispersive effects of exchangeable Na. In the present study involving saline sodic soils, this potential benefit seems to have been offset by the high soil salinity as well as by the high salinity of water used for leaching. However, the ability of plants to concentrate soil solutions can be significant in reclamation of sodic soil with low salinity as reported by Robbins (1986).

The most well-established mechanism for reclamation of sodic soil with the use of reclamation crops is enhanced dissolution of CaCO_3 through respiration, which helps remove exchangeable Na. The data obtained here present mixed results. The data shown in Fig. 7 indicate that the concentrations of Ca were generally higher in sodded cases than in nonsodded cases, especially during the first season when the leaching fraction exceeded 25%. This set of the data can be interpreted as a positive sign. The strongest evidence appeared in Fig. 8, where the quantities of Na removed increased with sodding, at least in Harkey soil. However, the SAR of the soils measured at the end of the experiment (Fig. 11) was greater in sodded cases than in nonsodded cases. This apparent discrepancy is related to the fact that the leaching fraction was not large enough to cause Na leaching during the second growing season as shown in Fig. 8 and 9. In other words, the process reverted to sodification, instead of reclamation. If irrigation were made to yield a greater leaching fraction, soil salinity as well as soil sodicity of the sodded lysimeters would have been lower. In Saneli soil, however, increased irrigation could have caused waterlogging.

Findings of this study raise some questions in regard to the effectiveness or appropriateness of the scheme which involves cultivation of salt tolerant plants with water of elevated salinity for reclamation of saline sodic soils. The use of saline water for leaching helps maintain soil permeability, especially when sodicity of the saline water is low. However, the use of saline water is likely to have no substantive effect of maintaining permeability of subsoils during the initial phase of leaching in saline sodic soils, since salinity of soil solutions already contains dissolved salts at high concentrations (Fig. 4). This means that the positive effect of maintaining permeability is likely to be limited to the soil surface layer, similarly to the cases involving chemical amendments. The real and most significant limitation of using saline water for leaching seems to appear in clayey soils with low permeability. In the present study, the use of saline water, even with the aid of gypsum or water-applied CaCl_2 , failed to provide permeability needed for adequate leaching in the sodium-affected silty clay loam. The solubility of gypsum is too low to attain necessary removal of exchangeable Na at the onset of leaching (Report 7). Likewise, application of CaCl_2 to leaching water at diluted concentrations has the same limitation. One can speculate that this was unavoidable, because of its texture which yields inherently low permeability. The data shown in Report 7, however, indicate that a high dosage of

high soluble CaCl_2 provides much greater sorptivity and permeability. The use of saline water for leaching may prove to be an effective option in coarse-textured sodic soils, but seems to have a limited value in clayey soils affected by sodium.

Sodding helped remove Na at least in Harkey soil, but not necessarily in Saneli soil. As reported earlier, dissolution of CaCO_3 increases with increasing pore water velocity or drainage. The positive effect of enhanced CaCO_3 dissolution, however, seemed to have been countered by the increase in sodicity caused by water-uptake. This problem is pronounced when saline water is used for irrigation. If soil permeability and/or irrigation quantities are insufficient to obtain drainage in excess of the quantity attained in nonsodded cases, the enhanced removal of exchangeable Na through cultivation of salt tolerance grass would be limited. This may account for the poor results obtained by Overstreet et al. (1951) and by Stroehlein et al. (1978). The water application strategy used in this experiment was to achieve the same quantity of drainage between sodded and nonsodded cases. A preferred option would be to use water application strategy which yields at least the same level of leaching fractions as nonsodded cases. This will, however, require additional amounts of irrigation. It is difficult to assess if permeability improvements achieved through sodding can accommodate such water application strategy, especially during the summer peak period. The use of cool season grass, in addition to the classic concept of saline water dilution method (e.g., Reeve and Bower, 1960), may help alleviate the increase in sodicity caused by water uptake.

In conclusion, this study, which is preliminary in nature, indicates that additional quantitative investigations, including modeling, are required before vegetative means of reclaiming Na-affected calcareous soils can be recommended with certainty. At present, the available data seem to indicate that the best scenario for using reclamation crops is under nonsaline sodic conditions in coarse textured soils where the benefit of enhanced CaCO_3 dissolution can be maximized. In the case of saline sodic soils, the presence of high salts not only lower potential benefits, but can potentially lead to soil sodification if leaching is not adequately maintained or soil permeability is insufficient.

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Table 1. Some properties of the soils used for the lysimeter experiment.

Experiment Soil type	Saturation water g kg ⁻¹	Satur. Extract					Cation Exch mmol _c kg ⁻¹
		pH	EC dS m ⁻¹	SAR	Na mmol _c L ⁻¹	Ca mmol _c L ⁻¹	
Harkey silt loam	455	8.2	19.6	38	211	40	171
Saneli Si C loam	560	7.9	15.1	26	141	30	237

Table 2. Composition of saline solutions used for the lysimeter experiment.

Soln. No.	EC	TDS	SAR	Na	Ca	Mg	HCO ₃	Cl	SO ₄
	dSm ⁻¹	mmol _c L ⁻¹							
1	1.0	10	10.0	8.54	1.06	0.40	2.4	4.2	3.4
2	2.5	25	10.0	18.3	4.46	2.24	2.4	14.2	8.4
3	4.5	50	10.0	31.0	22.6	6.4	2.4	31.0	16.6
2 Ca	2.9	30	7.5	(Soln 2 + 5 meq L ⁻¹ CaCl ₂)					
3 Ca	5.5	60	8.1	(Soln 3 + 10 meq L ⁻¹ CaCl ₂)					

Table 3. An outline of the treatments imposed on the lysimeter experiment.

Soil	Treatment	Gypsum		Mulch		CaCl ₂ Rate	Type of water		
		Rate	No.	Rate	No.		I ^{1]}	II ^{1]}	III ^{1]}
		Mg ha ⁻¹		Mg ha ⁻¹		Mg ha ⁻¹			
Harkey									
1	No sod	0	0	0	0	0	3	2	1
2	No sod, saline	0	0	0	0	0	3	3	3
3	No sod, gypsum	5.2	3	0	0	0	3	2	1
4	No sod, gyp. Saline	5.2	3	0	0	0	3	3	3
5	Sodded	0	0	0	0	0	3	2	1
6	Sodded, saline	0	0	0	0	0	3	2	2
7	Sodded, saline	0	0	0	0	0	3	3	3
8	Sodded, gypsum	5.2	1	0	0	0	3	2	1
9	Sodded, gyp, saline	5.2	1	0	0	0	3	3	3
Saneli									
1	No sod	0	0	0	0	0 ^{2]}	3	3	2
2	No sod, CaCl ₂	0	0	0	0	12	3ca	3ca	2ca
3	No sod, mulch, CaCl ₂	0	0	10	2	11	3ca	3ca	2ca
4	No sod, gypsum	7.5	3	0	0	0	3	3	2
5	No sod, mulch, gyp	7.5	3	10	2	0	3	3	2
6	Sodded, CaCl ₂	0	0	0	0	18	3ca	3ca	2ca
7	Sodded, mulch, CaCl ₂	0	0	10	2	18	3ca	3ca	2ca
8	Sodded, gypsum	7.5	1	0	0	0	3	3	2
9	Sodded, mulch, gyp	7.5	1	10	2	0	3	3	2

^{1]} I.: June 10 - July 7, 1998. Preplanting irrig. and transplant establishment

II: July 16 - April 30, 1999. The first season growth.

III: May 1 - July 27, 1999. The second season growth.

^{2]} For concentrations of CaCl₂ applied to water, refer to Table 2.

Table 4. The depth of irrigation and intervals used for the lysimeter experiment.

Soils	Nonsodded				Sodded			
	Depth	Events	Interval	Cumul.	Depth	Events	Interval	Cumul
Start Dates	cm	No	days	cm	cm	No.	days	cm
Harkey silt loam								
1. Preplant irrigation & transplant establishment								
6/10	7.5	2	0	15	7.5	2	7	15
6/16	7.5	4	7	45	7.5	4	7	45
2. First year growth								
7/14	7.5	6	7	90	7.5	6	7	90
8/25	11.25	2	7	113	11.25	2	7	113
9/08	3.8 ~ 7.5	5	8	135	15 ~ 30	5	8	240
3. Post harvest off-season								
10/22	5.6 ~ 11.25	3	15 ~ 25	159	7.5 ~ 17	3	15 ~ 24	281
4. The second year preseason								
1/07	11.25	4	15 ~ 28	204	11.25	4	15 ~ 28	326
5. The second year growing season								
1/26	15 ~ 23	3	13 ~ 23	303	30 ~ 42	3	13 ~ 17	504
6. The grand total								
7/27	-	31	-	303	-	31	-	504
Saneli silty clay loam								
1. Preplant irrigation and plant establishment								
6/10	7.5	2	0	15	7.5	2	7	15
6/16	7.5	4	7	45	7.5	4	7	45
2. First year growth								
7/14	7.5	6	7	90	7.5	6	7	90
8/25	11.25	2	7	113	11.25	2	7	113
9/08	3.8 ~ 7.5	5	8	135	15 ~ 30	5	8	240
3. Post harvest off-season								
10/22	5.6 ~ 11.25	3	15 ~ 25	159	7.5 ~ 17	3	15 ~ 24	281
4. The second year preseason								
1/07	11.25	4	15 ~ 28	204	11.25	4	15 ~ 28	326
5. The second year growing season								
1/26	15 ~ 23	3	13 ~ 23	303	30 ~ 42	3	13 ~ 17	504
6. The grand total								
7/27	-	31	-	303	-	31	-	504

Table 5. Dry weights of a salt and wheatgrass mix harvested in October 1998 and August 1999.

Soils Treatments ^{1]}	gypsum Mg ha ⁻¹ times	mulch Mg ha ⁻¹	water types		Dry top weight		
			98	99	98	99	Total
Harkey					----- kg m ⁻² -----		
5	0	-	2	1	2.16a	2.46a	4.62a
6	0	-	2	2	2.20a	2.52a	4.72a
7	0	-	3	3	2.00a	2.48a	4.48ab
8	5.2 x 1	-	2	1	2.14a	2.56a	4.70a
9	5.2 x 1	-	3	3	1.87b	2.44a	4.31b
Saneli							
6	0	0	3ca	2ca	1.23a	3.10a	4.33a
7	0	10 x 2	3ca	2ca	1.02ab	3.02a	4.04a
8	7.5 x 1	0	3	2	1.21a	3.13a	4.33a
9	7.5 x 1	10 x 2	3	2	0.91ab	3.18a	4.09a

^{1]} Refer to Table 2 for details.

Table 6. The water balance during the first and the second growing seasons.

Soils Treatments	Irrigation				Drainage			Evap. Trans.		Leaching Fraction	
	I ¹	II	III	Total	II	III	Total	II	III	II	III
	----- cm -----				----- cm -----			----- cm -----			
Harkey											
1	45	93	140	278	57	79	135	36	61	.61	.51
2	45	93	140	278	58	80	138	35	60	.62	.57
3	45	93	140	278	59	78	137	34	62	.63	.56
4	45	93	140	278	59	73	140	34	67	.63	.52
5	45	226	237	507	63	43	105	163	194	.28	.11
6	45	220	237	502	63	54	116	157	183	.29	.23
7	45	212	233	491	64	58	123	149	175	.30	.25
8	45	218	238	501	63	44	106	165	194	.29	.18
9	45	216	229	490	67	47	114	149	182	.31	.21
Saneli											
1	55	93	123	271	20	20	40	73	103	.21	.16
2	55	83	133	266	23	20	47	60	113	.28	.75
3	55	74	125	254	26	26	52	48	99	.35	.21
4	55	91	127	273	24	23	47	67	104	.26	.18
5	55	71	125	251	25	31	56	46	94	.35	.25
6	55	137	212	404	30	8	38	107	204	.22	.04
7	55	132	227	414	31	10	41	101	217	.23	.04
8	55	130	226	411	33	12	45	97	214	.25	.05
9	55	120	240	415	32	10	42	88	230	.27	.04

I: June 10 - July 7, 1998; Preplanting irrig. & transplanting

II: July 14 - Dec 31, 1998; The first year growth

III: January 1 - August 13, 1999; The second year regrowth

Table 7. The time required for ponded water to infiltrate into Harkey and Saneli soils.

	Harkey Loam			Saneli s.c. loam		
	Water	Depth	Duration	Water	Depth	Duration
	#	cm	hr	#	cm	hr
Preplant irrigation						
1 st application						
Control	3	7.5	1.48a ^{2]}	3	7.5	3.9a ^{2]}
Gypsum	3	7.5	1.52a	3	7.5	4.2a
CaCl ₂	-	-	1.52a	3 ca	7.5	4.0a
2 nd application						
Control	3	7.5	4.56a	3	7.5	19.2a
Gypsum ^{1]}	3	7.5	4.37a	3	7.5	12.3b
CaCl ₂	-	-	-	3a	7.5	18.5a
Weekly irrigations for transplant establishment						
3 rd and 4 th averaged						
Control	3	7.5	3.88a	3	7.5	20.6a
Gypsum ^{1]}	3	7.5	4.09a	3	7.5	18.3b
CaCl ₂	-	-	-	3ca	7.5	20.1a
5 th & 6 th averaged						
Control	3	7.5	3.97a	3	7.5	36.5a
Gypsum ^{1]}	3	7.5	3.87b	3	7.5	35.3b
CaCl ₂	-	-	-	3ca	7.5	36.4a
Summer irrigation season						
14 th Irrigation						
Nonsodded						
Control	3	7.5	16.81a	3	7.5	67a
Control	2	7.5	13.3b	-	-	-
Gypsum	3.2	7.5	4.15a	3	7.5	49ba
CaCl ₂	-	-	-	3ca	7.5	57a
Sodded						
Control	3.2	11.3	2.26a	-	-	-
Gypsum	3.2	11.3	2.28a	3	11.3	32c
CaCl ₂	-	-	-	3ca	11.3	39c

^{1]} Gypsum application rate: 5.2 Mg ha⁻¹ in Harkey and 7.5 Mg ha⁻¹ in Saneli (Table 3)

^{2]} The significance of the treatment mean differences was evaluated using a block design with uneven replicate numbers.

Table 8. The salt and cation balances after the 1st and 2nd growing seasons; Harkey, Saneli.

Treatment	Na			Ca			Mg		
	Drained	Added	Removed	Drained	Added	Removed	Drained	Added	Removed
Harkey									
First Season									
1	9.42	1.46	7.96	0.53	0.58	-0.05	1.67	0.22	1.45
2	11.80	2.67	9.13	0.85	0.88	-0.02	1.90	0.37	1.53
3	11.64	2.62	9.01	0.82	0.87	-0.05	1.95	0.36	1.59
4	13.03	4.00	9.03	0.85	2.92	-2.07	2.24	0.83	1.41
5	9.38	2.14	7.24	0.49	1.56	-1.07	1.81	0.44	1.36
6	9.60	1.46	8.15	0.52	0.58	-0.06	1.88	0.22	1.66
7	12.41	2.61	9.81	0.76	0.86	-0.10	2.09	0.36	1.73
8	12.79	4.05	8.74	0.84	2.95	-2.12	2.16	0.84	1.32
9	9.56	2.14	7.42	0.52	1.56	-1.04	1.79	0.44	1.35
Second Season									
1	2.10	0.89	1.21	0.24	0.18	0.07	0.98	0.08	0.90
2	2.18	1.48	0.70	0.27	0.29	-0.02	0.81	0.14	0.67
3	3.63	2.17	1.46	0.27	0.53	-0.26	1.37	0.27	1.10
4	3.13	3.62	-0.48	0.34	2.64	-2.29	1.03	0.75	0.28
5	2.07	1.76	0.31	0.29	1.28	-1.00	0.86	0.36	0.50
6	1.55	0.89	0.66	0.24	0.18	0.06	0.78	0.08	0.70
7	2.38	1.51	0.87	0.25	0.30	-0.05	0.90	0.14	0.76
8	3.72	3.46	0.26	0.34	2.52	-2.18	1.22	0.71	0.51
9	2.33	2.17	0.15	0.29	1.58	-1.29	0.90	0.45	0.45
Saneli									
First Season									
1	5.36	2.11	3.24	1.93	1.54	0.39	1.12	0.44	0.68
2	5.36	1.91	3.45	2.11	2.01	0.10	1.33	0.39	0.93
3	6.99	2.86	4.13	2.62	3.01	-0.39	1.46	0.59	0.87
4	5.39	1.82	3.57	1.70	1.91	-0.22	0.86	0.38	0.49
5	6.89	2.78	4.11	2.44	2.92	-0.48	1.58	0.57	1.01
6	5.72	2.17	3.55	1.84	1.58	0.26	1.24	0.45	0.79
7	5.91	2.73	3.18	2.49	1.99	0.50	1.58	0.56	1.02
8	5.22	1.78	3.44	1.84	1.30	0.54	1.09	0.37	0.72
9	6.09	2.57	3.52	2.73	1.87	0.86	1.72	0.53	1.19
Second Season									
1	2.58	0.98	1.60	0.13	0.58	-0.45	0.25	0.18	0.07
2	2.86	1.41	1.44	0.17	1.19	-1.02	0.29	0.25	0.04
3	1.54	2.01	-0.48	0.09	1.25	-1.16	0.16	0.33	-0.16
4	3.24	1.49	1.74	0.15	1.27	-1.12	0.32	0.26	0.06
5	1.76	2.12	-0.36	0.11	1.31	-1.20	0.18	0.34	-0.16
6	3.06	1.53	1.53	0.16	0.85	-0.69	0.32	0.27	0.05
7	2.32	2.18	0.15	0.12	1.04	-0.93	0.26	0.36	-0.10
8	3.63	1.49	2.14	0.22	0.82	-0.60	0.39	0.26	0.13
9	1.89	2.28	-0.40	0.12	1.09	-0.97	0.22	0.37	-0.16

FIGURES

- Fig. 1. Plant heights measured over the experimental period covering two growing seasons.
- Fig. 2. Cumulative irrigation and drainage depths over the experimental period.
- Fig. 3. Cumulative depths of water intake into Harkey and Saneli soils with and without sods during winter months.
- Fig. 4. Salinity of drainage water as a function of the cumulative drainage depth.
- Fig. 5. Sodidity of drainage water as a function of the cumulative drainage depth.
- Fig. 6. The concentrations of Na in drainage water as a function of the cumulative drainage depth.
- Fig. 7. The concentrations of Ca in drainage water as a function of the cumulative drainage depth.
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- Fig. 9. The quantities of Na removed from the soils as a function of the cumulative irrigation depth.
- Fig. 10. Salinity of the saturation extract at the end of the 2nd growing season.
- Fig. 11. Sodidity of the saturation extract at the end of the 2nd growing season.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

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