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SALINISATION, ALKALINISATION and SODIFICATION
on irrigated areas in Pakistan.

Characterisation of the geochemical and physical processes and the impact of irrigation
water on these processes by the use of a hydro-geochemical model

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March, **1997**

International Irrigation
Management Institute - Lahore
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FOREWORD

This report is the thesis or final report for the Master of Science Program of Mr. Nicolas Condom. He completed the requirements for an M.S. degree in Agricultural Engineering (Génie Rural in French) under a graduate program organised by the Universite des Sciences et Techniques du Languedoc, but enrolled at the Ecole Nationale du Genie Rural des Eaux et des Forêts (ENGREF) in Montpellier. He spent three months in Pakistan during 1996 to complete all of the necessary field work and analysis. This reproduction is identical with the document accepted by ENGREF in the fall **of 1996,** except for some additional editing.

We have a number of national and international students participating in the research program of the Pakistan National Program of the International Irrigation Management Institute. Their theses and dissertations are retained in our library for ready reference. Only a few of these documents are selected for publication in our research report series. The principal criteria for publishing is good quality research and a topic that would be of interest to many of our national partners.

This report is an output of a collaborative research program with CEMAGREF, the French national research organisation for agriculture, water and forests. However, this research is part of our program under the project "Managing Irrigation for Environmentally Sustainable Agriculture in Pakistan" funded by the Government of The Netherlands.

The advisor for this collaborative research was Dr. Serge Marlet of the Centre for International Cooperation in Agricultural Research for Development (CIRAD) in Montpellier. This was undertaken as part of the salinity research program being supervised Mr. Marcel Kuper of IIMI.

Nicolas Condom began a Ph.D. program this month (March 1997) that is being funded **by** the French Government. He will continue to do research on modeling hydro-geochemical processes. However, his field research will be done in West Africa.

Gaylord **V.** Skogerboe, Director
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ABSTRACT

Irrigated soils in arid areas are often affected by soil salinisation processes, which include the neutral salinisation, the alkalinisation, and the scdification processes. This is the case in Pakistan where the percentage of salt affected irrigated lands have been strongly increasing for more than thirty years. This is explained by the use of brackish tubewell water to supplement or replace canal water when the supply is deficient.

This study aims at the characterisation of the different salinisation processes, of their causes (irrigation water) and of their effects on soil (soil degradation).

Firstly, the study of the processes based on soil samples shows that the different paths of salinisations can be found in the study area, in the Punjab.; different levels of the processes chracterize also the soils of the area. All of these processes are assessed by chemical indicators.

Then, it is shown that several types of soil degradation in the surface soils could be found on irrigated fields that are linked to soil sodicity levels.

In a third step, the relations between water quality, soil chemical processes and soil degradation are studied with the help of a geochemical model and a hydro-geochemical model (which takes into account both the water and solute transports and the geochemical processes). The results show that the effect on the soil salinisation processes strongly depends on the irrigation water characteristics and on the soil texture. A classification framework for water quality is then proposed.

Key Words : SALINISATION, SODIFICATION, ALKALINISATION, SALMITY, SODICITY. ALKALINITY, GEOCHEMISTRY, IRRIGATION, WATER QUALITY, DEGRADATION, SOIL CRUSTS, MODEL, PAKISTAN

ACKNOWLEDGEMENTS

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INTRODUCTION

A. INSTITUTIONAL AND SCIENTIFIC CONTEXT OF THE STUDY

This report is the final output of a seven months thesis *wafer sciences* at *l'Ecole du Génie Rural des Eaux et des Forêts* (ENGREF) and *at* the department of *wafer* resources, *Montpellier, University of sciences.* It was the opportunity of new collaboration between the International Irrigation Management Institute (IIMI-Pakistan) and the Centre for International Cooperation in Agricultural Research for Development (CIRAD-France).

Pakistan has one of the largest contiguous gravity irrigation systems in the world, irrigating annually an area of about 16 million hectares.

There are a few processes influencing the overall present irrigation management in the Punjab, resulting in stagnant agricultural production (wheat, rice and sugarcane) and less sustainability overall. The main problems affecting the overall performance are : 1. the increasing demand of canal water supply due to the intensified cropping patterns; 2. increase in saline tubewell water use, which may result in a negative effect on production due to die increasing salinity and sodicity in the agricultural plots; 3. sever waterlogging at the lower parts of the system due to bad drainage and intensive irrigation; 4. limited resources for proper inaintenance and operation of the actual system by the Punjab Irrigation and Power Development ; and 5. non technical problems due to political and social constraints resulting in water theft and illegal irrigation practices (Visser, 1996).

IIMI has been working since 1989 on inter-related issues of canal irrigation nianagement, groundwater extraction, agricultural production and salinity/sodicity. The main objective of this research *is* **to** devise management interventions that have a potential to contribute to increased agricultural production and mitigate salinity/sodicity. Research efforts have focused on die Fordwah/Eastern Sadiqia area (FES) in south-east Punjab, where a multidisciplinary teams works on the various research components. The Chishtian Sub-division, located in the northern part of FES has traditionally been IIMI's research area.

B. SALINISATION IN A FEW WORDS

Salinisation is a global term used to describe several processes such as neutral salinisation (often merely called salinisation), alkalinisation and sodification. They are all caused by a gradual process of concentration of the soil water due to soil and crop evaporation and transpiration. All of these processes are linked. These three processes can be distinguished in terms of the processes (geochemical and physical processes), the environmental conditions of occurrence, their rate of development, and their effects on soils and crops.

Soil salinity and sodicity is of common occurrence in arid and semi-arid regions wherever irrigated agriculture has been practised. About 23 percent of presently cultivated land in the world is affected by salinity and sodicity (Postel, 1989, Tyagi, 1996,). Tanji (1990) estimates that 340 millions ha are covered by saline soils whereas the area under alkali soils (degraded soils resulting from

alkalinisation and sodification processes) occupies 560 millions ha. Table 1 provides some information on saline and sodic soils in the top five irrigation countries.

SOME FEATURES OF PAKISTAN

LAND:

Pakistan covers an area of 796 095 km². It comprises four provinces; Baluchistan, North West Frontier (NFWP). the Punjab and Sind. 40 % of the area form in the north west and west of Pakistan is a highly mountainous terrain, while the remaining presents a flat surface. The whole land, excluding must of Baluchistan, is drained by the Indus River system.

CHINA

AFGHANISTAN

INDIA

Chishtian
Subdivision
(study area)

IRAN
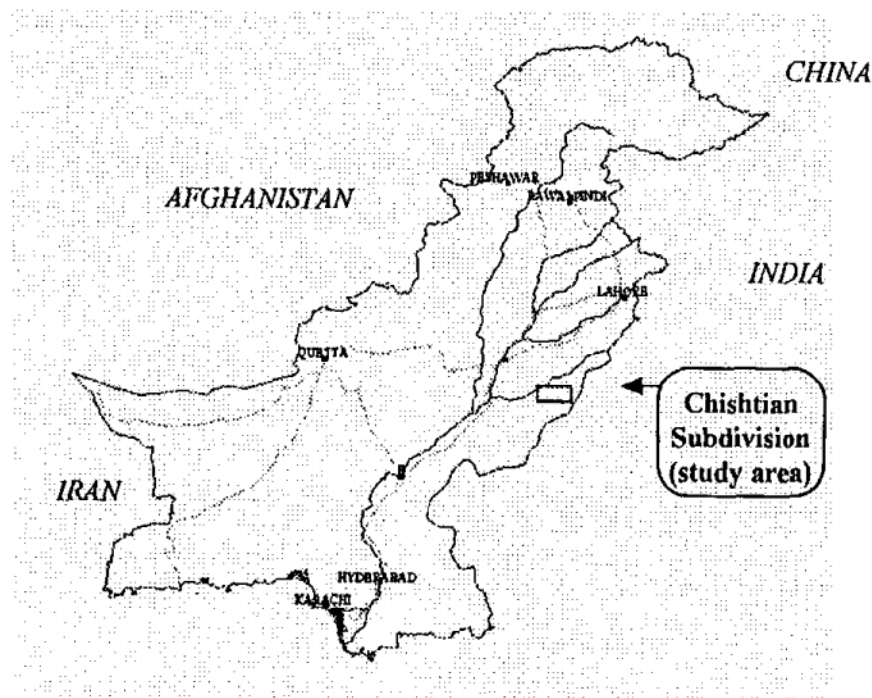
CLIMATE:

The spatial and temporal variation in rainfall is high. The average annual rainfall varies largely from more than 1200 mm in the Himalayan sub mountain area to less than 200 mm in the south. Around 75 per cent of the mean annual rainfall occurs in July and August (monsoon period). There are two cropping seasons in Pakistan. The summer season (*Kharif*) extends from May lo October. The winter season (*Rabi*) extends from November lo April. The distribution and intensity of rainfall is inadequate for two cropping seasons in most of Pakistan: some water is wasted in the monsoon period as well as it is not sufficient for crop water requirements during the rest of the year.

The annual evaporation is higher than annual rainfall. The total annual pan evaporation in the Indus Plain, in Punjab is about 2000 mm. Evaporation is lowest in January and highest in May.

The spatial and temporal variation in temperature is high. Pakistan possesses a great range of climatic diversity, from some of the hottest places in the world in its south western pan lo the snowy and cold region in the north. In the Indus plain. temperatures range from 32 to 49°C during summer to 13°C during winter.

POPULATION:

The population was estimated at about 112 million in *1990* with an annual growth rate of 3.1 percent in these last ten years[1]. 72 % of the total population lives in rural areas.

AGRICULTURE:

Thb is the largest and most important single sector in Pakistan's economy. Agriculture accounts for 26% of the QDP and exports generate about 70 percent of the total foreign exchange earnings in the country. This is the single largest source of employment accounting 52 percent for the labour force (1992)[2].

[1]World Bank, 1992

[2]Government of Pakistan, Financial Division, 1993.Economic survey 1992-1993

Wheat, cotton, sugar cane and rice are the major crops. The total production (1991-1992) and yields is 15.6 MT and 2.0 t/ha for the wheat, 9327 bales and 566 kg/ha for cotton, 3.1 Mt and 1.5 t/ha for rice and 38 Mt and 43.4 t/ha for sugarcane. Minor crops (less than 2% of the cropped surface) are represented by maize, oil seeds, chillies, pulses, potato, onions and fruit.

The Pakistani **agriculture is** Irrigated. 26 percent of the total land is cultivated: 78% (16.2 M ha) of which is irrigated: irrigated agriculture accounts for more than 90 per cent of the total agriculture production of the country.

- ## Surface water

The principal **source of water supply is provided** by the Indus River. *The* Indus River and its tributaries drain most **parts of** Pakistan. It originates in the Tibetan plateau at **an** altitude of 5500 meters above **the** sea level. **The** average annual flow measured at Tarbela, when the River arrives at plain, is of 83×10^9 m^3. **The** Indus water resource is shared between the four different provinces,

The chemical water **quality of** the Indus system **is excellent** for **irrigation.** The average salt **content is** about 300 to 420 mg/l. 70 per cent of the average annual flow is diverted into **the** irrigation **systems.**

A **gigantic** Irrigation **system.** Although irrigation has a 3000 year history in the Indus River Valley, the **first** canals were **constructed five** centuries ago. The present **system** was built in the nineteenth **century by** the British. This irrigation system is often referred to as the **largest** single irrigation system in the world. Today it includes more **than** 89,000 watercourses (tertiary unit) which irrigate 16 Mha. The length of the irrigation network of canals **is** more **than** 1.5 times the length of the equator.

- ## Ground water

The aquifer has a high yield and **substantial storage capacity.** Ground water is contained **in** interbedded deposits of alluvial **sand** and silt. Hydrogeologically, the whole of the Indus alluvial complex can be **treated as** a huge. single. unconfined aquifer with high hydraulic conductivity (30 to 60 m/d) and an average storage coefficient of 12 per cent (Rathur in Ghussem and **al.,** 1995). **The** water stored in the aquifer **is** 50 to 100 times higher than the annual volume of the Indus River.

The ground water **ranges from fresh to poor quality.** Quality depends on the climatic parameters, nature of the surface **flow.** topography, extent *of* seepage and irrigation practicer. The quality deteriorates from the mountains (Total Dissolved Solids of less than 1000 mg/l) to **the** Arabian sea (Total Dissolved Solid **of more** than 3000 mg/l). In general, saline ground water in the Indus Plain occurs in **the form** *of* lenses below the surface surrounded by fresh ground water or, just below the surface with gradual increase in salinity with depth. In Punjab, the quality is good for more than 60% of the areas and poor for 20 % (Water and Power Development Authority. **1988).**

Pumped water **provides 33% of the total** supply. Pumped ground water serves several objectives such as supplementing canal irrigation supplies during critical summer and winter periods; irrigation water **supply** in areas not sewed by **canal** water, reclaiming salt affected **area and** lowering watertable. More **than** 475 000 private **tubewells** and 16000 public **tubewells** are reported to be in operation.

- ## Drainage system

Horizontal drainage is not developed extensively. Instead, vertical drainage by means of tubewells has been adopted causing a drop in water tables in large **parts of the** Punjab.

Country	Irrigated area damaged (Million ha.)	Share of irrigated land (percent)
INDIA	7	15
CHINA	5.4	10
USA	5.2	21
PAKISTAN	3.2	20
SOVIET UNION	2.5	12
TOTAL	23.3	

Table 1: Irrigated land damaged by salinisation in top five irrigation countries (from Postel, 1989, Tyagi, 1996).

C. SOIL SALINITY AND SODICITY IN PAKISTAN

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1. CAUSES, EXTENT AND CONSEQUENCES

a) Causes

Part of the Indian subcontinent, including the Indus Plain, was fonned from sediments transported by rivers into a shallow sea. The receding sea has left behind residues of salt, both in the soil profile (presence of gypsum horizon) and in the aquifer. In addition, minerals in parent rocks release significant quantities of salts into the soil solution during weathering. Under the prevailing arid and semiarid climatic conditions, salts released through weathering are not leached out of the soil profile (GHASSEM et. al., 1995). The salinisation which occurs naturally is called primary salinisation.

Secondary salinisation is related to the modern irrigation system ; it is the result of, either accelerated redistribution of salts in the soil profile due to high water table, or the use of insufficient water to leach the salts, or the use of groundwater for irrigation with high contents of salts. The water table has risen due to irrigation causing waterlogging and salinity problems (Awan and Latif in Ghassem et. al., 1995). However, on the area studied by IIMI, the watertable is reported to have gone down due to pumping from ground water. In the Chishtian Subdivision (see map, appendix I) the level of the water table is lower than 3 meters depth.

As a result, nowadays, irrigation with poor quality tubewell water is assumed to be the main cause of the salinisation processes.

b) Extent and evolution

Nearly one fourth of the 16 millions hectare irrigated in Pakistan arc reported as being saline (Ahmad and Chaudhry in Ghassem et. al., 1995).

c) Economic consequences

In 1988, it was estimated that the economy of the country suffered a loss of approximately 4.3 billion Rupees (US$ 300 million) annually in the upper Indus plain (North West Frontier and Punjab provinces) on account of decreases in farm production on soils slightly to moderately affected by salinity (Water and Power Development Authority, 1988).

Apart from the economic damage due to production loss, Pakistan invests a lot of money on projects to alleviate salinity problems

2.   THE DIFFERENT PERCEPTIONS OF THE SALINITY/SODICITY STATUS AND OF THE SALINISATION/SODIFICATION PROCESSES

Different perceptions of soil and water salinity/sodicity, of the salinisation processes and of the soil degradation can be distinguished in Pakistan. We will pay attention, **on** one hand, to the perception of the farmers, who directly face these problems, and, **on** the other hand, to the perception of scientists (Soil Survey of Pakistan, International Irrigation Management Institute, Agricultural University of Faisalabad, etc.) which carry out surveys or research **on** these topics.

a)   The farmer's perception

Farmers approach the salinisation processes by the observation of their effects **on** soil (degradation of the soil structure) and **on** plants (decrease of crop performance). For this, they use different indicators that were reported and analysed by Kielen (1996).

Soil salinity/sodicity indicators are based **on** physical soil characteristics. They relate to the soil surface colour[3], the presence of a surface crust[4], or the hardness of the soil. Sonic indirect indicators as the time period of water standing **on** the surface after irrigation are directly linked to soil degradation.

Water quality indicators are related to the effects of irrigation water **on** the soil. The famiers distinguish canal water quality which does not cause any **fonn** of salinity from the tubewell water which may often have effects on the soils[5].

Crop indicators are based **on** crop performance. Poor germination, irregular crop growth, stunted crop growth and yellow leaf bum are evidences of soil salinity and sodicity.

Farmers replace all of the degradation states in a global process and relate the changes in soil appearance and structure due to different irrigation, tillage and cropping practices.

b)   The scientific perception

Research programs that have been carried out were aimed at understanding the causes (relations between irrigation quality and salinity) and the effects of salinisation on soil and crops. Most of them were focused on the cliaracterisation of the states (salinity and sodicity). The different processes (salinisation, alkalinisation and scdification) have **not** been **so** studied.

Salinity and sodicity states are usually assessed by chemical indicators : tlie two widely used indicators are the Electrical Conductivity (ECe) and the Sodium Adsorption Ratio (SAR) of **an** extract of saturated soil paste extract prepared in a laboratory[6]. The degradation of the soil is sometimes quantified by the pH value measured in a laboratory on a soil paste. From these indicators, and referring

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[3] White surface color which is commonly associated to the presence of salts on the soil surface is called "Chitta Kalar" (white colour). Black colour on surface. which is supposed to be due to the organic matter dispersion at high pH level, is reported as Kala Kalar (black colour) when it is associated with a hard upper layer.

[4] The crust presence and hardness is assessed by indicators based on visible perception (presence or absence) or sound perception (changes in the sound of walking through a field after irrigation).

[5] The canal water is reported as excellent water quality which leaches the salt and gets the soil soft. The tubewell waters quality strongly depends on the tubewell location: it ranges from good quality to "water causing white soil surface" or "hard soil".

[6] These indicators are detailed in Part II

to the classifications based on these ones, the soils are classified in terms of their salinity (EC) or sodicity (SAR) level; the different classes are defined by threshold values.

Only the water and solute transport aspect of the salinisation processes have been studied. For this, a hydro-solute transport model (SWAP 93) was calibrated and validated on four sample fields monitored by IIMI (Smets, 1996). The geochemical processes have been slightly studied, but never taken into account in the modelling of the salinisation processes ; thus, the processes of alkalinisation and sodification based on geochemical processes (mineral precipitation, solute exchanges) have only been partly approached.

In conclusion, there are two different approaches of the same processes (salinisation processes), the same soil or water status (salinity, sodicity) and at the same level (field level). The farmer's one is based on soil physics (the degradations of the soil structure) whereas the scientific one is based on soil chemistry (chemical indicators) ; the connection between these two perceptions has **been** slightly established yet. Moreover, several studies have been focused **on** the soil or water salinity/sodicity status, but not **on** the processes; the geochemical processes have never been modelled yet.

D. OBJECTIVES OF THE STUDY

To improve the water management with regards to tlic salinity problems, it is necessary to cliaractcrise and understand the processes, the causes and the effects. In this purpose, the following objectives were defined for this study :

1. The characterisation of:

   - the geochemical processes in order to distinguish the different salinisation processes (neutral salinisation, alkalinisation, sodification) ; and

   - the soil degradation which may be caused by these processes and encountered **on** the fields and the relations between structural soil status and geochemical processes.

2. The relationships between irrigation water, salinisation process and soil degradation. Irrigation is the major cause of salinisation in the study area. The purpose is to connect the type of irrigation water quality with the processes of salinisation.

E. APPROACH OF THE STUDY

1. Identification **of** the different salinisation processes, of their effects **on** soils, and of the way to characterise them.

   This part is based **on** a literature review. It aims at making the distinction between the different salinisation paths by studying the geochemical processes, at reporting the most usual methods to cliaracterise them, and at analysing the consequence on soils. The purpose is to identify precisely the processes which occur in the study area in Pakistan and to define a methodology for this study to characterise the geochemical and physical processes (soil degradation).

2. Analytical and modelling characterisation **of** the salinisation processes **in** the study area and study of the effects of water quality **on** the processes .

The geochemical processes arc identified and quantified with the help of chemical soil analysis made from a large sample of soils collected both on cultivated and barren fields in the study area. The relevance of cliemical indicators to assess the processes is pointed out.

3. Characterisation of the soil degradations caused by the salinisation processes.

A characterisation of the soil degradation that can be induced by tlie salinisation processes is conducted. Some physical and chemical measurements are done and the relevance of indicators based either on physical or chemical soil characteristics is discussed. The relations between physical and chemical properties of the soils are then analysed.

4. Study of the relations between irrigation and processes.

In this last step, the effects of irrigation water, and specially the influence of the water quality on the processes are analysed.

First, only the water quality component is taken into account. A geochemical model, calibrated on I5 soil samples, is used to highlight tho salinisation hazardous of irrigation water. A gradual concentrating process of soil water, resulting of a mixing between initial soil water and a single irrigation supply, is simulated to follow the trend of the main chemical components in the solution and on the soil complex.

In a second step, a hydro-gcoclieniical model (including the water flow, solute transport and geochemical components) is used to assess the effect of irrigation practices (water quality, quantity, frequency of the supplies) on the salinisation processes along one year of cultivation.

The steps I, 2, and 3 are respectively detailed in the three main sections of the report The theoretical knowledge based on the literature review is presented at the beginning of each section.

SECTION I - CHARACTERISATION OF THE GEOCHEMICAL PROCESSES OF SALINISATION

In this part, the objective is to study the geochemical processes that might occur in irrigated or **not** irrigated soils in order to: on the one hand, to distinguish the different types of salinisation processes (neutral salinisation, alkalinisation and sodification) in the case of the soils of the Chishtian Subdivision and, on the other hand, to discuss of the relevance of chemical indicators to assess them.

Two main steps will be distinguished:

- first, the geochemical processes will be detailed and the chemical indicators will be presented. This part is based on a literature review; and

- then, a methodology of soil processes characterisation will be applied to the soils of the study area.

A. THEORETICAL KNOWLEDGE ON SOIL SALINISATION PROCESSES

1. DIFFERENTIATION BETWEEN THE SALINISATION PROCESSES

The differentiation between the neutral salinisation, the alkalinization and the sodification is based on a geochemical law of mineral precipitation (T-law) and a geochemical concept (The Residual Alkalinity) which allows the prediction of the evolution of alkalinity with concentration.

a) The Mineral precipitation

The concentration process of soil water is the first step for all types **of** salinisation processes: it may he caused by high evaporation rate (especially in the arid areas) and water absorption by roots. Consequently, some minerals precipitate in order of their **own** solubility; from the less soluble ones, (e.g. calcite, $CaCO_3$) to the most soluble ones (e. g. NaCl).

Two steps can be distinguished in the concentration process of a solution containing two ions A^+ and B^+:

- below the mineral saturation threshold: the two ions concentrate simultaneously following the progressive concentration of the solution; and

- at and over the saturation threshold: the ions precipitate together as follows:

$$A^+ + B^- \rightleftharpoons AB \text{ with } K_S = (A^+) \times (B^-) \qquad (1)$$
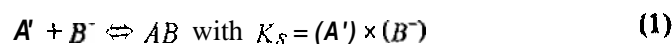
(A^+) and (B^-) are the chemical activities of A^+ and B^-
Ks: solubility product at equilibrium (constant temperature and pressure).

Then, the solution still concentrates, but the mineral is present. From Equation I, the activities of both elements cannot increase simultaneously (Ks is constant). Consequently, if the concentration of one mineral increases, the concentration of the second one decreases. This characteristic is known as the T-law.
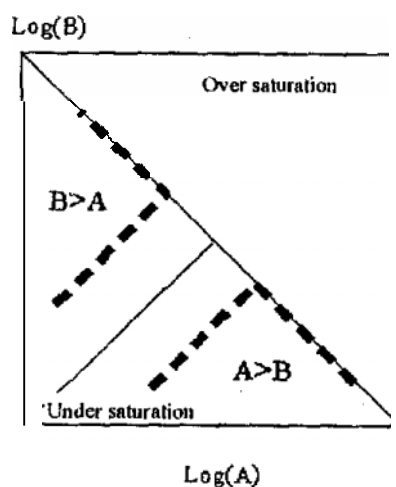
h B represent molality, (A) and (B) represent activities

Figure I-1: The T law: saturation of a mineral AB (from Marlet, **1996).**

Several minerals may be involved in the salinisation processes. Among them, calcite plays a major role because it is reported as the first mineral to precipitate in the soil concentration process. This property will first be explained by therdonynamic considerations and, then, the other minerals succptible to precipitation in the concentration process of the soil water will be listed.

(I)   The carbonate minerals

The main carbonate minerals involved in precipitation are listed below:

MINERAL	FORMULA	-log Ks (@ 25°C)
Rhodochrosite	$MnCO_3$	**11.13**
Siderite	$FeCO_3$	**10.89**
Calcite	$CaCO_3$	**8.48**
Aragonite (non stable)	$CaCO_3$	**8.34**
Magnesite	$MgCO_3$	8.24
Dolomite	$CaMg(CO_3)_2$	**17.09**

Table I-1: Mineralogy and solubility of some carbonates (thermodynamic data from Nordstrom et al., **1990).**

Regarding the solubility products, the minerals with a similar structure (all of them except dolomite) precipitate in the following order: rhodoehrosite, siderite, calcite, aragonite, magnesite.

- Siderite and rhodochrosite precipitate before the calcite but, in situ, these minerals are often present in very low quantity;

- Calcite precipitates as follows:

$$2HCO_3^- + Ca^{2+} \Leftrightarrow CaCO_3 + CO_2 + H_2O \qquad (2)$$
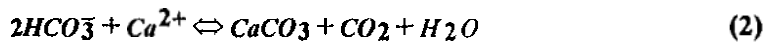
- Aragonite is less stable than calcite. Water equilibrium with aragonite is oversaturated for calcite so that aragonite dissolves and calcite precipitates;

- Magnesite precipitates when the solution is highly saturated in calcite; and

- Dolomite shows a high degree of ordering of Ca and Mg atoms which complicates its precipitation from aqueous solutions at low temperature.

In soils solution with high carbonate content, calcite precipitates as long as calcium is present. When calcium has disappeared , the solution become saturated for other carbonate minerals. As a consequence, calcite is considered by most of the authors as the main carbonate mineral in the salinisation process: other carbonate minerals are neglected.

This approximation can be criticised because:

- it assumes that the ion calcium is prevailing over divalent cations and especially magnesium. Nevertheless, it has to be kept in mind that some magnesium atoms may substitute for calcium in calcite. Resulting minerals containing calcite and magnesite are called Mg-calcite'. These Mg-calcites are far different from dolomite (which contains also calcium and magnesium) which is characterised by an organised structure. In most cases, Calcite is not a pure mineral.

- the solubility product depends on temperature, For each mineral, relationships between solubility product and temperature are different; as a consequence, some changes in temperature can modify the solubility products and, therefore, change the order of the precipitation between the minerals'. In semi-arid areas, temperatures higher than **25°C** is frequently encountered.

(2)   **Other minerals involved in the salinisation process**

In weathering conditions, other minerals may precipitate after the calcite.

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1 The Mg-calcite minerals split into the low Mg-calcites ($[Mg]<5$ mole %) and high Mg-calcite ($[Mg]>5$-30 mole %) (Appelo and Postma, 1995).

2 For calcite, Nordstrom el al. (1990) suggest the following relation between Ks and T:

$$\log Ks_{(T)} = -1228732 - 0.299444T + 35512.75/T + 485818\log T$$

NAME	FORMULA
Calcite	$CaCO_3$
Sepiolite	$MgSi_3O_6(OH)_2$
Gypsum	$CaSO_4.2H_2O$
Silica, chalcedony	SiO_2
Trona	$NaHCO_3.Na_2CO_3H20$
Magnesite	$MgCO_3$
Illite*	$Si_{3.5}Al_{2.3}Mg_{0.25}O_{10}(OH)_2K_{0.6}$
Kaolinite*	$Si_2Al_2O_5(OH)_4$
Paragonite*	$Si_3Al_3O_{10}(OH)_2Na$

Table **1-2**: List and formulas of the minerals suceptible to precipitation in the concentration process of fresh water (Appelo and Potsma, 1996; * Marlet, 1996).

b) The alkalinity

The alkalinity of a solution can be defined as *the sum of anions which may accept protons* (Bourrié, 1976):

$$Alkalinity = 2CO_3^{2-} + HCO_3^- + OH^- + S^{2-} + HS^- + H_3SiO_4^- + ... - H^+ \quad (eq/l) \qquad (3)$$

For most of the soil solutions, alkalinity is due to carbonate species HCO_3^- and CO_3^{2-} (Valles, 1985). The percentage of HCO_3^- of total CO_2 depends on the pH; between 6 and 10.3^3, HCO_3^- is dominant; for pH less than 8.3, only one percent of carbonic acid is present as CO_3^{2-}. In most of the soils, CO_3^{2-} can then be neglected for pH values below 10.3 (Appelo, 1996).

Combining this equation with the electroneutrality equation, alkalinity can then be deducted from the difference between the main cations and the main anions in the solution (Guillobez, 1989 in Marlet, 1996):

$$\textbf{Alkalinity} = Ca^{2+} + Mg^{2+} + K^+ + Na^+ - Cl^- - SO_4^{2-} + ... \quad (eq \; ll) \qquad (4)$$

By this formula, alkalinity can be deducted from the concentration in the main solutes that are determined easily in the laboratory,

c) The Residual Alkalinity concept

(I) Definitions

As described before, some minerals may precipitate in the concentration process. The Residual Alkalinity can be applied to the precipitation of each mineral.

The Residual Alkalinity is defined with reference to a mineral which may precipitate. This concept will be explained for calcite, calcite/sepiolite and calcite/sepiolite/gypsum, by the way of three examples: the Calcite Residual Alkalinity (CRA), the « Calcite Sepiolite » Residual Alkalinity (called Residual Sodium Carbonates, RSC) and the « Calcite-Sepiolite-Gypsum Residual Alkalinity (CSG-RA).

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[3] 6 and *10.3* refer, respectively, to the minus logarithm of the two dissociation constants of the carbonic acid (H_2CO_3).

(a)   The Calcite Residual Alkalinip

Referring to the T-law, when a solution is concentrated to the point that calcite precipitates, alkalinity and Ca^{2+} molality cannot increase together. Two different cases can then be distinguished:

- if the concentration in calcium $[Ca^{2+}]^{4}$ exceeds the alkalinity equivalents in the original soil solution, alkalinity decreases and $[Ca^{2+}]$ increases; and

- if alkalinity equivalents exceed $[Ca^{2+}]$ equivalents, alkalinity increases and $[Ca^{2+}]$ decreases.

The Calcite Residual Alkalinity (C-RA)is formulated as follows:

$$C - RA \; = CO_3^{2-} + HCO_3^- - Ca^{2+} \qquad (eq/l) \qquad\qquad (4)$$

(b)   The Calcite-Sepiolite Residual Alkalinity

The concept of residual alklinity can be applied to the precipitation of calcite and sepiolite. In this case, the Residual Sodium Carbonates (RSC) are used, which were first described by Eaton (1950). RSC is defined as:

$$RSC \; (eq/l) = CO_3^{2-} + HCO_3^- - Ca^{2+} - Mg^{2+} \qquad (eq/l) \qquad\qquad (5)$$

RSC assesses the balance between, on the one hand, the alkalinity and, on the other hand, calcium and magnesium.

(c)   The Calcite-Sepiolite Gypsum Residual Alkalinip

If calcite, sepiolite and gypsum can precipitate in the solution, the « Calcite-Sepiolite-Gypsum» Residual Alkalinity (CSG-RA) appears relevant, which is defined as:

$$CSG - RA \; (eq/l) = CO_3^{2-} + HCO_3^- - Ca^{2+} - Mg^{2+} + SO_4^{2-} \qquad (eq/l) \qquad\qquad (6)$$

(2)   Use of the Residual Alkalinity concept

The Residual Alkalinity is a conservative indicator; it means that its value is not modified by the precipitation of the mineral. It is used to predict the type of salinisation path that can occur in the soils.

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[4] $[Ca_2^+]$ represent the molarity of calcium (in mol/l or meq/l). (Ca_2^+) refers to the molality

- If the Residual Alkalinity is negative, tlie precipitation of calcite, sepiolite and other minerals causes a relative increase in calcium and magnesium molarities (T-Law) and a decrease of alkalinity: this is the neutral path of salinisation (merely called salinisation) (Clieverry, 1974; Servant, 1986). This process leads to saline soils. Nevertheless, mineral precipitation consumes Calcium and at high concentration levels (which occurs later in the process), the sodium becomes prevailing and is adsorbed on the soil complex: this is the sodification process.

- IF the Residual Alkalinity is positive, there is an increase in alkalinity and therefore of the pH: this is the alkalinization process called alkaline path of salinisation (Clieverry, 1974; Servant, 1986). Because of the continuous precipitation of calcite, which lowers the calcium concentration, sodium becomes prevalent over the calcium in the soil water. This imbalance leads to preferential adsorption of Na^+ on the soil exchange complex: this is the sodification process. It may lead first to sodic soils, which are not degraded but are characterised by high sodium content on the exchange complex. The structure of these soils is unstable and can be quickly degraded; then it forms alkali soils (see « effect of salinisation on soils», section II). In the literature, sodic and alkali soils are often mixed up; the sodic soils are often supposed as degraded.

These two salinisation paths and the different processes are presented on the following Figure 1-2.
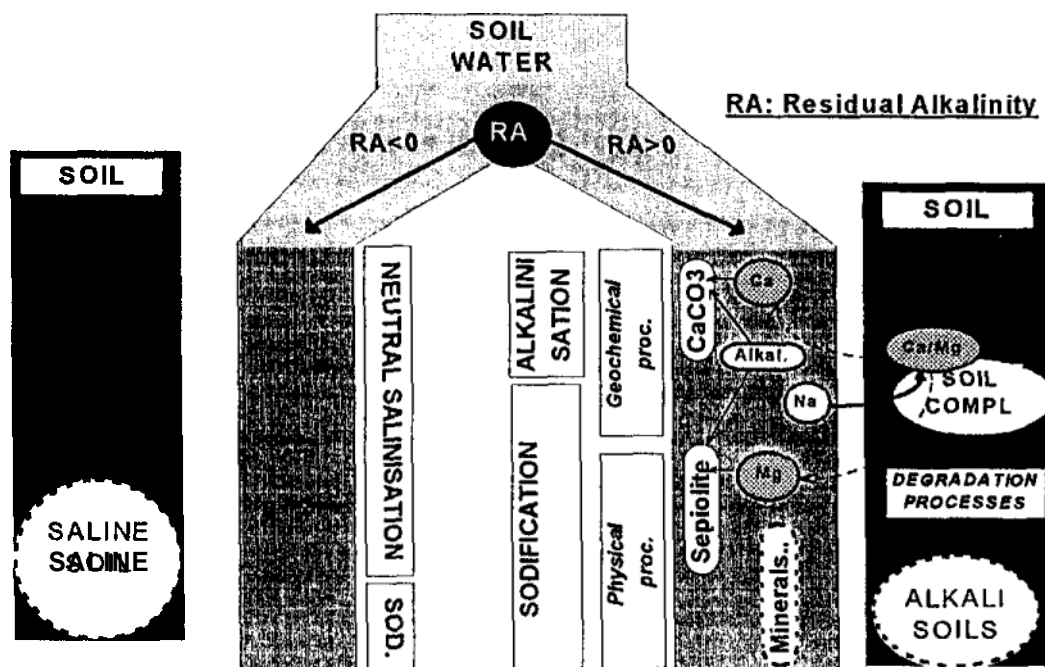

Figure 1-2: The different salinisation paths and processes.

(3) **Limits of the Residual Alkalinity concept**

This indicator is based on mineral precipitation and does not take into account the exchanges between soil solution and soil that may immediately induce some modifications in the soil solution composition. Vallès **(1985)** showed that these exchanges have to be considered when the Residual Alkalinity value is close to 0, because calcium and magnesium desorption can influence the sign of the C-RA, and thus, the salinisation paths.

Only carbonates are taken into account; other ions like S^{2-}, HS^{-} or $H_3SiO_4^{-}$ are neglected

2. NEUTRAL PATH OF THE SALINISATION

a) The process

The « neutral path of the salinisation » is called ((neutral salinisation » in this report. It occurs in soils during weathering when the Calcite Residual Alkalinity value is negative. This increases the concentration of dissolved salts in the soil water. Even though there is calcite and sepiolite precipitations, the calcium reamins prevailing over sodium: thus, there are only a few exchanges between calcium of the soil complex and sodium of the soil water,

b) The chemical indicators

(1) The Electroconductivity (EC)

The Electrical Conductivity (EC, in dSiemens/m) of a solution (surface and ground water, soil water) is widely used as an indicator to assess the level of concentration of the solution, and therefore of the salinity. For the soils, the Electroconductivity (EC_e) is measured from an extract of a saturated paste at 25°C (refer Appendix 3 for protocol).

EC is related to the ions which are present in solution; for EC values up to around 2 dS/m, the following relation is verified (Appelo and Postma, **1995):**

$$\sum anions = \sum cations(meq / l) = 10 \times EC(dS / m)$$

(7)

(2) The Total Dissolved Solids (TDS)

The Total Dissolved Solids (TDS in $mg.l^{-1}$) is also an indicator of the concentration of a solution. It is calculated from the residue on evaporation ,determined by evaporating an aliquot of water to dryness in a dish on a steam bath followed by heating the dish and residue in an oven for one hour at 180°C.This measurement is widely used as it does provide a measure of the total salt load that may be derived from various sources.

Some authors mention relations between EC and TDS (Tanji et al., **1975,** Al Jaloud and Hussain, **1992).**

3. ALKALINE PATH OF SALINISATION

a) The process

Alkalinization results from the concentration of the soil solution when the Residual Alkalinity is positive. It is characterised by an increase of alkalinity and consequently of the pH of the soil solution. It leads to a decrease of the calcium and magnesium concentration in the soil water (T-law).

b) Chemical indicators

(a) The alkalinity

The definition and the way to calculate the alkalinity has been previously presented; it can be obtained either by titration of the bicarbonates, or calculated as a difference between the cations and anions (Equation **4).** In both of the cases, the values obtained in the laboratory can differ noticeably from the real values in situ because:

- when the soil solution is brought to the surface for sampling, it is exposed to physical and chemical conditions which are different from those in situ. Alkalinity is particularly sensitive to changes in carbon dioxide concentration. In the soil conditions, the pressure in Carbon Dioxide (ranging from $10^{-3.5}$ to $10^{-1.5}$ atm) is higher than in the air $(pCO_2=10^{-3.5}$ atm$)^5$. Furthermore, degassing of CO_2 may provoke calcite precipitation (Equation 2) (Suarez, 1987), and consequently, a decrease in alkalinity.

- wetting of the soil samples in the laboratory induces dissolution of minerals. As a consequence, laboratory analysis may provide some overestimated alkalinity values.

(b) The Residual Alkalinity

This ((concept» has already been presented previously, which allows for the distinction between the different paths of salinisation. It can also be used as an indicator to evaluate the stage of the alkalinisation process; the more C-RA is positive, the more alkaline is the soil. The limits have already been presented.

(c) pH indicator

pH is traditionally measured in an extract of saturated soil paste (see the protocols in Appendix 3). The use of this indicator is hazardous because it highly depends on the conditions of measurement for the same reason as for the alkalinity.

The conclusion can be reached that pH and alkalinity can be used carefully as indicators and discussed in respect of the protocol (sampling, time period between collection and laboratory analysis). The Residual Alkalinity is invariant with respect to mineral dissolution/precipitation and, thus, is not sensitive to these problems caused by the experiments.

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[5] In the soil, and specially within the root zone, biochemical processes (root respiration, organic matter degradation) produce CO_2.

4.   THE SODIFICATION PROCESS

a)   The process

Sodification is a process of exchange between sodium present in the soil water and divalent cations (mainly Ca^{2+}) adsorbed on the exchange complex. It occurs when the sodium is present in higher concentration than the divalent one. Three main causes can result in sodification: alcalinisation, neutral salinisation (if the soil water has reached a high concentration level) and irrigation with high concentrated water. A high amount of sodium on the exchange complex may negatively affect the soil structure and aggregate stability (Ahu-Sharar et al., 1987a). Unstable soil may then he degraded by physical and chemical processes. This point is studied in Section II.

b)   Indicators of soil sodification

(a)   The Sodium Adsorption Ratio (SAR)

The sodium absorption ratio is defined as follows (USSL, 1954):

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+}+Mg^{2+})/2}} \tag{8}$$

SAR In $(meq.l^{-1})^{0.5}$, Na^+, Ca^{2+} and Mg^{2+} in $meq.l^{-1}$

This ratio appraises the relative proportion of Na^+ over divalent cations $(Ca^{2+}$ and $Mg^{2+})$. These three cations are the main elements involved in the exchanges between soil and soil water.

The SAR is calculated from laboratory analysis using an extract of a soil saturated paste or of a soil dilution (see protocol Appendix 3); it requires a simple and low-cost analysis of water. SAR is also often used directly or indirectly to assess sodicity in the soil profile.

The use of SAR as an indicator for soil sodicity presents some limitations:

- it assumes a direct relationship between soil water sodicity and soil sodicity. It does not take into account the soil conditions (texture, structure). Nevertheless, it can be used to assess indirectly the percentage of sodium on the soil complex (Exchangeable Sodium Percentage).

- the magnesium is taken into account similar to the calcium. This assumes that these two cations have the same geochemical behaviour. This point is controversial: some authors have shown that, contrary to calcium, adsorption of magnesium leads to degradation of the soil structure (Boulaine, 1957, Girdhar, 1994)) and may cause clay dispersioii (Shainberg et al., 1988). Its influence seems to be intemiediatc between Na and Ca (Azib, no date).

For irrigation water quality, there exists some other formulations of the SAR taking into account the environmental conditions of the soil surface on which the water is applied. Suarez (1981) proposes a SAR adjusted to the pressure of CO_2, the alkalinity, and the concentration level of water when it is in contact with the soil:

$$adj. R_{Na^+} = \frac{Na^+}{\sqrt{(Ca_x^{2+}+Mg^{2+})/2}} \tag{9}$$

Na^+, Mg^{2+} : calcium and magnesium concentrations in the irrigation water (meq/L);
$Ca^{2+}x$: calcium concentration adjusted to water concentrations when it is in contact with the soil (EC). to the ratio $HCO3^-/Ca^{2+}$ and to the partial pressure in CO_2 at the soil surface.

Jaloud et Hussain (1993)remarked that the adj. $Rna+$ and SAR are highly correlated,

This approach implies a source of calcite in the soil, but no precipitation of magnesium **as** sepiolite; this assumption is to be discussed.

Ayers and Westcots (1985)suggest another relation:

$$adj. \ SAR = SAR\left[1 + (8.4 - pH_c)\right] \qquad (10)$$

with $pH_c = \left(pK_2 + pK_{calcite}\right) + p\left(Ca^{2+} + Mg^{2+}\right) + p \ HCO_3^-$

p is the decimal logarithm;
K_2 second dissociation constant of carbonic acid;
Kc sniubility product of calcite;
The concentrations of Ca^{2+}, Mg^{2+}, and HCO^{3-} concentrations are expressed in meq/L;
pHc: theoretical pH calculated in contact with calcite in equilibrium with the pCO_2.

In this last relation, the magnesium **is** taken into account.

(b)   *The Exchangeable* Sodium Percentage *(ESP)*

The most frequently used indicator to assess soil sodicity is the Exchangeable Sodium Percentage (ESP). The **ESP** gives the proportion of sodium on the exchangeable complex,

$$ESP = 100Na^+/CEC \qquad (11)$$

Na^+ In eq/l;
CEC (eq/l) refers to Exchangeable Cationic Complex.

This formulation includes the type of soil by the way of the CEC. It can be calculated from the composition of the soil exchange cationic complex; for this, some complicated analyses are required. That is the reason why the ESP is usually calculated from the SAR value by the help of empirical relations (USSL, 1954,RAO and al., 1968,CRUESI, 1970).The **USSL** (1954)proposes:

$$ESP = 100 \frac{0.0147 SAR - 0.0126}{1 + (0.0147 SAR - 0.0126)} \qquad (12)$$

This relation assumes that there is a direct relation between the soil solution and the soil matrix. It does not take into account the soil conditions (texture, structure). These types of relations are criticised by several authors.

An **ESP** value of 15 % is generally admitted **as a** threshold value **for** sodic **soils** degradation (U. S. Salinity Laboratory, 1954, Servant, 1975). Over this value, the capacity of soil swelling increases proportionally to the **ESP.** The structure becomes very unstable. Such soil can then be quickly degraded when in contact with **a** soil water solution having **a low** concentration of salts.

Some authors modulate the threshold value as a function of soil or soil solution characteristics:

- the ESP threshold value depends on the soil texture: the Cationic Exchange Capacity (CEC) increases with the clay proportion in the soil. Ramadan (1991) verifies on Indian soils that ESP is correlated to clay percentage. ESP depends also on the types of clay minerals. Richards (1954), Oster and Shainberg (1981) show that the dispersion of clay minerals occurs at lower ESP levels for illites than for montmorillionites. Richards (1954) suggests, respectively, an ESP value of **5%** and 13%.

- the ESP threshold value depends **on** the concentration of tlie soil water: soil degradation can occur even **at** low ESP values in dilute solutions (Quirk and Scofield, 1955; Shainberg et al., 1981). Crescimanno et al. (1995) show that ESP values ranging from 2 to **5** %, associated with low concentrations of solution causes a reduction of hydraulic conductivity by 25%, or even more. Mc hityre and Shofield (1955). Rengasamy et al., (1984) and Agassi et al., (1985) propose **an** ESP>5 % to define a sodic soil irrigated with fresh water.

Some recent investigations tend to show that soil behaviour at increasing ESP appears **to** be a continuum. According to Sumner (1993), the establishment of a critical ESP threshold may be very arbitrary because the characteristics exhibited by the so-called sodic soils are simply the upper end of a continuum of behaviour that extends across tlie full range of Na saturations, being increasingly dependent **on** reduced concentration of tlic soil solution. While in pure clay water systems, the existence of a critical ESP can be clearly shown, in actual soils, a multitude of factors may influence the relationship between ESP **and** other soil physical parameters, and mask the critical value (So and Aylmore, 1993). On disturbed clayey sample soils, Crescimanno et al. (1995) **show** that **no** critical ESP threshold can be found.

The ESP appears **as** a relevant indicator to assess the soil sodicity: it is better if it is calculated directly from the composition of the soil complex and not from the SAR of the soil water. The existence of a ESP threshold for soil degradation is under question. It is may be necessary to take into account the concentration of the irrigation water to predict the degradation.

B. CHARACTERISATION OF THE GEOCHEMICAL PROCESSES IN THE PAKISTAN CONTEXT

1. METHODOLOGY

There is a need to cliaractcrise the geochemical processes that can be found in the soils of tlie study area in order to model them later (Section 111).

This part is based on analytical data obtained from two sets *of* soil samples. Tlie soils were sampled at tlie same time. Thus, it is not possible to cliaractcrise the temporal evolution of the salinisation processes. Moreover, it does not appcar relevant to consider that all of tlie soils are the result of the same process of salinisation. Indeed, there is a great variability in tlie types of irrigation water quality; the soil characteristics are not only determined by soil water concentration (caused by soil weathering) but also by a mix of irrigation quality which may dissolve or precipitate tlic minerals and, thus, may change the soil chemical cliaracteristics (soil water and soil complex).

In consequence, the processes will not be studied with time. but tlic analysis of tlie equilibrium of each sample will provide some information to identify the salinisation processes.

In a first step, tlic mineral will be identified from a detailed data set of 15 *soil* samples (see Appendix 7). The saturation of the solution with respect to calcite and gypsum precipitation will also be verified on a larger data set of 100 soil samples [6] (see Appendix 8). The protocol of tlic experiments is presented in Appendix 3.

In a second step, tlie concentration values in tlie different components of tlie soil water will be interpreted with respect to the equilibriums between the minerals and soil water.

2. CHARACTERISATION OF THE MINERALS

(1) Identification of tlic minerals

Charts of saturation of tlic soil water with regard to the precipitation of calcite, sepiolite, gypsum, illite and paragonite arc represented here. The composition of tlic solution is provided by detailed laboratory analysis on soil dilutions (1:1, 1:5, 1:10, 1:20). The activity of tlie different species is calculated by tlie model AQUA (Vallès and DeCockborne, 1992) from tlic molarity *of* the species present in tlie solutioii. The pressure in CO_2 is calculated from tlic alkalinity (carbonates and bicarbonates measured in the laboratory) and pH.

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[6] These samples were collected in the Chishtian Subdivision by the Soil Survey of Pakistan in November 1995 (SSoP, 1995).
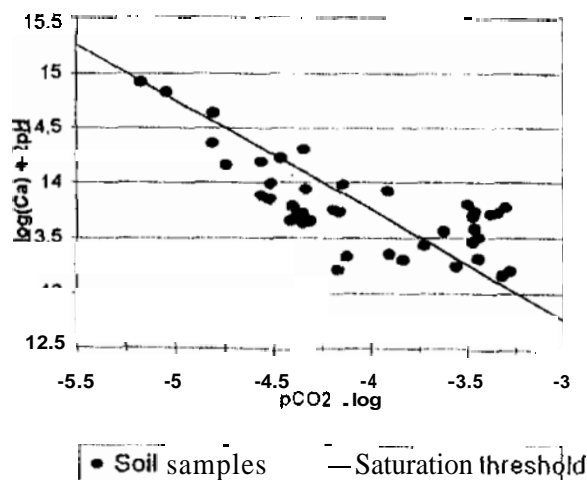
(a)   Calcite (CaCO₃)

Figure **1-3:** Saturation chart of calcite.

Overall, the soil samples show a chemical condition for calcite precipitation: some of them are slighty oversaturated, some others undersaturated. As it was said before. the solubility of calcite is low and this mineral precipitates even at low concentrations of the soil water, the Electrical Conductivity of the samples presented here ranges from 0.3dS/m to 2.9dS/m and is 5.2 for one of them.
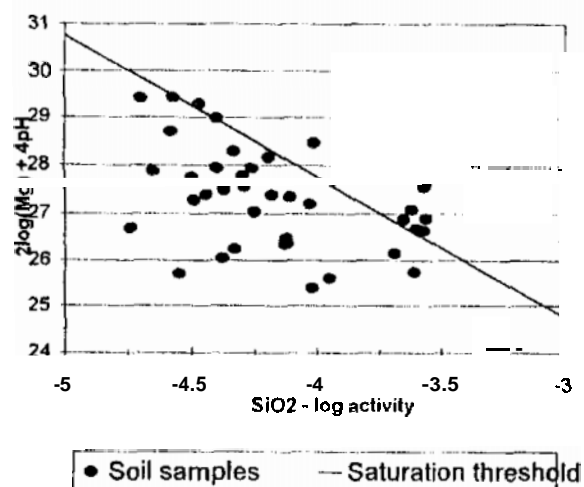
(b)   Sepiolite (MgSi₃O₆(OH)₂)

Figure **1-4:** Saturation chart of sepiolite.

This mineral is used to explain tlie absorption of the magnesium. The niagnesium is partly absorbed by the Mg but also by silicates containing some aluminium whose concentration in soils is difficult to measure. For this reason, the sepiolite. which is reported as precipitating in sequence of soil weathering, is used even though other Mg-minerals may also precipitate.
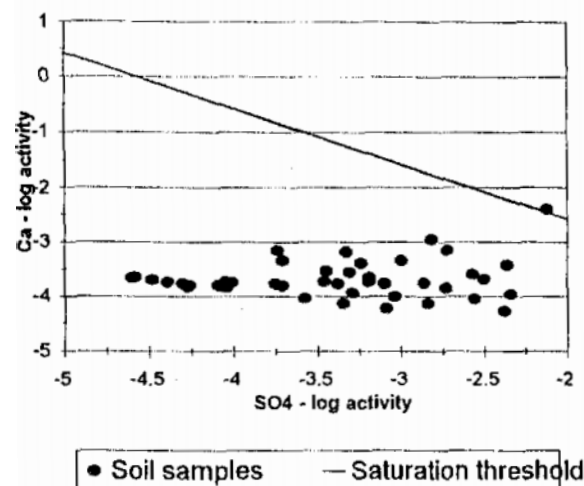
(c)   Gypsum (CaSO₄)

Figure **1-5: Saturation chart of gypsum.**

All the soils, but one of them, are quite undersaturated in relation to gypsum precipitation. It shows that at low concentration values, gypsum may not precipitate. One single point reaches the saturation threshold; the Ec value (dilution 1:1) is of 5.1 dS/m. This would imply that either some gypsum was applied on this field (which would change the chemical equilibrium and would not be a result of a concentrating process) or there is gypsum precipitation at high concentration.

The concentrations value in magnesium (7.6 meq/l), potassium (4.5 meq/l), sodium (35.6 meq/l) and chlorides (11.4 meq/l) are widely higher than for the other samples. The RSC is negative whereas the Calcite-Sepiolite-Gypsum Residual Alkalinity is positive: thus, the second assumption appears relevant. This should be confirmed on another data set with a wide-range of soil water concentrations.

(d)   *Illite $(Si_{3.5}AL_{2.3}Mg_{0.25}O_{10}(OH)_2 K_{0.6})$*
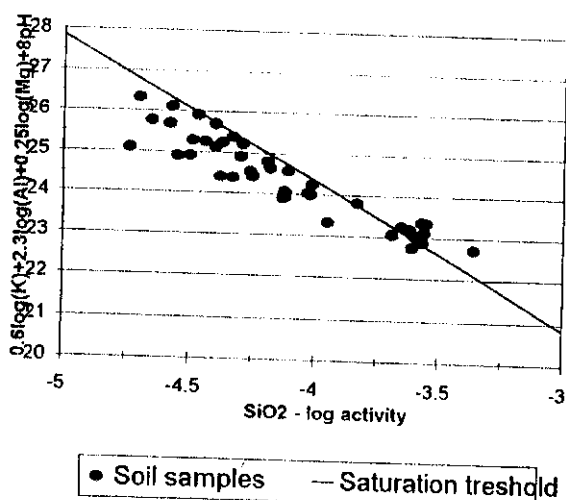

Figure I-6: Saturation chart of illite.

The calculation of the activity of aluminium was made taking into account an equilibrium between the illite and the sepiolite (Marlet, 1996). The trend of the soil samples is nearly parallel to the saturation line, which means that the mineral(s) which may be involved in the process may have a similar composition as the silica.

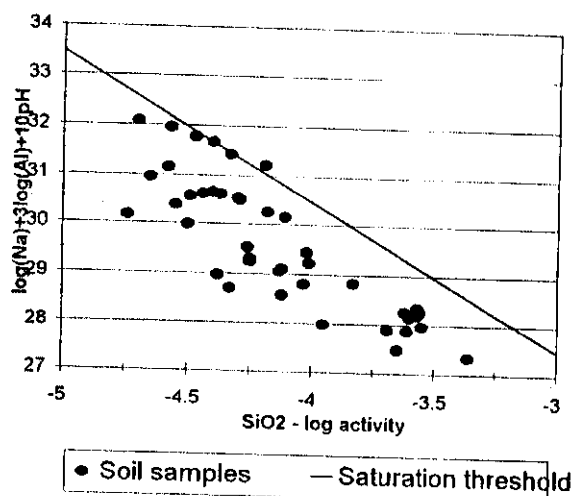(e)   *Paragonite($Si_3Al_3O_{10}(OH)_2Na)$*

Figure I-7: Saturation chart of the paragonite.

The calculation of the activity of aluminium was made taking into account an equilibrium between the paragonite and sepiolite (Marlet, 1996). Most of the authors assume an absorption of the sodium by a clay mineral. However, this mineral is not clearly identified. The choice of the paragonite is commonly made. The trend of the soil samples is similar to the one for the saturation line; this indicates that the composition of minerals involved in the process may be close to that of the paragonite.

(2)   Validation of the choice of minerals

In this part, the saturation level of the soil water in calite and gypsum are analysed on a data set of 100 soil samples collected by the Soil Survey of Pakistan in November 1995, including soil more concentrated than in the previous case. The concentration values in the main component are provided by chemical analysis on an extract of saturated paste (see Appendix 3).

The chemical activities were calculated by AQUA. For the calculation of the activities, the concentration in potassium, which was not available in this data set, was taken as 0.2 meq/l for concentrated soil water and 2 meq/l in the other cases; this approximation is based on the study of chemical analysis, including potassium concentration, that were made on 15 soil samples which have just been presented in the previous part. The concentration in Ca+Mg was divided up similarly between calcium and magnesium.[7] The pH measured in the field was taken as an input for this model

The concentration in silica was not available: thus, the saturation in sepiolite, illlite and paragonite are not studied here.

The samples are split up into two groups in function of the sign of the RSC value. As was seen before, this indicator is widely used and allows the distinction between the neutral salinisation process and the alkalinisation process (while gypsum does not precipitate). Thus, it appears interesting to study these two cases separately.
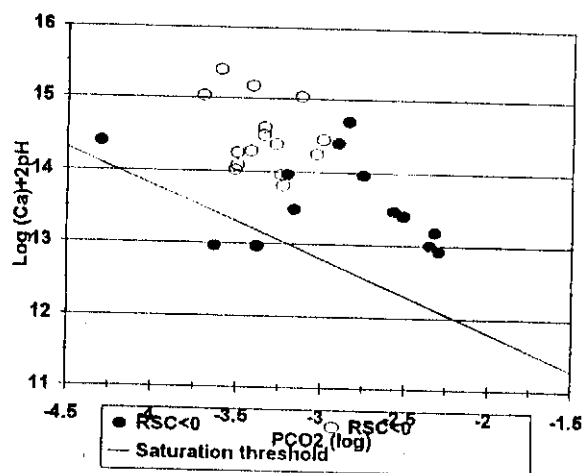
(a)   The Calcite

Figure I-8: Saturation chart of calcite.

Both in the case of RSC positive and negative, the soil samples are oversaturated in calcite.Thus, the precipitation of calcite occurs at low concentration values of the soil water. This oversaturation is an evidence of non equilibrium of the soil water and the minerals when the measurements were made: the extraction might occur too early.

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[7] This is approximated from the data set of 15 soil samples (See Appendix 7).

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