SOME CHARACTERIZATION STUDIES

OF SALT AFFECTED SOIL MATERIAL

CONTAINING SODIUM ZEOLITE

by

Nazmi Oruc

A Thesis Submitted to the Faculty of the

DEPARTMENT OF AGRICULTURAL CHEMISTRY AND SOILS

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 6 6

STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at the University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the library.

Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgement of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in their judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: _____

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

_____   _____1/18/66_____
        Stanley Walter Buol   Date
Assoc. Professor of Agricultural
    Chemistry and Soils

ACKNOWLEDGEMENT

TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Exchangeable-sodium percentages of over 100 were found in some salt affected Turkish soils. Also Gothard clay loam soil from southern Arizona was found to release Na^+ even after being saturated with Ca^{++}.

X-ray diffraction techniques were employed to determine the presence of sodium zeolites, namely analcime, thomsonite, stilbite, pectolite, chabazite, and natrolite, in salt affected soils of (Typic Natrargids) from Turkey, and Arizona. Analcime was found to be the only sodium zeolite found in the soils studied.

The replacing power of divalent cations Mg^{++}, Ba^{++}, Ca^{++} and Sr^{++} and monovalent cations K^+ and NH_4^+ in analcime was studied. A geological sample of analcime, the Turkish soil (Profile 1, 0-15 cm. layer) and a Na^+ free Red Desert soil (Typic Haplargid) were repeatedly washed with $1 \underline{N}$ solutions of these cations. The amount of released Na^+ was determined after each of seven washings. Washings with $MgCl_2$, $BaCl_2$, $CaCl_2$, and $SrCl_2$ solutions released approximately the same amount of Na^+. The amount of released Na^+ sharply decreased after two months of saturation with solutions of divalent cations. On the other hand K^+ and NH_4^+ released as much as three times more Na^+, especially from the analcime than

did the divalent cations. There was no sharp decrease in the amount

of released Na^+ in analcime and in the Turkish soil even after two

months of saturation with K^+ and NH_4^+ solutions.

INTRODUCTION

Adsorbed (exchangeable) sodium is widely recognized as an important constituent of the alkali soils in arid and semiarid regions. As is well known, the properties of these soils are usually influenced markedly by the relative amounts of the different adsorbed cations present (32).

Experience has shown that the determination of exchangeable bases, especially in soils of arid regions is not precise owing to the fact that the salt solutions employed for extraction, tend to dissolve various soil minerals and thereby bring bases into solution, which are not truly exchangeable. Therefore, it is to be expected that values obtained for the exchangeable sodium contents of saline and alkali soils will vary with the nature of the salt solution and the extraction procedure employed in making the determination (8)(28) (5).

Difficulties are frequently encountered in the determination of exchangeable sodium in salt affected soils. For example, it is not uncommon to find that the exchangeable sodium exceeds the NH_4OAc [1] exchange capacity by substantial margins (4)(24).

---

[1] NH_4OAc is used exclusively in this thesis as a notation for CH_3COONH_4.

1

Anomalous behavior of some salt affected Turkish and Willcox, Arizona soil samples with respect to high exchangeable-sodium percentages indicates that a great deal remains to be learned about cation exchange properties and the nature of the cation exchange material in these soils.

There is some evidence (16)(24) which indicates that the extraction of alkali soils with an excess of 1 $\underline{N}$ NH_4^+ solution may remove appreciable quantities of Na^+ in addition to that which is exchangeable and water soluble. Knowledge presently at hand regarding exchange properties and exchange materials do not explain the anomalous behavior of these soils. All indications suggest that these particular soils contain mineral components quite different from the recognized mineral species common in most soils.

Certain alkali soils have been found to contain noticeable quantities of a zeolite mineral, analcime[2] ($NaA \, l \, Si_2O_6H_2O$) (16) (1) (29). It is suggested that the zeolite, which has probably formed in these soils by recombination of Si^{+4} and Al^{+3}, and very probably other unusual compounds that may exist in strongly alkaline solutions,

---

[2]Analcime (Analcite was disapproved as the mineral name by a British-American minerological committee on nomenclature.) In this thesis analcime is used exclusively, except in references where the term analcite was used by the authors.

is responsible, at least in part, for the unusual properties of these soils (16).

The primary concern of this thesis is to determine a reason for the anomalous behavior of the problem soils by using x-ray diffraction techniques in examining the clay fractions for analcime. Some of the cations like K^+, NH_4^+, Mg^{++}, Ba^{++}, Ca^{++}, and Sr^{++} were also tested to determine the exchange rate of each cation against Na^+ fixed in analcime.

LITERATURE REVIEW

Difficulties in the determination of the exchangeable cations have been known since Way (33) first observed the property of soil to adsorb cations.

In 1930, Chapman and Kelley (8) discussed the available methods for, and the errors involved in, the determination of the exchangeable cations. They concluded that the determination of the exchangeable cations is complicated by the fact that various kinds of soil substances react with extraction solutions, and such constituents are probably most important in relatively young soils of arid and semi-arid regions.

Schollenberg and Simon (28) pointed out that the determination of exchange capacity and of exchangeable cations between a soil and a salt solution is not very precise in a quantitative sense because of the slowness in attaining equilibrium between coarse material particles in the soil and the solutions, and the indefinite nature of this equilibrium. The possibility of other reactions with colloidal substances in the humus-silica-sequioxice-base-acid-salt solution system were considered for the indefinite nature of this equilibrium.

Bower et al. (5) pointed out the difficulties involved in the determination of exchangeable cations in saline and alkali soils. These

difficulties arise from the presence of calcium and magnesium carbonates, soluble salts, and from the slow permeability of solutions and alcohols in soil materials. Solutions generally used for extracting replaceable bases from soils, dissolve all or most of the soluble salts and large amounts of Ca^{++} and Mg^{++} carbonates, if present. Consequently it becomes necessary to determine the soluble cation contents independently and to correct the exchangeable cation analysis, by substracting the soluble cation content from extractable cation content.

Kelley (16) criticized the cation exchange capacity determination method suggested by Bower et al. (5). According to Kelley their method (Bower et al.) can hardly give accurate results with all alkali soils for two reasons: "(a) Many alkali soils are much more alkaline than pH value of 8.2, hence their content of adsorbed cations is likely to exceed that held at pH value of 8.2 (b) It is practically certain that not all adsorbed Ca^{++} and Mg^{++} can be replaced by 1 N NaOAc".[3] By citing the work of Osthaus (21), Kelley (16) stated that several samples of montmorillonite still contained significant amounts of exchangeable Ca^{++} and Mg^{++}, after having been leached with 1 N NaOAc.

---

[3] NaOAc is used as a notation for CH_3COONa.

In the past 15 years, several workers in the United States have suggested that soils of arid regions, particularly those having high pH values, may contain Na^+ compounds or minerals which are insoluble in water, but which dissolve or decompose upon extraction with salt solutions such as NH_4OAc.

Bower (4) observed that a number of alkali soils, examined at the Salinity Laboratory in Riverside, California, exhibited significi-cantly greater exchangeable-sodium than cation exchange capacity when measured by the NH_4^+ adsorption method. He found that the extraction of alkali soils with excess of 1 $\underline{N}$ NH_4OAc solution may remove signifi-cant amounts of Na^+ from the soil in addition to that which is exchange-able and water soluble.

Overstreet et al. (23) stated that in other research, to be reported in another place, the calculated values for exchangeable-sodium percentage exceeded 200 per cent as a result of an error in the determination of the cation exchange capacity by using NH_4^+. This error was attributed to the fact that this particular soil possessed an usual capacity for the fixation of NH_4^+ ion in a difficultly exchangeable form.

Kelley (16) reported that certain alkali soils of San Joaquin Valley in California, were found to contain noticeable quantities of sodium zeolite namely analcime. The sodium zeolite as described by

Kelley is an alumina silicate, not commonly present in normal soils and differs from highly reactive zeolites, such as chabasite, scolecite, stilbite by undergoing cation exchange much less readily. He thought that chemically alkaline solutions are very good solvents for SiO_2 and Al_2O_3 and the products formed would be expected to combine in different ways depending on the conditions. Some unusual properties of alkali soils were related to the presence of analcime, which was formed by the recombination of soluble Si^{+4} and Al^{+3}, and very probably to other unusual compounds which do not exist in most other soils.

During the reclamation of nonsaline-alkali soils of Fresno in California, Overstreet et al. (24) reported that exchangeable-sodium percentage values occasionally may exceed 100 per cent. They concluded that there are evidently some Na compounds or minerals present in these soils, which are insoluble in the saturation extract but which are dissolved or decomposed upon extraction with $1 \underline{N}$ neutral NH_4OAc.

Babcock (1) found the evidence of Na^+ fixation in salt affected soils by using isotopic Na^{22}. He observed that adsorbed Na^+ in salt affected soils may be replaced with isotopic Na^+ but not with Ca^{++} and NH_4^+ ions. He also pointed out that a solid form of Na may be present in these soils, which dissolves in normal extracting solutions but not in water.

X-ray analysis of the soil samples collected from Magna, California by Schulz et al. (29) revealed that the Magna soil contains about 35 per cent of the zeolite mineral, analcime, in addition to the usual clay minerals.

The presence of zeolites and possibly other unknown Na bearing materials in salt affected soils may very well contribute to the observations that suggest alteration of layer silicate minerals in certain salt affect soils. Kelley (18) mentioned that Antipov and his coworkers in 1937 announced the synthesis of a new clay mineral called geodrizite, as a major component of the colloids in certain Russian alkali soils which showed so-called Solonetz morphology. Since they found that the very thin eluvial horizon above and the horizon below the horizon containing the zeolite, did not contain geodrozite, they concluded that the chemical conditions, such as high pH and Na^+ saturation, which prevail in that horizon of the solonetz soil, are responsible for the formation of geodrizite.

During the work on the colloidal constituents of American alkali soils, Kelley et al. (18) found that the inorganic colloids of several alkali soils gave indistinct x-ray diffraction lines, indicating that the clay minerals had been altered or the presence of amorphous material or both. They suggested that these soils may possibly contain fine grained substance of permutite like nature, formed in these soils,

under the influence of chemically alkaline solutions.

As a result of the examination of the clay distribution in a solodized-solonetz soil profile of the Sacramento Valley, California, Whittig (34) suggested the possibility of clay formation in situ, within the B horizon. Highly alkaline conditions during solonization and early solodization would be suitable to solubilization of Si^{+4} and Al^{+3}. During the downward movement of these soluble substances into the zones of higher electrolyte content, they may have been combined with cations, forming secondary minerals.

Although analcime has been recognized in the chemistry of salt affected soils only very recently, geologists have worked on the analcime since the last decade of the 19th century.

Analcime was found to be associated with volcanic mineral fragments in the Green River formation by Bradley (6). He concluded that the analcime was formed in place on a lake bottom as a result of the interaction between salts dissolved in the lake water, and the dissolution products of volcanic ash which fell into the lake.

During the investigations near Wikiup, Arizona, Ross (26) suggested that playa deposits often contain beds of exceedingly fine grained or colloidal clay and it is possible that reactions between colloidal hydrous aluminum silicates and Na salts may have produced analcime. Additional studies by Ross (27) in this area showed that

analcime was evidently derived from glassy volcanic ash. It was

proposed that the material deposited in the playa and undoubtedly Na

salts were the factors that resulted in analcime rather than bentonite

which is the normal product when glassy volcanic ash alters.

The formation of analcime in the Popo Agie was explained by

Keller (15) to be originated from the reaction of hydrous alumino

silicate clay minerals with Na^+ rich waters of a large interior marsh

lake. Since no evidence of volcanic material was found, it was suggested

that the derivation of Si^{+4} and Al^{+3} is probably from hydrous alumino

silicate clay minerals.

As a result of investigations of the mineral assemblages of

the Green River formation, Milton and Hans (20) reported that the

analcime can easily form at the interface between saline and tuffaceous

beds or more commonly during recombination by contact of alkali

solutions with siliceous materials containing the necessary amounts

of Al^{+3}.

Analcime and other authigenic silicate minerals were found in

samples of clay and tuff in recent sediments of Searles Lake,

California (13). It was suggested that strongly aklaline solutions which

saturate the surface and sub-surface sediments, and supply Na^+,

K^+, and B^{+3} can be responsible for the formation of authigenic

minerals. Solutions of quartz plagioclase and montmorillonite most likely supplied the Si^{+4} and Al^{+3} for authigenic silicates in clays.

The x-ray studies of the mineral associations in Stanley-ville, Congo by Vernet (31) have revealed that montmorillonite in addition to illite, was accompanied by analcime. He concluded that analcime generally formed from the products of the alteration of materials of volcanic origin under the chemically alkaline conditions.

The origin of the authigenic zeolites was reviewed by Pipkin (25). He virtually excluded the diagenesis of volcanic glass or direct precipitation of alumino silicate gels to form analcime. It was suggested that diagenetic destruction of kaolinite to form analcime occurred in Willcox, playa Arizona for the following reasons:"(a) Kaolinite is unstable in alkaline environment and all but few of the 200 pH values obtained, fell between pH 9.0-9.5; (b) Kaolinite is forming in minor amounts in the same area today; (c) High pine pollen counts in the cone interval 6-69 feet are indicative of higher precipitation and conditions more favorable for kaolinite genesis".

During the mineralogical investigations in the Pittsburgh coal mine, analcime has been found in sedimentary rocks by Foster and Feicht (10). They proposed that in all cases analcime has been

formed under alkaline conditions and decomposed by acid. It is suggested that alkaline solutions containing Na^+ reacted with clay to form analcime.

The structure of analcime as a member of the zeolite family of minerals has been worked out by several investigators in great detail over the past 40 years.

Investigations of the structure of analcime by Gruner (12), Taylor (30), Bragg (7), and Beattie (3) can be summarized as follows. Analcime possesses a definite composition of $NaAlSi_2O_6H_2O$ and its external form displays cubic holohedral unit cell with an edge of length 13.68 $\pm$ 0.04$\overset{o}{A}$. The main structural feature being the presence of diagonal channels which do not cross each other, and are surrounded by six fold rings of silica tetrahedra. Each unit cube contains 16 molecules of $NaAlSi_2O_6H_2O$ and is based on an arrangement of linked tetrahedra of oxygen ions. The negative charge of the framework is balanced by Na^+. Each Na^+ ion lies between four oxygen atoms and two water molecules.

The possibility of replacing Na^+ from analcime structure and synthesis of analcime have been studied by several workers in the last quarter century.

Bragg (7) assumed that the structures of zeolites are generally more open than felspars and the possibility of replacing Na^+ by other

cations suggests that the Na^+ atom must be expected as continuously changing from one position to another even at ordinary temperatures. He concluded that this movement permitted Na^+ to diffuse out of the crystal and Ag^+ to go into the structure when analcime was placed in a $AgNO_3$ solution.

Bragg (7) reported that the channels in the unit cell are wide enough to give ample room for water molecules and cations to pass in or out through analcime structure. The presence of water and existence of alternative empty positions in the neighborhood of each Na^+ ion are also thought to be contributers to the cation exchange in analcime and other minerals.

The ion exchange properties of the analcime was investigated by Barrer (2) by using different methods. He reported that the ions Na^+ (radius 0.98 $\overset{o}{A}$) Tl^+ (radius 1.49 $\overset{o}{A}$) and Rb^+ (radis 1.48 $\overset{o}{A}$) can pass into analcime crystal, but Ca^+ (radius 1.65 $\overset{o}{A}$) cannot because of the ion sieve affect. It was shown that leucite and analcime are readily inner convertible by ion exchange. (Na^+ + H_2O interchanges with K^+ + H_2O). Although retaining the analcime structure closely, the ion exchanged forms of analcime showed small adjustments in the alumino silicate framework.

The difficulties of obtaining Ca^{++} and Ba^{++} rich analcites were related to the ion sieve effect. According to Barrer (2), " In analcite

crystals, the interstatial channels suffer periodic restrictions suffici-

ent to prevent diffusion of Cs^+. The bivalent cations cannot easily

occupy positions at the restrictions in the channels for steric reasons;

on the other hand, their presence in only half of the sites normal for

univalent cations leads to a state of local disbalance of cationic and

anionic change. Since neither configuration is then very stable ex-

change of univalent for bivalent cations in analcime will be limited in

extent. Other factors are also considered to contribute the extent of

exchange. Very small ions such as Li^+ and Mg^{++} do not interchange

freely, but this may be associated with high energy of hydration in

the solution and with changes in the degree of hydration during ex-

change. Consequently it becomes clear that variety of factors may

operate in controlling ion exchange in the analcime structure."

During the x-ray diffreaction studies on the Magna California

soils Schulz et al. (29) has observed that when the clay fraction of the

soil sample was saturated with K^+ the analcime was converted into

leucite as determined by x-ray diffraction pattern. Also, a leucite-

like diagram formed when the clay sample, containing analcime, was

saturated with NH_4^+. No change was obtained when the sample was

saturated with Ca^{++}, and the analcime pattern disappeared.completely,

leaving only the x-ray diagram of the usual clay minerals, when the

sample was leached with 0.1 $\underline{N}$ HCl.

The analcime was formed synthetically by several investigators including Barrer (2) under the controlled environments. For example, Barrer (2) obtained synthetic analcite by treating gels of approximate composition of Na_2O, $Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$ with distilled water at $200^{\circ}C$ in steel autoclaves.

MATERIALS

Description of Sampling Sites

Most of the soil samples were taken from soils of the Igdir Plain which is located between the Aras River and the Agri Mountains in the eastern part of Anatolia, Turkey (22). On the basis of its geological and topographic characteristics together with the semiarid climate, cause 36 per cent of the total area of the Igdir Plain (2105 km^2 or 520,150 acres) to be classified as saline-alkaline soils. All the surface waters from the Aras River in the north and floods from the Agri Mountains in the southern part of the valley drained toward the basin and created a small salty lake in the bottom of the basin. The lake was artificially drained in 1960. Alluvial soils of the plain have been formed mainly by the Aras River.

At Igdir the mean annual temperature is 12°C (33.6°F), the mean annual rainfall 256 mm. (10 inches). The average hottest month of the year is July with 26°C (73°F) and the coldest is January with -3.1°C (26.4°F) (22).

The vegetation of the saline-alkali soils of the Igdir Plain is characterized by salt tolerant grasslands and bushes.

16

One of the x-rayed soil samples was taken by Hajra[4] from Willcox playa which is located in southern Arizona just south of the town of Willcox. It is a broad alluvial-filled valley without external drainage. All the surface waters in the northern part of the valley are collected in the playa which is a dry lake bed of pluvial Lake Cochise.

At Willcox the mean annual temperature is 58.7°F, the mean annual rainfall is 11.76 inches.[5] Desert grasslands and shrubs constitute the main vegetation in the basin.

Turkish soil samples were taken from representative saline-alkali areas. Sample depths were surface crusts, 0 to 15 cm. and 15 to 45 cm. (22).

One of the soil samples was collected by Hajra[4] from a depth of 0-8 inches in Willcox playa. The profile description of another pit a few yards from the sample site is given by Jay and Richardson.[6]

---

[4] Hassan Hamzo Hajrah The effect of cation exchange on gypsum requirement of soils. M.S. thesis. Dept of Ag. Chem. and Soils, Univ. of Arizona. 1965

[5] Arizona Climate. Edited by C. R. Green and W. D. Sellers. The Univ. of Arizona. Tucson. 1964

[6] James Jay and M. L. Richardson. Gothard clay loam saline alkali (564 Ari 2-2-21-1 through 8) Profile description written (USDA SCS) Oct. 20, 1965

The Red Desert soil sample (Typic Haplargid) from a desert grass-
land area was taken by Buol, Havens and Neiring.[7]

Profile Description of the Turkish Soils (Profile 1)

Location: Southeast of Igdir county 600 m. northwest of Hanoko Village

Vegetation: Very few scattered annual grasses

Slope: from 0°/o to 0. 1°/o to the Hanoko drainage ditch

Surface characteristics: Scattered salty crusts

Natural drainage: poorly drained

Ground water table: 240 cm.

Sampling date: July 1, 1962 (22)

Description of the Profile

Depth cm.	Characteristics
Surface crust	Salty crust, hard when dry
0-15	Light gray (19 YR 7/2) clay loam, salt crystalls apparent, structureless, sticky when moist, few roots.
15-45	Light gray (10 YR 7/2) clay loam, fine granular structure, slightly sticky when wet.

---

[7] Buol, S. W., Havens, Y. H. and Neiring, W. A. Profile description
    of a Red Desert soil near Oracle, Arizona. Ag. Chem. and Soils
    Dept. Univ. of Ariz and USDA, SCS. April 4, 1963.

| 45-75 | Light gray (2.5 Y 7/2) loam, weak blocky structure, slightly sticky when wet. |
| 75-105[t] | Light gray (2.5 Y 7/2) Sandy loam. |

(Profile 2)

Location: One km northeast of Asagi Camurlu Village

Vegetation: Scattered, salt tolerant plants (Tamarix gallica L. and salicornia species)

Slope: Nearly level plain

Surface characteristics: Many salty crusts, surface cracking is common.

Natural drainage: Very poor.

Ground water table: 150 cm.

Sampling date: July 9, 1962 (22)

Description of the Profile

Depth cm.	Characteristics
Surface crust	Salty crusts
0-15	Light gray (10 YR 7/2) loam, friable structureless
15-45	Light gray (10 YR 7/2) loam, weak blocky structure
45-75	Light gray (10 YR 7/2) clay loam, blocky structure
75-105	Light gray (10 YR 7/2) clay loam, blocky structure

105 ± 135[#]   Light gray (10 YR 7/2) clay loam

Profile Description of the Gothard clay loam Soil.

Location: Northern Cochise County Area, Arizona. 16 miles south and 1-1/4 miles east of Willcox, Arizona via Kansas Settlement Road. 1050' east and 350 north of the S1/4 corner Sec. 21 T 16S R25E. Photos: 1953 AMS 4064 and 1954 DUH 2N-63

Date: October 20, 1964

Description by: James Jay, M. L. Richardson

Classification: Typic Natrargid. Fine, loamy, mixed, thermic family

Vegetation: Grassland - principally alkali sacation, few shadscale and annual grasses

Climate: Mean annual ppt. 12.0". Mean annual temperature (Willcox) 58.4°F. Mean Jan. T. 41.3°F, mean July T. 77.6°F. Soil temperature at time of sampling 2' = 69.5°F; 4' = 71°F; 6' = 71°F.

Parent Material: Mixed alluvium mainly from ryholite, ignimbrite and andesite

Topography: Nearly level plain adjacent to Willcox playa. Slopes are very slightly concave and about 2°/o.

Elevation: 4190'

Drainage: Moderate internal, Slow external, Very slowly permeable Water table 50 to 100' deep.

Soil Moisture: Slightly moist. 25-50°/o field capacity.

Description of the Profile

Horizon	Depth	Characteristics
A_2 (S64 Ariz-2-21-1)	0-2"	Grayish brown and light gray (10 YR 6/2 and 7/1) fine sandy loam brown (10 YR 5/3) moist; moderate, medium and coarse structure; slightly hard, very friable, nonsticky, nonplastic; plentiful fine and medium roots; common discontinuous fine tubular pores; strongly effervescent with HCl; strongly alkaline pH 8.6 (1:5 Thymal blue); abrupt smooth boundary.
B_2t (S64 Ariz-2-21-2) Sampled for BPR	2-7"	Light brown (7.5 YR 6/4) clay, brown (7.5 YR 5/4) moist, moderate fine and medium prismatic breaking to moderate fine and medium angular blocky; hard, friable, sticky and plastic; many fine, medium and coarse roots; many fine exped and a few fine and very fine tubular pores; few thin clay skins on peds and in pores; strongly effervescent-lime disseminated and a few fine faint mottless; strongly alkaline pH 9.4; gradual smooth boundary.
Cca (Sa?)	7-20"	Light gray (10 YR 7/1) and many fine faint mottles of white mottles of white (10 YR 8/1) light clay, light grayish brown (10 YR 6/2) and light gray (10 YR 7/2) moist; massive breaking to moderate medium angular and subangular blocky; slightly hard, friable; sticky and plastic; plentiful fine and medium roots; few fine and very fine tubular and common fine interstitial exped pores; few thin clay bridges; strongly effervescent; very strongly alkaline pH 9.4 gradual wavy boundary.

IIB2tcab	20-40"	Matrix pinkish gray (7.5 YR 6/2); patchy clay films - brown (7.5 YR 5/4) and many medium to large distinct mottles, of white (N8), clay, brown (7.5 YR 5/2) brown to dark brown (7.5 YR 4/4) and light gray (10 YR 7/2) when moist; massive breaking to moderate medium angular and subangular blocky; very hard firm, sticky and plastic; few fine exped roots; many fine and very fine and a few medium tubular pores; common thin clay films on ped faces and lining pores; strongly effervescent in matrix and violently effervescent in mottles; very strongly alkaline pH 9.4 gradual wavy bounday.
IICIcr (b)	40-51"	Pinkish gray (7.5 YR 6/2) matrix with patchy coating of light brown (7.5 YR 6/4) and a few fine faint mottless of pale olive (5 Y 6/3) clay loam, brown (7.5 YR 5/4) brown to dark brown (7.5 YR 4/4) and olive (5 Y 5/3) when moist; massive and weakly cemented; extremely hard, firm, sticky and plastic; few fine roots; many fine and very fine tubular pores; slightly and strongly effervescent; very strongly alkaline pH 9.4; gradual smooth boundary.
IIIC2	51-58"	Light gray (10 YR 7/1) with common fine to medium mottless of light yellowish brown (10 YR 6/4) and a few fine mottles of white (8/N), light sandy loam or loamy sand, gray (10 YR 6/1), yellowish brown (10 YR 5/4) and light gray (10 YR 7/2), when moist massive and weakly cemented by silica (?); extremely hard brittle; firm, nonsticky, slightly plastic; no roots; common fine tubular pores; slight and strong effervescent; very strongly alkaline pH 9.4, clear smooth boundary.

IIIC3   58-69"   Matrix color is light gray (5 Y 7/1) with
                                varicolored mottles of yellowish red
                                (5 YR 5/6), dark reddish brown (5 YR 3/2)
                                olive brown (2.5 Y 4/4), and light brown
                                (7.5 YR 6/4), loamy sand stratified with
                                thin sandy clay loam lenses, gray (5 Y
                                6/1) with mottles brown (7.5 YR 4/4 and
                                5/4) light reddish brown (5 YR 6/4) and
                                olive (5 Y 3/4) when moist; massive, and
                                weakly cemented by silica (?); extremely
                                hard, firm, nonsticky, slightly plastic; no
                                roots; common fine tubular and a very few
                                very coarse tubular pores; slight efferves-
                                cence in spots strongly alkaline pH 9.0,
                                abrupt wavy boundary.

IIIC4   69-80" +   Light brownish gray and yellowish brown
                                (10 YR 6/2 and 5/4) sand, grayish brown
                                and dark yellowish brown (10 YR 5/2 and
                                4/4) when moist, massive and weakly
                                silica (?) cemented; very hard, friable;
                                nonsticky and nonplastic, no roots, common
                                fine tubular pores; noneffervescent;
                                strongly alkaline pH 9.1

Profile Description of Red Desert Soil.[8]

Area: Oracle Road

Date: April 4, 1963

Classification: Red Desert

Vegetation: Semi-desert, grassland (palo verde, cholla)

Climate: Semiarid

---

[8] After Buol et al. op. cit.

Parent Material: Granite, quartzite (alluvium, from metamorphic granite.)

Physiography: Old alluvial fan.

Relief: Nearly level to gently sloping

Elevation: 30.00'

Aspect: Top of slope

Drainage: Well drained

Ground water: Deep

Moisture: Moist

Root distribution: Normal

Stoniness: Common to plentiful fine gravel on surface

Erosion: slight

Permeability: Moderate

Horizon	Depth	Characteristics
Al[9]	0-3"	Yellowish-red (5 YR 5/6) sandy loam, yellowish-red (5 YR 4/6) when moist; weak coarse slaty structure, slightly hard, friable, nonsticky and nonplastic; few fine roots; 10 % fine gravel.
B1	3-10"	Yellowish-red (5 YR 4/6) sandy loam, dark reddish brown (5 YR 3/4) when moist; weak fine and medium subangular blocky breaking to weak fine granular structure; slightly hard, friable, slightly arid (pH 6.5); gradual smooth boundary.

---

[9] Sampled for laboratory analysis.

B21	10-16"	Yellowish-red (5 YR 4/6) gravelly sandy clay loam or sandy loam, reddish-brown (5 YR 4/4) when moist; weak fine and medium subangular blocky structure; hard, friable, slightly sticky and slightly plastic; few fine and medium roots; 20 % fine gravel; neutral (pH 7. 0); clear wavy boundary.
B22	16-23"	Reddish-brown (5 YR 4/4) gravelly light sandy clay loam, reddish-brown (5 YR 4/4) when moist; weak fine and medium subangular blocky structure, hard, friable, slightly sticky and slightly plastic; very few fine roots; 30 % fine and medium gravel; neutral (pH 7. 0); abrupt wavy boundary.
B23	23-27" +	Yellowish-red (5 YR 5/6) gravelly sandy loam, yellowish-red (5 YR 4/6) when moist; weak fine and medium subangular blocky structure; hard, friable, slightly sticky, plastic; very few fine roots; 30 % fine and medium gravel; neutral (pH 7. 0).

Natural Minerals.

The sodium zeolites used in this experiment were ordered from Ward's Natural Science Establishment, Inc., Rochester, New York. They were: Analcime (West Patterson, New Jersey), Thomsonite (Lake Superior), Natrolite (Nova Scotia), Pectolite (West Patterson, New Jersey), Stilbite (Nova Scotia), and chabazite (Nova Scotia).

The three strongest x-ray lines of the mineral pattern and their relative intensities, as given by the American Society for Testing and Materials, are shown below:

Mineral	d Å	Relative Intensity
Analcime	3.43	100
($Na_2O . Al_2O_3 . 4SiO_2 . 2H_2O$)	5.61	80
	2.93	80
Chabazite	2.95	100
$[(Na_2Ca)Al_2Si_6O_{16} . 6H_2O]$	4.35	90
	9.5	70
Thomsonite	2.86	100
$[(Na_2Ca)O . Al_2O_3 . 2SiO_2$	2.95	80
$2-1/2 H_2O]$	2.68	80
Stilbite	4.08	100
$[(Na_2Ca)Al_2Si_6O_{16} . 6H_2O]$	3.1	90
	4.68	90
Natrolite	2.86	100
($Na_2OAl_2O_3 . 3SiO_2 . 2H_2O$)	5.90	64
	4.38	64
Pectolite	4.08	100
($NaCa_2Al_5Si_{13}O_{36} . 14H_2O$)	9.1	90
	4.68	90

EXPERIMENTAL PROCEDURES

Chemical Analysis of the Soil Samples.

In the analysis of the saline-alkaline soils of the Igdir Plain generally the methods proposed by the USDA Salinity Laboratory were used (32).

Soil Reaction: The pH value of the saturation paste of the Turkish soil samples was determined by the glass electrate method (14).

Electrical Conductivity: EC of the Turkish soil samples were determined by using the method No: 4a given by the USDA Salinity Lab (32).

Calcium and Magnesium: Ca was determined by EDTA filtration (USDA Salinity Lab Staff, Method No. 7). Magnesium was found by substraction of the Ca from Ca plus Mg.

Carbonate and bicarbonate: $CO_3^=$ and HCO_3^- were determined by sulfuric acid filtration (USDA Salinity Lab Staff, Method No. 12).

Chloride: Chloride was determined by precipitating sulfate with $BaCl_2$ (USDA Salinity Lab Staff, Method No. 14).

Sodium: Ammonium extractable and water soluble Na^+ content of the Turkish soil samples were determined by flame photometer.

(USDA Salinity Lab Staff, Method No. 10a and 18, respectively).

A Dr. Lange Model 6 flame photometer was used to determine the Na^+.

In the experiment, where the KCl, NH_4OAc, $MgCl_2$, $BaCl_2$, $CaCl_2$ and $SrCl_2$ extractable Na^+ contents of the analcime, Turkish soil sample (Profile 1, 0-15 cm. layer) and Red Desert soil (A1 horizon) were determined, 1 N solutions of these salts were prepared. Five grams of soil material from the Turkish soil (Profile 1, 0-15 cm. layer) and the Arizona Red Desert soil (A1 horizon) were used whereas only two grams of ground analcime were used. The samples were then washed three times with distilled water and the effluents were discarded after five minutes of centifugation at 10,000 rpm[10], prior to washing with the salt solutions. Each washing consisted of three, thirty-three ml aliquates of the 1 N salt solutions.

Potassium: NH_4OAc extractable and water soluble K contents were determined, according to the Method No. 11a and 18 as described by the USDA Salinity Lab Staff (32). The Dr. B. Lange Model 6 flame photometer was used to determine the K concentration in solution.

---

[10]Sorvall SS-3 Automatic superspeed centifuge.

Cation Exchange Capacity: C. E. C. of the Turkish soils were determined by sodium saturation and NH_4OAc displacement (32).

Exchangeable-Sodium-Percentage: ESP was calculated by the following formula:

$$ESP = \frac{\left(\begin{array}{c}NH_4OAc \\ \text{extractable } Na^+\end{array}\right) - \left(\begin{array}{c}\text{water} \\ \text{soluble } Na^+\end{array}\right)}{C.\,E.\,C.} \times 100 \qquad (32)$$

Soil Moisture Content: Soil moisture content of the Turkish soil samples was determined by oven drying to $105^{\circ}C$. All results are based on oven-dry basis.

Willcox, Arizona soil sample was calcium-saturated in the following manner.[4] The $CaCO_3$ in the soil was partially removed by using HCl and adjusting the pH value between 6 and 7. The soil was saturated with calcium by leaching with a solution containing 100 meg Ca/1 of $CaCl_2$ solution. The soil then was leached with distilled water after the effluent was free of chloride as shown by the $AgNO_3$ test. After air drying, the soil was passed through a 2-mm. sieve. Exchangeable sodium of calcium saturated sample was determined by using NH_4OAc, as described in USDA Handbook (32).

In the chemical analysis of the Red Desert soil[7] exchange capacity was determined by saturation with Na^+ ion, and displacement

---

[4]See page 17

[7]See page 18

with NH_4^+ ion and determination of Na^+ displaced by using a Beckman

model DU spectrophotometer. The exchangeable cations Na^+, K^+, Ca^{++}

were displaced with NH_4OAc, the K^+ and Na^+ being determined on the

Beckman model DU spectrophotometer and the Ca^{++} and Mg^{++} deter-

mined by EDTA titration (14). Subsamples were oven-dried at $105^{\circ}C$

and all calculations were based on an oven-dry basis.

X-ray Diffraction Studies

In order to determine whether the various reagents will alter

the structure of analcime, x-ray diffraction studies of the standard

samples of geologic specimens were made. The procedure proposed

by Kittrick and Hope (19) was followed.

Analcime from West Patterson, New Jersey, was ground and

washed with distilled water. Particles less than 44 micron were

separated by using a sieve. Five grams of <44 micron samples were

placed in a 250 ml centrifuge bottle, one hundred of pH5. NaOAc

solution was added to remove carbonates and soluble salts. The

bottle was heated at about $80^{\circ}C$, for at least a half hour, and stirred

several times. After cooling the bottle was centrifuged at approxi-

mately 1500 rpm for five minutes and effluent was discarded, the

sample was then prepared for x-ray examination.

The same weight of another sample received the same

NaOAc treatment plus a second treatment for removal of organic

matter. About 20 ml. of water was added to the residue in the bottle to prevent the sample from going to dryness. The sample was heated to 80°C. Then 1 ml., of 30°/o H_2O_2 was added to the bottle. Since there was no organic matter, no more H_2O_2 is required. No Antifoam B was used. The sample was washed with alcohol, dried and prepared for x-ray examination.

A third sample received one additional treatment for the removal of iron oxide coatings. After the first and second steps, the sample was removed from the hot plate and 15 ml. of saturated NaCl solution was added. It was stirred, centrifuged and decanted. One hundred ml. of pH 7.3 citrate buffer was then added. The sample was then placed in a 80°C water bath. One teaspoon of dithionite was added to the solution. The bottle was kept in the water bath for 15 minutes, then cooled, centrifuged and decanted. The sample was then washed with alcohol and dried in oven at 105°C prior to preparation for x-ray examination.

Turkish soil samples (Profile I) also received the treatments for the removal of carbonates and soluble salts, organic matter, and iron oxide coatings as described above. Then by using International Equipment Co. centrifuge head No. 277, with 250 ml. centrifuge bottles marked with a 10 cm. line and a 1 cm. of sediment, the clay fraction was collected by centrifuging at 750 rpm for 5.3 minutes (19).

Instrumentation

A Norelco x-ray recording diffractometer was used with nickel-filtered copper Ka radiation (2 = 1.5418 Å) for the x-ray diffraction studies of the soils and geological samples. The x-ray tube power was 40 kv. and 20 ma. Divergence and scatter slits used were $1/4^O$ (2^O to 10°, 2 0), $1/2^O$ (10° to 16°, 2 0) and 1^O (16° to 50°, 2 0). The 0.003 inch receiving slit was used. Standard Norelco specimen holders (aluminum, capped flat to 0.002" 10 mm. x 20 mm. sample) were used. The specimens were scanned at 2^O, 2 0 per minute, with recorder settings of time constant = 4 and counting rate = 100.

Modified Pretreatment Procedures for X-ray Powder Techniques

After the personal communication with Professors Barshad and Whittig and reviewing the work of Schulz et al. (29), which indicated that acid solutions and long treatment procedures could destroy the analcime, different pretreatment methods were used. Instead of using Kittrick's method (19) which uses a pH5 solution of NaOAc for removal of soluble salts and carbonates the soil samples were only washed with distilled water, then clay fraction was separated by using the centrifuge technique. The collected clay fraction was then dried in an oven at 105^OC and powdered with an agate mortar and pestle.

X-ray Powder Camera Technique

A powder sample of the soil was put in a Lindiman tube (1/100 mm. wall thickness, 1 mm. inside diameter) and exposed to Ni filtered Cu Ka radiation for four hours with the x-ray tube power 40 kv. and 20 ma. Kodak no-screen medical x-ray film was used. In order to decrease the partial absorption of both the incident and diffracted beams by the air in the camera, Helium gas was introduced into the camera. Norelco, type 12045/3, x-ray equipment was used.

Heavy Liquid Separation

Different mineral species can be separated according to their density by using heavy liquid, which is simply a sink or float technique. The specific gravity of analcime varies from 2.22 gm. cm.$^{-3}$ to 2.29 gm. cm.$^{-3}$ (11). Two grams of Turkish soil sample (Profile 1, 0-15 cm. layer) which was previously prepared for x-ray diffraction was placed in a 125 ml. seperatory funnel with 18.8 ml. of nitrobenzene of specific gravity of 1.2 gm. cm.$^{-3}$ and 31.2 ml. of S-tetratromoethane of specific gravity of 2.96 gm. cm.$^{-3}$. The measured final density of this mixed liquid was 2.3 gm. cm.$^{-3}$. The separatory funnel was kept in constant temperature room for 12 hours at 23.3 - 24.3°C. It was presumed that most of the clay particles having specific densities of greater than 2.3 gm. cm.$^{-3}$, like kaolinite 2.60 - 2.63 gm. cm.$^{-3}$, chlorite group 2.65 - 2.96 gm. cm.$^{-3}$, feldspars 2.7 gm. cm.$^{-3}$,

mica 2.8 gm. cm.$^{-3}$, sink and the particles with specific densities of less than 2.3 gm. cm.$^{-3}$ were floating. The floating part of the suspension was recovered from the separatory funnel. After washing with alcohol, the sample was dried and prepared for the x-ray powder film.

RESULTS AND DISCUSSION OF RESULTS

Chemical Analysis of the Soil Samples.

The chemical analysis of the two Turkish soils, the Gothard

clay loam and the Red Desert soil are given in Tables 1, 2, 3 and 4

respectively.

The electrical conductivity of the saturation extract from the

Turkish soil was greater than 4 mmhos./cm. and the exchangeable-

sodium percentage exceeded 15, therefore, they are classified as

saline-alkali soils. The chemical analysis of the Turkish soils

(Profile 1) gave exchangeable sodium percentage values very close

to 100 per cent. Profile 2 soils yielded exchangeable sodium per-

centages well over 100 and exchangeable sodium percentages of the

both profiles were found to be considerably higher than the sodium

adsorption ratio of the saturation extracts.

Exchangeable sodium percentages of over 100 per cent are

considered theoretically impossible. Exchangeable sodium percent-

age of over 100 per cent and also the high sodium adsorption ratio

can be explained if it is hypothesized that during the determination of

the exchangeable sodium, replacement of Na^+ by NH_4^+ takes place

in sodium zeolites. Consequently higher Na^+ concentrations are ob-

tained than in soils which do not contain the sodium zeolites.

Table 1. Chemical Analysis of Turkish Soil (Profile 1) Soil Determinations

Soil Determinations

Soil Depth	Saturation	pH Value of saturation paste	Cation exchange capacity	Exchangeable Na^+	Exchangeable Na^+
cm.	%		meq./100 gm.	meq./100 gm.	%
Crust on the surface	42.9	8.9	13.67	47.98	350
0-15	42.4	8.8	19.14	17.41	90
15-45	41.3	8.7	15.78	14.68	92

Saturation Extract Determination

Soil Depth	Electrical conductivity	Cations (meq./l.)					Anions (meq./l.)				
cm.	$Ec \times 10^3$ mmhos./cm.	Na^+	K^+	Ca^{++}	Mg^{++}	Total	$CO_3^=$	HCO_3^-	Cl^-	$SO_4^=$	SAR
Crust on the surface	112	771.5	14.9	44.6	131.4	962.4	10.0	27.0	280.0	643.2	95.2
0-15	83	302.1	2.3	36.8	231.2	572.4	1.2	18.8	301.0	247.3	26.1
15-45	57	204.3	1.1	34.6	173.4	413.4	0.0	9.6	294.1	106.6	20.0

Table 2. Chemical Analysis of Turkish Soil (Profile 2) Soil Determination

Soil Depth	Saturation	pH Value of saturation paste	Cation exchange capacity	Exchangeable Na^+	Exchangeable Na^+
cm.	%	meq./100 gm.	meq./100 gm.	meq./100 gm.	%
Crust on the surface	42.8	8.6	18.0	68.00	377
0-15	57.9	8.4	24.67	43.17	174
15-45	74.6	7.7	26.72	34.46	128

Saturation Extract Determination

Soil Depth	Electrical conductivity	Cations (meq./l.)					Anions (meq./l.)				
cm.	$Ec \times 10^3$ mmhos./cm.	Na^+	K^+	Ca^{++}	Mg^{++}	Total	$CO_3^=$	HCO_3^-	Cl^-	$SO_4^=$	SAR
Crust on the surface	215	510.8	1.0	37.4	40.6	589.8	2.2	4.6	324.7	252.7	181.8
0-15	104	171.7	0.6	50.0	10.2	232.5	0.8	4.2	148.7	77.2	31.3
15-45	66	113.0	0.3	37.8	9.7	160.8	0.0	4.2	98.3	58.8	23.2

Table 3. Chemical Analysis of the Gothard Clay Loam Soil (after Hajrah op. cit.)

Exchangeable Cations in the Original Soil and Ca-Soil Meq/100 gm

Soil Depth (inches)	Original Soil						Ca-Soil			
	C. E. C.	Ca^{++}	Mg^{++}	Na^{+}	Ca^{++}	Mg^{++}	Na^{+}	C. E. C.	$(Ca^{++}+Mg^{++})$	Na^{+}
0-8	19.10	9.21	3.09	6.80	8.24	2.86	8.00	17.42	13.42	4:00

Table 4. Chemical Analysis of the Red Desert Soil (after Buol et al. op. cit.)

Soil Depth (inches)	Cation exchange capacity meq./100 gm.	Exchange-able Na^{+} meq./100 gm.	Exchange-able Ca^{+} meq./100 gm.	Exchange-able K^{+} meq./100 gm.	Exchangeable Mg^{++} meq./100 gm.
0-3	5.4	0.0	3.36	0.30	1.34

Exchangeable-sodium percentage of the Turkish soil was calculated by using the following formula (32):

$$\text{Exchangeable sodium percentage} = \frac{\left(\dfrac{Na_4OAc\ extractable}{Na^+}\right) - \left(\dfrac{water\ soluble}{Na^+}\right)}{cation\ exchange\ capacity} \times (100)$$

Ammonium acetate extractable Na^+ consists of NH_4OAc soluble Na^+ from the sodium zeolite plus exchangeable Na^+, plus water soluble Na^+. Therefore, an increase of the Na^+ in the NH_4OAc extractable Na^+ concentration, due to the presence of the sodium zeolite, gives higher exchangeable-sodium percentages during the calculation. This hypothesis was confirmed with the presence of the sodium zeolite (analcime) in the Turkish soil profile 1 and 2 after the x-ray powder film analysis of these soils.

The geological specimen of analcime, the Turkish soil (Profile 1, 0-15 cm. layer) and the Red Desert soil were treated with 1 N solutions of KCl, NH_4OAc, $MgCl_2$, $BaCl_2$, $CaCl_2$ and $SrCl_2$ in order to determine the amount of Na^+ released from three different soil samples and to check whether structural changes would occur in the samples, with different cations. Figures 1, 2, 3, 4, 5, and 6[11] show the amount of released Na^+ in meg. /100 gm. from different samples after the subsequent washings with 1 N solutions of KCl, NH_4OAc, $MgCl_2$, $BaCl_2$,

---

[11] "Leachings" has been used in these figures and should be considered to be the same as "washings" in the text.
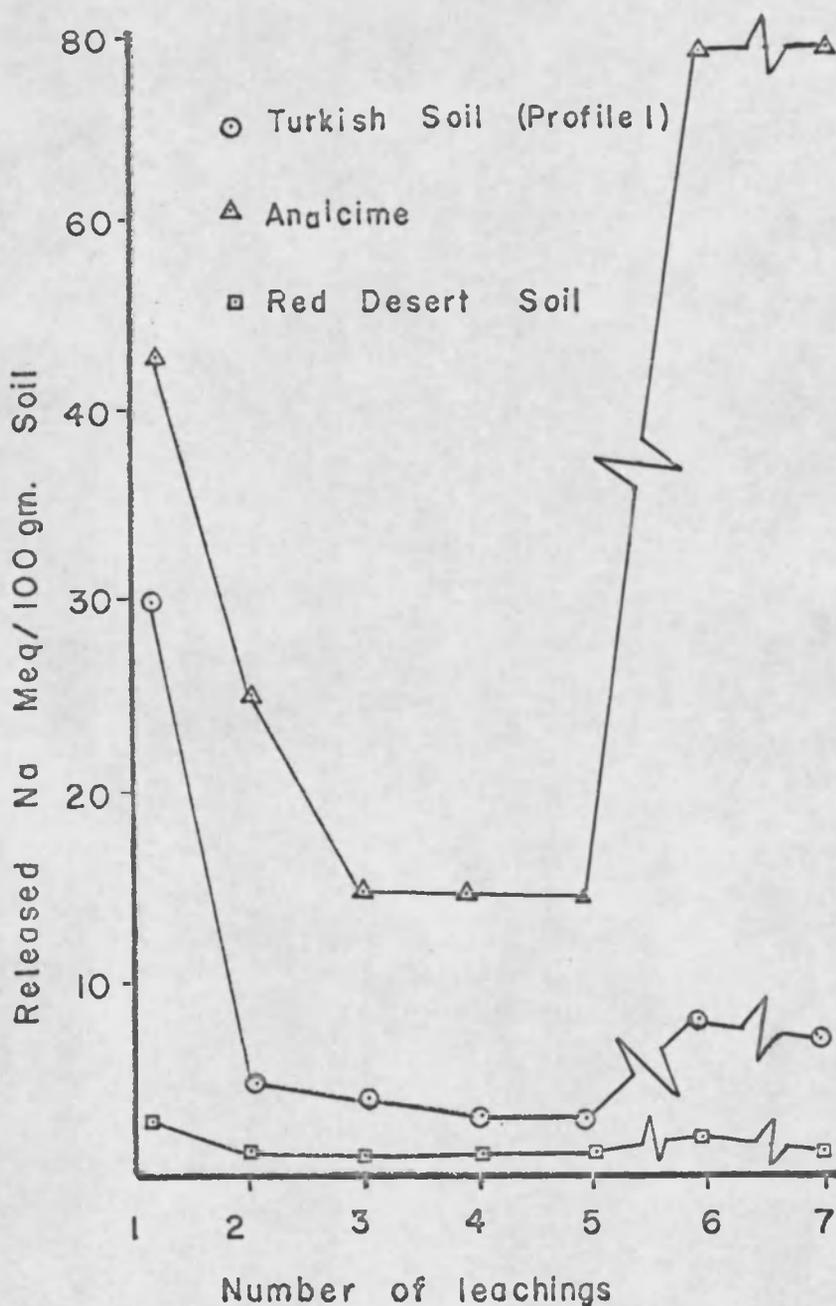
Figure 1. Released Na by KCl treatment. Leachings 1, 2, 3, 4 and 5 after 24 hours of saturation, No. 6 after 30 days, No. 7 after 60 days of saturation.
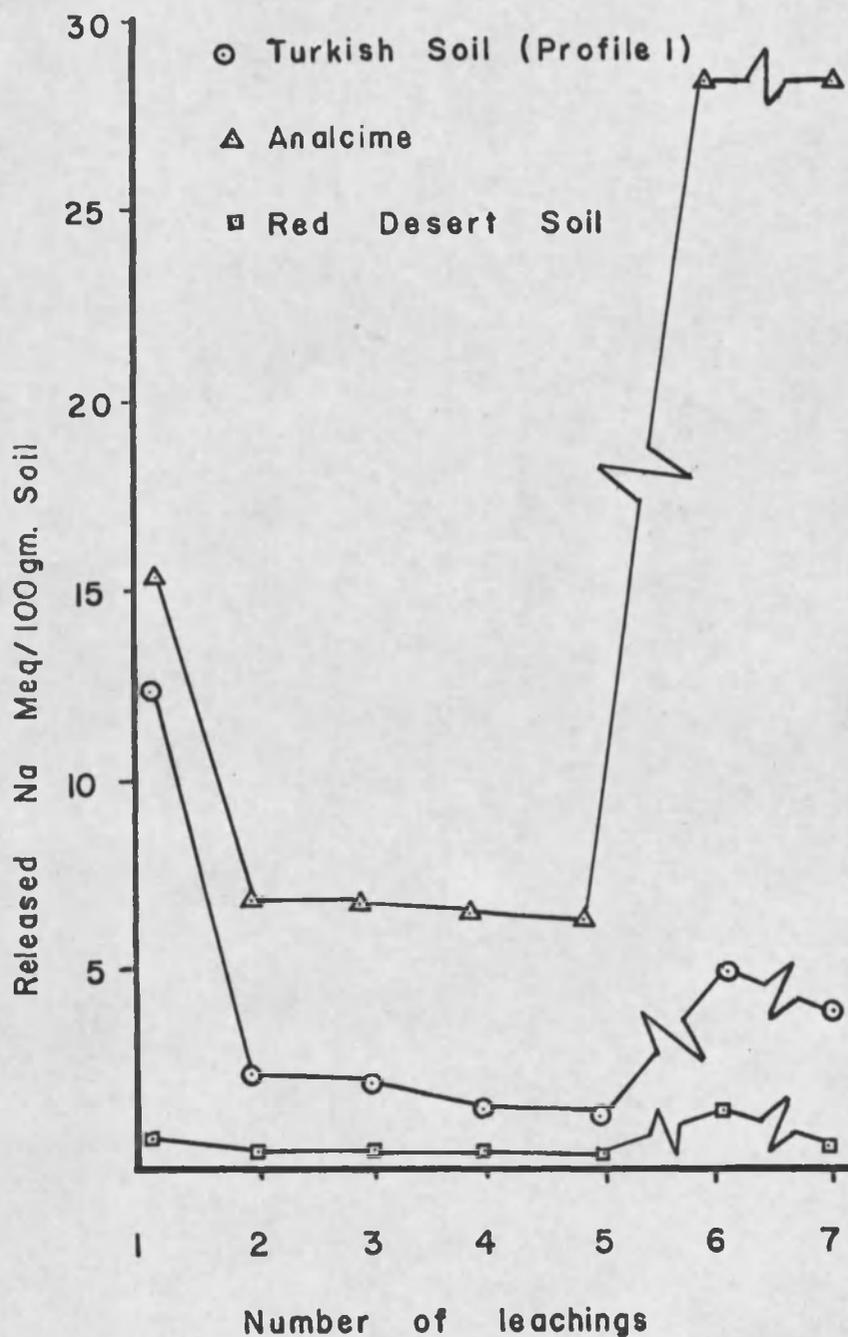
Figure 2. Released Na by NH_4OA_c treatment. Leachings
1, 2, 3, 4 and 5 after 24 hours of saturation,
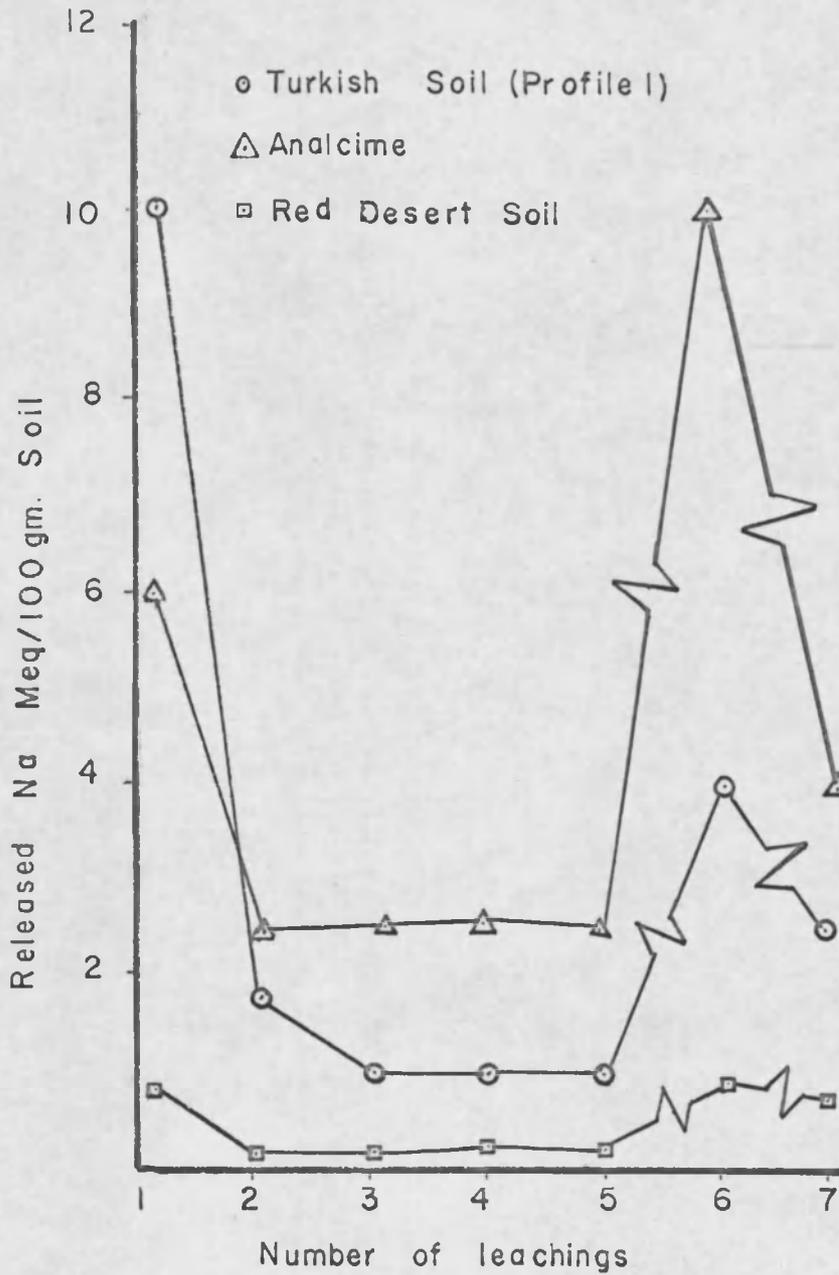No. 6 after 30 days, No. 7 after 60 days of
saturation   .

Figure 3. Released Na by MgCl$_2$ treatment. Leachings
No. 1, 2, 3, 4 and 5 after 24 hours of satur-
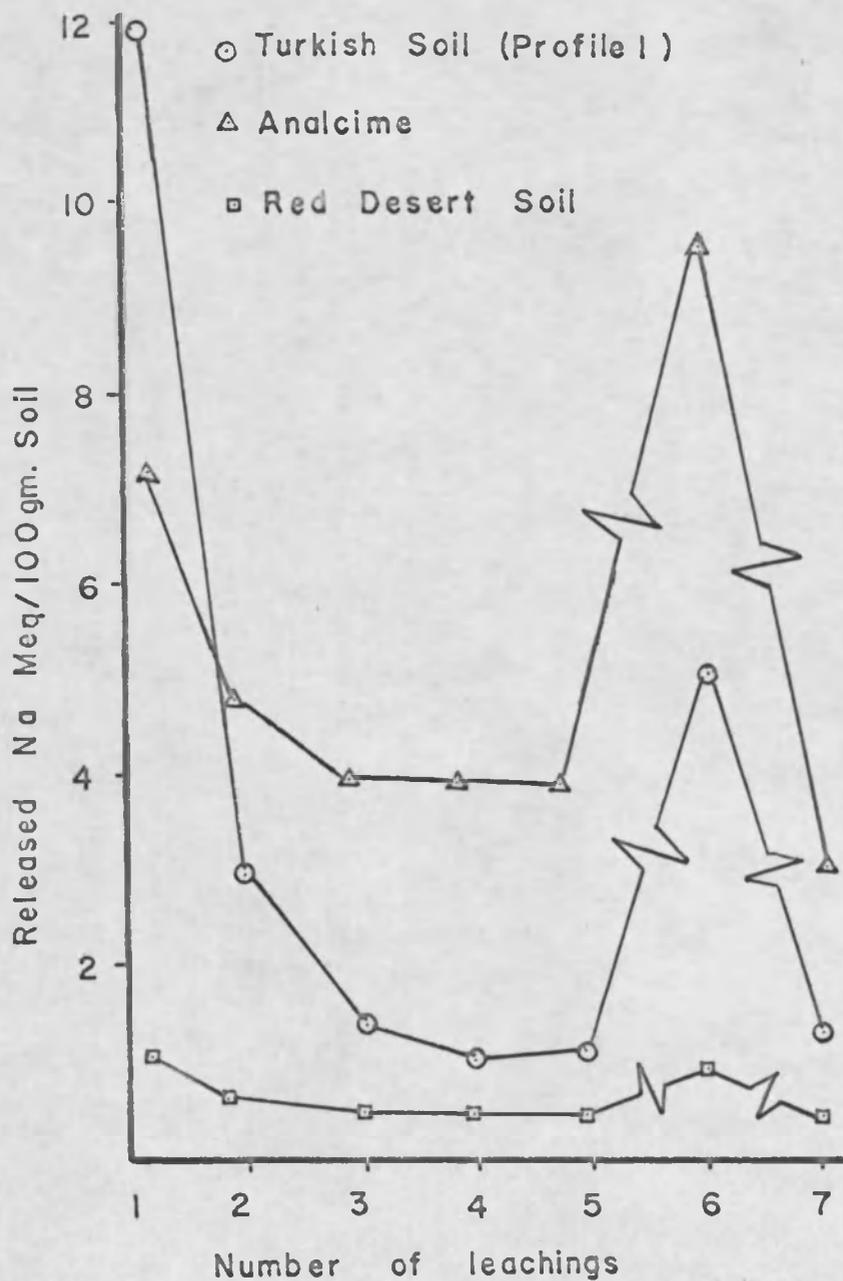ation, No. 6 after 30 days, No. 7 after 60
days of saturation

Figure 4. Released Na by BaCl$_2$ treatment. Leachings No. 1, 2, 3, 4 and 5 after 24 hours of saturation, No. 6 after 30 days, No. 7 after 60 days of saturation.
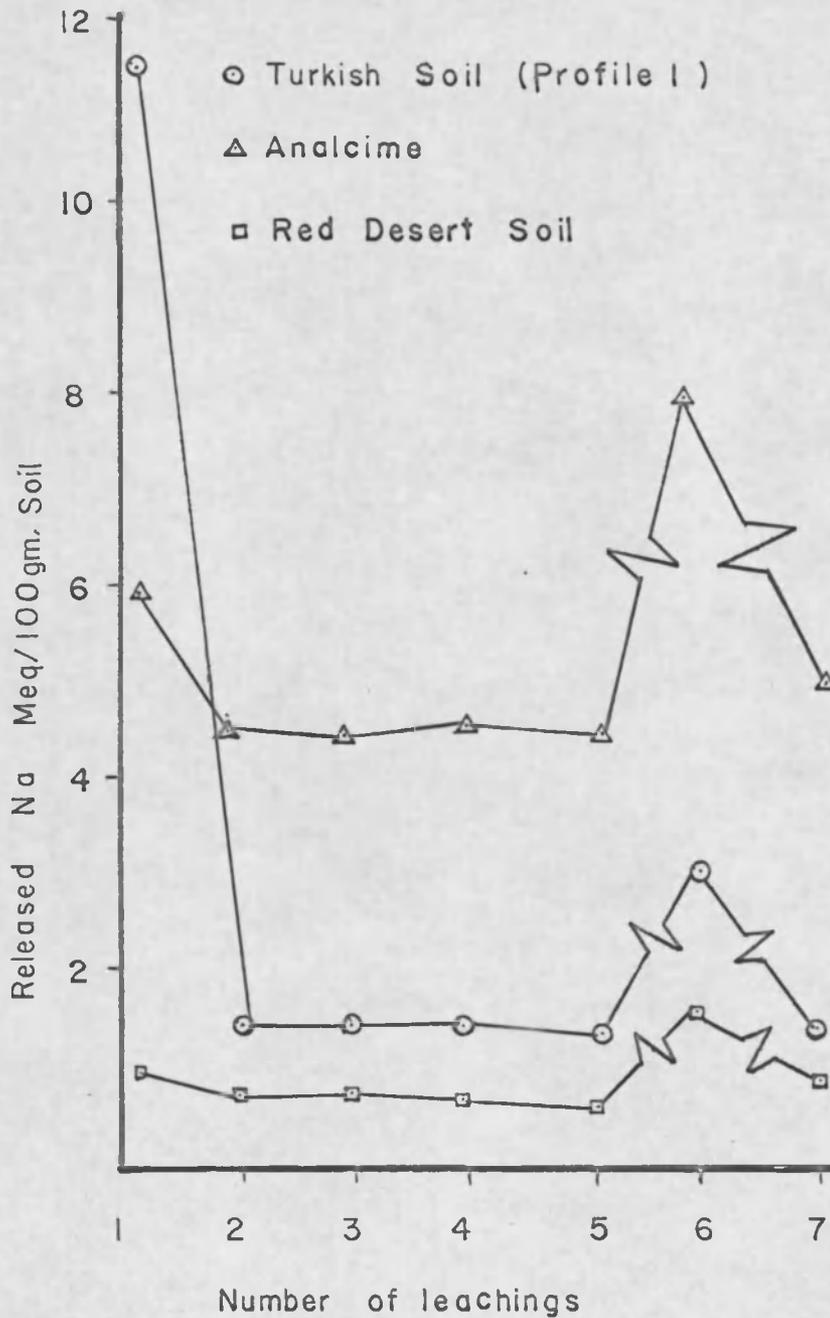
Figure 5. Released Na by CaCl$_2$ treatment. Leachings No. 1, 2, 3, 4 and 5 after 24 hours of saturation, No. 6 after 30 days, No. 7 after 60 days of saturation.
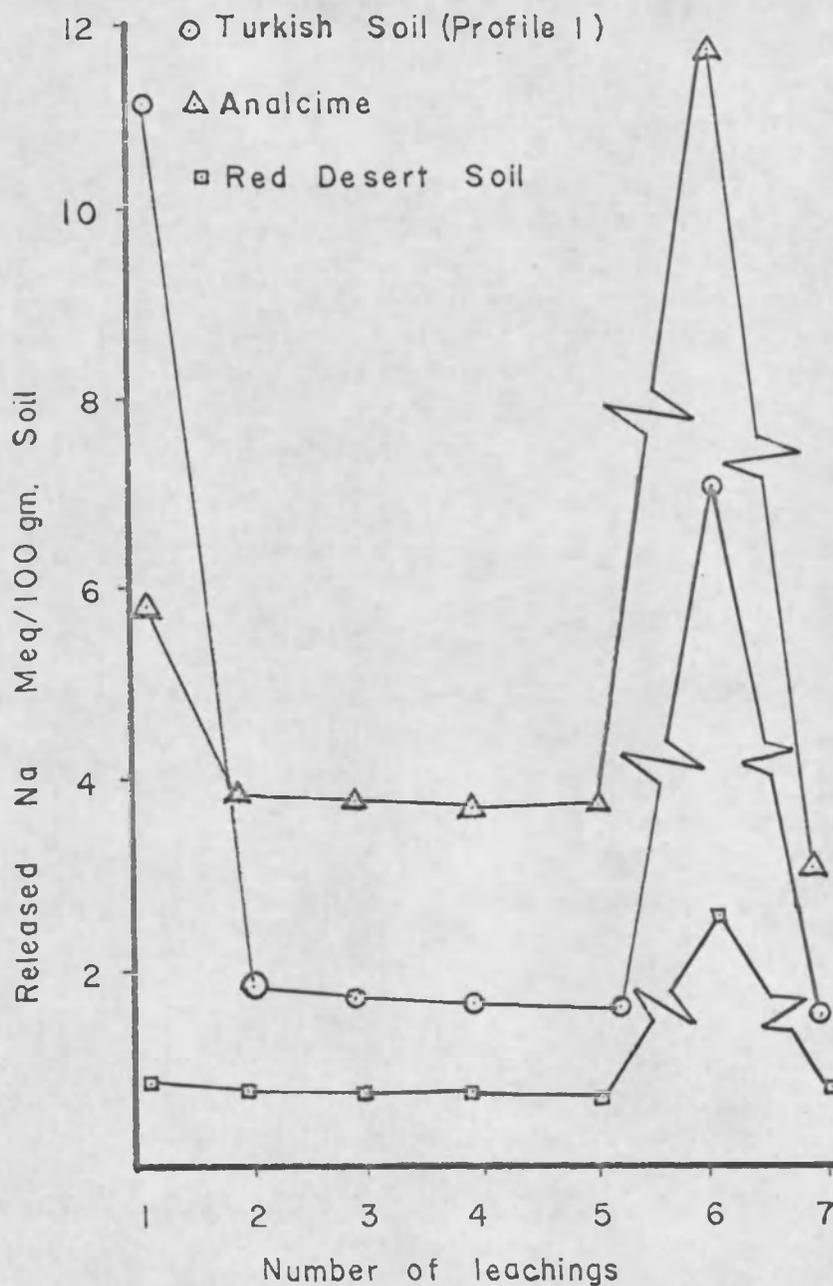
Figure 6. Released Na by Sr_2Cl treatment. Leachings No. 1, 2, 3, 4 and 5 after 24 hours of saturation, No. 6 after 30 days, No. 7 after 60 days of saturation.

$CaCl_2$ and $SrCl_2$.

It was assumed that the analcime initially would release and continue to release much more Na^+ than any of the soils. It has been further assumed that the Turkish soil would release more Na^+ than the Red Desert soil because of the presence of analcime. It was also assumed that after the first washing additional released Na^+ would come from the replacement of Na^+ in the analcime structure or from the decomposition of analcime, in addition to the gradual dissolution of other Na^+ bearing minerals, which are generally found in soil.

Washings with $MgCl_2$, $BaCl_2$, $CaCl_2$ and $SrCl_2$ solutions released approximately the same amount of Na^+ (Figures 3, 4, 5, and 6). Higher amounts of Na^+ were released from the Turkish soil sample in the first washings, than were released from either the analcime or the Red Desert soil. Upon additional washings the analcime released more Na^+ than either of the other two samples. All of the samples continued to release additional Na^+ upon subsequent washings. After one month of saturation the amount of released Na^+ was higher from the Turkish soil than from the Red Desert soil, but lower than from the analcime. The amount of the released Na^+ sharply decreased, in all samples, after two months (washing 7) of saturation with solutions of the divalent cations.

Monovalent cations, K^+ and NH_4^+ caused a greater release of Na^+ than did the divalent cations. In agreement with the ion sieve affect theory of Barrer (2) KCl and NH_4OAc solutions released as much as three times more Na^+, especially from the analcime and the Turkish soil sample than did the divalent cations. The analcime was found to release more Na^+ than the Turkish soil and the Red Desert soil in all washings with KCl and NH_4OAc. However, each KCl washing released two or three times more Na^+ from the analcime and the Turkish soil than did the NH_4OAc washings (Figures 1 and 2). After one month (washing no. 6) in the KCl solution, released Na^+ was highest from the analcime sample and less in the Turkish soil and the Red Desert soil, respectively. The KCl treated analcime continued to release the same amounts of Na^+ and also there was no sharp decrease in the amount of released Na^+ for the Turkish soil even after two months of saturation (washing 7). After two months in the NH_4OAc solution no decrease in the amount of the released Na^+ was observed for the analcime and only a slight drop was found for the Turkish soil. However, the concentration of the released Na^+ was still higher in all samples than when the samples were washed with solutions containing divalent cations.

Continued release of Na^+ from the Turkish soil during KCl and NH_4OAc washings may be considered as a method to indicate the

presence of the analcime.

X-ray Diffraction Studies of the Soil Samples

The different pretreatments for the removal of carbonates, organic matter and iron oxide coatings did not alter the structure of the geological analcime specimen. Conformation on nonalteration may not be accepted definitely, since there was a high concentration of analcime in the sample. In order to determine the amount of analcime in the sample before an analcime x-ray diffraction pattern could be seen one and ten per cent analcime was added to bentonite samples. One per cent was not detectable in x-ray diffraction patterns. With ten per cent analcime in bentonite x-ray diffraction lines due to analcime were as strong as those from pure analcime samples. These results not only indicate the difficulties of obtaining noticeable analcime patterns at the one per cent level, but also indicate the difficulties involved in quantitative determinations of the analcime.

With these difficulties in mind the heavy liquid separation technique was used to concentrate the analcime in the Turkish soil (Profile 1, 0-15 cm. layer). The technique was found helpful and the x-ray powder film of the floated part of the soil indicated the weak to moderate lines of the analcime (Figure 8). The third layer of the same profile, which has not received heavy liquid separation failed to give satisfactory indication of the analcime lines. However, the
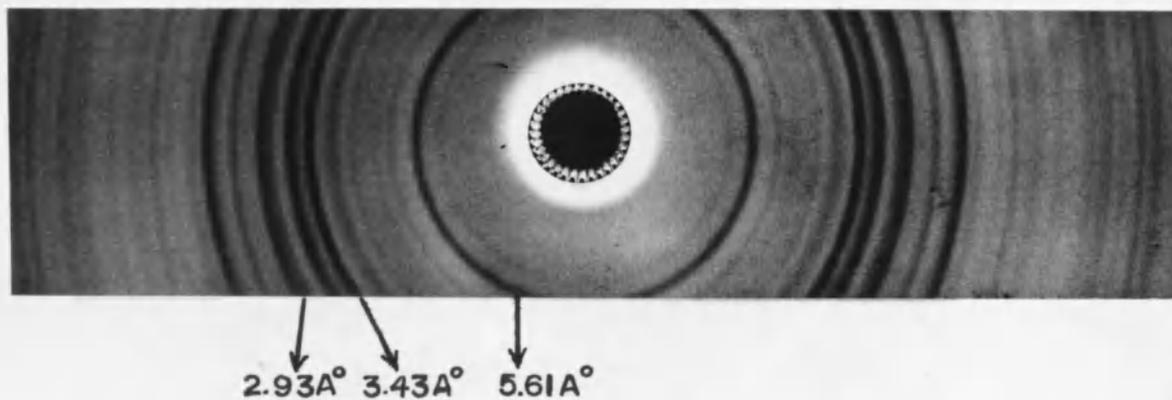
49

Figure 7. X-ray powder photograph of geological Analcime sample
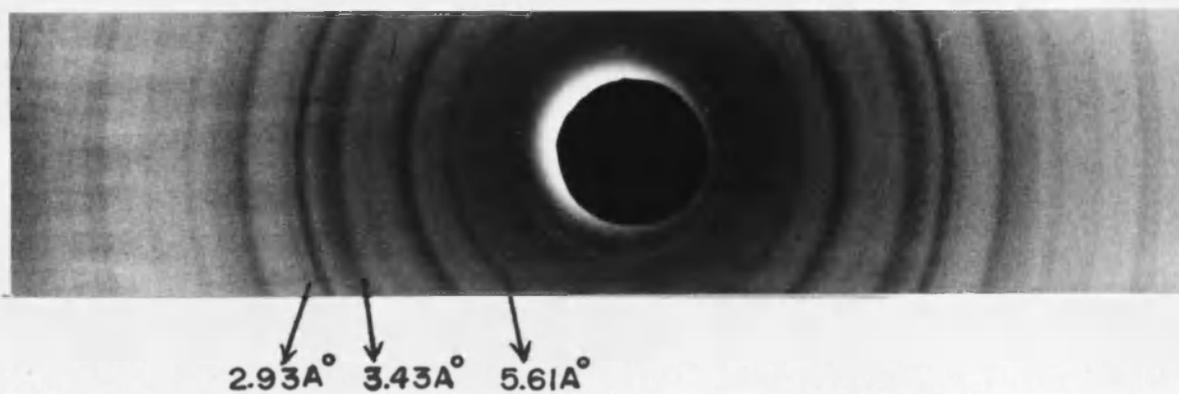showing the three strongest x-ray lines of analcime

Figure 8. X-ray powder photograph of Turkish soil (Profile
1.0-15 cm layer) showing the analcime lines.

2.93A° 3.43A° 5.61A°
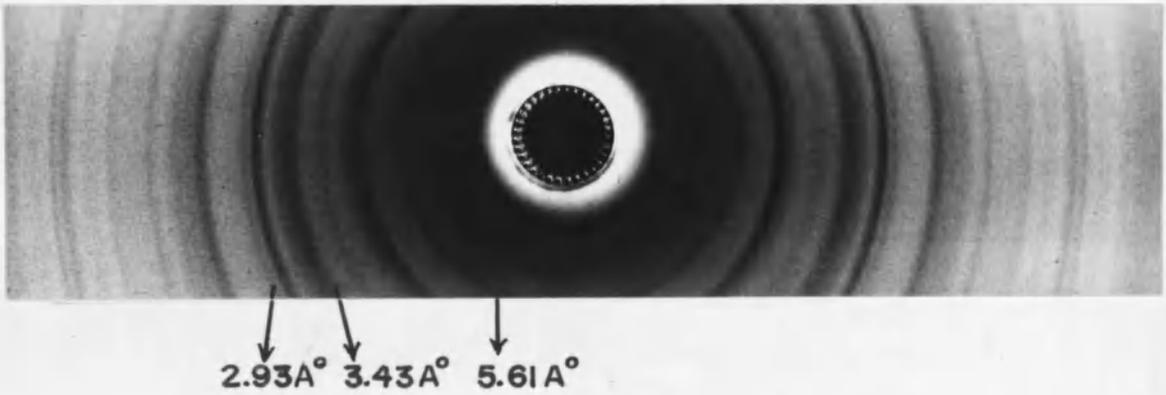
Figure 9.   X-ray powder photograph of Turkish soil (Profile
            2. 0-15 cm layer) showing the analcime lines

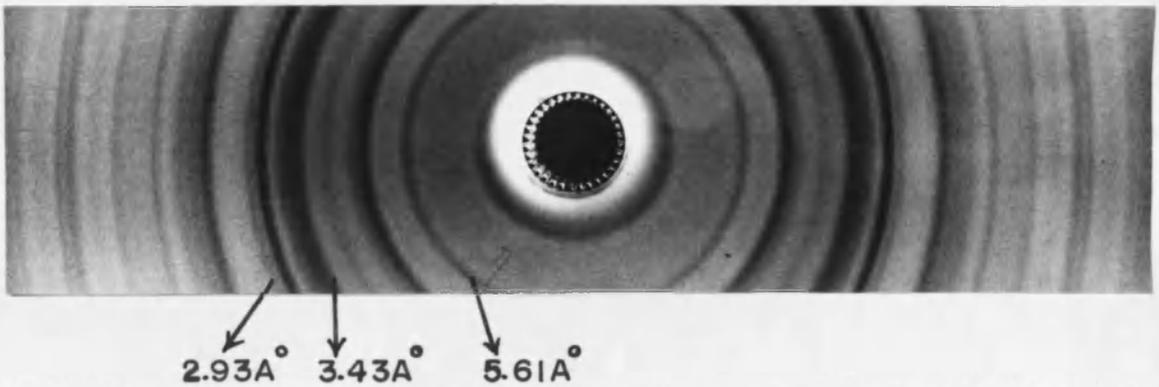2.93A°   3.43A°   5.61A°

Figure 10. X-ray powder photograph of Arizona.   Gothard Clay
            Loam soil, showing the analcime lines

x-ray powder film of the Turkish soil (Profile 2, 0-15 cm. layer)

has revealed the weak to moderate lines of the analcime (Figure 9)

even without concentrating the analcime by the heavy liquid technique.

The presence of the analcime in the surface layers of these soils is in

close agreement with higher accumulation of the salts and high pH

values of the upper 15 cm. of the soils. The high exchangeable-

sodium percentages of the Turkish soils, upon extraction with NH_4OAc

could be related to the presence of analcime.

The x-ray analysis revealed that Turkish soils contained no

thomsonite, natrolite, peitolite, stilbite and chabazite. Analcime was

the only sodium zeolite found to be present.

No evidence of the analcime was observed in the salty surface

crusts of the Turkish soil profiles. High exchangeable-sodium

percentages, over 100 per cent, of these soils could be attributed to the

presence of the larger amounts of Na salts, dissolving upon NH_4OAc

extractions.

The Gothard clay loam soil was found to contain the analcime

lines, with the x-ray powder film analysis (Figure 10). Although this

soil was saturated with Ca^{++} three times, it still yielded 4 meg./100

gm. of exchangeable-sodium upon extraction with NH_4OAc (Table 3).

The unexpected amounts of exchangeable sodium could be attributed to

the presence of the analcime which readily exchanges its Na^+ with

NH_4^+ in this soil.

X-ray powder films of the $MgCl_2$, $BaCl_2$, $CaCl_2$ and $SrCl_2$ saturated analcime samples indicated that the main analcime lines have not disappeared upon saturation with these divalent cations. On the other hand, in a very close agreement with the results of Schulz et al. (29) NH_4OAc treated analcime sample was shifted to leucite-like mineral and KCl treated analcime sample was also shifted very close to the leucite lines (29).

CONCLUSIONS

Exchangeable-sodium content over 100 per cent in some of the salt affected Turkish soils, and unexpected exchangeable sodium values in calcium saturated Gothard clay loam soil again indicates the difficulties of the analysis of the exchangeable cations in certain salt affected soils.

The two Turkish soil samples and the Gothard clay loam were found to contain the analcime, with x-ray powder film analysis.

The alkalization processes in the soil not only increases the amount of the adsorbed Na^+ and pH value of the soil, but also indirectly causes some alterations in the finer fractions of the soil, which ultimately leads to the formation of some new minerals. In the areas where the Turkish soil samples and the Gothard clay loam sample were collected the deposited mineral materials have been subjected to an alkali environment in the geologic past and also in present days. Alkali solutions are excellent solvents for Si^{+4} and Al^{+3}. Because of the limited leaching conditions in arid and semiarid climates, solubilzed constituents have little opportunity to leave the soil profile. Resynthesis of components would be the expected. The analcime has probably formed in these soils by recrystallization of soluble silica and alumina and its presence can account for the unusual properties of these certain saline-alkali soils.

In an agreement with previous works (2) (29) monovalent cations appeared much more efficient than divalent cations in replacing the sodium from the analcime.

Continuous release of sodium from the Turkish soil sample and the Gothard clay loam sample upon extraction with NH_4OAc could be attributed to the presence of the analcime.

In light of these results, it would seem more advisable to use divalent cation solutions such as calcium and barium for the determination of exchangeable sodium content and cation exchange capacity of certain salt affected soils, instead of using NH_4OAc solution.

SUMMARY

The exchangeable sodium is probably the most widely used measurement for characterizing the Na^+ status of soils. It is also used as a basis for the definiation of the alkali soils. It is well established that exchangeable cation analysis of saline and alkali soils is subject to difficulties not ordinarily faced with other soils. These difficulties not only arise from Ca^{++} and Mg^{++} carbonates, but also from the presence of some sodium zeolites.

During the chemical analysis, some of the salt affected Turkish soils gave exchangeable-sodium percentages well over 100 per cent which is theoretically impossible. Calcium saturated Gothard clay loam soil from Arizona yielded unexpected amount of exchangeable-sodium upon extraction with NH_4OAc.

Following the literature review of the problem, this study was undertaken to determine whether these soils contained any mineral which rapidly releases Na during the exchangeable cation analysis. X-ray diffraction techniques were employed to determine the presence of some sodium zeolites, namely analcime, thomsonite, stilbite, pectolite, chabazite, and natrolite ain salt affected soils from Turkey and Arizona. Analcime was the only sodium zeolite found in the soils studied.

Exchangeable-sodium percentages of over 100 per cent and the

unexpected release of Na^+ from Ca^{++} saturated soil can be explained

by the fact that during contact with NH_4OAc, Na^+ in the analcime is

replaced by NH_4^+. Consequently, higher Na^+ concentrations are

obtained than in other soils which do not contain analcime.

The geological specimen of analcime, the Turkish soil, and

a Red Desert soil which was used as a check, were washed with $1\underline{N}$

solutions of KC1, NH_4OAc, $MgCl_2$, $BaCl_2$, $CaCl_2$, and $SrCl_2$ in order

to determine the amount of Na^+ released from the three different

samples and to check whether structural changes would occur in anal-

cime with different cations. Washings with $MgCl_2$, $BaCl_2$, $CaCl_2$,

and $SrCl_2$ solutions released approximately the same amount of Na^+.

The amount of released Na^+ sharply decreased after two months of

saturation with solutions of the divalent cations. Monovalent cations

K^+ and NH_4^+ released as much as three times more Na^+, especially

from analcime and the Turkish soil sample than did the divalent cations.

Also there was no sharp decrease in the amount of released Na^+ in

analcime and the Turkish soil sample even after two months of satu-

ration. These results were found in agreement with the ion sieve

affect theory of Barrer (2). Continued release of Na^+ during washings

with NH_4OAc and KC1, may be considered as a method to indicate the

presence of analcime.

The Turkish soil samples and the Gothard clay loam soil samples collected from areas that have been subjected to alkali conditions for long periods of time were found to contain analcime. The obviously erroneous exchangeable Na^+ contents obtained by using the NH_4OAc extracting solutions can be related to the presence of analcime. According to the results obtained during this study, use of divalent cation solutions such as Ca^{++} or Ba^{++} for exchangeable sodium content and cation exchange capacity determinations of soils, containing analcime is suggested.

LIST OF REFERENCES

(1) Babcock, K. L. Evidence for sodium fixation in salt affected soils. Soil Sci. Soc. Am. Proc. 24:85-86, 1960.

(2) Barrer, R. M. Ion exchange and ion-sieve processes in crystalline zeolites. J. Chem. Soc. p. 2342, 1950.

(3) Beattie, I. R. The structure of analcite and ion exchanged forms of analcite. Acta Cryst. 7:357-359, 1954.

(4) Bower, C. A. Rapid tests for soluble and exchangeable sodium in saline and alkali soils. J. Am. Soc. Agron. 40:1100-1105, 1948.

(5) Bower, C. A. Reitemeir, R. F. and Fireman M. Exchangeable cation analysis of saline and alkali soils. Soil Sci. 73:251-261, 1952.

(6) Bradley, W. H. The occurrence and origin of analcite and meerschaum beds in the Green River formation of Utah, Colorado, and Wyoming. U. S. Geol. Survey professional paper 158. 1. 1-7, 1929.

(7) Brag, W. L. Atomic structure of minerals. Cornell Univ. Press. Ithaca, N. Y. 1937.

(8) Chapman, H. D. and Kelly, W. P. The determination of the replaceable bases and the base exchange capacity of soils. Soil Sci. 30:391-406, 1930.

(9) Cullity, B. D. Elements of x-ray diffraction. Addison-Wesley Publishing Company, Inc., 1956.

(10) Foster, D. W. and Feicht, L. F. Minerology of concretions from Pittsburgh Coal seam, with special reference to analcite. Am. Minerologist, 31-357, 1946.

(11) George, R. D. Minerals and rocks, their nature, occurrence and uses. D. Appleton-Century Company, Inc., 1943.

(12)   Gruner, J. W.   The use of the oscilliation method in determining
          the structure of analcite. Am. Minerologist, 13:174-194,
          1928.

(13)   Hay, R. L. and Moiria, R. J.   Authigenic silicate minerals in
          Searles Lake, California. Sedimentology. 2:312-332, 1963.

(14)   Jackson, M. L. Soil chemical analysis. Prentice-Hall, Inc.,
          1958.

(15)   Keller, W. D. Analcime in the Popo Agie, Member of Chug-
          water formation. J. Sed. Ret. 22:70-82, 1952.

(16)   Kelley, W. P. Adsorbed Na$^+$, cation exchange capacity and
          percentage Na$^+$ saturation of alkali soils. Soil Sci. 84:
          473-478, 1957.

(17)   Kelley, W. P. and Brown, S. M. Base exchange in relation to
          alkali soils. Soil Sci. 20:477-495, 1925.

(18)   Kelley, W. P., Dove, W. H. and Page, J. B. Colloidal con-
          stituents of American alkali soils. Soil Sci. 51:101-124,
          1941.

(19)   Kittrick, J. A. and Hope, E. W. A procedure for the particle
          size separation of soils for x-ray diffraction analysis. Soil
          Sci.   96:319-325, 1963.

(20)   Milton, C. and Engster, H. P. Mineral assemblage of the
          Green River formation. Researches in geochemistry,
          editor Abelson, P. H. John Wiley and Sons, Inc. p. 119-
          150, 1959.

(21)   Osthaus, B. Kinetic studies on montmorillonites and nontronite
          by acid-dissolution technique. (Fourth National Conference
          on Clays and Clay Minerals) Nat. Research Council Pub.
          456:301-321, 1956.

(22)   Oruc, N. Some physical and chemical characteristics of salt
          affected soils of Igdir Plain. University of Ataturk, College
          of Agriculture. Erzurum, Turkey, 1964.

(23)   Overstreet, R., Reardin, J. C. and King, H. M. Gypsum,
          sulfur, and sulfuric acid for reclaiming an alkali soil of
          the Fresno series. Hilgardia 21:113-127, 1951.

(24)   Overstreet, R. and Schulz, R. K.   The effect of rice culture on a nonsaline sodic soil of the Fresno series. Hilgardia 27:319-332, 1958.

(25)   Pipkin, W. B.   Clay minerology of the Willcox Playa and its drainage basin, Cochise County, Arizona.   Ph. D. Dissertation.   Univ. of Arizona, 1964.

(26)   Ross, C. S.   Sedimentary analcite.   Am. Minerologist. 13: 195-197, 1928.

(27)   _____   Sedimentary analcite.   Am. Minerologist.   26: 627-629.   1934.

(28)   Schollenberger, C. J. and Simon, R. H.   Determination of exchange capacity and exchangeable bases in soil - ammonium acetate method.   Soil Sci.   59:13-24, 1945.

(29)   Schulz, R. K., Overstreet, R., and Barshad, I.   Some unusual ionic exchange properties of sodium in certain salt affected soils.   Soil Sci.   99:161-165, 1965.

(30)   Taylor, W. H.   The nature and properties of alumina silicate framework structures.   Proc Royal Soc.   London, Series A 145, p. 80, 1934.

(31)   Vernet, J. P.   Concerning the association montmonllonite-analcime in the series of Stanleyville, Congo.   J. Sed. Petrology.   31:293-295, 1961.

(32)   U. S. Salinity Laboratory.   Diagnosis and improvement of saline and alkali soils.   USDA Handbook 60, 1954.

(33)   Way, T.   The power of soils to adsorb manures.   J. Roy. Agr. Soc.   England 2:313-379, 1850.

(34)   Whittig, L. D.   Characteristics and genesis of solodized solonets of California.   Soil Sci. Soc. Am. Proc. 23:469-473, 1959.