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MINERALOGY OF THE SALT-EFFLORESCENCES FROM TYPIC SALORTHID PAKISTAN

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Of 12 salt-efflorescences collected in the winter of 1989-90, from the Rechna doab, all qualified as "saline" with pH ranging from 8.1 to 10.5, EC 34.4 to 89.7 dS m^{-1}. Solution (1:10) chemistry was dominated by $SO_4^{2-} > Cl^- > HCO_3^- + CO_3^{2-}$ and $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. X-ray diffraction analysis (XRDA) showed that the mineralogy of the 8 selected efflorescences was dominated by thenardite (Na_2SO_4), accompanying this mineral in varying amounts were trona-$Na_3H(CO_3)_2.2H_2O$ (major); calcite-$CaCO_3$ (minor) together with traces of natron ($Na_2CO_3.10H_2O$), burkeite [$Na_6CO_3(SO_4)_2$] and halite (NaCl). The most common mineral assemblage detected is thenardite-trona-calcite.

INTRODUCTION

Of the many ailments peculiar to the soils of Pakistan, salinity and sodicity are most prevalent. About 9% of the reported area of the country is affected by salinity and sodicity to varying degree (Mian, 1990).

Salt-efflorescence is a feature of poorly drained salt-affected soils in the semi-arid regions of Pakistan. It is formed at the surface by capillary rise and subsequent evaporation. These salt-efflorescences, unlike evaporites have not been studied extensively (Stewart, 1963) due to their less economic significance. But they hinder germination through their sealing effect and facilitate soil dispersion. Studies of the dynamics of salts in the soil, however, greatly aid in the management of salt-affected soils.

Present investigation was, therefore, started on the salt-efflorescences from typic salorthid (Khurrianwala soil series) in the Rachna doab for establishing their true nature and quantity of minerals prevalent in salt-crusts.

MATERIALS AND METHODS

Twelve salt-efflorescences involved in the investigation were collected during winter 1989-90 from various sites (Fig. 1 a). Disturbed efflorescences were collected for chemical and mineralogical analyses.

All samples were subjected to pH (1:10 soil:water) and EC (1:10) analysis. Other determinations were made by the methods of Richards (1954). Mineralogical assessment of various salt-efflorescences was made by XRD technique.

Only 8 out of 12 salt-efflorescences have been studied by XRD. These were ground in an agate pestle and mortar and the fine powder was filled in an aluminium window. This was then used for XRDA which was done on a Philips wide range goniometer (PW 1050/23). The XRD was equipped with a PW 1011 generator producing Mn filtered FeKα radiation at 56 kv and 16 mA. Signals were further subjected to pulse height analysis. A scanning rate of $1°2\theta$/minute from 2° to 52° was used at the scanning speed 1°2Θ/cm, slit system i.e., (divergent/receiving/scattering 1°/ 0.1/1°) and 2 seconds damping time. The chart speed was maintained at 1cm/minute. Usually 1 x 10^3 counts per second (cps) were used.

The d-spacings of various salt minerals on the X-ray diffractograms were calculated using the Bragg's law ($n\lambda = 2d\sin\Theta$). The minerals were identified on the basis of d-spacing using the Finks Index (Smith and Beward, 1963). Relative abundance based on the peaks height of the minerals has been given as dominant (4 = 50 to 100%); major (3 = 30 to 50%); minor (2 = 10-30%) and traces (1 = less than 10%).

above 40 dS m^{-1} and 2 between 30 and 40 dS m^{-1} and hence are classified as "saline" (Richards, 1954) and "strongly saline" (FAO/UNESCO, 1974). Sulphates were dominant among the anions and sodium among the cations in all the salt-efflorescences. The salinity of all the salt-efflorescenses is, therefore, identified mainly due to Na^+ and SO_4^{2-} and only partly due to chlorides, bicarbonates and carbonates. Sodium is a dominant cation in all the salt-crusts accompanied by various amounts of potassium, calcium and magnesium.

By using the approaches (Richards, 1954; Yegorov and Gorina, 1975) devoted to soluble salts which are usually dissolved from the soil/salt mixture and the total amounts of salts and/or concentrations of various ions in the solutions determined. The anions and cations are then associated into various combinations of salts which ap-

Table 1. Chemical characteristics of the salt-crusts used in the study

Salt crust No.	pH (1:10)	EC dS m^{-1}	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	$Ca^{2+}+Mg^{2+}$
			....	....	..... me l^{-1}	.....	....	....	....
1	8.30	85.0	Nil	10	13	1124	1103	18	26
2	8.35	89.7	"	8	24	1148	1128	26	27
3	9.00	52.9	"	10	58	664	706	22	4
4	9.25	58.4	4.0	2	6	797	763	22	20
5	8.40	71.8	Nil	4	2	959	930	15	20
6	8.30	81.7	"	4	8	1072	1040	15	28
7	10.50	64.9	96.0	20	33	704	795	54	4
8	9.25	67.1	8.0	6	28	887	896	27	6
9	8.10	55.1	Nil	6	7	750	721	20	22
10	8.20	36.6	"	4	6	475	444	21	20
11	8.15	41.4	"	4	5	543	510	21	21
12	8.25	34.4	"	4	8	436	417	20	11

RESULTS AND DISCUSSION

The pH (1:10) ranged from 8.1 to 10.5 (Table 1). Nine out of 12 salt-crusts studied have EC (1:10) greater than 50 dS m^{-1}, 1 pear as hypothetical salt-minerals. It is concluded from Table 1 that thenardite (Na_2SO_4) or mirabilite ($Na_2SO_4.10H_2O$) may be dominant salt-minerals in all the salt-crusts.

Table 2. X-ray diffraction analysis of the salt-crusts

a. Relative abundance of various salt-minerals detected in the salt crusts

Salt crust No.	tnd	tro	cal	nat	bkt	hal
1	4	3	2	-	-	-
3	4	3	2	-	-	1
5	4	3	2	-	-	-
6	4	3	2	-	-	-
7	4	3	1	1	1	1
8	4	3	2	-	-	-
9	4	3	2	-	-	-
11	4	3	2	-	-	-

Key: dominant (4 = 50-100%); major (3 = 30-50%); minor (2 = 10-30%); traces (1 = less than 10%); - = not detected; tnd = thenardite; tro = trona; cal = calcite; nat = natron; bkt = burkeite; hal = halite.

b. Salt-minerals assemblage in various salt-crusts

Salt crust No.	Assemblage
1	tnd, tro, cal
3	tnd, tro, cal, hal
5	tnd, tro, cal
6	tnd, tro, cal
7	tnd, tro, cal, nat, bkt, hal
8	tnd, tro, cal
9	tnd, tro, cal
11	tnd, tro, cal

Mineralogical investigations by XRD: XRDA has been utilised in the present investigation to resolve the pragmatic ideas of various scientists about the dominance of halite (NaCl) or thenardite (Na_2SO_4) in the salt-crusts of Pakistan.

The X-ray diffractograms of only two salt crusts have been presented (Fig. 1 b). Details of all the salt-crusts is given somewhere else (Rasool, 1991). The semi-quantitative analysis of the salt-minerals detected in various salt-crusts and mineral assemblages are given in Tables 2 a and 2 b, respectively.

The X-ray diffractogram (Fig. 1 b) shows the presence of three salt-minerals (salt-1) and four minerals (salt-3). The salt-1 shows the presence of thenardite, trona and calcite and salt-3 revealed the presence of thenardite, trona, calcite and halite. The semiquantitative analysis based on the peaks height suggests the dominance of thenardite over the other minerals. Trona appeared to be the second dominant (major) mineral and calcite was present in minor amount. The dominance of thenardite in all the salt

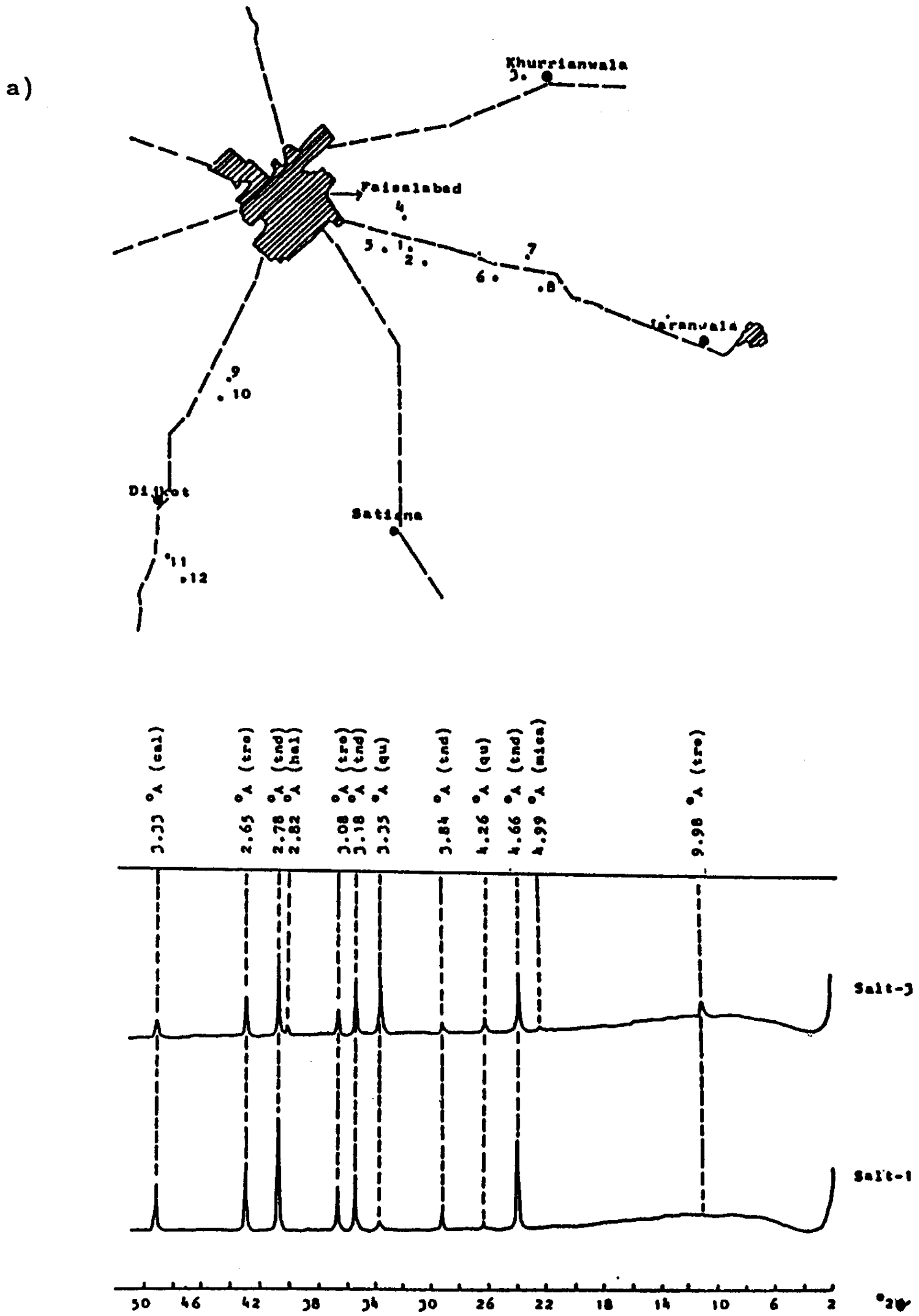

Fig. 1. a. Map showing the sites of salt-crusts collection.
b. X-ray diffractograms of the salt-crusts.

crusts could also be correlated with the chemical composition of the soil solutions (1:10), where Na^+ has been found to be dominant among the cations and SO_4^{2-} among the anions. Such a dominance of Na^+ and SO_4^{2-} could have better chances to crystallise together which ultimately results the mirabilite ($Na_2SO_4.10H_2O$) at the early stage which on further dehydration may lead to transformation to thenardite. Mirabilite is always found below the surface, where there may be regularly fed of capillary water from the groundwater table. The overlying horizon being dried, mirabilite looses water at the surface and gradually turns into thenardite (Tursina, 1980). Unfortunately the salt crusts involved were collected from the surface and no special precautions were made to preserve mirabilite. It has been further reported by Tursina (1980) that the change of mirabilite to thenardite is very rapid process, due to which mirabilite has not been detected, but thenardite, which suggests that the mirabilite was probably confined to the lower layer of the salt-crusts. In Pakistan, the temperature during the winter season ranges between 6.1 to 28.2 °C (Chaudhry, 1977). The literature shows (Tursina, 1980) that if the mirabilite is left open in air at about 26 °C for a longer time, this may change into thenardite.

The dominance of thenardite can also be correlated to the composition of under groundwater. The analysis of under groundwater collected from a tubewell situating near to the site of collection of salt-1, also revealed the dominance of Na+ and SO_4^{2-}. Similar studies have also been reported by Keller *et al.* (1986) on the mineralogy and stability of soil evaporites in North Dakota.

Assemblages of salt-minerals, i.e. thenardite/trona/calcite has also been detected in salt number 5, 6, 8, 9 and 11 and hence shows their relevance to the composition of salt-1, and to the composition of the under ground water. Only in salt number 3 and 7, different assemblage were detected. In salt-7 the assemblage was composed of thenardite/trona/calcite/natron/burkeite/halite. The crystallisation of natron ($Na_2CO_3.10H_2O$) and burkeite-$Na_6CO_3(SO_4)_2$ in the particular salt crust may be related to the high amount of CO_3^{2-} (96 me l^{-1}) and HCO_3^- (20 me l^{-1}) contents in this particular salt crust. The high pH (10.5) suggest the crystallisation of natron and burkeite which is also supported by the presence of high CO_3^{2-} and HCO_3^- contents in the soil solution of salt-7. This is in contrast to the soil solutions of other salt-crusts where these two minerals were not detected.

The present study shows the dominance of thenardite as the dominant mineral and thenardite/trona/calcite the most common assemblage, although small amounts of other salts (burkeite, halite and natron) are also present. On the other hand the solutions (1:10) contain other cations and anions capable of combination and subsequent recrystallisation as salt minerals, but these have not been detected in the present study as they are perhaps present below the sensitivity limit of the technique (XRDA) employed (less than 3%). The low amounts of various salt-minerals in the salt-efflorescences are overlapped by the most abundant and easily detected minerals due to dilution effect.

The crystallisation of dissolved solids as salt-minerals at the surface restricts crop production. Presence of salts increases osmotic pressure of soil moisture and consequently affect plant growth through physiological drought, a typical phenomenon for plant growing in saline conditions. Indirectly salinity affect the plant growth by causing deterioration of soil structure.

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