

## CHANGES IN POTASSIUM MINERALOGY OF A CALCAREOUS SALINE SODIC SOIL DURING RECLAMATION WITH ACIDS

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In a field study, gypsum, in addition to HCl and H<sub>2</sub>SO<sub>4</sub>, equivalent to 100% gypsum requirement, was used to reclaim a dense saline sodic clay loam soil during rice cultivation. Soil samples collected at two depths after the rice crop were analysed for total K<sup>+</sup> and mineralogy. Mica was the major K<sup>+</sup> mineral in the soil. Total K<sup>+</sup>, mica and smectite decreased more profoundly in acid treated soil than in the gypsum and untreated soils. It is suggested that the proton (H<sup>+</sup>) from acids extracted interlayer K<sup>+</sup> from mica and converted it to vermiculite which fixed applied K<sup>+</sup>. This could explain the reason of K deficiency in wheat sown after rice in acid reclaimed saline sodic soils.

Key words: acids, potassium mineralogy, reclamation, saline sodic soil

### INTRODUCTION

Soil salinity is a serious constraint for crop production in most arid and semi-arid areas of the world. Gypsum (CaSO<sub>4</sub> 2HP) is commonly used to reclaim saline sodic soils for economic crop yields. Recently, strong acids HCl and H<sub>2</sub>SO<sub>4</sub> generally available as industrial by products have been successfully used for the amelioration of calcareous saline sodic soils (Poonia and Bhumbra, 1974; Prather *et al.*, 1978 and Ahmad *et al.*, 1986). Wheat following rice in such reclaimed fields showed K<sup>+</sup> deficiency and responded well to its application (Ahmad, 1992: personal communication). On a clay loam soil, HCl dissolved and transferred an appreciable proportion of K to lower depths in soil columns (Ahmad *et al.*, 1985 and Akhtar and Niazi, 1986). Micaceous minerals are principal sources of K in most soils of Pakistan (McNeal, 1966 and Bajwa, 1987). Hydrogen saturated ion-exchange resins have successfully been used to extract non-exchangeable K from soils rich in feldspar and micaceous K<sup>+</sup> - bearing minerals (Sparks, 1986 and Rahmatullah, 1991). Improvement in water infiltration properties of such soils by acid reclamation may disturb soil K equilibria and hence alter soil K<sup>+</sup> mineralogy. This paper reports changes in K<sup>+</sup> mineralogy of a calcareous saline sodic soil reclaimed either by HCl, H<sub>2</sub>SO<sub>4</sub> or CaSO<sub>4</sub> 2HP with consequences upon K<sup>+</sup> nutrition of plants.

### MATERIALS AND METHODS

Soil reclaimants, HCl, H<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub> 2HP were

applied @ 100% of gypsum requirement, in addition to control treatment for rice cultivation on a Sindhelianwali (Typic Natrargidsi, clay loam soil (pH 8.6, ESP 91.6 and CaCO<sub>3</sub> 7.4 %) at Saline Agricultural Research Substation, Sadhoke (near Lahore) of Pakistan Agricultural Research Council. Gypsum requirement of surface 15 cm soil was 5.5 tons per acre and one ton gypsum was equal to 1.28 tons of 34 % HCl. Composite soil samples for this investigation were collected after rice cultivation at 0-22 cm and 22-44 cm depth. Soil samples were air dried and ground to pass through a 2 mm sieve.

For X-ray identification of clay minerals, the samples were treated with 1N NaOAc (pH5) to remove carbonates. Organic matter was oxidized with H<sub>2</sub>O<sub>2</sub> in 1N NaOAc and free iron oxides were removed with dithionite-citrate-bicarbonate solutions (Mehra and Jackson, 1960). Sand was separated by wet sieving. Silt and clay were fractionated by centrifugation (Jackson, 1965). Clay was further fractionated into coarse clay (2-0.2-μm) and fine clay (<0.2-μm). Separated clay samples were saturated with Mg<sup>2+</sup> and K<sup>+</sup> before preparing oriented specimens on glass slides. After preliminary examination of K<sup>+</sup> saturated clay at room temperature, specimens were heated for two hours at 550°C and were X-rayed again. Mg<sup>2+</sup> saturated specimens were X-rayed at room temperature after glycerol salvation. Samples were studied using Diano X-ray diffractometer with Cu K $\alpha$  radiation at 30 Kv and 18 mA.

Total K<sup>+</sup> in clay fraction was estimated by digesting its sub-portions in Tenon beakers with concentrate HNO<sub>3</sub>, HF, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> (Follet and Lindsay, 1970). The amount of micaceous minerals in <2 $\mu$ m (clay) fraction was determined by fusion with sodium pyrosulphate (Kiely and Jackson, 1965). The relative amounts of smectite and vermiculite in the clay fraction were estimated from cation exchange capacity measurements according to Alexiades and Jackson (1965).

## RESULTS

**Mineral Composition of Clay Fraction:** Coarse (2-0.2  $\mu$ m) and fine (<0.2  $\mu$ m) clay fractions, separated from composite soil samples collected from control plots, depicted a 10 Å peak for mica (Fig. 1). The peak was more intense in coarse clay. The two clay fractions had a 14 Å peak which could be attributed to vermiculite, smectite and chlorite. The presence of smectites was confirmed by partial expansion of 14 Å peak to 18 Å and by lesser intensity of the 14 Å peak upon glycerol salvation in Mg<sup>2+</sup> saturated samples. Chlorite was identified by persistence of a 14 Å peak in K<sup>+</sup> saturated samples X-rayed after heating at 300 and 550°C. Intensified 10 Å peak upon heating in K<sup>+</sup> saturated samples indicated the existence of vermiculite. Kaolinite was identified by a peak at 7 Å that disappeared upon heating to 550°C.

Evidently, Sindhelianwali clay loam had a mixed clay mineralogy where mica was the principal K<sup>+</sup> bearing mineral. These findings agree with those of the other investigators (McNeal, 1966; Bajwa, 1987 and Rahmatullah, 1991).

**Soil Reclamation and Potassium Mineralogy:** Total K content in the <2  $\mu$ m fraction of the soil samples was

2.5 to 3.7% as was found normally in our agricultural soils (Table I).

Reclamation with either H<sub>2</sub>SO<sub>4</sub> or HCl decreased the proportion of total K<sup>+</sup>, mica and smectite in 0-22 cm and 22-44 cm layers. Decrease in total K<sup>+</sup>, mica and smectite was relatively more in surface than in sub-surface layer. Relative decrease by reclamation with the two acids ranged from 17 to 26% for total K<sup>+</sup>, 16 to 32% for mica and 8 to 27% for smectite at the two soil depths. Nitric acid and H-saturated ion-exchange resins have been frequently used as proton (H<sup>+</sup>) source to replace interlayer K<sup>+</sup> from minerals, soils or soil fractions rich in feldspars and micaceous K<sup>+</sup>-bearing minerals (Quemener, 1979; Sparks, 1986 and Rahmatullah, 1991). However, proportional increase in vermiculite was 31 to 48% by reclamation with the two acids. Increase in vermiculite was more in 0-22 cm layer than in 22-44 cm layers.

Reclamation with gypsum increased the Proportion of either total K<sup>+</sup>, mica or smectite by about 8% in 0-22 cm layer. Gypsum did not affect the proportion of vermiculite in 0-22 cm layer but increased it by 7% in 22-44 cm layer. These changes due to gypsum treatment, either in the Proportion of total K<sup>+</sup>, mica, smectite or vermiculite, are within the error for X-ray diffraction technique.

## DISCUSSION

Most salt affected soils of Pakistan are developed under semi-arid to arid climate from alluvium deposited by the Indus river and its tributaries from Himalayas and the adjoining uplands (Wadia, 1966; Razzaq and Herbillon, 1979 and Ahmad, 1986). Predominantly, these soils

Table I. Distribution of total K<sup>+</sup>, mica, smectite and vermiculite in clay (<2  $\mu$ m) fraction of a soil reclaimed with strong acids (HCl and H<sub>2</sub>SO<sub>4</sub>) and gypsum

Reclamation treatment	Depth (cm)	Total K	Mica	Smectite %	Vermiculite
Control	0-2	3.4	32.6	12	8.9
	22-44	3.6	34.4	11	7.3
Sulphuric acid	0-2	2.5	27.4	10	12.5
	22-44	3.0	23.5	8	10.8
Hydrochloric acid	0-2	2.8	24.9	11	11.7
	22-44	3.0	27.1	8	10.8
Gypsum	0-2	3.7	35.3	13	8.9
	22-44	3.3	31.7	12	7.8

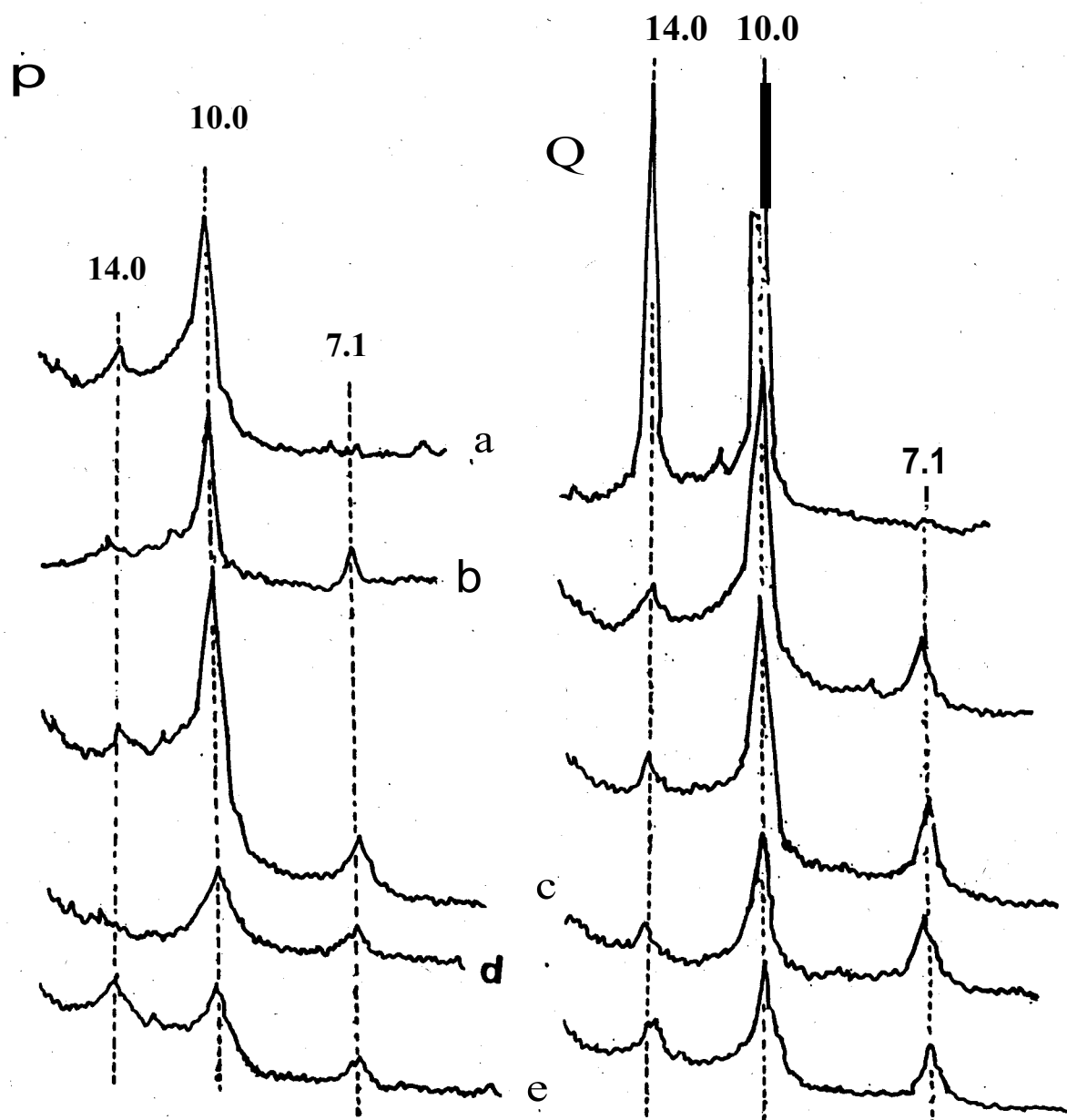


Fig. 1. X-ray spectra of fine (0.2-2  $\mu$ m, P) and coarse (0.2-2  $\mu$ m, Q) clay fraction of control plots after different treatments; [a = K + heating at 550°C; b = K + heating at 330°C; c = K at room temperature; d = Mg + glycerol and e = Mg saturation].

have mixed clay mineralogy containing mica as the principal K<sup>+</sup>-bearing mineral (McNeal, 1966; Ahmad, 1986 and Bajwa, 1987). Crop responses to K<sup>+</sup> application on such soils are sporadic (Sillanpaa, 1982). Hydrogen saturated ion exchange resins and HNO<sub>3</sub> have been used as proton (H<sup>+</sup>) source to extract

interlayer/non-exchangeable K<sup>+</sup> for monitoring its bio-availability for crop production in different soil-plant situations (Quemener, 1979; Sparks, 1986 and Rahmatullah, 1991). Other than dissolution of free lime during reclamation of a calcareous saline sodic soil, some protons (H<sup>+</sup>) either from H<sub>2</sub>SO<sub>4</sub> or HCl can also

release interlayer K<sup>+</sup> in mica rich soils (Table 1). The gradual release of K<sup>+</sup> from positions in the mica lattice results in the formation of illite (hydrous mica) and eventually vermiculite (McLean, 1979; Nielsen and Moberg, 1984). Vermiculite can fix applied K<sup>+</sup>. In Pakistan, rice is grown under submerged soil with free leaching conditions. This can facilitate the mobility of released K<sup>+</sup> to lower soil horizons. Hence, response of wheat to K<sup>+</sup> application after rice cultivation on a soil reclaimed by acid can be observed.

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## REFERENCES

- Ahmad, M., B.H. Niazi and G.R. Sandhu. 1985. Hydrochloric acid as a reclamation agent for calcareous sodic soils. I. Dissolution and transfer of ions under restricted leaching conditions. *Pak. J. Agri. Res.* 6(3): 197-203.
- Ahmad, M., B.H. Niazi, Rahmatullah and G.R. Sandhu. 1986. Reclamation of calcareous saline sodic soils by gypsum and HCl under rice cultivation. *Trap. Agri. (Trinidad)*. 63(4): 271-272.
- Ahmad, M. (Ed.). 1986. Proceedings XII International Forum on Soil Taxonomy and Agrotechnology Transfer, Vol. I & H. Soil Survey of Pakistan, Lahore.
- Akhtar, M.S. and B.H. Niazi. 1986. Nutrient dynamics during the reclamation of calcareous saline-sodic soil with hydrochloric acid. *Pak. J. Agri. Res.* 73: 221-226.
- Alexiades, C.A. and M.L. Jackson. 1965. Quantitative determination of vermiculite in soils. *Soil Sci. Soc. Am. Proc.* 29: 522-527.
- Bajwa, M.I. 1987. Potassium mineralogy of Pakistan soils and its effect on potassium response. In *Proceedings of Workshop on Potassium and Fertilizer Use Efficiency*, pp.203-216. National Fertilizer Development Centre, Islamabad.
- Follet, R.H. and W.L. Lindsay. 1970. Profile distribution of zinc, iron, manganese and copper in Colorado soils. *Colorado State Univ. Expt. Stn. Tech. Bull.* No. 110.
- Jackson, M.L. 1965. *Soil Chemical Analysis: Advanced course*. Published by the author, Department of Soil Science, University of Wisconsin, Madison, Wisconsin.
- Kiely, P.V. and M.L. Jackson. 1965. Quartz, feldspar and mica determination for soils by sodium pyrosulphate fusion. *Soil Sci. Soc. Am. Proc.* 29: 159-163.
- McLean, E.O. 1979. Influence of clay content and clay composition on potassium availability. In *Proceedings of Workshop on Potassium in Soils and Crops* (Ed.G.S. Sekhon), pp. 1-13. Potash Research Institute of India.
- McNeal, B.L. 1966. Clay mineral variability in some Punjab soils. *Soil Sci.* 102(1): 53-58.
- Mehra, O.P. and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*, 7:317-327.
- Nielsen, J.D. and J.P. Moberg. 1984. The influence of K-depletion on mineralogical changes in pedons from two field experiments and in soils from four pot experiments. *Acta Agricultura Scandinavica*, 34:391-399.
- Poonia, S.R. and D.R. Bhumbla. 1974. Effect of H<sub>2</sub>SO<sub>4</sub>, HCl and Al<sub>2</sub> (SO<sub>4</sub>) on the yield, chemical composition and Ca<sup>+</sup> uptake from applied 45CaCO<sub>3</sub> by dhairicha (*Sesbania aculeata*) in a saline alkali soil. *Plant Soil*, 40:557-564.
- Prather, R.J., J.O. Goertzen, J.D. Rhodes and H.Frenkel. 1978. Efficient amendment use in sodic soil reclamation. *Soil Sci. Soc. Am. Proc.* 42:782-786.
- Quemener, J. 1979. The measurement of soil potassium. *Int. Potash Inst. Res. Topic No.4*.
- Rahmatullah. 1991. Plant uptake of potassium released from sand, silt, and clay fractions of some alluvial and loess derived soils of Pakistan. Ph.D. Thesis, Justus-Liebig Univ., Giessen, Germany.
- Razzaq, A. and A.J. Herbillon. 1979. Clay mineralogical trends in alluvium-derived soils of Pakistan. *Pedologie (Ghent)*, 29(1):523.
- Sillanpaa, M. 1982. Micronutrients and the nutrient status of soils. A global study, FAO, Rome.
- Sparks, D.L. 1986. Potassium dynamics in soils. *Adv. Soil Sci.* 6: 163.
- Wadia, D.N. 1966. *Geology of India*. The English Language Book Society of MacMillan and Co., London.