CHAPTER VII

PATTERNS OF CHANGES IN CHEMICAL PROPERTIES OF SALINE-ALKALI SOILS DURING WEACHING AND INTERACTION OF SEA WATER AND WEACHED SOILS AND FURTHER DESALANIZATION.
It has been reported that sea-water flooded soil containing high percentage of soluble salts and high percentage of exchangeable sodium, potassium and magnesium, can be leached out of its soluble salts by interaction with water; but exchangeable sodium, potassium and magnesium will be removed only slowly. We know that sodium is responsible for the break-down of soil structure after removal of the bulk of soluble salts. A study under natural conditions of leaching of salty marshes has been carried out by Molen (9), Kelley (3), Bower (1) and other workers have studied the effect of various treatments on pH salinity and ESP of soils. The actual regeneration of a soil includes the following seven stages:

(1) Concentration - changes in the soil solution.
(2) Hydrolysis

(3) Reaction with water containing carbon-dioxide.

(4) Reaction with dissolved calcium carbonate.

(5) Reaction with dissolved gypsum.

(6) Reaction with other dissolving Ca-compounds.

(7) Uptake of ions by plant roots.

Thus degree of salinity, proportion of calcium carbonate and gypsum which are often present in saline soils become important factors in deciding the course of regeneration. In the absence of gypsum, regeneration takes place with calcium carbonate in many saline-alkali soils. During the regeneration Na⁺, K⁺ and Mg²⁺ ions are replaced by the more strongly adsorbed Ca ions. The resulting pH change will be indicative of the interaction during leaching of soluble salts. The ions usually decrease in the order Cl⁻ > Na⁺ > K⁺ > Mg²⁺ as suggested by Molen (10). According to experimental data on regeneration of sea-inundated soils reported by Molen (10), in a period of 4 years on application of gypsum, Na decreased from 12.9 to 2.0 percent,
K decreased from 3.6 to 2.1 percent and Mg decreased from 17.7 to 17.5 percent. It is thus indicated that Na ion is fast replaced than other ions, while Ca increased from 33.8 to 45.7 percent.

The resulting changes of various salinity levels in different saline soils may be predicted on theoretical grounds.

(1) With decrease in salt concentration, there will be the phenomenon of hydrolysis of Na-clay and the adsorbed Na ions will be exchanged with $H_3O^+$ originating from auto-protolysis of water.

\[
H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \]

\[
Na\text{-soil} + H_3O^+ \rightleftharpoons H_3O^-\text{-soil} + Na^+ \]

The OH\textsuperscript{−} ions resulting from the process will increase pH considerably.

(2) In the presence of CO\textsubscript{2}, however, the pattern of reactions will be as follows:

\[
CO_2 + H_2O \rightleftharpoons H_2CO_3 \]

\[
H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \]

\[
Na\text{-soil} + H_3O^+ \rightleftharpoons H_3O^-\text{-soil} + Na^+ \]
At this stage, if hydrolysis and the reaction with CO₂ proceed simultaneously, high amounts of carbonate ions will be produced according to the equation:

\[ \text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{CO}_3^{2-} \]

Due to the presence of carbonate ions, pH will not increase to that height as in the case of absence of calcium carbonate.

It is noted by Molen (11) that by simple hydrolysis, only 20 percent of exchangeable Na is released from a clay, while in the presence of carbon dioxide Na may be released to the extent of even 100 percent. Thus release of exchangeable Na will be a function of CO₂. It is therefore suggested that in calcareous soils, reaction with calcium bicarbonate will greatly predominate over the hydrolysis reaction. In calcareous soils Na is replaced by Ca rather than H₂O⁺.

(3) In soils rich in exchangeable Na (i.e. soils with high ESP) even a slight degree of hydrolysis will increase the soil pH to a large extent.

(4) In sea-inundated soils, when salts are removed and the soil contains calcium carbonate, the increase in pH is proportional to the ESP of the soil.
(5) The dissolved calcium carbonate will also influence the equilibrium for replacement of Na from the soil. In presence of a slight amount of carbon dioxide, bicarbonate ion will form according to the following equation:

$$\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{Ca}^{++} + 2\text{HCO}_3^-$$

The Ca ions so produced, will react with exchangeable Na according to following equation:

$$\text{Na}_2\text{-soil} + \text{Ca}^{++} \rightleftharpoons \text{Ca} - \text{soil} + 2\text{Na}^+$$

This will also influence pH of the soil suspension. In fact, this is the most important stage in regeneration of calcareous saline-alkali soils.

(6) The rate of replacement of Na by Ca may not be as expected, because presence of K and Mg in sea-inundated soil will interfere and therefore subsequent increase in pH can be attributed to the presence of Mg in soils.

(7) One more type of reaction prevails in the gypsy-ferous soils. In these soils the pH will be lowered depending upon the amount of gypsum. Gypsum may occur in soils of arid-regions.
Therefore a close study of patterns of pH and salinity changes during leaching will be a guide line to the processes taking place during regeneration. The varieties of patterns obtained during leaching suggests that inspite of water being freely available, different soils produce different equilibrium systems and a close study of such systems will be of great assistance in designing reclamation procedures for different types of salines.

(8) In highly saline soils there will be the reflection of the interaction of soil and salt solution only, during its first leachate.

INTERACTION OF SEA WATER WITH THE LEACHED SOILS

The saline-alkali soils leached repeatedly with quantities of distilled water will assume H-Ca-soil form, if the soil contains salts of calcium. When seawater is added to the leached soils, the first step will be the attainment of equilibrium between the adsorbed ions and the ions in solution. Kelley (2), Kunin and
Myers, Samuelson, Lederer and Lederer, and Wiklander (7), have studied the kinetics of ion-exchange. The equilibria are highly complicated in character. As there will be more than one electrolyte present in ion-exchange reaction with sea water, the Donnan distribution coefficient for the various ions can be given as follows according to Molen (8).

\[
\frac{a''Na}{a'Na} = \frac{a''K}{a'K} = \frac{a''Mg}{a'Mg} = \frac{a''Ca}{a'Ca} = \frac{a'Cl}{a''Cl} = \frac{a'SO_4}{a''SO_4} = \lambda
\]

The activity coefficients of ions will be involved in considering the ionic concentrations. The equilibrium Na-Ca and Mg-Ca can be given by the following equations:

\[
\begin{align*}
\frac{f^{2/3} + NaCl \cdot m_{Na}}{3/2 + CaCl_2 \cdot m_{Ca}} & = \frac{f^{2} + NaCl \cdot m_{Na}}{3/2 + CaCl_2 \cdot \sqrt{m_{Ca}}} \\
\frac{f^{3/2} + MgCl_2 \cdot m_{Mg}}{f^{3} + CaCl_2 \cdot m_{Ca}} & = \frac{f^{3} + MgCl_2 \cdot m_{Mg}}{f^{3} + CaCl_2 \cdot m_{Ca}}
\end{align*}
\]

The exchange of Na - Ca will take place according to the following equation of Krishnamoorthy and Overstreet (4, 5, 6).
The changes in pH on sea-water inundation for a non-calcareous soil has also been studied by Molen (11).

Diagrams 7.1 to 7.14 and Figures 7.1 to 7.8 present experimental results on leaching with distilled water, salinization of leached soils with sea-water distilled and again desalinization with distilled water.

The experimental technique followed for leaching, salinization and desalinization was as follows. 10 gms of the soil was taken and leached with 200 ml. of distilled water every time. The suspension was stirred two or three times and the extract was taken out every 24 hours. The extract so obtained was used for measurement of pH and electrical conductivity. For salinization experiment, the leached soil was treated with artificial sea-water prepared as follows:

**NaCl**  
26.52 gms.

**MgCl₂**  
2.45 gms.
MgSO₄          3.31 gms.
CaCl₂          1.14 gms.
KCl            0.73 gms.
NaHCO₃         0.20 gms.
NaBr           0.08 gms.

dissolved in one litre
distilled water. Finally leaching was again done with
distilled water as in the beginning.
Figure 7.1

Leaching Curve
Dhandhua - Patana Area

Figure 7.2

Salinization and Desalinization Curve
Dhandhua - Patana Area
LEACHING CURVE
CAMBAY—VADGAM AREA

- 489 C (0.8 EC → 0.09 EC)
- 489 B (7.2 EC → 0.09 EC)
- 489 A (7.99 EC → 0.08 EC)
- 480B (0.15 EC → 0.07 EC)
- 480A (0.18 EC → 0.09 EC)

PH

NUMBER OF EXTRACTS

FIG. 7.7

SALINIZATION AND DESALINIZATION
CAMBAY—VADGAM AREA

489 A
480 B
480A

PH

SALINIZATION DESALINIZATION

NUMBER OF EXTRACTS

FIG. 7.8
LEACHING CURVE
CUMBAH-DHURVARAN AREA

SALINIZATION AND DESALINIZATION CURVE
CUMBAH-DHURVARAN AREA

FIG. 7.9

FIG. 7.10
DISCUSSION

DHANDHUKA - PATANA AREA : (Semi-Ariel Region : Soda Soils)

The soils are characterised by a very high proportion of calcium carbonate in the soils, being greater than 20 percent in all the samples. These are the black alkali soils. Even during the leaching of soils of low salinity, the patterns differ widely. This is an indication of high exchangeable sodium in soil complex. A combined effect of hydrolysis of complex, and the interaction of calcium bicarbonate solution with the soil is reflected. Thus, a complicated equilibrium is set up in the soils, which have a non-saline alkali character. Differences in patterns can be attributed to variations in nature of soils, e.g. sample 120 A which has a very low salinity, does not show a prominent decrease in pH value upto its 12th leaching which indicates requirement of high proportion of Ca to replace Na from the soil.

The first stage of salinization with sea-water is indicated by lowering of pH and the other two stages indicate steady pH, due to high electrolyte content. Further desalinization follows a similar procedure to desalinization of naturally salinized soils.
pH significantly rises due to removal of salts, representing the ESP level of the soil. Once again there is gradual lowering of pH and steady attainment, which is almost parallel to the naturally salinized soils.

DHANDHUKA - DHOLDERA AREA: (Semi-Ariel Region; Old Coastal Intrusion: Calcareous soils)

The samples selected, show a wide variation in salinity range as well as percentage of exchangeable sodium. Proportion of calcium carbonate in most of the samples is fairly high. With decrease in initial salinity level, hydrolysis of Na-soil and the interaction of calcium carbonate are reflected up to 5th leaching. Subsequently, there is very little change. Of course, the steady pH attainment at low salinity has different values for different samples, which incidently can be correlated with low calcium carbonate content. The presence of calcium carbonate also appears to hasten the Na replacement reaction.

The first stage in salinization in a significant lowering of pH, but in the second stage there is slight increase in pH, suggesting alkalization. Further stages of desalination are followed by increase in pH
by about 1.5 units. And the final steady state attainment is similar to initial desalinization, but resultant equilibrium pH are high by about 0.5 pH units. This is difficult to explain except as contribution from dissolution of CaCO$_3$.

SURENDRANAGAR – MAL LAKE AREA: (Semi-Ariel Region: Old Sea Intrusion: Gypseferous soils)

These are gypseferous soils containing 3 to 30 percent calcium carbonate, the ESP values in most cases is below 50. The salinity levels are also low for many soils samples. The curves are peculiar. They differ from curves of other areas in that, there is no sharp increase in pH in early stages of leaching. Again attainment of highest pH in four out of five samples is 8.8 pH, while it is 9.7 in sample number 238 B, which has an ESP of only 37. The soils with low salinity level show an equilibrium pH upto 7.4 which is comparatively low.

The salinization and alkalization taking place simultaneously, is reflected by low equilibrium pH values. The desalinization state follows a pattern of increase in pH indicated by representation of the ESP with decreasing salinity levels. It is curious to note that, in such saline soils, containing gypsum, the steady...
state pH is higher by about 0.5 to 1.0 unit indicating that gypsum present is exhausted due to a large number of leachings and there is no buffer action of gypsum.

CAMBAY - VADGAM AND CAMBAY - DHUVARAN AREAS: (Humid coastal Region: Fresh Sea-Intrusion)

Soils of these two areas give the same pattern of leaching curves. Soils with low salinity attain a quick equilibrium, while those with high salinity indicate large changes in pH on leaching. Soils of Cambay - Dhuvaran tract attain a quick equilibrium to normal soil condition while soils of Cambay - Vadgam inspite of low BSP level show alternate increase and decrease, which perhaps may be attributed to Ca - Na reaction.

In Cambay - Vadgam area the salinization curve indicates decrease in pH and the steady pH due to salinization and the formation of saline-alkali soils. The desalinization curve for sample 480 A and 480 B is indicative of the original soil pattern, because it agrees with the general type of curves.

Thus a study of this type can throw light on the regional characteristics of the soil in any area. The desalinization, of sea-water treated soil, has a
same pattern as the natural coastal saline soils. This indicates that initial desalinization and desalinization after sea-water treatment are nearly the same for coastal salines, but they would differ in the case of arid - zone salines, which generally contain modifying constituents such as CaSO₄ and gypsum.

For soils of Cambay - Dhuvaran area the same remarks as Cambay - Vadgam area apply. A highly salinized and highly alkalized soil becomes desalinized and dealkalized by parabolic process, in contrast to the odd behaviour of naturally salinized soils.

BROACH - JAMBUSAR - KAVI AREA : (Humid Region : Recent Sea - Intrusion)

In this area, soils have extremely high salinity levels for the saturation extracts. These soils are coastal tidal salines in continuous equilibrium with sea-water. Here, the saline soils have pH from 7.5 to 7.7 which rises upto 9.0 pH in the third extract, indicating a very high sodiumization of the soil complex. pH gradually falls down continuously from 3rd to 9th extract. In three out of four samples, it becomes steady. The sudden increase in pH after the 3rd leaching may be attributed to complete leaching away of salts, and the hydrolysis of Na-soil complex.
In this area the patterns of salinization and desalinization are similar to other coastal salines. But it differs from desalinization of natural samples. The desalinization of natural samples follow an unpredictable non-flexible behaviour.

**NAVSARI - DANDI AREA** : (Humid Region : Fresh Sea Intrusion).

These coastal saline soils are high in exchangeable magnesium. The process of desalinization in this area differs from other areas. Equilibrium attainment after the 10th extract is indicative of a slow process. Proportion of high magnesium in soil complex appears to be the only explanation, as the calcium carbonate content is not very high. The alternate increase and decrease can also be attributed to release of hydroxyl ions as well as its precipitation by the magnesium released from soils by the action of $\text{H}_3\text{O}^+$ or calcium.

In this area, there is lowering of pH with increasing salinization. There is a slight increase in pH after second stage of salinization. But stage number 4 is curious in indicating a low equilibrium pH value, e.g. in sample 442 A the value attained is 6.5. During the stage of desalinization there is an increase in pH and direct steady state attainment without lowering of pH. In this aspect, the nature of this soil differs from soils of other areas.
BIBLIOGRAPHY


