SOFTENING OF SEAWATER

4.1 Experimental and results

Tulsion 14 cation-exchange resin

4.1.1 Effect of flow rate of the influent on breakthrough capacity

A glass column, 100 cm in length and of 2.5 cm$^2$ cross section area, was filled to 60 cm height with Tulsion 14 cation-exchange resin in the sodium form. Sea water (of composition given in Table 7) was passed through the resin bed at exhaustion flow rates ranging from 7.5 ml/minute to 25.0 ml/minute. The effluent was collected in 100 ml fractions after discarding the void volume. Every fraction was analysed for total hardness. The exhaustion was continued till the effluent and influent hardness were the same. Appearance of traces of calcium and magnesium was taken as the basis for determining breakthrough capacity. Total exchange capacity was determined by computing the calcium and magnesium ions exchanged for sodium on the resin. The results are presented in Table 1.

4.1.2 Effect of resin bed height on breakthrough capacity

Keeping the exhaustion flow rate constant at 7.5 ml/minute, experiments as described in 4.1.1 were repeated
for different bed heights ranging from 60 cm to 90 cm.
The breakthrough and total capacities realised at
different bed heights are presented in Table 2.

4.1.3 Effect of regenerant concentration on regenera-
tion efficiency

The resin bed (height 60 cm) was exhausted with seawater
at a flow rate of 7.5 ml/minute till the influent
and effluent hardness were the same. The column was
next backwashed and then eluted with 3.0 N sodium
chloride solution at a flow rate of 7.5 ml/minute till
there was no calcium and magnesium in the effluent. The
experiment was repeated using 1.0 N and 0.5 N sodium
chloride solution. The effluent was collected in 50 ml
fractions and analysed for calcium and magnesium ions.
The results are presented in Table 6.

Zekarb 225 cation-exchange resin

4.1.4 Effect of flow rate of the influent on break-
through capacity

The procedure described in 4.1 was adopted using
Zekarb 225 cation-exchange resin in the sodium form.
Resin bed height was kept at 60 cm and exhaustion flow
rates ranged from 7.5 ml/minute to 25.0 ml/minute in
different experiments. The results are presented in
Table 1.
4.1.5 Effect of bed height on breakthrough capacity

Keeping the exhaustion flow rate constant at 7.5 ml/minute experiments were carried out for different bed heights ranging from 60 cm to 90 cm using Zeokarb 225 cation-exchange resin in the sodium form. The results are presented in Table 2.

The product of the selectivity coefficient and the capacity of the resins (KQ) were calculated using the data from Table 1 & 2 which are presented in Table 3 & 4.

4.1.6 Effect of regenerant concentration on regeneration efficiency

Keeping the height at 50 cm, the bed was exhausted with sea water at a flow rate of 7.5 ml/minute. The resin bed was then washed with deionised water and eluted with 3.0 N sodium chloride solution at a flow rate of 7.5 ml/minute till there was no calcium or magnesium in the effluent. The experiment was repeated with 1.0 N and 0.5 N sodium chloride solution as regenerant. The results are presented in Table 5.
Table - 1

Effect of flow rate on breakthrough capacity for (calcium + magnesium)

Resins : Sodium form of Tulsion 14 and Zeokarb 225 (mesh size -30 + 52)

Resin bed height : 60 cm                  Resin bed volume : 150 ml

<table>
<thead>
<tr>
<th>Flow rate (ml/min)</th>
<th>Total capacity of the resin in meq.</th>
<th>Total uptake of calcium plus magnesium (Ca^{++} + Mg^{++}) in meq.</th>
<th>Breakthrough capacity for Ca^{++} + Mg^{++} realised at breakthrough point</th>
<th>Per cent capacity realised at breakthrough point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tulsion 14</td>
<td>Zeokarb 225</td>
<td>Tulsion 14</td>
<td>Zeokarb 225</td>
</tr>
<tr>
<td>7.5</td>
<td>105</td>
<td>225</td>
<td>48.00</td>
<td>108.1</td>
</tr>
<tr>
<td>15.0</td>
<td>-</td>
<td>-</td>
<td>48.20</td>
<td>108.5</td>
</tr>
<tr>
<td>25.0</td>
<td>-</td>
<td>-</td>
<td>48.03</td>
<td>107.6</td>
</tr>
</tbody>
</table>
Table - 2

Effect of resin bed height on breakthrough capacity for calcium and magnesium ions

Resins : Sodium form of Tulsion 14 and Zeckarb 225 (mesh size = 30*52)

Flow rate : 7.5 ml/minute

<table>
<thead>
<tr>
<th>Resin bed height (cms.)</th>
<th>Bed volume ml.</th>
<th>Total capacity of the resin (meg)</th>
<th>Total uptake of Ca++ Mg++ at equilibrium (meg)</th>
<th>Breakthrough capacity of Tulsion Zeckarb (14, 225)</th>
<th>Per cent capacity realised at breakthrough point (14, 225)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca++ Mg++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tulsion Zeckarb 14</td>
<td>60</td>
<td>150.1</td>
<td>225.3</td>
<td>48.2</td>
<td>84.1</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>175.2</td>
<td>262.0</td>
<td>55</td>
<td>119.1</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>225.0</td>
<td>347.1</td>
<td>73.6</td>
<td>163.5</td>
</tr>
<tr>
<td>Tulsion Zeckarb 225</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Flow rate : 7.5 ml/minute

Table 2: Effect of resin bed height on breakthrough capacity for calcium and magnesium ions. Resins: Sodium form of Tulsion 14 and Zeckarb 225 (mesh size = 30*52).

<table>
<thead>
<tr>
<th>Resin bed height (cms.)</th>
<th>Bed volume (ml.)</th>
<th>Total capacity of the resin (meg)</th>
<th>Total uptake of Ca++ Mg++ at equilibrium (meg)</th>
<th>Breakthrough capacity of Tulsion Zeckarb (14, 225)</th>
<th>Per cent capacity realised at breakthrough point (14, 225)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca++ Mg++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tulsion Zeckarb 14</td>
<td>60</td>
<td>150.1</td>
<td>225.3</td>
<td>48.2</td>
<td>84.1</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>175.2</td>
<td>262.0</td>
<td>55</td>
<td>119.1</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>225.0</td>
<td>347.1</td>
<td>73.6</td>
<td>163.5</td>
</tr>
<tr>
<td>Tulsion Zeckarb 225</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Flow rate : 7.5 ml/minute
Table 3

Effect of flow rate on equilibrium RNa+ Sea water system

Bed height = 60 cm

<table>
<thead>
<tr>
<th>Flow rate (ml/min)</th>
<th>Capacity of the resins (meq/ml)</th>
<th>$q_D$ (meq/ml)</th>
<th>$q_M$ (meq/ml)</th>
<th>$C_D$ (meq/meq)</th>
<th>$C_M$ (meq/meq)</th>
<th>$K_M$ (ml/ml)</th>
<th>$K_D$ (ml/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>0.700 1.500</td>
<td>0.320 0.720</td>
<td>0.380 0.780</td>
<td>0.140 0.341</td>
<td>1.84 0.98</td>
<td>1.302</td>
<td>1.470</td>
</tr>
<tr>
<td>15.5</td>
<td>0.700 1.500</td>
<td>0.320 0.720</td>
<td>0.380 0.780</td>
<td>0.140 0.341</td>
<td>1.84 0.98</td>
<td>1.302</td>
<td>1.470</td>
</tr>
<tr>
<td>25.0</td>
<td>0.700 1.500</td>
<td>0.320 0.720</td>
<td>0.380 0.780</td>
<td>0.140 0.341</td>
<td>1.84 0.98</td>
<td>1.302</td>
<td>1.470</td>
</tr>
</tbody>
</table>
Table - 4

Effect of resin bed height on selectivity coefficient value $K_M^D$ for Tulsion 14 and Zeokarb 225 cation-exchange resins

<table>
<thead>
<tr>
<th>Bed height in cm</th>
<th>Capacity of the resin meq/ml</th>
<th>$q_p$ meq/ml</th>
<th>$q_M$ meq/ml</th>
<th>CD meq/meg</th>
<th>CM meq/meg</th>
<th>$K_M^D$ Tulsion 14</th>
<th>$K_M^D$ Zeokarb 225</th>
<th>$K_M^D$ Tulsion 14</th>
<th>$K_M^D$ Zeokarb 225</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.0</td>
<td>0.700 1.500</td>
<td>0.320</td>
<td>0.720</td>
<td>0.380</td>
<td>0.780</td>
<td>0.140 0.341</td>
<td>1.84</td>
<td>0.98</td>
<td>1.288 1.470</td>
</tr>
<tr>
<td>70.0</td>
<td>0.700 1.500</td>
<td>0.320</td>
<td>0.749</td>
<td>0.380</td>
<td>0.751</td>
<td>0.140 0.341</td>
<td>1.84</td>
<td>1.10</td>
<td>1.288 1.650</td>
</tr>
<tr>
<td>90.0</td>
<td>0.700 1.500</td>
<td>0.320</td>
<td>0.778</td>
<td>0.380</td>
<td>0.727</td>
<td>0.140 0.341</td>
<td>1.84</td>
<td>1.24</td>
<td>1.288 1.860</td>
</tr>
</tbody>
</table>
Regeneration of the exhausted Zetikarb-225 cation-exchange resin bed with different concentration of sodium chloride

<table>
<thead>
<tr>
<th>Volume of regenerant required in ml</th>
<th>Concentration of the regenerant NaCl in N</th>
<th>Meq of Ca(^{++}) + Mg(^{++}) on the resin phase</th>
<th>Meq of Ca(^{++}) + Mg(^{++}) eluted out</th>
<th>Per cent conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>3.0</td>
<td>108</td>
<td>107.1</td>
<td>99.0</td>
</tr>
<tr>
<td>900</td>
<td>1.0</td>
<td>108</td>
<td>107.1</td>
<td>99.0</td>
</tr>
<tr>
<td>1200</td>
<td>0.5</td>
<td>108</td>
<td>75.6</td>
<td>70.0</td>
</tr>
</tbody>
</table>
Table 6
Regeneration of exhausted cation-exchange Tulsion 14 resin

<table>
<thead>
<tr>
<th>Volume of regenerant required in ml.</th>
<th>Concentration of the regenerant NaCl in N</th>
<th>Meq of Ca(^{++}) + Mg(^{++}) on the resin phase</th>
<th>Meq of Ca(^{++}) + Mg(^{++}) eluted out</th>
<th>Per cent conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>3.0</td>
<td>48.0</td>
<td>47.80</td>
<td>99.5</td>
</tr>
<tr>
<td>400</td>
<td>1.0</td>
<td>48.0</td>
<td>43.38</td>
<td>90.3</td>
</tr>
<tr>
<td>600</td>
<td>0.5</td>
<td>48.0</td>
<td>39.04</td>
<td>81.2</td>
</tr>
</tbody>
</table>
Table 7

Analysis of sea water

<table>
<thead>
<tr>
<th>Concentration of cations in meq/litre</th>
<th>Concentration of anion in meq/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>341.8</td>
</tr>
<tr>
<td>K⁺</td>
<td>140.0</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>140.0</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>481.8</td>
</tr>
</tbody>
</table>
4.2 Discussion

The formation of scale has always been a problem in
the production of fresh water from sea water by flash
distillation methods. It poses problems in using sea
water as coolant. Such scale formation not only retards
the heat transfer but also sometimes leads to fatal
accidents.

Two approaches for overcoming this difficulty are
(i) removal of scale and (ii) removal of calcium and
magnesium ions from the water before using it in the
process viz., prevention of scale formation. Ion-exchange
technique is widely used for the removal of scale
forming constituent ions like calcium and magnesium
from hard water. In the softening of seawater by ion-
exchange technique, it is passed through the sodium form
of a cation-exchange resin. The reaction taking place
during the operation is expressed by the following

\[ R \, Na^+ + \left[ Ca^{++} + Mg^{++} \right]_X \rightarrow R \left[ Ca^{++} + Mg^{++} \right] + NaX^- \]

Thus, Na\(^+\) form of cation-exchange resin can take up
Ca\(^{++}\) and Mg\(^{++}\) ions from sea water. However, sea water
contains a large concentration of sodium salt. Hence,
it was essential to study the uptake of scale forming
ions from sea water by ion-exchange technique in the
process of excess sodium ions. Charles\textsuperscript{203} has reported that exhaustion flow rate and bed height are the important factors which influence the capacity utilisation of the resin bed. Therefore these factors were first studied to find out the optimum conditions for softening of sea water.

\textbf{Effect of flow rate of the influent on breakthrough capacity.}

It can be seen from the data in Table 1 that in case of Zeokarb 225 cation-exchange resin, the per cent capacity realised at breakthrough remained practically constant when the flow rate was increased from 7.5 ml/minute to 15 ml/minute. However, when the flow rate was increased from 15 ml/minute to 25 ml/minute the per cent capacity realised at breakthrough decreased appreciably, showing thereby that the flow rate had a downward effect on breakthrough capacity when the flow rate was higher than 15.0 ml/minute.

In case of Tulsion 14, the per cent capacity realised at breakthrough, decreased appreciably when the flow rates were increased from 7.5 ml/minute to 25.0 ml/minute, showing thereby that the change in flow rates had a pronounced effect on per cent capacity realised at breakthrough.
It can also be seen from results in Table 1 that the uptake of calcium and magnesium at equilibrium condition remained constant at all flow rates showing that flow rate had no effect on equilibrium. Further, the uptake of calcium and magnesium on the resin bed at equilibrium was lower than the available capacities of both the resins. Due to the large concentration of sodium ions in seawater, at a certain stage equilibrium is established between sodium, calcium and magnesium ions exchanged on the resin bed and sodium, calcium and magnesium ions in sea water. Therefore further uptake of Ca\(^{++}\) and Mg\(^{++}\) may not be possible and thus lower capacity was observed.

It can be seen from Table 2 that in case of Zeokarb 225 when the height was 60 cm, the per cent capacity realised at breakthrough was 37.3, but when the height was increased to 70 cm and 90.0 cms, the per cent capacity realised at breakthrough was 45.5 and 47.1 respectively, showing thereby that there was visible increase in per cent capacity realised at breakthrough when the height was increased up to 70 cm but not much from 70 to 90 cm.
Helfferich has described the advantages and disadvantages of increasing resin bed height. An increase in bed height increases both the total and breakthrough capacities. However, an increase in bed height beyond a certain limit does not increase the degree of utilization. In this investigation for Zeokarb 225, the percent capacity realised at breakthrough increased appreciably with the resin bed height up to 70 cm but not appreciably above 70 cm.

Similarly, in case of Tulsion 14, the percent capacity realised at breakthrough increased gradually as the resin bed height was increased from 60.0 cm to 90 cm showing thereby that bed height had an effect on the degree of utilization even at 90 cm bed height.

Equilibrium study of the system
Sodium form of cation-exchange resin and sea water

The total uptake of divalent ions (Ca$^{++}$ + Mg$^{++}$) and monovalent ions (sodium) retained on the resin bed was calculated.

Equilibrium can be described by the separation factor, selectivity coefficient and distribution coefficient. Helfferich has reported that the selectivity coefficient
is more convenient for theoretical studies. The selectivity coefficient can be defined as

$$k_B = \frac{C_A}{C_B} \frac{|Z_B|}{|Z_A|}$$

Where $C_A$ and $C_B$ are the concentrations of ions A and B in the resin phase and $C_A$ and $C_B$ are concentrations of ions A and B in the solution phase. $Z_A$ and $Z_B$ are the valencies of the ions. Gerhard Klein, Vermeulen and coworkers have studied the performance of Dowex 50 W-X4, Dowolite C 25, and many other cation-exchange resins in the seawater softening process. They found by the batch method that the theoretical performance is governed by the numerical product of the selectivity coefficient $k_M^D$ and the resin capacity Q. They used the following equation.

$$k_M^D = \frac{q_D}{q_M} (\frac{C_M}{C_D})^2 \quad (1)$$

where $q_D$ and $q_M$ are the concentrations of di and monovalent ions in the resin phase viz. meq/g dry resin. $C_D$ and $C_M$ are the concentration of di and monovalent ions in seawater.
In the present investigation the same equation can be used to study the performance of Zeckarb 225 and Tulsion 14 cation-exchange resins. The only difference is that concentrations of divalent and monovalent ions are expressed in meq/ml. The modified equation will be

\[ K_M^D = \frac{q_D}{C_D} \left( \frac{C_M}{q_M} \right)^2 \]  

(2)

where \( q_D \) and \( q_M \) are the concentrations of divalent and monovalent ions in the resin phase expressed in meq/ml. \( C_M \) and \( C_D \) are the concentrations of the monovalent ions in sea water.

**Evaluation of values \( q_D \) and \( q_M \)**

Suppose initially the resin bed contains '2' meq of sodium ions. When sea water is passed \( Ca^{++} + Mg^{++} \) ions are taken up by the resin bed and equivalent ions of sodium are released. Suppose \( X \) meq of \( Ca^{++} + Mg^{++} \) are taken up at equilibrium then \( \frac{X}{V} \) is equal to \( q_D \).

Similarly retention of sodium ions on the resin bed is

\[ \frac{Z - X}{V} = Y \]

\[ q_M = \frac{\gamma}{V} \quad \text{(concentration of monovalent ions in meq/ml)} \]
computing the values of $q_D$ and $q_M$ the values of $K_M^D$ were calculated.

It can be seen from the data contained in Table 3 that in case of both the resins, the selectivity coefficient $K_M^D$ is independent of the flow rate of the influent. The obvious reason for this is that $C_D$ and $C_M$ are constant because the same sea water was used throughout the experiments. The values of $K_M^D$ depend on the values of $q_D$ and $q_M$. Total uptake of (Ca$^{++}$ and Mg$^{++}$) under equilibrium condition was the same at different flow rates therefore $K_M^D$ remained constant at different flow rates for both the resins.

The selectivity coefficient depends on the type of the resin and on the concentrations of the ions. Here, concentrations of mono and divalent ions are the same. It was expected that selectivity coefficient value will not change with the bed height. It can be seen from data in Table 4 that in case of Tulsion 14 the values of $K_M^D$ remained constant showing that bed height has no effect on selectivity coefficient. However, in case of zeokarb 225 a change was observed, the value increased from 0.98 to 1.24 as the bed height increased from 60 cm to 90 cm showing
that the bed height has pronounced effect on $K^D_M$.

It can also be seen from data in Tables 3 and 4 that selectivity coefficient values for Tulsion 14 were higher than that for Zeokarb 225, showing that Tulsion 14 has higher affinity for divalent ions ($Ca^{++} + Mg^{++}$) than Zeokarb 225. To compare the performance of the two resins $K^D_M Q$ was used where $Q$ is the capacity of resins in meq/ml.

It can be seen from results in Table 3 that $K^D_M Q$ values of both the resins were almost equal 1.30 and 1.47 in case of Tulsion 14 and Zeokarb 225 respectively. Further, it is also revealed from the data in Table 4 that $K^D_M Q$ values for Zeokarb 225 slightly increased with the resin bed height. However, $K^D_M Q$ value does not increase with resin bed height in case of Tulsion 14.

Since the concentration of the regenerant is an important factor, different concentrations of sodium chloride were used for regeneration. It can be seen from data contained in Table 5 that in case of Zeokarb 225, 99.1 per cent regeneration was obtained with 1.0 N and 3.0 N sodium chloride solution. The volume of regenerant required for 99.0 per cent regeneration was
900 ml and 450 ml respectively; comparing the amount of regenerant required in gms viz (on weight basis), the amount of regenerant required in case of the 1.0 N sodium chloride was lower than the amount needed when 3.0 N sodium chloride was used as regenerant. It can be seen from data in Table 6 that for Tulsion 14, 99.5 per cent regeneration was obtained when 3.0 N sodium chloride solution was used as regenerant. However 90.3 and 81.2 per cent regeneration was obtained with 1.0 N and 0.5 N sodium chloride solution. The probable reason for this is that, Tulsion 14 has a preference for divalent ions and hence higher concentrations of sodium chloride are needed to displace the calcium and magnesium ions from the resin.

Conclusion
Thus the investigation revealed the practical utility of an indigenously available resin for treating sea water to remove the scale forming constituents.