A SCIENTIFIC ANALYSIS OF THE PROCESS OF MANUFACTURE OF SALT (NaCl) AND BYPRODUCTS FROM SEA WATER USING SOLAR ENERGY

by

S.A.S. Perera

Abstract

Sea water is the most abundantly available chemical resource in Sri Lanka. However, its commercial exploitation to produce salt and byproducts, remains at an extremely unsatisfactory level. Considering the fact that, solar energy (sunshine), which is the main source of energy for salt manufacture, is abundantly available in all parts of Sri Lanka, and the fact that, very large extents of land area are available in the coastal belt of the island, that cannot be used for agriculture, due to the lack of water and the salinity of the soil, it is extremely important that these lands are used for the manufacture of solar salt, for the economic development of the country.

In this paper, the process of manufacture of salt and byproducts by solar evaporation of sea water is scientifically analysed. The theoretical aspects have been discussed and a material balance has been carried out to determine the requirement of sea water and the production of byproducts with reference to a salt production capacity of 30000 MT. Some simple processes for the manufacture of chemicals from sea water have also been discussed.

The main objective of this paper is to highlight the scientific aspects of salt manufacture and to motivate more and more scientists, engineers and entrepreneurs to get involved in this great industry for the economic development of Sri Lanka.

1.0 Sea water

Seawater contains a large number of salts, besides the more important constituent, sodium chloride (NaCl) or common salt. The average composition of Indian Ocean seawater (Bollena, 1967), with respect to its principal constituents, is given in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>2.783</td>
</tr>
<tr>
<td>MgSO4</td>
<td>0.238</td>
</tr>
<tr>
<td>MgCl2</td>
<td>0.353</td>
</tr>
<tr>
<td>CaSO4</td>
<td>0.118</td>
</tr>
<tr>
<td>KCl</td>
<td>0.051</td>
</tr>
<tr>
<td>Other salts</td>
<td>0.010</td>
</tr>
<tr>
<td>Total</td>
<td>3.553</td>
</tr>
</tbody>
</table>

From Table 1, it can be seen that seawater is a dilute source of salts, having more than 96% water. Hence, to crystallise salts from seawater, a very high portion of water has to evaporated out. Since, evaporation of water is energy intensive, a high input of energy is required for this process. If this energy is to be artificially supplied by burning biomass or fossil fuels, the fuel cost will be so high, that, manufacture of salt from seawater will be uneconomical.

Sri Lanka, is surrounded by the sea and its coastal areas have easy access to seawater. Moreover, more than 90% of the coastal belt has long periods of dry, sunny weather too. Hence, these areas have all the natural ingredients for economic manufacture of salt and byproducts.

2.0 Theory of crystallization of salts from brine

In Sri Lanka, salt and byproducts are manufactured from seawater by solar evaporation. This process has been developed, by considering the following properties of inorganic chemicals and their aqueous solutions.

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a) The maximum weight of a solute that can be dissolved in 100g of water at a given temperature is called its solubility. The product of ionic concentrations in a saturated solution of a solute is called its solubility product. As an example, consider a univalent ionic solute AB which ionises into A⁺ and B⁻: when dissolved in water, the solubility product of AB, denoted by Ksp(AB), is given by the following equation.

\[ \text{AB} + \text{H}_2\text{O} \rightarrow A^+ + B^- \]

\[ K_{\text{sp(AB)}} = (A^+)^n \times (B^-)^m \]  

For a multivalent solute AxBy, the Ksp value is calculated as follows.

\[ \text{AxBy} + \text{H}_2\text{O} \rightarrow xA^+ + yB^- \]

\[ K_{\text{sp(AxBy)}} = (A^+)^x \times (B^-)^y \]  

b) If the product of ion concentrations in a solution, exceeds the Ksp value at that temperature, there will be precipitation of the excess solute.

c) The solubilities and the Ksp values of the major components of seawater (brine) are given in Table 2. The Ksp values have been calculated from solubility data (3) using equations (1) and (2).

Table 2 - Solubilities and Solubility Products of Salts in Seawater (Brine)

<table>
<thead>
<tr>
<th>Component</th>
<th>Solubility at 30°C (g/l)</th>
<th>Solubility Product (g/l)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>370.0</td>
<td>32662</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>588.6</td>
<td>2.88x10⁷ (g/l)^3</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>393.2</td>
<td>24737</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>2.332</td>
<td>1.130</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.012</td>
<td>3.456x10⁵</td>
</tr>
<tr>
<td>KCl</td>
<td>363.3</td>
<td>32924</td>
</tr>
</tbody>
</table>

d) Since, brine is a mixture of several solutes, the solubility of each solute is affected by the presence of the others to a limited extent. If two or more solutes have common ions, the concentration of the common ion can have a major influence on the solubilities of each of these solutes. This phenomena is known as the common ion effect.

In brine, the common ion Cl⁻ will influence the solubilities of the solutes, NaCl, MgCl₂, and KCl, while, the common ion SO₄²⁻ will influence the solubilities of CaSO₄ and MgSO₄.

As a result of the common ion effect, all the above salts exhibit a lower solubility in brine than in water.

e) In addition to the "common ion effect", there is the "steric effect", which reduces the solubility of each solute in a multicomponent system. This effect arises as a result of the reduction of free space due to the interference of ions and molecules in solution. The "steric effect" generally depends on the electro negativity and the size of the ions in solution.

f) If the constituents of brine are listed out in the order of increasing solubility product, it would be as given in Table 3.

Table 3 - Salts in brine listed in the order of increasing Solubility Product

<table>
<thead>
<tr>
<th>Component</th>
<th>Solubility Product (g/l)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>3.456x10⁵</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>2.4737</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>2.88x10⁷</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.30</td>
</tr>
<tr>
<td>KCl</td>
<td>3.2924</td>
</tr>
</tbody>
</table>

Table 4 - Salts in brine listed in the decreasing order of concentrations

<table>
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<tr>
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<th>Concentration (g/100g)</th>
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<td>0.051</td>
</tr>
</tbody>
</table>

h) To determine the order of crystallisation of salts from brine, the three factors, solubility product, steric effect and the concentration should be analysed. When brine undergoes solar evaporation, the weight ratio of salts to water increases resulting in the increase of ionic concentrations.

i) With progressive evaporation, the volume of brine decreases, resulting in a net increase of density. Density is the physical parameter which
is measured, monitored and controlled in the salt manufacturing process. The density is measured using a “Beaume Meter” in “Degrees Beaume” (°Be). The °Be unit gives the percentage of dissolved solids, with a fair accuracy. Hence, the density of seawater (brine), which contains 3.553% solids will give a density reading of 3.5 °Be, when measured using the “Beaume Meter”.

i) The products of ionic concentrations in fresh brine (seawater), can be calculated from the chemical composition of seawater and are as follows.

\[
\begin{align*}
(\text{Na}^+) (\text{Cl}^-) &= 216.3 \ (\text{g/l})^2 \\
(\text{Mg}^{2+}) (\text{Cl}^-)^2 &= 535.5 \ (\text{g/l})^2 \\
(\text{Mg}^{2+}) (\text{SO}_4^{2-}) &= 3.74 \ (\text{g/l})^2 \\
(\text{Ca}^{2+}) (\text{SO}_4^{2-}) &= 0.93 \ (\text{g/l})^2 \\
(\text{K}^+) (\text{Cl}^-) &= 5.34 \ (\text{g/l})^2
\end{align*}
\]

j) When brine undergoes solar evaporation, the water content is progressively reduced, resulting in a progressive increase in concentrations of all the ions. The variations in the concentrations of the major salts when sea brine is subjected to solar evaporation, are given in Figures 1, 2, 3 and 4.

3.0 The process of manufacture of salt

In the actual process of manufacture of salt, the theoretical aspects discussed in the proceeding sections have been incorporated as follows. Salt is manufactured in Sri Lanka, by solar evaporation of seawater in salterns. A saltern consists of a large number tanks constructed on the earth. Brine is concentrated in these tanks, stage wise, by solar energy. The stage wise concentration process is described below.

a) Stage 1: Brine is concentrated from 3.5 °Be to 9 °Be, in large tanks called primary condensers in a saltern. No salts crystallise out during this stage.

b) Stage 2: Brine is concentrated from 10 °Be to 25 °Be, in tanks called secondary condensers. Gypsum (\(\text{CaSO}_4 \cdot 2\ \text{H}_2\text{O}\)) crystallises out in these tanks.

c) Stage 3: Brine is concentrated from 25° Be to 29° Be, in tanks known as the crystallisers in a saltern. Around 75% of common salt (\(\text{NaCl}\)) available in brine crystallises out during this stage.

d) The 29° Be, liquid residue of the crystallisers, called bitterns for its bitter taste, has very high
concentrations of MgCl₂ and MgSO₄. Although it also contains some NaCl, it is unsuitable to crystallise any more NaCl because the product could get contaminated with magnesium salts. At present this magnesium rich liquid is sent back to the sea, although it can be used to recover several valuable chemicals.

4.0 Material balance calculations to determine quantities of brine and the ratio of areas (primary condensers:secondary condensers:crystallisers)

Basis: 10000 litres of 3.5°Be (1.025 g/cc) brine (sea water) subjected to solar evaporation until salt is produced

(a) Primary evaporation of brine from 3.5°Be (1.025 g/cc) to 13°Be (1.1 g/cc)

If we assume that X litres of water evaporates during this process, X could be determined from the following material balance equation.

Mass of 10000 litres of 3.5°Be (1.025g/cc) brine = Mass of (10000 - X) litres of 3.5°Be (1.025g/cc) brine + X

10000 x 1.025 = (10000 - X) x 1.1 + X

Hence, X = 7500 litres = mass of water evaporated from the brine during the process.

Hence, the volume of 13°Be (1.1 g/cc) brine left over = 2500 litres

(b) Secondary evaporation of brine from 130Be (1.1 g/cc) to 250Be (1.205 g/cc)

During this process it has been practically observed that around 12 kg of gypsum (CaSO₄·2H₂O) crystallizes out. If the volume of water evaporated during the process is Y, Y could be determined from the following materials balance equation.

Mass of 2500 litres of 130Be (1.1 g/cc) brine = Mass of (2500 - Y) litres of 3.50Be (1.025g/cc) brine + Mass of Gypsum deposited + Y

2500 x 1.1 = (2500-Y) x 1.205 + 12.5 + Y

Hence, Y = 1340 litres

Hence, the volume of 250Be (1.205 g/cc) brine left behind = 1160 litres

(c) Crystallisation of Salt (NaCl) from 25°Be (1.205 g/cc) to 29°Be (1.25 g/cc)

During this process it has been practically observed that around 200 kg of salt (NaCl) and around 0.6 kg of gypsum (CaSO₄·2H₂O) crystallizes out. If the volume of water evaporated during the process is Z, Z could be determined from the following materials balance equation.

Mass of 1160 litres of 25°Be (1.205 g/cc) brine = Mass of (1160 - Z) litres of 29°Be (1.25g/cc) brine + Mass of Gypsum deposited + Z

1160 x 1.205 = (1160-Z) x 1.25 + 0.6 + Z

Hence, Z = 1010 litres

Hence, the volume of 290Be (1.25 g/cc) brine left behind = 150 litres

The 150 litres of 29°Be brine, called bitterns, due to its bitter taste, has a very high concentration of magnesium salts, that can be extracted by solar evaporation followed by crystallisation.

From the above materials balance calculations, the following results can be obtained by simple arithmetic.

To produce 30000 MT of solar salt per annum, using the above mentioned process, the volumes of brine to be handled, mass of gypsum formed and the ratio of condensation and crystallization areas are as follows.

a) sea brine = 1.5 x 109 litres
b) 130Be brine = 3.75 x 108 litres
c) 250Be brine = 1.74 x 108 litres
d) 290Be brine = 2.25 x 107 litres
e) Evaporation = 1.48 x 109 litres
f) Mass of gypsum formed = 1800 MT

5.0 Present status of the sea water and salt based industry in Sri Lanka

At present only solar salt and a small quantity of gypsum is produced from sea water, in Sri Lanka. However, there is high scope for production of sea water based chemicals, such as, epsomsalt (MgSO₄·7H₂O), kieserite (MgSO₄·H₂O) Clauber’s salt (Na₂SO₄·10H₂O), schoenite (K₂SO₄·MgSO₄·6H₂O) and potassium chloride (KCl).

Where the salt based industry is concerned, the current status is that there are a few private companies which are producing table salt by refining solar salt (solar salt...
has impurities such as sand and clay) to supply for direct human consumption as well as industries, such as, food and beverage, soap, paper, textiles and hotels. Very important salt based chemicals, such as, caustic soda (NaOH), soda ash (Na₂CO₃), chlorine (Cl₂), bleaching powder (Ca(OCl)₂), hydrochloric acid (HCl) and other chlorine based inorganic and organic chemicals are not produced in Sri Lanka. There is a high local and foreign demand for most of these chemicals and it is high time that the local entrepreneurs got interested in this industry.

6.0 Some simple processes to manufacture chemicals from sea water

6.1 Manufacture of fertilizer grade epsom salt (MgSO₄·7H₂O)

a) Solar concentration of brine (bitterns) from 29⁰Be to 34⁰Be to remove residual salt (NaCl).

b) Cooling of 34⁰Be to 0⁰C. During this stage, epsom salt (MgSO₄·10H₂O) crystallizes out.

c) Centrifugation of (b) and washing the crystals collected with a saturated solution of epsom salt.

d) The crystals from (c) can be sloar dried to obtain dry epsom salt (MgSO₄·10H₂O).

6.2 Manufacture of fertilizer grade schoenite (K₂SO₄·MgSO₄·7H₂O)

a) Solar concentration of brine (bitterns) from 29⁰Be to 34⁰Be to remove residual salt (NaCl).

b) Further solar concentration of brine (bitterns) from 34⁰Be to 36⁰Be. During this stage a crystalline aggregate called mixed salt, containing all the salts available in bitterns, is formed.

c) The mixed salt obtained in (b) is crushed to a fine particle size and is rigorously agitated in a high speed mixer with water. During this stage, all the other salts get dissolved in water and schoenite crystallizes out separately.

d) Centrifugation of (c) to obtain schoenite crystals.

e) The crystals from (d) can be sloar dried to obtain dry schoenite.

6.3 Manufacture of magnesia (Mg(OH)₂)

a) Reaction of 29⁰Be bitterns with a solution of caustic soda. During this stage, a magnesia precipitates out.

b) Filtration of the precipitate and washing.

c) Solar drying of the precipitate.

6.4 Manufacture of Glauber's salt (Na₂SO₄·10H₂O)

a) Reaction of 29⁰Be bitterns with a solution of caustic soda. During this stage, a magnesia precipitates out.

b) Filtration of the precipitate and obtaining the filtrate.

d) Cooling of the filtrate to crystallize out Glauber's salt.

e) Centrifugation and washing the crystals with a saturated Glauber's salt solution.

f) Solar drying of the product.

References:
1. Beaume and Bitterns, 1967, 8, Solar salt production, Bolena