The Dead Sea—A live pool of chemicals

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The Dead Sea has been a source of chemicals since ancient times. Large scale production of potash by solar evaporation started in 1931 and today the Dead Sea is intensively exploited by Israel and Jordan as a major source of potash, bromine, and magnesium, for agriculture and the chemical and automotive industries. A smart coupling of solar evaporation and knowledge of the complex phase diagram allows a one-to-one easy separation of the principal salts present in the brine. A description of the properties of the Dead Sea is provided together with a chemical engineering analysis of the processes used to realize its commercial potential.

Of the several hypersaline water bodies present on the surface of the earth, the Dead Sea is the one that has attracted and attracts the most attention. The most probable reasons for this unusual fact are possibly religious. Interest was renewed strongly after extensive geochemical research that suggested the commercial potential of the salt composition of the brine and after discovery of the Dead Sea Scrolls.

The Dead Sea is mentioned in several books of the Bible as a landmark for several historical events (for example, the destruction of Sodom and Gomorrah), geographical pointers, and battles. It appears for the first time in the book of Genesis (Genesis 14:3) as Yam-Hamelach (the Salt Sea). The peculiar properties of its brine were noted by many writers, for example, Aristotle (384-322 B.C.E.) in his treatise Meteorologica, book II, part III, he wrote: "If there were any truth in the stories they tell about the lake in Palestine it would further bear out what I say. For they say that if you bind a man or beast and throw him into it he floats and does not sink beneath the surface; and that the lake is so bitter and salty that there are no fish in it, and if you wet clothes in it and shake them out it cleans them".

The Greeks called it Lacus Asphalitidis (Lake Asphaltites) because of the lumps of asphalt that were periodically thrown out from its depths, particularly after earthquakes. This asphalt was used by the early inhabitants of the area for waterproofing baskets, for decorative purposes, and to glue flint implements to wooden handles. Later, it became an important trading commodity for the people of the area. According to Diodorus Siculus (ca. 50 CE) the Nabateans took the asphalt to Egypt and sold it for embalming the dead.

Christians of the Middle Ages also knew it as the Devil's Sea, and their Arab contemporaries referred occasionally to the Stinking Lake, presumably because of the smell of sulphur emitted from several places along the shore.

Sir Walter Scott (1771-1832) used the Dead Sea region as the setting for his novel The Talisman. In the opening page he wrote: "...was placing slowly along the sandy deserts which lie in the vicinity of the Dead Sea, or as it is called, the Lake Asphaltites, were the waves of the Jordan pour themselves into an inland sea, from which there is no discharge of waters".

The Dead Sea was first mentioned in the scientific literature during the first half of the nineteenth century when Angelot discussed the nature of several brackish bodies located in the Mediterranean area and proposed that all had originated from an old sea that was centered where the three continents meet.

Antoine Laurent de Lavoisier (1743-1794) made the first chemical analysis of seawater and also the first quantitative analysis of Dead Sea. Gay-Lussac also analyzed the water of the Dead Sea; one of his objectives was to check the presence of small animals. No "microscopic animals" were found. Nissenbaum has discussed in detail the results of all the papers published between 1778 and 1830, related to the chemical analysis of Dead Sea water and made an estimate of the corresponding salts. Some of his results are summarized in Table 1.
It is the purpose of this paper to review the characteristics of the Dead Sea and describe how the industrial chemical potential of its waters is being realized for the large-scale production of commodities.

Geochemistry

The Dead Sea is a hypersaline lake located at the deepest part of the Jordan-Arava rift, in the East African Rift Valley. It forms part of a long fault trench that extends from Lebanon over the Arava Valley to the Dead Sea.

The Dead Sea is the world’s saltiest natural lake, with an average salinity of 280 g/kg compared with the ocean’s average of 35 g. Both the lake’s salinity and its low location make it a valuable natural resource for the production of chemicals and electricity. Israel and Jordan are already exploiting it for the large-scale production of commodities such as potash and bromine. Both countries have proposed plans to build a canal connecting one of the surrounding seas to the Dead Sea, to realize the lake’s potential as a sink for the generation of electric power.

The Dead Sea presents some unusual geochemical features. Its surface, today at 412 m below the Mediterranean Sea level, is the lowest surface on the face of the earth. It covers an area of about 970 km², has a volume of 135 km³ (nine times that of the Great Salt Lake, Utah), and length 80 km. The lake is divided into two parts, very different in character and almost separated one from the other by the Lisan Peninsula protruding from its eastern shore. The southern part covers 244 km² and is very shallow, rarely exceeding 10 m in depth. The north basin covers an area of 757 km² and reaches a depth of 401 m.

The area is highly arid; it has 300 cloudless days during the whole year and an average rainfall of about 50-mm. Average air temperatures vary between 17°C in January to 34°C in August, with maximum day temperatures 11°C and 30°C, respectively. Average relative humidities during the daytime in April to September are 30 to 40%.

Since the Dead Sea has no outlets the balance between precipitation, runoff, and evaporation determines its level and size. The major supply of water comes from the Jordan River. Additional amounts of water are supplied by the Arnon River and by a large number of fresh water springs and runoff and floods during the rainy winter. The annual flow of the Jordan River varies considerably; until the late 1950s its annual discharge into the Dead Sea was about 1,200×10<sup>6</sup> m<sup>3</sup> while the total average annual intake of the Dead Sea was about 1,600×10<sup>6</sup> m<sup>3</sup>. More than one percent of the Dead Sea water was renewed annually. Increased use of the waters of the Jordan River by Israel and Jordan for agricultural purposes has resulted in a substantial decrease of the input into the Dead Sea, and hence, a decrease in its level. Since the 1960s, the level has decreased continuously from −397 m to −412 m in 1999 and would have resulted in the disappearance of the southern portion, where it not for the artificial evaporation pans built by Dead Sea Works.

The large amount of water lost annually by evaporation (−1,600×10<sup>6</sup> m<sup>3</sup>) has resulted in a natural increase of deuterium; in the surface of the southern Dead Sea basin it reaches 0.01626 mole% in the hydrogen.

As seen in Table 1, the water of the Dead Sea is characterized by a very high salinity, higher than that of any large lake known. The water is of the chloride

<table>
<thead>
<tr>
<th>Analysis of Dead Sea water (g/100 g)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Macquer&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Marcel&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Klaporth&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Guy-Lussac&lt;sup&gt;e&lt;/sup&gt;</th>
<th>Gmelin&lt;sup&gt;f&lt;/sup&gt;</th>
<th>DSW&lt;sup&gt;+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10.2</td>
<td>10.1</td>
<td>11.3</td>
<td>15.3</td>
<td>11.8</td>
<td>14.8</td>
</tr>
<tr>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>8.3</td>
<td>3.8</td>
<td>5.4</td>
<td>4.0</td>
<td>3.1</td>
<td>4.1</td>
</tr>
<tr>
<td>NaCl</td>
<td>6.3</td>
<td>10.7</td>
<td>7.8</td>
<td>7.0</td>
<td>7.1</td>
<td>7.4</td>
</tr>
<tr>
<td>KCl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>MgBr&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Total salts</td>
<td>24.8</td>
<td>24.6</td>
<td>24.5</td>
<td>26.3</td>
<td>24.1</td>
<td>28.0</td>
</tr>
<tr>
<td>Density</td>
<td>1.241</td>
<td>1.211</td>
<td>1.245</td>
<td>1.228</td>
<td>1.211</td>
<td>1.233</td>
</tr>
</tbody>
</table>

<sup>a</sup>Dead Sea Works Ltd.
type, with unusually high content of magnesium and bromine, and unusually low sulphate and carbonate content (bicarbonate probably less than 100 mg/L). In terms of total cation content, the amount of calcium of 15.75%, is again, unusually high. The Dead Sea is currently saturated with respect to halite (NaCl), which is being precipitated in the lake and raising its bottom. The composition of the Jordan water alone would adequately explain the presence and quantities of most of the salt contained in the Dead Sea, with the exception of bromine of which only traces can be found in the river.

An additional characteristic of the Dead Sea is the presence of a definite chemical stratification; the composition of the water varying with depth. The composition of the water of the Dead Sea is unique in the nature and amount of the ions it contains. It is very concentrated in Cl and also contains an abnormally high amount of Br. The Cl:Br ratio is 35:1, only about one third that of the tributary waters carry considerable amount of bromine and iodine. Consequently, it is most likely that bromine in the Dead Sea originated from the concentration of fossil residual salt brines, which formed during the Tertiary. This assumption is supported by the actual operation of the solar evaporation pans of Dead Sea Works. The residual brines are very rich in bromine. Specifically, mother brine having a specific gravity of 1.192 contains about 4.0 ppm bromine. After precipitation of halite and carnallite (MgCl2:KCl 6H2O) the residual brine has a

Origin

It is generally accepted that the Dead Sea formerly occupied a much larger area and that its volume was 4 to 5 times the present one. Similar to the Atacama Desert, the origin of the unique salt concentration and composition of the Dead Sea has been the subject of many speculations. Bentor has given a very detailed account of the geological history of the Dead Sea: Towards the end of the Mesozoic times tectonic disturbances and fault formation resulted in the sinking of part of the Jordan-Arava rift, followed by lacustrine deposition. These Neogene lakes must have been sometimes communicated with the open sea, as suggested by the presence of Mugil priscus Ag, in the upper tertiary Sodom formation of Mount Sodom and marine micro fauna of Pliocene age.

In the late Pliocene, or in the early Pleistocene, an extended inland lake, the first of the three lakes that occupied the Jordan-Sea area during this period, rapidly filled the inland depression. This first lake (Lake Samara) was full with fresh water that eventually turned salty and was replaced by the Lisan Lake. After several hundred thousand years the Lisan Lake started to shrink and the present Dead Sea became established in late Pleistocene times in the lowest part of the area originally occupied by the lakes.

According to Bentor the geological history of the area suggests that Lisan Lake contributed only a small part of the total amount of salts in present-day Dead Sea. The salts must, therefore, have been carried into the Lake mainly by rivers, floods, and springs.

It has been mentioned above that one of the most characteristic geochemical features of the Dead Sea is its high concentration of bromine. The total amount of bromine now present in the Dead Sea is about 900 million tons. Its distribution over a large area and almost constant association with calcium chloride, make a common origin almost certain. According to Bentor, the following facts may explain the origin of these salts:

(a) Volcanic activity has been present in the near past of the area. The corresponding emanations from the interior of the earth may have carried HCl. This acid could have reacted with the limestone layers that form a large part of the geological section on both sides of the Jordan Valley, and formed CaCl2.

(b) Existence of organic material may lead to bromine enrichment. It is well-known that most oil waters carry considerable amount of bromine and iodine. Since the Br:I ratio in the Dead Sea water is larger than 10, it is almost certain that the origin of the bromine is not organic. Consequently, it is most likely that bromine in the Dead Sea originated from the concentration of fossil residual salt brines, which formed during the Tertiary. This assumption is supported by the actual operation of the solar evaporation pans of Dead Sea Works. The residual brines are very rich in bromine. Specifically, mother brine having a specific gravity of 1.192 contains about 4.0 ppm bromine. After precipitation of halite and carnallite (MgCl2:KCl 6H2O) the residual brine has a
specific gravity of 1.341 and contains 8,750 ppm Br. It is conceivable that the most soluble salts contained in these lakes never crystallized, and that these solutions were trapped at depth\textsuperscript{13}.

Under the present conditions rains from the Mediterranean deposit at least about 75,000 tons of chloride ions in the Dead Sea area; ground waters and floods carry this deposition into the closed basin of the Rift Valley. The almost entire absence of iodine in the Dead Sea is a characteristic feature of air borne salts. It has been calculated that to balance the quantities of bromide in the Dead Sea at least 200\times10^9 tons of NaCl must be buried in the Rift Valley\textsuperscript{15}.

Some researchers have postulated that the main source of chloride in the Dead Sea area is ancient seawater that penetrated the Dead Sea rift in the Neogene and after evaporation gave rise to the large amount of salt which exists in the area. Yechiel et al.\textsuperscript{16} have rejected this claim on the basis that such source would have very little \(^{36}\text{Cl}\) as the \(^{36}\text{Cl}/\text{Cl}\) ratio in seawater is very low due to the very long residence time of chloride in the sea. Moreover, since the half-life of \(^{36}\text{Cl}\) is 301,000 years the \(^{36}\text{Cl}\) would eventually have decayed to zero during the ensuing millions of years.

Another interesting phenomenon that took place recently in the Dead Sea is water inversion. Historically, the fresh water that flowed into the Dead Sea mixed to a small extent with the much saltier lake water and formed less saline layers floating over a dense column of fossil water. Increased use of Jordan River water for agricultural purposes stopped this process and started making the surface water saltier and denser. Eventually, in 1979, the age-old gradient disappeared and the water column turned over\textsuperscript{17}.

**Life in the Dead Sea**

Arguments about the existence of living organisms in the Dead Sea have taken place for many years\textsuperscript{18}. It has already been mentioned that in 1819 Gay-Lussac looked for and did not find microscopic animals. It took more than one-hundred years until it was proven that lower organisms could exist and proliferate in the hypersaline environment; Wilkansky\textsuperscript{19} showed that bacterial organisms could grow in water taken from the sea at depth up to seven meters and that microscopic examination revealed the presence of phytotflagellates. Further investigations have shown that the biota of the sea is very limited in variety and is composed of the chlorophyton *Dunaliella* and a few species of the halo-obligatory bacteria. According to Nissenbaum\textsuperscript{20} the number of recorded species is very low but the total biomass is reasonably high (about 105 bacteria/mL and 104 algal cells/mL). The indigenous flora is comprised mainly of obligate halophilic bacteria, such as the pink, pleomorphic *Halobacterium* sp., a *Sarcina*-like coccus, and the facultative halophilic green alga, *Dunaliella*. These organisms possess unusual properties. The *Halobacterium* sp. has extremely high intercellular K\textsuperscript{+} concentration (up to 4.8 m) and extraordinary specificity for K\textsuperscript{+} over Na\textsuperscript{+}. The biota microorganisms exert a critical influence on some biogeochemical processes occurring in the lake. For example, bacteria reduce the precipitated sulphate to sulphide and generate bicarbonate. The bicarbonate causes precipitation of calcium carbonate. It is also possible that bacteria feed on the glycerol liberated by lysing algal cells.

Nissenbaum\textsuperscript{20} has discussed in particular the fact that *Halobacterium* and *Dunaliella* have found two distinct means of adjusting to their hostile environment. *Halobacterium* is an obligate halophile that represents a complete adaptation to the Dead Sea. Its cytoplasmic ionic content is very different from the external composition but has about the same osmotic pressure and similar ionic strength. The green alga *Dunaliella*, is an excellent example of biological flexibility; it is capable of standing wide ranges of salt concentration, and it is not an obligate halophile. According to Nissenbaum *Dunaliella* has solved the problem of differences in osmotic pressure by developing a unique metabolic pathway of producing large amounts of intracellular glycerol as a response to the changes in the external environment\textsuperscript{20}.

**Thermodynamic properties of the solutions**

The reader interested in the thermodynamic analysis of complex aqueous inorganic solutions should read the very detailed papers written by Lerman\textsuperscript{21}, Marcus\textsuperscript{22,23}, and Krumgalz et al.\textsuperscript{24} on the subject. It has already been mentioned that the salinity of the Dead Sea is some eight times that of ocean water and that is the saltiest large body of water on the surface of the earth. A balance among solar radiation absorption, surface water evaporation, replenishing by the Jordan River, and surface mixing by wind and waves, results in a nearly constant surface temperature of 25°C, both of the lake and of the pans.
The ionic composition of the Dead Sea is also different from that of ocean water, the main differences being deficiencies in sulphate and bicarbonate and in excess of bromide ions.

Lerman\(^{21}\) calculated the mean activity coefficients of NaCl, KCl, and MgCl\(_2\) and the solubility of halite and carnallite in the Dead Sea brine, and from these parameters he determined the dissociation constants of carnallite and bischofite at 25\(^\circ\)C as \(\log K_{\text{carn}}=4.00\) and \(\log K_{\text{biho}}=4.445\). From these values he concluded that the ground brines from the Dead Sea coastal areas were close to saturation with respect to halite but unsaturated with respect to sylvite (KCl) and carnallite. In addition, his results indicated that the Dead Sea had not evolved through a stage of brines more concentrated than the present.

In a first publication, Marcus\(^{22}\) suggested that the multistage crystallization process presently used for separating several of the components of the brine could theoretically be replaced by another based on a membrane semipermeable only to KCl and water. To analyze this possibility he recalculated the activities of KCl and water in Dead Sea water using several approaches dealing with multicomponent electrolyte solutions, and obtained values substantially higher than those of Lerman\(^{21}\). Anyhow, Marcus came to the conclusion that the Dead Sea brine could not be simultaneously in equilibrium with respect to both water and KCl. That is, a hypothetically perfect semipermeable membrane could not lead to a state of equilibrium between the brine and aqueous KCl of any concentration.

Since Dead Sea water was composed mostly of chlorides Marcus assumed\(^{23}\) it to be a quinquenary common ion aqueous electrolyte solution, composed of the chlorides of sodium, potassium, magnesium, and calcium. In particular, the surface water of the sea could be assumed to be equivalent to an aqueous solution of 1.752 m NaCl, 0.174 m KCl, 1.555 m MgCl\(_2\), and 0.427 m CaCl\(_2\) at 25\(^\circ\)C. This concentrated solution had an ionic strength 7.874 m, osmolality of 9.799 m, and a total chloride concentration of 5.891 m.

Marcus then used different models to calculate the activity of the different species present in this model surface water and arrived at the values

\[
\begin{align*}
 a_{\text{H}_2\text{O}} &= 0.7514, \log a_{\text{NaCl}} = 1.198, \log a_{\text{KCl}} = -0.102, \\
 a_{\text{MgCl}}_{2, \text{H}_2\text{O}} &= 1.591, \log a_{\text{CaCl}}_{2, \text{H}_2\text{O}} = 0.788, \text{and} \\
 a_{\text{KMgCl}}_{3, \text{H}_2\text{O}} &= 1.489.
\end{align*}
\]

Table 2—Dead Sea mineral composition and reserves\(^{14}\)

<table>
<thead>
<tr>
<th>Composition (g/L)</th>
<th>Reserves (10^6 ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium chloride</td>
<td>190.2</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>91.8</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>52.4</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>15.9</td>
</tr>
<tr>
<td>Bromide</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3—Quantities of minerals produced presently

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Quantity (ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potash (potassium chloride)</td>
<td>3,000,000,000</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>500,000,000</td>
</tr>
<tr>
<td>Bromine</td>
<td>250,000,000</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>100,000,000</td>
</tr>
<tr>
<td>Magnesium chloride</td>
<td>1,000,000</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>10,000,000</td>
</tr>
<tr>
<td>Magnesium</td>
<td>35,000,000</td>
</tr>
</tbody>
</table>

*Under construction*  

As mentioned already, Dead Sea water is unsaturated with respect to its chloride salt components. Concentrated by partial evaporation in the solar salt pans, it reaches a point where halite starts to precipitate, the halite point. According to Marcus, it was possible to use the calculated activities to establish how much water would have to be evaporated isothermally from a given amount of solution, in order to reach the halite point. For the model composition, evaporation of 192 g of water from an amount of solution containing 1000 g of water was enough to reach the solubility product of sodium chloride. More evaporation resulted in halite precipitation. Similarly, it was possible to calculate how much halite would precipitate when given amounts of water were removed by evaporation, as well as to follow the change of activity of the different components as a function of the weight of water evaporated.

According to Marcus' model the "end brine" would be a solution constituted mainly of magnesium (4.24 m) and calcium (1.30 m) chlorides, with small amounts of sodium (0.42 m) and potassium (0.06 m) chlorides, having an ionic strength of 17.0 m, a water activity of only 0.371, and a density of 1.342 kg/L.

It has already been mentioned that nowadays water evaporation from the Dead Sea exceeds the input from precipitation and runoff. Evaporation increases the ionic strength of water and decreases its activity in
the liquid phase. This process will end when the chemical potential of water in the sea's surface and on the adjacent air layer will become equal. Different approaches have been used to investigate how long it will take to achieve this equilibrium state. Klein performed a water budget balance and concluded that this state would be reached at the end of 360 years, when the water level had dropped to -680 m. Gavrieli and Yechiali built a model for water depletion based on climate, water input, and diminishing evaporation, and calculated a final level of -500 m to be reached in about 400 years. Krungalz et al. used a thermodynamic approach, based on Pitzer's ion interaction parameters, to develop a model that allowed calculation of the amount of water removed from the brine and the amount of precipitated minerals and ionic concentrations. Under the present climate conditions, the model predicted that equilibrium would be reached when the level dropped to -500 m. At that time, the volume and surface of the sea would have decreased from 146 to 88 km³ and from 815 to 526 km², respectively.

The phase diagram of different sections of the brine system has been determined, for example, Sheshtakov and Pelsh and Zdanovskii have published data for the quaternary system H₂O-KCl-NaCl-MgCl₂.

Exploitation

In the 19th and 20th century, The Dead Sea attracted many explorers and scientists. The first expedition to study the chemical aspects of the Sea was probably that of C. Costigan, an Irishman. In 1853 he descended in a boat from the Lake Kinneret (Sea of Galilee) to the Dead Sea. There he was caught in a storm, thrown up on the Lisan Peninsula and died of hunger and thirst before he could be rescued. Further explorations were by E. Robinson (1832), W. F. Lynch (1848), L. Lartet (1848), and M. Blanckenhorn (1894 to 1930).

In 1911 began the practical chemical investigation and experimental work of the Dead Sea resources that in 1930 would lead to formation of the concern Palestine Potash Limited. On the initiative of Moshe A. Novomeysky (1873-1961), a mining engineer from Siberia who received a concession from the British mandate administration, the first potash and bromine works were built in 1930 at Ramat Ashlag in the northwest corner of the Dead Sea. Novomeysky's process of selective precipitation is still the basis of production by the Dead Sea Potash Works.

An interesting historical fact is that Palestine Potash Ltd., the forerunner of Dead Sea Works Ltd., was practically the only source of potash and bromine for the British Commonwealth during the Second World War. Production level was 110,000 ton/yr.

Basically, the process consisted in piping sea water into a series of shallow evaporation pans where each of the various salts precipitated at its concentration reached the saturation point. Gypsum crystallized first, followed by sodium chloride and then carnallite when the brine reached a specific gravity of 1.3 g/cm³. The carnallite was then broken into its components by water treatment and the potassium chloride further refined. A small fraction of the remaining "end brine" was treated with chlorine gas to extract bromine.

The northern facility was destroyed during Israel's War of Independence (1947-1948) and the southern facility was reactivated in 1952 under the ownership of the new company, Dead Sea Works Ltd. Production began again in 1955 at a level of 200,000 ton/yr and a series of expansions in the later years brought the level of production up to the present level of 2.8 million ton/year.

The Jordanian facility, Jordan Dead Sea Industries, was established in 1999 on the eastern shore of the sea.

The quantities of minerals (tons/year) produced at present are as shown in Table 3.

Derivative products, processed from the above minerals, include potassium nitrate, phosphoric acid, chlorine, caustic soda, potassium carbonate and sulphate, and bromine compounds. The Dead Sea is thus the central mineral source of Israel and Jordan, supporting a considerable export trade and supplying raw materials for a large variety of local manufacturing plants.

A short description of the production process of the different commodities is presented below.

Potash production

Potash production begins with a first stage of solar evaporation. The waters of the sea are pumped into large evaporation pans, which cover an area of about 130 km². Almost all of this area is separated from the sea by dikes built into the shallow southern part. Evaporation is enhanced by the climatic conditions prevalent in the area.

The first salt that crystallizes out is calcium sulphate. Water evaporation continues until the salt...
concentration in the pans reaches about 17% (350 g/L of total dissolved salts). At this point (halite point) sodium chloride begins to crystallize and continues until the volume of the water has diminished to about half of its original value. At the beginning of the crystallization stage a typical brine contains (g/L) MgCl₂, 165; CaCl₂, 48; NaCl, 105; KCl 14.5, and CaSO₄ 1.0. At the end of this step about 90% of the sodium chloride and more than 95% of the calcium sulphate is crystallized. Sodium chloride accumulates at the bottom of the pond and causes an increase of its height.

Concentration of the brine by solar evaporation is carried on a second series of pans. When the specific gravity of the brines reaches a value of 1.300, corresponding to a total salt content of about 32% at 35°C (carnallite point), a new solid phase (in addition to NaCl), consisting of carnallite (KCl·MgCl₂·6H₂O), begins to separate. A typical brine composition at this point is (g/L): MgCl₂, 295; CaCl₂, 85; NaCl, 20; KCl 27, Br⁻ 9, and CaSO₄ less than 0.1. The pans are used as storage for the carnallite. An important technological feature is that carnallite tends to crystallize in separate crystals rather than in continuous layers as sodium chloride, forming a loose layer amenable to slurry pumping from the bottom of the pans.

When the specific gravity of the brines reaches 1.350, the ratio between evaporation and crystallization becomes unfavourable; the evaporation process is terminated and the end brine returned to the sea. A typical composition of the end brine is MgCl₂, 360; CaCl₂, 110; NaCl, 7; KCl 5, and Br⁻ 12 g/L. A small amount of it is used for the production of bromine and hydrochloric acid.

Further evaporation of such brines, possible only during 2-3 months every summer, to a specific gravity of 1.365, brings about the crystallization of bischofite (MgCl₂·6H₂O).

Analysis of the above figures indicates that evaporation by solar energy has increased the concentration of KCl of about 1% weight in the original brine to about 20% as carnallite.

Carnallite ores are not found in other parts of the world and are normally associated with salt, kieserite (MgSO₄·H₂O) and insoluble clays. The carnallite deposits are processed for potash only in areas where the sylvinitic resources are limited. The carnallite obtained by solar evaporation of Dead Sea brines is different in several aspects from the mined variety: it contains very little slimes and sulphates, and the potassium chloride content is relatively high.

The carnallite slurry (10-20% solids) is now pumped to thickeners, where it is concentrated to 40-50% solids, and then to filters to yield a cake containing 85-88% solids. Separation of carnallite into its components and impurities (mainly NaCl), is carried by partial crystallization/solution, taking into advantage of the different solubilities of the salts. Addition of water causes solution of all the magnesium chloride and most of the potassium chloride. The solid phase is a mixture of sodium and potassium chloride (sylvinite), containing 50-65% potassium chloride on a dry basis.

The major portion of the potash produced at the Dead Sea Works is by hot leaching of sylvinite. This process utilizes the fact that KCl is much more soluble at high than at low temperatures, while NaCl has an almost constant solubility over a wide temperature range. Sylvinite is now contacted with hot (105°C) recycle brine that is unsaturated with respect to KCl but saturated in NaCl. Potassium chloride is dissolved and separated by centrifugation from the residual solid phase (NaCl). The hot brine is fed to vacuum crystallizers to generate a solid phase having a typical composition (g/L) of KCl, 19-20%; NaCl, 11-15%; MgCl₂, 28-30%; CaCl₂, 0.5-1.0%, and H₂O, 37-40%.

After centrifugation and washing, the product contains only some 2% NaCl, it is dried in rotary kilns and separated on vibrating screens to different grades: coarse, standard, and fine.

Another alternative to produce KCl is flotation. Here sylvinite is slurred in a suitable brine, long chain fatty amines are added as flotation reagents, and the mixture pumped to flotation cells. The froth of these cells is enriched with KCl but may still contain appreciable amounts of sodium chloride. The KCl crystals are small and tend to stick together and agglomerate with NaCl crystals, probably by electrostatic attraction. As a result the flotation tops contain only 65-75% KCl and require extensive washing to remove NaCl and obtain a 95% KCl product. Agglomeration is reduced by addition of substances that are habit modifiers for sodium chloride, e.g., sodium ferrocyanide and nitritolriacetamide. The final product is centrifuged and dried in rotary kilns giving a very fine grade of potassium chloride.
By products of potash production  

Sodium chloride

Sodium chloride separated from the sylvinitic is used for producing chlorine and caustic soda by electrolysis and for other industrial uses. Table salt is produced by a salting-out process.

Bromine

The process depends on the oxidation of bromide to bromine and consists of simultaneous chlorination and steam blowing. The end brine from the carnallitic pans contains 11-12 g/L of bromine in the form of bromide salts. This is the highest concentration of bromine found in the world and compared favorably with other sources of bromine such as salt brines in the U.S. (3-4 g/L) and sea water (70 ppm).

The end brine is sent to the top of the blowing-out packed tower where it flows counter current to live steam and chlorine. The chemical reaction taking place is:

\[ \text{Cl}_2 + 2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{Cl}^- \]

The brine is usually heated to near-boiling point to reduce the partial pressure of bromine to nearly zero.

The exit top stream contains excess steam and impure bromine. After cooling it separates into two phases, the bromine phase is distilled to remove the dissolved chlorine and then dried with concentrated sulphuric acid. The water content must be less than 30 ppm to prevent corrosion of metal transporting and storage containers.

The Dead Sea Bromine Co. and its subsidiary Bromine Compounds produce a series of bromine derivatives from the bromine produced at the Dead Sea. The main uses of bromine are in flame retardants, drilling fluids, brominated pesticides (mainly methyl bromide), water treatment chemicals, photographic chemicals, and rubber additives.

An important growing application of bromine is in the manufacture of fire retardants either of the additive- or reactive-type.

Magnesium and magnesium derivatives

Magnesium chloride

Bischofite brine is used for the production of MgCl₂·6H₂O, magnesia and HCl. The purified MgCl₂ liquor is sent to evaporators to yield the solid salt, which is then purified by repeated crystallization. The final product finds application in the manufacture of cement, ceramics, textiles, paper, water purification, and sewage treatment chemicals.

MgCl₂ is also converted into aqueous magnesium chlorate that is sold as a defoliant agent and desiccant.

Magnesium oxide by thermal hydrolysis

On heating solid MgCl₂·6H₂O it melts and begins dissolving in its own water of crystallization. This makes heat transfer difficult and completion of the hydrolysis process not economical. The problem was resolved by the Aman process in which the thermal hydrolysis is performed in a spray reactor. The Aman process allows production of high purity magnesia (99.3%) and hydrochloric acid. Thermal hydrolysis takes place in a relatively short residence time.

\[ \text{MgCl}_2 + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HCl} \]

The raw magnesium oxide is separated from the accompanying salts by hydration to magnesium hydroxide followed by water washing. High purity magnesium oxide is then produced by calcination.

The main outlet for this highly pure periclase is in the production of high grade refractory bricks for the basic oxygen furnaces used by the steel industry.

Magnesium metal by electrolysis

Dead Sea Magnesium, a joint venture between the Magnesium Division of Dead Sea Works, and Volkswagen AG of Germany, inaugurated production of magnesium metal in 1997 at the Dimona Plant, near Sodom. Magnesium is considered a critical material because of its extensive use in industrial and military applications. Its low density has encouraged its use in structural applications and motor vehicles, where it competes with aluminium.

The process is based on the electrolysis of molten anhydrous MgCl₂ prepared under controlled operating conditions to minimize its decomposition into MgO and HCl. The carnallite is first fed to a chlorinator operating at 700°C where it melts and the traces of MgO are converted to MgCl₂. Afterwards, it flows to an electrolytic cell provided with a graphite anode and iron plate cathode. Magnesium deposits on the cathode and by it’s being lighter than that of the electrolyte, it floats. Chlorine is produced in the anode and proper cell partitions prevent its reaction with the molten metal. Although it is possible to electrolyze MgCl₂ pure, it is not done because of technological drawbacks such as the high fusion temperature of the salt (712°C), instability in contact with air, low...
electrical conductivity, and density similar to that of pure magnesium. To improve the process chlorides of calcium, potassium, and sodium are added to the electrolyte bath. These salts, in proper concentration, lower the fusion temperature of MgCl₂ to about 500°C. A typical electrolyte contains between 10 to 15% MgCl₂.

The spent electrolyte is solidified and sent back to the potash plant where it is processed into fertilizer. The molten crude magnesium is delivered to the foundry for further refining and casting into ingots.

Lithium

The Dead Sea contains approximately 2 million tons of lithium with a concentration of 14 to 15 mg/L. This concentration increases to over 30 mg/L during the evaporation process of the brine to produce the main chemicals. Under present conditions about 3,000 tons of lithium pass annually through the pond system. Tandy and Canfy have described a pilot plant scale process developed by Dead Sea Works to extract most of lithium present, based on its selective precipitation as lithium phosphate, using a highly concentrated solution of sodium diphosphate.

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