2.1 - Bromine from the Dead Sea. Why?

Even before Balard's discovery of bromine, there was much interest in the composition of the Dead Sea waters, and evidence exists that as early as the 17th and 18th centuries several analyses were carried out.

The search for bromine in the Dead Sea started immediately after bromine was discovered. The first to analyze Dead Sea water was Lavoisier, followed by Gay-Lussac and Gemlin. In 1827 Gemlin's laboratory produced results for the bromine ion concentration in the Dead Sea that deviated only 20% from its true value. During the 19th century Dead Sea water was analyzed many times and the investigators realized that it contained very high concentrations of bromine ions.

Several theories have been advanced to explain the origin of the Dead Sea and its high salt concentration

Scientists believe that the Dead Sea was created hundreds of millions of years ago, in a very early geological period. The Jordan Valley, where the Dead Sea is situated, is part of a narrow and long strip of land that sank into the earth's crust and is called the "Syrian-African rift". During this geological period a number of ancient lakes were created in the Jordan Valley, which are termed "tongue-shaped lakes". These lakes gradually expanded, until they covered almost the entire region. Fifteen thousand years ago a tongue-shaped lake covered the entire area between the Sea of Galilee in the North and the Hazeba region in the South. Later, with the onset of dry periods in the region, the water in the lake began to evaporate. Its wet surface area shrank gradually until all that was left was the Dead Sea.

We should remember that the Dead Sea has no other natural outlet except evaporation into the desert air. The special climatic conditions of the desert are:

- *High temperature throughout most of the year*
- *Low air humidity and little rainfall*
- *Constant winds*

In a process lasting millions of years during which all these factors played a role, the salt concentration of the lake increased, while a large amount of salt accumulated at the bottom.

The following table shows the enormous amounts of salts found in the Dead Sea, amounting to approximately 45 billion ton:

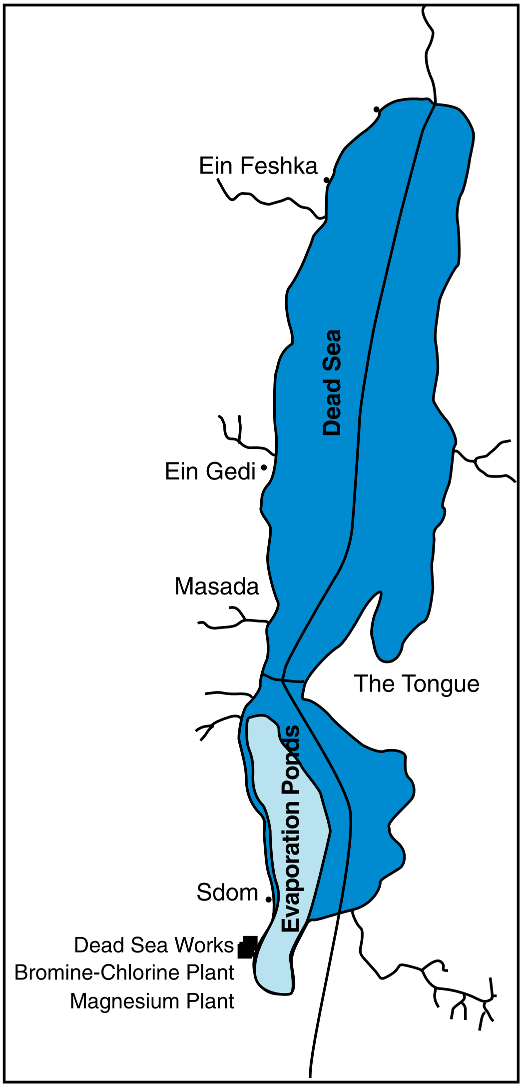
Table No. 2.1. Amounts of salts found in the Dead Sea

Salt	Amount (billion tons)
$MgCl_2$	22
NaCl	12.5
$CaCl_2$	6
KCl (potash)	2
$MgBr_2$	1
$CaSO_4$ (gypsum)	0.215

The Dead Sea: Geographical data

Height	400 meter below sea level
Length	80 km
Maximum width	17.5 km
Surface area	1000 sq.km.
Average depth	Northern basin: 390 meter
Southern basin:	Dried up, today used as area for evaporation pools
Average ambient temperature	10°C(winter) to 40°C (summer)
Atmospheric pressure	1.05 atm
Rainfall (Sdom)	47 mm
Seawater density	1.22 gram per cc
Salt concentration	300 gram per liter

The Dead Sea: The lowest sea in the world.
It has a salt concentration greater than that of any other sea in the world.



The location of The Dead Sea Works

Table No. 2.2. Ion concentrations in Dead Sea water and regular seawater (gram per liter)

Ions	In Dead Sea	In regular seawater
Cations		
Sodium Na^+	39	10.7
Magnesium Mg^{2+}	39.2	1.27
Calcium Ca^{2+}	17	0.42
Potassium K^+	7	0.4
Anions		
Chloride Cl^-	208	19.4
Bromine Br^-	5	0.07
Sulfate SO_4^{2-}	0.5	3.6
Total	315	33.68

The average salt concentration in Dead Sea water is approximately 30% (about 310°g/liter) while in regular seawater the concentration is approximately 3-4% (about 33°g/liter). The ratio between chlorine ions and bromine ions in the Dead Sea is 40:1, much less than in other sources. In Mediterranean seawater, for example, the ratio is 280:1.

A theory has been put forward to explain the relatively high bromine ion concentration claiming that the source of the salt layer on the bottom of the Dead Sea stems from the period of the ancient lake. By dissolution of this layer and precipitation of sodium chloride NaCl, chalk $CaCO_3$ and gypsum $CaSO_4$, a solution rich in bromine ions was formed. Another theory focuses on the possibility of the underwater formation of wells rich in bromine ions.

For generations the Dead Sea was composed of two basins: The northern and the southern ones, separated by a peninsula called "the tongue". The southern part was shallow and extended to Masada. The northern part is deep and extends 50 km to the North. Its total length was 80 km and its maximum width about 17 km. Evaporation rate was always controlled by three factors: rivers flowing into the Dead Sea, floodwaters and underwater wells or wells originating from salt layers on the bottom of the Dead Sea. The rivers, and in particular the Jordan River, replaced about 60% of the evaporated water, floodwaters about 30% and springs about 10%. Years of drought and exploitation of the Jordan River waters (the

Israel National Carrier project and the diversion of the Jordan sources carried out in the sixties) caused a severe shortage of water reaching the Dead Sea, resulting in a gradual reduction of its area.
The southern basin disappeared in 1977 and the sea terminates opposite Masada.

Today the water reservoirs in the southern basin are in fact the evaporation pools of the Dead Sea Works. The company has installed enormous pumps that pump part of the water from the northern basin (positioned lower) and transfers it through a canal built especially for the purpose to the evaporation pools built in the southern basin. These are shallow and open pools that exploit the great advantage of the Dead Sea – **solar energy**.

Feeding canal

- *What is the advantage of shallow and open evaporation pools?*
- *What is the advantage of using solar energy for evaporation?*
- *Are there also disadvantages in using solar energy for evaporation of water? If yes, give details.*

Note that the burning of 1 gram of coal releases the equivalent of 32.8 kJ of energy.
In the evaporation pools 36x106 cm^3 water are evaporated per year.

- *Assuming that the average water temperature is 35°C, how much coal is needed to evaporate this amount of water?*

In the evaporation pools the evaporation process and salt precipitation take place, as will be detailed later (see Page 59). In the process solutions with bromine ion concentrations of 10-12 gram/liter are obtained (the ratio chlorine ions to bromine ions reaches 17:1). These solutions, which are called brine, constitute the raw material for the production of bromine.

Brine: a concentrated salt solution

The ion concentration in the Dead Sea varies with depth and with the seasons. Table No. 2.3 gives the average annual ion concentrations at two different depths, in gram/liter:

Table No.2.3. Average annual ion concentrations

Ions	Up to 40 meter	From a depth of 100 meter
Cations		
Na^+	38.5	39.7
Mg^{2+}	36.1	42.4
Ca^{2+}	16.4	17.6
K^+	6.5	7.6
Anions		
Cl^-	197.0	219.0
Br^-	4.6	5.3
SO_4^{2-}	0.58	0.42
HCO_3^-	0.23	0.22
Average saltiness	300	332

- *What are the reasons for the seasonal differences in ion concentrations?*
- *What are the reasons for the differences in ion concentrations at different depths?*
- *Where is the water to the southern basin pumped from? Explain.*
- *In which seasons is the water pumped to the southern basin? Explain.*

Pump station

2.2 - Weighing the pros and cons of building up the bromine industry in Israel

> "...And so these waters of ours are much richer than all other waters in the entire world. That same old legend about a treasure case that drowned in the sea comes back to my mind. Infants believe that this treasure was made up only of golden necklaces, golden rings orgolden coins, but the salts of the Dead Sea are gold as well.
> The amount of bromine in these waters cannot be found in any other natural brine. And you know how expensive bromine is, and how many and varied the products we produce in addition to all those in that fertile region of our country, that before was the most desolate of all, the dead..."

In this way, in 1902, Benjamin Zeev Herzl described the future bromine industry, to be developed in the vicinity of the Dead Sea in his book "Altneuland". Although his vision was not realized exactly as he predicted in his book, this man of genius undoubtedly did envision the developments.
The first efforts to exploit the resources of the Dead Sea on an industrial scale began in 1921 by the engineer M.A. Novomeisky, who arrived in Israel from Russia his birthplace.
Novomeisky saw the enormous opportunities hidden in the Dead Sea and worked tirelessly to obtain a concession from the mandatory government to exploit the Dead Sea's reserves.
In 1930, after the concession was granted and the Potash Company founded, the first attempts were made to produce bromine from the Dead Sea. The production method was based on oxidation of bromine ions in brine by chlorine, a method similar to that used 100 years before by Balard, leading to his discovery of bromine and described in Section 1.2. The first bromine installations were built from basalt plates and the bromine was stored and transported in clay pots.
In 1931, bromine production was started from brine obtained after separation of potash. It was reasonable that the installations for the production of potash and bromine were located close to the Dead Sea. The first installations were built in Kalia, in the northern Dead Sea area. The site was chosen because of the location of roads for transport of materials and a supply of sweet water and crude oil for electricity production that were more accessible than the roads in the southern Dead Sea area.
Only two years after production began it became clear to Novomeisky that the production installations had to be relocated in the southern Dead Sea area. There the water was shallower and conditions more favorable for the construction of

bigger evaporation pools, based on exploitation of solar energy.
In 1934 a start was made with the building of the potash plant at the southern end of the Dead Sea, in Sdom. The Sdom plant got its sweet water from the village of Safi, on the opposite bank of the Jordan. Most of the employees, who were mainly Bedouins living in the region, also came from the other side of the Jordan.
Supplies and crude oil for the production of electricity arrived by boat from the northern Dead Sea area. The products of the potash plant were also transported this way to the north of the Dead Sea and from there, via Jerusalem, the potash and the bromine (the bromine was then produced only in the northern Dead Sea) reached the ports of Jaffa and Haifa.

Ever since establishment of the industry, which exploits the Dead Sea resources, we are faced with a **complex of considerations to determine the location of the plant:**

1. *Proximity to raw material source*
2. *Suitable construction site for production plants.*
3. *Good service facilities such as sweet water supply and electricity.*
4. *Easy access roads*
5. *Availability of manpower*

It is not always possible to find an ideal site that combines all these factors. In most cases a compromise had to be made in order to find the most suitable place.
In the case of building the potash plant it was the second consideration that was decisive in favoring the southern plant.

Before the Second World War the amount of bromine produced reached 500-700 tons per year, and during the war it increased (see Section 1.3).
In 1948, during the Israel War of Independence, the northern Dead Sea plant was destroyed leaving only the Sdom plant, which was cut off from its access roads and sweet water supplies. Production stopped. The industrial activity around the Dead Sea was renewed only four years later, in 1952, with the foundation of the Dead Sea Works and the building of a new potash plant in the southern Dead Sea area.
In 1955 the Dead Sea Bromine Company was founded, and one year later the

plant for the production of bromine was built in Sdom. Bromine production started in 1957 with a production of a few hundred tons per month. A plant for the production of EDB close to the bromine plant was installed in the same period.

The bromine plant was gradually enlarged with improvements and progress in technology and building materials. Glass replaced granite and clay. The next step was the use of glass-coated iron and finally noble metals.
The increased global demand for bromine and bromine compounds led to the foundation of the subsidiary company Bromine Compounds Ltd in 1960 with 50% foreign ownership. The objective was to produce more sophisticated bromine products, in order to increase profitability.

In 1963 the plant built in the industrial area of Beer Sheba started to produce bromine compounds. The establishment of this plant far away from its raw material source may seem odd, but the reasons for it are complicated and are connected mainly with considerations of recruiting suitable manpower for the work in the plant. **The tough climatic conditions** in Sdom and the **geographical distance** from city centers reduced the availability of suitable **manpower**. Producing compounds, which is much more complicated than producing bromine, required more and better educated personnel: engineers, technicians, researchers, etc. The Beer-Sheba region was better suited for this purpose than Sdom and made it easier to find trained and skilled personnel.

Bromine from the Dead Sea Bromine from the Dead Sea

The Bromine Compounds Ltd. plant- early days

Map of Dead Sea Bromine facilities

The next important step in the development of the Dead Sea Bromine Group was the establishment of a subsidiary company in Europe. In 1966, Broomchemie B.V. was founded in Woerden, The Netherlands. The purpose was to establish a plant for the production of bromine compounds in the European Common Market, to increase sales and to penetrate the global market for bromine compounds. It has been a great success.

In 1971, management of the Dead Sea Bromine Company and Dead Sea Works was transferred to Israel Chemicals Ltd., the largest chemical corporation in Israel.

The increased demand for bromine and bromine compounds led to the expansion of bromine production in Sdom and as a result a chlorine production plant was built in 1975 (until then chlorine was brought in containers from the Frutarom company in the north of the country).

In 1976 the Broomchemie plant was enlarged and moved to the city of Terneuzen in the south-west of the Netherlands.

In 1978 a new plant for bromine compounds was founded in the new industrial area in Ramat-Hovav. The government's decision to establish this industrial area, 15 km south from Beer-Sheba, was influenced by the growing awareness of environmental issues.

The choice of Ramat-Hovav as the site for the plant was based on the following considerations:

- *The site was remote from populated areas.*
- *There was a reasonable possibility of recruiting suitable manpower.*
- *There was a network of roads and a railroad.*
- *Research showed that the geological composition of the soil would not permit deep penetration of waste materials in groundwater.*
- *Research showed that wind directions in the area would not endanger the quality of life of Beer-Sheba residents.*
- *Water supply to the site was good.*
- *The site was not too far removed from the raw material source in Sdom and the access roads were relatively convenient.*

Over the years, the production capacity of bromine grew with the addition of both chlorine and bromine production plants. Likewise, the production of bromine compounds was increased in quantity as well as in variety. At the same time an international marketing network was built up, composed of companies for the marketing, sales and distribution of bromine compounds in different parts of the world.

It is clear that we are dealing here with a dynamic organization needing to change and develop in line with the requirements of the market and the management conception of the company's directors. The organization was totally owned by the state until 1995 and complete control was turned over to private hands by the year 2000 [1].

[1] In the year 2000 the Dead Sea Bromine Group became a privately owned company which does not trade on the stock exchange. Therefore financial data are not published as of that year.

Milestones

1924 –	*First attempts at industrial exploitation of the Dead Sea resources by the engineer M.A. Novomeisky*
1929 –	*M.A. Novomeisky received a concession to exploit Dead Sea resources*
1930 –	*Foundation of the company "Land of Israel Potash Ltd" and building of the plant in the northern Dead Sea area (Kalia).*
1931 –	*Start of bromine production*
1932 –	*Start of potash production. First shipments of bromine and potash.*
1934 –	*Start of developmental work for building a plant in the southern Dead Sea area (Sdom).*
1948 –	*War of Independence, northern Dead Sea plant is destroyed and production in southern Dead Sea is halted.*
1952 –	*Foundation of the company Dead Sea Works*
1955 –	*Foundation of the company Dead Sea Bromine Ltd, a subsidiary company of Dead Sea Works Ltd and managed by the latter.*
1956 –	*Establishment of bromine production plant in southern Dead Sea area (Sdom) with an overall production capacity of 10,000 ton/year.*
1957 –	*First bromine plant in Sdom is operational with production capacity of several hundred tons of bromine per month.*
1957-58 –	*First production of bromine-containing organic compounds.*
1961 –	*Foundation of the company Bromine Compounds Ltd in Beer-Sheba.*
1962 –	*Opening of plant for the production of bromine compounds (Industrial area, Beer-Sheba).*

1967 –	*Foundation of the company Broomchemie Ltd for the production of bromine compounds, Woerden, The Netherlands*
1971 –	*Management transfer of Dead Sea Bromine Ltd from Dead Sea Works to Israel Chemicals Ltd.*
1973 –	*Production of the 100,000-th ton of bromine in Sdom.*
1977 –	*First chlorine plant in Sdom operational (Diaphragm system) with production capacity of 45,000 ton per year.*
1977 –	*Enlargement of Broomchemie plant and its relocation in Terneuzen, the Netherlands.*
1978 –	*Enlargement of Bromine Compounds Ltd. plant and its relocation from Beer-Sheba to Ramat-Hovav.*
1987 –	*Second chlorine plant in Sdom operational (membrane system) with production capacity of 45,000 ton of chlorine per year.*
1995 –	*Conversion of Dead Sea Bromine Ltd to a public company.*
1995 –	*New bromine plant in Sdom operational with production capacity of 50,000 ton of bromine per year.*
1995 –	*Acquisition of 50% of the American company Clearon, manufacturer of water treatment products.*
1996 –	*Establishment of the magnesium plant with production capacity of 50,000 ton of chlorine per year.*
1998 –	*The total production capacity of all bromine factories together in Sdom is 250,000 ton per year.*

Concepts studied in Chapters 1 and 2

Brine:
A concentrated salt solution

Considerations when choosing the location of the plant:
- Proximity to raw material source
- Suitable construction site for production plants.
- Availability of good services such as sweet water supply and electricity.
- Easy access roads
- Manpower availability

Corrosion:
Deterioration process of solid material (usually metallic) as a result of contact with other material(s). Deterioration is usually accompanied by formation of holes, cracks or disintegration of the material. The process causes a change in the mechanical properties of the material, which may no longer suit its purpose.

Israel's advantage in bromine production:
- Dead Sea is a surface sea.
- Bromine ion concentration in the Dead Sea is the highest in the world.
- Dead Sea is located in a hot area with a high rate of evaporation, and the all year round availability of solar energy cheapens the production costs of bromine in a highly significant way.

Photochemical process:
Chemical process occurring by means of light absorbed by the system.

Leaded fuel:
Fuel to which Tetra-ethyl Lead is added to prevent self-combustion and "knocking engine".

Profitability of production of any product depends on:
- Uses generating a demand for the product.
- Existence of suitable raw material sources.
- Technological capability
- Financial means

Unleaded fuel:
Fuel without addition of Tetra-ethyl Lead.

Questions about Chapters 1 and 2

1. Bromine is an element belonging to the family of halogens.

a. List the properties of bromine:
Electron configuration
Ionization energy
Electron affinity
Electronegativity
Standard reduction potential
Possible oxidation states

b. How do these properties influence the reactions of bromine with other substances?

c. Bromine is the only non-metal that is a liquid at room temperature. Explain.

2. The following is a list of different bromine compounds:
$CH_2BrCOOH$, CH_3Br, PBr_3, $PbBr_2$, Br_2O, $BrCl$, $MgBr_2$

a. Show the bonds existing in each of the compounds

b. Give the representative electron configuration for each of the compounds.

c. Determine the oxidation state of the bromine atoms in each of these compounds.

d. Determine in which compounds the bromine may act as oxidant, as reductant or both oxidant and reductant. Explain.

3. The following is a list of substances, some of which may react with a hydrogen bromide solution. Each time a reaction occurs, write the equilibrium equation for the reaction and indicate the kind of reaction: precipitation, oxidation-reduction, acid-base, etc.

a. Solid lead nitrate

b. Chlorine gas

c. Hydrogen chloride gas

d. Carbon dioxide gas

e. Solid lithium carbonate

f. Solid calcium hydroxide

g. Solid calcium carbonate

4. Use the Table No. 1.1 on Pages 28 - 29 and arrange the bromine compounds in groups according to the following classifications:
a. Inorganic compounds
b. Organic compounds (according to functional groups)
c. Oxidizing agents
d. Acids
e. Solutions
f. Corrosive agents
g. Substances that decompose under heating and release toxic gases
h. Main applications

5. Bromine chloride (BrCl), which is formed by a reaction between bromine and chlorine, is a liquid at room temperature. It is impossible to isolate pure bromine chloride. Explain why.

6. 1,2 dibromo ethane (EDB.) was used for a long period for two main purposes:
- Fuel additive
- Soil pest control and long-term storage of agricultural products

a. What were the reasons for the increased demand for EDB?
b. What were the reasons for the drop in use of EDB?

7. It is customary to name a certain period in history after the materials that were used. For example, there are people who think that our period will be called the Plastics Age. Look at the Table No. 1.4 on Page 36 and try to find a connection between the development of certain materials and human needs in the corresponding periods. Explain.

8. What are the advantages of bromine production from Dead Sea water compared to its production from other sources? Explain.

9. What are the factors that may influence the profitability of bromine production in Israel?

10. Why are the USA and Israel the most important manufacturers of bromine and bromine compounds in the world?

11. Look at the Table No 2.2 on Page 42 showing the concentrations of the most important ions in Dead Sea water, and answer the following questions:

a. Write the chemical formulas of the salts that may be formed during the evaporation of Dead Sea water.

b. What factors determine which salts are actually formed during evaporation?

c. What are the main salts obtained in the evaporation pools of the Dead Sea?

12. **a.** What were the reasons for choosing the sites of the following Bromine Compounds factories:
Bromine-chlorine plant in Sdom
The Bromine Compounds plant in Ramat Hovav
The Broomchemie plant in the Netherlands

b. Compare the reasons you gave for each plant with the general considerations appearing on Page 47.