

A Comparative Study of the Artificial Evaporation of Underground and Sea Brines

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Evaporation of underground and sea brines were monitored artificially. The rates of evaporation for both the samples were almost same. Various parameters were analyzed at different Baume degrees. A comparative study was carried out regarding the presence of Ca^{2+} , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} ions and sodium chloride in both samples.

Key Words: Physico-chemical parameters, Brines.

INTRODUCTION

Sodium chloride, naturally called common salt, is widely distributed on this earth. The constituents of sodium chloride, *i.e.*, sodium and chlorine, are two of the twelve dominant elements in the human body. Directly or indirectly, salt finds application in more than 14,000 ways¹.

Today, only 6% of the world's annual salt production is directly used for human consumption. As the frontiers of the chemical industry grow, new applications for salt and its derivatives are constantly being discovered².

Salt is produced by mining of solid rock deposits and by the evaporation of sea, lake and underground brines. In higher concentration, it occurs in sea-water and inland saline lakes. Repeated pumping of underground water makes the water more saline.

The following are the various methods possible for the manufacture of salt³:

- By the solar evaporation of either sea water or natural brines from lakes or wells.
- By the artificial evaporation of brine by direct fire or steam.
- By freezing of sea brine which forms a saturated brine followed by separation of salt. This method is being followed in North European countries, which have excessive cold climate.
- By mining rock salt by dry method or by injecting water to get a saturated salt solution.

Of all the above methods, the solar salt manufacture is of greater importance, since our country is having a long warm summer.

The present work involves the monitoring of artificial evaporation of both underground and sea brine samples to investigate the process of evaporation.

EXPERIMENTAL

For the comparative study of artificial evaporation of underground and sea brines, samples were collected from two different places, *viz.*, the salt-pans at Puthalam, which is located 8 km away from Nagercoil, the headquarter of Kanyakumari district of Tamil Nadu, where underground water is used. The salt-pans at Kovalam which is located 20 km from Nagercoil and just 5 km away in the west of Kanyakumari, the southern tip of the country, where sea brine is used.

10 litres of brine samples from Puthalam (underground) and Kovalam (sea brine) were collected separately. The atmospheric temperature and the Baume degrees were noted. Then both the samples were exposed to sunlight in separate plastic buckets. Each bucket was labelled and the atmospheric temperature and the Baume degree ($^{\circ}\text{Be}$) were recorded daily. The rate of evaporation was found out by measuring exactly the remaining amount of the samples left in the bucket daily.

Gypsum formed between 16°Be and 25°Be was collected daily, dried and weighed accurately. Similarly, the sodium chloride crystallized between 25°Be and 30°Be was also collected daily, dried and weighed accurately.

Parameters such as temperature of the brine, atmospheric temperature, pH, electrical conductivity, percentage of chloride, sulphate, calcium and magnesium were analyzed at 10°Be , 15°Be , 20°Be , 25°Be and 30°Be using standard procedures⁴. The amounts of sodium and potassium present in the above samples were also determined by using flame photometer.

pH was determined by standardized pH-meter and the electrical conductivity by the Elico conductivity bridge.

RESULTS AND DISCUSSION

During the course of evaporation, gypsum was collected from the underground and sea brine samples daily. The weight of dry gypsum in the underground sample was 28.35 g and that of the sea-brine was 33.20 g. It was observed that sea brine was having higher concentration of calcium sulphate than the underground brine (Table-1).

Similarly, the sodium chloride formed between 25°Be and 30°Be was also collected. The amount of dry sodium chloride in the underground brine was 310.45 g, while in the sea brine, it was 416.95 g (Table-1). This indicated that sea brine was more saline than the underground brine.

TABLE-I
COMPARISON OF AMOUNT OF SODIUM CHLORIDE FROM TWO SOURCES

No.	Source	Vol. of sample (L)	Wt. of gypsum (g)	Wt. of sodium chloride (g)
1	Underground brine	10	28.35	310.45
2	Sea brine	10	33.20	416.95

At the beginning of the evaporation, the decrease in volume for the two samples was around a litre a day and as it proceeded, the volume reduced by approximately 300–400 mL per day. At 30°Be, volume of the underground and sea brine samples reduced to 0.250 mL and 0.230 mL respectively (Table-2).

TABLE-2
EVAPORATION RATE WITH °Be

Underground brine (Puthalam)		Sea brine (Kovalam)	
°Be	Volume (L)	°Be	Volume (L)
4.00	10.000	6.00	10.000
5.00	9.200	6.50	9.100
5.25	8.665	7.00	8.710
5.50	8.210	7.25	8.300
6.00	7.520	8.00	7.620
6.50	6.800	8.50	6.950
7.00	6.275	9.50	6.460
7.50	5.725	10.00	5.940
8.50	5.150	11.25	5.375
9.25	4.800	12.00	5.000
10.00	4.400	12.75	4.625
10.75	4.075	13.50	4.325
11.75	3.725	14.25	4.000
12.25	3.650	15.00	3.850
14.00	3.000	15.50	3.725
15.50	2.550	16.50	3.350
17.50	2.200	18.00	2.975
20.00	1.870	20.00	2.625
22.50	1.575	22.00	2.300
25.00	1.350	25.50	1.820
26.50	1.050	26.00	1.570
27.50	0.760	26.50	1.320
29.00	0.475	27.00	1.000
30.00	0.250	27.50	0.770
—	—	29.00	0.470
—	—	30.00	0.230

Initially both samples had the same pH value, *i.e.*, 7.2. There was a gradual increase for both samples at 10°Be. The pH was 7.6 for the underground brine and for the sea brine, it was 7.3. At 15°Be, both samples had the same value, *i.e.*, 7.7. At 20°Be, the values decreased to 7.4 and 7.6. Then further reduced to 7.3 and 7.5 at 25°Be. But at 30°Be, the values further reduced to 6.6 for the underground and 7.2 for the sea brine samples. As maximum amount of calcium sulphate was collected between 16°Be and 20°Be, there was a decrease in alkalinity. This was evident in the gradual fall of pH values (Tables 3 and 4).

TABLE-3
PHYSICO-CHEMICAL PARAMETERS OF UNDERGROUND BRINE (PUTHALAM)

A	B	C	D	E	F	G	H	I	J	K
4	29.0	31.0	7.2	52	3.0	0.40	0.065	0.32	7803	170
10	30.5	32.0	7.6	81	5.8	0.56	0.120	0.60	11699	185
15	30.0	30.5	7.7	102	9.7	0.92	0.182	0.96	14811	186
20	31.5	31.0	7.4	103	14.6	1.16	0.099	1.51	16517	189
25	30.0	30.5	7.3	105	18.4	1.64	0.077	1.85	18220	200
30	31.0	31.0	6.6	101	22.7	3.86	0.068	3.90	14058	206

TABLE-4
PHYSICO-CHEMICAL PARAMETERS OF SEA-BRINE (KOVALAM)

A	B	C	D	E	F	G	H	I	J	K
6	29.0	31.0	7.2	67	4.0	0.74	0.046	0.25	9504	160
10	32.0	31.0	7.3	91	6.5	1.28	0.058	0.41	13725	166
15	28.5	28.0	7.7	102	10.5	1.70	0.099	0.59	17016	185
20	30.5	31.5	7.6	104	13.0	2.11	0.074	0.78	17511	193
25	31.0	30.5	7.5	106	18.8	2.41	0.065	1.08	18273	202
30	31.5	30.5	7.2	102	19.0	4.92	0.062	2.99	14323	208

A = Baume degree (°Be)

B = Temperature of the brine (°C)

C = Atmospheric temperature (°C)

D = pH

E = Electrical conductivity (10^{-3} mho)

F = percentage of chloride

G = Percentage of sulphate

H = Percentage of calcium

I = Percentage of Magnesium

J = Sodium (mg/L)

K = Potassium (mg/L)

Both underground and sea brines possessed almost similar electrical conductivity values in the beginning, *i.e.*, 52 for the underground brine and 67 for the sea brine. As the °Be increased, the values of electrical conductivity also increased steadily, *i.e.*, at 10°Be it was 81 and 91 for underground brine and sea brine respectively; at 15°Be, it was the same for both the samples, *i.e.*, 102. At 20° and 25°Be the values were almost similar, *i.e.*, 103 and 104 for both samples and at

25°Be, the values were 105 and 106 respectively. But at 30°Be, there was a sharp decrease in the electrical conductivity for both the samples, *i.e.*, 101 and 102 respectively. This indicated that around 80% of Na⁺ and Cl⁻ ions were removed as sodium chloride before reaching 30°Be (Tables 3 and 4).

Considering the percentage of chloride ion, for both the samples, there was a gradual increase and the values reached a maximum at 30°Be. Though a large amount of sodium chloride was removed before 30°Be, this high value was due to the remaining sodium chloride, potassium chloride and magnesium chloride. Both the underground and sea brine samples had similar percentage of chloride ion in the beginning, *i.e.*, 3.0 and 4.0 respectively. At 10°Be, they were 5.8 and 6.5. But at 15°Be, there was a sudden increase, *i.e.*, 9.7 and 10.5. At 20°Be, the values were 14.6 and 13.4. At 25°Be, the values were almost similar, *i.e.*, 18.4 and 18.1. But at 30°Be, the underground brine had the highest value of 22.7 while the sea brine had 19.1. This revealed that the underground brine had more amount of magnesium chloride and potassium chloride, compared to the sea brine.

There was a gradual increase in the values of sulphate ion concentration and reached the ultimate values. Though calcium sulphate was separated in the earlier level, the high value of sulphate was due to the presence of magnesium sulphate and potassium sulphate, and they got precipitated only after 30°Be. At the beginning, the percentage of sulphate was 0.40 and 0.74 for the underground and sea brines respectively. At 10°Be, the values were 0.56 and 1.28. Then at 15°Be, the values were 0.92 and 1.70. At 20°Be, they were 1.16 and 2.11. The values were 1.64 and 2.41 at 25°Be. But at 30°Be, these were 3.86 and 4.92. The high value of sulphate ions in the sea brine at 30°Be showed that it had more amount of magnesium sulphate and potassium sulphate than the underground brine.

The percentage of calcium ions was found to increase up to 15°Be for both the underground and sea brine samples. Then, as gypsum was collected before reaching 20°Be, from 20°Be onwards, there was a gradual decrease in the percentage of calcium ions and reached a minimum at 30°Be. Initially, the values were 0.065 and 0.046 for the underground and sea brines respectively. At 10°Be, the percentages of calcium ions were 0.120 and 0.058. But at 15°Be, the values were 0.182 and 0.099. Then, at 20°Be, as all the gypsum was removed, the value got reduced, *i.e.*, 0.099 for the underground brine and 0.074 for the sea brine. At 25°Be, the values were somewhat similar, *i.e.*, 0.077 and 0.065 and at 30°Be also, the values were somewhat similar, *i.e.*, 0.068 and 0.062. This showed that both the underground and the sea brine samples had almost similar calcium contents at various Baume degrees.

Considering the percentage of magnesium ions, both the underground and the sea brine samples possessed almost similar values initially, *i.e.*, 0.32 and 0.25 respectively. But at 10°Be, the value was greater for the underground brine, *i.e.*, 0.60, while it was only 0.41 for the sea brine. At 15°Be, these were 0.96 and 0.59. But at 20°Be, the values were 1.51 and 0.78. The values were 1.85 and 1.08 at 25°Be. The underground brine had the highest value, *i.e.*, 3.90 and for the sea brine it was 2.99 at 30°Be. This indicated that the underground sample, at 30°Be, had higher percentages of magnesium chloride and magnesium sulphate.

Regarding the amount of sodium, as expected, the underground brine had lesser

quantity than the sea brine, *i.e.*, initially it was 7803 mg/L for the underground brine and 9504 mg/L for the sea brine. At 10°Be, these were 11699 mg/L and 13725 mg/L. The values were 14811 mg/L and 17017 mg/L at 15°Be. At 20°Be, the values were 16517 mg/L and 17512 mg/L. At 25°Be, the values were 18220 mg/L and 18273 mg/L. Then there was a sudden decrease in the value at 30°Be for both samples, because, around 70% of sodium chloride was removed. The values were 14058 mg/L for the underground brine and 14323 mg/L for the sea brine. The above values revealed that some sodium chloride remained with the samples at 30°Be.

Regarding the values of potassium ions, as there was no separation of potassium salts, up to 30°Be, the values went on increasing for the two samples and reached the highest value at 30°Be. This was evident that KCl and K₂SO₄ crystallized only between 36°Be and 38°Be. Initially, the underground brine had the value 170 mg/L and that of the sea brine had 160 mg/L. At 10°Be, the values rose to 185 mg/L and 166 mg/L. At 15°Be, the values increased somewhat similarly, *i.e.*, 186 mg/L and 185 mg/L. But at 20°Be, the values were 189 and 193 mg/L. At 25°Be they were 200 and 202 mg/L. At 30°Be the values were almost similar, *i.e.*, 206 and 208 mg/L. This indicated that both the underground and sea brine samples possessed almost equal amount of potassium salts, *viz.*, KCl and K₂SO₄.

Conclusion

The underground brine was enriched with magnesium chloride and potassium chloride while the sea brine was enriched with sodium chloride, gypsum, epsom and potassium sulphate. The rates of evaporation for both the samples were almost same.

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