

ON THE PHYSICO-CHEMICAL CHARACTERISTICS OF BRINES

P.V.Shirodkar, P.V.S.S.Durga Prasad Rao and S.Y.S.Singbal
National Institute of Oceanography
Dona Paula, Goa - 403004

ABSTRACT

Analyses of the natural brines from the salt lakes, salt pans and the artificial brines obtained after the solar desalination of seawater respectively, showed wide differences in their physico-chemical characteristics. The natural brines are marked by significant increases in density, salinity and the major element composition relative to the artificial ones. The salinity of the salt pan brines though varied from 287.78 to 329.44 PSU, an apparent uniformity was observed in their chemical composition. The salt lake brines on the contrary varied in salinity from as low as 13.34 to as high as 473.46 PSU and indicated greater diversion in their chemical composition. The observed properties of the solar still brines range between the two types of natural brines.

The elemental composition of boron, calcium and magnesium, though showed an enrichment in all these brines relative to seawater, the salt lake brines were more richer followed by the salt pan brines with lowest concentrations in the solar still brines. Most of the salt lake brines showed 10-20 fold increase in calcium, 50-95 fold increase in magnesium and 15-20 fold increase in boron content relative to seawater. Magnesium always remained higher to calcium in these brines. The increase in elemental composition of the natural brines was found to be related to the geological features, the climatic condition and to the presence of source waters in the area.

The boron isotopic composition ($\delta^{11}\text{B}$) studied from the surface and interstitial brines of the salt lakes varied from 2.94‰ to 10.37‰ and indicated a non-marine origin of the salt lake brines as compared to the well known salt pan and the solar still brines of marine origin.

The physico-chemical characteristics of these brines thus indicated a greater potential of the salt lake brines followed by the salt pan brines, the least solar still brines for the exploitation of their resources.

INTRODUCTION

Brine, a significantly rich and an important alternate source of chemicals of economic importance occurs in nature mainly as the geothermal brine, the salt lake brine and the salt pan brine of the solar salt works. Artificially, the brine occurs as a by-product of the desalination of seawater at the solar desalination plants.

The significance of most of the chemical elements occurring in brines is due to their role in day to-day life. Apart from the minor elements which are either used in medicine or chemical and/or ceramic industry, the common salt is one such example playing an important role. The other major elements like Ca, Mg, K etc. are used by various other industries and fertilizers respectively (Mc Ilhenny, 1975). However, the elements such as boron, lithium, vanadium and few others are economically important because of their use in nuclear industries and in medicine (Xiao et al, 1988; Lui and Edmond, 1988). Boron and lithium are good absorber of neutrons and so are used in neutron shielding in nuclear industries (Ramkumar et al, 1984; Xiao et al; 1987). Uranium is also a well known nuclear fuel.

The depleting terrestrial reserves and the increasing demand for the economically important chemicals has focussed more attention on brines to develop new technologies for their extraction from brines. In the Third World as well as in the developed countries, extensive research is being done on the tedious task of the extraction of some important chemicals from brines. India, a geographically well placed country on the surface of the earth is surrounded by the sea and is gifted with the natural resources of brines like the Sambhar lake and other associated lakes in Rajasthan, some lakes in Orissa and West Bengal. Apart from this it has a number of salt works along its coast like those in Gujarat, Maharashtra, Orissa, Andhra Pradesh, Tamil Nadu etc., all of which provide large quantities of brins and bittern for the exploitation of their resources.

In this particular investigation, the properties of different types of brines have been studied that will help in future for the development of methods for the quantitative extraction of economically important chemicals from brines.

GEOGRAPHICAL FEATURES OF THE AREA

a) Salt Pans

Goa, a tiny state along the west coast of India experiences a tropical climate and is influenced by three seasons - the pre-monsoon, monsoon and the post-monsoon. It receives plenty of sunlight throughout the year and the temperature variation is mostly from 21 to 36° C. The highest temperature is observed in summer during the day. The summer season is followed by monsoon, during which heavy rainfall from the SW monsoon (av. 100"-120") is observed. This is followed by the post-monsoon, the receding period, giving a little bit of rain from the NE monsoon. The air is sometimes humid.

The salt works in Goa are mostly situated inside the sea coast and at the route of small creeklets or channels and are at a lower level than the sea or tide level. All the salt works are smaller in size, about 5 to 10 hectares. The soil in these salt works is mostly brown and contains silt, clay and fine particles of sand. In most of the places, the soil is impermeable and non-porous and is suitable for preparing crystallizer beds.

These salt works are provided with a storage area for seawater and the area of the salt works is divided in different compartments called the salt pans Fig. 2. The salt pans are the pools for obtaining salt by natural evaporation of seawater. During high tide, the seawater entering the storage area is allowed to evaporate by solar radiation. The brine thus formed of lower density is then taken into the salt pans at higher level and then allowed to flow by gravity to the lower level pans. The depth of the brines is kept at a minimum. During the evaporation of saturated brine in the salt pans, the salt separates out and settles to the bottom and is periodically raked with wooden pawdi. This helps in making salt crystals more compact and therefore voids and adherence of magnesium impurities are reduced considerably. Salt is harvested by making heaps in the pans and allowing it to drain (Shah and Rathod, 1990). After the removal of salt, the mother liquor called bittern is left behind that contains very high concentrations of the elements of economic importance. This bittern is then stored in bittern storage pans depending upon its use.

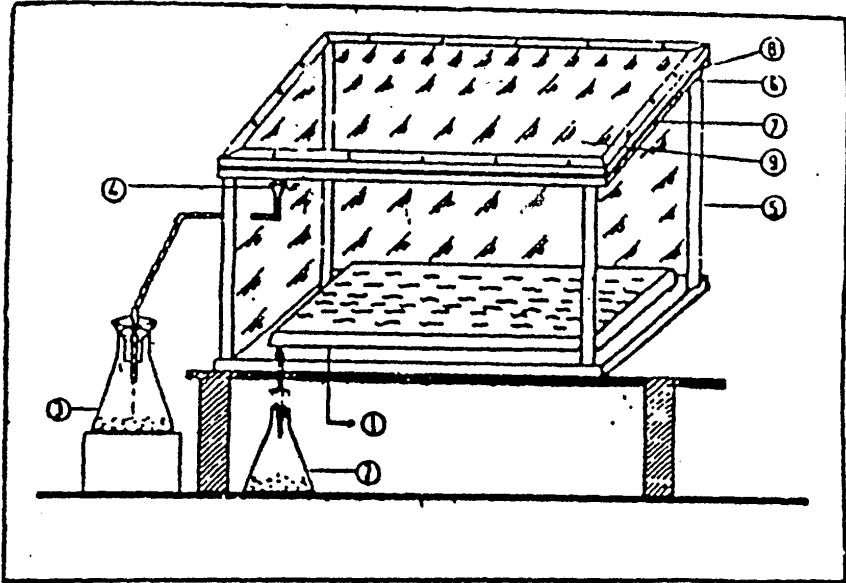


Fig. 1 (a) : Schematic diagram of the new prototype solar still.

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| (1) G. I. sheet water basin. | (5) Wooden pillar. |
| (2) Side walls' condensate. | (6) Wooden beam. |
| (3) Top cover condensate. | (7) Rubber gasket. |
| (4) Condensate collection gutter made of copper sheet. | (8) M. S. nut-bolt. |
| | (9) Glass sheet top Cover. |



Fig. 1 (b) : Experimental set up to study the improvement in efficiency of multi-surface solar still.

- 1 & 2. : Measuring cylinders for condensate collection from the top cover (1) and side walls (2)
- 3. : Saline water bottle with inlet tube.
- 4. : Rain water collection bottle.
- 5. : Multi-surface solar still.

b) Salt Lakes

The Qinghai Plateau in the north western region of China is provided with hundreds of lakes, both freshwater and saline. Most of the saline lakes occur in Qaidam Basin that is situated in the Kunlun-Tangula mountains in the NW part of Qinghai Plateau and is at an altitude of more than 2600 m above sea level Fig. 3. It is typically a terrestrial basin evolved during the Jurassic (Sun and Lock, 1990) and is surrounded by mountain ranges composed of metamorphic rocks and the granites of volcanic origin, It experiences a continental climate. The air is arid and cold with an annual precipitation less than 50 mm and the annual evaporation far exceeds precipitation. Due to severe cold, aridity and the strong winds, the salt lakes here are filled with brine rich in minerals and the chemicals of economic importance (Sun et al, 1982).

MATERIALS AND METHODS

Five seawater samples of varying salinities were collected and desalinated by solar desalination in solar stills to get the artificial brines. Another six samples of natural brines from the salt pans along the Goa coast (India) and seven samples from the salt lakes in Qaidam Basin, China were analysed for their physico-chemical properties and the elemental composition.

Temperature and density of the samples were noted at the time of collection whereas, the salinity was measured at the laboratory by argentometric titration method, after diluting the brine sample to seawater salinity (Strickland and Parsons, 1979). The pH of the brines was measured by Centron Dynamics pH meter with an accuracy of ± 0.01 units. Boron in brines was estimated by the Non-aqueous solvent method of Hulthé et al, (1970), whereas, calcium and magnesium were analysed by methods developed by the Qinghai Institute of Salt Lakes, China (1988) for their estimation in brines. The isotopic measurements of boron were carried out after its separation by ion-exchange as per the method outlined by Xiao et al, (1983). 10 ml portion of the surface and interstitial brine sample each was first slightly acidified with 1:1 HCl and then passed through a

specially made ion-exchange column (provided with a sintered glass) consisting of a mixture of strongly acidic cation exchange resin (Shanghai No. 1) in the H^+ form and a weakly basic anion exchange resin (Ion exchanger II) in the HCO_3^- form. It was then shaken for 7 to 10 rats and the boron was eluted with 60 ml high purity water. The eluate was centrifuged to 0.5 ml volume and loaded onto the filament of the Mass Spectrometer for boron isotopic measurements, using the procedure given by Xiao et al, (1988).

RESULTS

Solar still brines: The results of investigation (Table 1) showed the salinity of brines to vary from 187.86 to 255 PSU with an exceptional value of 0.64 PSU for one of the seawater samples of very low salinity. The temperature of these samples varied from 28-35° C while the density showed a variation from 1.125 to 1.212 and the pH varied from 7.45 to 7.77.

The calcium of these brines ranged from 320 to 1450 $mg\ l^{-1}$ whereas the magnesium showed an increase from 770 to 7000 $mg\ l^{-1}$. The lowest concentrations of calcium and magnesium of 5.0 and 8.0 $mg\ l^{-1}$ respectively, were observed in the samples with lowest salinity. The boron in these brines varied from 7.45 to 30.70 ppm with an exceptionally low value of 0.4 ppm for one of the samples whose salinity is significantly low. The average concentration of boron in these brines was 13.18 ppm and it showed a linear variation with salinity (Table 1).

Salt pan brines : All the brines were found to be hypersaline and showed high salinity varying from 287.78 to 329.44 PSU. The temperature difference for these samples was observed from 28.8 to 40.0 °C. The density of the samples ranged from 1.183 to 1.246 and the pH from 6.63 to 7.26 (Table 1).

Sample No.	Volume (ml)	Temp. (°C)	Salinity	pH	Density (gm/cc)	Volume (ml)	Temp. (°C)	Salinity	pH	Density (gm/cc)	Boron (ppm)	Calcium (mg/l)	Magnesium (mg/l)
SEA WATER													
SOLAR STILL BRINES													
1.	3500	32.0	0.11	8.09	1.011	8.0	35.0	0.64	7.45	1.212	7.45	5.0	8.0
2.	5000	29.5	36.06	8.08	1.014	660.0	35.0	255.00	7.70	1.169	30.7	980.0	7000.0
3.	5000	29.0	30.38	7.57	1.020	770.0	35.0	193.18	7.75	1.140	17.76	1200.0	4420.0
4.	5000	28.0	22.23	8.22	1.015	580.0	35.0	187.86	7.77	1.125	9.6	1450.0	3330.0
5.	4000	31.0	ND		1.002	6.2	35.0	ND	-	1.043	0.40	320.0	770.0
SALT PANS													
SALT PAN BRINES													
1.	Siridao -1	-	-	-	-	-	40.0	329.44	6.63	1.246	16.20	1040.0	37500.0
2.	Siridao -2	-	-	-	-	-	39.0	312.09	6.83	1.233	14.92	990.0	37600.0
3.	Siridao -3	-	-	-	-	-	28.8	328.33	7.02	1.217	41.02	500.0	18420.0
4.	Siridao -4	-	-	-	-	-	29.0	287.78	7.04	1.183	32.66	320.0	18700.0
5.	Arpora -1	-	-	-	-	-	37.5	319.62	7.23	1.205	9.70	1470.0	17300.0
6.	Arpora -2	-	-	-	-	-	38.0	310.91	7.26	1.203	8.48	1790.0	14330.0
SALT LAKES													
SALT LAKE BRINES													
1.	Potassium Lake - 1	-	-	-	-	-	34.0	471.9	4.58	>1.300	30.17	9852.0	112145.0
2.	Potassium Lake - 2	-	-	-	-	-	22.0	473.5	4.62	1.136	93.87	8177.0	113998.0
3.	Buo Buxian Lake	-	-	-	-	-	23.0	330.7	5.63	1.263	69.40	886.6	62349.0
4.	Gau Quan Potassium Factory (Interstitial brine).	-	-	-	-	-	16.0	-	6.31	1.246	77.45	-	-
5.	Lenghu Lake	-	-	-	-	-	24.0	3.84	7.76	1.002	2.18	235.8	156.5
6.	Gansen Lake	-	-	-	-	-	15.0	-	8.64	1.008	3.52	-	-
7.	Qinghai Lake	-	-	-	-	-	10.05	13.34	9.09	1.011	12.07	14.13	727.5

Table 1. The chemical composition of Brines from different sources. ND - not detected.

The calcium of these brines ranged from 320 to 1790 mg l^{-1} and magnesium from 14330 to 37600 mg l^{-1} . The boron varied from 8.48 to 41.0 ppm with an average of 20.5 ppm. The salt pan brines do not indicate direct relationship of boron with salinity (Table 1).

SALT LAKE BRINE

The brines observed were of two types. In one type the samples showed vary low salinity ranging from 3.84 to 13.34 PSU while in the other type, the samples showed high salinity in the range of 330.67 to 473.46 PSU. The temperature was found to be as low as 10.05 to as high as 34 $^{\circ}$ C. The pH ranged from acidic (4.58) to alkaline (9.09) and the density variation was from 1.001 to > 1.30.

In the low salinity brines, the calcium and magnesium varied from 14.13 to 253.8 mg l^{-1} and from 156.5 to 727.5 mg l^{-1} , respectively. In the high salinity brines, their variation was observed from 886.6 to 9852mg l^{-1} and from 62349 to 113998 mg l^{-1} , respectively.

Boron, however, followed the trend of calcium and magnesium variation and ranged from 2.18 to 12.07 ppm in the low salinity brines and from 30.17 to 93.87 ppm in the high salinity brines. The average values of boron calculated for these (two types) brines were 5.9 ppm 67.72 ppm respectively for the low and high salinity brines.

The boron isotopic composition of a few of the salt lake brines taken as a representative of the salt lakes in Qaidam Basin, depending upon their salinity, indicated the isotopic ratio, $^{11}B/^{10}B$, for the surface brines to vary from 4.0614 to 4.0838 with $\delta^{11}B$ varying from 4.40‰ to 10.37 ‰. However, the boron isotopic composition of the interstitial brine (Table 2) gave a very low $\delta^{11}B/^{10}B$ ratio of 4.0555 with low $\delta^{11}B$ value of 2.94 ‰.

No.	Brine	11B/10B ratio	$\delta^{11}\text{B}(\text{‰})$
1.	Potassium Lake - 2	4.0856	10.37
2.	Potassium Lake - 1	4.0838	9.95
3.	Qinghai Lake	4.0614	4.40
4.	Gao Quan Potassium factory (interstitial brine)	4.0555	2.94

Table 2. Boron isotopic composition of salt lake brines.

DISCUSSION

All the brines studied have been arranged in order of their increasing pH (Table 1). The data indicated that these various types of brines are hypersaline with salinities 10 -15 times higher than that of seawater. The brines of the salt lakes are very significant in their physico-chemical properties relative to the salt pan and solar still brines. This significance is mainly due to the degree of evaporation and depends on the environmental factors such as solar radiation, atmospheric temperature, wind and humidity and is indirectly related to their heat content.

Generally, a temperature of 35 °C and above of a water body increases the chances of brine formation. It is also augmented by the wind flow. Even in the deep sea, wherever there is a restricted water movement, the brine formation has been found to take place if the temperature of water goes beyond 35 °C. The brine pools below depths of 1000 - 1500 m in the deep basin of the Red sea were observed to have the same temperature between 36 - 40 °C (Swallow, 1969).

The nature of formation of these brines indicates that the solar still brines and the salt pan brines were formed due to the solar heating of water. All the solar still brines were formed at a uniform temperature of 35 °C (Table 1). As the latter were made to form in a wooden tray painted black from inside (Fig.1), they had no contact with the earth's surface and were also cut off from the wind due to a closed assembly. The salt pan brines on the contrary were made to form on the surface of the earth in the salt pans (Fig.2) and so had a direct contact with the bottom sediments. Their exposure to sunlight apart from other environmental factors, however, showed wide variations in their temperature from 28.8 to 40 °C, indicating the different heat capacities for these brines. This reveals that other factors mainly in sediments influence these brines greatly.

The salt lake brines depicted a reverse picture as compared to the other two types of brines. These brines were found to have significantly low

temperature from 10.05 to 34° C and therefore indicate hardly any influence of solar radiation. It was therefore, the other environmental factors related to geography of the area seem to influence these brines. These brines are influenced by severe cold, dry and arid air and the strong winds all of which increase their rate of evaporation. This has led to the formation of hypersaline brines. Although the brines are hypersaline, the natural brines apart from showing increased salinity and increase in their chemical composition relative to the artificial ones, show differences among themselves. This difference within the natural brines could be related to their formation and origin. However, these brines are found to be similar in their properties to those from Bannock and the Tyro Basins (Bregant et al, 1990; Lange and Edmond, 1990)

Considering the the origin of these brines, the artificial brines and the salt pan brines are of marine origin, as they were obtained by the evaporation of seawater. However, the origin of salt lake brines was studied using boron isotope as a tracer. The boron isotopic composition of the salt lake brines indicated that the values of the boron isotopic composition ($\delta^{11}\text{B}$) of these brines does not exceed 10.4 ‰. This value is much lower compared to that of seawater which is 39.5‰ (Spivack, 1986). Several early studies indicated that the samples with $\delta^{11}\text{B}$ values of around 40‰ belong to that of marine origin. Studies by Sun Da Peng et al, (1989) and others on brines from most of these salt lakes observed $\delta^{11}\text{B}$ values below 30‰ and they characterised these brines to be of non-marine origin. Supported by these findings, the observed brines from the salt lakes in this investigation can be considered to be of non-marine origin.

The brines of marine origin obtained from the salt pans and the solar stills when compared with those of the seawater brines formed under natural conditions at great depths in the Red Sea, indicate similarity in their chemical composition. The salinity of the former brines falls in the range of 187.86 to 329 PSU whereas for the latter brines the salinity was around 320.4 PSU. The salt lake brines on the contrary, showed very high and exceptionally low salinities. A close examination of the chemical composition of lake brines showed significant

differences in their ionic composition when compared with the standard seawater. All the brines in Table 1 are enriched in Na, Ca, Mg, and B. In the case of solar still brines, however, due to the lack of contact of the brine with the earth surface, the variations in ionic compositions of their elements resulting from exchange reactions between seawater and sediments during the brine formations are not observed. Their observed concentrations only indicate the result of evaporation of water.

Coming to the salt pan and the salt lake brines, though one is of marine origin and the other of the non-marine origin, their compositions usually depend on the factors such as geography of the area, the presence of the type of rocks and minerals and the presence of source waters to these lakes. Generally, the enrichment of Na and Ca in the lake brines can be expected to be due to the leaching of halite and gypsum in sediments. Studies on the mineralogy of these lakes indicated that apart from the clay minerals, these lake sediments contain other minerals such as carnallite, sylvite, halite and bischofite of the chloride type and the mirabilite, picromerite and polyhalite mostly of the sulphate type which are found always in association with epsomite, bloedite, mirabilite and gypsum. The boron minerals found in these lakes were ulexite, pinnoite and borax (Zheng Xiu, 1974; Sun Da Peng and Lock, 1990; Sun Da Peng et al, 1991; Vengosh et al, 1994). The mountain ranges surrounding these salt lakes are composed of metamorphic rocks of the Paleozoic age along with granite of varying ages. The granitic rocks occupy about 2/3 of the total area of the drainage basin. These rocks contain B, K, Li etc., the concentrations of which are several orders of magnitude higher than the ordinary rocks. The streams draining from these snow capped mountains at the basin margin terminate in a series of saline lakes and leach out lot of boron thereby accounting for an increase in boron content.

It is also known that the salt lakes in Qaidam Basin are fed by waters from various sources such as the hot springs, riverine surface freshwater and the saline and hypersaline underground fluids characterised by different chemical and boron isotopic composition (Huang Chi, 1974; Li Xianyong, 1985; Xiao et al, 1992; Vengosh et al, 1994). As these waters flow over the host country rocks

enroute to lakes, they are subjected to various processes including evaporation that bring about changes in their chemical composition.

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