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Chemical Parameters of Brine at Various Stages of Solar Salt Production in South Tamil Nadu, India

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Abstract - **It deals with the chemical parameters of brine at various stages of four selected salt production works, two from Kanyakumari District (SW1,SW2) and other two from Tuticorin District (SW3,SW4) Tamil Nadu. Estimation of ionic content of the various ions like chloride, sulphate, fluoride, calcium, magnesium, sodium and potassium were studied. The mean and standard deviation value of chloride, sulphate, fluoride, calcium, magnesium, sodium and potassium content (gl^{-1}) at various stages of salt production process of the selected salt works were evaluated. The concentration of different ions in each samples were almost same. The calcium ion content was minimum in bittern stage of sub soil brine and below the detection level in sea brine.**

Keywords: **Sea Brine, Subsoil Brine, Chemical Parameters, Salt Works**

I. INTRODUCTION

Common salt is one of the most plentiful substances on earth (J.C. Hocquet *et al.,* 1987, L.G.M. Bass Becking, 1931). Salt production in solar salterns has been a traditional wealth of source from ancient times, being developed in salterns in which brines started from sea water evaporation, as well as in those brines were obtained directly from salty wells and sources, usually located inland far from the sea shore(F. Amat,1986). In India, nature has endowed with long periods of dry weather, which aids natural evaporation of sea water. The technique of solar salt production involves fractional crystallization of salts in different ponds to obtain sodium chloride in the purest form possible (eg. up to 99.7% on dry weight basis) (P. Sorgeloos *et al.,* 1990). Since solar salt is produced by the action of sun and wind on sea water or natural brines, temperature plays a very important role, in addition to many other factors. Temperature being an important ecological master factor, it never remains constant in the brine sources. These variations are exclusively due to the seasonal changes and the rainfall (P. Haridas *et al.,* 2000). Salt production, the salt pans water evaporates in successive ponds, until the brine is fully concentrated and salt crystallizes on the floor of crystallizers. Over sixty elements are found in sea water, and among them, the most important ones are sulphate, carbonate, calcium, chloride, sodium, magnesium and potassium (M.L. John, 1964). Five ions sodium, magnesium, potassium, chloride, and sulphate dominate to such as extent that sea water is often considered as a quinary system (A.G. Taher *et al.,* 1995).

For the manufacture of salt from sea water, the knowledge both the composition of sea water and its phase chemistry is necessary. While studying the phase chemistry of salt manufacture, brine concentration is given on the Baume scale, (^{o}Be). The phase chemistry of solar salt production is conveniently divided into four distinct phases (H.W. Fiedelman *et al.,* 1969). The first phase is from 3 to l3^{o}Be, when most of the carbonates of calcium, magnesium and iron precipitate. The second phase extending from 13 to 25.4°Be, centres around gypsum, $CaSO_4.2H_2O$, which crystallizes as needle shaped crystals from 13 to 16.4^{o}Be, and thereafter as anhydrous $CaSO_4$, 85% of $CaSO_4$ present is precipitated in this phase. The third phase extends between 25.6 and 30^{o}Be, in this phase common salt, is precipitated out. The crystallization starts at 25.6^{o}Be and its rate rapidly increases at the initial stages. 72% of the total amount is precipitated by 29^{o}Be and 79% by 30° Be (Febvre, 1962). At higher saturation, crystallization slows down considerably and is complete only with the completion of evaporation. The concentration at which sodium chloride starts to crystallize is known as the "salting point" and the mother liquor at this point is called "pickle". At the end of this phase, where the concentration is 30°Be and above, the liquor is called “bittern”, because of the characteristic bitter taste.

The salt works that use sea water for salt production should be located closer to the sea. The topography of a salt pan is made in such a position, so as to pump sea brine to the salt pans in a cost - effective manner. The area requirement and the ratio of reservoir, condenser and crystallizer ponds vary from place to place depending on the salinity of brine and the seepage losses. Normally the ratio of reservoir, condenser and crystallizer ponds is 30:60:10 (W.T. Lambe, 1951).

The ideal depth of the brine in the salt works is between 15 and 20 cm (T.R.Rajagopalan, 1981). Solar salt production may be from the sea water, inland lake or underground brines. The brine from different sources has different mineral concentration (D.C.Hahl *et al.,* 1969). India produces 75% of salt by solar evaporation of sea water, 20% from sub soil brine and inland lakes and the rest from backwater. Tuticorin, the major salt producing District of Tamil Nadu, uses subsoil brine and sea water equally for salt production (C.Govindasamy *et al.,* 2000). In

Kanyakumari District, the total salt production contributes a little to the overall salt production of Tamil Nadu and the Manakudy Lake (estuary) forms the prime source for salt production in addition to sea water and subsoil brine. But excessive dilution by heavy rains can be an important factor responsible for lowering down the values of different ions in the brine (A.C. Cumming *et al.,* 1968).

II. MATERIALS AND METHODS

The present study was carried out over a period of one year. Water samples were collected monthly from the different stages of the salt production process such as source, reservoir, condensers, crystallizer and bittern in all the four salt works, Kovalam (SW_1), Puthalam (SW_2), Vepalodai (SW_3) and Sahupuram (SW_4). The chemical parameters, the concentration of ions like chloride, sulphate, fluoride, calcium, magnesium, sodium and potassium were determined. The mean and standard deviation were taken of the data presented monthly during the study period. The determination of all the chemical parameters was done by the standard procedures (A.I. Vogel, 1961). Estimation of sodium and potassium using flame photometer (C.S. Rao, 1995). The fluoride concentration was carried out using fluoride ion selective electrode, ORION fluoride electrode in combination with the direct combination readout specific ion meter (Model: ORION 720A) (Sujit Pal *et al.,* 2004).

III. RESULTS AND DISCUSSION

TABLE I THE MEAN AND STANDARD DEVIATION VALUE OF CHLORIDE, SULPHATE, FLUORIDE, CALCIUM, MAGNESIUM, SODIUM AND POTASSIUM CONTENT (GL^{-1}) AT VARIOUS STAGES OF SALT PRODUCTION PROCESS OF THE SELECTED SALT WORKS

Salt Works	**Various Stages**	**Chloride (gl^{-1})**	**Sulphate (gl^{-1})**	**Fluoride (gl^{-1})**	**Calcium (gl^{-1})**	**Magnesium (gl^{-1})**	**Sodium (gl^{-1})**	**Potassium (gl^{-1})**
SW1 Sea brine	Source	18.82±0.69	3.18±0.15	0.81±0.017	0.20±0.01	0.34±0.03	5.30±0.24	0.29±0.04
	Reservoir	20.39±1.95	5.72±0.61	0.83±0.016	0.14±0.01	0.86±0.04	7.30±0.30	0.43±0.02
	Condenser	133.6±8.9	18.02±1.82	0.89±0.017	0.10±0.07	5.67±0.77	35.20±3.53	2.07±0.10
	Crystallizer	193.79±8.72	43.89±6.06	0.92±0.017	0.080±0.01	13.12±0.23	51.56 ±2.27	2.97±0.36
	Bittern	206.10±6.41	87.74±6.58	0.97±0.025	-	21.06±0.58	13.54±0.44	5.27±0.12
SW2 Sub soil brine	Source	13.06±2.36	3.87±0.41	0.48±0.020	0.28±0.07	0.67±0.03	4.28±0.24	0.32±0.02
	Reservoir	37.58±4.96	12.41±1.42	0.51±0.023	0.32±0.03	2.11±0.11	11.74±0.81	0.47±0.02
	Condenser	116.5±12.2	29.64±1.88	0.57±0.024	0.07±0.04	9.86±0.97	44.32±3.07	1.98±0.19
	Crystallizer	178.57±13.85	49.39±3.95	0.60±0.034	0.04±0.01	13.79±2.11	52.09 ±1.31	2.71±0.18
	Bittern	202.34±3.61	63.70±4.09	0.64±0.021	0.0049±0.001	29.26±4.20	23.54±0.25	3.65±0.15
SW3 Sea brine	Source	18.57±1.01	3.37±0.20	0.85±0.026	0.27±0.03	0.35±0.03	5.74±0.14	0.31±0.01
	Reservoir	29.48±4.42	5.54±0.40	0.89±0.025	0.13±0.03	0.83±0.04	8.12±0.13	0.50±0.02
	Condenser	135.8±11.2	18.72±2.10	0.91±0.022	0.18±0.06	6.97±0.29	39.39±5.34	2.30±0.50
	Crystallizer	200.79±2.44	52.08±0.98	0.93±0.024	0.07±0.02	15.66±0.49	55.90 ±2.24	3.55±0.58
	Bittern	213.94±5.41	77.36±3.90	0.99±0.021	-	21.89±1.13	13.19±0.22	5.94±0.26
SW4 Sub soil brine	Source	15.51±0.93	3.82±0.53	0.44±0.021	1.01±0.06	2.61±0.32	9.41±0.61	0.33±0.02
	Reservoir	44.32±4.40	8.06±0.46	0.48±0.028	1.36±0.19	4.57±0.25	19.70±1.02	0.72±0.05
	Condenser	124.5±11.4	13.74±0.59	0.51±0.031	0.86±0.03	11.97±0.80	40.22±2.07	2.04±0.18
	Crystallizer	182.88±3.59	23.13±0.55	0.54±0.025	0.58±0.07	16.74±0.34	52.80 ±1.30	3.27±0.16
	Bittern	201.0±0.93	53.66±2.50	0.58±0.039	0.07±0.01	24.67±0.80	13.32±0.47	6.12±0.40

A. Chloride (gl^{-1})

Chloride ion is one of the dominant anions in the brine in concentration from the source to the bittern stage. The chloride ion concentration in the source samples of various salt works ranged from 13.06 ± 2.36 to 18.82 ± 0.69 gl^{-1}. In the bittern samples of various salt works ranged from 201.0 ±0.93 to 213.94 ± 5.41 gl^{-1}.The chloride concentration increases from source to bittern stage. Though the crystallizer pond discharged chloride, the concentration of chloride continued to increase, in the subsequent bittern stage. Earlier reports too have confirmed this observation, which was due to factors like the incomplete crystallization of sodium chloride in the crystallizer stage (76%) and the presence of highly soluble potassium chloride and magnesium chloride in the bittern (P.Subramanian,1981).

B. Sulphate (gl^{-1})

The mean sulphate concentration in the source water samples ranged from 3.18 ± 0.15 to 3.87 ± 0.41 $gl^{-1}$and 53.66 ± 2.50 to 87.74 ± 6.58 gl^{-1} in the bittern. In the present study, the sulphate ion concentration of the brine sample increased from source to the bittern stage, which is in accordance with earlier works (Vaithyanathan *et al.,* 2001). According to the phase chemistry of solar salt production, sulphate gets eliminated as gypsum $CaSO_4$. $2H_2O$ and $CaSO_4$ in the condenser stage where the salinity is around 13°Be. Yet the sulphate concentration was on the increase in sulphate concentration as $MgSO_4$ and K_2SO_4 during evaporation than the deposition as gypsum and anhydrous calcium sulphate.

C. Fluoride (gl^{-1})

The mean fluoride concentration in the source samples ranged from 0.44 ± 0.021 to 0.85 ± 0.026 mg l^{-1}. The mean fluoride concentration in the bittern samples ranged from 0.58 ± 0.039 to 0. 99± 0.021 mgl^{-1}.In the present study, the fluoride ion concentration of the brine increased from source to bittern stage. The high fluoride containing water has lower concentration of calcium. These findings are in agreement with the present study (A.K.Tripathi *et al.,* 1996, S.L.Choubisa,1995).The concentration of magnesium is high in samples containing higher concentration of fluoride. This may be due to the higher solubility of magnesium fluoride than calcium fluoride in water. The present study is also in agreement with the earlier findings (K. Krishnamohan *et al.,* 1996).

D. Calcium (gl^{-1})

The source sample of various salt pans, the mean concentration of calcium ranged from 0.20 ± 0.01 to 1.01 ± 0.06 gl^{-1}. The reservoir sample of various salt pans, the annual mean concentration of calcium ranged from 0.14 ± 0.01 to 1.36 ± 0.19 gl^{-1}. The condenser sample of various salt pans, the mean concentration of calcium ranged from 0.07 ± 0.01 to 0.86 ± 0.22 gl^{-1}. The crystallizer sample of various salt pans, the annual mean concentration of calcium ranged from 0.04 ± 0.01 to 0.58 ± 0.07 gl^{-1}. In the present study, the concentration of calcium in source samples was comparatively lower than the other ions. SW_2 and SW_4 salt works (uses subsoil brine) the values slightly increased from source to reservoir.

Salt works (uses sea water) the calcium concentration decreases from source to reservoir might be due to the deposition of $CaCO_3$ at early stages (reservoir). The decrease in calcium thereafter was due to the deposition of calcium as gypsum and as calcium sulphate, in the condenser ponds as thick deposits from 13°Be till the end of phase II and at the beginning of phase III. Low concentration of calcium in the crystallizers confirmed the maximum elimination of calcium. Trace amount of calcium in the crystallizer and bittern stages may also be attributed to the excessive organic matter complexed with calcium in high saline concentrating ponds that leads to deposition of this mineral (M. J. Barcelona *et al.,* 1978, J.S. Davis,1990). This leads to the concentration of calcium, below the detection limit in the bittern in SW_1 and SW_3 (uses sea brine) and very low value in SW2 and SW4 (uses sub soil brine). The salt production using sea brine, there was no calcium in bittern was also confirmed by earlier report (S.Sundaresan, 1986). The present study is in agreement with the earlier report.

E. Magnesium (gl^{-1})

The source sample, the mean magnesium concentration of various salt works ranged from 0.34 ± 0.03 to 2.61 ± 0.32 gl^{-1}. The bittern sample, the mean magnesium concentration of various salt works ranged from 21.06 ± 0.58 to 29.26 ± 4.20 gl^{-1}. The magnesium concentration gradually increased from source to bittern stage. It was due to the fact that during the course of evaporation, magnesium chloride and magnesium sulphate stay in the solution on the account of their greater solubility and can be crystallized only after 30°Be, bittern stage (A.F. Nylander *et al.,* 1964).

F. Sodium (gl^{-1})

The source sample, the mean sodium concentration of various salt works ranged from 4.28 ± 0.24 to 9.41 ± 0.61 gl^{-1}. The crystallizer sample, the mean sodium concentration of various salt works ranged from 51.56 ± 2.27 to55.9 ± 2.24 gl^{-1}. The bittern sample, the annual mean sodium concentration of various salt works ranged from 13.19 ± 0.22 to 23.54 ± 0.25 gl^{-1}. The concentration of sodium ion the principal cation of brine samples, increased from source to the crystallizer. In the crystallizer, as sodium increases it as sodium chloride, decreasing its concentration in the subsequent bittern stage, as confirmed by earlier report (A.Mnif *et al.,* 2001). Between 25.4 and 28°Be, 72 to 76% sodium chloride had crystallized and the remaining sodium had been in the bittern.

G. Potassium (gl^{-1})

The source sample, the mean potassium concentration of various salt works ranged from 0.29 ± 0.04 to 0.33 ± 0.02 gl^{-1}. The bittern sample, the mean potassium concentration of various salt works ranged from 3.65 ± 0.15 to 6.12 ± 0.40 gl^{-1}. Potassium ion was present in lesser amount than other cations in all stages of salt production. As potassium salts are highly soluble, no potassium salt is found to be crystallized before the bittern stage which is in accordance with earlier findings (C.R.Goldman *et al.,* 1963).

IV. CONCLUSION

The present study was concluded that the ionic content of chloride, sulphate, fluoride, magnesium, and potassium except sodium and calcium increases from source to bittern stage. The increasing in sulphate ion concentration as $MgSO_4$ and K_2SO_4, which was more than the deposition as sulphate of calcium. It was due to the fact that during the course of evaporation, magnesium chloride and magnesium sulphate stay in the solution on the account of their greater solubility and can be crystallized only after the bittern stage. As potassium salts are highly soluble, no potassium salt is found to be crystallized before the bittern stage. The concentration of sodium ion the principal cation of brine samples, increased from source to the crystallizer. In the crystallizer, sodium increases it as sodium chloride, decreasing its concentration in the subsequent bittern stage. The calcium ion concentration of the brine decreased from source to bittern stage. Calcium ion concentration is decreased, due to the deposition of calcium as gypsum and as calcium sulphate in the condenser ponds. The calcium ion content was minimum in bittern stage of sub soil brine using salt works and below the detection level in sea brine using salt works.

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