YIELD IMPROVEMENT OF SALTS WITH INCREAING THE RATIO OF SODIUM TO MAGNESIUM IN SATURATED BRINE

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Abstract: The present state of brine making system in solar salt production enterprise was introduced. The brine making system introduced in this work was compared with the one generally used in making saturated brine. The reason and the disadvantages was analyzed for the low ratio of sodium to magnesium. The technology for increasing the yield of salt was proposed based on the principle of increase the ratio of Na to Mg in the brine making system with the method of mixing salting-out brine with the fresh brines.

Key words: sodium, magnesium, yield

The general used management index of brine making system in sea-salt enterprises is the concentration of seawater, say °Bé of the brine, rather than the ratio of sodium to magnesium. However, the ratio of sodium to magnesium will be much lower in the brine than in the coastal water when the NaCl in the brine is saturated. The concentration of Mg^{2+} and SO_4^{2-} are higher while the concentration of NaCl in the brine is lower.

The value of Na/Mg in saturated brine varies with the time and the batch when the brine was made during the year. It was not controlled in the process so that the value of the Na/Mg was varied very much in the production system.

1. Brine making condition and reason of the low value of Na/Mg in the brine

As reported by Sun Zhinan, the seawater was continuously evaporated untill to the 31.33 °Bé。The components of the brine at different stage of evaporation are listed in Table 1

Table 1 Experiment resulrs of seawater evaporation

Concentration °Bé	Relative Dendity d_4^{20}	concentration of Salts g/1000ml								
		$CaSO_4$	$MgSO_4$	$MgCl_2$	KCl	NaCl	NaBr	H_2O	Na^+/Mg^{2+}	Mg^{2+}/Mg^{2+}
3.51	1.0240	1.274	2.190	3.028	0.768	25.35	0.127	991.26	8.23	1.72
7.04	1.0502	2.571	4.581	6.330	1.581	53.73	0.263	981.14	8.34	1.74
13.44	1.1015	4.273	9.266	13.35	3.304	112.14	0.552	958.62	8.38	1.82
17.94	1.1408	3.264	13.65	19.47	4.710	163.47	0.797	935.44	8.35	1.80
25.04	1.2086	1.471	20.39	30.60	7.593	251.06	1.216	896.27	8.30	1.89
26.76	1.2264	0.815	31.82	53.23	12.13	233.94	2.026	892.39	4.62	2.12
28.48	1.2444	0.391	53.96	93.94	21.68	174.79	3.456	896.18	1.99	2.20
31.33	1.2760	0.162	84.70	157.95	34.28	95.73	5.764	897.41	0.68	2.36

From table 1 we can see that the density of the brine is 25.67 °Bé when the 3.51°Bé seawater was continuously evaporated to the NaCl saturated. Meanwhile the value of

Na/Mg is always about 8.3 that accord with the value of coastal water. The concentrations of the salts in the brine are: NaCl 255.50 g/l, Mg_2SO_4 21.06g/L, $MgCl_2$ 31.73g/L, KCl 7.8g/L. With the NaCl was salt out, the ratio of Na/Mg declines. At the end of the experiments, the density of the brine is 31.33 °Bé the ratio of Na/Mg in the brine is 0.68.

In the real salt production system, the salt-out rule is just like the Table 1 under the condition of no adding the desalination brine into the brine making system. The value of Na/Mg is the same both in the brine and in the coastal seawater before the NaCl saturated. In general the brine contains NaCl 250~260 g/L $Mg^{2+} \leq 13$ g/L and SO_4^{2}- ≤ 18 g/L.

The value of Na/Mg in the brine system is lower in salt production system, however, because of some objective factors such as salt field configuration and technology of making brine and so on. So that the concentration of NaCl in the brine is lower than that in seawater and concentration of Mg^{2+} and SO_4^{2-} are higher than that in the seawater.

As an example the components of NaCl saturated brine which was taken from the ChangLu salt company are listed in Table 2.

Table 2 Components of NaCl Saturated Brine in Some Seasalts Enterprises (g/L)

Salt Field	Na^+/Mg^{2+}	SO_4^{2-}	Mg^{2+}	NaCl	$MgSO_4$	$MgCl_2$	KCl
One in HeiBei	4.52	28.03	18.74	215.3	35.12	45.60	11.70
One in TianJin	4.87	26.44	19.14	236.23	33.13	48.73	13.31
General saturated brine		<18	<13	250~260			

From table 2 we can see that the ratio of Na/Mg in the saturated NaCl brine from real production system is much lower than the one in the seawater. The minimum is 4.52 and the average is 4.7. Meanwhile quantities of Mg^{2+} and SO_4^{2-} are much lower than the one in the saturated seawater. It indicates that there are different levels mixed with salt-out brine into the brine making system.

The case of salt plant in TangShan is showed in order to elaborate the value of Na/Mg at different time and place, just as table 3 and table 4.

Table 3 Values of Na/Mg in the Brine Pool in Other Years

Pools	Offering waterway	Reservior	Evaporation 1	Evaporation 2	Evaporation 3	Regulated	Crystallization
Na^+/Mg^{2+}	8.10	8.10	7.81	6.26	5.25	4.52	3.02

Table 4 Mean Value of Na/Mg on the Saturated Brine Month

Month	1	2	3	4	5	6	7	8	9	1/	11	12
Na^+/Mg^{2+}	2.66	2.90	3.22	4.95	5.12	5.23	4.50	4.19	3.51	4.12	4.23	2.98

Table 3 shows the ratio is the highest in the way of water supplying and in the reservoir, and then it becomes lower in crystallization ponds. It suggested that the amount of salt out mother liquor was mixed less amount with the system brines at different stage of the production.

From the table 4 it can be seen that the value of Na/Mg is lower in saturated brine than in coastal water whenever the harvest season is. The maximum is 5.23 on June, the best is on January 2.66. It also showed mixing quantities are higher before June.

It disobeys the condensation law. The difference may be explained by following reasons: wrong technical index or incorrect operation or uncontrolled brine mixing.

Technical index could cause: taking the brine mixing in order to reduce Na/Mg , for example in HeiBei province CangZhou salt plant has the making brine as 'brine backmixing quick and well after rainfall. Set-up the returning system.

Positive mixing could cause: in the transportation some desalination brine which come out of crystallization ponds was added into brine making e process in order to enhance the density as soon as possible.

Negative mixing could cause: after rainfall the density of crystallization pond is higher than seawater, it should take the reasonable mixing based on the original density.

The results of the mixing were that some desalination brine goes back to original system which makes the ratio lower and brine quality decline.

2. THE DISADVANTAGE OF BACK-MIXING OF THE DESALINATION BRINE

There are two disadvantages of back-mixing. Firstly the capacity of salt field goes down and the yield of salt production decreases. Secondly, the quality of salt will be low because the impurity increase.

The degree of the effect depends on the back-mixing quantity of salt-out brine. The result is proportional to back-mixing.

2.1 The effect of salt yield

The brine contains lots of Mg_2SO4 and $MgCl_2$ after salt-out. Back-mixing makes Na/Mg decrease. In the same environment the mixing evaporation index decrease and resistance of brine in the system increase. This will affect the evaporation in the solar pond. Meanwhile, the concentration of NaCl in the brines decrease and saturated point changes. So the technical operation is out of order.

Consequently the technology of mixing salting-out brine with making brine system decline quality and quantity of the brine.

The quality of saturated brine has an effect on the NaCl crastallization as well as the salt yield. The more the brines was mixed, the lower the Na/Mg is.

Table 5 show the relationship between the saturated brine with different Na/Mg and salt yield

Table 5 Analysis of Brine Composition and Salt-out Quantity

Brine Composition			$1m^3$ Saturated Brine Condensed				
Denaturalization ratio	Na/Mg	Saturated point °Bé/ 30℃	Separated quantity of NaCl at 28°Bé t	Separated quantity of NaCl at 29°Bé t	Separated quantity of NaCl at 30°Bé t	Separated quantity of NaCl at 31°Bé t	Separated quantity of NaCl at 32°Bé t
2	1.481	29.3	0	0.008	0.043	0.074	0.100
	3.066	27.22	0.052	0.102	0.133	0.156	0.174
	5.194	26.35	0.136	0.173	0.200	0.217	0.229
	6.209	26.05	0.162	0.182	0.213	0.226	0.237
	8.457	25.56	0.250	0.222	0.237	0.245	0.250
3	1.465	28.4	0	0.04	0.082	0.105	0.120
	3.078	26.8	0.092	0.134	0.158	0.174	0.185
	4.693	26.04	0.015	0.181	0.200	0.210	0.218
	6.274	25.5	0.186	0.208	0.222	0.231	0.237
	8.257	25.15	0.221	0.237	0.242	0.254	0.257
4	1.59	27.9	0.007	0.071	0.104	0.123	0.130
	3.033	26.38	0.117	0.147	0.167	0.174	0.187
	4.645	25.70	0.172	0.196	0.212	0.220	0.20
	6.202	25.57	0.201	0.219	0.232	0.237	0.20
	8.421		0.225	0.241	0.250	0.255	0.20

Comparing the different ratios of Na/Mg among the same brine with density of 30°Bé it can be seen that the difference of the NaCl yield is about 15% . The lower of the ratio of Na/Mg is, the lower the salt yield is .

Taking the salt field saturated brine as the materials in the technology of refine salts manufacture process, the ratio of Na/Mg has a strong effect both on the refine salt productivity and production cost. The productivity and the cost of the production will be improved if the ratio of Na/Mg was taken as an index in the production..

Table 6 show the relationship between the saturated brine with different Na/Mg and salt yield under the same environment and salt field.

Table 6 Yield of NaCl per Millimiterare by Different amount of Saturated Brine

Na^{+}/Mg^{2+}	°Bé/ 20℃	Quantity of brine making 1t NaCl m^3	Yield of NaCl per Milli-miterare Kg	Comparison %									
8.36	25.88	4.19	13.83	100.00									
7.94	26.00	4.25	13.42	97.04	100.00								
5.41	26.50	4.82	13.00	94.00	96.87	100.00							
3.98	27.00	5.54	12.55	90.74	93.52	96.54	100.00						
3.06	27.50	6.47	12.09	87.42	90.09	93.00	96.33	100.00					
2.41	28.00	7.73	11.63	84.09	86.66	89.46	92.67	96.20	100.00				
1.97	28.50	9.30	11.19	80.91	83.38	86.08	89.16	92.56	96.22	100.00			
1.59	29.00	12.14	10.72	77.51	79.88	82.46	85.42	88.67	92.18	95.80	100.00		
1.31	29.50	16.66	10.27	74.26	76.53	79.00	81.83	84.95	88.31	91.78	95.80	100.00	
1.08	30.00	25.69	9.84	71.15	73.32	75.69	78.41	81.39	84.61	87.94	91.79	95.81	100.00
0.9	30.50	52.49	9.41	68.04	70.12	72.38	74.98	77.83	80.91	84.09	87.78	91.63	95.63

From the table 6 we can see the lower the ratio of Na/Mg is, the less the capacity of unit production is. When the ratio is 3.98 the capacity of the unit production has been reduced by 9.26%.

Combining the data of table 5 and table 6 we can conclude that there at least is 10% effect on the production capacity when the ratio of Na/Mg is lower than 5. This means that if there is no salt-out brine back-mixing and maintains the ratio of Na/Mg in saturated brine is as the same as seawater, the capacity of the production could be increased about 10 percent without enlarging the salt field area.

2.2 The effect on the purity of salt

Because the back-mixing of the salt-out brine the Na/Mg in the brine was decreased, It will increase the concentration of Mg^{2+} and SO_4^{2-} The high impurity will results in the more impurity in the product.

3 MEASURES IN IMPROVING THE NA/MG IN THE BRINE

3.1 Modifying the brine making operation regulations

It should be specified that back-mixing in the process will be avoided.

3.2 Negative mixing of salt-out brine and

solar evaporation separately of making brine

The area of the brine making, crystallization has to be separated.. Make sure no mixing in the making brine system.

4 CONCLUSIONS

The reason for the decline of Na/Mg in the brine and its disadvantages was analyzed. The salt production capacity and salt quality could be improved by using the technology of separation solar evaporation area and by avoiding the mixing between the brines in production system with that in the salt out brine.

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