

# THE NON-EQUILIBRIUM SALT FORMING PHASE DIAGRAM: APPLICATION TO EFFECTIVELY UTILIZE BRITTEN RESOURCE

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**Abstract:** The non-equilibrium state salt forming phase diagram, include primary region and extended Region, are different from solubility phase diagram and metastable phase diagram, which can be used to express the salt forming regions in the non-equilibrium state of evaporation and crystallization process in the high temperature for the multi-component salt-water systems. In this paper the residual brine resource of Tulantai salt-lake(China), Dongtai Salt-lake(China), Jilantai Salt-lake(China), Qarun Salt Lake(Egypt) and Seawater which after precipitation of pure sodium chloride, was analyzed. The benefit strategy needed by bittern utilization was given by compare 'Na<sub>2</sub>SO<sub>4</sub> based plan' with 'MgSO<sub>4</sub> based Plan'. The operations required by evaporation processes at 25°C, 75°C, 100°C and 150°C were simulated by a path through the solubility diagram and salt-forming diagram of Mg<sup>2+</sup>-Na<sup>+</sup>//SO<sub>4</sub><sup>2-</sup>-Cl<sup>-</sup>-H<sub>2</sub>O system. The yield and recovery rate of salt and sulfate were calculated. The results show, (1) more benefit of MgSO<sub>4</sub> based plan than that of Na<sub>2</sub>SO<sub>4</sub> based plan. (2) MgSO<sub>4</sub> based plan can be putted in practice, but in the middle temperature and vacuum evaporation process. (3) the yield of NaCl for the several bittern in the MgSO<sub>4</sub> based plan were 1.53, 2.01, 2.95, 19.48 and 6.8 times respectively than that of Na<sub>2</sub>SO<sub>4</sub> based plan in the normal temperature, the recovery rate of sulfate were increased by 18.46%, 27.51%, 38.23%, 55.13% and 79.99% respectively.

**Keyword:** Phase Diagram, Non-Equilibrium State, Britten, Salt Lake, Seawater, Salt

## 1 INTRODUCTION

A path through the salts solubility diagram allows the simulation of any operation required for the separation of a salt from bittern or other salt resource. Normally, the salt resource belongs to the sub-seawater type solution for the seawater, salt-lakes and salt-mines. The solubility phase diagram of Na<sup>+</sup>,K<sup>+</sup>,Mg<sup>2+</sup>//Cl<sup>-</sup>,SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O system at 25°C was determined by J.H.Vanth'off in the end of 19<sup>th</sup> century. But in spite of the great number of available data in literature, the sea-water system is still under-exploited, due to the complexity of the system, or to the lack of reliable data in some solubility fields, or to the complexity of the mate-stable phenomena.

The salt forming sequence in the evaporation process is largely different from the solubility diagram. H.C.K. Купляков (1938) got another phase diagram, named solar phase diagram or mate-stable phase diagram, for the system of Na<sup>+</sup>,K<sup>+</sup>,Mg<sup>2+</sup>//Cl<sup>-</sup>,SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O (partial) at 25°C by the method of isothermal natural evaporation. Using the same method, Jin Zuomei (1980,2001,2002)<sup>[3,4,5]</sup> got the mate-stable phase diagrams at 25°C,35°C and 15°C. R. Cohen-Adad<sup>[6]</sup> (2002) given an presentation to tentatively forecast or improve an extractive process for the Balck sea water, which based on the data of mate-stable phase diagram.

However, the multi-effect evaporation

process, which widely adopted in the salt plants, are run in the boiling temperature usually from 50 to 120°C, and the data lack for the salt-forming characters or the mate stable phase diagram at that high temperature and the strongly evaporation process. For this reason, we focus on the investigation of salt forming behaviour in the boiling evaporation process for the seawater type solution, in which the several progresses have been made. The Non-equilibrium behavior of Salt-Forming in Boiling Evaporation Process for the Systems of  $\text{Na}^+, \text{Mg}^{2+} // \text{SO}_4^{2-} - \text{H}_2\text{O}$  system at 100°C<sup>[7]</sup> and  $\text{K}^+, \text{Mg}^{2+} // \text{SO}_4^{2-} - \text{H}_2\text{O}$  system at 75°C<sup>[8]</sup> have be published, the systems of  $\text{Na}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$  system<sup>[9]</sup> and  $\text{K}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$  system will be published. The initial conception of non-equilibrium state salt forming phase diagram was formed and have be successfully applied to the Qarun project.

The main goal of this paper is to introduce the conception of non-equilibrium state salt-forming phase diagram, and to develop a procedure to effectively utilize the salt resource of Tulantai salt-lake (China), Dongtai Salt-lake (China), Jilantai Salt-lake (China), Qarun Salt Lake (Egypt) and Seawater.

## 2 The initial conception of non-equilibrium state salt forming phase diagram

The study of solid liquid phase relationship in the non equilibrium state of boiling evaporation process was carried out by the method of isothermal boiling evaporation and crystallization. The characteristic regions in the salt-water phase diagram stably occurs in the high temperature and strong evaporation process, which the Primary-Region, Extended-Region and conditional-Region, so called Non-equilibrium state salt forming phase diagram, are largely different from the solubility diagram, and can be applied to improve the process of extracting valuable material from salt resource.

### (1) Primary-Region

Primary-Region, the Primary-salt forming region, is the part of salt-water system phase diagram. Locating in that region, the brine could occurs same salt primary nucleation in the evaporation process. The difference between the primary region and the equilibrium region is show in Fig-1 for the  $\text{MgSO}_4 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$  system at 100°C. The  $\text{Na}_2\text{SO}_4$  Primary-region is 1.56 times large than that in solubility phase diagram, contrarily the Loewite Primary-region is 0.62 times little than that equilibrium region. In fig-2, the Primary-region of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  in  $\text{Mg}^{2+} - \text{Na}^+ // \text{SO}_4^{2-} - \text{Cl}^- - \text{H}_2\text{O}$  system are 1.94 and 1.92 times large than that in solubility phase diagram

### (2) Extended-Region

Extended-Region, the extended salt forming region, is the possible maximum salt forming region, which is larger than the Primary region due to the existing of crystal seeds, that reduce the salt forming potential barrier extended. The extended-region of  $\text{Na}_2\text{SO}_4$  and Vanthoffite in Fig-1, are 7.72 and 8.81 respectively bigger than the Primary region in  $\text{MgSO}_4 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$  system at 100°C. The Extended-Region of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  in the  $\text{Mg}^{2+} - \text{Na}^+ // \text{SO}_4^{2-} - \text{Cl}^- - \text{H}_2\text{O}$  system at 100°C are shown in Fig-2 ( pink diagonal lines).

### (3) Conditional-Region

Conditional-Region is the overlap region caused by the different salt Extended-Regions. Locating in the region, the kind of salt forming is based on the kind of crystal seeds and the operational condition. The wide of the Conditional-Region is 18.03% of total Phase region in the  $\text{MgSO}_4 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$  system at 100°C, and is 47.25% of total Phase region in the  $\text{Mg}^{2+} - \text{Na}^+ // \text{SO}_4^{2-} - \text{Cl}^- - \text{H}_2\text{O}$  system at 100°C. The existing of Conditional-Region makes it possible to control the kind of salt forming by control the crystal seeds and the operational condition.



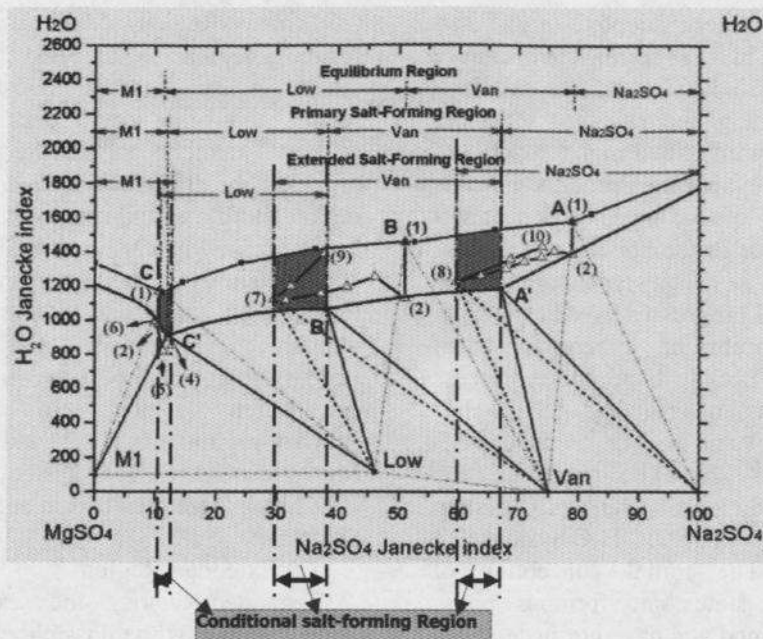


Fig-1 Salt-forming behavior and salt-forming regions in the non-equilibrium state of boiling evaporation process of  $\text{MgSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  system at 100 °C

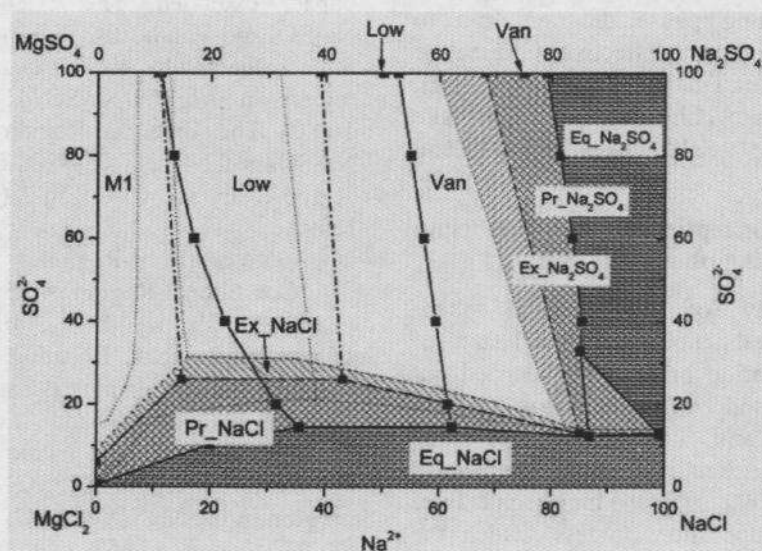


Fig-2 The Non-Equilibrium Phase Regions which include Equilibrium Region, Primary region, and Extended Region for  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  in the non-equilibrium state of boiling evaporation process of  $\text{Mg}^{2+}\text{-Na}^+/\text{SO}_4^{2-}\text{-Cl}^- \text{H}_2\text{O}$  system at 100 °C

### 3 Bittern resource

The bittern resources data of Tulantai salt-lake (A), Dongtai Salt-lake (B), Egypt Lake Qarum (C), Jiantai Salt-lake (D) sea salt residual brine (E) are shown in table 1 and table 2. The points of these bitterns in the  $\text{K}^+$  free diagram of  $\text{Mg}^{2+}\text{-Na}^+/\text{SO}_4^{2-}\text{-Cl}^- \text{H}_2\text{O}$  are

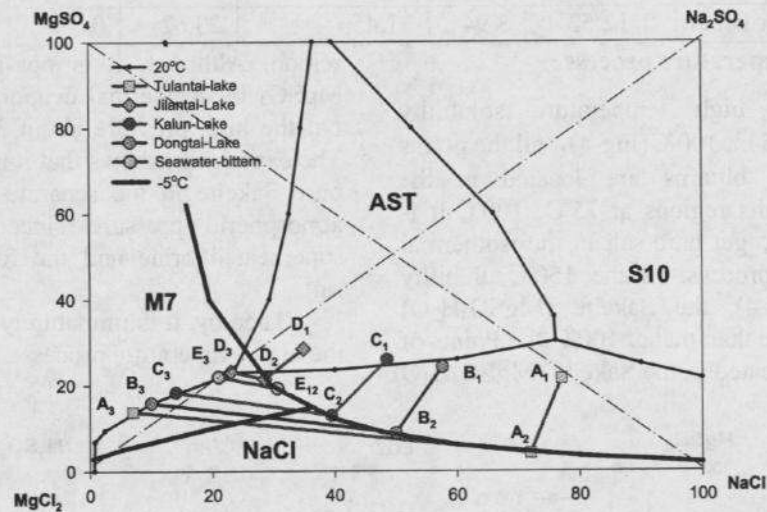
shown in the fig-3 for the natural temperature 20 °C (summer) and -5 °C (winter), and fig-4 for the high temperature 100 °C and 150 °C. In the fig-3, the resources points are located near the co-saturated curves of  $\text{NaCl}$  and other compounds at 20 °C since the bittern were formed by natural evaporation.

**Table 1. The composition of water free Britten in the form of Ionic Pair**

Water Free Britten (100g)	Content of Ionic Pair				
	K <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>
(A)Tulantai Lake	0.00	30.56	4.72	17.53	47.19
(B)Dongtai Lake	4.54	22.85	7.32	19.67	45.62
(C)Egypt Lake Qarun	2.98	19.76	9.93	21.67	45.67
(D)JilanTai Lake	0.00	14.86	14.33	24.59	46.22
(E)Seawater Bittern	3.98	12.72	14.24	15.88	53.19

**Table 2. The composition of water free Britten in the form of Compound**

Water Britten (100g)	Free	Content of Compound					
		(I) Based on MgSO <sub>4</sub> (g)			(II) Based on Na <sub>2</sub> SO <sub>4</sub> (g)		
		NaCl	MgCl <sub>2</sub>	MgSO <sub>4</sub>	NaCl	MgCl <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>
(A)Tulantai Lake		76.93	0.69	21.96	55.42	11.61	26.07
(B)Dongtai Lake		57.51	5.75	24.65	33.37	18.00	29.27
(C)Egypt Lake		49.74	10.93	27.15	23.16	24.43	32.23
(D)JilanTai Lake		37.41	19.94	30.81	7.24	35.26	36.57
(E)Seawater		32.01	25.15	19.90	12.53	35.04	23.62



**Fig-3 The Processes of Bittern Utilization which Based on the Solubility Phase Diagram of Mg<sup>2+</sup>-Na<sup>+</sup>//SO<sub>4</sub><sup>2-</sup>-Cl<sup>-</sup>-H<sub>2</sub>O at -5°C and 20°C. Tulantai(A), Dongtai(B), Qarun (C), Jilantai(D) and Seawater bittern (E)**

From Fig3, since the five points of the resource bitterns are located in the triangle of NaCl- MgSO<sub>4</sub>- MgCl<sub>2</sub>, or NaCl- Na<sub>2</sub>SO<sub>4</sub>-MgCl<sub>2</sub>. So the ionic composition of these bitterns could be compound to two type salts in the MgSO<sub>4</sub> based type of NaCl- MgSO<sub>4</sub>-MgCl<sub>2</sub> or in the Na<sub>2</sub>SO<sub>4</sub> based type of NaCl-Na<sub>2</sub>SO<sub>4</sub>-MgCl<sub>2</sub>. The Content of salts are very difference in the two type salts, such as the content of NaCl in the MgSO<sub>4</sub> based Type is 76.93, 57.51, 49.74, 37.41, 32.01 respectively, which is very bigger than that 55.42, 33.37, 23.16, 7.24, 12.53 in the

Na<sub>2</sub>SO<sub>4</sub> based type. It is more benefit to recover salt and valuable compound in the routine which is depended on the MgSO<sub>4</sub> based salts type.

#### 4 The strategies of bittern utilization

To find the effective method for the utilization of bittern resource, the three technical routines were considered, that are normal temperature process, high temperature process and middle temperature vacuum process.



#### 4.1 Normal temperature process

The operation process in the summer and winter are arranged in the Fig-3. Since the composition of the five points are located near the co-saturated curve of NaCl and other compounds at 20°C, so the yield or recover rate of NaCl are lower in the process of evaporating continually at the normal temperature. The benefit routine is cooling the bittern in the winter to recover Glauber's salt, and evaporate the residual brine to recover salt in the summer. The yield and

recover rate of NaCl and  $\text{Na}_2\text{SO}_4$  in this process are shown in table -3, which were calculated by the solubility data at 20°C and -5°C. However, this process couldn't be applied to the high temperature region, such as Egypt Lake. It is necessary to use mechanical refrigeration to recover Glauber's salt.

From table-3, the recover rate both NaCl and  $\text{Na}_2\text{SO}_4$  are very lower in this process (except the Tulantai Lake brine). The sulfate recovered are only in form of Glauber's salt.

**Table 3. The Yield and Rate of recovery of salt and sulfate in the natural temperature process**

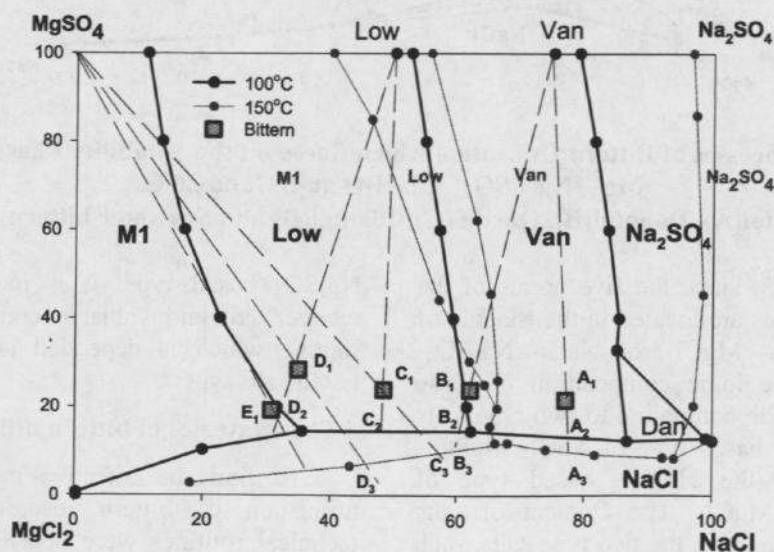
Water Free Bittern (100g)	NaCl			of	$\text{Na}_2\text{SO}_4$			of
	Content	Yield	Rate		Content	Yield	Rate	
	(g)	(g)	(%)		(g)	(g)	(%)	
(A)Tulantai Lake	55.42	50.03	90.28		26.07	21.05	80.74	
(B)Dongtai Lake	33.37	26.7	80.00		29.27	18.64	63.68	
(C)Egypt Lake	23.16	14.95	64.56		32.23	16.26	50.44	
(D)Jilantai Lake	7.24	1.4	19.30		36.57	9	24.61	
(E)Seawater Bittern	12.53	3.94	31.45		23.62	0	0.00	

#### 4.2 High temperature process

In the high temperature solubility diagram of 75°C, 100°C(Fig-4), all the points of the five bitterns are located in the compound salts regions at 75°C, 100°C. It is not possible to get pure salt in the isothermal evaporation process. In the 150°C solubility diagram (fig-4), the Sakeite ( $\text{MgSO}_4\cdot\text{H}_2\text{O}$ ) region is large than that at 100°C, the Points of BCDE are located in the Sakeite ( $\text{MgSO}_4\cdot\text{H}_2\text{O}$ )

region. Although it is possible to recover  $\text{MgSO}_4$  by isothermal evaporation at 150°C, but the high pressure about 3atm is needed. The experiment shows that it is difficult to get pure Sakeite in the separate process in the atmospheric pressure since the flash of superheated brine and the form of mixture salt.

Thereby, it is immature technology for the high temperature process.



**Fig-4 The Processes of Bittern Utilization which Based on the Solubility Phase Diagram of  $\text{Mg}^{2+}\text{-Na}^+/\text{SO}_4^{2-}\text{-Cl-H}_2\text{O}$  at 100°C and 150°C.**

Tulantai(A), Dongtai(B), Qarun (C), Jilantai(D) and Seawater bittern (E)

### 4.3 Middle temperature and vacuum process

In the solubility diagram of 75°C (Fig-5), all the biterms are located in the loeweite and vanthoffite region. so it is theoretically no possible to get pure salt in the isothermal evaporation process. However, it is the true fact that the existing of NaCl extended-region in the boiling evaporation process, and the extended-region at 75°C is bigger than that at 100°C. All the points of those biterms are located in the NaCl extended-region in the  $\text{Mg}^{2+}\text{-Na}^{+}\text{///SO}_4^{2-}\text{-Cl}^{-}\text{-H}_2\text{O}$  system (see Fig-5).

It is high-efficiency to recover salt for all the biterms by the method of vacuum evaporation and crystallization control, which based on the Non-equilibrium stable state phase diagram, although all the procedures are running in the compound salt region in the solubility diagram.

(1) Recycle part of the cooling mother liquid to form the mixture solution, and evaporate it to recover salt for the biterms of ABC, and cooling the salt residual liquid to recover epsom salt.

(2) Evaporate the biterm of DE to recover salt and cooling the salt residual liquid to recover epsom salt.

The yield and recover rate of NaCl and sulfate are calculated for these routines, which based on the data we got for the non-equilibrium stable state phase diagram, and all the results are shown in table-4. Compare the table 4 and the table 2,

(1) the NaCl yield in the middle temperature is 1.53、2.01、2.95、19.48 and 6.8 times respectively than that of  $\text{Na}_2\text{SO}_4$  based plan in the normal temperature. Based on 100g water free biterm, the NaCl yield was enhanced from 14.95g to 44.05g for Qarun biterm, and from 3.94g to 26.79g for the seawater biterm.

(2) the recovery rate of sulfate were increased by 18.46%、27.51%、38.23%、55.13% and 79.99% respectively than that of  $\text{Na}_2\text{SO}_4$  based plan in the normal temperature. The sulfate recovery rate was enhanced from 50.44% to 88.67% for the Qarun biterm, and form 63.68% to 91.19% for the Dongtai Salt lake biterm.

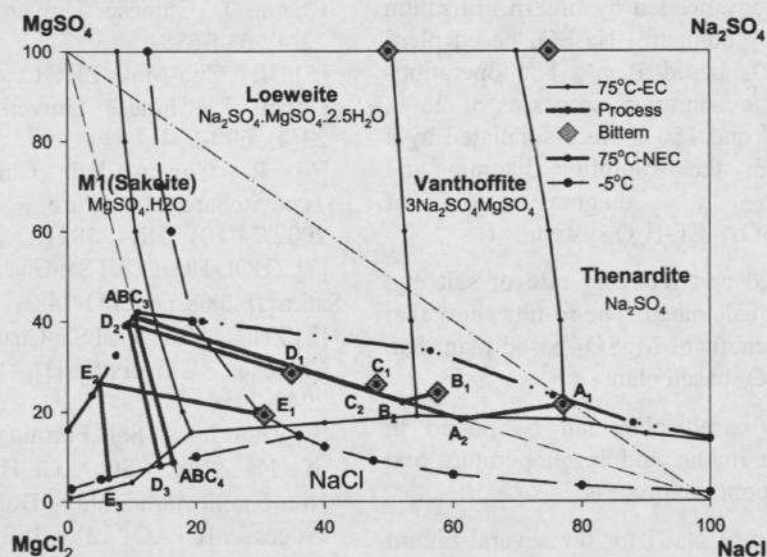


Fig-5 The Processes of Biterm Utilization which Based on the Non-equilibrium States Salt Forming Phase Diagram. Tulantai(A), Dongtai(B), Qarun (C), Jilantai(D) and Seawater Biterm (E)



**Table-4 The Yield and Rate of Recovery of Salt and Sulfate in the Non-equilibrium State Process**

Water Free Bittern (100g)	NaCl			MgSO <sub>4</sub>		
	Content	Yield	Rate of Recovery	Content	Yield	Rate of
	(g)	(g)	(%)	(g)	(g)	(%)
(A)Tulantai Lake	76.93	76.66	99.65	21.96	21.78	99.20
(B)Dongtai Lake	57.51	53.56	93.14	24.65	22.48	91.19
(C)Egypt Lake Qarun	49.74	44.05	88.57	27.15	24.07	88.67
(D)Jilantai Lake	37.41	27.22	72.76	30.81	24.57	79.74
(E)Seawater Bittern	32.01	26.79	83.68	19.90	15.92	79.99

## 5 conclusion

(1) The non-equilibrium state salt forming phase diagram, include primary region and extended Region, are different from solubility phase diagram and metastable phase diagram, which can be used to express the salt forming regions in the non-equilibrium state of evaporation and crystallization process in the high temperature for the multi-component salt-water systems.

(2) The residual brine resource of Tulantai salt-lake(China), Dongtai Salt-lake(China), Jilantai Salt-lake(China), Qarun Salt Lake (Egypt) and Seawater was analyzed. The benefit strategy needed by bittern utilization was given by compare 'Na<sub>2</sub>SO<sub>4</sub> based plan' with 'MgSO<sub>4</sub> based Plan'. The operations required by evaporation processes at 25°C, 75°C, 100°C and 150°C were simulated by a path through the solubility diagram and salt-forming diagram of Mg<sup>2+</sup>-Na<sup>+</sup>//SO<sub>4</sub><sup>2-</sup>-Cl<sup>-</sup>-H<sub>2</sub>O system.

(3) The yield and recovery rate of salt and sulfate were calculated. The results show that it is more benefit of MgSO<sub>4</sub> based plan than that of Na<sub>2</sub>SO<sub>4</sub> based plan.

(4) MgSO<sub>4</sub> based plan can be putted in practice, but in the middle temperature and vacuum evaporation process.

(5) The yield of NaCl for the several bittern in the MgSO<sub>4</sub> based plan were 1.53, 2.01, 2.95, 19.48 and 6.8 times respectively than that of Na<sub>2</sub>SO<sub>4</sub> based plan in the normal temperature, the recovery rate of sulfate were increased by 18.46%, 27.51%, 38.23%, 55.13% and 79.99% respectively.

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