# STUDY ON THE SALTS CRYSTALLIZATION BEHAVIOURS DURING BITTERN BOILING EVAPORATION AT 70℃

ZHOU Xiuyun [1] CHEN Xia [2]

1.Salt Research Institute, China National Salt Industry Corporation 300450
2. Tianjin University of Science and Technology 300457

**Abstract:** Normally the production process to deal with the bittern includes three steps: KCl production with 2-effect vacuum evaporation of the mixture of bittern and mother liquor after KCl production; $Br_2$ extraction through distillation process, and $MgCl_2 \cdot 6H_2O$ production by mono-effect evaporation. For the production of KCl, Most of the salt industry plants will mix the bittern and mother liquor after its production in the first evaporator, and separate the NaCl and $MgSO_4$ solids from the mother liquor in the second evaporator. In the second evaporator, the operation temperature is 65～70℃, but the concentration is controlled by operation experience only, that may lead to the NaCl and $MgSO_4$ solids can not be separated from the liquor completely, then the output is low, meanwhile big quantity of mother liquor is mixed in the solid, so the throughout of KCl product wiill be low also, and the further separation of the NaCl and $MgSO_4$ solids will be not easy. Based on the analysis of $Na^+$、$K^+$、$Mg^{2+}//SO_4^{2-}$、$Cl^-$—$H_2O$ phase diagram and the experimentation of the bittern evaporation in the laboratory, this paper studies the salt crystallization behaviours of the bittern evaporation under 70℃, which will supply reliable data for operation of the second evaporator in the production of KCl product.

**Keywords:** bittern, phase Diagram, boiling evaporation, crystallization behaviour of salts

## 1. INTRODUCTION

Bittern, the mother liquor discharged from solar salt field after sea water ( underground brine) concentration in evaporation ponds and NaCl crystallization in the crystallization ponds, it is rich of $Mg^{2+}$、$K^+$、$Na^+$、$Cl^-$、$SO_4^{2-}$、$Br^-$. At present, the total output of solar salt is more than 22,000,000tons, and 1 ton raw salt will discharge $0.8m^3$ bittern with concentration of 30 $^0Be'$, so the total quantity of by-produced bittern is about $18,000,000m^3$ But only 10% of it is recovered, most of the bittern is discharged directly, that wastes available resource and leads to serious environment contamination [1].

From 1960's, China started to study the process of the comprehensive utilization of the bittern, and found bittern chemical industry with products of KCl, $Br_2$ and $MgCl_2$. Firstly, KCl is produced with vacuum evaporation of the mixture of bittern and mother liquor after KCl production; then $Br_2$ is extracted through distillation process from the mother liquor after KCl production, finally $MgCl_2 \cdot 6H_2O$ is recovered by mono-effect evaporation of the mother liquor discharged from $Br_2$ workshop.

Up to the present, the above production process of the comprehensive utilization of the bittern is used continuously, which recovered the bittern resource, guarantee the sustainable development of solar salt industry and prevent marine environment from pollution.

With the above production process, the production capacity of KCl reached

50,000ton/year, it used as the main KCl resource of other industries in China from1970's to 1980's . The detailed production process is as follows:

First step: the bittern is mixed with the mother liquor after KCl production in a mixing tank, and NaCl solid (low temperature salt) is separated from the liquor.

Second step: The liquor concentrated by vacuum evaporation, and the NaCl and $MgSO_4 \cdot H_2O$ solids will crystallize with the withdrawal of the water.

Third step: the gained slurry is transported to heat-insulated settler to separate the solid from the liquor. The separated solid is called high temperature salt.

Fourth step: The resulted liquor is discharged to cooling crystallizer, in which carnallite crystallize with the flashing of water.

Fifth step: Carnallite is discomposed by hydrolysis and raw KCl is gained,

Last step: The raw KCl is purified by washing and final KCl is produced.

In second step, two evaporators are employed. The crystallized NaCl and $MgSO_4 \cdot H_2O$ solid in the second evaporator will enter the first evaporator together with the liquor, in which solid crystallize continuously with the further concentration of the liquor, then the mixture of the solid and concentrated liquor enter the heat-insulated settler.

Inside the settler, the solid is separated from the liquor at high temperature and discharge to other steps to recover NaCl and $MgSO_4 \cdot H_2O$, so big quantity of heat energy is wasted. And because of the high solid content inside the first evaporator and the settler, and running loads of them are high, also the heating tubes are easy to be scaled, blocked and abrased, that reduce the continuous running time of the production line and shorten the life time of evaporators.

Otherwise, base on the above production process, the particle size of low temperature salt is small and the impurities content is high, it can not share good market.

In order to overcome the above mentioned problems, most of the bittern chemical plants renovate the old process. They mix the bittern and the mother liquor in the first evaporator, and discharge the result mixture of solid and concentrated liquor from second evaporator to the settler. The advantages of the new process are:

(1) the quantity of the high temperature salt is lower the that in the old process, the discharged quantity of the concentrated liquor mixed in the solid will below, it will improve the yield of KCl product.

(2) the chemical composition of the high temperature salt differences from that of the old process, the value of $MgSO_4$ / NaCl is improved, from 1(in old process) to 2 (in new one), which is useful for the recovery of $MgSO_4 \cdot H_2O$ product[2].

For the renovated process, the main point is to find the suitable concentration in the second evaporator in order to guarantee NaCl solid crystallize as more as possible, ant other salts don't crystallize. At present, the bittern chemical plants control the concentration in the second evaporator by their operation experience only, so some problems still exist during the running of the production line, some times NaCl can not crystallize adequately, some times the total quantity of high temperature salt is high and the content of NaCl in it is also high.

In order to get the reasonable concentration data, firstly we analyze the phase diagram of $Na^+$、$K^+$、$Mg^{2+}$//$SO_4^{2-}$、$Cl^-$—$H_2O$ at 75℃ as the theoretical basis, then make the experimentation of the bittern evaporation in the laboratory under 70℃. Base on the analysis of phase diagram and the experimentation data, this paper studies the salt crystallization Behaviours of the bittern evaporation, which will supply reliable data for practical operation of bittern chemical plants.

## 2. Analysis of phase diagram

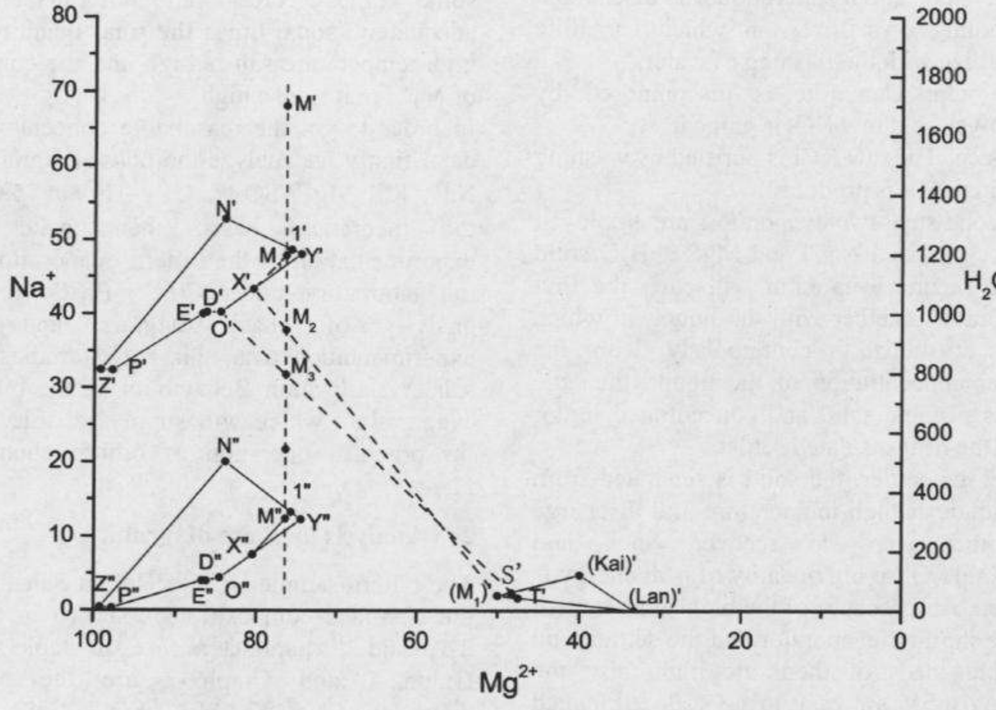
The bittern sample is from Hangu Salt Plant, the chemical composition is shown in table 2-1, and J′ parameters are in table 2-2. Graph2-1 and Graph2-2 are the phase diagrams of $Na^+$, $K^+$, $Mg^{2+}$//$SO_4^{2-}$, $Cl^-$—$H_2O$ at 75℃, Graph2-1 shows the contents of $Na^+$ and $H_2O$, Graph2-2 shows the contents of $K^+$, $Mg^{2+}$, $SO_4^{2-}$, in which the M point, M' point and M'' point indicate the chemical content of the bittern sample. The M point, M' point and M'' point are called system point.

**Table 2-1 chemical composition of bittern（g/L）**

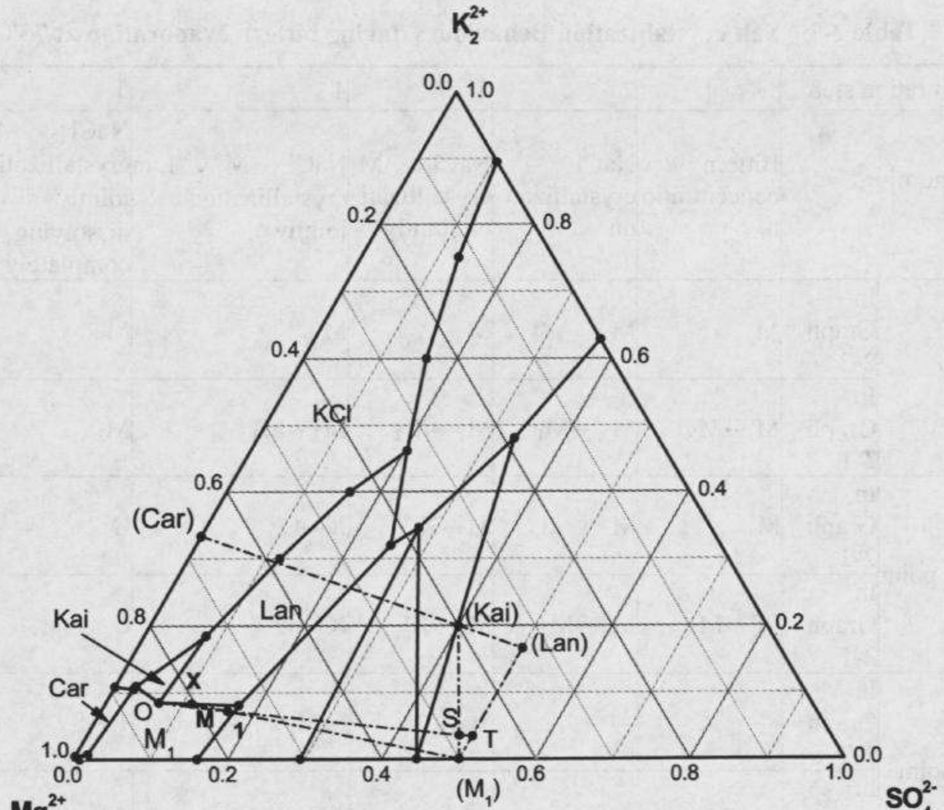
| Material | ${}^{0}$Be′/℃ | $Mg^{2+}$ | $Cl_2^{2-}$ | $K_2^{2+}$ | $SO_4^{2-}$ | $Na_2^{2+}$ | $H_2O$ |
|---|---|---|---|---|---|---|---|
| Bittern | 28.5/15 | 54.25 | 192.69 | 16.67 | 46.43 | 34.74 | 901.32 |

**Table 2-2 J′ parameters of bittern**

| Material | ${}^{0}$Be′/℃ | $Mg^{2+}$ | $Cl_2^{2-}$ | $K_2^{2+}$ | $SO_4^{2-}$ | $Na_2^{2+}$ | $H_2O$ |
|---|---|---|---|---|---|---|---|
| Bittern | 28.5/15 | 76.22 | 92.79 | 7.28 | 16.50 | 25.80 | 1708.4 |




**Graph 2-1 Na$^{+}$ Phase diagram of $Na^{+}$、$K^{+}$、$Mg^{2+}$//$SO_4^{2-}$、$Cl^{-}$— $H_2O$ system at 75℃**




**Graph 2-2 $H_2O$ and NaCl free Phase diagram of $Na^+$、$K^+$、$Mg^{2+}$//$SO_4^{2-}$、$Cl^-$— $H_2O$ system at 75℃**

See the M' point and M" point in Graph 2-1, at the beginning, the bittern sample is not saturated for NaCl. When the bittern is evaporated for concentration, M' point moves to $M_1$ point and NaCl crystallize from the liquor. According to Graph2-2, the M point is situated in M1（$MgSO_4 \cdot H_2O$）section of the diagram, so if the liquor is evaporated continually, NaCl and M1（$MgSO_4 \cdot H_2O$）will crystallize jointly, the detailed process of bittern concentration and salts crystallization Behaviours are shown in table 2-3. by calculation, we can see when the bittern sample concentrates to M1（$MgSO_4 \cdot H_2O$）saturation point, 1liter liquor crystallize 46.3g NaCl; Evaporate $H_2O$ 272.88g; and the yield of NaCl is 52.26%。

Table 2-3 **Salt crystallization Behaviours during bittern evaporation at 75℃**

| Concentration step | | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Concentration process | | Bittern concentration | NaCl crystallization | NaCl& $M_1$ crystallization jointly | NaCl、$M_1$、Lan crystallization jointly | NaCl、M1、Kai crystallization jointly，Lan dissolving completely |
| System point | In Graph 2-2 | M | M | M | M | M |
| | In Graph 2-1 | $M' \rightarrow M_X$ | $M_X \rightarrow M_1$ | $M_1 \rightarrow M_2$ | $M_2 \rightarrow M_3$ | $M_3$ |
| Liquor point | In Graph 2-2 | M | M | M→X | X→O | O |
| | In Graph 2-1 | $M' \rightarrow M_X$ | $M_0 \rightarrow M_1$ | $M_1 \rightarrow X'$ | X'→O' | O' |
| Solid point | In Graph 2-2 | — | — | ($M_1$) | ($M_1$) →T | T→S |
| | In Graph 2-1 | — | — | ($M_1$) | ($M_1$) →T' | T'→S' |
| Solid crystallization | | — | NaCl | NaCl+$M_1$ | NaCl+$M_1$+Lan | NaCl、M1、Kai crystallization jointly，Lan dissolving completely |

**Note:** $M_X$ point in Graph2-1 can not be defined by phase diagram, that can be confirmed by experiment data.

### 3. The experimentation of the bittern evaporation

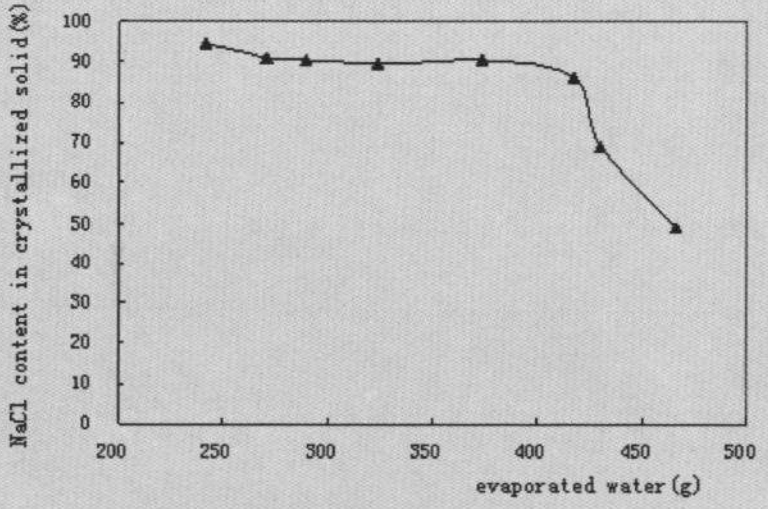
The bittern sample mentioned in item 2 is used in the evaporation experiment. According to the practical situation of KCl production, in the second evaporator, NaCl should crystallize as more as possible, and other salts don't go out, so this experiment is mainly for the study of NaCl crystallization during bittern evaporation at 70℃. Based on 1liter bittern sample，we get the experiment data that show in the below Table 3-1, Table 3-2, Graph 3-1, Graph3-2 and Graph3-3.

**Table 3-1 the chemical contents of liquor during evaporation of bittern at 70℃**

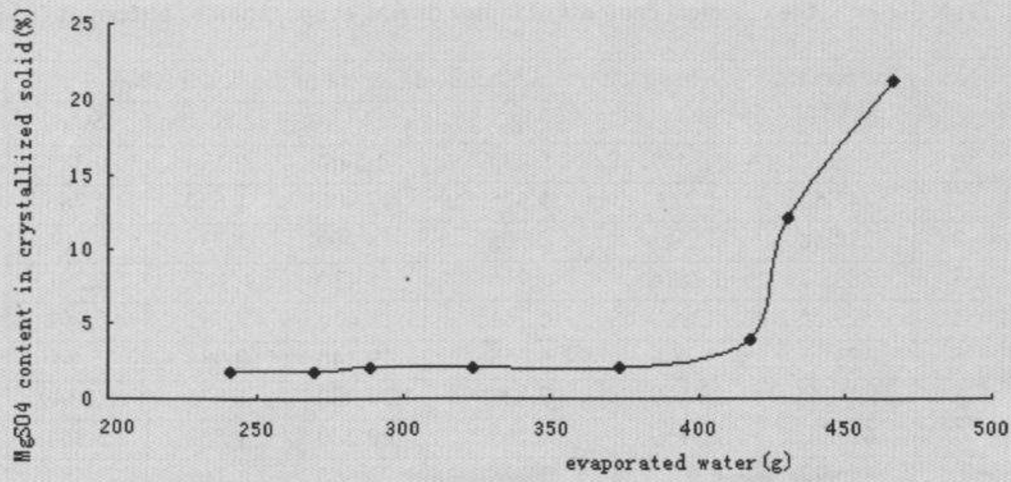
| No. | Evaporated $H_2O$(g) | Density | Chemical content of the liquor (%) | | | |
|---|---|---|---|---|---|---|
| | | | $Mg^{2+}$ | $Cl^-$ | $K^+$ | $SO_4^{2-}$ |
| 0 | 0 | 1.2461 | 0.435 | 1.546 | 0.134 | 0.373 |
| 1 | 241.57 | 1.283 | 5.575 | 17.900 | 1.634 | 4.766 |
| 2 | 270.18 | 1.285 | 5.785 | 18.060 | 1.734 | 4.901 |
| 3 | 288.97 | 1.2876 | 5.916 | 18.430 | 1.8475 | 5.291 |
| 4 | 323.25 | 1.2998 | 6.381 | 18.670 | 1.985 | 5.462 |
| 5 | 373.16 | 1.314 | 6.758 | 19.140 | 2.088 | 5.84 |
| 6 | 419.565 | 1.3169 | 7.127 | 20.060 | 1.875 | 5.2349 |
| 7 | 429.76 | 1.3159 | 7.168 | 20.280 | 1.562 | 5.364 |
| 8 | 465.77 | 1.3072 | 7.728 | 21.660 | 1.161 | 3.385 |

**Table 3-2 the chemical contents of the solid crystallized during bittern evaporation**

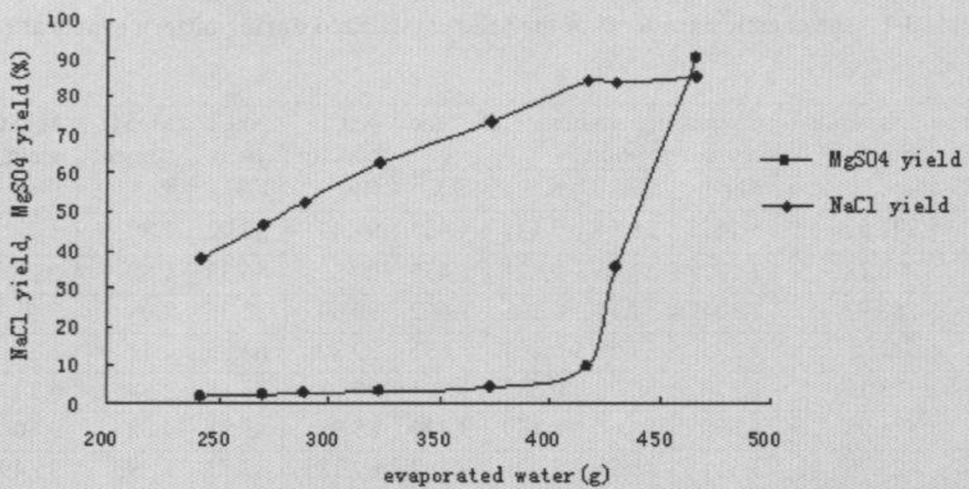
| item | Evaporated water (g) | Chemical content of the crystallize solid/% | | | | NaCl content (%) | NaCl yield (%) | $MgSO_4$ content % | $MgSO_4$ yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | $Mg^{2+}$ | $Cl^-$ | $K^+$ | $SO_4^{2-}$ | | | | |
| 1 | 241.57 | 0.7478 | 58.44 | 0.141 | 1.437 | 94.49 | 38.02 | 1.80 | 1.77 |
| 2 | 270.18 | 1.171 | 57.45 | 0.221 | 1.435 | 90.82 | 46.39 | 1.80 | 2.25 |
| 3 | 288.97 | 1.1042 | 57.14 | 0.208 | 1.662 | 90.60 | 52.36 | 2.08 | 2.95 |
| 4 | 323.25 | 1.295 | 57.51 | 0.467 | 1.681 | 89.80 | 62.85 | 2.11 | 3.39 |
| 5 | 373.16 | 1.230 | 56.7 | 0.585 | 1.708 | 90.41 | 73.17 | 2.14 | 4.24 |
| 6 | 416.98 | 1.660 | 55.66 | 1.139 | 3.210 | 85.98 | 83.81 | 4.02 | 9.60 |
| 7 | 429.76 | 3.541 | 48.31 | 3.391 | 9.562 | 69.18 | 83.73 | 11.98 | 35.49 |
| 8 | 465.77 | 5.400 | 39.92 | 7.596 | 16.85 | 49.00 | 85.10 | 21.11 | 89.74 |




Graph 3-1 Crytallized NaCl-evaporated water diagram




Graph 3-2 crystallized MgSO4-evaporated water diagram




Graph 3-3 NaCl yield, MgSO4 yield-evaporated water diagram

According to the above experiment data, the more the quantity of evaporated $H_2O$ is, the more the quantity of crystallized NaCl will be. When the evaporated $H_2O$ is more than 400g, the content of $MgSO_4$ in the solid will increase quickly, that means $MgSO_4$ starts to crystallize. By the crystal form, the solid should be $MgSO_4 \cdot H_2O$.

## 4. Discussion

From the above experiment result, for 1liter bittern, when the evaporated $H_2O$ is 400g, only NaCl solid crystallize, the density of the liquor is about 34°Be′, the content of NaCl in the crystallized solid is 90%, and NaCl yield reach 80%.

Compared the experiment data with the result of the analysis of phase diagram, the evaporated $H_2O$, the crystallized NaCl and the yield of NaCl from the experiment are much more than these from the analysis of phase diagram. The main reason is that the analysis of phase diagram is base on equilibrium state, but during the boiling evaporation process, because of the high evaporation rate, the system point leave the equilibrium state, so the crystallization Behaviours of salts is different from it in phase diagram.

The chemical composition of the bittern is complex, and there are many factors such as temperature, evaporation rate and agitation rate that will affect the crystallization Behaviours of salt, and until now we don't find the report for the crystallization Behaviours of salts during bittern boiling evaporation. So we suggest the experiment result in this paper be used as the operation data of KCl production in bittern chemical industry.

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