The ancient, latter-day and coming technology of feed grade salt recovering in Yuncheng salt lake: an introduction of Salt-forming diagram application

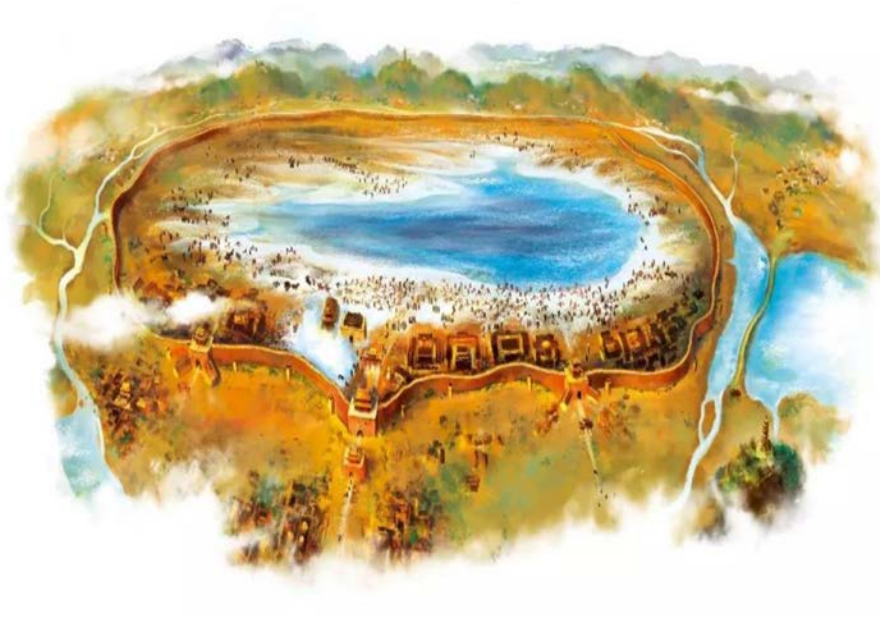
Huan Zhou （周桓）

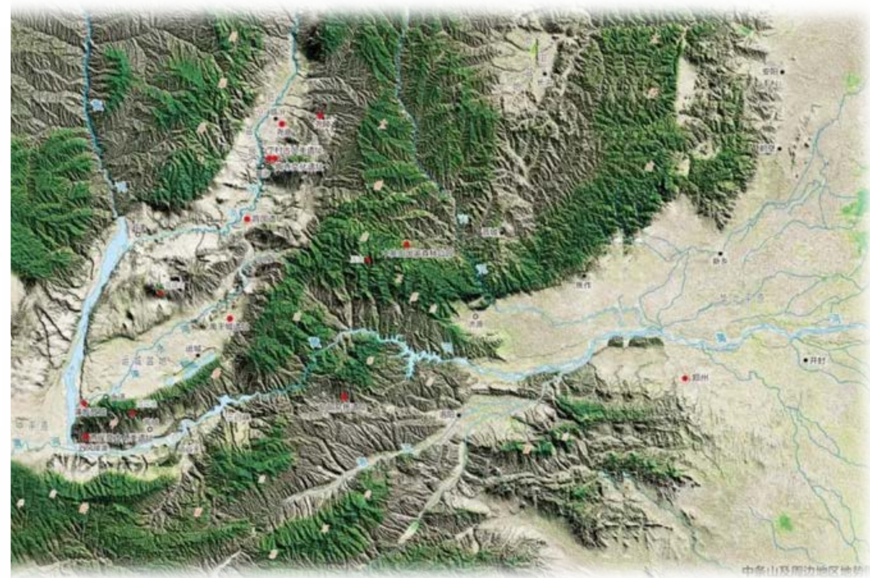
Tianjin University of Science and Technology (TUST)
No.29, the 13th Street, TEDA, Tianjin, P.R.China
Email: zhouhuan@tust.edu.cn
Mobile:13702119692

1.0 Yuncheng salt lake *vs* Chinese civilization

Yuncheng salt lake is located in the center of China

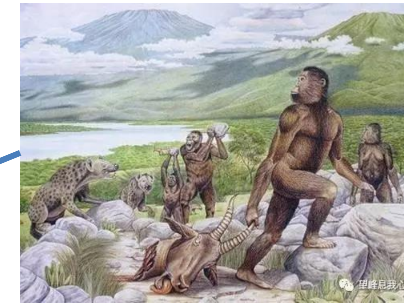
Yuncheng salt lake





- Sodium sulphate type salt lake
- 30 kilometers long from east to west, 4 kilometers north to south.
- The development of salt lake has a history of more than 4,000 years.
- It is a common goal for all the tribes in the ancient China.

1.0 Chinese civilization *vs* Yuncheng salt lake

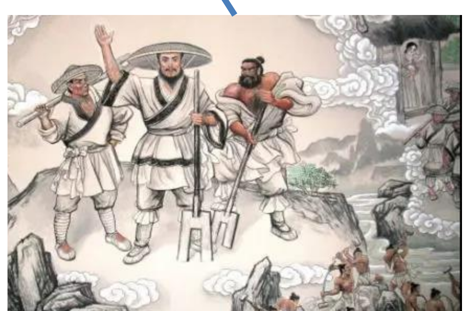


45 million years ago
(earlist ancientsn)

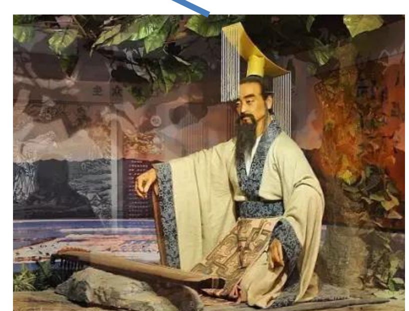
黄帝 2717 BC

尧 **2377BC**

夏朝 **Xia** dynasty (2070 BC)



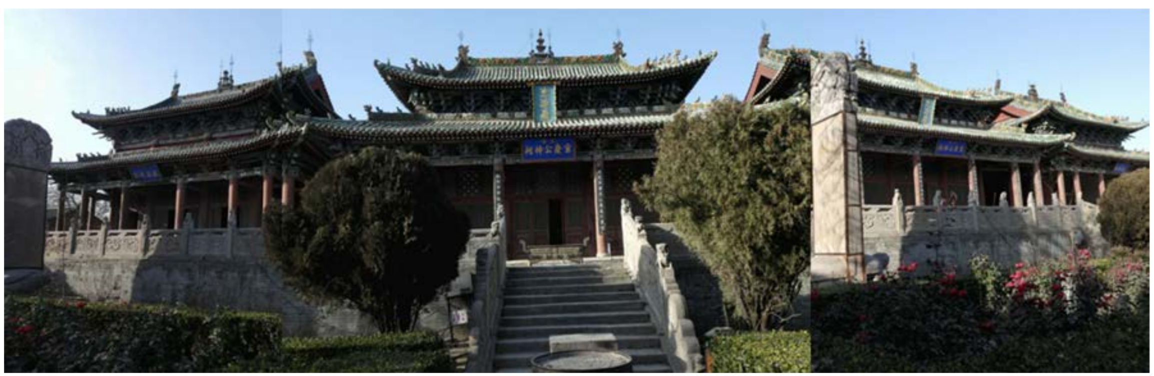
禹



舜 **2277 BC**

1.0 Yuncheng salt lake *vs* Chinese civilization

- With the monopoly of salt industry for more than 2000 years, Yuncheng salt has been the main source of state financial funds in successive dynasties.



Yuncheng temple of salt

Panoramic view

2.0 The technique of ancient salt-making

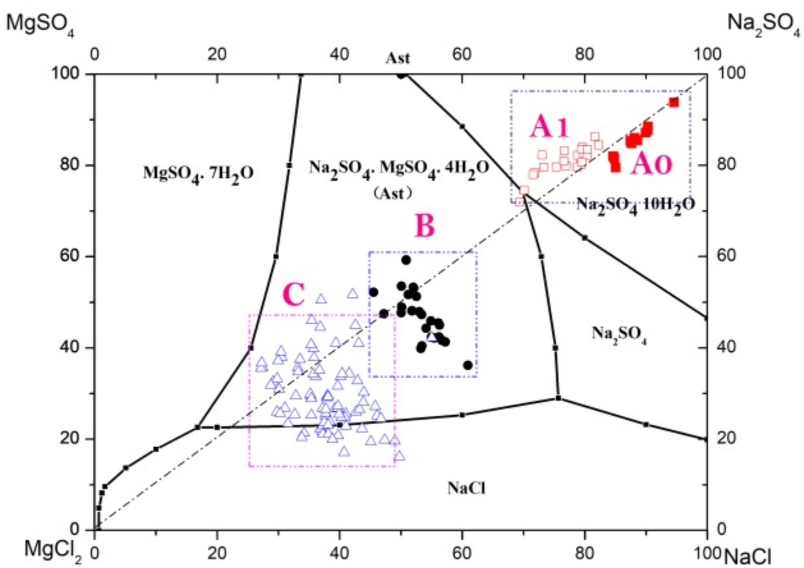


Figure 1. Brine composition in Yuncheng salt-lake (phase diagram at 25 ° C).

'■'Mine brine at present; '□'Earliest record of salt-lake brine; 'Δ' Waste bittern of current production '●' Feed brine of mirabilite production.

- How can food-salt be produced under the natural conditions of Yuncheng salt-lake, which is rich in Na_2SO_4 but not NaCl?

- Why the salt recovery processes in ancient times were sustainable with no obvious environmental impact?

2.0 The technique of ancient salt-making

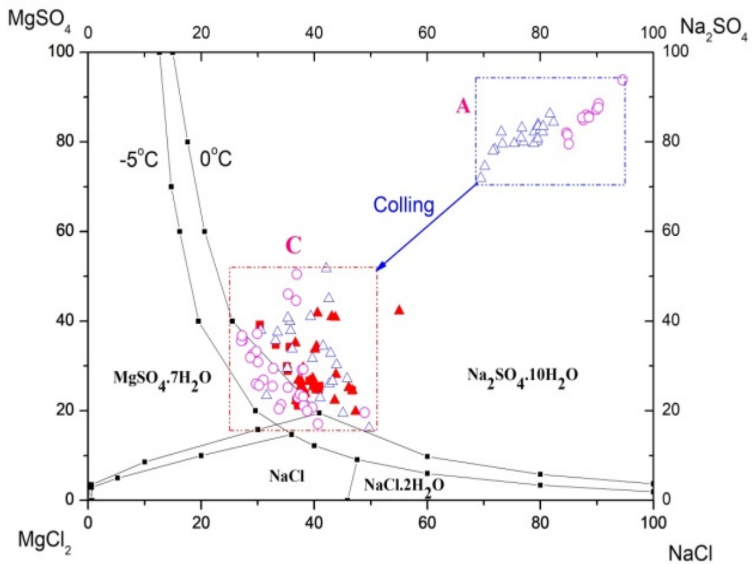


Figure 2. Na_2SO_4 recovery process (phase diagrams at 0 ° C and −5 ° C). '■'Mine brine at present; '□'Earliest record of salt-lake brine; 'Δ' Waste bittern of current production

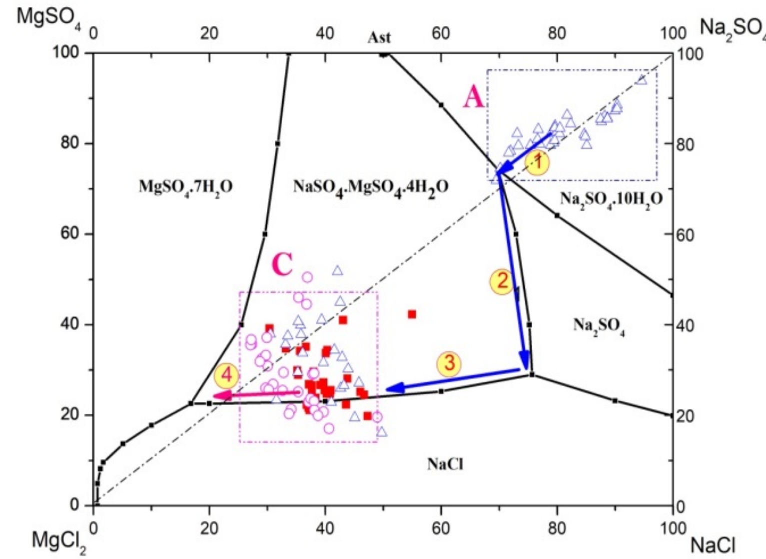


Figure 3. Process analysis of evaporation based on solubility diagram at 25 ° C

- However, the conclusion of 'impossible to produce pure salt (NaCl)' can obtained via phase diagram analysis at temperature range from -5 to 35 ° C (Figs. 2 and 3).

2.0 The technique of ancient salt-making

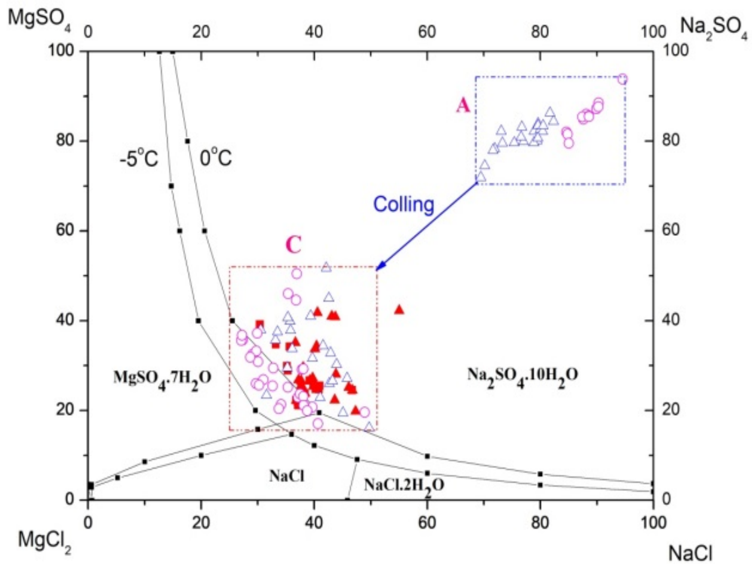


Figure 2. Na_2SO_4 recovery process (phase diagrams at 0 ° C and −5 ° C). '■'Mine brine at present; '□'Earliest record of salt-lake brine; 'Δ' Waste bittern of current production

Mirabilite ($Na_2SO_4 \cdot 10H_2O$)

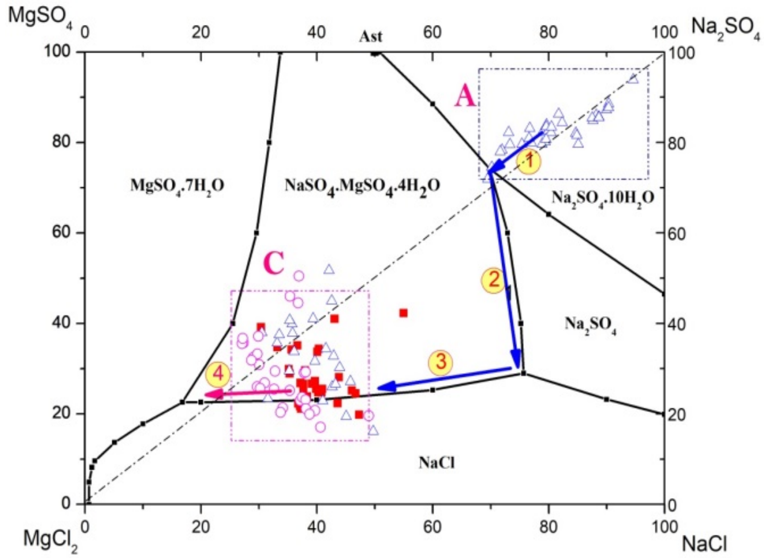


Figure 3. Process analysis of evaporation based on solubility diagram at 25 ° C

(1) Mirabilite ($Na_2SO_4 \cdot 10H_2O$)
(2) Astrachanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$)+Thenardite ($Na_2SO_4$)
(3) Astrachanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$)**+ NaCl**

- The conclusion of 'impossible to produce pure salt (NaCl)' can obtained via phase diagram analysis at temperature range from -5 to 35 ° C (Figs. 2 - 3).

2.0 The technique of ancient salt-making

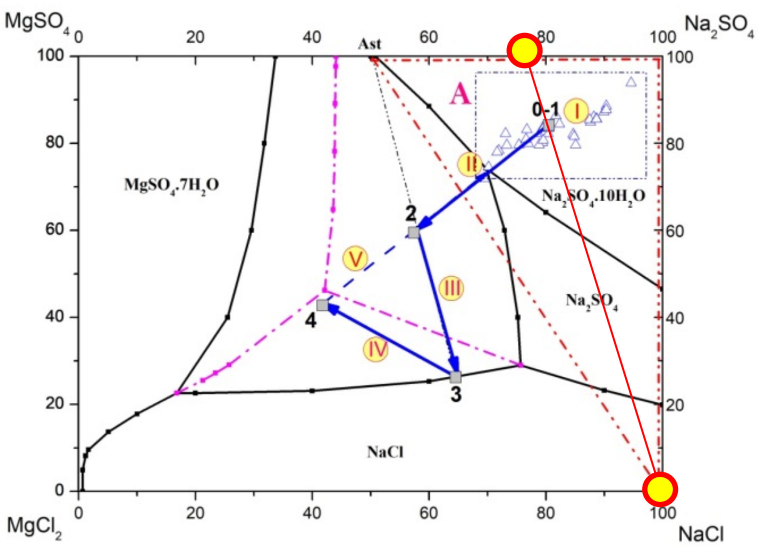


Figure 4. Actual process of ancient salt

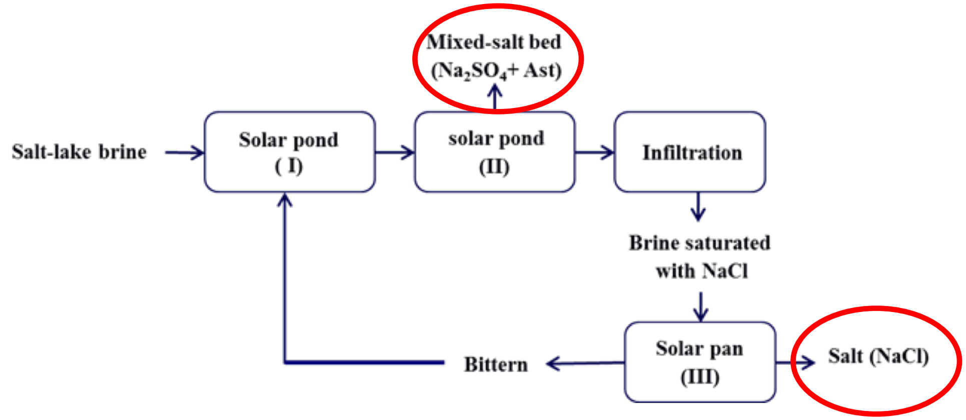


Figure 5. Ancient salt-productio processes in Yuncheng salt-lake.

One primitive sustainable process

- Solar pond (I) : raw brine is concentrated until sulfate is saturated.
- Solar pond (II) : the sulfate salt precipitates and forms the so-called 'sulfate bed.'
- Natural filtration: the mother liquor of the sulfate salt is filtered through the sulfate bed and gathers in the outside trench. ——contains a high concentration of NaCl.
- Solar pond (III) : food-salt crystallizes out from the filtered brine.
- The mother liquor of the filtered food-salt is discharged into solar pond (I).

3. Sodium sulphate production in latter-day

- This salt-making process persisted for thousands of years until the 1960s, when the mass extraction of Na_2SO_4 was replaced.

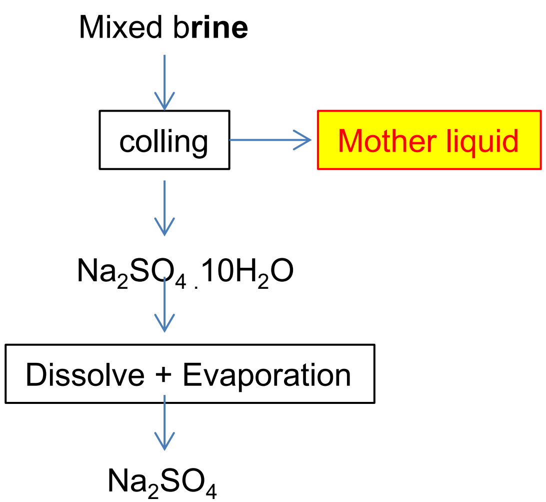


Figure 6a. Na_2SO_4 production

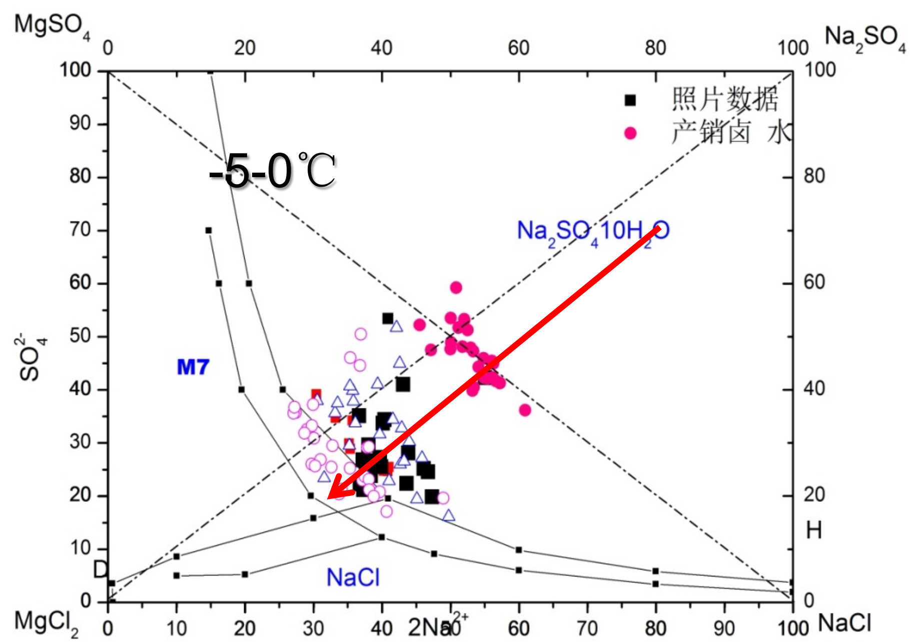
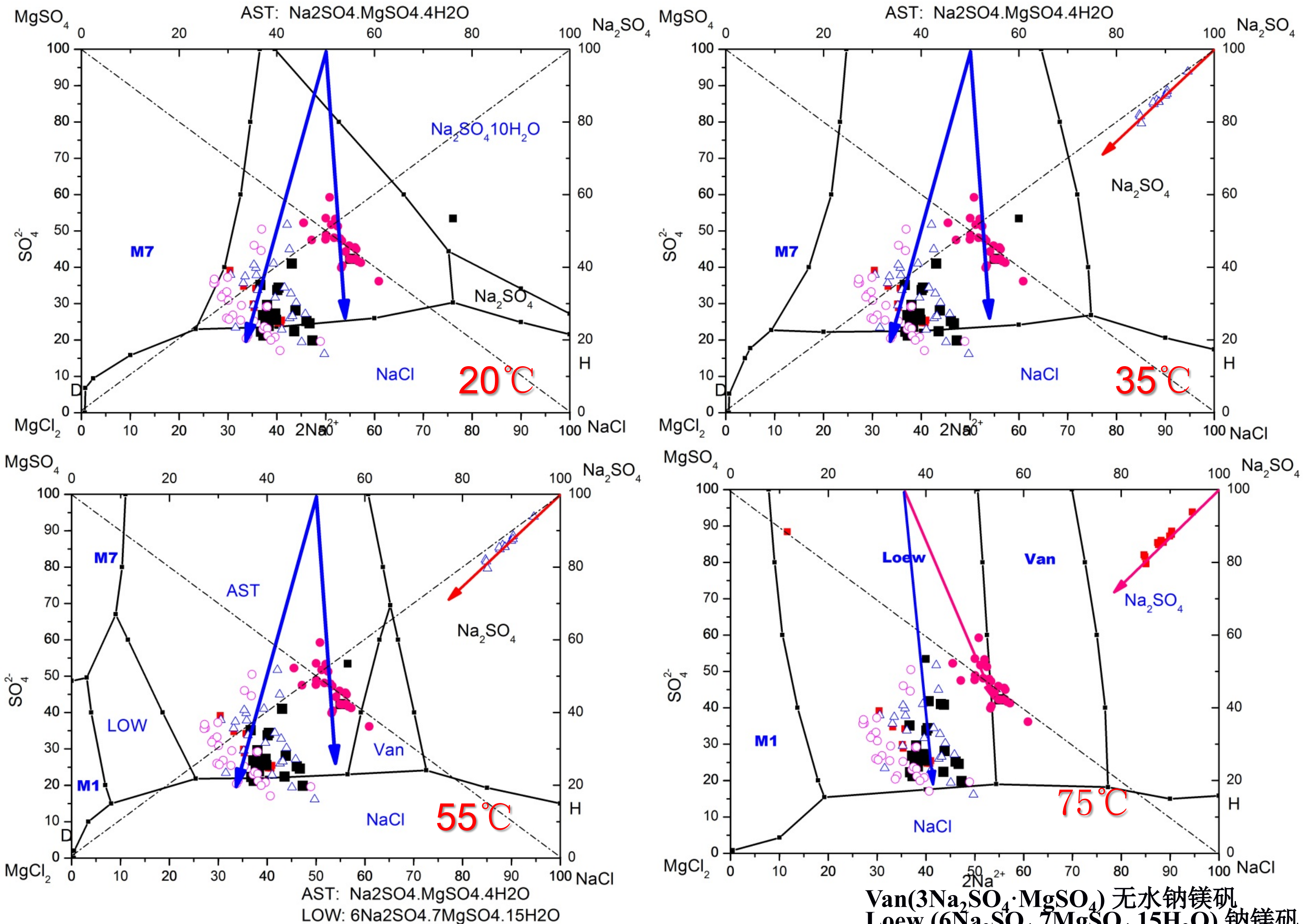


Figure 6b. $Na_2SO_4 \cdot 10H_2O$ production in winter (phase diagram at -5-0℃)

Problem: $MgCl_2$ riched brine

4.0 New comprehensive utilization system

- 4.1 Process planning on solubility phase diagram



Van($3Na_2SO_4 \cdot MgSO_4$) 无水钠镁矾

Loew ($6Na_2SO_4.7MgSO_4.15H_2O$) 钠镁矾

4.0 New comprehensive utilization system

- 4.1 Process planning on solubility phase diagram

150℃： 0.36-0.48 mPa

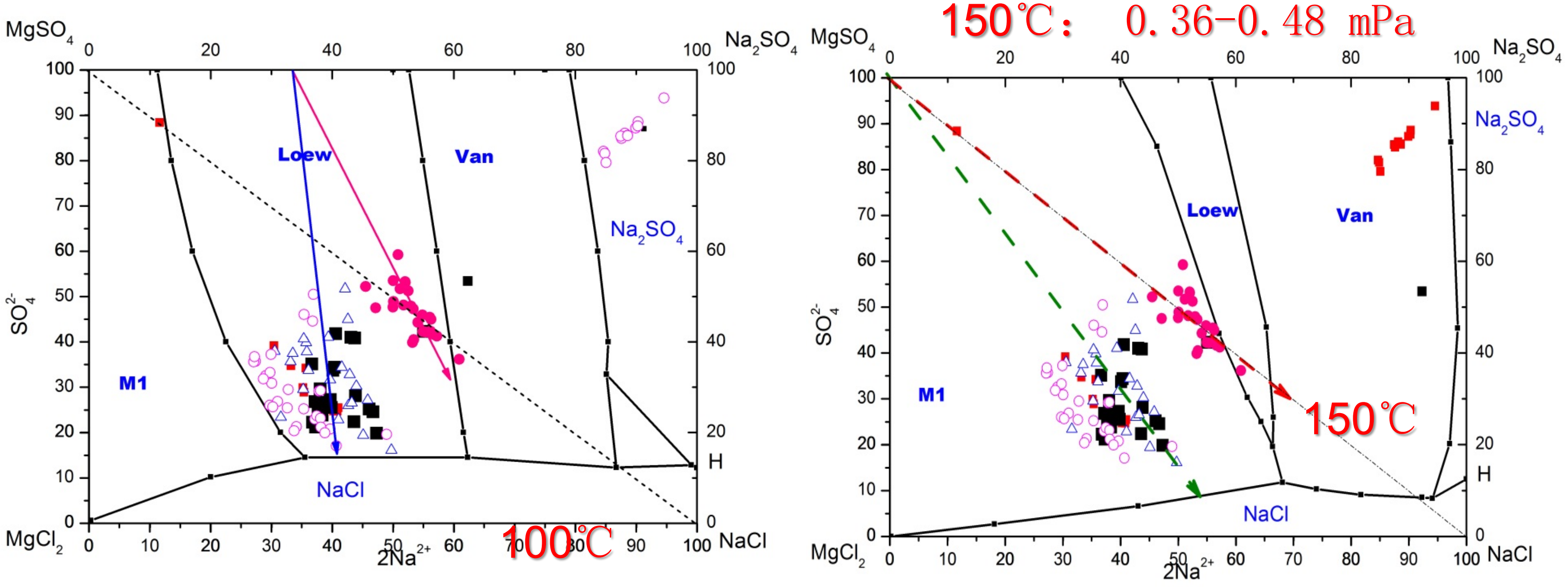


Figure 6 Process planning on multiple temperature phase diagram
Ast: $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ (Astrachanite); Loe: $6Na_2SO_4 \cdot 7MgSO_4 \cdot 15H_2O$ (Loeweite);
Van: $3Na_2SO_4 \cdot MgSO_4$ (Vanthoffite); M1: $MgSO_4 \cdot H_2O$ (Kieserite)

The single salt or hydrate of $Na_2SO_4 \cdot 10H_2O$, $MgSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot H_2O$ can be produced at low temperature of < 0 ℃ or at high temperature about 150 ℃

4.0 New comprehensive utilization system

- 4.1 Process planning on solubility phase diagram

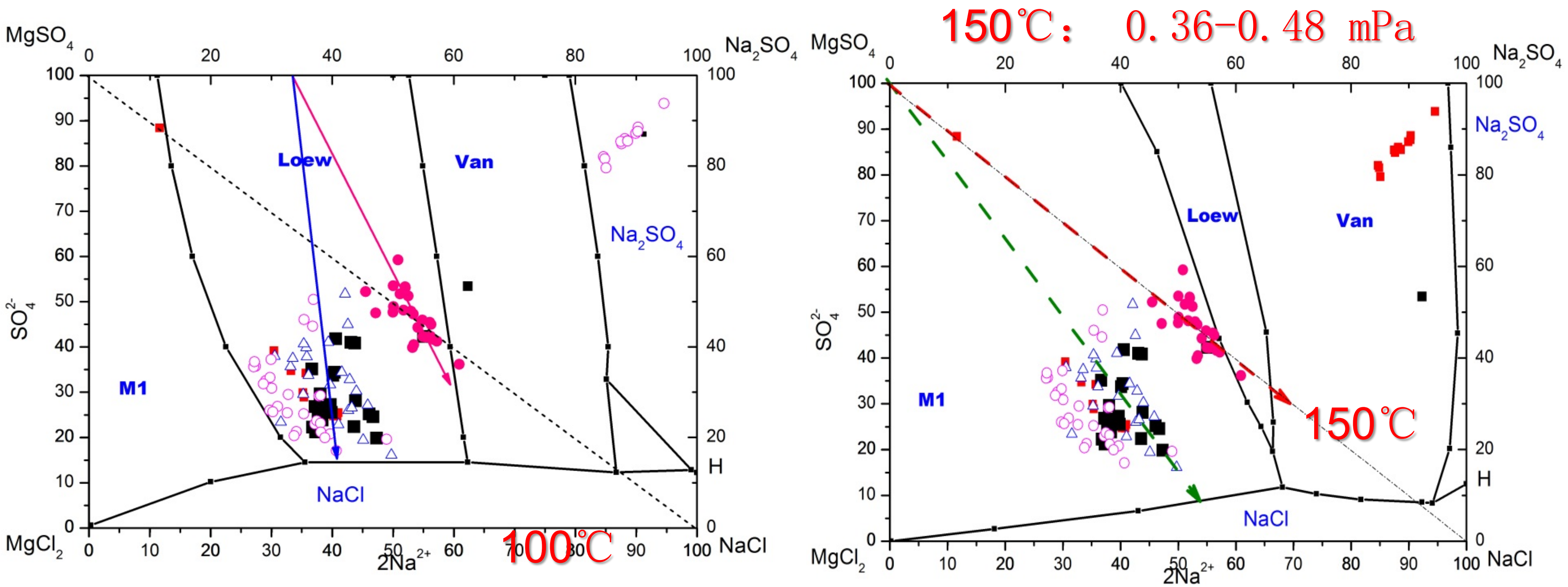


Figure 6 Process planning on multiple temperature phase diagram
Ast: $Na_2SO_4·MgSO_4·4H_2O$ (Astrachanite); Loe: $6Na_2SO_4·7MgSO_4·15H_2O$ (Loeweite);
Van: $3Na_2SO_4·MgSO_4$ (Vanthoffite); M1:$MgSO_4·H_2O$ (Kieserite)

The single salt or hydrate of $Na_2SO_4·10H_2O$, $MgSO_4·7H_2O$ and $MgSO_4·H_2O$ can be produced at low temperature of < 0 ℃ or at high temperature about 150 ℃

4.2 Phase Equilibria and Phase Daigram

（1） Solubility Phase Diagram

——Equilibrium state —Stable Phase Diagram

Began with van't Hoff, and continued by a lot of scientists, and has taken over 100 years of continuous solubility investigations within the salt-water systems.

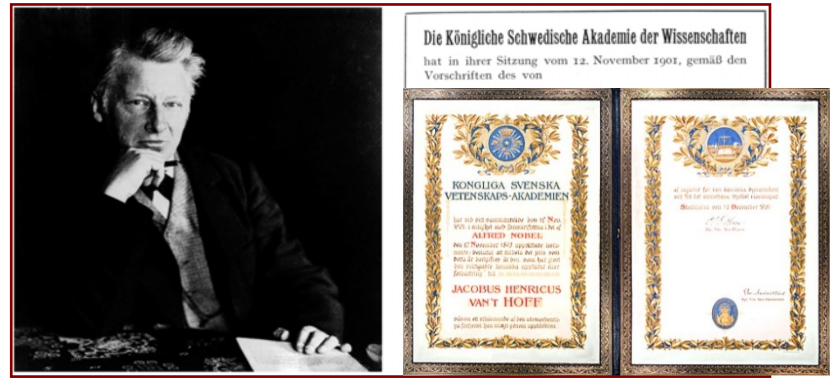


Figure 1 J. H. van't Hoff, the first winner of a Nobel prize in chemistry in 1901

（2） Matestable Phase Diagram

——Matestable State Phase Diagram

——Evaporation Phase Diagram Matestable phenomenon occurs in some salt-water systems

Phase regions are usually different from that in solubility diagrams

Н.С.Курлаков (25°C 1938)
Zuomei JIN (25°C 1980)
(15°C 2001)
(35°C 2002)

Process

_natural evaporation _surface evaporation

_no Stir or Mixing

Evaporate intensity

0.04-0.08g/(day. cm²)_15℃,

0.2-0.3g/(day. cm²)_35℃

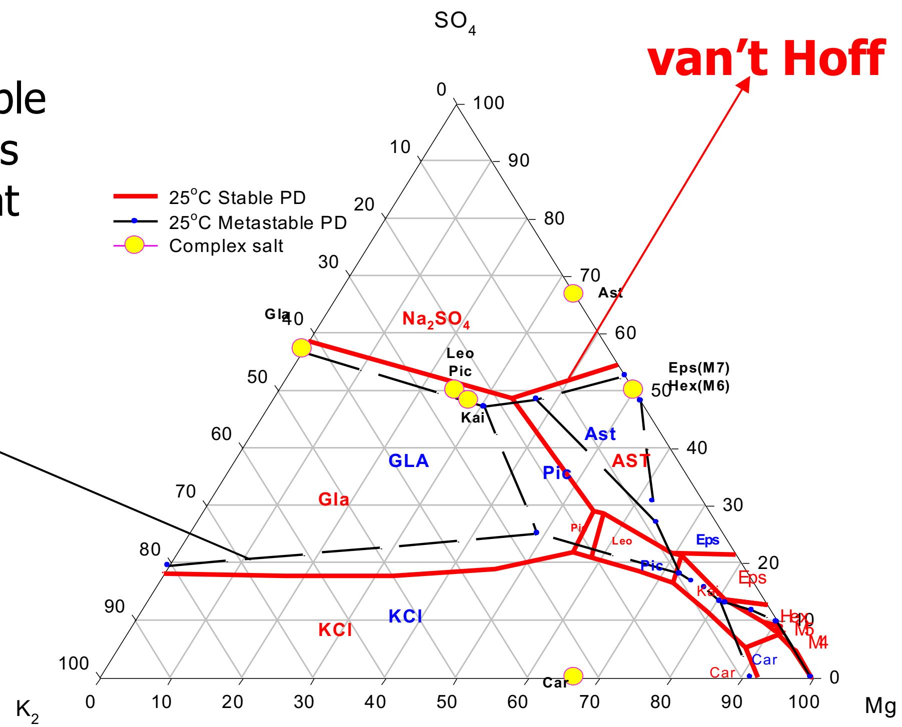


Fig-1 Stable phase Diagram and Metastable Phase Diagram of Na^+, K^+, Mg^{2+} // Cl^-, SO_4^{2-}-H_2O System at 25°C

Н.С.Курлаков, Николаев В.И. Фи3-Хим. Аналн3а АН СССР. Х.1938. 333-306

4.3 Salt-forming Dynamic

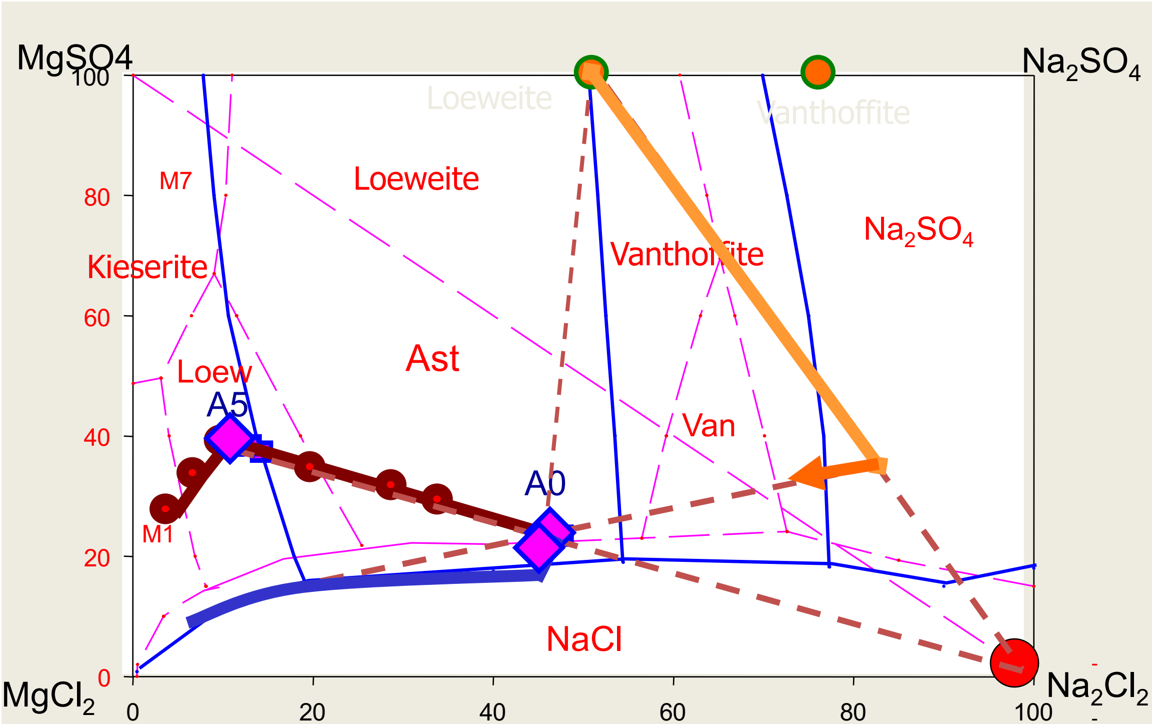


Figure 3 Boiling evaporating process of A0 solution at 75°C

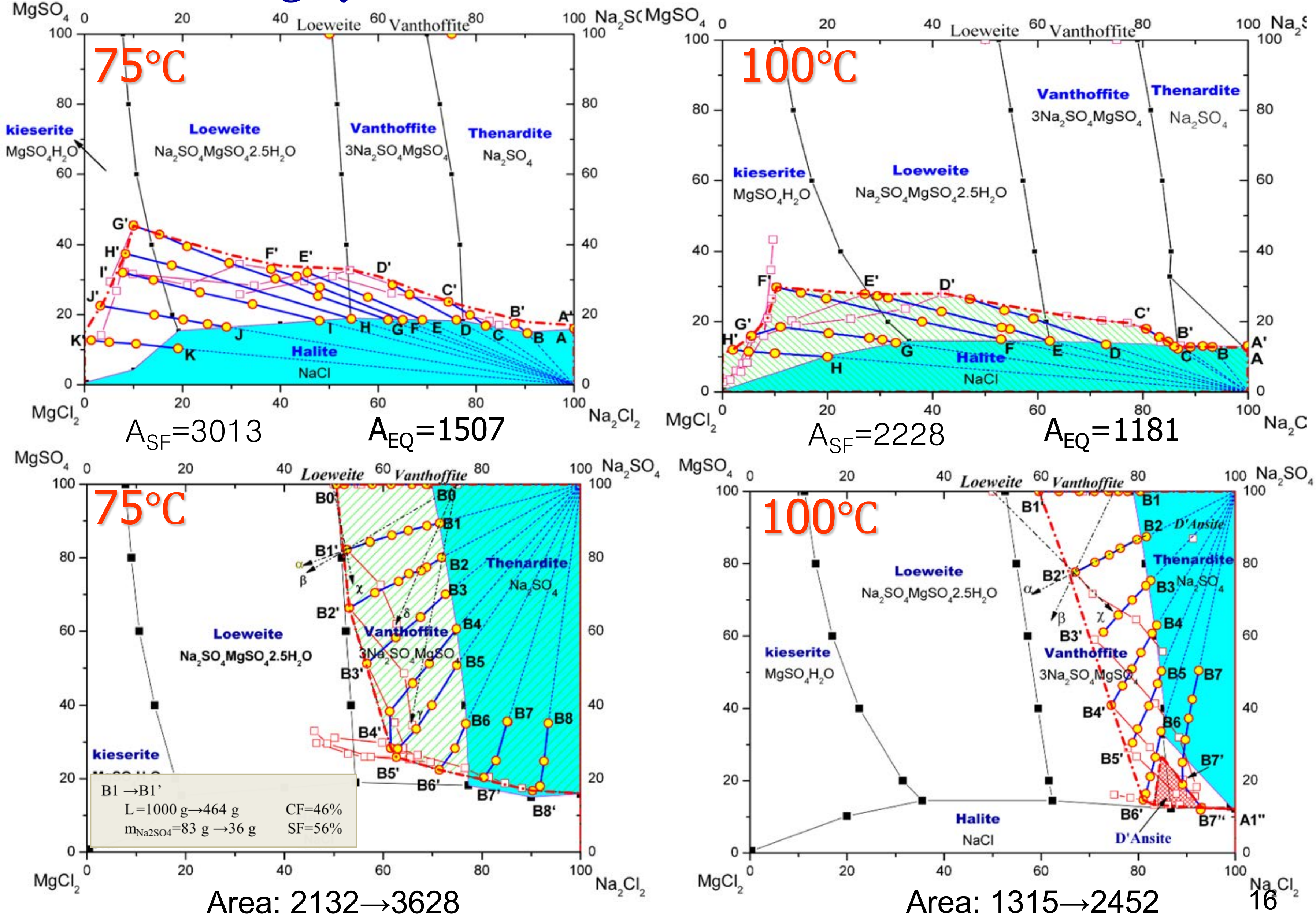
bule curve 75 °C ——pink curve 55 °C

Salt Recover from Bittern in Hangu Salt Plant

Epsomite Recover from Bittern in HanGu Salt Plant

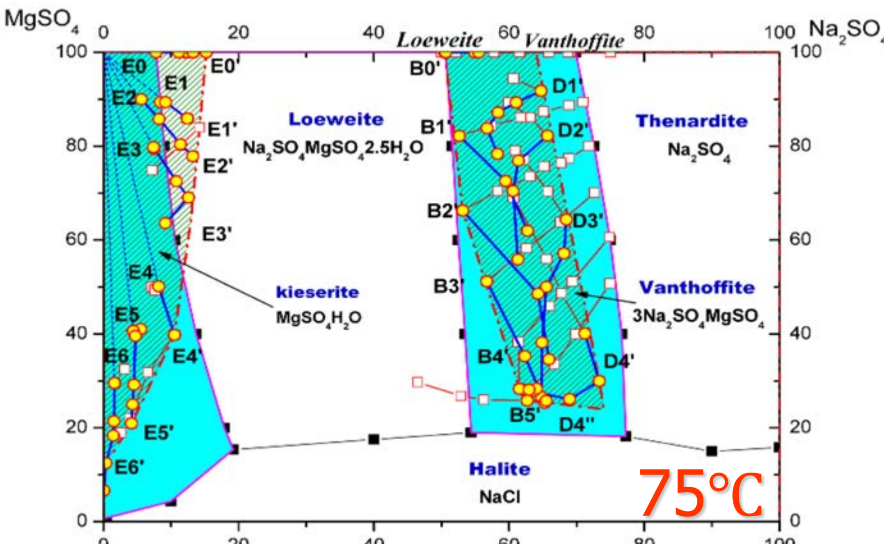
Epsomite and Salt joint Production from Bittern

4.3 Salt-forming Dynamic

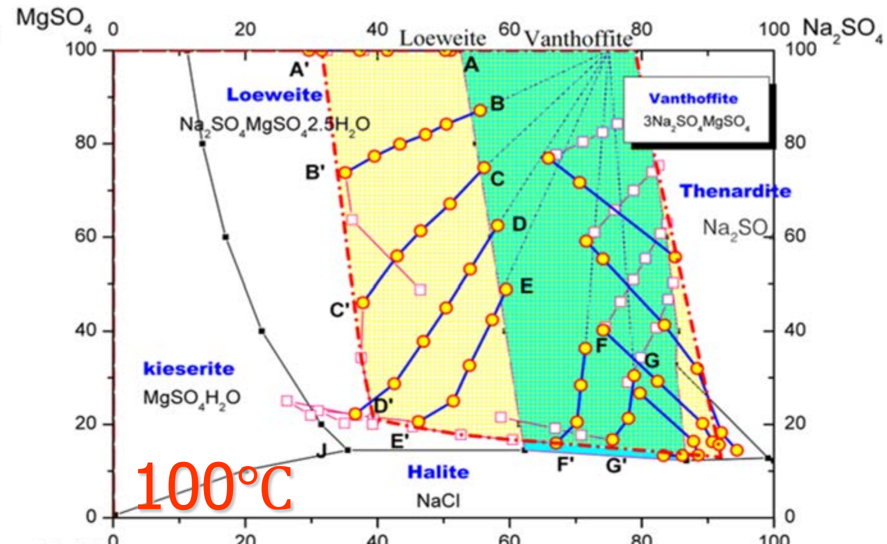


Huan Zhou,* Hongli Zhang, Yadong Chen. Chem. Eng. Data 2012, 57, 943−951
Huan Zhou,* Jianbo Zhang, Hongli Zhang. J. Chem. Eng. Data 2012, 57, 1192−1202

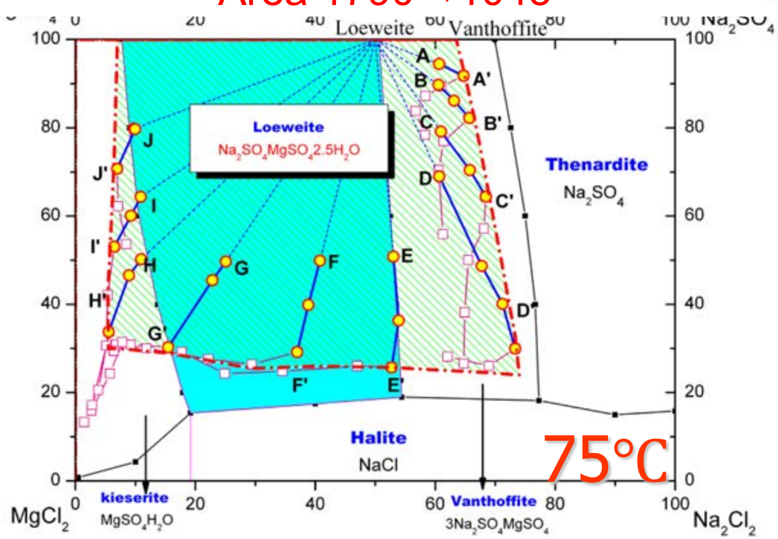
1.3 Salt-forming Dynamic



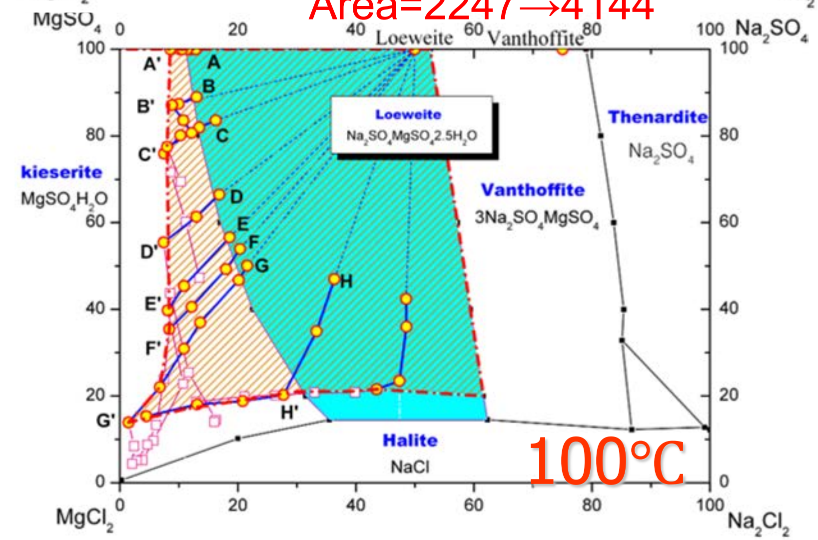
Area 1790→1045



Area=2247→4144



A_{SF}=4635 A_{EQ}=3380



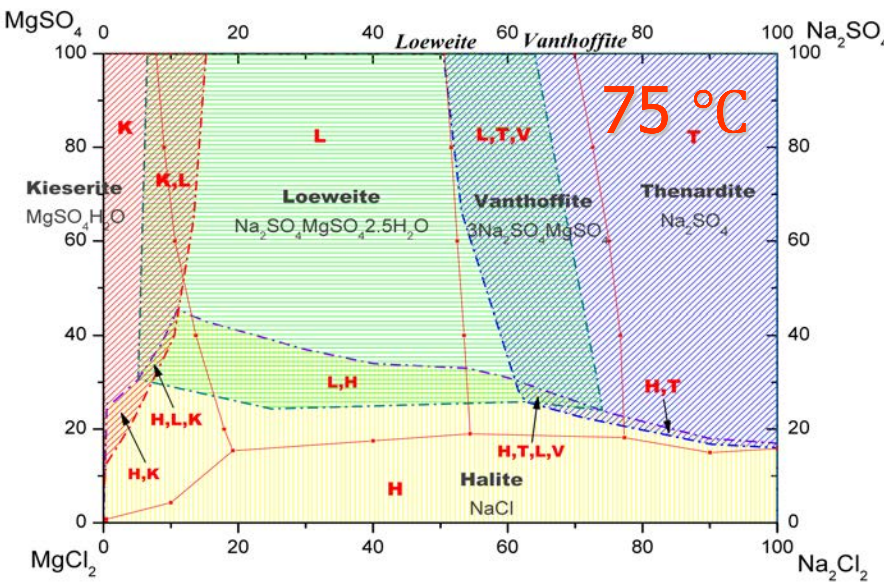
A_{SF}=4003 A_{EQ}=3241

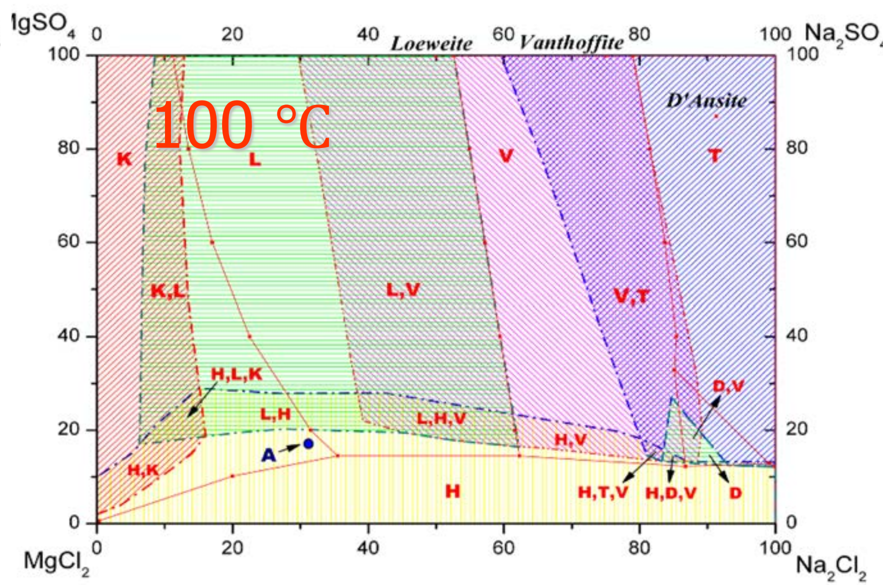
Huan Zhou,* Hongli Zhang, Yadong Chen. Chem. Eng. Data 2012, 57, 943−951

Huan Zhou,* Jianbo Zhang, Hongli Zhang. J. Chem. Eng. Data 2012, 57, 1192−1202

4.3 Salt-Forming Diagram

(1) First type *Conditional Salt-forming Region* (C-R)





C-R accounts for 22.12 % area

C-R accounts for 40.28 % area

(i) The overlap region we called as Conditional Salt-forming region.

(ii) The salt species precipitated depends on the crystal seed (kind, amount) and evaporation intensity

Huan Zhou,* Hongli Zhang, Yadong Chen. Chem. Eng. Data 2012, 57, 943−951

Huan Zhou,* Jianbo Zhang, Hongli Zhang. J. Chem. Eng. Data 2012, 57, 1192−1202

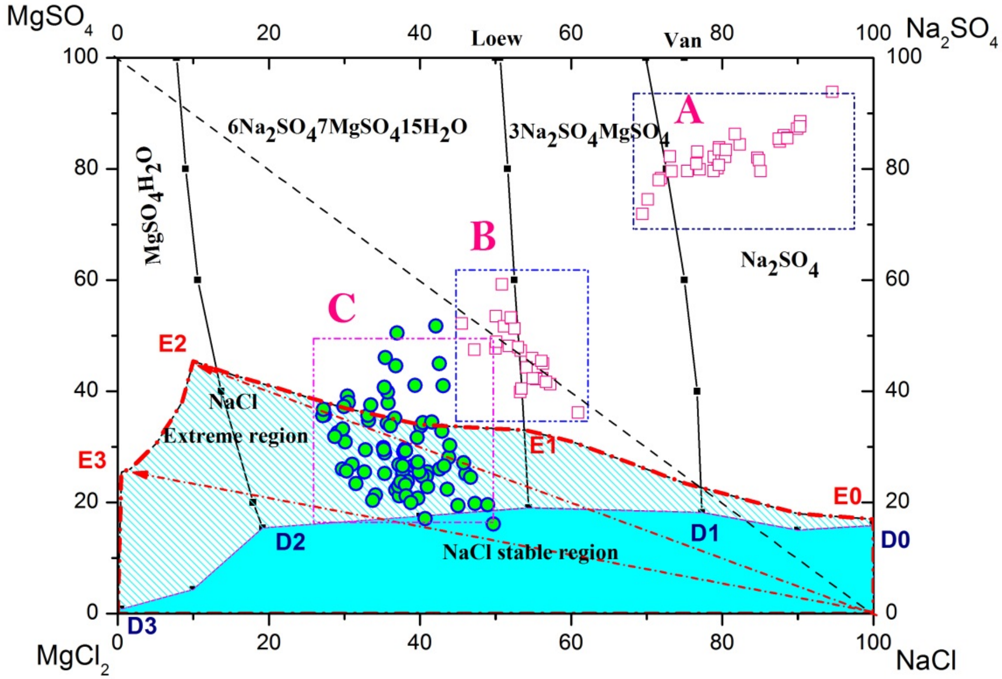


Figure 7. Salt-forming diagram of Na^{+}, $Mg^{2+}//Cl^{-}$, SO_4^{2-} - H_2O system for NaCl production at 75 ° C

4.4 Experiments

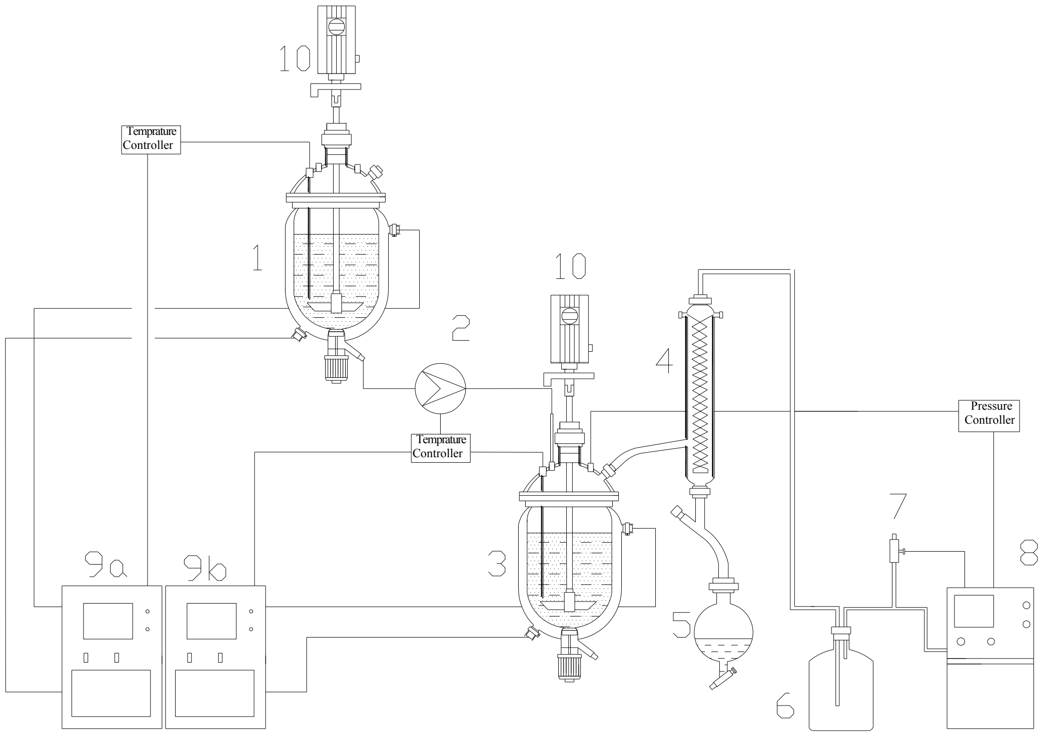


Figure 8. Experimental apparatus
1—Oil and vacuum jackets glass thermostat (Feed tank); 2—Feed pump; 3—Oil and vacuum jackets glass evaporating crystallizer; 4—Water vapor condenser; 5—Water collector; 6—Buffer bottle; 7—Vacuum control valve; 8—Vacuum pump; 9 (a,b)—Thermostatic oil bath; 10—Heidolph Stirrer.

4.5 NaCl process

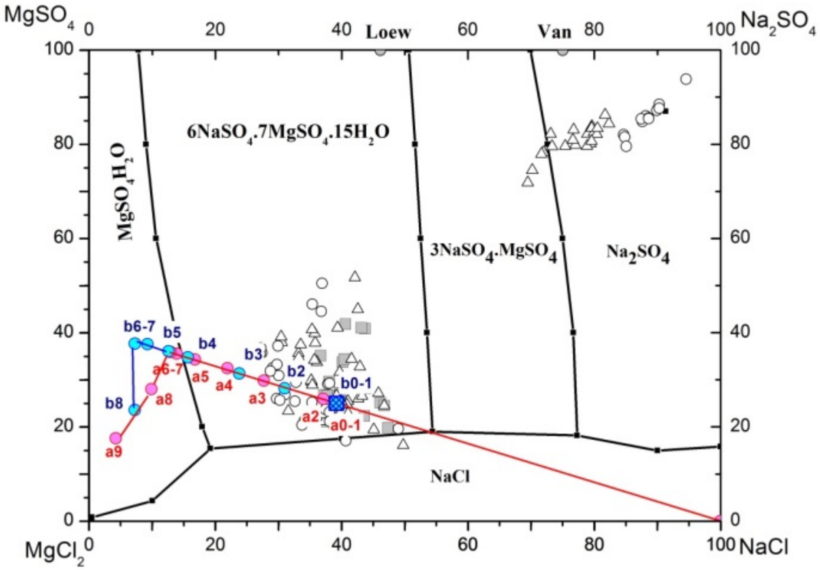


Figure 9. Liquid points in the evaporation process under vacuum and at atmospheric pressure;

- Isothermal evaporation was carried out at for raw brine a_0
- until the sulfate begins to precipitate at a_7, the vapor pressure reduced to 180 mbar, the concentrated ratio of the liquid phase and the output ratio of NaCl were 46.6% and 75.2%, respectively.

- Constant pressure evaporation was carried out
- When NaCl begins to precipitate，the boiling temperature is 53.2 ° C. Until sulfate starts to precipitate at b_8, the temperature has risen to 61.3° C, where the liquid phase is concentrated to 45.1%, and an 84.1% output of NaCl was achieved.

4.6 $MgSO_4$ process

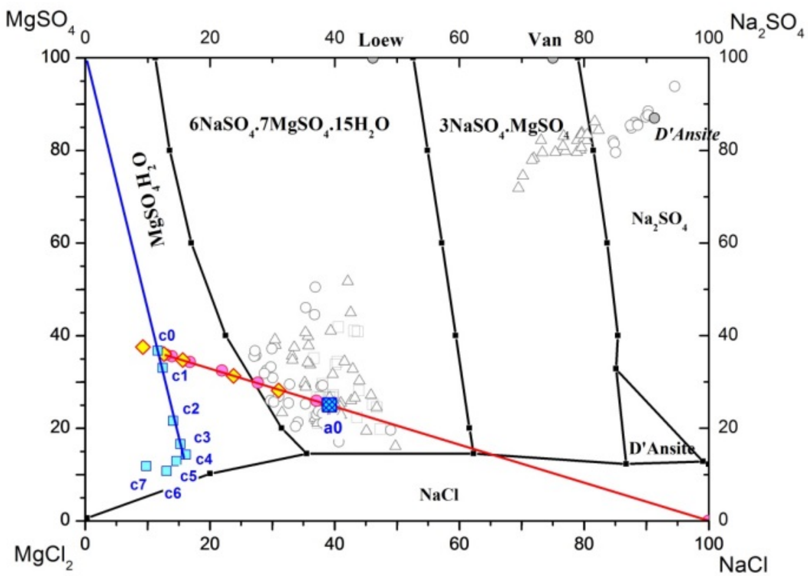


Figure 10. Liquid points in the evaporation process under atmospheric pressure; The background phase diagram is at 100 ° C

The mother liquid of salt was evaporated under normal pressure (~1013 ± 2.0 mbar)

The boiling temperature is from 107.7 ° C to 116.3 ° C. The one solid region for monohydrate MgSO4 is from c1 to c4 with corresponding temperatures from 107.7 to 115.4 ° C.

The output ratio of $MgSO_4$•H_2O reaches 72.2%

4.7 Comprehensive utilization system

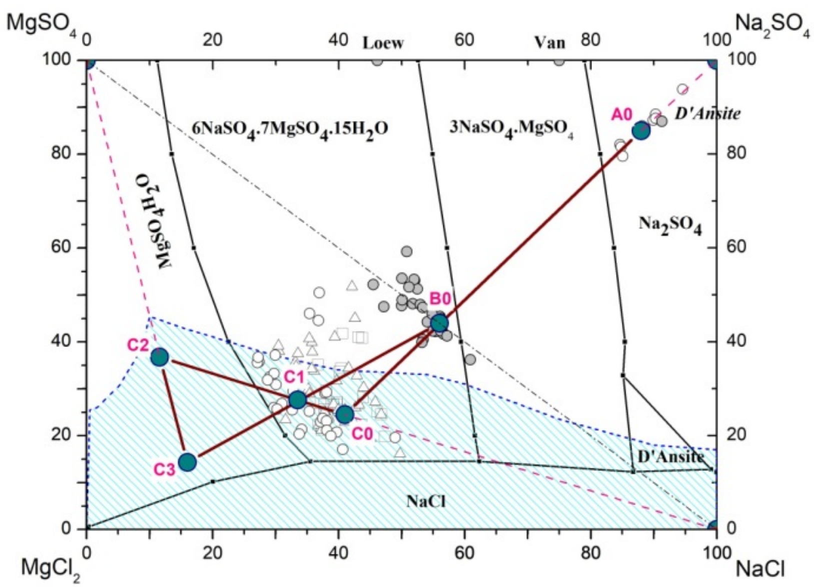


Figure 11. The integrated processes for Yuncheng salt-lake resource utilization. The background phase diagram is at 100 ° C, the background salt-forming region for NaCl is at 75° C

- (1) mixing the raw brine A_0 with waste brine C_0 to form the feed brine B_0, where B_0 is located on the diagonal line of NaCl - $MgSO_4$;
- (2) mixing the feed brine B_0 with the recycle brine C_3 to form the solid-liquid mixture C_1;
- (3) evaporating brine C_1 via multi-effect evaporation to produce salt and the mother liquor C_2;
- (4) evaporating brine C_2 at high temperatures to produce monohydrate $MgSO_4$ and to recycle brine C_3.

5 Conclusions

- Based on the salt-forming phase diagram in the non-equilibrium state, the technical secrets of Yuncheng salt-making in ancient China were revealed. In order to utilize the large amount of residual brine produced in the Na_2SO_4 recovery process and to eliminate its environmental impact, one system of comprehensive utilization was proposed and experimentally tested.
- This system includes a vacuum salt-making process and a normal pressure Kieserite process. The experiments confirm that the salt-making process can stably run in the double salt region without double salt formation and show that the Kieserite-salt process can produce crystalline monohydrate $MgSO_4$, which can be easily separated and purified.
- The evaporative crystallization process stably running in the extreme region of NaCl, proves the feasibility of salt-forming regions in industrial application. Thus the salt-forming diagram would be extremely valuable to industry process design and control, especially, the treatment of concentrated brine.

Acknowledgments

The authors gratefully thank the financial support of the National Natural Science Foundation of China (U1407204)

天津科技大学
Tianjin University of Science & Technology

国家自然科学基金委员会
National Natural Science Foundation of China

Thanks for your attention