The ancient, latter-day and coming technology of salt recovering from Na_2SO_4 type brine in Yuncheng salt-lake of China: The typical application of salt-forming diagram

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Abstracts: The comprehensive utilization and environment-friendly processes for fresh water or valuable salt recovering from seawater, salt-lake or brine resource are very important for sustainable development. Yuncheng-salt in the ancient of China produced from the sodium sulfate type brine for thousands of years and no obvious environmental impact, but the mass extraction of single product of Na_2SO_4 in latter-day reduces large amount of waste liquid. In this research, depending on salt-forming region in non-equilibrium state, the technical secrets of ancient salt technique were uncovered, and one comprehensive utilization system was proposed and experimentally tested. The new system includes vacuum salt-making process and normal pressure Kieserite-process. The experiments confirm that the salt-process via vacuum evaporation can stably run in the double-salt region but no double-salt forming, and show that Kieserite-process can produce crystal monohydrate magnesium sulfate. This comprehensive utilization system can gradually eliminated waste liquid and will help for the sustainable development of Yuncheng salt-lake, and contribute to environment improvement.

Key word: phase equilibria，salt-lake brine，process systems，sustainability，waste water

1 Introduce

Salt resources widely exist in seawater, salt lakes, and mineral deposits. The bulk processes such as seawater desalination, valuable salt recovering, are needed for human development. For sustainability, the comprehensive utilization and environment-friendly processes are very important.

Yuncheng salt-lake locates in the middle inland of China, which close neighbor the ancient capital cities of xi'an and Luoyang, had been the main salt-producing area for thousands of years and played an important role in the history of Chinese civilization[1][2]. Since the salt-lake brine is not sodium chloride type but sodium sulfate, the special salt-making process has been seen as one great invention in ancient China. This salt-making process lasted over thousands of years until the 1960s, when the mass extraction of sodium sulfate was replaced. However, the single product of sodium sulfate for nearly 50 years resulted in the significant change of the salt-lake composition and environment. The comprehensive utilization and environmentally friendly technology needs to be developed urgently.

Salt-water system phase diagrams expressing aqueous salt solubility and solid-liquid phase equilibrium behaviours for a multicomponent salt-water system is the most common tool for process analysis, design, and integration [3]. However, besides that metastable behaviors are typically found, evaporative crystallization processes are often operated at non-equilibrium state due to high evaporation rates. In such case, the salt-forming regions can be different and more complex than expected based on the equilibrium diagram. Therefore, we propose the concepts and principle of salt-forming regions including primary region, extreme region, and conditional region to present the complex behaviors of salt-formation [].

In this study, depending on the salt-forming diagram, the ancient technical secrets were uncovered, and one comprehensive utilization system for the joint production of industrial sodium chloride and monohydrate magnesium sulfate was developed with no waste liquid and consuming the existed residual bittern.

2. Brine composition

Brine composition of Yuncheng salt-lake [4] from 1950s to the present was summarized in table 1 and plotted on the phase diagram of $Na^+,Mg^{2+}//Cl^-,SO_4^{2-}$ - H_2O quaternary system[3] at 298.15K as figure 1(a). The compositions located in region ‘A’ are the earliest record of the salt-lake before 1950s and the record of the mine-brine at present. It indicates that (1) the primordial salt-lake belongs to Na_2SO_4 type; (2) salt-lake composition wasn’t significantly changed with salt-making process for thousand years [1]. However, it had been largely changed in latter-day caused by recovering a mass of single product Na_2SO_4, and the composition of the waste bittern located in the region ‘C’ as figure 2. If this process continues, it will eventually cause all the raw brine into the waste bittern.

Table 1 The composition of Yuncheng salt-lake(a)

Year	Na^+	Mg^{2+}	SO_4^{2-}	Cl^-		
	Chemical composition (Dry salt based %)				J Na_2^{2+}	J SO_4^{2-}
1955	27.39	3.89	57.79	10.92	78.84	79.61
1956	26.65	4.30	58.80	10.25	76.59	80.90
1957	24.62	5.79	56.37	13.23	69.22	75.88
1980	18.86	9.34	59.03	34.58	51.63	77.35
2011	16.57	12.89	28.27	29.71	40.46	33.05
2016	22.99	8.17	36.53	32.31	59.81	45.49
2017	23.46	8.18	31.75	36.61	60.24	39.02

(a) [][]

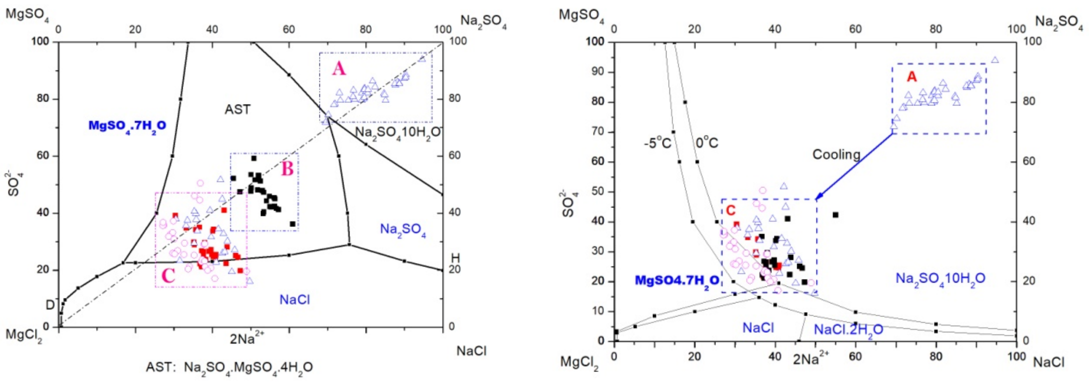


Figure 1Brine composition in Yuncheng salt-lake (phase diagram at 25°C)

A. Original composition before 1950s; B. Mixed brine to produce mirabilite in winter during the years between 2010 to 2017; C. Residual brine after Na_2SO_4 recovering.

Ast: $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ (Astrachanite)

Figure 2. Na_2SO_4 recover process (phase diagram at 0°Cand -5°C)

A. Original composition of mine brine; C. Residual brine after Na_2SO_4 recovering

3. The technique of ancient salt-making

3.1 The process analysis based on phase diagram

How to produce food-salt under the natural conditions from Yuncheng salt-lake which rich in sodium sulfate but not sodium chloride? Why the salt-recovering processes in ancient times were sustainable and no obvious environmental impact? Using the stable phase diagram analysis, there are no answer to these questions. For example, three processes shown in figure 2-3 can be arranged by the phase diagrams between the temperature region from -5 to 35℃:

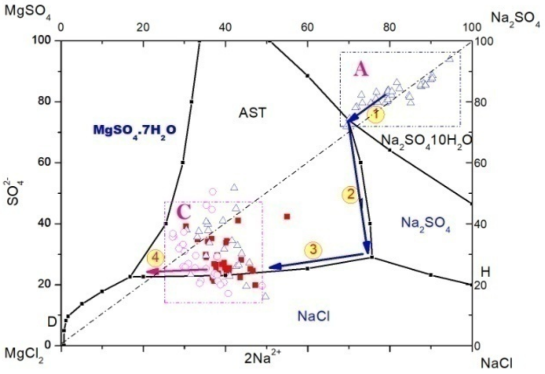


Figure 3The process analysis of evaporation based on solubility diagram at 25℃.

Ast: $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ (Astrachanite)

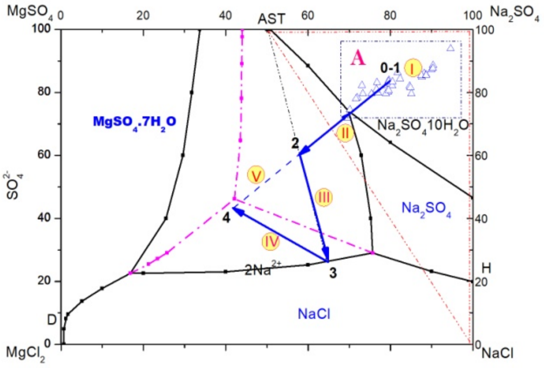


Figure 4 Actual process of ancient salt

i). Brine concentrated; ii). Mirabilite process; iii). Infiltration process; iv. Salt crystallization; v. Brine recycle.

Ast: $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ (Astrachanite)

(1) Cooling the salt-lake brine in winter under the ambient temperature around 0℃ to -5℃ as shown in figure 2, there is only Mirabilite ($Na_2SO_4 \cdot 10H_2O$) region, but no single salt (NaCl) in the cooling process.

(2) Evaporating the salt-lake brine in summer under ambient temperature around 25℃ to 35℃, as shown in figure 3, three steps exist in the evaporation process: (i) brine concentrated and Mirabilite crystallizing-out; (ii) Astrachanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) and Mirabilite or Thenardite (Na_2SO_4) co-saturated and crystallizing-out; (iii) Halite (NaCl) and Astrachanite co-saturated and crystallizing-out. In those steps, it is no region for NaCl singly crystallizing-out.

(3) Cooling or evaporating the residual brine in region ’C’, as shown in figure 3, it is no region for NaCl singly crystallizing-out.

3.2 The actual process of ancient salt-making

The conclusion based on the stable phase diagrams seems that it is impossible to recover pure salt from Yuncheng salt-lake under natural conditions. However, the ancient salt-making was actual processes which included five steps [3], as shown in figure 4-5, and summarized as follows:

(1) Solar pond (I) for first step evaporation: raw brine concentrated until sulfate saturated;

(2) Solar pond (II) for second step evaporation: the sulfate-salt precipitate from the saturated brine and forms the so-called ‘sulfate-bed’;

(3) Natural filtration: the mother liquid of sulfate-salt filtrated through the sulfate-bed, and come together to the outside trench. The filtrated brine would be normally high concentrated with sodium chloride;

(4) Solar pond (III) for third step evaporation: food-salt crystallize-out from the filtrated brine.

(5) The mother liquid of food-salt was discharged into solar pond (I).

All the steps were controlled by the skilled technician relying on experience. The processes were repeated over and over again for a thousand years.

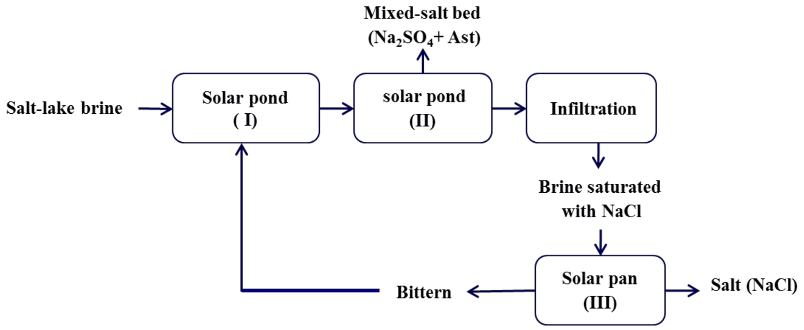


Figure 5 Ancient salt-production processes in Yuncheng salt-lake

3.3 Uncover the principle of ancient salt-making

In fact, it is found that the behaviors of stable and metastable solid-liquid phase equilibria had been wisely and naturally used in the ancient salt-making process.

Metastable data in $Na^+,Mg^{2+}//Cl^-,SO_4^{2-}$ - H_2O system at 298.15K [5], the pink curves in figure 4, shown as follows: (1) there is no solid region for Astrachanite; (2) the surface evaporation in second solar pond would form the solids of Mirabilite or Thenardite and the liquid which saturated with metastable phase of Astrachanite; (3) Astrachanite would fully precipitate in long period of filtrate process, and the final brine has already been stable and saturated with sodium chloride.

The filtrated brine locates on NaCl region of metastable diagram, the only salt of NaCl crystallize-out until Epsom salt saturated.

3.4 One primitive sustainable process

The residual brine of salt-making in third evaporation step was discharged to the first evaporation step. It is very important for the high efficiency of NaCl recovering, and for the sustainability of resource utilization. The compositions of salt-lake locate at the triangle area of NaCl-Ast-Na_2SO_4 in figure 4, and the solid products are food-salt and sulfate-bed which composed by Astrachanite and Na_2SO_4. Thus, the recycling of residual brine forms one sustainable process with the following advantages: (1) no residual brine discharge; (2) all the chloride content transformed into salt product;

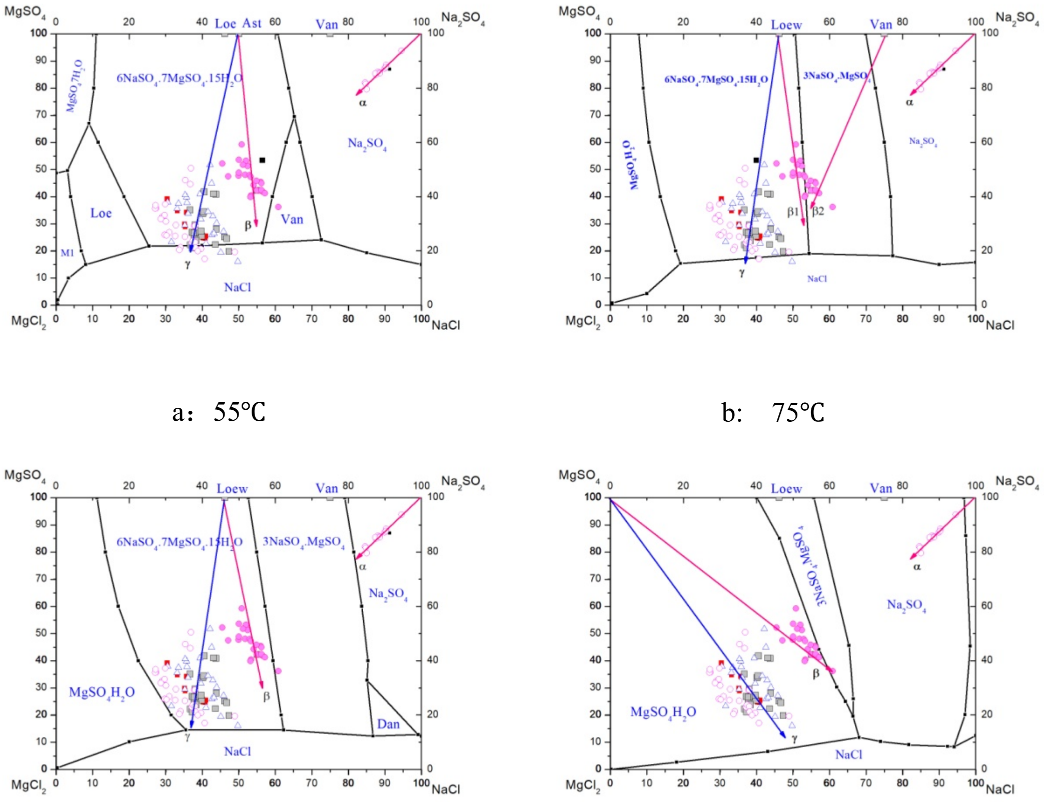
(3) all the sulfate and magnesium contents form the deposition of sulfate-bed. (4) salt-making processes are separated from the salt-lake, and the composition of salt-lake has not been affected by salt-making.

Thus, the ancient salt-making process is a primitive sustainable process and a truly great invention in ancient China.

4. New comprehensive utilization system

4.1 Process planning on solubility phase diagram

In order to develop one sustainable and optimized process for the utilization of the salt-lake resources, we plot the brine of ‘A’、‘B’ and ‘C’ on the phase diagram of multiple temperature from -5℃ to 150℃as figure 6(a) 55℃, (b) 75℃, (c) 100℃, and (d) 150℃.



a： 55°C

b: 75°C

c: 100°C

d: 150°C

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)

At temperature from -5 to 0℃(Fig 2), the brine ‘B’ locate at the region of $Na_2SO_4·10H_2O$, and the brine ‘C’ near to the co-saturated curve of $Na_2SO_4·10H_2O$ and $MgSO_4·7H_2O$; at temperature from 25℃to 55℃, both B and C are locate at Astrachanite region; at temperature 75℃to 100℃, both B and C are locate at Loeweite ($6Na_2SO_4·7MgSO_4·15H_2O$) region; and at 150 ℃, both brine ‘B’ and ‘C’ locate at Kieserite ($MgSO_4·H_2O$) region, and brine ‘B’ near to Loeweite region.

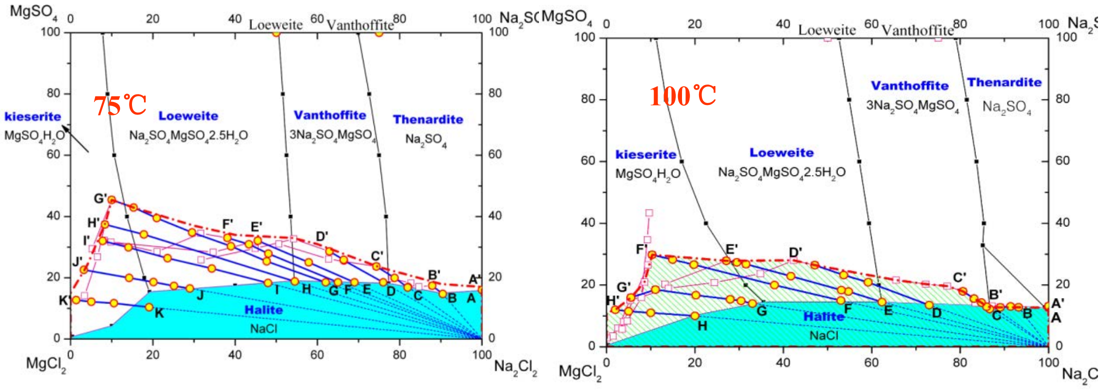
From those diagram, the single salt or hydrate of $Na_2SO_4·10H_2O$, $MgSO_4·7H_2O$ and $MgSO_4·H_2O$

can be produced at low temperature of < 0 ℃ or at high temperature about 150 ℃, however, it is a pity that the production at those temperatures are undesirable, e.g., the production at low temperature has already produced the large amount of waste liquid, and by the contrary, the operation at high temperature need high pressure which would result in the difficult of solid-liquid separation and high cost of operation.

4.2 The analysis based on salt-forming diagram

It is known from the previous research [], salt-forming behaviors in the evaporation process for Na$^+$,Mg^{2+}//Cl$^-$,SO$_4^{2-}$-H$_2$O system are largely different from the stable phase diagram. For example, the salt-forming region of NaCl at 75℃and 100℃[6-8] were shown in Figure 7. The concepts and principle of salt-forming diagram has been proposed on the paper [9]. Since the driving force needed for crystal growth of sodium chloride is far less than the driving force of primary nucleation for double salts, which results in stably crystallizing-out of NaCl from double salt solid-region. Comparing the salt-forming region of NaCl in Figure 7, the extend region of NaCl at 75℃is more larger than that at 100℃.

Thus, it is possible to produce salt (NaCl) from brine ‘C’ via multi-effect evaporation. During evaporation process, the mother-liquid points move along with the vector line of NaCl crystallize to the limited curve of G’H’I’J’ (figure 7a) or F’G’H’ (figure 7b) where kieserite starts to precipitate. Figure 7 shows that the mother-liquid of salt-making is enriched in MgSO$_4$, and composition points locate in the middle of Kieserite region. Therefore, sodium sulfate hydrate can be easily produced.



(a) (b)

Figure 7 Salt-forming diagramof Na$^+$,Mg^{2+}//Cl$^-$,SO$_4^{2-}$ - H$_2$O system for NaCl at 75℃ [ ]and 100℃ [ ]

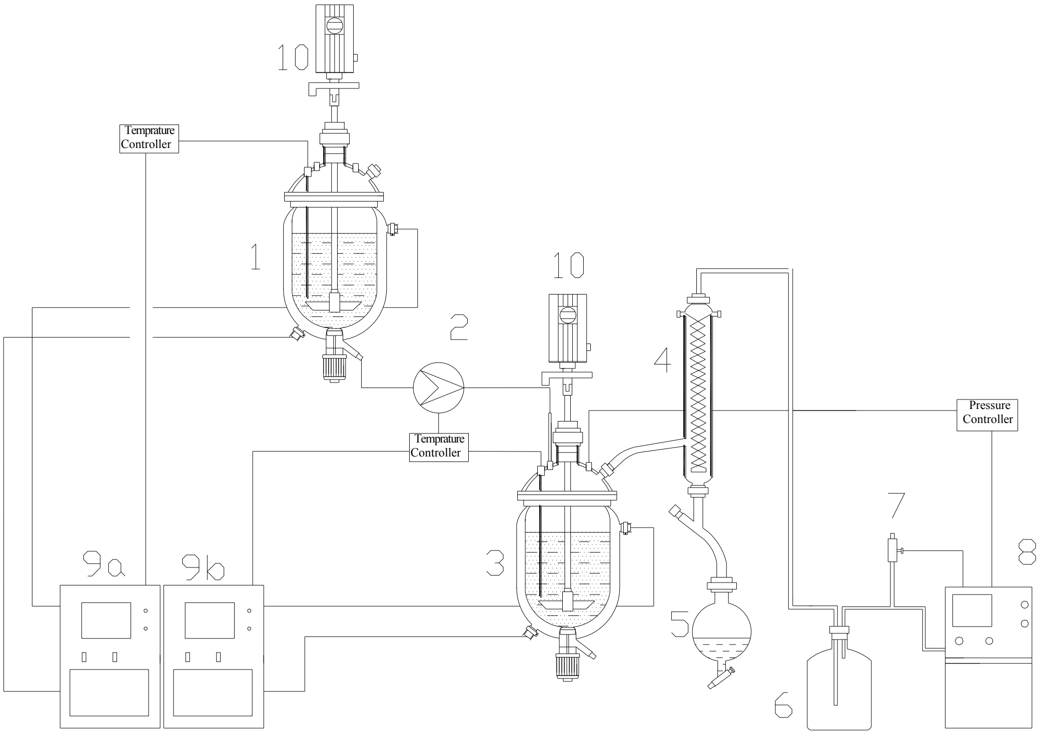


Figure 8. Experimental apparatus

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.

4.3 Experiments

Apparatus

Figure 8 shows the experimental apparatus. 2 L jacketed glass evaporating crystallizer (Chemglass) with a stirrer (Heidolph), water vapor condenser with a water collector, thermostatic oil heating bath (Huber, Unistat Petite Fleur), chemistry diaphragm pump (vacuubrand, PC 610 NT), pressure-temperature controller and online recorder system were used.

Vacuum boiling evaporation to produce salt

Two set vacuum boiling evaporation processes of isothermal process and constant pressure process were carried out, and controlled by adjusting vapor pressure. The heating temperature difference(⊿*T*) for the whole process was kept at 40℃. Solid and liquid samples were took by discharging solid-liquid mixture through the bottom valve and separated via the isothermal filtering method []. The compositions of samples were analyzed via chemical method.

Isothermal evaporation process was carried at 75℃ for raw brine A_0, and the results were listed in table 2 and plotted on figure 9a., NaCl starts to precipitate at point A_1 where the boiling pressure is 310 mbar. Continuing the evaporation process until the sulfate starts to precipitate at A_7, the concentrated ratio of liquid phase and the output ratio of NaCl achieved at 46.6 % and 75.2% respectively.

Constant pressure boiling evaporation was carried under 100 mbar for raw brine B_0 (same with A_0), the results were listed in table 3 and plotted on figure 9a. The boiling temperature at NaCl starts to precipitate is 53.2℃. Until sulfate precipitated at B_8, the liquid phase has been concentrated to 45.1 %, and the output of NaCl achieved at 84.1%.

It was worth notice, the experiments confirm that the vacuum boiling evaporation for salt-making process can stably run in double salt (Loeweite) region and $MgSO_4 \cdot H_2O$ region, and no double salt precipitated, the purities of salt and $MgSO_4 \cdot H_2O$ can achieve at 99.1% and 95.0%.

Table 2 The isothermal boiling evaporation at temperature 75℃

No.	Temperature	Pressure	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	H_2O	Solid
	℃	mbar			mass %			
A0	20.0	1013	4.03	3.33	11.95	5.40	75.29	---
A1	75 ± 1.0	310	5.05	4.17	14.96	6.76	69.06	NaCl preipitate
A2	75 ± 1.0	300	4.63	4.16	14.29	6.75	70.18	NaCl
A3	75 ± 1.0	265	3.18	4.41	12.49	7.15	72.77	NaCl
A4	75 ± 1.0	240	2.79	5.35	13.50	8.68	69.69	NaCl
A5	75 ± 1.0	222	2.36	6.24	14.37	10.12	66.91	NaCl
A6	75 ± 1.0	206	2.14	7.14	15.59	11.58	63.55	NaCl
A7	75 ± 1.0	195	2.14	7.70	16.54	12.49	61.14	NaCl
A8	75 ± 1.0	180	1.65	7.97	18.56	9.81	62.01	$NaCl+MgSO_4 \cdot H_2O$
A9	75 ± 1.0	165	0.69	8.18	20.54	5.94	64.65	$NaCl+MgSO_4 \cdot H_2O$

Table 3 Boiling evaporation at constant pressure of 100 mbar

No.	Temperature	Pressure	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	H_2O	Solid
	℃	mBar			mass %			
B0-B1	53.2	100±2.0	4.03	3.33	11.95	5.40	75.29	Boiling point
B2	54.7	100±2.0	3.57	4.73	13.66	7.67	70.28	NaCl
B3	56.3	100±2.0	2.96	5.66	14.28	9.18	67.33	NaCl
B4	57.4	100±2.0	2.30	6.37	14.47	10.33	65.88	NaCl
B5	58.3	100±2.0	1.98	6.78	14.67	10.99	64.64	NaCl
B6	59.0	100±2.0	1.59	7.24	14.82	11.74	64.49	NaCl
B7	59.6	100±2.0	1.42	7.38	14.81	11.97	62.81	NaCl
B8	61.3	100±2.0	1.13	7.58	14.86	12.18	61.30	$NaCl + MgSO_4.6H_2O$
B9	67.0	100±2.0	1.14	7.67	18.44	7.71	65.05	$NaCl + MgSO_4.6H_2O$

Table 4 Boiling evaporation at normal pressure of 1013 mbar

No.	Temperature	Pressure	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	H_2O	Solid
	℃	mBar			mass %			
C0	107.7	1013 ± 2.0	1.85	7.75	16.18	12.57	61.66	Boiling point
C1	113.2	1013 ± 2.0	1.85	7.06	16.19	9.83	65.07	$MgSO_4 \cdot H_2O$
C2	113.6	1013 ± 2.0	2.07	6.83	18.18	6.70	66.22	$MgSO_4 \cdot H_2O$
C3	114.3	1013 ± 2.0	2.21	6.76	19.41	5.05	66.57	$MgSO_4 \cdot H_2O$
C4	114.8	1013 ± 2.0	2.30	6.80	20.17	4.36	66.37	$MgSO_4 \cdot H_2O$
C5	115.4	1013 ± 2.0	2.37	6.89	20.81	3.98	65.95	$MgSO_4 \cdot H_2O + NaCl$
C6	116.0	1013 ± 2.0	2.01	7.06	21.14	3.45	66.34	$MgSO_4 \cdot H_2O + NaCl$
C7	116.3	1013 ± 2.0	1.39	6.78	19.32	3.52	68.99	$MgSO_4 \cdot H_2O + NaCl$

Normal pressure evaporation to produce monohydrate magnesium sulfate

The mother liquid ‘C0’ produced from salt-making process via the previous vacuum boiling evaporation, were evaporated under normal pressure about 1013 ± 2.0 mbar and with the heating temperature difference of 40℃. The results were listed in table 3 and drawn in figure 9b. The boiling temperature is 107.7 ℃. The one solid region for monohydrate magnesium sulfate is from C1 to C4 with the corresponding temperature from 107.7 to 115.4 ℃. NaCl would precipitate when the boiling temperature is higher than 115 ℃. From C0 to C4 the amount of liquid phase was concentrated only to 80.2 % and water evaporated ratio is only 13.6%, however, the output ratio of $MgSO_4 \cdot H_2O$ has been achieved at 72.2 %. It means $MgSO_4 \cdot H_2O$ precipitated mainly caused by the temperature enhance, but not evaporation.

It is found that the monohydrate magnesium sulfate produced from this process could forms spherical crystal, as figure 10, and the solid-liquid mixture could be easy separated by filter, and the high pure product of monohydrate magnesium sulfate could be easy obtained.

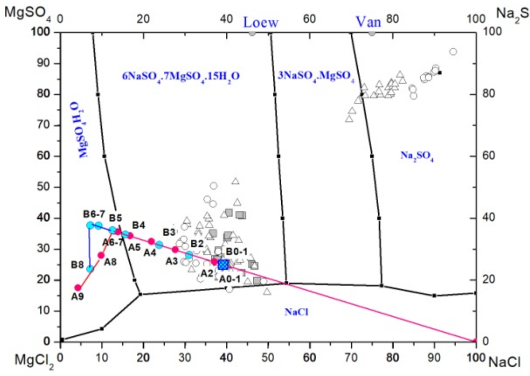


Figure 8a Liquid points in the evaporation process under vacuum and atmospheric pressure

The background phase diagram is at 75℃

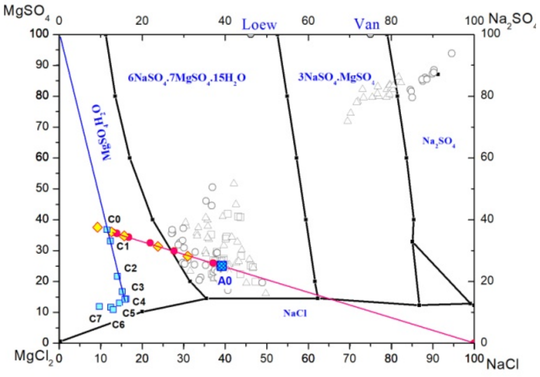


Figure 8b Liquid points in the evaporation process under atmospheric pressure

The background phase diagram is at 100℃

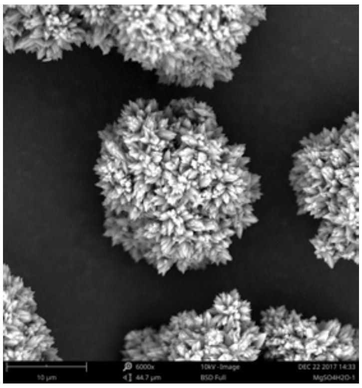


Figure 10 The crystal shape of monohydrate magnesium sulfate produced from brine via normal pressure evaporation

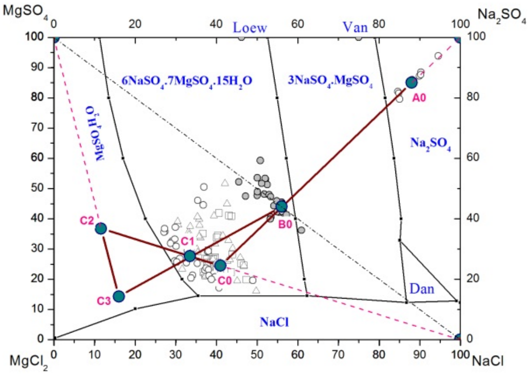


Figure 11 Integrated processes of salt-lake resource utilization in sustainable

Table 5 The main parameters for the integrate process of brine sustainable utilization.

Material	Temperature ℃	Pressure mbar	Mass Kg	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	H_2O
				mass %				

B0	20.0	1013.0	1000.00	6.87	2.39	10.71	9.29	70.74
C1	115.0	1013.0	1811.91	4.82	4.37	14.95	7.08	68.78
C2	61.5	115.0	1012.12	1.85	7.75	16.18	12.57	61.66
C3	115.0	1013.0	811.91	2.30	6.80	20.17	4.36	66.37
NaCl			174.65	39.34		60.66		
$MgSO_4 \cdot H_2O$			132.26		17.56		69.42	13.02
water1			622.23					100.00
water2			85.17					100.00

4.4 Comprehensive utilization system

From the experimental results, the sustainable system for brine comprehensive utilization can be integrated. As figure 11, the system includes four sub-processes:

(1) mixing the raw brine A_0 with waste brine C_0 to form the feed brine of B_0, where B_0 located on the diagonal line of NaCl and $MgSO_4$;

(2) mixing the feed brine B_0 with the recycle brine C_3 to form solid-liquid mixture C_1;

(3) evaporating brine C_1 via multi-effect evaporation to produce salt and mother liquid C_2;

(4) evaporating brine C_2 at high temperature to produce monohydrate magnesium sulfate and recycle brine C_3.

The main parameters for brine B_0 utilization were exampled shown in table 5. In this process, all components of raw brine are transformed to the target product. The evaporation amount account 88% and 12 % respectively for salt-making and sulfate-making process, meanwhile, the recycle brine C_3 is necessary.

Based on this system, all the raw brine in ‘A’, ’B’, or ‘C’ regions can be arranged to produce salt, monohydrate magnesium sulfate. The comprehensive utilization of mine brine ’A’ and residual brine ‘C’ can gradually eliminate the existing waste liquid.

5 Conclusion

Depending on the salt-forming phase diagram in 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 sodium sulfate recovering process, and eliminate its environmental impact, one comprehensive utilization system was proposed and experimentally tested.

The comprehensive utilization system includes vacuum salt-making process and normal pressure Kieserite process. The experiments confirm that salt-making process can stably run in the double salt region but no double-salt forming, and show that Kieserite-salt process can produce crystal monohydrate magnesium sulfate which can be easy separated and purified.

This comprehensive utilization system will help for the sustainable development of Yuncheng salt-lake, and contribute to environment improvement.

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