HOT RECIRCULATION PROCESS FOR THE CO-PRODUCTION OF SALT AND THENARDITE OF NACL-NA_2SO_4-H_2O SYSTEM

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Abstract: The hot recirculation new process for the co-production of salt and thenardite with the NaCl-Na_2SO_4-H_2O type brine was proposed by compare the present process of hot recirculation and the mixed brine recirculation process.

Key words: Hot Recirculation Process, Co-production of Salt and Thenardite

1. THE PRESENT HOT RECIRCULATION PROCESS FOR THE CO-PRODUCTION OF SALT AND THENARDITE

The compositions of rock salt mine and sodium sulfate type brine refer to table 1, which the mainly solutes of those resources are NaCl and Na_2SO_4, and can be roughly considered as the ternary system of NaCl-Na_2SO_4-H_2O. The phase diagram data for the ternary system refers to table 2. The solubility of NaCl and Na_2SO_4 was influenced by temperature, which increases for NaCl and decreases for Na_2SO_4 along with the rising of temperature. Based on these habits, several processes were designed to produce salt and thenardite.

Table 1 Composition of Some Rock Salt and Sodium Sulfate Brine

Producers	Unit	NaCl	Na_2SO_4	$CaSO_4$	$MgSO_4$
Sino-Salt Zhenjiang Salt Mine	g/l	290	13.86	3.64	0.33
Jiangsu Huaerun Company	g/l	300	22.0	2.50	0.80
Anhui Yangtze Salt Mine	g/l	286	16.17	2.20	0.27
Guangdong Longgui Salt Mine	g/l	280	15.0	0.69	0.13
Hunan Xiangfeng Salt Mine	g/l	300	32.0	1.28	1.53
Jiangxi Sale Mine	g/l	300	25.0	1.60	0.80
Hubei 728 Salt Mine	g/l	288	17.3	2.51	0.65

Table 2 Phase Diagram Data of $NaCl-Na_2SO_4-H_2O$ System

Temperature °C	Unit	NaCl	Na_2SO_4	H_2O	Solid Phase
150	g/l	349	59	808	$NaCl+Na_2SO_4$
105	g/l	316	53	841	$NaCl+Na_2SO_4$
100	g/l	307	54	849	$NaCl+Na_2SO_4$
90	g/l	308	54	847	$NaCl+Na_2SO_4$
75	g/l	302	57	850	$NaCl+Na_2SO_4$
60	g/l	298	63	849	$NaCl+Na_2SO_4$
55	g/l	296	62	852	$NaCl+Na_2SO_4$
50	g/l	293	65	853	$NaCl+Na_2SO_4$
45	g/l	284	70	857	$NaCl+Na_2SO_4$

1.1 Salt-out Method

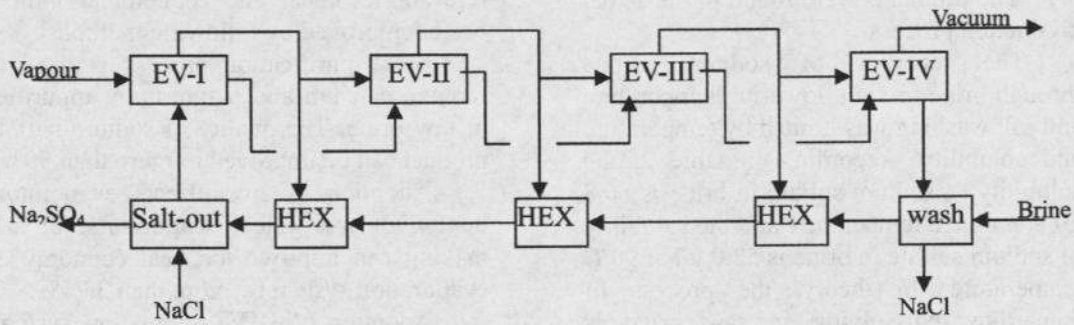

Fig.1 The Process flow diagram of the Co-production of salt and thenardite in Salt-out Method

The process flow diagram of the Co-production of salt and thenardite in Salt-out Method was show in figure 1,in which the four effects evaporation process was taken, both the salt slurry and mother liquor are in co-current in the process. Salt slurry is discharged from the last effect of evaporator. The thenardite which crystallized with salt in the evaporation process was redissolved by mixing the slurry with raw feed brine in normal temperature. The washed salt becomes the finished product salt after dewatering and drying. The salt washing brine was heated up to 90°C with condensate and secondary steam, and be added salt to salt-out thenardite. The finished product of thenardite is produced through salt-out, washing, dewatering and drying. The actual production data were shown in table 3.

Table 3 Production Data of Salt Out Process of Co-production of Salt and Thenardite in

Yunying Region in Hubei Province

Items	Unit	°C	NaCl	Na_2SO_4	$CaSO_4$	$MgSO_4$	H_2O
Raw brine	g/l	25	270.5	26.46	1.52	1.05	
Settled matter of primary brine washing	%	30	26.94	8.70	1.90	0.06	62.4
Salt washing brine	g/l	30	285.25	78.06	0.66	1.18	
Feed liquor to I effect	g/l	140	311.0	54.52	0.33	0.29	
Feed liquor to II effect	g/l	125	305.0	54.86	0.41	0.36	
Feed liquor to III effect	g/l	100	306.7	56.58	0.21	1.09	
Feed liquor to IV effect	g/l	60	304.2	56.36	0.21	5.45	
Salt washing mother liquor	g/l	90	306.7	56.58	0.21	1.18	
Thenardite after salt out	%	90	9.82	50.44	31.36	0.46	7.92
Refined salt	%	70	95.09	0.37	0.02	0.01	4.36

(1) The problems were found in the actual production process

The recovery of sodium sulfate through brine mixing, lowering temperature and salt washing was limited by temperature and solubility. According to table 2, the solubility of sodium sulfate in brine is 80.8 g/l at ambient temperature and the solubility of sodium sulfate in brine is 52.0 g/l at 90°C temperature. In theory, the process of thenardite redissolving in raw brine is limited when the concentration of sodium sulfate in the raw feed solution is more than 30 g/l.

Scaling occurs in the pre-heating process of salt washing brine. According to table 3, the process of pre-heating of salt washing brine and salt-out include the process of sodium chloride dissolving and the process of sodium sulfate and calcium sulfate separation. The secondary steam pre-heater is affected by scaling and frequent flushing.

The impurities compounds of calcium and magnesium separated out from brine. According to table 3, calcium sulfate is separated out in the process of salt washing, pre-heating and salt-out, Magnesium sulfate are separated out in the process of pre-heating and salt out. The quality of sodium chloride and sodium sulfate products is affected by these impurities compounds.

The heat economy of four effects evaporators is lower.

(2) The improvement methods

Based on the progress of production technique and automation technology, the relevant technical and economical indices can be improved by following methods

Brine purification process is used to remove calcium and magnesium impurities in raw brine. The quality of sodium sulfate product can be improved to more than 99%.

Adoption of five effects evaporators instead of four effect evaporators for salt making can improve the heat economy of evaporation system by more than 3.79%.

Adoption of DCS automation system, the production system was running continuously and stably. The annual effective production period can be increased to more than 320 days.

Salt product can be improved to more than 99.1% with the method of refined brine washing and mother liquor recirculation.

It is helpful to control the quality of thenardite product, that instead of salt-out for thenardite separation by evaporation the salt washing brine to produce thenardite.

1.2 The Imported technology

The imported evaporation process of co-production of salt and thenardite was shown in figure 2.

In the process, the purified brine is fed in co-current through pre-heating with condensate and secondary steam. Salt is produced through evaporators of 201 to 304, and discharged after washing with purified brine in the evaporator's salt leg. Salt product was formed after dewatering and drying. The mother liquor of salt making is fed into 301 hot pump and thenardite evaporator after pre-heating with secondary steam from302 flashing tank and 301

thenardite making tank. Thenardite product is produced through washing of thenardite slurry with 304 salt making mother liquor, dewatering and drying. The relevant actual production data refer to table 4.

Table 4 Production Data of Imported Evaporation Process of Co-production of Salt and Thenardite with Sodium Sulfate Brine

Items	Unit	℃	Operation Data		Saturated Liquor		Remarks
			NaCl	Na_2SO_4	NaCl	Na_2SO_4	
Purified brine	g/l	30	300.0	15.0	277.0	80.8	
201 feed liquor	g/l	107	339.0	21.07	306.0	54.3	
202 feed liquor	g/l	85.6	329.0	29.85	305.0	53.7	
203 feed liquor	g/l	63.3	310.0	47.16	299.0	58.2	
304 feed liquor	g/l	47.9	296.0	62.29	294.0	64.0	
301 feed liquor	g/l	98	309.0	53.74	307.0	53.7	
302 feed liquor	g/l	78.2	305.0	53.97	304.0	55.2	
Sodium sulfate	%	70	0.80	99.0			
Refined salt	%	70	99.5	0.20			

According to the actual production situation, due to the limit of compression ratio of thermal pump, the thermal transfer capacity for unit area is lower and the heating area is bigger, thenardite mother liquor flash tank 302 and salt mother liquor pre-heaters 305 and 306 are apt to scaling for the adoption of thermal pump four effects evaporators for salt making. Based on the progress of automation technology and relevant technical, the economical indices can be improved by taking the following measures:

(1) Thenardite quality can be improved to more than 99.5% by using the thenardite solution to wash the thenardite slurry circularly.

(2) Evaporation thermal economy was improved to more than 3.79 for salt making by instead of four effects evaporators with five effects evaporators.

(3) Eliminating the thermal pump for salt making evaporation can increase the evaporation capacity of unit area for salt making, and can improved the adaptability of the process on the variation of thenardite concentration in raw brine.

(4) Eliminating of flashing tank can avoid the scaling in thenardite production system, keep the stability of production process, and extend the effective production period.

(5) Adopting the heat exchanger with forced solid recirculation (patented equipment) can minimize the scaling of pre-heaters 305 and 306.

2. New Hot Recirculation Process

Based on the analysis of above processes for co-production of salt and thenardite, a new process (patent No. 200610114043) were recommended to improve the process of the co-production of salt and thenardite(or thenardite and salt).The process flow are shown in figure

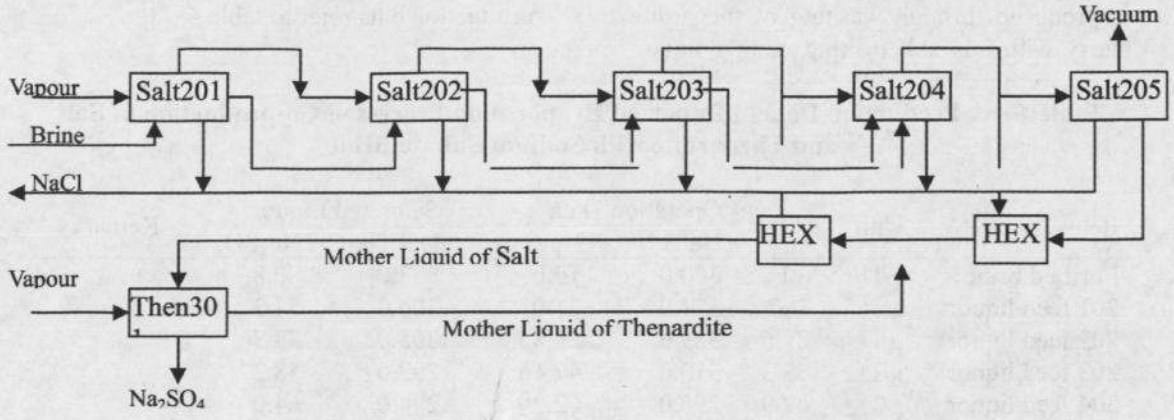

Fig. 3 Flow Diagram of Recirculation Process of Co-production of Salt and

The Purified brine is fed into deaerator for evaporation and concentration after heat exchange with condensate. The deaerated purified brine is pre-heated by the secondary steam from the evaporators of I to IV effects, and flows in co-current into I to V effect evaporators for salt making. The salt slurry is treaded by washing, dewatering and drying. The mother liquor of salt making from V effect evaporator is pumped to thenardite evaporator to produce thenardite, after two steps pre-heat by the secondary steam from IV effect evaporator and thenardite making evaporator. The thenardite slurry is treaded by washing, dewatering and drying. The mother liquor of thenardite making flows to the salt making system.

The following are the main operation parameters (table 5) and equipment (table 6) of the new recirculation process of co-production of salt and thenardite for a 600,000 t/a refined salt and 30,000 t/a sodium sulfate plant based on the composition of raw brine of NaCl 286 g/l, Na_2SO_4 16 g/l, $CaSO_4$ 1.0 g/l and $MgSO_4$ 0.6 g/l.

Table 5 Evaporation Process Parameters

Items	I Effect	II Effect	III Effect	IV Effect	V Effect	Thenardite Making
Steam temperature in heating chamber °C	140	118	100	82	63	100
Pressure in heating chamber MPa (a)	0.34	0.19	0.10	0.05	0.02	0.10
Liquid temperature in evaporation chamber °C	130	110	90	69	48	90
Pressure in evaporation chamber MPa (a)	0.19	0.10	0.05	0.02	0.01	0.05
Na_2SO_4 content in feed liquor (g/l)	19.2	24.6	33.2	55.0	62.0	54.0
Na_2SO_4 content in saturated brine (g/l)	54.8	54.5	51.6	56.5	64.0	51.6
Brine flow rate at inlet m^3/h	274	234	182	135+429	92+411	448
Brine flow rate at out let m^3/h	234	182	135	92+411	448	429

Table 6 List of Major Equipment of Evaporation and Pre-heating

SN	Items	Size	Quantity	Remarks
1	Salt making evaporator	F=1000 m^2	5	
2	Concentrator deaerator	F=200 m^2	1	
3	Purified brine pre-heater	F=300 m^2	5	
4	Salt making mother liquor pre-heater	F=1000 m^2	2	
5	Thenardite making evaporator	F=1000 m^2	1	

(1) The five effects evaporators for salt making: I effect evaporator steam pressure is 3 kgf/cm^2 (g) and temperature is 143°C. V effect evaporator vacuum is 0.092 MPa and feed liquor temperature is 48°C. The ratio of solid and liquor in salt slurry is 15-30% for each effect evaporator, and 50% for discharge in purified brine washing. The flow rate of purified brine is 280 m^3/h. The recirculating volume of salt making mother liquor is 448 m^3/h. The Salt production is 78 t/h. The evaporator of forced recirculation and feeding in axial direction is adopted.

(2) The concentration and deaeration of purified brine: Purified brine is pre-heated with mixed condensate to 48°C. Purified brine flow rate is 280 m^3/h. Purified brine is then heated, evaporated and concentrated with the secondary steam from IV effect evaporator. The vacuum in deaerator is 0.092 MPa. Feed liquor temperature is 48°C. The deaeration evaporator of forced recirculation and feeding in axial direction is adopted.

(3) Pre-heating of purified brine with secondary steam: After concentration and deaeration purified brine is pre-heated with the secondary steam from the evaporators of I to III effects. The initial temperature of purified brine is 48°C and final temperature is 115°C. Concentrated purified brine production is 274 m^3/h. Tube type heat exchanger is adopted.

(4) Vacuum system: Mist spray condensing tower, secondary steam injector and primary water injector are used for the vacuum system of V effect evaporator for salt making. The vacuum is 0.092 MPa. Recirculating cooling water supply temperature is 32°C and return water temperature is 38°C.

(5) Pre-heating of salt making mother liquor: The temperature of salt making mother liquor pre-heated with the secondary steam from IV effect evaporator is 48°C at the inlet and 56°C at the outlet. The temperature of the salt making mother liquor pre-heated with the secondary steam from thenardite making and III effect evaporator is 56°C at the inlet and 75°C at the outlet. Salt making mother liquor flow rate is 448 m^3/h.

(6) Thermal pump evaporation for thenardite making: The working pressure is 3 kgf/cm^2 (g). The temperature is 151°C. Feed liquor temperature is 90°C. Compositions of thenardite making mother liquor are Nacl 308 g/l and Na_2SO_4 54 g/l. Thenardite making mother liquor flow rate is 429 m^3/h. Solid and liquor ratio for washing thenardite slurry with recirculating thenardite water is 50%. Forced recirculation and feeding in axial direction evaporator is adopted.

(7) Product quality: Purity of refined salt has NaCl content more than 99.5%. Absolute thenardite has Na_2SO_4 content more than 99.5%.

3. The benefits of the new process

(1) Five effects equal area evaporators are used in the process for salt making, which is favorable for domestic manufacturing of standard and non-standard equipment of 1,000,000 t/a capacity plant.

(2) Flashing tank is eliminated and forced recirculating pre-heater is used for salt making mother liquor, which is favorable for simplifying the process flow, minimize scaling issue in thenardite system and extend effective production period.

(3) This process is favorable for the secondary steam from IV effect flashing for thenardite making to carry out evaporation, concentration and deaeration of purified brine, incease the thermal economy of the system, minimize corrosion issue of the equipment of evaporation system and balance the five effect evaporation system for salt making and the evaporation system for thenardite making.

(4) The recirculating thenardite solution is used for thenardite slurry washing in the process, which is favorable for improving

thenardite product quality to more than 99.5%.

(5) The thenardite system is simplified in the process, which is favorable for lowering investment.

(6) This process has a strong adaptability on the variation of thenardite content in raw brine, which is favorable for extending service lifetime of brine well. This principle process flow is also adaptable for co-production of salt and thenardite.

(7) The thermal economy of the evaporation system in the process is increased to 3.35. Energy consumption is decreased. Quality of salt and thenardite products is improved. Both technical and economic indices of the process are better than the those both at home and abroad. Competitive power of the products is strengthened. It has a broad application prospect.

4. Conclusion

To sum up, the recirculation process of co-production of salt and thenardite can produce economically and reasonably salt and thenardite with $NaCl\text{-}Na_2SO_4\text{-}H_2O$ salt system.

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Peng Saijun, male, deputy chief engineer of China BCEL International Engineering Co., Ltd., mainly engaged in the research and design works on salt chemicals.