

VOL. 61, 2017



DOI: 10.3303/CET1761287

#### Guest Editors: Petar S Varbanov, Rongxin Su, Hon Loong Lam, Xia Liu, Jiří J Klemeš Copyright © 2017, AIDIC Servizi S.r.I. ISBN978-88-95608-51-8; ISSN 2283-9216

# Simulation and Optimization of Salt-Production Process from Desalination Brine

# Lianying Wu\*, Teng Sun, Yangdong Hu

College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, Shandong, China wulianying@ouc.edu.cn

A novel multi-salt crystallization process is presented to separate the salts from the desalination brine and is optimized using the gradual optimization integration strategy based on T-H diagram. Firstly, the process is simulated by Aspen Plus software to obtain the cold and hot load curve and the bottlenecks and unreasonable heat transfer processes are analysed. Secondly, considering the energy utilization and conversion procedure, the turbine and/or heat pump are introduced to improve the process. Then the parameters of production process and utility system are adjusted. Thirdly, the new stream information is obtained by process simulation and the new composite curves are drawn, which will guide the further adjustment of the system. If the new composite curves do not satisfy the process demand, then the above steps are repeated. Through several improvements, two approximate parallel hot and cold stream curves are constructed. The hot streams and cold streams are maximum possible matched, and the amount of utility and power consumption is significantly reduced. In a case study, two optimization schemes are adopted: the feed brine is preheated by the flash steam and the heat pump crystallization technology is introduced. The results show that the energy consumption of two optimized processes is 94.8 kW and 90.1 kW, and the total energy loss decreased 86.7 % and 87.3 %.

# 1. Introduction

Seawater desalination is one of the most useful modern technologies to open up new water resources in largescale and plays an important role in solving the water shortage problem (Kim D. H., 2011). But desalination produces concentrated brine which can cause a series of problems to marine and underground habitat. The treatment of the brine has presented technical, economic and environmental challenges.

Some researchers have focused on the issues and several techniques are used to remove dissolved solids from brine including electro-dialysis (ED) (Korngold, et al.,2009) and ion exchange membrane (Kobuchi et al.,1983), mechanical vapor compression systems (MVC) (Ericsson and Hallmans, 1996), Solar salt-works (Sedivy, 2009) and solar evaporation ponds (Ravizky and Nadav, 2007). Apart from the above processes, newer processes such as SAL-PROC also exist where brine is sequentially crystallized using both evaporation and chemical processing (Ahmed, et al., 2003). The supercritical water desalination (SCWD) process is used to treat the saltwater streams with zero liquid discharge (Odu et al., 2015). In Tianjin Northern power plant, the brine is introduced into HanguChanglu salt field, which can greatly improve the efficiency of salt-production. The annual output can rise by 500,000 t and the salt-production mother liquor is introduced into the chemical products, such as bromine, potassium chloride, magnesium chloride, magnesium sulphate. and zero discharge is achieved (Zhang et al., 2008). More recently, membrane distillation (MD) (Tun et al., 2005) and integrated membrane distillation-crystallization (Creusen et al. 2013) have emerged as an alternative technology for an integrated brine concentration and crystallization process including crystallization of concentrated salts–flux and crystal formation.

Improvement in energy consumption is important to the multi-salt crystallization process. In this paper, considering the energy utilization and conversion procedure, the turbine and/or heat pump are introduced to improve the process and the optimal crystallization separation scheme is obtained using the gradual optimization integration strategy.

1735

# 2. Mathematical model

The schematic of evaporation and crystallization is shown in Figure 1. The system includes evaporator, crystallizer and centrifuge. The raw material liquid is sent to the evaporator through a circulating pump. Then it goes into the crystallization evaporator chamber after being heated. The solution is delivered straight to the bottom of crystallizer after the secondary steam is separated, where the concentrate solution is super-saturation and crystal grain is obtained. When the particles grow to a specific size, the suspension liquid goes out from the bottom of crystallizer and is pumped into the centrifuge to separate. The liquid is recycled to the evaporator and the crystal products are sent to be dried.



Figure 1: The evaporation crystallization process flow diagram

# 2.1 Evaporator model

The mass balance and energy balance of the evaporator are formulated as Eq(1) and Eq(2).

$$F \cdot X_0 = (F - W) \cdot X_1 \tag{1}$$

$$D \cdot H + F \cdot H_0 = W \cdot H' + (F - W) \cdot h_1 + D \cdot h_W + Q_L$$
<sup>(2)</sup>

where *F* is the flow rate of liquid raw materials [kg/h], *W* is the water steam flow rate of the evaporation in a unit time [kg/h],  $X_0$  is quality fraction of raw material liquid,  $X_1$  is quality fraction ofconcentrated solution from the crystalizer bottom, *D* is the heating steam flow rate [kg/h], *H* is the enthalpy of steam heating [kJ/kg],  $h_0$  is the enthalpy of raw material liquid [kJ/kg], *H*' is the enthalpy of secondary steam [kJ/kg],  $h_1$  is the enthalpy of complete solution [kJ/kg],  $h_w$  is the enthalpy of condensation water [kJ/kg], and  $Q_L$  is heat loss [kJ/kg].

# 2.2 Crystallizer model

The mass balance and energy balance of the evaporator are formulated as equation (3) and equation (4)

$$F \cdot C_1 = G + F \cdot (1 - V) \cdot C_2 \tag{3}$$

$$V \cdot F \cdot r_s = F \cdot C_p \cdot (t_1 - t_2) \cdot (1 + C_1) + r_{cr} \cdot G \tag{4}$$

where  $C_1$  and  $C_2$  are the mass concentration of material liquid and recycling liquid [kg/m<sup>3</sup>], *G* is the quantity of crystallization [kg/h], *V* is the amount of evaporation solvent [kg/h],  $r_{cr}$  and  $r_s$  are heat of crystallization and vaporization [kJ/kg],  $t_1$  and  $t_2$  are initial and end temperature of solution [K], and  $C_p$  is specific heat of solution [kJ/kg k].

# 3. Optimization scheme

The optimization and design of the salts production process from the brine is performed using the gradual optimization integration strategy (GOIS), which is put forward by author (Wu et al., 2013). The basic idea of the GOIS is described as following steps.

- (1) The initial technological process is determined and the character of cold and hot utility stream is specified.
- (2) The process is simulated by Aspen Plus software to obtain the cold and hot load curves. The bottlenecks and unreasonable heat transfer processes are determined through analysing composite curves of hot and cold load.

1736

- (3) To overcome or improve the bottlenecks and unreasonable processes, a turbine or heat pump is introduced to the initial process after considering the energy utilization and conversion procedure. The new production process is then conducted and the parameters of production process and utility streams are adjusted to meet the new process.
- (4) The new stream information is obtained by process simulation and the new composite curves are drawn, which will guide the further adjustment of the system.
- (5) If the new composite curves do not satisfy the process demand, then the above steps are repeated until finally two approximate parallel hot and cold stream curves are constructed. The optimal production process is then obtained. The heat is reasonably used, the hot streams and cold streams are fully matched, and the amount of utility and power consumption is significantly reduced.

While the process is improved, economic evaluation of the improvement process also has been made.

# 4. Case study

# 4.1 Crystallization separation scheme

A crystallization separation scheme is proposed as shown in Figure 2. The process includes a reactor and four crystallizers. As the magnesium ion is easy to generate double salt and the number of crystal water of magnesium salt is uncertainty, the lime is added to make Mg<sup>2+</sup> translate to Mg(OH)<sub>2</sub> sediment firstly. In order to obtain the highly purified CaCl<sub>2</sub> crystal, the other positive ions must be crystallized as much as possible before entering the CaCl<sub>2</sub> crystallizer. and the optimal crystallization sequence of various salts is Mg(OH)<sub>2</sub>—CaSO<sub>4</sub>—NaCl—KCl—CaCl<sub>2</sub>.



Figure 2: Crystallization separation scheme flow chart

#### 4.2 Determination of crystallization conditions

The crystallization separation scheme is simulated by Aspen Plus software, which determines a suitable crystallization temperature and pressure. The aim is to obtain the maximum of salt crystallization production and also meet the salt purity and other salts precipitate as little as possible. In the simulation, the amount of evaporation water and crystallization changes through constantly adjusting the temperature, pressure and other parameters. Considering the crystal purity and yield, the best crystallization temperature and pressure are obtained. Then the load of process stream and utility streams are determined. The composite curve of cold and hot streams is drawn on the T-H diagram.

#### 4.3 Simulation results

The feed rate is 1,000 kg/h, the feed temperature is 25 °C and the feed pressure is 101 kPa. Crystallization temperature and pressure of various salts are in Table 1. The simulation results of crystallization separation scheme are in Table 2.

	-		•	
Salts	CaSO <sub>4</sub>	NaCl	KCI	CaCl <sub>2</sub> •4H <sub>2</sub> O
T, ⁰C	118	60	100	135
P, kPa	137	12	10	101

Table 1: Crystallization	temperature and	l pressure of	<sup>r</sup> various salts
--------------------------	-----------------	---------------	----------------------------

Salts	CaSO <sub>4</sub>	NaCl	KCI	CaCl <sub>2</sub>	Mg(OH) <sub>2</sub>
Feed rate, (kg·h <sup>-1</sup> )	1,051.6	193	28.2	14.1	1,057.4
Feed temperature, °C	118	60	70	135	25
Crystilization temperature, °C	118	60	70	139	25
Crystilization pressure, kPa	137	12	10	101	101
Crystal, kg h <sup>-1</sup>	6.78	45.94	2.98	12.30	5.76
Purity, %	100	99.9	41.9	98.2	100
Recovery, %	99.1	96.1	92.3	100	99.6
Total energy consumption, kW			710.5		

The separation of various ions has been achieved and pure inorganic salt crystals have been obtained. Zero discharge of brine has also been realized. The Composite Curves of original and optimized processes are shown in Figures 3, 5 and 7.



Figure 3: The Composite Curve of original process

As shown in Figure 3, the original process has no energy matching and needs much external utilities. Two improvement schemes are proposed to decrease the load of utility. One is that the feed is preheated by the secondary steam, the other is that the heat pump is introduced to separation process.

#### 4.4 Improvement scheme I- feed preheating process

It will cause huge waste of energy if the secondary steam is condensated directly, which is separated from evaporation chamber. Therefore, the first improvement scheme is proposed that the secondary steam is used to preheat feed brine (Figure 4a).



Figure 4: (a) Flow chart of preheating brine process. (b) The composite curve of preheating feed process

As shown in Figure 4b, through the secondary steam recycling to evaporator to preheat the feed stream, the composite curve of heat and cold stream match better than that of initial separation scheme. The integrated energy of inside process stream is 615.7 kW. The required quantity of heat utility and cold utility is 26.4 kW and 68.4 kW. The total energy consumption is 94.8 kW. The quantity of heat utility approximately is reduced 86.7 % than the initial separation scheme.

#### 4.5 Improvement scheme II- heat pump crystallization process

To further reduce the energy consumption, the heat pump crystallization scheme is introduced to the separation process (Figure 5a). The steam separated from the evaporation chamber is compressed by the heat pump compressor and is sent back to the evaporator as heating steam. The composite curve of this process is shown as Figure 5b.



Figure 5: (a) Flow chart of heat pump process. (b) The composite curve of heat pump process

In Figure 5b, the composite curves of the hot and cold streams are good match with two almost parallel composite curves being constructed. The amount of integrated energy of inside stream reaches 642.1 kW and external hot utility is not required. The total energy consumption is 90.1 kW. The energy consumption of compressor is converted to thermal energy. The energy consumption comparison of the original process to the improved processes are given in Table3.

Table 3: Energy consumption of original process and improved processes

	Energy integration, kW	Hot utility, kW	Cool utility, kW	Compressor, kW
Original	—	642.1	68.4	_
Improvement scheme I	615.7	26.4	68.4	—
Improvement scheme II	642.1	0	68.4	21.7

# 5. Conclusions

In this paper, a comprehensive utilization scheme of desalination brine is proposed. Brine sequentially passes through several evaporation crystallizers and reactors, then valuable inorganic salt products, such as Mg(OH)<sub>2</sub>, CaSO<sub>4</sub>, NaCl, KCl and CaCl<sub>2</sub> are collected in a specific sequence. Zero discharge of brine is achieved. The separation process is simulated by Aspen Plus to determine the technological parameters.

The process of salt-production from brine is optimized based on the gradual optimization integration strategy. Two improvement schemes are put forward: (1) the steam separated from the evaporation chamber is used to preheat the feed brine and (2) The heat pump crystallization technology is introduced to the separation process. The energy consumption of the two improvement schemes is 94.8 kW and 90.1 kW. The total energy consumption decreased 86.7 % and 87.3 %. The heat pump crystallization process is better than the feed preheating process.

# Acknowledgment

This work was financially supported by the National Nature Science Fund Program of China (No.21376231).

# Reference

Ahmed M., Arakel A., Hoey D., Thumarukudy M.R., Goosen M.F.a., AlHaddabi M., Al-Belushi A., 2003, Feasibility of salt production from inland RO desalination plant reject brine: a case study, Desalination, 158,109–117.

- Chen G., Lu Y., Krantz W.B., Wang R., Fane A.G., 2014, Optimization of operating conditions for a continuous membrane distillation crystallization process with zero salty water discharge, Journal Membrane Science, 450,1–11.
- Creusen R., van Medevoort J., Roelands M., van Duivenbode A., Hanemaaijer J.H., van Leerdam R., 2013, Integrated membrane distillation-crystallization: process design and cost estimations for seawater treatment and fluxes of single salt solutions, Desalination, 323, 8–16.
- Ericsson B., Hallmans B., 1996, Treatment of saline wastewater for zero discharge at the Debiensko coal mines in Poland, Desalination, 105, 115–123.
- Kim D H. 2011, A review of desalting process techniques and economic analysis of the recovery of salts from retentates. Desalination, 270, 1–8
- Kobuchi Y., Terada Y., Tani Y., 1983, The first salt plant in the Middle East using electrodialysis and ion exchange membranes, Sixth Int. Symp. Salt II., Toronto, Canada, 541–555.
- Korngold E., Aronov L., Daltrophe N., 2009, Electrodialysis of brine solutions discharged from an RO plant, Desalination, 242, 215-227
- Meng S., Ye Y., Mansouri J., Chen V., 2015, Crystallization behaviour of salts during membrane distillation with hydrophobic and super hydrophobic capillary membranes, Journal Membrane Science, 473,165–176.
- Odu S.O., van der Ham A.G.J., Metz S., Kersten S.R.A., 2015, Design of a process for supercritical water desalination with zero liquid discharge, Industry Engineering Chemical Research, 54, 5527-5535.
- Ravizky A., Nadav N., 2007, Salt production by the evaporation of SWRO brine in Eilat: a success story, Desalination, 205, 374–379.
- Sedivy V.M., 2009, Environmental balance of salt production speaks in favour of solar salt works, Global NEST J., 11, 41–48.
- Tun C.M., Fane A.G., Matheickal J.T., Sheikholeslami R., 2005, Membrane distillation crystallization of concentrated salts–flux and crystal formation, Journal Membrane Science, 257, 144–155.
- Wu X., Wu L., Hu Y., 2013, Total site gradual energy integration and optimization strategy based on T-H diagram, Journal of Chemical Industry and Engineering, 64, 1696-1703.
- Zhang N., Su Y., Su H., 2008, Review on the comprehensive utilization of concentrated seawater in desalination industry, Marine Sciences, 6, 85-88.