The application of structured packing in industrial extraction of bromine from concentrated seawater

Qi Zhang, Wei Liu, Shujing Chai, Zejiang Wang, Xiaoyu Yu, Wenyuan Zhang, Xiaocui Hao, Dan Wu, Tao Li, Xiping Huang*

The Institute of Seawater Desalination & Multipurpose Utilization, Tianjin, China

*Corresponding author e-mail: xipinghuang@163.com

Abstract. In this paper, a pilot plant for bromine extraction with the consumption of 500 m³/d concentrated seawater was designed, built and operated based on the Henry’s constant. The energy consumption and yield of the blowing-out tower filled with structured packing and traditional random packing were compared by the air blowing-out method. It showed advantages applying the structured packing than the random packing according to the experiment dates, and it will achieve great market prospect that combining seawater desalination with bromine extraction.

1. Introduction

Bromine which is described as “marine elements” is an important industrial raw material [1,2]. In China, the air blowing-out method is commonly used to extract bromine from underground brine with low concentration of 200~300 mg/L. The process includes the following steps of oxidization, blowing-out, absorption, distillation, condensation and purification. However, there are some bottlenecks in China bromine industry. First, the underground brine is becoming less and less with nearly 30,000 tons of bromine being imported every year. Second, the blowing-out towers applied in the industrial production are usually filled with the random packing-polypropylene cascade ring packing, the yield is low due to the poor contact state between the gas and the liquid phases, and the ratio of gas/liquid is about 120~150:1, energy consumption is larger [3,4]. So, the demand for the new resource of extracting bromine with low cost is very urgent.

Now, it will achieve a bright prospect that extracting bromine from the concentrated seawater instead of underground brine with the increasing number of desalination projects. There are some advantages for concentrated seawater as the resource to extract bromine. First, the supply is very stable and large. Extracting bromine from underground brine is often subject to policy restrictions for environmental consideration in China. However, the supply of concentrated seawater containing bromine from desalination projects is non-stop. It is estimated that the amount of concentrated seawater discharged from a desalination plant with a capacity of 100,000 m³/d is sufficient for a bromine factory with a capacity of 3,500 t/a. Second, the temperature of the concentrated seawater is high enough for extracting bromine, which will increase the yield of bromine. It’s reported that the yield is only about 60% when the temperature is under 10 ℃, and it is 85% when the temperature is 30 ℃. Third, compared with the seawater, the concentration of bromine has been doubled, which helps to reduce the cost of extraction. Forth, the concentrated seawater is very clean without precipitation of CaSO₄ in the bromine production.
When the underground brine is used as bromine resource, the packing is often blocked by the precipitation of CaSO\textsubscript{4} leading to the production stoppages. Though the random packing is relatively easy to replace and clean, it should be avoided. Therefore, due to its advantages of large surface area, small pressure drops, uniform fluid and high mass transfer efficiency, the new structured packing represented by orifice corrugated packing can be used to replace the traditional random packing when there is no blockage in the production, which has been used in the improvement of desorption towers successfully in many industrial fields.

In this paper, based on the equilibrium data of concentrated seawater-bromine system, the energy consumption and productivity of the blowing-out tower filled with structured packing were compared with those of random packing in the bromine factory. The results will help to make the best use of the concentrated seawater in the commercial extraction of bromine.

2. Methodology
A pilot plant for bromine extraction with the consumption of 500 m\textsuperscript{3}/d concentrated seawater was designed, built and operated. The pilot plant consisted of blowing-out tower, absorption tower, purification tower and a fan, the process was the same as that of the factory. The diameter of the towers is 0.8m with 6.5m of the packing height in the blowing-out tower. And there were 4 spray nozzles in the tower. The experiments were conducted by comparing the pressure drop and yield of the tower filled with polypropylene structured packing SNB100 and DN38 polypropylene cascade ring packing in the same condition with the air blowing-out method.

In the experiment, the concentrated seawater with the bromine concentration of 150 mg/L was subject to acidification and oxidation in the conveying pipeline of the bromine factory, so that the bromine ions in concentrated seawater transformed into free bromine. Free bromine-containing concentrated seawater and purified air were introduced from the top and bottom of the blowing-out tower respectively for counter-current contact, and then the concentrated seawater left by bromine was discharged from the bottom of the blowing-out tower, while free bromine was blew out by air and brought into the absorption tower from the top of the blowing-out tower. In the absorption tower, the free bromine in the air reacted with the absorption solution to become bromine irons, and then the air without bromine went back to the blowing-out tower after flowing through the purification tower. The yield was calculated by using the concentration of the bromine ions in the concentrated seawater at the top and bottom of the blowing-out tower, and the pressure drop was measured by electronic differential pressure gauge with the measurement points at the top and bottom of the packing layer.

3. Research results and discussion
3.1. Characteristics of Structured Packing Tower in Extracting Bromine
Based on the above date, the diameter of the structured packing towers designed is 0.8m, the height of the packing is 6.5m. SNB100 orifice corrugated packing and DN38 cascade ring packing were chosen as the representatives of structured packing and random packing to filled in the blowing-out tower, respectively. The calculation process is omitted here.

3.2. Characteristics of Pressure Drop
The pressure drop curve with the gas velocity was shown in Figure 1. It can be seen that at the same gas velocity and the same spray density, the pressure drop of structured packing is lower than that of the random packing by about 30%~40%. There was flooding appeared at experiment conditions when using cascade ring packing, while there was no flooding appeared in all the experiment conditions when using SNB100. So, when the blowing-out tower needs upgrading in the further, it will largely increase the capacity of blowing-out tower or decrease the energy consumption by applying SNB100 instead of traditional cascade ring packing with the same packing height.
3.3. Characteristics of yield

The relationship of the yield with the gas/liquid ratio by DN38 cascade ring and structured packing SNB100 were shown in figure 2. When the gas/liquid ratio is 80~100:1, the yield is both near to 90%, which means the packing height is enough to extract bromine in this experiment. However, at the same gas/liquid ratio, the yield increased with the increase of the liquid spray density when using DN38 cascade ring. This may because the accumulation of random packing was not ideal, the packing wasn’t completely wet when the liquid spray density is low, the effective mass transfer area of packing increase with the increase of liquid spray density. While the yield stayed nearly the same when using structured
packing SNB100, which means the theory plate height of structured packing changed little with the spraying density, the contact station of gas and liquid is good enough even at low liquid spray density.

![Diagram of yield with gas/liquid ratio](image)

**Figure 2.** Relationship diagram of yield with gas/liquid ratio

3.4. Energy consumption with separation efficiency

The separation efficiency can be expressed by the relationship of total pressure drop and yield. Because the concentration of bromine in the concentrated seawater is nearly all the 150 mg/L, the concentration of bromine in the effluent may also reflect the yield. In figure 3, it can be seen that when the concentration of bromine in the effluent reach 6ppm, it will take total pressure of 3000 Pa for DN38 cascade ring at the liquid spray density of 40m³/m²h, while only 1250 Pa for SNB100. On the other hand,
when the total pressure drop is 1500 Pa, the concentration of bromine in the effluent was 10 ppm for DN38 cascade ring, while it’s 6 ppm for SNB100. From above, it can be concluded that it will show higher separation efficiency and lower energy consumption for SNB100 instead of DN38 cascade ring.

![Graph showing relationship between total pressure drop and bromine concentration for DN38 cascade ring and SNB100.](image)

**Figure 3.** Relationship diagram of yield with total pressure drop

4. Conclusion
In this paper, a pilot plant of structured packing towers instead of random packing for bromine extraction with the consumption of 500 m$^3$/d concentrated seawater was designed, built and operated in the real factory based on the Henry’s constant for bromine-concentrated sea, which showed the energy
consumption decrease by 30% and higher separation efficiency under the same condition. Furthermore, the study on the scope of application of the structured packing is being investigated.

Above all, it will achieve great market prospect that combining seawater desalination and bromine extraction with structured packing instead of random packing, which can make the best use of the concentrated seawater and ensure the bromine supply with good economic benefit.

Acknowledgments

This work was financially supported by Public science and technology research funds projects of ocean (201505023), and Fundamental Research Funds for the Central Public Welfare Scientific Research Institution (K-JBYWF-2016-T6).

References

[1] L. C. Stewart. Commercial extraction of bromine from sea water, Industrial & Engineering Chemistry. 26 (1934) 361-369.
[2] M. E-H Amer. Chemical reaction engineering analysis of the blowout process for bromine manufacture from seawater, Industrial & Engineering Chemistry. 46 (2007) 3008-3015.
[3] J. Ren, P. L. Liu. After desalination process making bromide several water-saving improvement measures, Journal of Salt and Chemical Industry. 42 (2013) 36-37.
[4] W. LIU, R. H. Cai, Y. S. Zhang, etc. The application of tower equipment used in the industrial extraction of bromine, Journal of Salt and Chemical Industry. 39 (2013) 30-35.
[5] Q. S. Li, W. T. Ma, Z. T. Zhang. Research and development trend of column packing, Chemical Industry and Engineering Progress. 24 (2005) 619-624.