Development status and future development trend of bromine

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Abstract. Bromine is one of the important chemical raw materials. It is widely used in flame retardants, petroleum exploitation, fungicides, pesticides, photographic materials and medicine. Its preparation technology and application value are highly valued by scholars at home and abroad. This paper describes the production and sales of domestic and foreign bromine, introduces the process and advantages and disadvantages of industrial bromine extraction, and proposes the future development trend of bromine industry.

Keywords: Bromine; Production and marketing; Air Blowing

1. Introduction

Bromine is the first element discovered and separated from seawater. Bromine is widely used as a chemical raw material in flame retardants, petroleum extraction, fungicides, pesticides, photographic materials and medicine [1-4]. In 2016, the annual global production is about 820,000 tons. In recent years, with the rapid development of China's economy, market demand has grown strongly. However, compared with countries with large bromine resources such as Israel and the United States, the status quo of China's brine resources is worrying. The bromine industry faces the dilemma of the depletion of traditional bromine resources, making mining more and more difficult. China's bromine is mainly produced from the underground brine in Laizhou Bay, Shandong Province. Since the 1990s, the total amount of mining has exceeded 40% of the total bromine reserves of underground brines. The average bromine concentration of underground brines has also dropped from the original 350 g/m3. Up to now, about 200 g/m3, the shortage of supply and demand of bromine due to the sharp decrease in the total amount and grade of traditional brine resources has become the norm. Therefore, the full use of bromine resources in cultured brines can alleviate the problem of the shortage of bromine resources in China to a certain extent.

2. China's bromine production and sales

In 2008, the domestic production of bromine was about 160,000 tons, mainly distributed in Shandong, Hebei, Tianjin, Liaoning and other places. There are 140 bromine production plants and more than 200 sets. Among them, Shandong Weifang, Shouguang, Hanting and Changyi produced 40,000 tons each, Shandong Laizhou 15,000 tons, Dongying 0.4 million tons, Binzhou 0.8 million tons, Hebei 0.7 million tons, Tianjin 0.8 million tons, Liaoning, Jiangsu and other places small. Domestic bromine production

was about 130,000 tons in 2015, and domestic bromine production was about 150,000 tons in 2016. It can be seen from Figure 2 that from 2008 to 2016, there was no change in the main distribution areas of bromine production. In Shandong, Hebei, Tianjin, Liaoning and other places, Changchun produced the most, with a total output of 34,750 tons, and the total output decreased. The high concentration of underground brine in Sichuan has not developed much. The bromine of Yuncheng Salt Lake in Shanxi has been developed. The development and utilization of bromine in Xinjiang, Qinghai and Inner Mongolia has also attracted people's attention.

The total amount and grade of bromine resources in China are declining day by day. It is a consensus of academia and industry to develop new sources of bromine resources and develop low-energy and high-efficiency bromine extraction technologies.

The sales price of bromine in China has continued to rise in 2000-2018, especially the sales price of bromine has increased significantly in the past two years, which is related to the decrease in the total amount of bromine resources in China and the strong growth of market demand.

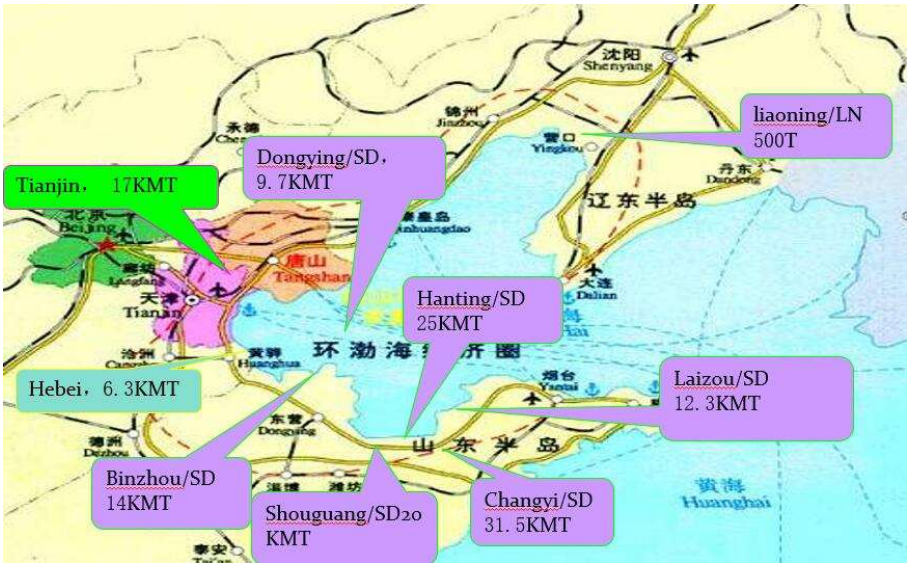

Figure 1. Distribution of bromine production in China in 2016

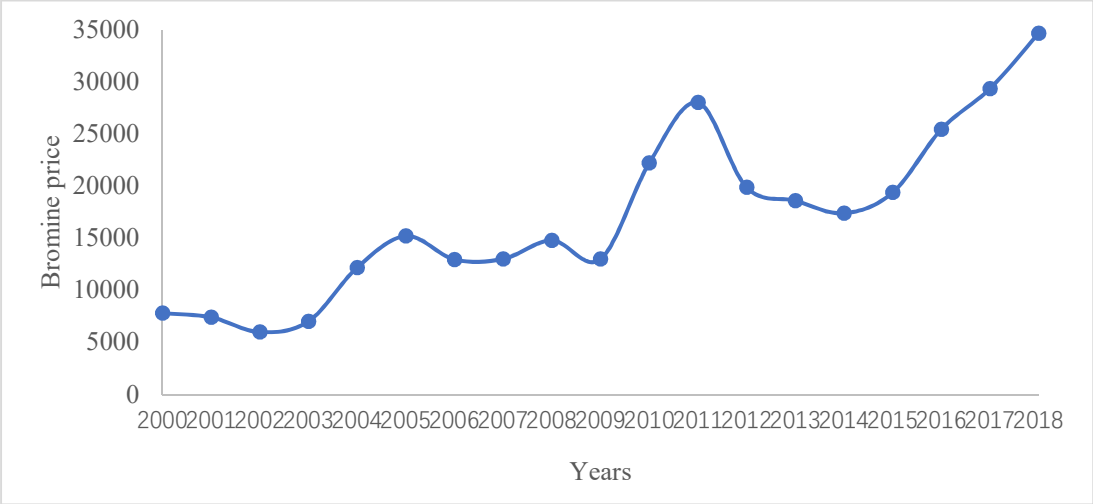

Figure 2. China's bromine sales price in 2000-2018

Table 1. Bromine imports from China

Years	Israel	Ke Juya	Albemarle	India	Japan	Total
2010	16000	1800	4800	0	0	22600
2011	16000	2600	4100	0	0	22700
2012	14600	4000	7700	0	0	26300
2013	21000	5400	7200	0	0	33600
2014	20000	9000	4800	600	0	34400
2015	14000	3400	3900	2500	17	23817
2016	19800	8200	6000	3200	0	37200

Although China is striving to find and develop new bromine resources, the year-on-year decline in production is a major trend. The amount of bromine used in China will increase or remain flat, and the contradiction between supply and demand of bromine will become more and more prominent. Before China can find large-scale, high-grade bromine resources, it can only rely on imports to balance this contradiction.

3. Bromine production and sales in the world

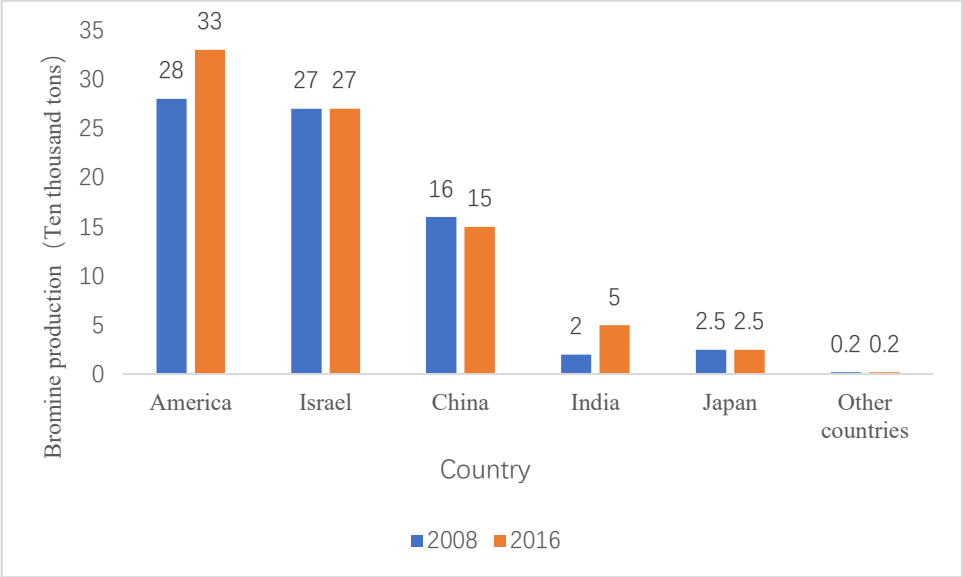

Figure 3. Bromine Capacity in 2008 and 2016

The production of bromine in the United States is declining due to the limitation of underground brine. The “Dead Sea” is controlled by Israel Chemical and American Albemarle. Their current bromine production capacity has exceeded 400,000 tons, which is more than half of the world's total production. With abundant resources, India's bromine capacity has developed rapidly, from 20,000 tons to 50,000 tons, and has been sold to China in bulk.

Some companies have begun to pay attention to the bromine resources of the salt lakes and lagoons in Iran's Umilye Salt Lake and some African countries. Countries such as Australia and Mexico that use seawater to make salt are also potential areas for the development and utilization of bromine resources. Domestic bromine production capacity is still the main raw brine in the Bohai Sea underground brine and sea salt field in recent years. Due to the year-on-year reduction of underground brines, bromine production capacity has been declining until new resources are discovered.

4. Industrialized bromine process

In 1934, the United States DOW Chemical Company first used soda ash as an absorbent to realize the industrial production of air blowing. By the early 1990s, 90% of the world's bromine was produced by this method [5]. China's bromine industrial technology was developed from the development of underground brine in Laizhou Bay in the 1980s. The process uses the “air blowing acid spray spray absorption and absorption tail gas closed cycle process”. This technology is increasingly mature, twice. He won the third prize of National Science and Technology Progress Award. With the over-exploitation of underground brines, the depletion of resources and the rising price of supply and demand in the bromine market, the country began to use the lower concentration to dilute the brine and seawater directly. The technology is still the traditional air-blowing acid spray. The foam capture and absorption tail gas closed cycle process, but improved in some technical details, the purpose is to improve the yield and reduce the production cost. Although domestic companies and research institutes have conducted experimental research on various methods, they have not been applied to the production process (resin adsorption method, membrane method, etc.).The process of producing bromine by acid method is that the concentrated seawater from the brine reservoir is input into the pipeline by the brine pump, and the acid and chlorine gas are added to the pump outlet pipeline, and further reacted by the oxidation tower to be sent to the blowing tower, and sprayed from the top of the tower. The blower blows air from the bottom of the tower to complete the gas-liquid exchange on the surface of the packing. The bromine in the brine is desorbed and blown out, and the waste liquid is discharged from the bottom of the tower. The bromine-containing air is discharged from the top of the tower, mixed with sulfur dioxide gas and fresh water spray added in the top air passage, and absorbed downstream, and formed small droplets of hydrobromic acid, which are enriched by the absorption tower and the trap to form bromine content. The higher hydrobromic acid completion liquid is passed through chlorine gas oxidation, steam distillation, condensation, washing and separation to obtain the finished industrial bromine. The simplified process flow of bromine by acid method is shown in Figure 4.

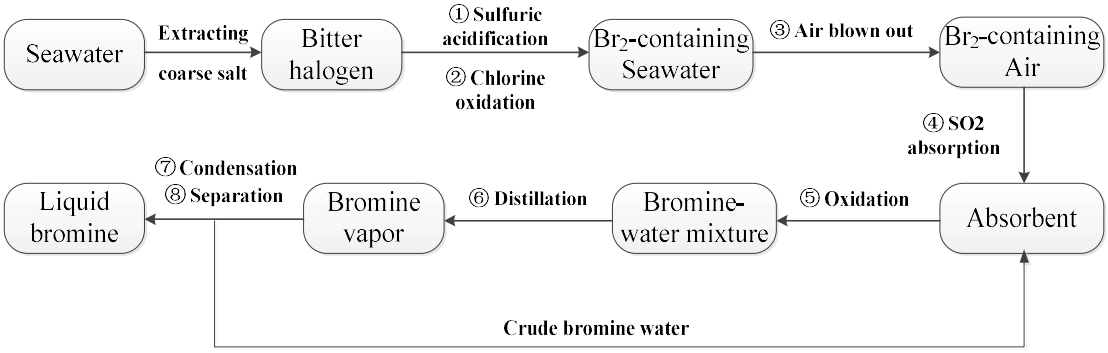

Figure 4. Acid Process Bromine Process

5. Future development trends

In terms of bromine extraction technology, at present, China mainly adopts the acid method air blowing bromine extraction process, which has the advantages of large operation flexibility, wide application range and simple operation, but also has the disadvantages of high energy consumption and low efficiency, which restricts efficient use of limited bromine resources in China. The reason is mainly because the process of blowing the tower multi-pile stepped ring is used as the packing, and the random distribution of the packing is large, which leads to poor flow contact between the gas and liquid two phases in the tower, and the non-ideal flow condition is serious, which affects Mass transfer effect; and in practical application, in order to improve the bromine blowing efficiency, the air blowing bromine extraction process is mostly operated under the condition of relatively large gas and liquid, the gas-liquid ratio is generally around 120-150, and the air amount and gas velocity are large, resulting in The

pressure drop of the whole tower is large, and the air transportation energy consumption is high. Therefore, it is urgent to upgrade industrial technologies and equipment to achieve efficient use of bromine resources and energy conservation and consumption reduction in the production process.

On the basis of the increasing shortage of resources in the bromine industry, finding new alternative resources is the trend of research today. For example, the application of culture brine, seawater desalinated concentrated brine and potassium-producing mother liquor [6], the development of brine extraction bromine new process, not only increased the source of bromine resources, but also to share the development cost of coastal saline-alkali tidal flat resources, improve the economic benefits of the industry Have a positive effect.

In view of the high energy consumption of bromine in the industry, the combination of bromine and electricity in the north is more economical. Using the resources of seawater cooling water from power plants to extract bromine and then make salt, from the perspective of circular economy, it is a project with multiple harvests. It is also an in-depth study of seawater desalination, concentrated saltwater utilization and circular economy in Beijiang Power Plant. The efficiency of this project will be more obvious with the electricity price before the power plant is connected to the Internet.

The finished bromine prepared by the industry has a purity of about 99.5%, and usually contains chloride ion impurities and organic impurities oxidized by chlorine and bromine. In some special cases, such as halogen lamps filled with tin bromide, spectrally pure bromine is required, so further purification of industrial bromine is required. In China, high-vacuum low-temperature purification method was reported. The sodium bromide was added to the raw material to remove free chlorine, and then heated to 850° C to remove organic impurities. Five vacuum reactors were used, and the first reactor was dried with magnesium perchlorate. The agent removes the moisture in the raw material; the latter four reactors are vacuumed and the temperature is lowered step by step. The experiment is selected to be as low as the liquid nitrogen temperature (-196 °C), and the partial pressure of the impurities under vacuum is much lower than the fraction of bromine vapor at low temperature. When pressed, the bromine is condensed at a low temperature, and the impurities remain in the last reactor, and finally ultra-high purity bromine is obtained, and the total mass fraction of all impurities is 1×10-7. This process is complicated and requires low temperature cold traps and high vacuum, thus hindering industrial applications [7].

6. Conclusions

Domestic bromine production capacity is still the main raw brine in the Bohai Sea underground brine and sea salt field in recent years. Due to the year-on-year reduction of underground brines, bromine production capacity has been declining until new resources are discovered.

Desalination of concentrated brine will provide greater capacity support for bromine production. However, due to the impact of environmental protection and comprehensive utilization of concentrated brine, the development and utilization of coastal areas without beach conditions are still under discussion. The utilization of cooling seawater for power generation in the northern coastal areas is currently limited to areas with beach conditions. Other places cannot be exploited due to lack of regulatory support and environmental pressure.

The preparation of high-purity bromine still has many difficulties and deserves the attention of researchers.

Acknowledgements

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