Application prospect of high efficiency and energy saving bromine extraction technology in the field of bromine-containing waste salt

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Abstract. Bromine has a strong resource dependence. With the sharp decline of the total amount and grade of traditional brine resources, the difficulty of mining is increasing day by day, and the shortage of bromine supply and demand has become a normal situation. Therefore, it is urgent to find new sources of bromine resources and develop corresponding extraction technologies. Bromine-containing waste salt is a new source of bromine. The mature technology achievements of bromine extraction in underground brine, concentrated seawater and other water are transferred to the field of bromine extraction from bromine-containing waste salt, which realizes the closed-loop recycling of resources and extends the industrial chain, and has a good application prospect.

key word: Bromine, solid waste, bromine-containing waste salt, bromine extraction.

1. Introduction

Bromine is widely used in flame retardants, pharmaceutical intermediates, pesticide chemicals, oilfield chemicals and water treatment [1-3]. A large amount of bromine- containing wastewater will be produced in the production process.

Zero discharge of wastewater is an important way to realize the utilization of sewage resources. At present, the basic idea of "zero discharge" wastewater treatment process is to separate salt and water, to obtain recycled water and crystallized salt. For most industries, due to the complex salt composition of wastewater, it is very difficult to achieve "zero solid waste" discharge by simply evaporating. Due to the immature process of salt separation, most enterprises get bromine-containing waste salt after treating high-salt sewage containing bromide, which is temporarily stored as solid waste or dangerous waste. This not only causes resource waste, but also aggravates potential environmental protection and safety risks. We should also attach great importance to the prevention and control of solid waste pollution. In the work plan of "waste-free city" construction during the 14th Five-Year Plan Period, the comprehensive utilization of solid waste has been mentioned for many times, and the overall goal has been clearly stated to promote the construction of "waste-free city" in about 100 cities at prefecture level and above. By 2025, the production intensity of solid waste will be reduced rapidly, the comprehensive utilization level will be significantly improved, and the solid waste treatment system and capacity will be significantly improved. It is pointed out that the green and low-carbon development of industry should be accelerated, the pressure of industrial solid waste treatment should be reduced, and the comprehensive utilization of industrial solid waste should be strengthened.

As a potential source of solid bromine, bromine-containing waste salt has not been used to extract bromine on a large scale. The high value utilization of bromine containing waste salt can greatly develop circular economy, realize the win-win situation of closed loop utilization of resources and environmental governance, and effectively promote the economical and intensive recycling of resources. It is of great significance to safeguard national resource security and support the construction of ecological civilization at a high level.

2. Current situation of bromine resources

2.1 Current situation of traditional bromine resources

The total amount of bromine reserves is small, the grade is low, and the resources are exhausted day by day. Chinese bromine resources mainly come from the underground brine of Laizhou Bay, Shandong Province, but the average concentration of bromine is only 200 g/m^3, and the rate of decrease is 10g/m^3 per year. In addition to underground brines, bromine extraction from medium brines in the salt-making process from seawater accounts

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for about 20% of the annual output. However, due to the policy restriction of salt production, it is difficult to increase the output of bromine extraction from medium brine effectively. After 2013, the production of bromine gradually decreased. As shown in Figure 1, in 2018, due to storm surge, safety inspection and other factors, many bromine plants in China stopped production and the annual output of bromine was about 85,000 tons. In addition to 2020, our annual output of bromine rebounded to 125,000 tons, other years the annual output of bromine about 70,000-90,000 tons.

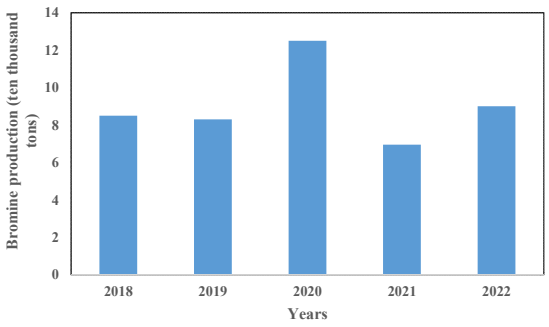

Figure 1. Variation of bromine production in China.

As shown in Figure 2, the average annual price of bromine has shown an oscillating upward trend in the past five years. The average annual price in 2021 is 45,502 yuan per ton, an increase of 53% compared with the previous year. The average bromine price in 2022 remained unchanged from 2021.

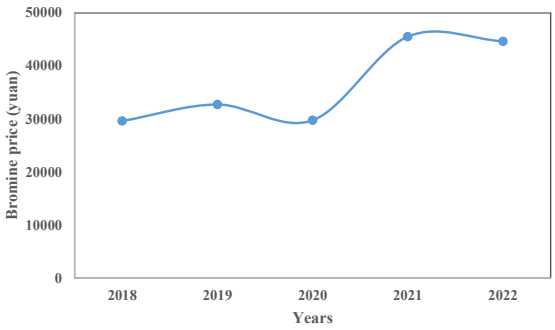

Figure 2. China's average annual bromine price in recent 5 years.

In terms of import, the accumulated import volume of bromine from January to November in 2022 is about 54,000 tons. Imported bromine is still an important supplement for domestic bromine. According to the import volume of bromine in previous years, the annual import volume of bromine is expected to exceed 60,000 tons in 2022.

Some places, such as Tianjin, have begun to extract bromine from desalinated concentrated seawater with a bromine content of only 80 g/m^3. Some domestic power plants and chemical plants have also planned to use warm seawater (50 ~ 60 g/m^3) discharged for bromine extraction. Relevant feasibility studies have been conducted, but due to the restriction of environmental protection policies, the construction has not started yet. Now, our country has become a net importer of bromine. The tension of bromine supply and demand caused by the shortage of resources has become normal. Many Chinese enterprises have gone to Africa, South America, Southeast Asia and other countries with insufficient supporting facilities to purchase brine resources to extract bromine. Therefore, developing new bromine resources is the necessary way to ensure the safe supply of bromine and realize the sustainable development of bromine and bromine industries.

2.2 Current situation of bromine resources in waste salt resources containing bromine

Bromine and bromides are widely used in flame retardants, medical intermediates, pesticide chemicals, oilfield chemicals and water treatment[1-3]. For example, bromoaniline as an important chemical intermediate, is widely used in medicine, dyes, pigments and other fine chemical products, and the synthesis of bromoaniline has a step of bromination reaction mainly using bromine as raw material. Therefore, in the synthesis process, it is inevitable to produce synthetic wastewater, which contains a large number of bromine ions not involved in the reaction. Direct discharge will cause serious harm to the environment and waste resources.

For most industries, due to the complex salinity of wastewater, it is very difficult to achieve "zero solid waste" discharge by simply evaporating. In the context of the state's efforts to control the discharge of wastewater, due to the immature process of salt separation, most enterprises get bromine-containing waste salt after treating high-salinity wastewater, which is temporarily stored as solid waste or dangerous waste. This not only causes a waste of resources, but also aggravates the potential risks of environmental protection and safety. The large-scale bromine-containing waste salt extraction project is still blank. According to the survey, the total amount of bromine-containing waste salt produced by 15 enterprises in a city can reach 15,000 tons/year, with an average bromine content of 13% (sodium bromide). If the resource treatment is carried out in a concentrated way, the annual output of bromine is expected to be about 1,500 tons. The annual average operating income is 66.9 million yuan (calculated at the average bromine price of 45,000 yuan/ton in 2022).

3. Current status of bromine extraction from bromine-containing waste salt

3.1 Current status of bromine-containing waste salt treatment technology

Bromine-containing waste salt is a potential source of solid bromine, and no large-scale bromine extraction projects have been carried out using bromine-containing waste salt. The literature reports mainly on how to treat bromine-containing wastewater to meet the emission standards[4]. Some bromine demand enterprises treat their own bromine-containing wastes mainly as bromine-

containing wastewater and on a small scale. Most of the solid waste treatment enterprises collect bromine-containing waste salt and do not achieve the recovery of high-valent elements (bromine), and only use the form of salt separation for harmless treatment. The reports on bromine extraction process of bromine-containing wastewater are mainly focused on patents [5]. There is no research on the impurity removal process of bromine-containing waste salt reported in the literature.

3.2 Problems need to be solved in extracting bromine from bromine-containing waste salt

Bromine-containing waste salt are characterized by a wide range of sources, variety and complex composition. There are two forms of bromine in bromine-containing waste salt, namely organic and inorganic salts. The source of bromine-containing waste salt may be organic product manufacturers such as pharmaceutical intermediates, pesticide chemicals, dyestuffs, etc., which may increase the chlorine consumption in the oxidation stage due to high COD and affect the quality of bromine products due to volatilization of organic matter in the distillation process. Therefore, the pretreatment process of bromine-containing waste salt needs to remove COD firstly, and the common method to remove COD is calcination, and the bromine distribution law after calcination is one of the key issues in the study of bromine extraction from bromine-containing waste salt. Theoretically, the bromine in organic matter will enter the absorption solution with the tail gas, while the bromine in inorganic salts (e.g., sodium bromide, etc.) will be retained in the solid phase waste salt. However, whether there are other influencing factors to change the bromine distribution in the actual production process, practical verification of the bromine distribution pattern after calcination is needed.

After calcination, whether the bromine is distributed in the tail gas absorption solution or in the waste salt, the next process step is to convert it into a bromine-containing waste salt dissolution with a certain salt concentration. The bromine-containing waste salt is mainly inorganic salts such as sodium bromide, and the proportion of bromine in the waste salt is high after calcination, so most of the cases need to get the bromine containing waste salt dissolution by salting. If the calcium and magnesium scale forming ions in the bromine containing waste salt are too high, it will affect the equipment of the subsequent water distillation process, and the scaling problem will occur easily. Therefore, the pretreatment process should also include the removal of calcium and magnesium plasma.

Although there are many kinds of bromine-containing waste salts, inorganic salts are still mainly sodium bromide. Considering the high value of bromine, the bromine-containing waste salt as solid waste will not have too high bromine concentration, and the bromine concentration in the raw material solution of bromine-containing waste salt obtained through the above pretreatment process may range from several hundred to several ten thousand g/m^3. Because of the wide range of concentration of raw material liquid, the bromine extraction process route needs to be determined according to the actual situation.

3.3 Prospects of high efficiency and energy saving bromine extraction technology in the field of bromine-containing waste salt bromine extraction

Air blow-out method and water vapor distillation method are the most widely used bromine extraction processes in domestic and foreign industries [6]. The air blow-out method can extract bromine from underground brine (about 100-300 g/m^3) or seawater (50-65 g/m^3). This method has been adopted by almost all the enterprises using underground brine or (concentrated) seawater to extract bromine in Shandong province. According to the different absorbents, this method is divided into two types: air-blown acid absorption method and air-blown alkali absorption method. Although the former method has relatively low steam and electric power consumption, it needs to prepare sulfur dioxide gas with sulfur incinerator; although the latter method has relatively high electric power and acid-base consumption, it is easy to control the absorption by lye only, and the chlorine consumption can be reduced by about 50%. Water vapor distillation method is suitable for the raw material liquid with bromine content above 2~5 kg/m^3, which is basically used in foreign countries with high bromine grade such as the United States and Israel. In addition, after the concentration of the finished bromine solution is enriched to 20~80 kg/m^3 in the air blowing method, water distillation method must be applied to finally produce liquid bromine.

Analyzing from the technical point of view, our team has been continuously researching in the field of high-efficiency separation of bromine with multiple magnitudes, wide sources and low concentrations for more than ten years, and has comprehensively mastered the bromine extraction technologies such as air blow-out and water distillation, and has achieved many research results in bromine extraction from seawater, concentrated seawater and underground brine, and realized the transformation of the results. In response to the difficulties of low resource utilization and high energy consumption in China's bromine extraction industry, the project team has built indoor R&D platforms of 30m^3/d and 500m^3/d and on-site pilot production units with the continuous support of several national and provincial vertical research projects. The project team developed the industrialization technology and key core equipment of high efficiency and low energy consumption of bromine extraction from concentrated seawater by air blowing method, which broke through the bottleneck of low yield and high energy consumption of this process. During the research and development process, many national invention patents have been applied, covering the whole process of bromine extraction, including new process, key tower core components, tail gas purification and emission, etc. A relatively complete patent protection system has been formed.

Based on the above results, in 2019, the project team presided over and completed the first domestic 1,000-ton concentrated seawater high-efficiency and low-energy bromine extraction industrialization demonstration plant project in Tianjin. After the transformation, the bromine content of the bromine extraction mother liquor is 30%

lower than that before the transformation, and the production capacity is increased by 7.5%; the resistance loss of the components in the tower of the energy-efficient bromine extraction plant is about 60% of that in the tower of the conventional bromine extraction plant, and the energy consumption per ton of bromine is reduced by 10% on average. The project has passed the process checking in winter and summer organized by the manufacturer and the acceptance of relevant experts, and has been operating stably for three years with high reliability and good economic benefits. While realizing the industrialized operation of bromine extraction from concentrated seawater, the project has expanded its achievements to the field of bromine extraction from underground brine and sun-dried seawater step by step.

On the other hand, the bromine-containing waste salt needs to be transformed into bromine extraction raw material liquid before bromine extraction, which involves treatment processes such as dissolving salt and removal of calcium and magnesium scale forming ions. Our team has long been committed to the research on resource-based treatment of high-salt wastewater, and has made significant technical breakthroughs and fruitful research results in the research fields of crystallization technology, equipment and high-salt wastewater treatment, and formed advantageous technologies with independent intellectual property rights, which have been successfully applied in more than 10 demonstration projects in the fields of high-salt wastewater treatment and resource-based utilization in electric power, metallurgy, chemical industry and mining industry. Among them are 4 projects of high calcium and magnesium wastewater disposal (concentration, calcium and magnesium removal).

Coupling our team's mature technology of bromine extraction in underground brine, concentrated seawater and other water and high calcium and magnesium wastewater disposal technology in the new field of bromine-containing waste salt, we have better technical support for the application of high efficiency and energy saving bromine extraction technology in the field of bromine-containing waste salt bromine extraction.

From the perspective of application prospect, the bromine market in China has long been in short supply and the price continues to run high, so the economic benefits of the bromine extraction project are extremely good. The bromine extraction technology is transformed in the new field of bromine-containing waste salt. After the successful indoor research and development, it can be directly promoted and applied with the mature equipment and operation process.

In summary, the transformation of high efficiency and energy saving bromine extraction technology in the field of bromine-containing waste salt bromine extraction is technically feasible and has good application prospects.

4. Conclusion

Bromine-containing waste salt is a potential source of solid bromine, and no large-scale bromine extraction projects have been carried out using bromine-containing waste salt. Bromine-containing waste salt are characterized by a wide range of sources, variety and complex composition. The key technologies for extracting bromine from bromine-containing waste salt include pretreatment process and determination of bromine extraction process route. By coupling the mature technology of bromine extraction in water and the disposal technology of high-salinity wastewater in the new field of bromine extraction from bromine-containing waste salt, the transformation and industrialization of high efficiency and energy saving bromine extraction technology will be realized. Construction of bromine extraction project of bromine-containing waste salt can realize high-value utilization of high-value element (bromine) recovery and low-value element conversion, and achieve a win-win situation of resource utilization and environmental governance.

Acknowledgments

This work was financially supported by Key R&D Program in Shandong Province (2019JZZY010807), National Key Research and Development Program of China (2022YFC290400503) and Special basic research fund for central public welfare institute of China (R-JBYWF-2021-T01).

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