DISCUSSION ON COMPREHENSIVE UTILIZATION OF CONCENTRATED BRINE FROM SEAWATER DESALINATION

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Abstract: Seawater desalination is one of the most important ways to settle the problem of water resources shortage in China. The direct drain of concentrated brine produced in the desalination would destruct the eco-environments to some degree. Furthermore it makes the comprehensive utilization of chemical resource more effective because of the high and stable concentration of the concentrated seawater. The comprehensive utilization processes of concentrated seawater including the process based on the traditional brine pond, the method of salt production by electrodialysis, the technology of synthetically extracting the chemicals from the brine and the RO-electrodialysis integrated membrane process are introduced. The advantages and disadvantages as well as the feasibility of those technologies application in China are discussed in detail. Some proposals about the development of concentrated seawater utilization in China also are put forward.

Key words: seawater desalination; concentrated brine; comprehensive utilization

INTRODUCTION

The shortage of water supplies for drinking and irrigation purposes is already a very serious problem for China, especially for the development of coastal cities. Seawater is an important component of water resources. Effectively usage of seawater is now considered to be a very attractive solution to the puzzle. With the build of large scale seawater desalination plant, the discharge problem of byproduct caused serious concern. Although there are no reports on the effect of direct discharge of the brine on environment, the harm of the direct discharge were paid more attention to, especially in closed water area with highly concentrated seawater. The impact is obvious. On the demand of the development of recycling economy and marine environmental protection, the development of concentrated brine utilization technology becomes more and more important.

The concentrated brine discharged by the desalination plant is rich in sodium, potassium, bromine, magnesium and lithium, most of which are rare mineral resources on the land. The concentration of these chemicals in the brine is twice the concentration of seawater. To extract equivalent resources, the brine needed is only half of the seawater, which can reduce the cost significantly. In addition, the equipments of intake and chlorine disinfection of seawater are omitted when extracting chemicals from the brine, which will save much investment. Since the temperature and flow rate of the discharged brine is stable, it facilitated the stable operation of the resource extraction. Therefore, it is necessary to make comprehensive utilization of the brine. In this article, some techinolgies on comprehensive utilization of the discharged concentrated brine were introduced and compared, and some proposals were also put forward.

1 PROCESS BASED ON TRADITIONAL BRINE POND

This program is based mainly on the traditional brine pond. In the brine pond process, seawater pumped into the pond is concentrated by solarization evaporation at natural conditions. Saturated brine is got through primary concentration zone, middle concentration zone and advanced concentration zone respectively. Brine is produced after sodium chloride crystals precipitation in the crystallization zone. It is transported to the brine chemical plant for the recovery of potassium, bromine and magnesium. After this process, all of the chemical resources in seawater are fully used. This program is widely used by domestic Saltern. Concentrated brine comprehensive utilization program based on traditional brine pond directly introduces the brine to corresponding concentration zone. The other process is unchanged.

The first advantage of this program is that all the concerned technology is mature. The existing area of brine ponds and the equipment in the marine chemical plant could meet the demand of production. With concentrated brine as raw material, more brine pond area is saved at the same salt production. But there are also some shortcomings.

First of all, there are a large number of organisms in the different concentrations of brine produced by natural evaporation. There are 17 kinds of algae, 13 kinds zooplankton, 14 kinds of protozoa and five kinds bacteria in brine about 6°B′e as measured[1]. A large number of domestic and foreign research data show that the organisms in brine play an important role in salt production. In low concentration zone, large numbers of algae can consume ammonia, phosphorus and other nutrients in the brine. At the same time, the absorption rate of solar is increased because the existence of algae deepened the color of the brine. In addition, the leakage of brine is effectively reduced by the biological cushion formatted by benthic organisms. In middle concentration zone, artemia propagate with algea from low concentration zone for bait. On the one hand, the quality of brine is enhanced since such suspended particles as algea, calcium sulfate and tiny soil is filtered. On the other hand, dead body of the artemia is food for the halophilic bacteria in high concentrate zone and crystallization zone. In high concentration zone and crystallization zone, red halophilic bacteria propagate goes through decomposition of the bodies of artemia. This turns the brine to red and the absorption rate of solar is enhanced. Therefore, in a normal

brine pond ecosystem, all kinds of organisms carry out their duties. The productivity and quality of the salt is improved through above process. To avoid the membrane fouling and reducing of equipment efficiency in desalination, chemical agents is added to kill the organisms in raw seawater. The ecological balance would be serious destroyed if directly discharge the concentrated brine to the salt pond. It is necessary to repair the ecosystem to the brine

Second, the desalination plant generally works all year long with a balance supply. While affected by the season and climate, salt productivity through brine pond is not balance in a year. 80% of the salt is generally produced in about six months. So a big reservoir is needed to balance the productivity of the two. For example, to treat the concentrated brine from a 200,000 t/d desalination plant, a reservoir with area of about 38% of the evaporation area should be built. It is reported that about 50% of the brine pond is saved using concentrated brine from desalination as raw materials. But space required for the reservoir significantly reduced this ratio.

Third, as a result of shortage of land resource and history, salt pond only exists in part of the coastal region. With rapid economic development of the coastal cities, the salt pond area is diminishing and far from the need of the desalination scale. The building of desalination project would be limited if program based on salt pond is the only technology being used.

2 PROGRAM BASED ON SALT PRODUCTION BY ELECTRODIALYSIS

Studies on salt production by electrodialysis were developed widely in Japan since 1950's and industrialization of this technology was realized in 1970's. The salt production technology by brine pond was abolished in Japan at present. All the output, about 1,500,000 t/a, was produced by electrodialysis. NaCl concentration produced reaches 200g / L and the power consumption to produce 1 t salt is about 150 kWh using ion-exchange membranes with monovolume ion selectivity. The brine produced by electrodialysis is evaporated and dried, salt was produced at the same time with byproduct of bittern.

Seawater desalination by ion-exchange membranes electrodialysis process is consisted by four main parts: electrodialysis, evaporation crystallization, drying and packing. Among them, the electrodialysis method to concentrate brine is the heart of the whole process, which is composed by three parts: seawater extraction, and electrodialysis and pretreatment is composed of three parts. If using the concentrated seawater as a feed, which is the by-product of desalination, the equipments of intake and chlorine disinfection of seawater can be omitted. In this way, investment and construction cost can be reduced substantially, and the concentrated water can be directly used for electrodialysis system.

Compared with the program based on the traditional brine pond, the program based on salt production by electrodialysis has more advantages. A lot of land was saved and was not impacted by season by this process. Moreover, investment and manpower was also saved using electrodialysis. For example, the area of the brine pond for a salt productivity of 150000t/a is about 500 hm2, while 20 hm2 is enough for a process using electrodialysis. The staff required in salt plant based on electrodialysis is only 1/10 ~ 1/20 of the brine pond process. Automation is also easy to realize. In addition, the quality of the salt produced by electrodialysis is better than that get by brine pond. Some disposal fees are saved if the salt is used to chlor-alkali industry. The main disadvantage of this technology is the difficulties on extracting chemical resources from the desalinated brine because of its low concentration. The productivity of potassium, bromine and magnesium is decreased. The cost of this process is more than that based on brine pond.

3 EXTRACTING CHEMICAL RESOURCES FROM CONCENTRATED BRINE DIRECTLY

The traditional program of extracting potassium, bromine, magnesium from bittern is limited by the scale of salt pond. Extracting chemical resources from concentrated brine directly was paid more attention to.

After more than twenty years of study, the technology of extracting potassium with modified ion-sieve directly from seawater was successfully developed. A serious of problems such as high potassium selectivity, high concentration ratio and high-efficient and energy-saving potassium separation technology were broken through. 100-tons pilot and industrial tests have been successfully completed. The results show that an enrichment rate of 200 times was reached for seawater. The quality of the products is up to excellent grade of imports while the cost is 30% lower than the imports. The discharged concentrated brine from desalination plant can be directly used as raw material in this technology. It is the first technology that extracting potassium from seawater economically in the world. The factory with productivity of 10,000 t KCl per year applying this technology has been built and put into production in Tianjin. Enterprises in Hebei and Shandong are also preparing for the construction of potassium extraction plants actively.

To extract bromine from seawater, technologies as air-blow, solvent extraction, adsorption and sedimentation have been reported. Among them, the main industrialized process is air-blow technology developed by U.S DOW Chemical Company. The best raw material for this process is the middle concentrated brine as discharged from desalination plant. Other technologies such as gas membrane were also studied in recent years.

After decades of development, the scale of magnesium hydroxide and high purity magnesium oxide production through precipitation has reached millions of tons abroad. Some countries pay more attention to studies on magnesium functional materials. The study on magnesium hydroxide slurry for environmental protection is going on in China. With the enhancement of environmental awareness, its market is with great potential.

On the basis of technologies mentioned above, the process for comprehensive utilization of the discharged brine is shown in Figure 1. In this process, the chemical resources in the brine are extracted fully and zero emission is realized.

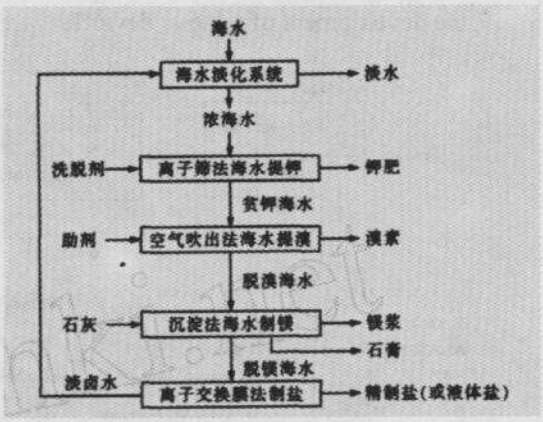

Fig 1 Process of extracting chemical resources from concentrated brine directly

4 INTEGRATED MEMBRANE PROCESS OF REVERSE OSMOSIS – ELECTRODIALYSIS

The process was put forward by Japanese researchers as shown in Figure 2: after pretreatment process, seawater was pumped into the multivalent ion adsorption tower. 60% of alkaline-earth metal ions were removed in the tower, such precipitation as $CaSO_4$, and $CaCO_3$ in the high concentration brine is relieved when desalination using reverse osmosis. Then the seawater is pumped to the high pressure reverses osmosis for desalination. Water recovery rate in this process could reach 70% ~ 80%. The concentrated water from reverse osmosis was passed to the electrodialyzer with monovalent ion selective membrane. Monovalent ion and multivalent ion were separated and concentrated at the same time. The solutions with monovalent ion and with multivalent ion were pumped into monovalent ion adsorption tower and multivalent ion adsorption tower for further separation respectively. Productions as water, salt, compounds of monovalent ion and compounds of multivalent ion were got after this process.

In this process, resources in seawater are completely separated. It is the direction of the seawater comprehensive utilization in Japan. A series of projects concerning this program were put forward, such as adsorbents with special ions selectivity, high pressure RO and

the development of relative devices.

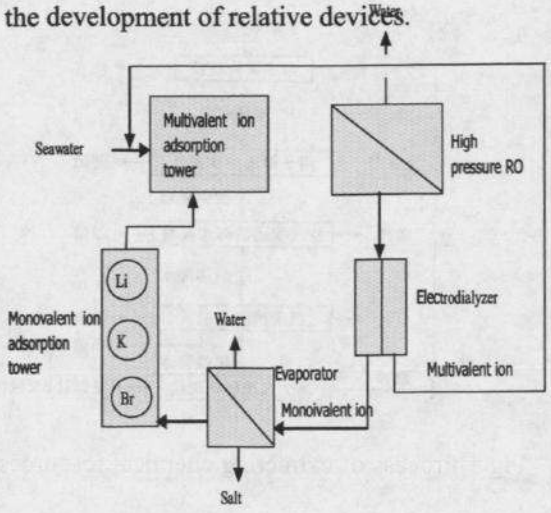

Fig 2 Reverse osmosis - electrodialysis integrated membrane process

5 Recommendations

Technologies of desalination and comprehensive utilization of the discharged concentrated brine were paid more attention to in China in the recent years. It is the prior themes of the key field in "the national medium and long-term science and technology plan" promulgated by the State Council. Projects of extracting potassium, bromine, magnesium from seawater or the concentrated brine were ratified as key projects in the "Special planning for seawater utilization" promulgated by National Development and Reform Commission. At the same time, projects of ten thousand-ton grade of potassium extraction, thousand-ton grade of bromine extraction and ten thousand-ton grade of magnesium extraction from seawater were supported by Ministry of Science and Technology in the "Eleventh Five-Year plan"

With the building of large-scale seawater desalination projects, the comprehensive utilization of the discharged concentrated brine has been concentrated on the agenda. A series of high technologies about seawater chemical resource extraction is required to ensure balanced development with the desalination. The authors think that more efforts should be taken to the following technologies. Membranes with monovalent ion selectivity, technology and equipment for large-scale electrodialysis for concentration, energy-saving technologies and equipments for direct extraction of potassium, bromine, magnesium from seawater, technologies of noble metals such as lithium, uranium, cesium extraction, development of packaged technology and equipment and demonstration of comprehensive utilization of the discharged concentrated brine.

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