EVOLUTION OF DEVELOPMENT OF TECHNOLOGIES FOR BITTERN UTILIZATION IN CHINA

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Abstract: The composition and distribution of bittern from Chinese sea salt works were investigated. The process principle, technology flow, technical and economic index and developing progress of the technologies of bittern complex utilization, including recovering potassium chloride from bittern by mixing brine method, preparing potassium sulfate using bittern and potassium chloride, extracting potassium sulfate using bittern and seawater by zeolite method were introduced in detail. The advantages and disadvantages of those kinds of technologies were discussed and the development trend of the new technologies of complex utilization of bittern was proposed.

Keywords: bittern; comprehensive utilization; developing progress

1 INTRODUCTION

Bittern is the by-product of sea salt production and high concentrations of potassium, magnesium, bromine and sulfate are contained in it. The production of sea salt in China has exceeded 22 million tons per year, which is on the first place of the production of sea salt in the world and the corresponding bittern produced is up to 18 million m^3. Bittern is a kind of abundant and sustainable liquid mineral resources. The study and development of bittern utilization in China originated from 1960's. After fifty years of hard work, the chemical industry of bittern with potassium, bromine, magnesium as product chains was founded. This contributes to making the best of the resource of bittern, the continuable development of the salt production trade and the protection of the marine environment.

2 BITTERN RESOURCE AND DISTRIBUTION CHARACTERISTICS

2.1 Compositions

The concentration of the chemical compositions in the bittern from different producing areas is shown in Table 1

Table 1 Main chemical composition of bittern

Density	chemical compositions/kg·m^{-3}					
/°B'e	KCl	NaCl	$MgSO_4$	$MgCl_2$	$MgBr_2$	H_2O
28-32	20-28	70-150	50-90	120-200	2-3	~850

As seen in Table 1, the total quantity of all kinds of salts in the bittern is in the range of 334.5~391kg/m^3, which is 10 times higher than that in the sea water (35‰), and the

concentration of elements such as potassium, bromine, magnesium is 30 times higher than that in the fresh sea water. This made bittern a good raw material to prepare products of potassium, bromine and magnesium. But the complicated composition and the similar solubility characteristic of salts in bittern made it much difficult to separate efficiently and economically.

2.2 Resource and distribution

The resource and distribution situation of bittern in China is shown in Table 2.

It can be concluded from Table 2 that although there are 10 provinces producing sea salt and bittern in China, production of salt mainly distributes in Shandong, Hebei, Liaoning, Tianjin, Jiangsu province, which possess 93.87% of the resource and the others only have few and scattering.

It can be also seen from Table 2 that those bittern contains 456,600 tons of potassium chloride, 1,369,600 tons of magnesium sulfate, 3,104,200 tons of magnesium Chloride, 45,900 tons of bromine and 1,641,000 tons of sodium chloride. The total salt amount is up to 5,018,600 tons and all of those resources are continuable resource.

Table.2 The resource and distribution of bittern

Province	Sea Salt Production /10^4 t·a^{-1}	Bittern amount /10^4 m^3·a^{-1}	Mineral resource amount/10^4 t·a^{-1}				
			KCl	$MgSO_4$	$MgCl_2$	Br_2	NaCl
Shandong	976	780	19.50	58.50	132.60	1.95	70
Hebei	497	398	9.95	29.85	67.66	1.00	36
Liaoning	287	230	5.75	17.25	39.10	0.58	21
Tianjin	226	180	4.50	13.50	30.60	0.45	16
Jiangsu	158	126	3.15	9.45	21.42	0.32	11
Fujian	49	39	0.98	2.93	6.63	0.10	3.5
Zhejiang	37	30	0.75	2.25	5.10	0.08	2.7
Guangdong	26	20	0.50	1.50	3.40	0.05	1.8
Hainan	18	14	0.35	1.05	2.38	0.04	1.3
Guangxi	11	9	0.23	0.68	1.53	0.02	0.8
The whole country	2285	1826	45.66	136.96	310.42	4.59	164.10

3. DEVELOPMENT EVOLUTION TECHNOLOGIES FOR BITTERN UTILIZATION

In order to make the most of the bittern resource and meet the demands of national economy, the marine chemistry scientists in China have made great efforts in bittern utilization since 1960's and a series of technologies for the integrated utilization of bittern were got. Those technologies are shown as follows.

3.1 Technology of recovering potassium chloride by mixing brine

The technology of recovering potassium chloride by mixing brine is a traditional technology of bittern integrated utilization which is widely used in the bittern chemical industry. Production of 50,000 tons per year (calculated by potassium chloride) has been reached since the technology is successfully developed in our country in 1960. This has contributed to the potassium usage in the industry in the 1970's and the 1980's.

The basic principle of the technology is as follows: the law of salt separation from bittern is based on the phase diagram of the system (K^+, Na^+, Mg^{2+} // SO_4^{2-}, Cl^--H_2O). The main product of potassium chloride is got after the process of adding bittern, evaporating, cooling, resolving and washing firstly. Then bromine is extracted by oxidation-distillation and $MgCl_2 \cdot 6H_2O$ is produced by evaporating and cooling the effluent liquor of bromine. The flow sheet of

the technology and its technical and economic index are shown in Fig. 1 and Table 3 respectively.

From Fig. 1 and Table 3 we can see that products of potassium chloride, bromine and magnesium chloride which is urgently needed in our country are gotten. However, it still has some problems. Firstly, the recovery rate of the elements in bittern is low. For example, the recovery rate of potassium in the bittern in most of the factory is only 50% and the maximum is still less than 70%. The recovery rate of the magnesium chloride is only 60%, and the sulfate is not used at all. Secondly, to produce 1 ton potash, more than 20 tons of steam and about 1000 kilowatt-hour of electricity were consumed. This make the manufacture cost of potassium chlorine per ton is 1000 Yuan higher than its selling price. So the integrated economic benefit of this technology is bad.

Table 3 Technical and economic index of the complex utilization of bittern by add-bittern method

Product	Quality	Consumption of raw materials /1·t	Energy consumption		Rate of recovery /%	Production cost /RMB·t^{-1}	Product structure /wt
			Steam/t·t^{-1}	Electricity /kwh·t^{-1}			
Potassium chloride	GB6549-1996 Ordinary grade	Brine: 50m^3	20-25	~1000	50-70	2500-3000	1.0
Bromine	QB2021-1994 Premium grade	Mother liquid of potassium:150m^3 Chlorine: 0.55t	20-22	350-400	~80	5000-6000	0.1
Magnesium chloride	QB/T3706-1999 First class	Bromine effluent: 1.1m^3	0.8-1	20-25	~60	200-250	10

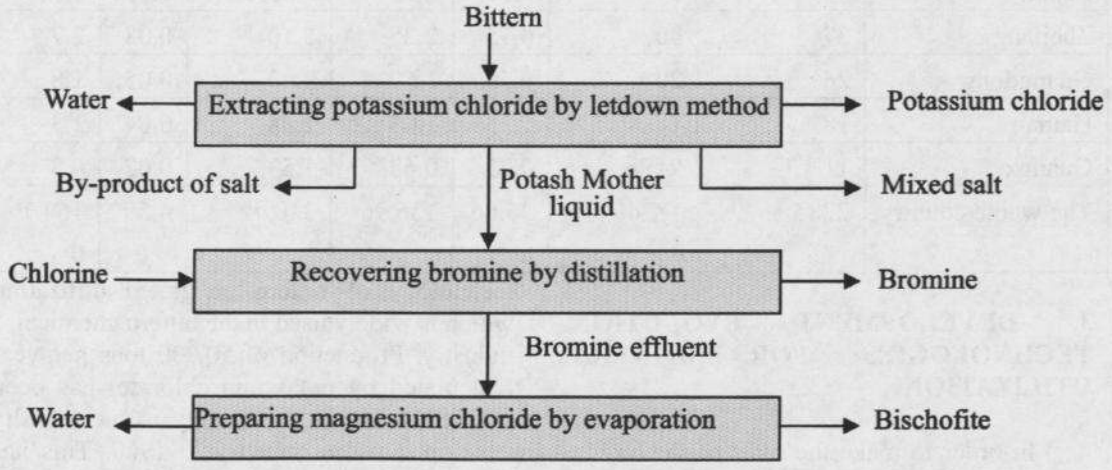

Fig.1 Flow sheet of integrated utilization of bittern by mixing brine method

Especially in recent years, with the increasing cost of energy, materials and labour expenses, the disadvantage of this technology in energy consumption and low recovery rate is outstanding. The results in worsening economic situation of the bittern chemical plant and half of the 20 bittern chemical plants in our country have closed.

Technical improvement was put aiming at the problems, including removing sulfur by adding calcium water to brine[2], the process of "three-high method"[3] and the technology of "controlling crystal" of potassium chloride[4]. This improved the technical recovery rate and reduced the energy consumption. But all the improvements didn't solve the problem of energy consumption fundamentally and failed to be implemented on a large scale.

3.2 Technology of producing potassium sulfate using bittern and potassium chloride

Potassium sulfate is a high-quality potassium fertilizer without chlorine, especially suitable for the economic crops. At the beginning of 1990's, with the fast development of the economic agriculture and the cancellation of replenish for importing fertilizer, the demand for the potassium sulfate increased sharply, which lifted the development of potassium sulfate at home. Because the international market price of potassium sulfate is nearly one time higher than the potassium chlorine's, it is new opportunity to improve the chemical enterprise's benefit through making potassium sulfate from bittern.

After the separation problem of sodium chloride and sulfate was break through successfully, a series of technologies of producing potassium sulfate from bittern were developed successively. According to the different separation methods, the technologies are separated to flotation, swirl, sieving and high-temperature salting out etc. The projects of 10,000 ton-class potassium sulfate have been set up in Daqinghe Salt Works in Hebei and Haihua Group in Shandong through separate method of flotation and swirl respectively.

The flow sheet and technical and economic index of the technology [6] of producing potassium sulfate from bittern and potassium chloride are shown in Fig.2 and Table 4 respectively.

Table 4 Technical and economic index of producing potassium sulfate using bittern and potassium chloride

Product	Quality	Consumption of raw materials/1·t^{-1}	Energy consumption		Rate of recovery /%	Production cost /RMB·t^{-1}	Product structure /wt
			Steam/t·t^{-1}	Electricity /kwh·t^{-1}			
Potassium sulfate	ZB/TG21006-89 Premium grade	Brine: 15m^3 potassium chloride: 0.7t	11.0	~300	80	1600-1800	1.0
salt	GB5462-2000 Premium grade				80		1.3
Bromine	QB2021-1994 Premium grade	Potassium mutterlauge:150 m^3 Chlorine: 0.55t	20-22	350-400	~85	5000-6000	0.04
Magnesium chloride	QB/T3706-1999 First grade	Effluent of bromine: 1.1m^3	0.8-1	20-25	~80	200-250	4

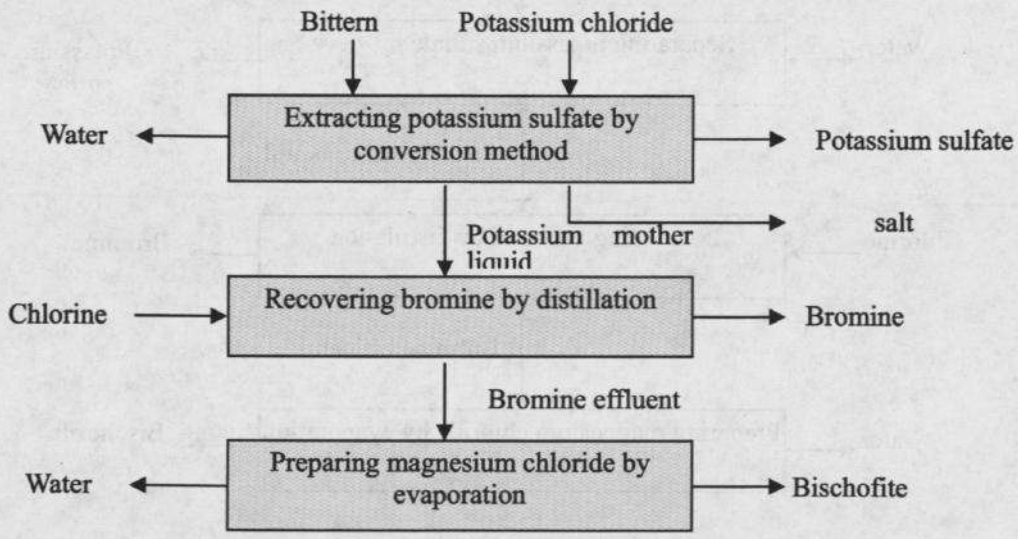

Fig.2 Flow sheet of producing Potassium sulfate and integrated utilization by the brine and potassium chloride

Fig.2 and Table 4 show that K^+,Na^+,Mg^{2+},SO_4^{2-},Cl^- in bittern were recovered by the above technology, so the recovery rate of the element and the integrated economic benefits are improved notably.

The production situation indicated that the economic benefit of bittern chemical industry plants were improved remarkably. This achievement was awarded the National Invention Prize in 1998. However, with the fierce competition of domestic market of potassium sulfate, especially the fast soaring of the price of potassium chloride recently, the defect that to produce one ton of potassium sulfate need to consume 0.7 tons of potassium chloride is outstanding. This results in the failure of application of the technology on a large scale in the salt chemical industry plant.

3.3 Technology of producing potassium sulfate from bittern and seawater by zeolite

In order to solve the problem of potassium source in producing potassium sulfate by bittern and potassium chloride, Hebei University of Technology has exploited the technology of producing potassium sulfate via bittern and seawater by zeolite [7]. The basic principle of this technology is that enriching the potassium in bittern and sea water using the effect of potassium ion-sieve of the modified zeolite and then extracting potassium sulfate directly from sea water is realized. The flow and the technical economic index of this new technology are show in Fig. 3 and Table 5 respectively.

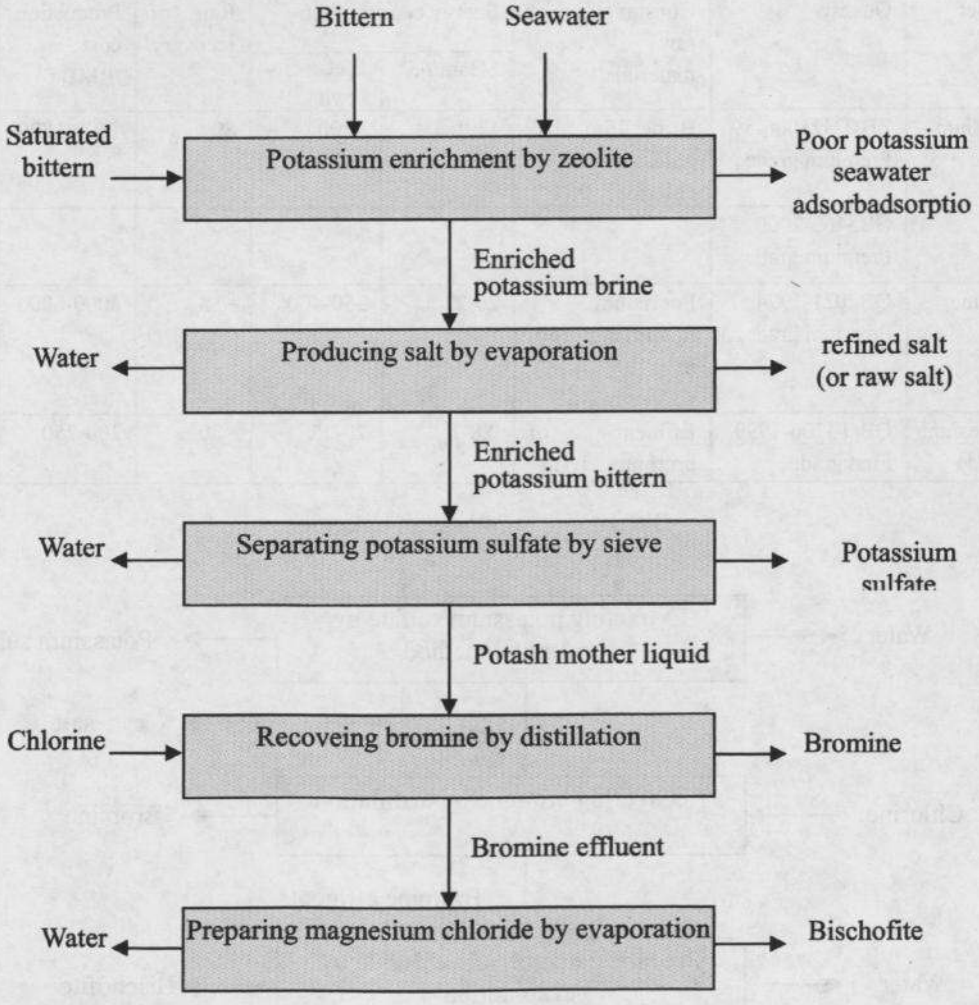

Fig.3 Flow sheet of producing Potassium sulfate from seawater and bittern by zeolite

Table.5 Technical index of comprehensive technology of producing potassium sulfate by zeolite

Product	Quality	Material consumption /1·t^{-1}	Energy consumption	Recovery rate /%	Production cost /RMB￥·t^{-1}	Product structure /wt	
			Steam /t·t^{-1}	Electricity /kwh·t^{-1}			
Potassium sulfate	ZB/TG21006-89 Premium grade	Bittern: 15m^3 Seawater:1000m^3	10.0	455	85	1200-1300	1.0
refined salt (raw salt)	GB5461-2000 (GB5462-2000) Premium grade	Saturated brine: 5.2 m^3	1.5	80	85	250-300	6.0
Bromine	QB2021-1994 Premium grade	Potash mutterlauge :150m^3 Chlorine: 0.55t	20-22	350-400	85	5000-6000	0.04
Magnesium chloride	QB/T3706-1999 First grade	Effluent of bromine:1.1m^3	0.8-1	20-25	80	200-250	4.0

As seen from Fig. 3 and Table 5, the technology of producing potassium sulfate from bittern and seawater by zeolite and the integrated utilization not only realized extracting potash directly from sea water, but also reduced the cost of potassium sulfate to 1300 Yuan/t which is far lower than the price of the imported potassium sulfate (2200 RMB Yuan/t). Every product in this product chain has good prospect and strong market competitiveness. In addition, because of the introduction of potassium resources from seawater, the production of the potash was improved by more than one time.

This new technology was passed the assessment presided over by the provincial scientific and technological commission of Hebei in January in 2000. The evaluation expert including academicians of the Chinese Academy of Sciences and Chinese Academy of Engineering asserted unanimously that this technology had reached the international leading level, and has extremely strong market competitive power. Under the supporting of the project of the tenth five-years of the state and key research projects of Tianjin from 2002 to 2004, a series of the key problems of the technology have been broken through and the one hundred -ton pilot-plant test had been finished successfully which offered design considerations for industrialization development of this new technology. The result of the pilot-plant test indicated that the high-efficient power-saving technology not only could be put into industrialization in saltworks, but also had higher comprehensive economic benefits and will made great contribution to the bittern chemical industry.

4 TREND AND PROSPECT OF THE TECHNOLOGY OF INTEGRATED UTILIZATION OF BITTERN

4.1 Market analysis of the products

Such bittern chemical products as the potassium, bromine and magnesium are the materials needed badly at home. The potassium is essentially nutrient for crops growth, but because of the lack of the resource, 80% of potassium relies on import in our country. In 2004, the import of the potassium in China was up to 7,300,000 tons, which ranked the third of the import goods and materials in our country, which laid after total import value of petroleum and the iron ore. Therefore, the exploitation of new potassium resources, especially 500 trillion tons resource in the seawater has great significance for the resource and economic security.

Bromine is an important refined chemical material, which was extensively used in fire retarding agent, fire extinguishing agent, refrigerating agent, sensitive material, remedy, pesticides and oil field. At present, the consumption of domestic bromine is about 100,000 tons. For a long time, domestic bromine can not satisfy the demand of production and quality and import is still needed.

The magnesium salt is a kind of basic industrial raw which is extensively used to make metal magnesium, the magnesia for steel-making, magnesium oxygen cement, burning retardant, snow thawing agent, antifreeze agent and food addition agent with the consumption of 1 million tons per year. Especially as the magnesium chloride (bischofite) substitutes the salt, which has strong corrosives to the road, as the snow off agent used in winter, the short supply of magnesium salt appeared.

In a word, enormous market demand has offered powerful force for the exploitation of bittern resources.

4.2 Trend of the new technology development

To efficiently exploit the resource of bittern and improve the integrated benefit of bittern plants, we should not only positively generalize the integrated technology of extracting potassium sulfate from seawater and bittern by zeolite in the salt-making trade, but also pay more attention to new technologies as follows.

(1) Technology of refined and serialized potash fertilizer

To meet the requirement of high quality potash fertilizer with high density, whole nutrition and no remainder, refined and serialized products such as potassium nitrate, potassium dihydrogen phosphate and nitre basis series of ternary compound fertilizer should be extracted from bittern and seawater. The fertilizer not only has high fertilizer efficiency, but also has a price of one or even several times higher than the price of potassium chloride and potassium sulfate. Presently, great progress has been made on drawing potassium nitrate, potassium dihydrogen phosphate from seawater by zeolite and extracting nitre base ternary compound fertilizer from seawater. The demonstration project of extracting potassium nitrate form seawater with a production of ten thousands tons per year is in progress. This is the sign that the new technology of the marine chemical industry has stridden forward to industrialization.

(2)New technology of extracting bromine from dilute brine and seawater

Presently, the major source of bromine is brine underground the area around Bohai in Shandong. With high-strength mine for many years, the concentration of the bromine in brine underground has declined and cann't ensures the continuable development for the bromine industry. Therefore seeking new bromine resource is urgently needed. On the other hand, extracting bromine from potassium mother liquor (strong brine) has a recovery rate of about 80%, that is to say, 20% of bromine has been lost in the process of drawing potassium form bittern and the recovery rate of the bromine in the seawater is only 15% during the process of salt producing. So to improve the utilization rate of the bromine resource, the process of extracting bromine is needed to be put forward and new technology of extracting bromine from sea water and dilute brine is need to explore. Nowadays many salt works have set up plants to extract bromine from middle degree brine(10-15°B^{1}e) using air purging method and technology of membrane and ion exchange process have also been improved greatly.

(3) Magnesium salt functional material

For a long time, the main product of magnesium salt of our chemical plants is powder or platy of $MgCl_2 \cdot 6H_2O$. The product is in low price and the market of it is influenced by season. Following the trend of the world, the new functional material of magnesium salt will become the advanced direction of magnesium salt of bittern in China. At present, the functional material of magnesium salt exploited includes exceeding-minute-powder material of magnesium salt (fire-retarding magnesium hydroxide, high-pure magnesia, advanced magnesia, etc.), whisker material of magnesium salt (magnesium hydroxide whisker, basic magnesium chloride whisker, basic magnesium sulfate whisker, magnesium euchlorine whisker, magnesium borate whisker, etc.), environmental magnesium plasm, etc. If these functional magnesium salts are researched and put into practice, it will contribute to improving the technical level of the salt-making trade.

5 CONCLUSIONS

Nowadays, every trade in our country is implementing scientific sight. Emphasize resource conservation and continuable utilization has become the guidance principle of development of resource. Bittern is a kind of minerals resource which can develop continuablely. Developing the utilization of the bittern resource would satisfy the need of potash fertilize of our country and ensure the continuable development of the salt-making

trade. This is not only according with the industrial policy of our country, but also the specific embodiment of the scientific development sight. We should grasp the good opportunity of developing bittern chemical industry and push forward the industrialization of the new technologies of bittern chemical industry, and form the new industrial chain of marine chemistry and make new contribution to the construction of national economy.

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