

# THE STATUS QUO OF BROMINE MAKING INDUSTRY IN CHINA

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### PREFACE

There was a close connection between the bromine industrial and salt industry(NaCl).The raw material of making bromine were seawater and salt brine(concentrated seawater).The existing form of bromine was mainly bromine ion in the marine or in the salt brine derived from paleo- seawater. The raw material of making bromine was salt brine before or after salting out. The concentrations of salt brine were different due to different resources in the world. Minority countries such as Japan extracted bromine takes seawater as raw material, such countries as China and India take brine of medium concentration in salt making or brine of high concentration after salting out as raw material, such countries as America and Israel take brine in paleo-ocean as raw material.

As concomitant output of salt production(non-rock salt), the bromine production is very important in economic status in salting making enterprises using sea water as raw material such as Shandong province . Since 19080's, Shandong province has devoted to balance development of salt

and bromine, and the annual yield of sea salt was 20 million tons and bromine was 150 thousand tons. According to average price of salt and bromine, the sales were nearly the same, but the economic benefit of bromine has imponderable advantages over salt industry. Further processing of bromine and bormide is the main source of economic benefit in the development of salt industry in Shandong province. The output value of salt accounted for 1/4 of that of bromine industry. The bromine accounted for the main part the traditional salt production of Potassium, Bromine, Magnesium and Sodium sulfate .

### INTRODUCTION ON THE PRODUCTION OF BROMINE AROUND THE WORLD

Annual yield of bromine come to 700 thousand tons in the world, including:

Albemarle Corporation of USA: Annual yield of bromine come to 170 thousand tons including 120 thousand tons in American homeland, and 50 thousand tons in Jordan(the Dead sea).

Great lake of USA: Annual yield of

bromine come to 170 thousand tons.

Israel:270 thousand tons.

India:20 thousand tons.(Extracting bromine form solution after salt making)

Japan: 22-25 thousand tons (Directly extract bromine from seawater)

China:160 thousand tons in (joint production of salt and bromine)

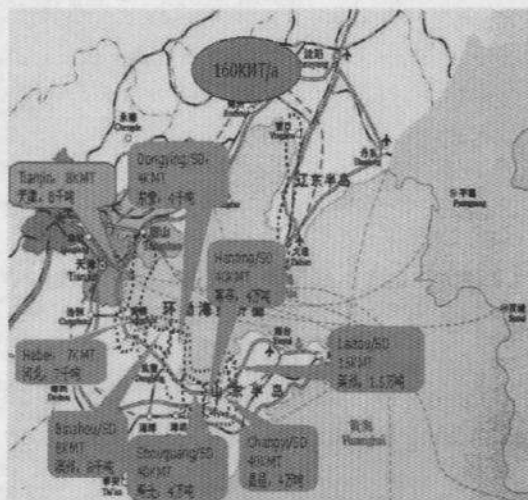
Ukraine and other areas around the world :around 2 thousand tons

## PRODUCTION OF BROMINE IN CHINA



The yield of bromine is 160 thousand tons every year in China so far. The manufacturers of bromine have more than 120 in Shandong, Hebei and Tianjin in China. The production equipments of bromine have more than 200.

Where, the yield of bromine in Shouguang, Hanting, Changyi in weifang of Shandong province is 4 thousand ton. And 15,000 tons in laizhou, 4000 tons in dongying, 8000 tons in binzhou, 7000 ton in Hebei province, 8000 ton in Tianjin. In addition, it also distributed in Liaoning province and Jiangsu province, but the yield is very small. The bromine factories of our company are distributed in hanting, changyi, laizhou, zhanhua and haixing in hebei province. The total yield is more than 4000 tons whit 5 sets of equipment using brine included bromine as raw material.



## APPLICATION OF BROMINE IN CHINA

Development of electronic appliances in the word promotes the development of bromine-contained flame retardant. The development of drilling fluid and completion fluid ( $\text{NaBr}$ ,  $\text{CaBr}_2$ ,  $\text{ZnBr}_2$ ) follow the extensive restarting of oil exploitation as the upsurge of oil price. The bactericidal algacide containing bromine has been developed as the protection of water resources in the world. At the same time, the medical products containing bromine also have a stable increase, and the downward market is very prosperous. In the world market, due to the market operation of main manufacturers making bromine and bromide, Great lake company in the USA had shutted down a 40000-ton bromine equipment in the Britain and purchased bromine and bromide from other companies instead. Albemarle Corporation of USA had shutted down bromine an equipment in France. At the same time, the production of bromine(mainly is Great lake company previously, now named Chentura company and Albemarle Corporation) had decreased by 3%~5% in the USA because of outdated production process and resources. As the change of balance of supply and demand, and the transfer of electronic appliances industry (laying copper plate industry transferred to China in large scale) in the world and other products (bronopol) transferred to China due to pressure of environmental protection. Additionally, some traditional bromine products(such as the



production of dyes) in China also give the companies of bromine and bromide in China a great development, which promote the market prosperity.

The yield of bromine in China increased from 80000 tons in 2002 to 150000~160000 tons in 2007, which promotes and supports the development of downstream bromine products in China. At the same time, the import volume of bromine was 4000~5000 tons in 2000 and 2001, nearly 10000 tons in 2002, nearly or exceeded 25000 tons in 2003, 2004 and 2005. Since 2006, the development of bromine and bromide gave international companies great pressure, which made them change strategy in the world. The import volume of bromine started decreasing. There are about 17000 tons in 2006 and only 13000 tons in 2007.

The bromine consumption is about 160000~170000 tons, which has reached historical high. And China has become the third country in bromine production and consumption, only less than American (about 240000 tons) and Israel (about 180000 tons).

Flame retardant markets, brominated flame retardant are still the main forces of world flame retardant markets which occupied 40% of the market, although many countries, organizations and enterprises made much great attacks because of business and political reasons. In the future, it will have a stable development in flame retardant markets in the world because of its excellent flame retardancy and relative economy. So it is in China. The production and consumption of bromine in brominated flame retardant was about 100 thousand tons, which occupied 62~65% of bromine output in China. They are mainly applied to the production of tetrabromobisphenol A, decabromodiphenyl oxide, octabromo-ether and tribromophenol.

Medicine market. Because of its complexity in this market, the products used bromine are very universal. But the consumption of bromine in many medicine manufacturers is very small, sometimes only a few tons every year. In 2007, the consumption of bromine in China market was about 28 thousand tons, which occupied 17~20% of bromine supply in the whole China. They were mainly applied to trimethoprim and its

intermediate benzaldehyde, chloramphenicol/thiamphenicol/florfenicol, amanterdine, cabamersapine and so on.

Organic and inorganic intermediates. Organic and inorganic intermediates in China are mainly made of hydrobromic acid which is byproducts of flame retardant and medicine production. For example, NaBr, CaBr<sub>2</sub>, bromopropane, bromine hexane, 2-bromopropane and bromoputane.

Another organic and inorganic intermediates are made of bromine in China. In 2007, the consumption of these products was about 12000~13000 tons, which mainly applied to production of HBr, PBr<sub>3</sub>, m-bromoanisole, NBS, bromobenzene, ethylene, partly bromobutane and partly NaBr and sodium bromate.

Water treatment agent/bactericidal algicide. The production of whole bactericidal algicide have greatly developed because of the need of clean water. Compared with other products, the bromine products have better performance on biocide, algae removal and the environmental pressure, the water treatment agent of bromine series had a great development. But the price is relatively high at present and mainly depends on export. In 2007, the bromine consumption of bactericidal algicide was about 8000~10000 tons, which occupied about 5%~7% in the whole bromine consumption in China. It mainly applied to bronopol, DBNPA, bromine chlorine/dibromohydantoin.

Dyeing industry. In dyeing industry, compared with F-, Cl-, I- with moderate activity products using bromine as raw materials have better quality and dyeing effect. The dyeing products containing bromine are mainly used to disperse dyes and their intermediate, such as 2,6-dibromo-4-nitroaniline, 6-Br-2,4-dinitroaniline, bromo-amino acid, No.56 dispersed brilliant blue and bromine indigo and so on. The whole consumption of bromine was about 6000~10000 tons, which occupied 3%~4% in bromine consumption in China. Because of the environmental pressure, the production enterprises in the south had transferred their production bases. They moved to the north of Jiangsu province and Shandong province. At the same time, the

whole output of dispersed dyes have decreased to some degree.

Pesticide industry. The bromine products are still mainly methyl bromide and other products such as profenofos, thiabendazole, bromadiolone and so on. The whole consumption of bromine is about 5000~8000 tons. Because methyl bromide were forbidden products of Montreal, it will influenced the production of methyl bromide. In contrary, the profenofos will develop to some degree as a substitute product.

In general, if we convert all the bromide into the bromine in 2007 and 2008, the production and application still has net export. In 2009, the production and application will reach to balance. From 2010, if we convert the bromine and bromide into bromine, it will has net import because of the restriction of the bromine in China if we can't find new resources.

## RESOURCES OF BROMINE

The bromine is a element found and separated from seawater. Although the bromine is widely distributed in lithosphere, its abundance is very low ( $<0.1\text{ppm}$ ). The bromine in seawater is a trace element of rich abundant with content is  $65\text{ppm}$ . The bromine is referred as marine element because about 99% of bromine is existed in seawater. The natural resources of the bromine are mainly seawater and sediment of Ancient Ocean namely rock salt mine and bittern mine, which come from seawater, too.

Precipitation regularity of seawater by natural evaporation is that,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  was firstly precipitated when the solution is condensated from 3 to 13 in baume degree,  $\text{NaCl}$  was then salted out when the concentration is 25.5 in baume degree, and after that  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  would salted out when the concentration is 36 in baume degree, finally ,with continual condensation, the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  will be salted out .The bromine is always existed in the mother liquid and become bromine resources, the mother liquid has high concentration of bromine

The brine in the Dead sea and underground brine in the USA are mines containing rich bromine where also has a high

concentration of  $\text{NaCl}$  ,  $\text{KCl}$  and  $\text{MgCl}_2$ . The concentration of bromine is  $3\text{kg} \sim 12\text{kg/cubic meter}$ .

China and other countries still doesn't find such brine, so we can only extract bromine from seawater, concentrated seawater and mother liquid of salt making.

At present, there isn't any large saltern in Japan , the annual output of extracting bromine from seawater is about 22 thousand tons.

Output of bromine in India from mother liquid after salt production is about 18 thousand tons.

In Australia, There are large salterns with medium brine and mother liquid of salt production, but they doesn't produce bromine.

There aren't any salterns with high concentration of bromine being found in China. Before 1972, the production of bromine used mother liquid of salt production and joint-production of K, Br and Mg. At present, the manufacturers using this technology are salterns in Hangu in Tianjin, Saltern in Tanggu, saltern in Nanpu in Hebei, saltern in Daqinghe and Jiangsu provinces and so on. The total output is less than 5000 tons.

There are rich underground brine resources in the coastal area of Laizhouwan in Shandong province. The original state is concentrated seawater. The content of containing salt and bromine is 3~6 times of seawater. The yield of sea salt in Shandong province is about 20 million tons every year. Bromine in china is just developed by these resources, and realized joint production of salt and bromine.

## PRODUCTION TECHNOLOGIES OF BROMINE

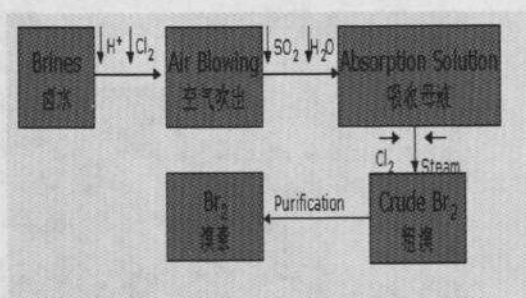
The bromine exists in the form of ions in natural. In 1825, chemist Baland in Germany used chlorine to treat brine, and found the method of extracting bromine. In 1877, this method was widely used to seawater system, and is still the base for making bromine in industry scale.

Because high-concentration brine hasains high concentration of bromine, the bromine making technology is distillation by chloride for one time, such countries as American, Israel and India adopt this technology.

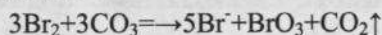


But low-concentration brine contains low concentration of bromine, this technology consumes plenty of steam. It is diseconomy. So they adopted secondary oxidizing method. The first time of oxidation is to enrich the mother liquid to a content of bromine of 50~150kg/cubic meter. The second time is to make bromine. Japan and France has stopped using such technology, and this technology is used in China.

The schematic diagram of the technology is as follow:

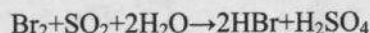


The technology of Alkali absorption was adopted in China in 1985, the reaction equation is:



Making bromine by adding acid and distillation, there was a production line in AGROCEL in India.

After 1985, SO<sub>2</sub> was used as absorbent in China, the reaction equation was:



And make bromine by adding chlorine to distillate.

The material consumption of making bromine(ton bromine)

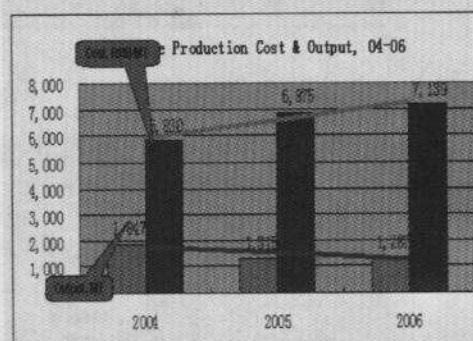
Electric:1200~1600 degree

Chlorine:1.2~1.3 ton

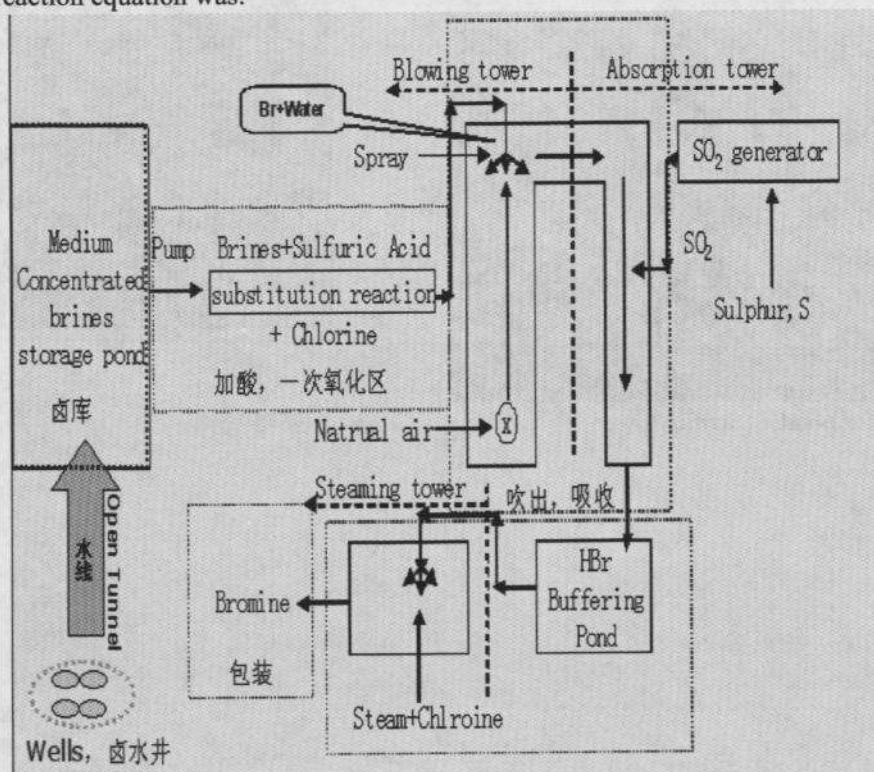
Sulfur:0.3~0.35 ton

Coal:0.3~0.4 ton

The cost of bromine in salt company  
盐业科技公司的溴素成本



Remarks: cost without VAT



Underground brine wells, water line



Brine library, reaction



Blow out, absorption



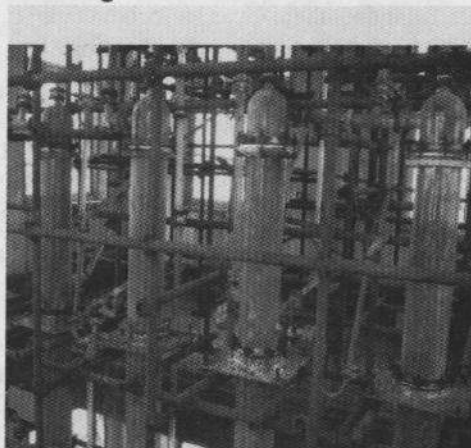
Buffer pond, steaming tower



Control room

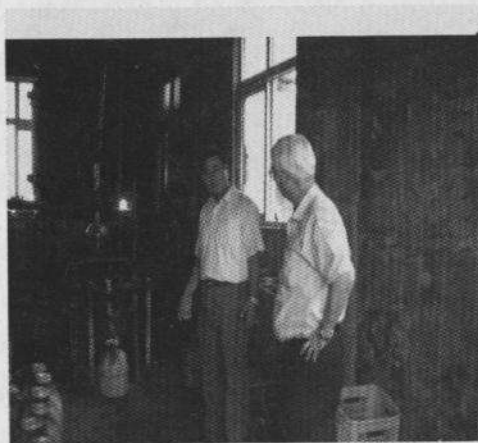


Steaming



Package





Storehouse



The brine of bromine extracting→ double extraction and making salt



## DEVELOPMENT TREND OF BROMINE INDUSTRY IN CHINA

The bromine and bromide industry have greatly developed in China in recently 20 years. At present, a supply of about 160 thousand tons of bromine cannot satisfy the market in China. And we need import bromine from Isreal and American every year.

The bromine in China is mainly used to make flame retardant, intermediate of pesticide and drug, intermediate of dye and bromine inorganic salt and so on.

The production of bromine in China mainly depends on underground brine in the coastal area in Laizhouwan. But because of the excessive development of salt and bromine, the underground brine is over explored. The reserve and content of bromine is decreasing every year. The decreasing rate is 5%~10%. In 3~5 years, the brine resource advantage of salt and bromine is no obvious. So the bromine market in China will appear the situation of shortage. Only two ways can solve this contradiction:

Import bromine

find new resources in China

At present, associated water of oilfield and underground brine in China are not used in Liaoning province.

There are plenty of salt mine, potassium ore, magnesium ore in the western China. And there may be bromine brine ore but not found.

Our company had completed the research on extracting bromine from seawater in 2005. The technology can meet the demand of seawater desalination and seawater cooling for electricity company. It can make bromine of 20 thousand tons in 5 years.

At present, the innovative technologies of producing bromine are solvent deresining (Ocean university of China), membrane extracting (Tangu saltern). These methods only limited to research stage, they can't apply to industrial production immediately.