EFFECTS OF THE COMBINED PRODUCTION OF SALT AND BR ON SEA –SALT PRODUCTION

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Abstract: In the technology of the combined production of salt and Br, some changes that occurred after extracting Br and the effects of the combined production of salt and Br on sea-salt production were introduced, and some improvements were also put forward.

Key words: Brine; Br; Sea – salt

PREFACE

Many salt production companies invest more in pro-
ducing bromine, enlarging the production capacity, with the recovery of bromine price in the recent two years.

Salt-bromine co-production process means that the medium brine (the concentration is about 9°Be′ ~14°Be′, clear, the bromine content is more than 150 g/m^3) is fed into the salt production system to vaporize after extracting bromine.

The bromine-refinery process includes six stages: acidification, oxygenation, blowing out, absorption, vaporization and condensation. The PH value and components both will be changed before and after bromine refinery. If the bittern is fed into the sea salt-production system, it is sure that the sea-salt quality will be affected.

This paper will take the closed circulation bromine production by blowing out acid to absorb end gas in TIANJIN CHANGLU HAIJING CO.LTD as an example to analyze the effect which is caused by the changes between before and after bromine-refinery from the medium bittern. The improvements are also listed.

THE CHANGES OF MEDIUM BRINE AFTER BROMINE REFINERY

The technological flow sheet of with blowing out acid by air to absorb acid closed circulation bromine production process is as follows.

The raw material bittern in the process is from the primary brine-producing area-WANGZI NO.9 and 4-4, 4-8 WANGZI in the salt production system. The concentration is about 10°Be′ ~ 13°Be′. It will return to the salt production system after acidification, oxygenation and blowing out. The complex physic and chemical changes will take place.

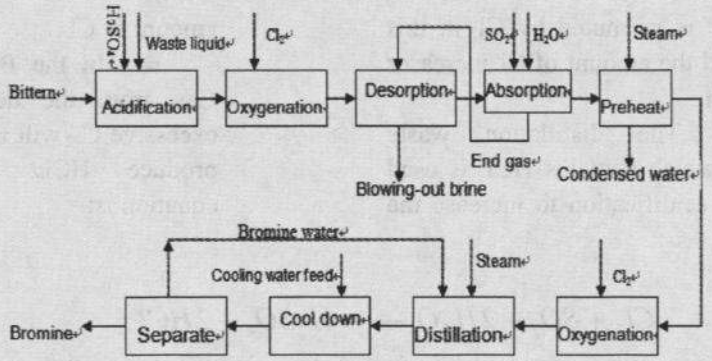

Figure 1. The technological flow sheet of Bromine-production

The change of PH value

The first process of refining bromine from bittern is acidification. The medium bittern is slight basic. The PH value is about 7-9. Under this condition, the bromine and chlorine molecule tend to decompose. In order to prevent the hydrolysis, decrease the chlorine consumption and increase the blowing out ratof bromine, the acid should be added during the process to lower the PH value.

In the operation, the bittern acidification utilized the waste acid. The main component of the waste acid is hydrochloric acid, sulfuric acid and a little hydrobromic acid. The PH value will be decreased to 2.5-4.0 after acidification. The HBr and H_2SO_4 mist will be taken in when blowing out cycling end-gas. This will also cause the decrease of PH value. The situation of changing of PH value is shown in the Table1.

Table 1. The changes of PH value

Position	Sample date	concentration (°Be′)	pH value Before refinery	After refinery
1 Department	2006 . 4 . 05	12 . 38	7 . 68	2 . 56
	2006 . 7 . 16	11 . 75	7 . 85	3 . 12
	2006 . 9 . 25	12 . 34	8 . 17	3 . 62
2 Department	2006 . 4 . 05	9 . 35	8 . 02	2 . 85
	2006 . 7 . 16	9 . 12	7 . 69	3 . 24
	2006 . 9 . 25	9 . 53	7 . 93	3 . 51

From table 1, it can be seen that the slight basic of bittern is changed into a little strong acidity. The PH value changed.

The changes of chemical components of bittern

The bromine refinery of medium bittern includes acidification, oxygenation, blowing out and vaporization. The complex physic and chemical changes take place, so the components of brine also have some changes. The analysis is as follows:

(1) The changes of chlorine ion

Three ways of causing the increase of Cl^- in the process are as follows:

The Br^- is oxidized by the Cl_2, the chemical equation is

$$2Br^- + Cl_2 \longrightarrow Br_2 + 2Cl^- \quad (1)$$

The Br^- is permuted by Cl_2 in this reaction, and the amount of Cl^- increases in the bittern.

- The distillation waste liquid which contains HCL is used during acidification to increase the amount of Cl^-

- In the Br_2 –Air mixture Gas from the desorption tower, excessive Cl_2 will react with SO_2 to produce HCL. The chemical equation is:

$$Cl_2 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl \quad (2)$$

The Cl^- will be increased in the distillation waste liquid after oxidation and vaporization. The Cl^- in the bittern will be increased, too.

(2) The changes of SO_4^{2-}

In this process, there are two ways to increase SO_4^{2-}, which are as follows, respectively:

① in this process, the acid-method absorption will be adopted, i.e. using SO_2 and water to absorb Br_2, the chemical equation is:

$$SO_2 + Br_2 + 2H_2O \longrightarrow 2HB_r + H_2SO_4 \quad (3)$$

The product bromine will be got after the absorption liquid is re-oxidized by Cl_2 and then rectified. It is clear that the main components of distillation waste liquid are H_2SO_4 and HCl, which can be used to acidate brine to increase SO_4^{2-}.

② If SO_2 is excess in the off-gas absorption process, the off gas which is fed into the blowing-out tower will contain SO_2, which will reduce the dissociative bromine that has been oxidized. And then the reaction (3) will take place, and the amount of SO_4^{2-} in the blowing-out liquid will be increased.

(3) The changing of free bromine and ionic bromine

① Lacking SO_2 in absorption process, the recycling end gas entering the blowing-out column will contain free bromine, so the waste liquid blown out will contain free bromine to make the brine redden. At the same time the end-gas comes from the absorption appliances contains the hydrobromic acid mist, which can carry some ionic bromine.

② Distillation waste liquid acidification brine contains a few hydrobromic acid and free bromine, which will change the content of the bromine in water.

Effect on the creatures in salt pan

After extracting bromine, the PH value and chemical composition of brine changed, which affects the ecosystem of the salt pan seriously. And the biocoenosis of brine also changed. The comparison between Artemia and Algae of salt pan is as follows:

(1) The production of Artemia declines: Because of the changes of the PH value and chemical composition of brine, the Artemia density of the salt pan after extracting bromine dropped. Like the experiment of a factory, the concentration in salt pan of medium brine before extracting bromine is 12°Be' and the density of the number of Artemia per liter is 180. After adding some brine with bromine extracted, the difference of concentration is less than 1°Be'; after a period of time, the density of the Artemia becomes 100 per liter.

(2) Coccochloris increases obviously: It's hard to find Coccochloris in the brine before extracting Bromine. After adding some brine that has extracted bromine, more than twenty kinds of algae were found such as coccochloris、dunaliella and navicula etc. Among them, coccochloris、dunaliella and navicula are dominant species, which account

for over 95% of the total, and coccochloris accounts for more than 65%.

ANALYSIS ABOUT THE EFFECTS OF THE SEA SALT PRODUCTION

In general, composition and PH value of the brine changes after extracting bromine. When it is fed into sea-salt production system again, the analysis about the effects on the output and quality is as follows:

Effect of PH value's changing

The PH value of the brine reduces after extracting bromine, changing from neutral to acidic, which leads to some changes of ecosystem of salt pan. It affects the growth of Artemia, reduces the production of Artemia obviously, lowers the quality of brine and reduces the evaporation of brine; Meanwhile, the coccochloris has mass propagation.

Coccochloris is a type of algae which have capsules, which is the archenemy of sea-salt production. The mass propagation of coccochloris makes the viscosity of the brine increase, affects the evaporation of brine, and reduces the production of the crude salt

High viscosity of the brine will affect the crystallization of salt, lead to produce the crude salt with small particles and many impurities, and lower the output and quality.

The effect of the changing of chemical composition

The increase of SO_4^{2-} in the brine would affect the growth of NaCl crystal, which is disadvantageous for the regular arrangement of Na+ 、 Cl-. In the crystallization process, raw salt crystals are loosening, soluble impurities increase, and the quality of the product goes bad.

The existence of bromine ion affects the regular arrangement of Na^+ and Cl^- during the crystallization process, and also increases the impurities in crude salt, reduces the quality of the product.

The increase of Cl^- is beneficial for the sea-salt production in a way.

EPILOGUE

Combined production of salt and bromine is a process that has high economic benefit, which achieved the cyclic utilization of the ocean economy to a certain extent. To achieve the win-win of the benefit and ensure the production & quality of sea-salt, some improvements are put forward.

(1) To treat the brine with bromine extracted reasonably. Mix brine with bromine extracted with certain brine without bromine extracted to control the PH value in alkalescence (PH = 7~9), and set a fixed area to run up the brine to avoid large-area pervasion.

(2) Rebuild the ecosystem of the salt pan. To reduce the content of coccochloris in the extracted brine, we can take large quantity of Artemia from the neighboring salt pan and cultivate them. By using the filter of the Artemia to control the propagation of Coccochloris, develop the Artemia species, rebuild the ecosystem of the salt pan, and improve the quality of brine and the production & quality of sea-salt.

(3) Perform "new, deep, long" crystallization process of sea salt strictly; strictly prohibit the reuse of old brine. When using subsection crystallization process, the concentration of the old brine and ratio of Na & Mg need to be controlled.

(4) Control the process conditions of all the sections in extracting the bromine strictly; minimized the content of free bromine and ion bromine blown out from the waste liquid.