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Study on Process Technology of Raw Material Water Pretreatment for Extracting Bromine

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Abstract. In view of the characteristics of different bromine raw materials such as seawater, desalinated concentrated seawater, and cultured salt brine, the raw material liquid is carried out by examining physical and chemical indicators such as temperature, turbidity, pH, Br^-, suspended solids, COD, residual chlorine and chemical components. Purification, acidification, oxidation and other pretreatment processes are studied to form a pretreatment process suitable for different bromine feedstocks. Satisfy the influent water quality requirements of different bromine extraction methods, form a mature pretreatment process, provide important support for the related vertical issues in the field of bromine and the application of horizontal development projects such as feasibility study and design, and help to achieve desalination projects and The scientific combination of bromine engineering.

Keywords: Bromine; Acidification; Oxidation; Pretreatment.

1. Introduction

Bromine is an important basic chemical raw material. In 2016, the annual global output was about 820,000 tons. It is widely used in medicine, pesticides, flame retardants, fire extinguishing agents, refrigerants, photographic materials, fine chemicals, oilfield mining and other fields[1-4]. There are many methods for the production of bromine, and currently 90% of the production of bromine is carried out by air-frozen acid absorption.A simplified process for the bromine process by acid is shown in Figure 1.

Liquid bromine is not directly distilled from bromine-containing seawater, but is subjected to "air blowing, SO_2 absorption, oxidation" because the content of bromide ions in seawater is small. Before seawater is extracted, bromine must be concentrated. The process of blowing, SO_2 absorption, and chlorination is actually a concentration process of Br_2, which is more efficient, less energy-consuming, and less costly than direct distillation of Br_2-containing seawater. [5]

The main cost of using bromine in concentrated seawater is in the blowing process. Therefore, controlling the ratio of concentrated seawater to acid and chlorination in the blowing process and bromine content in the absorbing liquid can play a decisive role in the cost of bromine.

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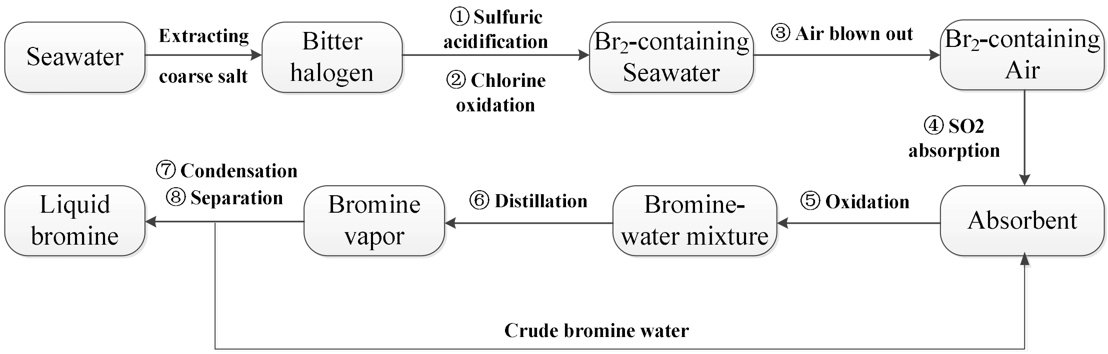

Figure 1. Acid Process Bromine Process

2. Research content

Study different chlorine ratios (100%, 110%, 120%, 130%, 140%, 150%, 160%) under different temperature (10°C, 20°C, 30°C), different pH values (2, 3, 4) to obtain the best process conditions for the oxidation effect of bromide ions in the raw materials; at the same time, obtain the comprehensive cost (acid and chlorine gas consumption) under the optimal conditions, and form the optimal pretreatment process for extracting bromine from different raw materials.

3. Experimental program

At a constant temperature, 10 L of the feed liquid was added to a 20 L stirred, temperature-controlled laminated glass reactor, and a certain amount of dilute sulfuric acid (20%) was added dropwise to adjust the pH, and then the mass flow meter and the corresponding shut-off valve were used. The chlorine gas was metered in. After the reaction was equilibrated, 100 ml of the feed liquid was taken from the bottom of the reaction vessel for partial detection. The bromine plant was used to determine the total amount of bromine chloride. The chlorine ratio was determined by using the industry standard. The bromide ion content in the feed liquid was determined and the oxidation rate was calculated to obtain the relationship between the chlorine distribution rate and the oxidation rate under the condition. After a set of experiments is completed, the waste liquid is discharged after passing through an excess of sodium hydroxide solution for neutralization. Replace the new material solution for the next set of experiments.

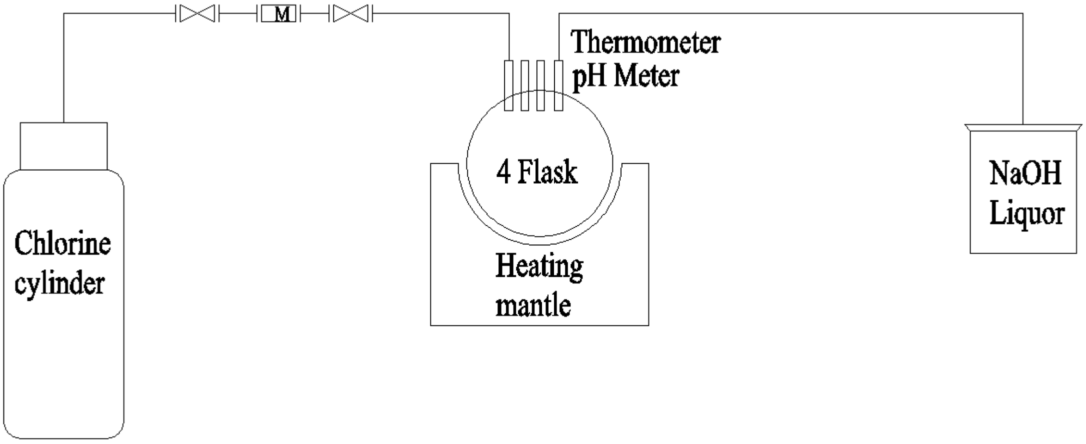

Figure 2. Acidification oxidation experiment equipment

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4. Experimental results

4.1. Raw material liquid analysis

In this project, different raw material liquids such as seawater, desalinated concentrated seawater and cultured salt field brine are taken as research objects. Physical and chemical indicators such as temperature, turbidity, pH, Br^-, suspended solids, COD and chemical components are investigated to purify the raw material liquid. Research on pretreatment processes such as acidification and oxidation.

Table 1. Analysis of raw material composition

	Seawater	Yantian brine	Bromine waste
Baume	4	3.6	3.75
Turbidity	2.56	2.63	3.52
P^H	8.21	6.95	5.66
SPM（mg/L）	12	32	12.5
Na^+（mg/L）	12428	11618	12058
K^+（mg/L）	459	403	417
Mg^{2+}（mg/L）	1308	1203	1265
Ca^{2+}（mg/L）	419	405	454
Cl^-（mg/L）	20452	19007	19737
Br^-（mg/L）	83	26	26
SO_4^{2-}（mg/L）	3275	3079	3176

In the industry, the bromine raw material liquid is subjected to coarse filtration to remove some impurities visible to the naked eye, and the large particles are screened out to ensure that the pipes and equipment are not blocked, and that calcium sulfate crystal precipitation does not occur.

According to the above data analysis, the brine of 83 mg/L of Br^- was selected as the raw material liquid, and the experimental study of the acidification oxidation process was carried out.

4.2. Acidification Oxidation Process

4.2.1. Effect of temperature on bromine production

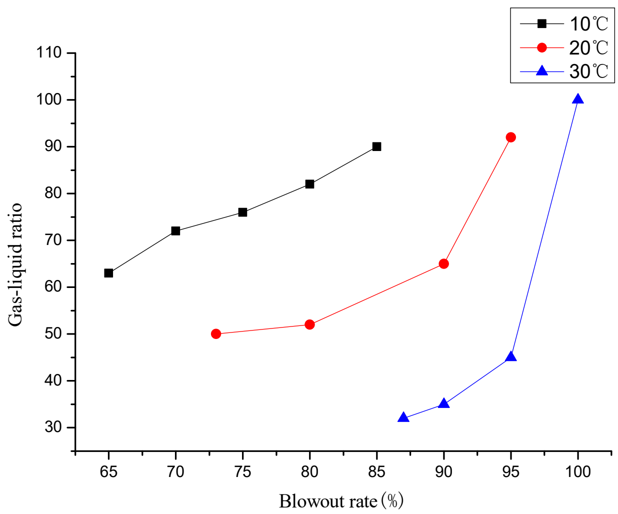

Figure 3. Seawater bromine blowing rate and gas-liquid ratio relationship diagram under different temperature

During the chemical reaction process, temperature is an important factor affecting the reaction rate. It determines the desorption process of bromine. When the temperature decreases, the equilibrium partial pressure of bromine decreases, the mass transfer driving force decreases correspondingly, and the conversion rate of bromine decreases accordingly. Achieving the same amount of blow rate requires an increase in the amount of blown air. The relationship between the seawater blowing rate and the gas-liquid ratio at different temperatures was studied experimentally, and the relationship between the bromine blowing rate and the gas-liquid ratio in seawater was obtained.

4.2.2. Effect of pH on bromine production

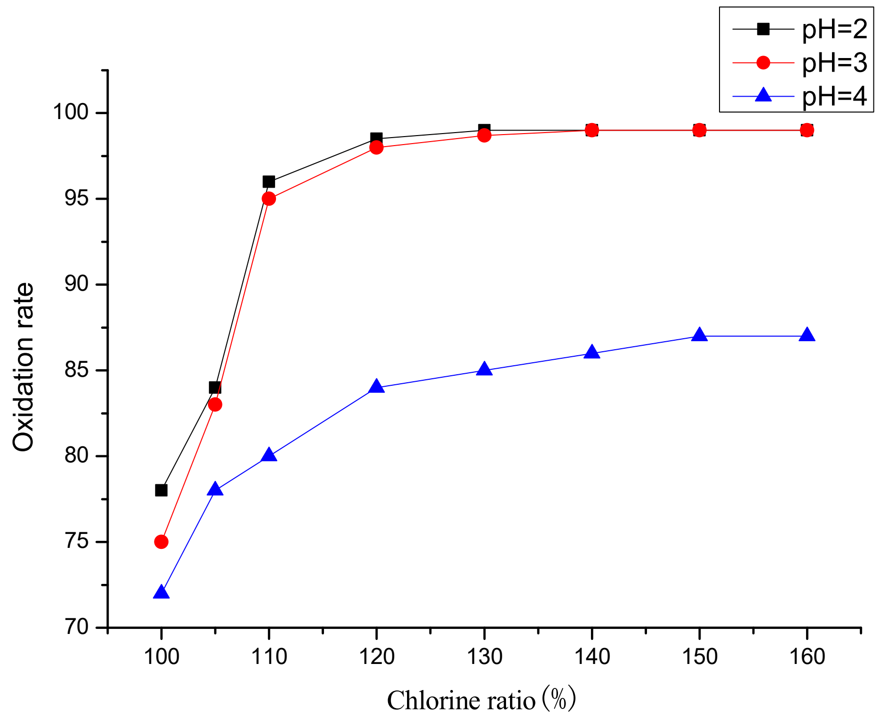

Figure 4. Relationship diagram of chlorine in oxidized liquid and bromine content in the solution under different pH

In the process of extracting bromine, the ionic state Br-Bromide in seawater is first oxidized to Br_2, and Br_2 is easily hydrolyzed. To prevent hydrolysis, it is necessary to increase the concentration of H+ in the solution, that is, to lower the pH of the solution. Cl_2 as an oxidant has stronger oxidizing ability under acidic conditions, and the change of free bromine content in solution at different pH values is obtained through experiments. According to the data analysis, the highest oxidation rate of bromine in the solution is about 86% when the pH value is about 4. When the pH value is about 2-3, the bromine in the solution is completely present in the molecular state Br_2, and when the acidity of the solution is stronger, Consume more concentrated acid, in order to reduce the production cost, control the pH value of the solution at about 3 can have a better effect.

4.2.3. Effect of chlorine distribution rate on bromine production. In order to increase the extraction rate of bromine in the solution, in order to reduce the chlorine consumption of the solution, the chlorine production cost can be reduced to reduce the production cost of bromine. Therefore, it is necessary to find the best chlorine distribution rate to achieve a win-win situation, the chlorine distribution rate and the oxidation rate. (Br_2 content in solution) diagram, it can be seen that under the premise of a certain temperature and acidity, it is more suitable to control the chlorine content, that is, the chlorine ratio is

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between 110% and 125%. At this time, the oxidation rate of bromine is above 98.0%, has reached the optimal level of bromine conversion.

5. Conclusion

In order to increase the blowing rate of concentrated seawater, the pH value is controlled at 3.0 according to the experimental data, and the chlorine distribution rate is 110%-125%. Since the bromine content of concentrated seawater is only 0.1 kg/m^3, according to the bromine yield of 70%, the extraction of 1t bromine requires about 14,000 m^3 of concentrated seawater. Under the different acidification pH value and chlorine distribution rate of the blowing process, the material The consumption is quite different. Therefore, strict control of production process parameters plays a crucial role in reducing costs.

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