STUDY ON DESULFURIZATION OF SODIUM SULFATE TYPE ROCK SALT BRINE BY FREEZING PROCESS

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INTRODUCTION

Nowadays, China is the biggest salt production and consumption country in the world, the yield of salt in our country is more than 60,000,000 tons/years. Amount it the edible salt consumption is approximately 7,500,000 tons/years, other major part of salt product functions as raw material for soda industry. In 2006, the yield of soda is approximately 31,000,000 tons, the consumption of crude salt is approximately 46,500,000 tons, amount it, major part is solid salt (sea salt and vacuum salt). But other production and consumption country use a lot of liquid salt in soda industry. The production of liquid salt accounts for 50% of the total output, but 95% of its soda production salt is the liquid salt. In Britain, France and former Soviet Union, the liquid salt account for 6O%, 72% and 5O% of their total output respectively.

The raw material of soda industry in our country mainly is sea-salt baked in the sun on beach and solid salt by vacuum evaporation from well rock salt, and small percentage is liquid salt. Until 2006, the yield of liquid salt is only 3,187,400 tons in all over the country, account for 5.6% of total output of salt in whole country. The production cost and energy consumption is quite difference between vacuum salt and liquid salt. In China, the vacuum salt's energy consumption is approximately 140~180 kg standard coal/ ton salt. But the liquid salt is approximately 4 kg standard coal/ton salt. In 2006, the total yield of salt in our country is around 56,557,000 tons, the output of well rock salt is approximately 15,565,000 tons, its proportion of energy consumption occupies the total energy consumption salt industry is high. If liquid salt can be promoted and produced, the cost of raw material may largely be reduced. In the production of soda, sodium chloride water solution function as the raw material is used in alkaline decomposition and ammonia - soda process. According to the technological structure of soda process in China, around more than 75% is using liquid salt as the raw material. The rock salt in our country mainly has two kinds of sulfates: the sodium sulfate and the calcium sulfate. The main component of sodium sulfate is sodium chloride, the impurity is sodium sulfate (approximately is 15~30 g/L). The raw material request of soda production is $SO_4^{2-} \leq 4$ g/L, therefore, the key point of promote the application of liquid salt is the selection of energy saving technology in desulphurization of rock salt brine.

The commonly used methods in desulphurization of sodium sulfate type rock salt brine are precipition and freezing sodium sulfate. The precipitation method usually is adding chemical agent to brine to causes insoluble salt precipitation by the

combination of chemical agent and sulfate radical in brine, then separation is following. For example, the reaction between calcium waste liquid and brine in ammonium alkali process of producing alkali in China Petrochemical Corporation, Nanjing Chemical Industrial Co., Ltd. is as follows:

$$CaCl_2 + SO_4^{2-} = CaSO_4 \downarrow + 2Cl^- \quad (1)$$

After precipitation and separation, the concentration of SO_4^{2-} in brine is 4~5 g/L, and apply in the production of soda. The application of $BaCl_2$ as the precipitator has made an obvious result.

The freezing principle is using the different solubility of sodium sulfate and sodium chloride under different temperature condition and the characteristic of sodium sulfate has lower solubility under low temperature condition, in order to precipitate sodium sulfate in the form of $Na_2SO_4 \cdot 10H_2O$. Nowadays, many enterprises is applying this method, the freezing temperature controls in the range of -8℃~-5℃, the content of sulfate radical usually is around 5 g/L in sodium sulfate mother liquor. But it still could not satisfy the production technique request in many situations. This article studied on reducing the freezing temperature and further reducing the sulfate radical in sodium sulfate mother liquor to obtain liquid salt with higher quality.

Analysis of phase diagram

Figure 1 shows the phase diagram of the system of NaCl-Na_2SO_4-H_2O at -5℃.

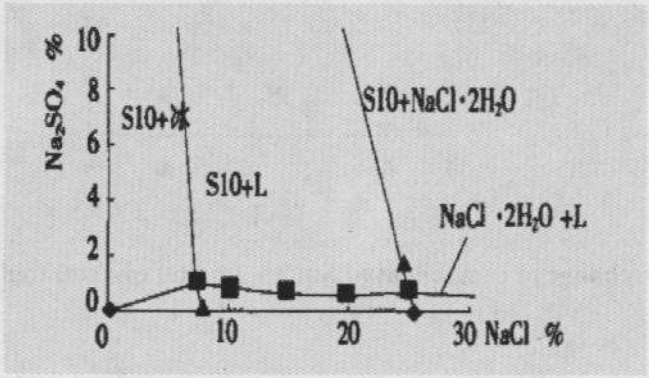

Figure 1. phase diagram of the system of NaCl-Na_2SO_4-H_2O at -5℃

In China, the composition of sodium sulfate type rock salt brine generally is 280~300 g/L of sodium chloride and 15~25 g/L of sodium sulfate. As spot F shown in Figure 1, nearby the linking line between of the co-saturated point of NaCl-Na_2SO_4-H_2O and the solid phase point of $Na_2SO_4 \cdot 10H_2O$ at -5℃ is the solid Glauber's salt by freezing brine process or the mixed salt from Glauber's salt and few $NaCl \cdot 2H_2O$.

The phase diagram of the system of NaCl-Na_2SO_4-H_2O under -5℃ still can not be found yet. According to Figure 2 and Figure 3, variation tendency of sodium chloride solubility in water and component of NaCl + Na_2SO_4 co-saturated solution along with temperature changing is analysis. Freeze brine below -5℃ could further reduce the solubility of sodium sulfate and sodium chloride, its balanced solid phase is existing by the form of $NaC1 \cdot 2H_2O$. The precipitated solid phase might be the mixed salt of Glauber's salt and $NaCl \cdot 2H_2O$.

EXPERIMENATAL

Experimental procedure

The preparation of brine used in laboratory is sodium chloride and sodium sulfate reagent (analytitcally pure), the composition is: NaCl 296.5 g/L, Na2SO4 21.16 g/L. Put the vessel with agitator which filled with brine in DL-4020 cryostat. Adjust the temperature in cryostat until it reaches the designated value, then keep stirring for 90 min. Stop agitation and carefully absorb supernatant liquor of brine, then analyze its composition.

Analysis on the composition of the material, the sulfate radical uses barium chloride gravimetry and chlorine ion uses silver nitrate titrimetry.

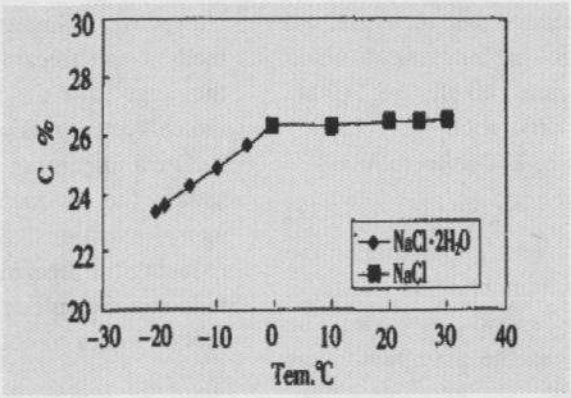

Figure 2. The change of NaCl solubility along with temperature

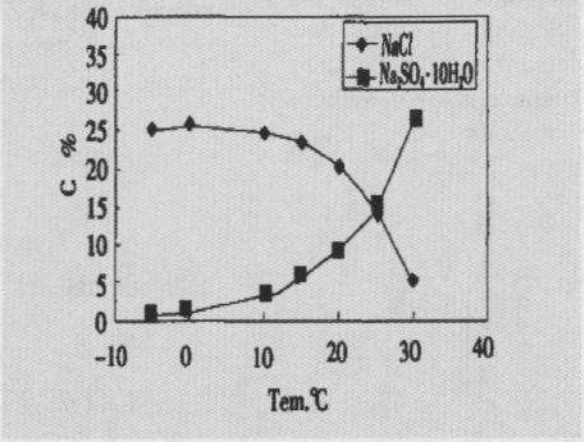

Figure 3. The change of component of NaCl + Na_2SO_4 co-saturated solution along with temperature

RESULTS

The freezing temperature in the test is in the range of 0~-20℃. Table 1 illustrate the composition of sodium sulfate mother liquor at different freezing temperature. The concentration of SO_4^{2-} and NaCl along with the change of temperature is shown in Figure 4 and Figure 5.

Table 1. The composition of sodium sulfate mother liquor at different freezing temperature

Serial number	Freezing temp. (℃)	Content of SO_4^{2-} (g/L)	Content of NaCl (g/L)
1	0	14.20	295.3
2	-3.5	6.647	295.3
3	-5	5.948	290.2
4	-8.3	3.684	288.4
5	-12.9	2.614	283.0
6	-14.1	2.202	281.6
7	-15.7	1.811	280.2
8	-19	1.317	269.8

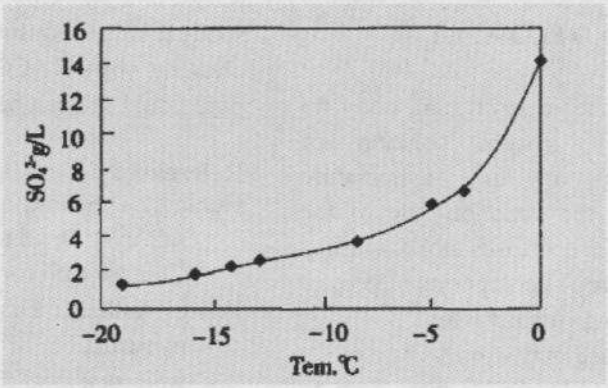

Figure 4. The concentration of SO_4^{2-} along with the change of temperature

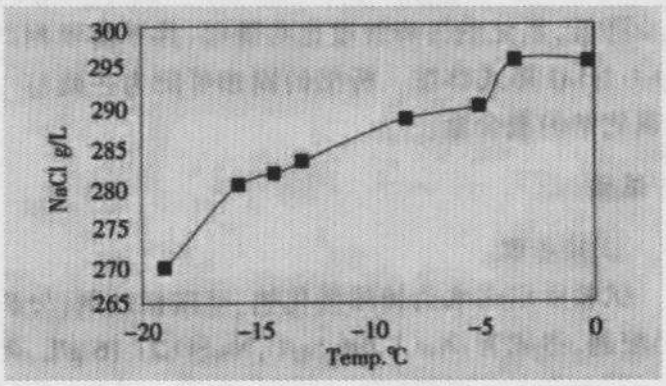

Figure 5. The concentration of NaCl along with the change of temperature

DISCUSSION

Base on the experimental results, the following can be found:

When the hydrous salt system solution of NaCl-Na_2SO_4-H_2O at the temperature between 0~-20℃, the solubility of Na2SO4 decreases along with the drop of temperature. In the range of 0~7℃, the solubility goes down fast, but when the temperature is lower than -7℃, the decreasing rate of solubility is smooth (Figure 4). When freezing temperature is -12℃, SO_{42-} in liquid phase may drop to below 3 g /L, when is -16℃, SO_4^{2-} may drop to below 2 g /L.

According to experimental data regression, in the range of 0~-20℃, the solubility along with the temperature change can be indicated as follow equation:

$$\ln C = -8112.6/T + 32.515 \quad (1)$$

where, C ---- the solubility of Na_2SO_4 (g/L);
T ---- temperature (K).

(3) Speaking of the raw brine in experiment, during the freezing process, Na_2SO_4 achieves saturated before NaCl, its saturation temperature is a little bit higher than 0℃. When the concentration of sodium sulfate in raw brine changes, the saturation temperature will also change. Generally speaking, along with the increase of Na_2SO_4 concentration the saturation temperature decreases.

(4) When the hydrous salt system solution of NaCl-Na_2SO_4-H_2O at the temperature between 0~-20℃,the solubility of NaCl also decreases along with the reducing of temperature (Figure 5). According to the related literature, the balanced solid phase of NaCl is NaCl·$2H_2O$. Speaking of this experimental with using brine, saturation temperature of NaCl·$2H_2O$ is between -3.5~-5℃.

CONCLUSION AND PROSPECT

(1) Through the experimental study on the hydrous salt system solution of $NaCl-Na_2SO_4-H_2O$ at the temperature between 0~-20℃, the variation rule of the solubility of Na_2SO_4 decreases along with the drop of temperature. The experiment proved that when freezing temperature is -12℃, SO_4^{2-} in liquid phase may drop to below 3 g /L and when is -16℃, SO_4^{2-} may drop to below 2 g /L.

(2) During freezing, NaCl can be precipitated by the form of $NaCl{\cdot}2H_2O$ together with Glauber's salt.

(3) According to the crystallization law of salt by freezing brine, the liquid salt which quality is higher than QB/T 1879-2001 standard can be produced by lower the freezing temperature, in order to satisfy the soda-making industry. With the auxiliary cleaning by Na_2CO_3-NaOH-$BaCl_2$ almost pure liquid salt can be obtained.

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