Discussion on the Process for Producing Liquid Salt Used to Make Alkali with Sodium Sulfate Type Brine

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Abstract: This paper mainly comparatively analyzes all kinds of processes of removing calcium and magnesium from sodium sulfate type brine. It also discusses the process for producing liquid salt used to make alkali with sodium sulfate type brine, in order to drive the development of domestic liquid salt.

Key Words: Discussion; sodium sulfate type brine; alkali making; liquid salt; process

1. PREFACE

As a basic industry , the salt industry plays an important role in people's life and national economy. There are sea salt, lake salt and well and rock salt in our national salt industry, which accounts for 30% of total production, however its Energy consumption accounts for 91% of the whole salt industry. In order to reduce energy consumption of well and rock Salt, the state development and reform commission encourage the development and use of liquid salt. In The guidance of Restructuring of the National Salt Industry ([2006]605), it raises the liquid mineral salt proportion from 12% in 2004 to 20%. In the end of 1980's, the proportion of solid salt and liquid salt in American are 50 to 50, while the liquid salt of soda industry account for over 95%; the proportion of liquid salt account for all the salt dosage are 60%, 72% and 50% in England, France and The former Soviet Union. The yield of liquid salt in our country accounts for 12% in well and rock salt production, 4.84% in national salt production, 5.73% in soda industry. Therefore, the production and use of liquid salt in our country leave a large gap with developed country. To greatly develop the liquid salt becomes the important subject of our salt industry, especially the well and rock salt industry. With the endeavor of enterprises which increase the use proportion of liquid salt to reduce the production cost, the emphasize of the functional departments and the development of our liquid salt production technology will make a great progress in production level and use dosage of our liquid salt.

Liquid salt can be divided into sodium sulfate type and plaster type liquid salt. They also can be divided into salt-making liquid salt and soda-makig liquid salt by usage. The paper will discuss the production method of soda-making liquid salt with sodium sulfate type brine in order to will promote the liquid salt develop.

2 . Quality requirement of soda-making liquid salt

2.1 The hazard of SO_4^{2-} in liquid salt to the soda industry

In chlor-alkali production, SO_4^{2-} will obstruct discharge of Cl^- and make OH^- discharge, which will reduce the current efficiency and consume the electrical energy and speed up the electrode corrosion. In soda production, SO_4^{2-} will block the tower of evaporating ammonia and the pipeline, which will shorten the production cycle. Production cost is expensive with removing the SO_4^{2-} from liquid salt and it has seriously impact on the usage of liquid salt in the chlor-alkali and soda industry. So, many enterprises have to

use refined salt as materials.

2.2 Quality standard of soda-making liquid salt

At present, the performing standard of national soda-making liquid salt is under the guidance of "The light industry liquid salt performing standard of the PRC"(QB/T1897-2001), the control index is as follow(Table 1): According to Table 1, the control index of liquid salt for soda-making is sodium chloride ,sulfate ion, magnesium ion and calcium ion. The index of sodium chloride , magnesium ion and calcium ion is easy to control for sodium sulfate well type brine.

Hence, it is the key point to remove the most sulfate ion from the sodium sulfate well type brine .

Table 1 Quality of soda-making liquid salt(g/L)

Items		Control Index		
		Excellent	Class I	Class II
NaCl	≥	290	280	260
SO_4^{2-}	≤	5.0	10.0	15.0
Mg^{2+}	≤		0.6	
Ca^{2+}	≤		2.0	

2.3 Quality requirement of input liquid for chlor-alkali production

The main quality requirement of input liquid for chlor-alkali production is :

NaCl 305 g/L , Na_2SO_4<5.5g/L, Ca 、Mg(total)<10ppm .

3. METHOD OF OBTAINING SODA-MAKING LIQUID SALT FROM THE SODIUM SULFATE TYPE BRINE

The main components of sodium sulfate type brine are:NaCl 270-305 g/L. $Na_2SO_4$10-35 g/L, $CaSO_4$ 1-3g/L, $MgSO_4$ 0.2-1.5g/L. According to quality requirement of input liquid salt for chlor-alkali production, sodium sulfate type brine needs to remove not only the sulfate ion, but also magnesium ion and calcium ion.

3.1 Choice of removal process of magnesium ion and calcium ion

There are three removal processes of magnesium ion and calcium ion in domestic: "lime and soda "process, "caustic soda and soda" process and "lime –sodium sulfate –flue gas" process. Among which, the lime-sodium sulfate-flue gas process are extensive applied in production of salt and sodium sulfate enterprises. The follow are explain of these removal methods.

3.1.1 Lime and soda process

Technological principle is expressed in the following equations

Main reactions are :

$$CaO+H_2O=Ca(OH)_2 \quad (1)$$
$$Ca(OH)_2+MgSO_4=Mg(OH)_2+Na_2SO_4 \quad (2)$$
$$Na_2CO_3+CaSO_4=CaCO_3+Na_2SO_4 \quad (3)$$

Process description: pumping raw brine, proper lime(solution), soda(solution) into reaction pot, which will react under stirring. Finally the flocculants were added to the solution in order to separate the solution from the precipitation. The purification of brine is a batch process.

Refined brine: Ca^{2+} ≤l0ppm Mg^{2+}≤5ppm.

3.1.2 Caustic soda and soda process

Technological principle is is expressed in the following equations

Main reaction are : Using the OH^- in the NaOH to remove the Mg^{2+}, and Using the CO_3^{2-} in Na_2CO_3 to remove Ca^{2+}

$$2NaOH+MgSO_4=Mg(OH)_2+Na_2SO_4 \quad (4)$$
$$Na_2CO_3+CaSO_4=CaCO_3+Na_2SO_4 \quad (5)$$

This method has the same principle with "lime-soda process". The main technological process is same, which replaces the lime place with caustic soda. Compared with "Lime and soda process", magnesium ion, calcium ion and impurity (dissoluble and not dissoluble) are introduced with lime. Consumption of soda is large, Magnesium ion

and calcium ion is more in the slurry.
Refined brine: : Ca^{2+} ≤10 ppm Mg^{2+}≤5 ppm.

3.1.3 "Lime –sodium sulfate –flue gas"

$$CaO+H_2O=Ca(OH)_2 \quad (6)$$
$$Ca(OH)_2+MgSO_4=Mg(OH)_2+CaSO_4 \quad (7)$$
$$Ca(OH)_2+Na_2S0_4=2NaOH+CaSO_4 \quad (8)$$
$$2NaOH+CO2=Na_2CO_3+H_2O \quad (9)$$
$$CaSO_4+Na_2C0_3=CaCO_3+Na_2SO_4 \quad (10)$$

Refined brine: Ca^{2+}<5ppm Mg^{2+}≤1ppm

The XiangYe salt Co.,Ltd is the first enterprise to use the "lime –sodium sulfate –flue gas" process. Because the lower level of technology and automatic control, this method is fail to apply. In1990s, XiangHeng salt mine of HuNan province introduce the technology and automatic control from Austria, this method got successful application and got great economic benefit. This method was popularized by Tianjin Salt Research Institute (SRI), which is affiliated to China National Salt Industry Corporation(CNSIC). At present, this method is also applied by Dongxing Salt Co.,Ltd of CSIC and Jiangsu JingSheng salt Co.,Ltd .

3.1.4Cost comparison of the three technological processes

Example is based on an annual output of 600 thousand tons of refined salt. The raw material brine: $CaSO_4$ ≤ 2g/L, $MgSO_4$≤0.2g/L, refined brine Ca^{2+}≤l0ppm, Mg^{2+}≤5ppm, The investment and cost analysis is shown in Table2.

Table 2 Investment and cost of the three methods

No.	Method	Investment	Cost
1	lime and soda	1200	22.00
2	Caustic soda and soda	1400	22.30
3	lime –sodium sulfate –flue gas	1800	12.90

Learned from the Table 2 that: (1) "Lime and soda" process: less capital investment, simple process, the higher cost of purification, less amount of calcium slurry;(2)"caustic soda and soda" process: more capital investment, relatively simple process, the higher cost of purification, larger amount of calcium slurry;(3)"lime –sodium sulfate –flue gas" process: high capital investment, relatively complex process, the less cost of purification, larger amount of calcium slurry. Considering the infrastructure investment and cost of treatment to the brine, it should adopt the "lime –sodium sulfate –flue gas" process to deal with the calcium sulfate type brine.

3.2 Removal of the sulfate ion

If we adopt the liquid salt production process.

Technological principle can be expressed by the following equations:

$$Na_2SO_4+BaC1_2=2NaCI+BaSO_4\downarrow \quad (11)$$

Less Na_2SO_4 content in the liquid salt production method with sodium sulfate type brine, it is necessary to reduce the sodium sulfate of the brine after the removal of magnesium ion and calcium ion of the raw brine. Recently, Research institutions at home and abroad developed several low-cost sulfate removal technologies.

It includes that $BaCl_2$ process, $CaCl_2$ process, freezing process, $BaCO_3$ process, NDS process, ion exchange resin method, membrane filtration method and so on. At present, the common sodium sulfate removal method in domestic are these: $BaCl_2$ process, SRS process, CIM process from the Kaimo corporation .

3.2.1 $BaCl_2$ process

The reaction equation:

This method: less one-time investment, high running cost, large displacement, pollution of the environment, because $BaCl_2$ is highly toxic material.

3.2.2 $CaCl_2$ process

The reaction equation:

$$Na_2SO_4+CaC1_2+2H_2O=2NaCl+CaSO_4\downarrow+2H_20$$

This liquid salt production: $Na_2SO4 \leq 6g/L$

This method: less one-time investment, low removal efficiency of sodium sulfate, large amount of removal calcium, high running cost, a large number of gypsum productions as by-production and so on.

3.2.3 $BaCO_3$ process

The way to remove sulfate with $BaCO_3$:

Injecting proper $BaCO_3$ into mixture tank, then we can make $BaCO_3$ suspension solution by stirring the tank. Putting the suspension liquid into the tank with sulfate and calcium from top, then the reaction will take place. After purification, the liquid was use to make salt, while the left $BaCO_3$ will circulate back to the reaction tank for repeat usage.

The reaction equation s is as follows:

$$BaCO_3+Na_2SO_4=BaSO_4+Na_2CO_3 \quad (12)$$
$$Na_2CO_3+Ca^{2-}=CaCO_3\downarrow+2Na^{+} \quad (13)$$

This liquid salt production has less Na_2SO_4.

This method can remove the sulfate and calcium ion at the same time, but $BaCO_3$ is highly toxic material. It is hard to deal with and time-consuming. It will produce large displacement, polluting the environment.

3.2.4 Freezing process

The separation principle of freezing process is to separate the sodium sulfate using the variation of the solubility, temperature, physicochemical characteristics. When the temperature is at -12~-10℃, sodium sulfate crystallized and it can be separated as the $Na_2SO_4 \cdot 10H_2O$ while anhydrous sodium sulfate is the by-production.

Liquid salt production: $Na_2SO_4 \leq 6g/L$

Freezing process: large investment, complex technology, high running cost. It is suitable for brine which nitrate is abundance.

3.2.5 NDS process

NDS process is a sodium sulfate removal method which is developed by Zhongyuan Chemistry Company of Japan. NDS process uses the zirconium hydroxide as the ion exchange body, removing sodium sulfate from salt water continuously and selectively.

Features of NDS process: non-toxicity. Zirconium hydroxide is not poisonous as the barium salt, it does not produce solid waste; low running cost, it has no impact on metal anode ion-exchange membrane, ion concentration is easy to control. NDS process has similar removal capacity as a barium sulfate, which can control the ion concentration at any range. The sulfate removal efficiency of NDS process has nothing to do with concentration of salt water. Zirconium hydroxide has chlorine tolerance. Zirconium hydroxide will not cause the chemical change when used to deal with the salt water in which chlorine was dissolved. Easy operation.NDS process adopt the automatic control technology, it needs less operators, faster reaction in sorption and desorption. Zirconium hydroxide absorbs the sodium sulfate selectively, so that loss of salt is less. Zirconium hydroxide exists as granular, and it is easy to deal with because its good Filter performance.

3.2.6 Ion exchange resin method

To reduce the cost and pollution of salt refined progress, Sanshan company from Japan and Ekotic company corporate in 1995. They use the ion exchange resin method to replace the $BaCl_2$ process. This method reduces the cost and has no salt slurry to deal with. This method adopts the selective ion exchange resin, which can absorb the sulfate of salt water and be reproduced through water elution. Its patent has three features: (1) Salt water treatment plant is flat-type (2) Fixed bed of full filled resin; (3) the size of ion exchange resin is small. The salt water flows from bottom to top, removing the sodium sulfate. When reproducing, fresh water through the resin from top to bottom to bring the sodium

sulfate out of the system. Its economical efficiency is better than the $BaCl_2$ process.

3.2.7 Membrane filtration method

Since the membrane separation is the separation of molecular and it is a physical process. There are no phase transition, No chemical reaction and No added chemicals. Filtrate's quality is good, and its operation system is relatively simple. Its running cost is low, and its scalability is good. At present, membrane filtration method is mostly using in Chlor-alkali works to deal with thin salt water, which is the development direction.

3.2.7.1 SRS technology for sodium sulfate removal

SRS is developed by CHEMETICS Company of Canada, its full name is sulphate removal system. It successfully used in the sodium sulfate removal equipment of electrolysis enterprises of an U.S. petrochemical company, its patent is protected in China and other countries. It is economic and environment-friendly in Chlor-alkali industry. There are 4 company in China has bought such equipment The CHEMETICS company's SRS adopt the nanofiltration Membrane, which is based on membrane pore size and electrostatic, the content of Na_2SO_4 in SRS Concentrated liquid is about 100g/L, the content of NaCl is 220g/L. At present, SRS method is mainly using to remove Na_2SO_4 from salt water of Chlor-alkali enterprises It still stands out of area of removal Na_2SO_4 from the high concentration brine.

3.2.7.2 LJ Membrane system

LJ Membrane Technology which is developed by Lufujin technology Co.,Ltd of Xiamen can be used to remove the sulfate from the high concentration salt water of NaCl. This company can process the brine with tiny impurities of Na_2SO_4 25g/L,NaCl 290g/L. After being processed by LJ Membrane, the liquid salt contains: Na_2SO_4 is less than 5g/L and Na_2SO_4 is more than 75g/L. The liquid salt production: NaCl 290g/L, Na_2SO_4<5g/L

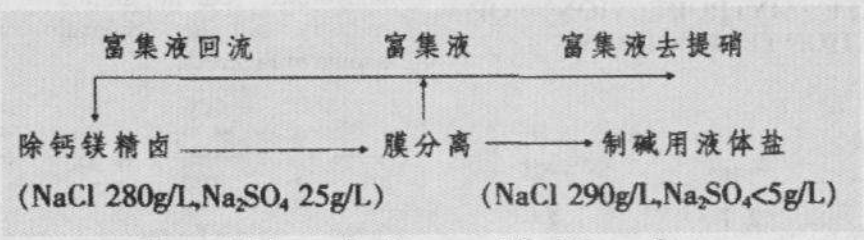

Figure 1 Schematic diagram of the LJ membrane

LJ Membrane system is suitable for Na_2SO_4 removal of small flow of brine, when dealing a large amount flow of brine, the cost will be relatively high. For example, when the volume of solution is 570m^3, the cost will be 62.5 million Yuan, which is not economical based on the current market.

3.2.8 Comparison about cost of sulfate removal technology

"$BaCl_2$ process" is suitable for brine with a bit of Na_2SO_4 , because the $BaCl_2$ is expensive. Its cost will be extremely high if the Na_2SO_4 content of production is required. Take the annual output 0.6 million liquid salt as example.

Refined brine: Na_2SO_4 25 L, liquid salt Na_2SO_4 <5 L.

Table 3 Cost comparison of those technologies (RMB:Yuan)

No.	Method	Cost	Note
1	$CaCl_2$	16.8	
2	$BaCO_3$	17.2	
3	$BaCO_3$	30.1	
4	Freezing	13.5	
5	Ion exchange resin Membrane	6.5	Thin salt water
6	NDS	10.8	No application in Chia
7	SRS	2.7	Thin salt water
8	LJ Membrane	4.0	Include microfiltration

As can be seen from above Table 3, the cost sequence of the eight sulfate removal technology is $BaCl_2$ process 、 $BaCO_3$ process 、 $CaCl_2$ process 、 freezing process 、 NDS process、 Ion exchange resin process 、 LJ membrane system process 、 SRS process. The cost of SRS process is lowest, but it still not applied in sulfate removal area of high concentration NaCl. Therefore, considering factors as energy, the environment protection, reducing the cost of brine purification and enterprises economical efficiency, LJ Membrane system method is more profitable to remove the sulfate.

To sum up, LJ Membrane system method should be adopt to remove the sodium from Na_2SO_4 type brine. It removes the most Na_2SO_4 of refined brine, which can be used to make the liquid salt for soda industry, however, the high concentration Na_2SO_4 are used to produce the anhydrous sodium sulfate and refined industry salt .

4. BRIEF INTRODUCTION OF PRODUCTION TECHNOLOGY

Based on the analysis of the removal technology of magnesium ion, calcium ion and sodium sulfate, the author think that we should adopt the "lime –sodium sulfate –flue gas" process to remove the magnesium ion and calcium ion and use LJ Membrane system method to remove the sulfate. The brief progress is as follows: The first step is to produce the material brine with water-soluble exploitation. The second step is to remove the magnesium ion and calcium ion in order to produce the refined brine with "lime –sodium sulfate –flue gas" process. The third step is to pump the refined brine into LJ Micro-filtration system in order to remove the slurry of magnesium ion and calcium ion and gypsum, the filtered solution is then pumped to the nanofiltration device to remove the Na_2SO_4 of the refined brine. Finally the solution after the nanofiletration is the soda-making liquid salt. Mixing the solution with high concentration of Na_2SO_4 and refined brine, the solution is just the raw material for the production of anhydrous sodium sulfate and refined industry salt.The schematic diagram is shown in Figure 2.

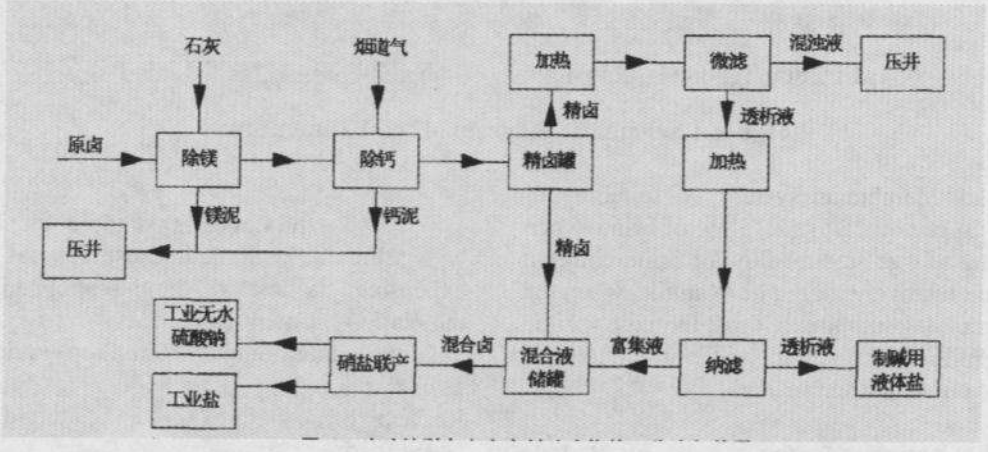

Figure 3 Schematic diagram of the proposed process

5 .CONCLUSION

This paper only compared different removal methods of magnesium ion and calcium ion and sulfate from sodium sulfate type brine so as to get a ideal production method of soda-making liquid salt. The "lime –sodium sulfate –flue gas" process is successful to remove the magnesium ion and calcium ion, but LJ Membrane system method has no industry example to remove the sulfate in high concentration and large flow. Therefore, it is hoped to develop the first production technology of soda-making liquid salt with sodium sulfate type brine in domestic and do some contribution to the development of the domestic liquid salt industry. This will rely on the nanofiltration technology research institutes and engineering institutes in domestic to do some deep research and development.