SELECTION FOR EXTRACTION PROCESS OF SODIUM SULFATE

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PREFACE

A new tide for expansion of rock and well salt production has been coming and developing, and more and more salt manufacturers have begun to build new salt plants or expanded the existing plants. Because most salt mine contains sodium sulphate, the manufacturers face a selection of sodium chloride production process in terms of extraction way of sodium sulphate. The selection of production process should be depended on the individual situation, plant site condition and brine composition of every manufacturer, avoiding to follow others unreasoningly and bring unnecessary loss.

In China the NaCl production processes with Na_2SO_4 extraction has three ways, which include freezing process, heat process and mother liquor recover process (called NaCl/Na_2SO_4 combined production). All the processes are according to the principle that Na_2SO_4 has the largest solubility at 17.9℃. Whenever temperature increases or decreases from the point, Na_2SO_4 solubility will decrease. Based on solubility behavior of NaCI- Na_2SO_4-H_2O ternary system, by controlling the system crystallization at different temperature we can realize the NaCl & Na_2SO_4 produced separately. Following is detailed discussion of the three processes.

DESCRIPTION OF FREEZING PROCESS

By freezing the brine at -4℃, the $Na_2SO_4 \cdot 10H_2O$ will crystallize from brine. By separation from liquor, re-dissolve, re-crystallization, and 1separation again and drying, the product Na_2SO_4 will finally be obtained. The brine after Na_2SO_4 extraction could be used to produce NaCl or used as liquid salt product. Because most raw brine has a low Na_2SO_4 content, manufacturer likes to adopt the bittern after NaCl crystallization or mixture of raw brine and bittern after NaCl crystallization as material to extract Na_2SO_4. Freezing procedure needs great quantity of refrigerating capacity consumption, and some freshwater is also needed to dilute the brine to avoid NaCl crystallization during freezing procedure. It not only increases energy consumption but also decreases the Na_2SO_4 content in brine which lowers the Na_2SO_4 extraction efficiency. Other problems are blockage of heating tubes during Na_2SO_4 production, making the evaporating system be washed frequently, actual working period becomes short, production operation is not stable and heat energy wastes a lot. On the other hand, the crystals of freezing is $Na_2SO_4.10H_2O$, it needs a process including re-dissolve, evaporation, separation and drying to finally produce Na_2SO_4 product. Three–effect evaporation is generally employed for Na_2SO_4 production, which needs high investment and consumes high heat energy. The representative enterprises adopting freezing process are Xiangli salt mine and Yipinglang salt mine.

The advantages of this process include technical maturity, high extraction efficiency

of Na_2SO_4 and high product quality of NaCl and Na_2SO_4. The disadvantages include production flow is too long; technical process is complicate; operation is difficult to control; too many equipments; high consumption; and high cost. The electrical and steam consumptions for each ton Na_2SO_4 are 450kwh
8~2t respectively. Generally speaking, the freezing process to produce Na_2SO_4 is not economical if only for obtaining high quality NaCl product.

But, if using the brine after extracting Na_2SO_4 as a type of liquid salt product, the freezing process shows a very good prospect. Because the procedures which transform liquid salt to solid salt in salt manufacturer, then transform solid salt to liquid salt in PVC-NaOH and Na_2CO_3 manufactures employs a lot of equipment and consume large energy, the new trend in production is to provide product qualified liquid salt directly from salt manufacturer to PVC-NaOH and Na_2CO_3 manufactures. In U.S.A the liquid salt covers 95% of total salt supplied to PVC-NaOH and Na_2CO_3 industries. In China the liquid salt ration is not high compared with total salt supply. It is caused firstly because of the geographic distribution of salt manufacturers and PVC-NaOH and Na_2CO_3 manufacture, secondly because salt industry and PVC-NaOH and Na_2CO_3 industries belong to two administration systems. With the opening of salt industry market, we suggest both large scale of chemical enterprises using salt and salt mine enterprises set up long term operation on liquid salt supply system. It is not only benefit to development of salt industry, but also propitious to development of PVC-NaOH and Na_2CO_3 industry. The freezing technology to extract Na_2SO_4 should be attached importance by enterprises with geographic convenience.

HEATING PROCESS

Heating process is a process developed in 1980's, which is based on the solubility behavior of Na_2SO_4, decreasing along with temperature increases when it is higher than 17.9 ℃. By heating the discharged mother liquor to 100℃, then adding fine salt to the liquor or sending the liquor to a Na_2SO_4 evaporator for concentration, the brine becomes NaCl saturated from unsaturated. Because of common-ion effect, Na_2SO_4 is saturated and crystallized to separate from the liquor, then the mother liquor is sent back to NaCl production system.

The advantages for this process include high heat utilization efficiency because of recovery of raw condensate water and withdraw of vapor from every effect evaporator to heat feeding brine; high solid rate which can reduce heat loss; process flow short and low investment without raw brine purification; brine is used with circulation, no mother liquor discharged, so brine consumption is low and environment pollution can be avoided. The disadvantages include small operation flexibility and low quality of product NaCl and Na_2SO_4. Because the impurity of calcium and magnesium in brine is not removed, the purity of Na_2SO_4 product only can reach 95%. So this process has not been spreaded and some manufacturer adopted this process gave it up later on. Only Lantian chemical plant still employs this process to produce Na_2SO_4 and achieves good economic effect through many years' operation experience and some technical modification.

Heating process is a way with low investment and high heat efficiency, but the discharged mother liquor is required having Na_2SO_4 content as high as 70 g/L during NaCl crystallization in order to produce Na_2SO_4 at next step, so NaCl crystals are not very pure. On the other hand, because this process doesn't employ brine purification, the impurity calcium and magnesium in raw brine makes the final product NaCl and Na_2SO_4 quality not very pure. If brine purification is implemented, the final product quality will be enlightened, but the investment of equipment and running cost will be increased too.

NACL/ NA_2SO_4 COMBINED PRODUCTION PROCESS

This process is a technology imported in 1990's. It is based on the solubility behavior of the NaCl-Na_2SO_4-H_2O ternary system, by controlling mother liquor circulation and technical parameters at different stages to

realize crystallize Na_2SO_4 at high temperature and crystallize NaCl at low temperature. It can guarantee not only produce high quality NaCl, but also produce high quality Na_2SO_4. The advantages of this process include low energy consumption; less blow down avoiding pollution to environment and high product quality. The raw material can be either raw brine or bittern after NaCl crystallization. With more than 10 years of running experience, this process has developed adequately in China, and evolved two branches. Following gives the description for each respectively.

NaCl/ Na_2SO_4 combined production process from raw brine

The procedures for this process are as follows: Firstly the raw brine is concentrated in the three evaporators, and when the content of Na_2SO_4 in brine reaches aimed index, it will be sent to the following three evaporators for next evaporation by circulation. During the evaporation at next stage of circulation, the brine is continued to concentrate, and NaCl will crystallize in a low temperature evaporator, and Na_2SO_4 will crystallize in a high temperature evaporator. By alternatively crystallization of NaCl and Na_2SO_4, a combined production is realized. Because when Na_2SO_4 crystallizes, NaCl is not saturated and when NaCl crystallizes, Na_2SO_4 is not saturated; in this process pure NaCl and pure Na_2SO_4 with high quality can be obtained if with help of an elutriation step after crystallization. Adopting heat pump technology and withdrawing vapor from each effect evaporator, the heat efficiency of this process is very high, and steam consumption of per ton product is about 1 ton. The representative enterprises for this process include Jiangxi salt mine and Jintan salt mine.

The NaCl/ Na_2SO_4 combined production process starting from raw brine features long flow; numerous equipments and high investment; and requiring the Na_2SO_4 content in raw brine limited under a defined figure. Because the NaCl evaporation section of this process is equivalent to a four-effect vacuum salt production system attached with a heat pump, NaCl evaporation section has high heat utilization efficiency, but the section for mother liquor recovery has relatively lower heat utilization efficiency. If the Na_2SO_4 content low in raw brine, the mother liquor quantity transferred from the NaCl evaporation section will be low, the average heat utilization efficiency for total process will be high. When Na_2SO_4 content exceeds 25 g/L, the heat economical advantage of this process will be not obvious. In China the Na_2SO_4 content in brine is between 15 to 30g/L in most situation, some exceeding 30g/L. All the salt mines containing Na_2SO_4 resource employ water dissolving exploit technology, so the Na_2SO_4 content in raw brine is usually lower at the beginning of exploitation, becomes higher with expansion of exploitation and probably folds at the end stage. This situation requires the equipment for Na_2SO_4 production has a designed surplus capacity for potential capacity increases in future, which will increase the investment and running cost. On the other hand, raw brine needs purification according to this process, and large quantity of raw brine's purification needs higher equipment investment and running cost. Now In Chinese domestic market, excellent grade salt product usually get same price as ordinary salt product in most situation except special demand-
ed products, so the advantages of NaCl/ Na_2SO_4 combined production process on product quality and on economic benefit have not been shown sufficiently.

NaCl/ Na_2SO_4 combined production process starting from bittern

It is based on almost the same principle as the process starting from raw brine, adopting original three evaporators in existing NaCl plant as the NaCl evaporation section of the new process, and all newly added apparatus belong to the mother liquor recovery section, which use the transferred mother liquor with high Na_2SO_4 content from the old evaporator apparatus as feeding material, evaporate the liquor to crystallize Na_2SO_4 in a high temperature evaporator and crystallize NaCl in a low temperature evaporator to produce NaCl and Na_2SO_4 respectively. This process features high quality; adapting to wide range of Na_2SO_4 content in raw brine; saving investment; but lower heat efficiency than the combined process starting from raw brine. Generally the

steam consumption for per ton product is 1.1-1.3 ton. In terms of brine purification method there are two types of production models for this process. Follows are the detailed descriptions.

Model of raw brine purification

The representative manufacturer of this model is the salt plant of Shuanghuan Co.Ltd., group. Firstly the raw brine is purified and sent to the original NaCl evaporation section for NaCl crystallization, then the discharged mother liquor after clarification is transferred to recovery section to produce Na_2SO_4 and NaCl respectively. Because the raw brine is cleaned, the NaCl product produced in NaCl evaporation section has a high quality, it is benefit to the utilization of PVC-NaOH manufacturers. But for most NaCl manufacturers facing the fact that excellent grade salt product can not obtain higher benefit from high price and more than 20 Yuan purification cost for per ton product, they provably give up raw brine purification and select bittern purification model.

Bittern purification model

The representative manufacturers of this model are the Changjiang salt chemical plant of China Salt Corporation and Jingshen Salt Company of Jiangsu Province. The procedures are as follows: Firstly the raw brine is directly sent to the original NaCl production section. After NaCl crystallization the discharged mother liquor (bittern) after clarification is transferred to the bittern purification apparatus. The purified bittern is then sent to the mother liquor recovery section as feeding material. Because of the quantity of bittern is only 1/3-1/4 of the quantity of raw brine, the required capacity for purification equipment is greatly reduced for the bittern purification model compared with brine purification model, and the purification cost is also greatly decreased. For glauberite type brine, by removing some glauberite sediment by clarification, it makes the bittern purification easier and running cost lower. With the bittern purification model, the NaCl product quality from the original NaCl section is a little lower than that of raw brine model, with lower production cost; the products from the mother liquor recovery section (NaCl/ Na_2SO_4 combined section) has very high quality with a little high running cost. So this process can meet different customer's requirements at different levels with better economic benefits.

This model of process adapts to the situation with varying composition of feeding brine, it can run with raw brine as feeding when the NaCl evaporation section is stopped sometimes, of course the economic benefit has a decrease at this situation. It is possible to purify the mixture of raw brine and bittern and use the mixture as feeding to produce NaCl and Na_2SO_4. This mixed feeding is especially suitable to the manufacturer employing raw brine with high Na_2SO_4 content.

CONCLUSION

The author select three representative Na_2SO_4 extraction processes to describe, following is a comparison to these processes on several aspects.

Comparison for three Na_2SO_4 extraction processes

Method	Freezing	Heating	NaCl /Na_2SO_4 combined with raw brine	NaCl /Na2SO4 combined with bittern	
				Raw brine purification	Bittern purification
NaCl quality	ordinary	ordinary	excellent	excellent	
Na_2SO_4 quality	excellent	low	excellent	excellent	
Investment	high	low	Very high	high	
Purification cost	None	None	high	high	low
Consumption	None	None	high	low	
Suitable situation	Liquid salt	Need modification	New project	Existing plant modification	

With the development of society and technology, more and more advanced processes and technologies will be developed. Because of higher and higher quality requirement from customers, when a plant is designed or made technical modification, investigation must be done sufficently on each aspect, such as brine composition and its varying trends, customers' requirement and its developing trends, geographic environment, etc. for making scientific and correct decision to realize the best economic benefits.