

A New Technical Process for the Joint Production of Sodium Chloride and Sodium Sulphate

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ABSTRACT

This paper introduces a new technical process for producing sodium chloride and sodium sulphate using the raw brine material mined by the drilling and water solubilizing method in chloride and sulphate salt mines. After the raw brine has been purified by eliminating the calcium and magnesium ion elimination, its content of NaCl and Na₂SO₄ is 270-300 g/l and 15-30 g/l, respectively. In the new process, the mother liquor, from which Na₂SO₄ has been salted out at a temperature of 70-100°C, is sent to the multi-effect evaporating system for making vacuum salt. Salt slurry drained from the last evaporating stage is washed twice with counterflow washing at normal temperature. Thus, fine salt with a content of 99.2% NaCl is obtained, and the content of Na₂SO₄ in the washing liquid is more than 70 g/l. Heating the washing liquid at a temperature of 70-100°C produces sodium sulphate which contains 98-99% Na₂SO₄. The mother liquor, which has crystallized out sodium sulphate, can be sent to the evaporator to crystallize salt. This represents the closed-cycle system of producing sodium chloride and sodium sulphate jointly.

INTRODUCTION

Many salt mines mined in China contain sodium sulphate together with sodium chloride. The brine obtained by the drilling and water solubilizing method generally contains 270-300 g/l NaCl, 15-30 g/l Na₂SO₄, 1-1.5 g/l CaSO₄, and 0.3-1 g/l MgSO₄. In the vacuum salt making factory, raw brine must be purified to eliminate calcium and magnesium ions. The purified brine contains few calcium and magnesium ions but its sodium chloride and sodium sulphate content changes little after this treatment. In the evaporating process, if the purified brine is used as the raw material for making salt, the concentrations of NaCl and Na₂SO₄ may saturate to the extent that they will crystallize together. Thus, the salt obtained may contain sodium sulphate as an impurity.

For a long time, salt containing about 95% NaCl has been produced. It is very poor in quality, and even with continual improvement, only a 98% NaCl content in the salt can be achieved. To obtain a high-purity salt using brine with a high Na₂SO₄ content as the raw material for salt production, the method of separating sodium chloride from sodium sulphate should be considered. The normal practice in industry is to freeze the Na₂SO₄ containing brine to a certain temperature and separate out mirabilite

(Na₂SO₄·10H₂O). The separation of sodium chloride and sodium sulphate can then be achieved. This method requires a freezing station and the mirabilite produced is an intermediate product which needs further processing to yield sodium sulphate. Thus, the process becomes more complex and requires more initial plant investment, high maintenance costs and high consumption of electricity and water. This makes that the production cost of sodium sulphate very high. Until now, there are very few factories using this kind of production process. Many of them operate by discharging the mother liquor, but this causes environmental pollution. Even if the mother liquor is sent back to the brine well, the consumption of raw brine and the number of mine wells will increase. This has been the main problem in the vacuum salt making industry.

Another method is to recover sodium chloride and sodium sulphate from the salt making mother liquor. In China, as the raw brine contains more than 20 g/l Na₂SO₄, its concentration in the discharged mother liquor will certainly be high in the process of salt making. As the heat efficiency of the mother liquor recovery equipment is much lower than that of the four-effect vacuum salt making equipment, this kind of method is not suitable for treating brine which contains high Na₂SO₄.

Producing sodium chloride and sodium sulphate together is a new method of salt making and sodium sulphate precipitation which is suitable for the real situation regarding China's raw materials. The new technical process is based on the NaCl-Na₂SO₄-H₂O ternary system phase diagram and has been subject to long-term laboratory tests in a pilot factory. Some factories have adopted this method for several years and have achieved satisfactory results.

THE BASIC PRINCIPLE OF SODIUM CHLORIDE AND SODIUM SULPHATE JOINT PRODUCTION

The basic principle of the joint production of sodium chloride and sodium sulphate is to utilize the difference in solubility between the NaCl and the Na₂SO₄. With an increase of temperature, the solubility of the NaCl and the Na₂SO₄ in the saturating solution of water will change, i.e. the solubility of the NaCl will increase and that of the Na₂SO₄ will decrease.

Figure 1 shows the phase diagram of NaCl-Na₂SO₄-H₂O. The points f and c represent the saturation points of NaCl and Na₂SO₄, respectively, at a temperature of 100°C or 30°C. Points efG, and abcd represent the solubility curves at temperatures of 100°C and 30°C, respectively. The raw material from which to produce sodium chloride and sodium sulphate jointly is a saturation solution of NaCl and Na₂SO₄ produced at a high temperature, such as 100°C. From Fig. 1, it can be seen that if the saturated solution is evaporated at 100°C, only mixed salt of NaCl and Na₂SO₄ (containing about 18% Na₂SO₄) can be obtained. This is marked by h on the figure. To obtain fine purified salt of good quality, the salt can be washed in raw brine (the composition is marked i on Fig. 1) at the normal temperature of 30°C. If the line A-c intersects line h-i at point j, the line segment of h-j means the weight of raw brine, while i-j means the weight of salt of solid phase. If line h-i intersects line c-d at point k, which is at the saturation curve of NaCl at 30°C, after washing, we can obtain NaCl and a saturated solution of NaCl and Na₂SO₄ at 30°C. At a temperature of 100°C, the saturation solution of NaCl and Na₂SO₄ at 30°C is in the crystallization area of Na₂SO₄. Heat the washing liquid to 100°C and let line B-c intersect curve e-f at point L. By adding a certain amount of NaCl (or evaporating part of the water), we obtain the Na₂SO₄ and a common saturation solution of NaCl and Na₂SO₄ at 100°C. In this way, the whole process circulates along the line fjcl.

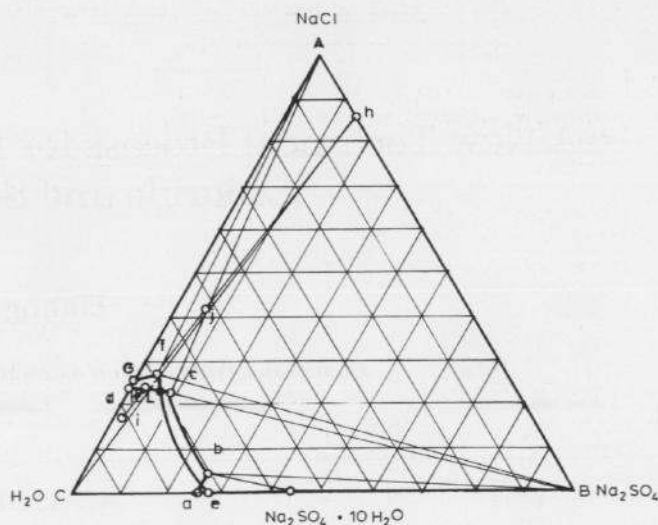


Fig. 1. NaCl-Na₂SO₄-H₂O phase diagram.

From the above analysis of the phase diagram, at 30°C, if NaCl (which is mixed with Na₂SO₄) is washed in raw brine, the Na₂SO₄ will dissolve in the liquid phase. Thus, pure NaCl is obtained. The common saturated solution, called the washing liquid, which contains NaCl and Na₂SO₄ at 30°C is heated to a temperature of 100°C and added salt can salt out (or evaporate) as Na₂SO₄.

THE TECHNICAL PROCESS AND ITS ADVANTAGES

According to the above principle of NaCl-Na₂SO₄-H₂O phase diagram analysis and combined with our actual experience in production, we constructed the following technical process for the joint production of sodium chloride and sodium sulphate.

Explanation of the process

Generally, in the vacuum salt making factory, purified brine is directly evaporated to make salt. However, this new process is different: firstly the purified brine washes the salt slurry from the last stage of the multi-effect vacuum evaporation equipment. Recently it has been realized that salt slurry flows along the process, i.e. the salt comes out of the evaporation system continually from the last stage, is thickened to 70% in density, and then is sent to the salt washer and mixed, washed with all the raw brine. The washing temperature is 30°C and the washing process is continual. After salt washing, fine salt with 99.2% NaCl and washing liquid with 70 g/l Na₂SO₄ is obtained. To obtain white sodium sulphate, the washing liquid must be clarified to remove insoluble impurities mixed during the

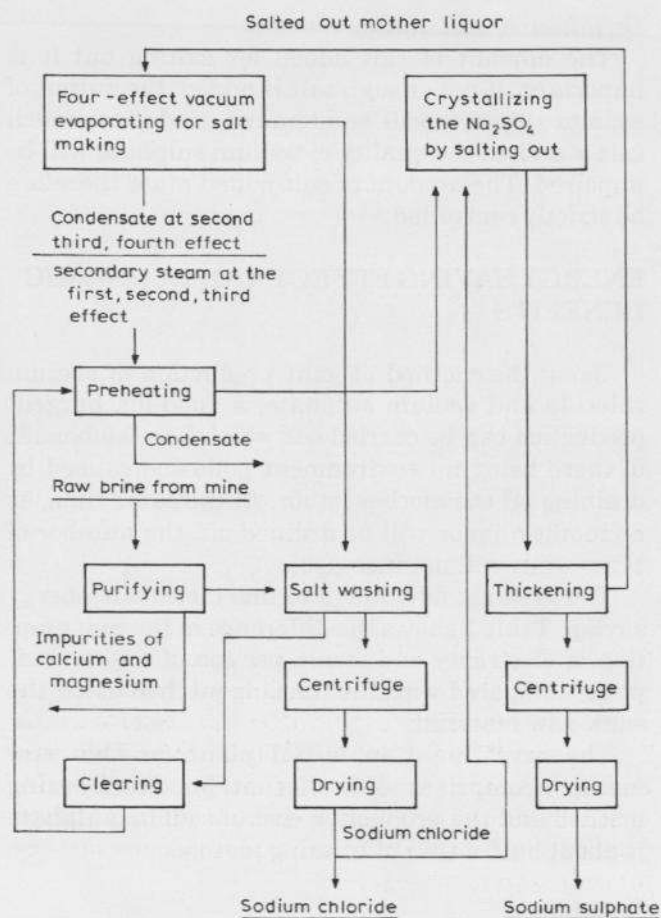


Fig. 2. Technical flow diagram of the joint production of sodium chloride and sodium sulphate.

process of washing. The washing liquid can be preheated by the second, third and fourth effect condensate from the four-effect vacuum salt making equipment with the plate type heat exchanger. Further heating is continued by the secondary steam of the first, second and third effect and can gradually be preheated to 100°C. The washing liquid is then sent to the crystallizer with the mechanical stirrer or circulating pump. At the same time, sodium chloride, which is necessary for salting out, is added. Sodium sulphate is then separated from the solution along with the solubilizing of sodium chloride. After thickening, centrifugal dehydration and drying, sodium sulphate which contains 98–99% Na_2SO_4 , is obtained. The mother liquor, heated to a high temperature, is directly sent to the first, second and third stage of the salt making evaporation equipment from the crystallizer and thickener.

Advantages of the process

In China, the content of Na_2SO_4 in raw brine is more than 15–30 g/l. In the solution mining process

the content of Na_2SO_4 can sometimes differ by more than 10 g/l in the same mine. The new process is effective even with this difference.

In addition, the new process differs from that of the general vacuum salt making factories. The high temperature saturated solution containing 55 g/l Na_2SO_4 is evaporated in the multi-effect vacuum salt making equipment with no adverse effects on the evaporation equipment such as scaling of the pipe wall of the heating chamber, and the wall near the liquid surface of the evaporation chamber. Long-term investigations have shown that using this new process, even in the factory where the raw brine is not purified, the evaporation equipment does not need to be cleaned after 20 days continual running and the effectiveness of the equipment remains normal. In factories where the raw brine is pre-purified, the salt making evaporator can of course run for longer.

From the above description of the process it can be seen that it is necessary to wash the salt and preheat the raw brine. The process of sodium sulphate precipitation is very simple and its energy consumption is low. Apart from the consumption of steam and electricity for drying, there is no other consumption of steam and water.

Before adding salt for salting out, the washing liquid contains 280 g/l NaCl, but the content of NaCl in the mother liquor of salted sodium sulphate increases at high temperature. During the evaporation process, the content of sodium chloride is increased by treating 1 m³ of brine. In this way, the salt used for salting out can be fully recovered which means that during the production process, the salt for salting out is not consumed but is kept in circulation.

The preheating process of the washing liquid is the same as the preheating of the raw brine for general vacuum salt making equipment, that is, by condensate of the vacuum salt making equipment and secondary steam to combine the salt making process with the sodium sulphate precipitation process.

In summary, the consumption of energy and sodium sulphate raw material is very low in this production process and as the process is simple, the equipment cost, depreciation charges and maintenance costs are also lower.

MAIN TECHNICAL DATA AND OPERATION CONTROL

Operation and control of the salt washing process

The salt washing process is very important for the joint production of sodium chloride and sodium sul-

phate. Whether good or bad quality salt is produced and the degree of enriched sodium sulphate in the washing liquid depends on the salt washing process. If the following operating conditions are adhered to, sodium sulphate mixed in sodium chloride may be completely solubilized.

Temperature for salt washing

As we know from the relationship of their common saturation in water and temperature of NaCl and Na₂SO₄ the solubility of Na₂SO₄ reaches its highest at a temperature of 17.9°C. Considering this point only, a temperature of 17.9°C can be regarded as being the most suitable temperature for washing salt. However, a cooling process is needed for the temperature of 17.9°C and thus the process becomes complicated and the cost increases. In the new process, the temperature of 30°C is chosen as the washing salt temperature. This is because when mixing the thickened salt slurry of 50°C and raw brine of 25°C can reach a temperature of 30°C. At the temperature of 30°C the solubility of Na₂SO₄ increases when NaCl and Na₂SO₄ are saturated in water. After salt washing, not only is fine salt obtained (NaCl content 99.2%), but sodium sulphate brought by the raw brine can also be completely extracted (except for that lost during the technical process). Moreover, all the technical indices are stable after long-term running. This shows that a temperature of 30°C for salt washing can meet the technical requirements.

Time for salt washing

To reach a balance between the liquid and solid phases during the salt washing process, it is necessary to have a certain reaction time because the solubility of sodium chloride and sodium sulphate is high in water.

Operation and control in the process of salting out sodium sulphate by adding sodium chloride

Definition of salting out temperature.

Using the phase diagram analysis of NaCl-Na₂SO₄-H₂O and experimental testing, the washing liquid with Na₂SO₄ was preheated and salt was added for salting out to complete the crystallization process of sodium sulphate. The definition of the salting out temperature is based on the temperature at which the saturation level of Na₂SO₄ is low. The washing liquid is preheated by the preheater of the evaporation equipment saturated with NaCl and Na₂SO₄ at a high temperature. In this way, a temperature of 100°C is quite suitable.

Definition of salt adding amount

The amount of salt added for salting out it is important. If not enough salt is added, the output of sodium sulphate will be impaired, and if too much salt is added, the quality of sodium sulphate will be impaired. The amount of salt added must therefore be strictly controlled.

ENERGY SAVING EFFECT AND ECONOMIC BENEFITS

Using the method of joint production of sodium chloride and sodium sulphate, a "non-discharged" production can be carried out which has the benefit of there being no environment pollution caused by draining off the mother liquor. At the same time, as no mother liquor will be drained off, the number of brine wells will not increase.

The greatest advantage of this method is energy saving. Table 1 shows the difference in the consumption of electricity and steam per ton of sodium sulphate compared with the freezing method using the same raw material.

The investment in initial plant for this new method comprises 60% of that for the freezing method and the production cost of sodium sulphate is about half of that of freezing method.

TABLE 1

Consumption of electricity and steam per ton of sodium sulphate

	Freezing method	Sodium chloride/sodium sulphate joint production
Steam (ton)	2	1.2
Electricity (kWh)	500	130

CONCLUSIONS

1. The raw brine that contains NaCl 270-300 g/l; Na₂SO₄ 15-30 g/l mined by the drilling and water solubilizing method from the chloride and sulphate salts mine is completely suitable for the new technical process of producing sodium chloride and sodium sulphate jointly.

2. The new technical process of producing sodium chloride and sodium sulphate jointly is similarly suitable for raw brine from which calcium and magnesium ions have not been eliminated. However, about 90% calcium sulphate in raw brine should be separated out together with sodium sulphate as it will reduce the quality of sodium sulphate. The crude

sodium sulphate can be solubilized and crystallized again to obtain a good sodium sulphate product.

3. With the new technical process, sulphate, the content of the product is: NaCl $\geq 99.2\%$ in good quality salt; Na₂SO₄ 98–99% in sodium sulphate.

4. Practice has showed that the new method can decrease energy consumption, and reduce both in-

vestment in initial plant and production cost in comparison with the freezing method.

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