Technological Basis for the Production of Sodium Sulfate by the Conversion of Sodium Chloride with Ammonium Sulfate

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Abstract

The production of sodium sulfate on the basis of conversion of sodium chloride with ammonium sulfate is based on the physicochemical properties of quaternary reciprocal aqueous system of chlorides and sulfates of sodium and ammonium and their constituent ternary systems.

Key words: *sodium chloride, ammonium sulfate, cooling temperature*

INTRODUCTION

To substantiate the conversion of sodium chloride with ammonium sulfate at elevated temperatures, the ternary system $(NH_4)_2SO_4$- $NH_4Cl - H_2O$ and the quaternary system $2Na^+, 2NH_4^+ // 2Cl^-, SO_4^{2-} - H_2O$ were studied by the isothermal method at 100^0C.

The process of filtration of the pulp which is formed in the processes of obtaining sodium sulfate and ammonium chloride by conversion of sodium chloride with ammonium sulfate has been studied. According to the obtained data, the filterability of the pulp with precipitate of ammonium chloride is slightly higher than the pulp with precipitate of sodium sulfate.

Material and methods. The creation of solid base for the long-term progressive development of all areas of the chemical industry necessitates accelerating the transformation processes of the industry, with taking into account the most advanced foreign experience.

Technological transformation of the chemical industry is considered the creation of multiple value chains from raw materials to finished products on the basis of new capacities for the production of semi-finished products from domestic raw materials, including through organic synthesis and nanotechnology. Together with this, a phased reduction in the export of unprocessed raw materials (natural gas, industrial salt, cotton cellulose, acetic acid and others) was carried out by organizing their deep processing on the territory of the country.

Sodium sulfate or sodium salt of sulfuric acid is extracted from mineral raw materials (for example, mirabilite). As a rule, reserves of sodium sulfate are concentrated in brine and deposits of salt lakes of the chloride-sulfate type. Another source of sodium sulfate production is considered by-products of various chemical processes, for example, the production of hydrochloric acid. Using spheres of sodium sulfate are varied; they depend on the specific region and many other factors. The main using sphere is considered the manufacture of detergents. In addition, sodium sulfate is used in the paper and cellulose, glass and textile industries, in nonferrous metallurgy, and Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) - in medicine and veterinary medicine, as well as in the production of starches, animal feed, and others.

As noted above, sodium sulfate intake depends on a number of factors. For example, one of the factors which is negatively affecting the consumption of sodium sulfate in the manufacture of detergents is considered to grow popularity of liquid synthetic washing products. Technical innovations, for example, in the pulp and paper industry, can have significant impact on the sodium sulfate market.

The Tumryuk mirabilite deposit is considered one of the main raw material sources of sodium sulfate which was characterized by the minimum content of impurity salts of halite, epsomite and gypsum. Each deposit of raw materials is unique in its own way and requires separate research to obtain a product.

In addition, it is promising to obtain sodium sulfate by conversion in aqueous medium of sodium chloride with ammonium sulfate.

The technological basis for the production of sodium sulfate by the conversion of sodium chloride with ammonium sulfate is based on the physicochemical properties of quaternary reciprocal aqueous system of sodium and ammonium chlorides and sulfates and its constituent ternary systems.

Results. The investigated quaternary system $2Na^+,2NH_4^+//2Cl^-,SO_4^{2-}-H_2O$ consists of four ternary water systems. The ternary systems $Na_2SO_4-NaCl-H_2O, Na_2SO_4-(NH_4)_2SO_4-H_2O$ and $NaCl-NH_4Cl-H_2O$ have been well studied in the temperature range 0-100^0C. $2Na^+,2NH_4^+//2Cl^-,SO_4^{2-}-H_2O$ system and its component of ternary system $(NH_4)_2SO_4$-NH_4Cl-H_2O was studied only for temperatures of 0,25, 40, 60 and 80^0C.

It follows from the results of the study of these systems that it is advisable to carry out the conversion of sodium chloride with ammonium sulfate at elevated temperatures, when the yield of sodium sulfate increases. In this regard, the ternary system $(NH_4)_2SO_4$- NH_4Cl-H_2O and the quaternary system $2Na^+,2NH_4^+//2Cl^-,SO_4^{2-}-H_2O$ were studied by the isothermal method at 100^0Cin order to substantiate the conversion of sodium chloride by ammonium sulfate at elevated temperatures.

The phase equilibrium in the system ammonium sulfate - ammonium chloride - water was established with constant stirring and thermostating within 3 days. In the quantitative chemical analysis of liquid and solid phases, well-known methods of analytical chemistry were used.

The obtained data were used to determine the compositions of solid phases according to Schreinemakers and to construct isothermal diagram of the solubility of the ternary system $(NH_4)_2SO_4$- NH_4Cl-H_2O at 100^0C.

The solubility diagram of the ternary system of ammonium sulfate - ammonium chloride - water at 100^0C consists of two crystallization branches of solid phases - ammonium sulfate and chloride. The crystallization branch of ammonium sulfate is larger than ammonium chloride. In the studied system, neither solid solutions nor new chemical compounds on the basis of the initial components are formed. The peculiarity of the solubility isotherm is that the components of the system have a mutual salting-out effect on each other. Due to its good solubility in this system, ammonium chloride has a greater salting-out effect on ammonium sulfate than ammonium sulfate on ammonium chloride.

Comparison of the solubility isotherm of the system $(NH_4)_2SO_4$- NH_4Cl-H_2O at 100^0C with isotherms at 0,25, 40, 60 and 80^0Cshows that the branch of crystallization of ammonium sulfate with increasing temperature expands, and ammonium chloride, on the contrary, decreases. Consequently, eutonic solutions of the ternary system with increasing in temperature $(NH_4)_2SO_4$- NH_4Cl-H_2O are enriched in ammonium chloride with simultaneous decrease in the content of ammonium sulfate.

Analysis of the solubility diagram of the system $(NH_4)_2SO_4$- NH_4Cl-H_2O at 25^0C consists of crystallization fields of sodium and ammonium chlorides, thenardite (Na_2SO_4), mirabilite

($Na_2SO_4 \cdot 10H_2O$), ammonium sulfate and compounds $Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ (Fig. 1.).

Fig. 1.

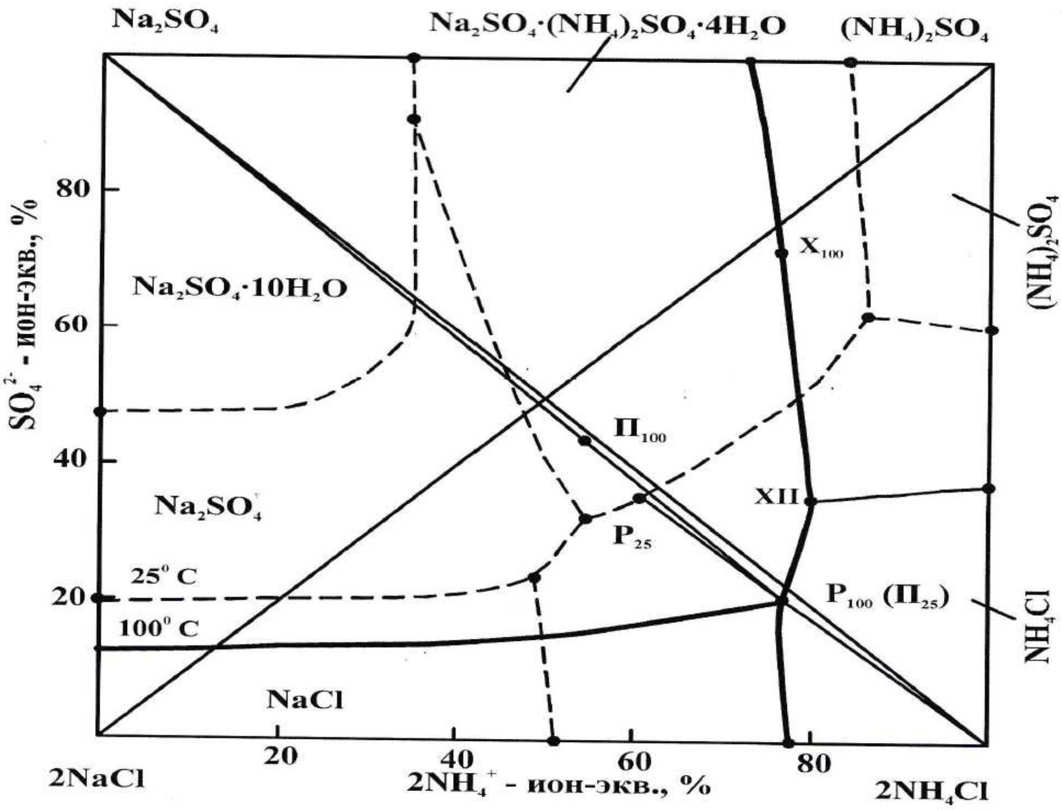

Diagram for substantiating the conversion of sodium chloride by ammonium sulfate on the basis of the isotherm of the system $2Na^+, 2NH_4^+//2Cl^-, SO_4^{2-} - H_2O$at 25 and 100^0C.

As the temperature rises, a qualitative change occurs in the composition of the crystallizing solid phases of the system. At 100^0C mirabilite and double salt $Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ do not exist in the system as independent equilibrium solid phase. As a result, the crystallization field of thenardite expands and the area of existence of ammonium chloride decreases. The isothermal solubility diagram takes on simpler form and consists of crystallization fields of sodium and ammonium chlorides and sulfates.

Discussion. The solubility diagram of the system $(NH_4)_2SO_4$- $NH_4Cl - H_2O$ at temperatures $25^0C$and 100^0Cshows that the diagonal $Na_2SO_4 - 2NH_4Cl$ for temperatures 25-100^0Calways intersects the lines of joint saturation and crystallization fields of sodium sulfate and ammonium chloride, which are the products of the exchange decomposition of sodium chloride and ammonium sulfate in aqueous medium. This indicates more complete conversion of sodium chloride with ammonium sulfate and the possibility of obtaining sodium sulfate and ammonium chloride under certain technological conditions. On the other hand, the crystallization field of thenardite expands with increasing temperature; while on the contrary, ammonium chloride decreases.

It follows from this that, the conversion of sodium chloride is expediently carried out at higher temperature as possible in order to obtain sodium sulfate. Ammonium chloride is obtained by cooling the mother liquor after the separation of sodium sulfate. Moreover, the lower the cooling temperature, the greater the yield of ammonium chloride and the productivity of the technological process. Another variant of the technological process is considered to carry out the conversion at low temperature, for example $25^0C$with obtaining ammonium chloride.

Sodium sulfate is separated from the lye enriched with sulfate ion at temperature 100^0C.

The saturated solution of the system is highly enriched in sulfate ion in the area of co-crystallization of thenardite with ammonium sulfate or double salt $Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$with ammonium sulfate. This indicates the inexpediency of carrying out the conversion at these sites in order to obtain sodium sulfate due to the fact that the sulfate ion accumulates in the liquid phase and the yield of the target product will be low.

The highest yield of sodium sulfate can be expected when the final composition of the liquid phase is at the triple point corresponding to the crystallization of sodium sulfate, sodium and ammonium chlorides.

The process of filtration of the pulp which was formed in the processes of obtaining sodium sulfate and ammonium chloride by conversion of sodium chloride with ammonium sulfate has been studied. The obtained results on the filterability of the pulp with precipitate of sodium sulfate and ammonium chloride at 100 and 25 ^{0}Care presented in Table 1. According to the presented data, the filterability of the pulp with the precipitate of ammonium chloride is slightly higher than the pulp with the precipitate of sodium sulfate.

Table 1. Filterability of pulp with sodium sulfate and ammonium chloride precipitate

The amount of pulp, g	Time (τ), seconds	Solid residue thickness (h), mm	Filterability (F 10-5), m4 / N · h	Filtration rate, kg / m2 · s		
				By pulp	Solid phase	By filtrate
Pulp with sodium sulfate precipitate						
400	28	6,6	0,204	2,247	0,456	1,791
300	18	4,9	0,176	2,621	0,531	2,090
200	11	3,3	0,129	2,860	0,580	2,280
100	5	1,7	0,074	3,145	0,638	2,507
Pulp with ammonium chloride precipitate						
400	26	9,8	0,332	2,420	0,469	1,951
300	16	7,4	0,305	2,949	0,572	2,377
200	9	4,9	0,240	3,495	0,678	2,817
100	4	2,5	0,138	3,932	0,762	3,170

Conclusion. The filtration rate of studied pulps in solid and liquid phases mainly depends on the thickness of the solid residue formed on the filter. The smaller the solids thickness, the higher the filtration rate.

Before using ammonium sulfate and sodium chloride, they were analyzed for the content of the basic substance and were used for conversion taking into account the amounts of these components. The results of the experiments showed that the possibility of obtaining sodium sulfate and ammonium chloride with basic substance content isconsidered at least 98%. The yield of the main products and the degree of conversion of sodium chloride with ammonium sulfate practically corresponds to the use of pure reactive sodium chloride and ammonium sulfate.

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