A REVIEW OF POTASSIUM SULFATE PRODUCTION

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Abstract: The main methods and processes for potassium sulfate production were briefly introduced as well as their characteristics and recent development. A new method of producing comparatively pure potassium sulfate from seawater using the natural zeolite as the ion exchange agent was introduced in particular.

Keywords: potassium sulfate; techniques; review

1. INTRODUCTION

Potassium sulfate is orthorhombic or hexagonal crystal or powder, with bitter taste, colorless or white. It is soluble in water, but insoluble in ethanol, acetone and carbon disulfide. It is a basic material for producing potassium salts including potassium carbonate and potassium aluminum sulfate. It is widely used in glass, dye and spices industry, and it is also used as a laxative in medicine.[1]

In agriculture, potassium sulfate is not only the main chloride-free potash fertilizer, but also an important supplement to the source of sulfur needed by crops. For those crops which can only be applied by potassium nitrate, potassium sulfate and potassium dihydrogen phosphate, the currently most widely used fertilizer is potassium sulfate. Since sulfur can not only improve agricultural output, but also improve its quality, so the sulfur in potassium sulfate is also an important nutrient element for plant growth. However, in recent years as a result of reduction of ammonium sulfate in fertilizer, the sulfur content in soil correspondingly became lower, which caused a lack of sulfur in some areas. In addition, potassium sulfate can be used in the manufacture of compound fertilizers by mixing with almost all existing fertilizers.

2. THE STATUS OF POTASSIUM SULFATE PRODUCING TECHNOLOGY

At present, the methods of producing potassium sulfate at home and abroad can be roughly divided into three types: first, extracted from the sulfate-based sea-lake salt brine and underground brine, with its output accounting for about 10-15%; second, extracted from natural potassium sulfate ore or solid potassium ore with complex components, with its output accounting for about 10%; third, transformed from sulfate-containing materials by reacting with potassium chloride, with its output accounting for about 75%. Some main processes currently used are introduced as follows.

2.1 Production of potassium sulfate from sea-lake salt brine and underground brine

At early stage, the methods for producing potassium sulfate from sea-lake salt brine mainly include the high temperature salt method, the evaporation bittern – flotation method and the ion exchange method.

2.1.1 High temperature salt method

High temperature salt, a by-product of potassium chloride production, is reacted with potassium chloride to conduct the first-step transform and to get a mixture of leonite and sodium chloride. And then the fatty-acid amine salts collector and the terpene alcohol-type foaming agents are added and mixed with the vitriol mother liquor produced to get the final mud which is then put into the flotation machine for separation to get the schoenite and industrial salt. After second-step transform of schoenite and potassium chloride in aqueous solution followed by separation, potassium sulfate products are obtained [2].

The disadvantages of this method are its high investment, high cost of equipment, long process and the negative effect of the flotation agents used on the quality of the products. Moreover, the reuse of the potassium chloride produced as a raw material again results in unnecessary duplication of work and an increase in production cost.

2.1.2 Bittern evaporation – flotation method

This process is the improvement of the high temperature salt method.[2,3] The self-produced carnallite is mixed with bittern and allowed to evaporate after removing the bitter salt generated until the solid mixture of NaCl, hydrated magnesium sulfate ($MgSO_4 \cdot H_2O$), langbeinite ($K_2SO_4 \cdot 2MgSO_4$), carnallite and potassium chloride is obtained. The pure langbeinite and hydrated magnesium sulfate are extracted from the above mixed salts, and then transformed into schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) at 15~66℃:

$$2(K_2SO_4 \bullet 2MgSO_4) + 2KCl + 18H_2O \rightarrow 3(K_2SO_4 \bullet MgSO_4 \bullet 6H_2O) + MgCl_2$$
$$2(MgSO_4 \bullet H_2O) + 2KCl + 4H_2O \rightarrow K_2SO_4 \bullet MgSO_4 \bullet 6H_2O + MgCl_2$$

The main remaining after solid-liquid separation is the mixture of schoenite, KCl and NaCl. After removing the NaCl salt by flotation, KCl and H_2O are added with a theoretical amount calculated based on the phase diagram of K^+, Mg^{2+}//Cl^-, SO_4^{2-}-H_2O at 25℃. After full reaction, the solid left is potassium sulfate.

$$K_2SO_4 \bullet MgSO_4 \bullet 6H_2O + 2KCl \rightarrow 2K_2SO_4 + MgCl_2 + 6H_2O$$

This method reduces the procedure of the high-temperature salt method. No potassium chloride is generated and the carnallite is directly mixed with the brine, leading to a simplified process and thus reducing losses and increasing the yield. At the same time, the method for producing potassium chloride was changed to production of potassium sulfate, raising the product value. However, this process still inevitably brings defects as a result of flotation.

2.1.3 Ion exchange method

The processes of this technology include (1) letting sea water go through the ion exchange column filled with natural adsorbents so that potassium ions were adsorbed on the adsorbents; (2) recycling the solution for additional adsorption; (3) eluting the potassium ions from the exchange column with hot saturated brine at a high temperature to get the enriched potassium eluting solution and recycling liquid; (4) returning the enriched potassium eluting solution to mix with the purge; (5) first-step evaporation after adjustment of the composition; (6) when the sodium chloride precipitated and the lamgbeinite become saturated, the solid is separated and washed with the enriched potassium eluting solution followed by separation and dryness to get purified salt; (7) evaporating the supernatant continuously to get more lamgbeinite precipitates but without precipitation of potassium chloride; (8) settling the final liquid under heat preservation, cooling the supernatant and geting carnallite and purge; (9) self-produced potassium sulfate mother liquor decomposes carnallite and get KCl and decomposition liquid, slurry separates kieserite and NaCl through flotation, adds water to kieserite and then reacts with KCl and gets potassium sulfate and potassium sulfate mother liquor.

This method solved the following problems in the production of potassium sulfate by brine [2]

(1) Potassium ion and sulfate radicals imbalanced in brine caused the need to add potassium chloride;
(2) This method can be used directly to extract potassium sulphate from seawater, and ultimately resolve the most pressing need for potassium sulfate in China and creates a new way for potassium fertilizer self-sufficiency in our country.

2.2 Production of potassium sulfate with Sylvite ore

This method includes a series of physical and chemical changes of potassium sulfate minerals (such as Polyhalite $K_2SO_4 \cdot MgSO_4 \cdot CaSO_4 \cdot 2H_2O$), kainite ($K_2SO_4 \cdot MgSO_4 \cdot 3H_2O$) and alunite ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 2Al_2O_3 \cdot 6H_2O$), etc. to produce potassium sulfate.[4]

Although China's Potassium Sulfate producing technology with sylvite ore has been identified, the only form of mass production plant is in Wenzhou, Zhejiang Province. Due to the lack, low-grade, regional distribution of available Sylvite resources in our country, as well as difficulty to deal with the separation, poor quality of the product and lower yield, the method of producing potassium sulfate with Sylvite ore has not received a wide range of the promotion and application

2.3 Potassium chloride transformation method

According to the use of different material with sulfate radicals, potassium chloride transformation can be divided into the following categories:

2.3.1 Mannheim process

At the end of the 19th century, Mannheim Vereim form Germany invented this method for producing potassium sulfate using potassium chloride and sulfuric acid as raw materials, that is, the so-called Mannheim process[5,6], which is the currently most mature production technology. The main reaction is:

$$2KCl + H_2SO_4 \rightarrow K_2SO_4 + 2HCl$$

From the reaction mechanism, the reaction should be carried out into two steps. The first step is that sulfate reacted with potassium chloride which is an exothermic reaction at a relatively low temperature,

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl + Q$$

The second step is that potassium bisulfate reacted with potassium chloride which is an endothermic reaction at a high temperature,

$$KHSO_4 + KCl \rightarrow K_2SO_4 + HCl - Q$$

The advantages of the method are that the quality of potassium sulfate produced is in a higher grade (K_2O 50% -51%), and with almost no losses, the yield of potassium is also relatively high.

The shortcoming of the method is the severe corrosion problem under the high reaction temperature and in strong acid environment. It is difficult to raise the single-furnace production capacity. The maintenance work is heave and the investment cost is high. Furthermore, it is difficult to sell the by-product---hydrochloric acid.

2.3.2 Association displacement process

The method is researched and developed by Chinese own--using potassium chloride, sulfuric acid and ammonia as raw material, by association, replacement and reconciliation, to produce potassium sulfate [7,8]. The basic principle for the process is based on the different affinity of organic solvents to hydrochloric acid and sulfuric acid to produce potassium sulfate. First, the sulfuric acid is associated with some organic solvents which are insoluble in water. Second, the sulfate ions are exchanged by the chloride ions using potassium chloride solution as the elution solution to get the potassium sulfate solution. Finally, this potassium sulfate solution is put into the crystallization system to produce pure potassium sulfate. In order to reuse the organic associated agent, ammonia is used for dissociation by combining the chlorine to generate ammonium chloride. The mother liquor after dissociation is reused.

This process is conducted under atmospheric pressure and low reaction temperature. Small corrosion, long life of equipment, high product quality, low investment, low cost and no pollution are the advantages of this method. The by-product, ammonium chloride, is also a very good fertilizer. However, the method in the process of industrialization encountered some problems which remain unresolved. The capacity of the factory is small, and the associated agent will be lost in some degree during production, or even "be poisoned". The requirement for material selection is high. All these problems result in an unsatisfactory state of this method.

2.3.3 Double decomposition method

Double decomposition method uses a variety of soluble salts containing potassium sulfate to proceed a double decomposition reaction with potassium chloride for production of potassium sulfate. According to different types of soluble sulfate, this method can be divided into the following types.

2.3.3.1 Potassium bisulfate method

Potassium bisulfate method refers to the neutralization of potassium bisulfite by adding alkali [5], namely through the reaction of potassium chloride and sulfuric acid to remove hydrogen chloride gas generated and at the same time adding an alkaline substance in order to undermine the structure of $KHSO_4$ and to get potassium sulfate directly. The reaction is proceeding at ambient temperature and pressure in aqueous system. Ammonia is commonly used as the best alkaline substance. Ammonia, in addition, can also reduce the solubility of potassium sulfate in water sharply to precipitate as pure crystals. The reactions included are:

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl \uparrow$$

$$KHSO_4 + KCl + NH_3 \bullet H_2O \rightarrow K_2SO_4 + NH_4Cl + H_2O$$

The advantages for Potassium bisulfate method are the low reaction temperature, low power consumption, low degree corrosion for equipments, extended life of equipment; completed and fast reaction, simple techniques, low cost; high yield of potassium, high purity and good quality. This process is applicable for all scales and various specifications of the production of potassium sulfate.

2.3.3.2 Ammonium sulfate - potassium chloride method

Ammonium sulfate - potassium chloride method is using solubility differences of ion reaction and production reacted of ammonium sulfate and potassium chloride, by controlling the concentration of reactant and reaction temperature, thereby to generate potassium sulfate and ammonium chloride [6]. Reaction is as follows:

$$(NH_4)_2SO_4 + 2KCl \rightarrow K_2SO_4 + 2NH_4Cl$$

Producing potassium sulfate with this method requires lower investment and the second conversion can also produce products with better quality, but higher production costs, smaller scale production and lower yield, poor economic returns are the shortages. Meanwhile there are some technical problems in practical production, for example, the crystallization of ammonium chloride is not good enough. So we can not develop this method blindly.

2.3.3.3 Calcium sulfate method

This method, also known as Gypsum method [5,6], is divided into one-step and two-step transformation. One-Step transformation method used ammonia as a catalyst. Gypsum and potassium chloride react directly in saturated solution of ammonia to produce potassium sulfate and calcium chloride is the by-product:

$$CaSO_4 \bullet 2H_2O + 2KCl \rightarrow K_2SO_4 + CaCl_2 + 2H_2O$$

Two-Step transformation method is based on ammonium bicarbonate reacted with gypsum to produce calcium carbonate and ammonium sulfate. Then, the ammonium sulfate and potassium chloride proceed a double decomposition reaction to producing potassium sulfate and ultrafine calcium carbonate:

$$CaSO_4 \bullet 2H_2O + 2NH_4HCO_3 \rightarrow (NH_4)_2SO_4 + CaCO_3 + CO_2 + 3H_2O$$

$$(NH_4)_2SO_4 + 2KCl \rightarrow K_2SO_4 + 2NH_4Cl$$

Liu Xiaohong makes some improvements in two-step transformation method [9]. Both the first step and second step are carried out at room temperature, getting the coarse particles of calcium carbonate and potassium sulfate in order to facilitate the separation of the two. This method can also save heating steam, reduce volatilization of ammonia, add organic solvents to increase the yield of potassium sulfate and use tank-in-series continuous reaction device to make operation easy, equipment production intensive and technical operation stable.

2.3.3.4 Glauber's salt - potassium chloride method

The theoretical basis for Glauber's salt -

potassium chloride method is the Na_2SO_4-KCl-K_2SO_4-H_2O phase diagram. Based on the difference in solubility at various temperatures, the salts can be separated by crystallization to produce potassium sulfate products. The by-product of this process is chlorine sodium. The first step reaction (at 25℃) is:

$$4Na_2SO_4 \bullet 10H_2O + 6KCl \rightarrow 3K_2SO_4 \bullet Na_2SO_4 + 6NaCl + 40H_2O$$

The second step reaction (at 60 ~ 100℃) is:

$$3K_2SO_4 \bullet Na_2SO_4 + 2KCl \rightarrow 4K_2SO_4 + 2NaCl$$

The advantages for this method are [10]: simple process, easy amplification for the installation, low investment, low energy consumption and free pollution, etc. The shortcomings are as follows. Since the Mirabilite ($3K_2SO_4 \cdot Na_2SO_4$) is a double salt with inconstant components, the potassium and sodium ratio being in the range of 2.1 ~ 2.7 and instable, once the potassium mirabilite mother liquor is over-heated, co-crystals of potassium and Glauber's salt will be generated. Therefore the quality of products and the purity of the salts are not easy to improve.

3 NEW TECHNOLOGY IN PRODUCING POTASSIUM SULFATE

This process is to use zeolites as ion-exchange agent and make the sea water go through the zeolite column. Potassium ions in sea water are adsorbed in the zeolite at room temperature and the zeolite was transferred from the Na^+-type into a K^+-type. At a certain temperature, ammonium sulfate solution is to be eluant, which accesses zeolite column. NH_4^+ in solution and K^+ in Zeolite proceeded ion exchange and then zeolite transferred into NH_4^+-type zeolite. The part of solution of having high potassium content is intercepted to be K-rich liquid. After that, using saturated sodium chloride solution renews zeolite column and the zeolite was re-generated to Na^+-type with adsorptive ability for potassium. This process keeps the cycle of zeolite conversion and collects the outflow of K-rich solution. Potassium sulfate fully precipitates using appropriate crystal seeds under certain conditions, which obtains more pure potassium sulfate crystals. The reaction as following:

$NaZ + K^+ = KZ + Na^+$
$2KZ + (NH_4)_2SO_4 = K_2SO_4 + 2NH_4Z$
$NH_4Z + NaCl = NaZ + NH_4Cl$

This technology can be applied to extract K^+ in sea water, brine, salt lake water. Advantages: Good technology applicability, simple process line and no waste discharge. The by-product-- ammonia can also react with sulfuric acid to produce ammonium sulfate in order to save cost.

4 CONCLUSION

To sum up, focus on the contradiction between supply and demand of K_2SO_4 in the world and the status of producing potassium sulfate in China, selecting methods of producing of potassium sulfate should consider the following points:

(1) Consider the local conditions to find the suitable production process and using raw materials, which is easy to get, produces potassium sulfate to enhance economic efficiency;
(2) Mild reaction conditions should be adopted and choose reaction process with low equipment corrosion;
(3) The production techniques chosen should be less in pollution, no "three wastes" from the production process;
(4) At the same time, it should be committed in a mature technology condition to develop industrialization of new technologies and new techniques to meet the requirements of market economy, enhance competitiveness of products in the market and improve the production of potassium sulfate in China.

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