Optimization of Experimental Conditions in Single-Stage Process for Preparation of Potassium Sulphate from Magnesium Sulfate and Potassium Chloride

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Abstract

A method and a system for Single-Stage conversion of magnesium sulphate and potassium chloride to potassium sulphate in aqueous alcoholic solution at 50-85°C were developed. Raw magnesium chloride was a by-product formed in the process. The effects of reaction molar ratio, methanol volume, evaporation, and magnesium chloride content on the purity and the conversion rate of potassium sulphate were studied. The product and by-product were purified and the metal ions contents were determined by Atomic absorption spectroscopy. Results showed that the washing with methanol had a certain impact on the purity and the conversion rate of potassium sulphate. The potassium sulphate reached to the qualified standard, when the molar ratio of $2KCl$ and $MgSO_4$ was 1:1. The recoveries of potassium sulphate (as final product) and potassium chloride (as raw material)in an aqueous alcoholic solution compound fertilizer were approximately 80% and 12.76%, respectively. Magnesium chloride had a significant influence on the purity and the conversion rate of potassium sulphate. Purities of products throughout can be controlled by using slight circuit adjustments and/or by additional water washes.

Keywords: Alcoholic solution, Potassium sulphate, Crystallization, Single-Stage Process, Atomic absorption spectroscopy analysis.

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Introduction

Potassium is one of the three essential elements for plants to maintain proper growth [1-3]. Potash fertilizers used in agriculture usually contain two types: one is potassium sulphate (K_2SO_4), which is a chlorine-free, high-quality, potent potash fertilizer, especially indispensable for tobacco, tea, potatoes, watermelon, sugar beets and other economic crops that are sensitive to chlorine, and the other is potassium chloride (KCl), which is harmful to some crops, increases soil salinity and pH of the soil [4-7]. Therefore, more favourable potassium sources in the preparation of multi-component fertilizers are potassium sulphate and potassium nitrate. Almost 90% of potassium sulphate produced in the world is consumed by the fertilizer industries. However, the amount of K_2SO_4 employed in the manufacture of potassium fertilizers represents only about 8% of the overall potassium consumption [8-12]. The problem of obtaining chlorine-free potassium fertilizers has been latterlyat the focus of specialists'attention both in CIS countries and in extended foreign countries. Currently, these fertilizers previously are or are to be manufactured in all countries producing potassium fertilizers, and also in Japan and Belgium, both having no potassium raw materials of their own. At the present-day amounts of produce and consumption of chlorine-free potassium fertilizers, they are in deficit. This shows that further development of the production of chlorine-free kinds of potassium fertilizers are needful. In the last years, particular attention has been given to a study of conversion methods for the manufacture of potassium sulphate, based on the interaction of potassium chloride and various kinds of sulfate-containing raw materials [13-16] by the reaction:

$$KCl + MSO_4 \rightarrow K_2SO_4 + MCl_n, \qquad (1)$$

$$\text{Where; } M = Na^+, NH_4^+, H^+, Ca^{2+}, Mg^{2+}, \text{ etc.}$$

Therefore, the described conversion methods are to use as raw material, potassium chloride, which is a product obtained in the processing of natural potassium salts and hence only replace one kind of potassium fertilizer with another, rather than raising the output of the product by the potassium industry. Potassium sulphate is recommended to be used as a fertilizer instead of potassium chloride because it has the following distinct advantages [17-20]:

1- It is a two–nutrient fertilizer (K+S) since it contains 50 % K_2O and 18 % S.

2-It contains a very low amount of chloride.

3-It has a low salt index, then it is better suited to utilize on saline-sensitive crops.

4-It possesses excellent physical properties and mostly is recommended for utilizing in high-quality crops.

For these reasons, many processes have been used to convert the potassium chloride, in the presence of a source of sulphate, into potassium sulphate. These processes include the Mannheim process by the reaction of potassium chloride with sulfuric acid, the Glaserite process by the reaction of potassium chloride with sodium sulphate, and the phosphogypsum process by the reaction of potassium chloride with phosphogypsum in the presence of ammonia and alcohol, and others [21-25]. In the word, potassium sulphate is produced from potassium chloride mainly by means of the energy-consuming Mannheim process. In this process, potassium chloride reacts with sulfuric acid forming first potassium bisulphate and hydrogen chloride. The final product, potassium sulphate can be formed at high temperature, about 600-700°C. Potassium sulphate can also be obtained by acidulation of potassium chloride at a lower temperature. Under such conditions, potassium hydrosulfate is formed [26]. Most previous studies on the dissolution of crystalline growth of potassium sulphate have been obtained by cooling or evaporation of its aqueous solutions. A different methodology for its crystallization is the addition of a second solvent which changes the conditions of the phase equilibrium. This change in the physical properties of the medium may produce changes in the size and form of the crystals obtained [27-28].

Abu-Eishah [29] studied the preparation of potassium sulphate from phosphogypsum and potassium chloride using aqueous solutions containing 33 wt.% and 7 wt.% methanol and The maximum conversion of KCl to K_2SO_4 obtained under these conditions was 97.2%.Mientkaand Grzmil [30] studied the effect of adding methanol to the mixture at ambient temperature. They found that methanol is better desalting out the medium for the potassium sulfate preparation than propane-2-ol, i.e. The higher amount and higher purity of precipitate K_2SO_4 were obtained. The preparation of pure K_2SO_4 (free of chlorides) using the desalting out process could be interesting taking into account the necessity of the solvent recovery and mother liquor recycles.

Fairchild [31] studied the recovery of potassium sulphate and mirabilite from glaserite at ambient temperature and using an aqueous solution containing alcohol as a catalyst for the reaction. The optimum condition that yields 95 % of the potassium contained in the glaserite raw material can be achieved with over 90% of the sodium being rejected as mirabilite.Jannet and Rokbani [32] found that the double decomposition reaction kinetics depends on the formation and dissolution rates of intermediate salt and potassium sulphate, respectively. Also, they realized the formation of schoenite outside of its crystallization field might indicate a metastable space extension of this domain to cover the potassium sulphate one and the formation kinetics rate of schoenite is quicker than the potassium sulphate one.Khlissa and Rokbani [33] studied the potassium sulphate can be produced by double decomposition reaction between potassium chloride and sodium sulphate. These actions are used in two of the principal stages of the process; firstly to induce the reaction

between sodium sulphate and potassium chloride to move in the desired direction, and secondly to selectively crystallize the potassium sulphate formed. They found thatin this work, the electrical conductimetric technique was used in order to determine the considered parameter as a function of temperature.Susarla and Chudasama [34] found that sodium sulphate present in brines and solid bitterns can be processed to glaserite, a valuable fertilizer product by its reaction with potassium chlorideunder optimized conditions and a simple method for recovery of glaserite from solid bitterns of the sambhar lake (Rajasthan) containing sodium sulphate has been worked out.

In this paper, a method and system for the preparation of potassium sulphate are obtained. The method comprises reacting a chloride of potassium with a magnesium sulphate in an aqueous-alcoholic solution, with recycling of magnesium sulphate and preparation of hydrochloric acid (at a temperature in a range between 50-85°C) where the recycling of magnesium is done by a reaction of sulfuric acid on results magnesium chloride with corresponding preparation of magnesium sulphate and hydrochloric acid.

Experimental

Materials and Instruments

Potassium chloride, magnesium sulphate, and methanol were used p.a. grade (Merckco). The potassium chloride was oven-dried at 120°C for 48 h to remove moisture. All solutions were prepared will Milli-Q quality distilled water. The concentration of metal ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, Cl^-) was determined by an atomic absorption spectrophotometer (AAS, AA-6880 SHIMADZU, Japan).

Preparations

For the precipitation of potassium sulphate, a warm methanolic solution (40°C) of magnesium sulphate (19.12 g of magnesium sulphate is dissolved in 200 ml of water at 65°C) is poured into the warm potassium chloride solution (23.74 g of potassium chloride is dissolved in 100-150 ml of water at 50-60°C) rapidly with good stirring there is a partial precipitation and the mixture is filtered, rinsed with 50 ml of methanol and dried at about 100°C giving a crop of 27.75 g of potassium sulphate. The determination of chlorides indicated 0.7% chloride ion into the potassium sulphate. For the recycling of materials, by evaporation of the mother-liquor and methanol rinsing, the methanol was recovered (40-50 ml) and the residual water solution evaporated to yield magnesium chloride hexahydrate.

Purification of potassium sulphate

The purification experiment was carried out as follows. First, a certain mass of potassium sulphate was added to a three-necked bottle that contained 1 L of water to obtain the desired liquid to solid ratio. The mixture was then stirred at a speed of 270 rpm for 15 min to achieve dissolution equilibrium at the desired temperature (100°C, 80°C or 60°C). Afterwards, the residues were separated at the above-desired temperature utilizing a qualitative filter paper. The filtrate was placed in an alternating damp-heat apparatus for spontaneous crystallization at the desired temperature (0–30°C). After a certain crystallization time, the solid phase was separated from the solution by using a qualitative filter paper. The obtained solid was dried at 105°C in an oven until a fixed weight was recorded. Finally, the purified potassium sulphate was obtained. The chemical composition of potassium sulphate was determined using the same method as that for potassium sulphate. The crystallization yield was calculated by using the following equation (2):

$$y = \frac{m_1}{m_2} \times 100\% \quad (2)$$

where m_1 and m_2 represent the mass of the crystallization solid and dosage of potassium sulphate.

Results and discussion

During the early stages of the system, quite a number of experiments were conducted at widely varying temperatures. Thereaction of potassium chloride with anhydrous magnesium sulphate in the presence of crystalline nuclei of the product (K_2SO_4) was investigated. At the first stage, a mixture of potassium chloride with magnesium sulphate was separated from the mother liquor after the separation of potassium sulphate through solvent evaporation followed by crystallization at temperature 30°C. During the second stage, magnesium chloride was separated from the solution obtained after the solvent evaporates and crystallization at 110 °C. Both, the mixture of solution and the remaining end-liquor were recycled to the conversion stage. Raw magnesium chloride was a by-product formed in the process. Potassium sulphate of purity higher than 95%is obtained by this reaction (Table1).TheK$_2$O, Na$^+$, SO$_4$$^{2-}$, Mg^{2+},Cl$^-$ metal ion contents were determined by AAS.

Table.1 Preparation of Potassium Sulphate.

Feed, grams				Solid Product, mole %				
$MgSO_4$	K_2SO_4	$MgCl_2$	KCl	K_2O	SO_4^{2-}	Mg^{2+}	Cl^-	Na^+
19.12	27.75	15.169	23.74	52.3	18.6	0.92	0.76	0.17

The fact that magnesium chloride forms a rather stable complex with methanol ($MgCl_2$. 6MeOH) might be the reason why the system represented by reaction (3):

$$2KCl + MgSO_4 . 7H_2O \rightarrow K_2SO_4 + MgCl_2.6H_2O + H_2O \quad (3)$$

Potassium sulphate is insoluble in methanol, although magnesium chloride is nearly soluble in this solvent. The precipitated potassium sulphateis filtrated and the end filtrate contains magnesium chloride in methanol and water. Methanol can be distilled off and recovery and magnesium chloride crystallized out after evaporation of extra water. Slight advantages with respect to yield are obtained for a given operation, if lower temperatures 0°C is employed. One the other hand, higher temperatures 100 °C increase the rate of reaction. The advantages of either high or low temperatures appear to be more than offset by the convenience and economy of operating at ambient temperatures. Ambient temperatures are found to be satisfactory for the first and second stages of preparation as well as for a subsequent washing stage. The temperature that is not critical for the preparation of the mixed sulphate is illustrated in table 1 where nearly similar results were obtained at 20 and 35 °C. If the water of hydration is a sufficiently high proportion of the total water in the system, it may be necessary to release it by increasing the temperature above 32°C.The high insoluble content had a negative effect on the dissolution of potassium sulphate (Table 1). Purification significantly and efficiently solved the problem. After comparing Table 1, it can be obviously seen that the insoluble content was efficiently removed and that the impurity content for the ions (Mg^{2+}, Ca^{2+}, Na^+, Cl^-) decreased after purification. Data in Table 2 show that magnesium sulphate of nearly 95% purity, on a mole percent basis, can be obtained.

Table 2. Recovery of magnesium sulphate.

Feed					Brine					Solid Product- MgSO$_4$				
Mole%					Mole%					Mole%				
K$_2$O	SO$_4^{2-}$	Mg^{2+}	Cl$^-$	Na$^+$	K$_2$O	SO$_4^{2-}$	Mg^{2+}	Cl$^-$	Na$^+$	K$_2$O	SO$_4^{2-}$	Mg^{2+}	Cl$^-$	Na$^+$
17.6	30.4	42.8	69.6	39.6	22.2	11.8	54.2	88.2	23.6	1.2	95.4	3.2	4.6	95.6
18.4	33.0	39.4	67.0	42.2	24.2	12.0	51.2	88.0	24.6	1.4	95.0	3.4	5.0	95.2

Potassium chloride is precipitated from the chloride rich brine of the previous operation by evaporating the brine to a specific gravity of 1.200. The salt content of the remaining brine is approximately 80% magnesium chloride (Table 3).

Table 3. Separation of potassium chloride from magnesium chloride.

Feed						Product (magnesium chloride)						Solids				
Mole%					SP.gr.	Mole%					SP.gr.	Mole%				
K$_2$O	SO$_4^{2-}$	Mg^{2+}	Cl$^-$	Na$^+$		K$_2$O	SO$_4^{2-}$	Mg^{2+}	Cl$^-$	Na$^+$		K$_2$O	SO$_4^{2-}$	Mg^{2+}	Cl$^-$	Na$^+$
23.0	12.2	51.4	87.8	25.6	1.185	8.4	15.6	82.6	84.4	9.0	1.300	44.0	5.6	6.8	94.4	49.2
20.6	10.0	55.0	90.0	24.4	1.184	2.0	12.0	86.6	88.0	7.4	1.300	43.4	7.2	6.6	92.8	50.0
22.2	11.8	54.2	88.2	23.6	1.175	7.6	16.8	82.8	83.2	9.6	1.303	47.0	3.4	5.8	96.6	47.2

If the magnesium chloride rich brine is evaporated until a boiling point of 158°C is reached, the impurities separate from the solution. This solution, when decanted at 120°C, solidifies on cooling to yield magnesium chloride hexahydrate (MgCl$_2$.6H$_2$O) of purity higher than 94% (Table 4).

Table 4. Purification of magnesium chloride.

Feed						purified magnesium chloride						Remaining Fraction				
Mole%					Total salt, g.	Mole%					Dry salt, g.	Mole%				
K_2O	SO_4^{2-}	Mg^{2+}	Cl^-	Na^+		K_2O	SO_4^{2-}	Mg^{2+}	Cl^-	Na^+		K_2O	SO_4^{2-}	Mg^{2+}	Cl^-	Na^+
5.8	16	85	84	9.2	1396	2.8	5.8	96.2	94.2	1	552	7.8	23.4	77.8	76.6	14.4
6.8	14.8	84	85.2	9.2	1419	2.6	2.8	96.4	97.2	1	442	9	20.8	77.6	79.2	13.4
6.6	17.4	85	82.6	8.4	1523	2.8	4	96	96	1.2	529	8.8	25.2	78.4	74.8	12.8

Contrasting with the convenient temperatures of the potassium sulphate circuit are (1) the low temperature (-8°C) required for precipitating the salt and (2) the high temperature (158°C) used for purifying magnesium chloride. Regulation of the temperature at 120°C is also required in the separation of magnesium chloride from its impurities. Inefficient temperature control during filtration in the laboratory has been blamed for the purity of magnesium chloride not exceeding 99%. Although data on the separation of potassium chloride from magnesium chloride do not report on the results, fractional crystallization following the conventional procedure is technically satisfactory, but in practice, costly, on account of high energy requirements. For an industrial operation, certain steps of the process outlined in this paper might have to be curtailed or omitted, but the present investigation has sought to indicate how high purities and high recoveries can be achieved. The degree of purity and the extent of recovery attained by industry would depend on many factors, including the size and nature of the operation and the cost of power.

Conclusions

By using phase data from the literature and experimental results from the laboratory, a batch process for the preparation of potassium sulphate has been devised. Yields of potassium sulphate have been improved by re-use of brine and by the recovery of magnesium sulphate and potassium chloride from the spent liquor. Potassium sulphate of purity higher than 99% can be obtained without loss of recovery by adding a washing stage of the circuit. Sulphates used for potassiumsulphate preparation can be of natural as well as of anthropogenic origin. The obtained potassium sulphate can be utilized for the preparation of multi-component fertilizers. Therefore, it should not contain heavy metals, the amount of which in fertilizers is limited. Hence, the use of raw materials for potassiumsulphate preparation is limited to sources free of the above-mentioned

impurities. This system allows the preparation of potassium sulphate of high purity, containing less than 1% chlorides. The temperatures of operation are low, typically below about 65°C and the recycling of magnesium sulphate takes place at temperatures typically below about 120°C, with the preparation of hydrochloric acid as a useful secondary product. With the recycling of magnesium sulphate as an intermediate step, the high temperature, low energy efficiencies and corrosive situations along with chloride contamination common to existing processes are thus avoided. Additionally, it was found that the temperature increased the heat capacities of the solution, with the concentration of potassium sulphate producing a reverse effect.

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