Single-Stage Process for Manufacturing of Potassium Sulphate from Sodium Sulphate*

B. U. GRZMIL** and B. KIC

Institute of Chemical and Environment Engineering, Technical University of Szczecin, PL-70 322 Szczecin
e-mail: barbara.grzmil@ps.pl

A single-stage process for the conversion of sodium sulphate (anhydrous or hydrated, of natural or anthropogenic origin) with potassium chloride in aqueous solution at 20—25 °C to potassium sulphate was developed. Both reagent grade sodium sulphate and that formed as a by-product during trimethylolpropane synthesis were used as raw material. Initial reaction mixture contained less than 30 mass % of salts with the calculated mole ratios $n(KCl) : n(Na_2SO_4) \geq 6$; $n(K_2SO_4 : n(NaCl) \geq 1$. Resulting potassium sulphate contained about 96 mass % of K_2SO_4, 0.5 mass % of Cl^-, and 0.2 mass % of Na^+.

At the first stage, a mixture of potassium chloride with glaserite was separated from the mother liquor after the separation of K_2SO_4 through solvent evaporation followed by crystallization at temperatures ≤ 2 °C. During the second stage, sodium chloride was separated from the solution obtained after the solvent evaporation and crystallization at 110 °C. Both, the mixture of KCl and $K_3Na(SO_4)_2$ and the remaining end-liquor were recycled to the conversion stage. Raw sodium chloride was a by-product formed in the process.

During the manufacturing of multi-component fertilizers, the main source of potassium is potassium chloride. This salt is the most widespread one in the world and currently 90 % of potassium fertilizers is produced using it [1]. The world potash production amounted to 25.8×10^6 t K_2O in 2001. However, potassium chloride is not a versatile potassium source. Plants demand of chlorine is limited on trace amounts only. Moreover, some of them are susceptible to this element, which, in higher loads, may reduce both the quality and the yield of crops. Therefore, more favourable potassium sources for the production of multi-component fertilizers are potassium sulphate and potassium nitrate. Almost 90 % of potassium sulphate produced in the world is consumed by the fertilizer industry. However, the amount of K_2SO_4 employed in the manufacture of potassium fertilizers represents only about 8 % [1] of the overall potassium consumption.

The production of potassium sulphate is based on the reaction of potassium chloride with either sulphates (of calcium, sodium, ammonium, magnesium, and iron) or with sulphuric acid [2, 3]. The raw materials may be either natural sulphates (langbeinite, leonite, schoenite, glaserite) or sulphates with anthropogenic origin. Nowadays, it seems to be advantageous to use sodium sulphate for the potassium sulphate production. This compound is formed as a by-product, *e.g.* during the processing of chromium ores, in the flue gases purification, in the manufacture of viscose fibres, rayon, hydrochloric acid, silica pigments, fatty acids, trimethylolpropane, and during the disposal of spent sulphuric acid [4]. As estimated, the global yearly production of sodium sulphate in 2002 was *ca.* 4×10^6 t, including a synthetic product (1.5—2.0×10^6 t). Sodium sulphate is often used for the production of soap and detergents (46 %), pulp and paper (13 %), textiles (12 %), glass (11 %), carpet fresheners (7 %), and miscellaneous (11 %) [4].

For the sake of thermodynamics constraints, the process of potassium sulphate production from sodium sulphate proceeds in two stages (reactions (A) and (B)) [2, 3].

$$6KCl + 4Na_2SO_4 = 2K_3Na(SO_4)_2 + 6NaCl \quad (A)$$
$$2KCl + 2K_3Na(SO_4)_2 = 4K_2SO_4 + 2NaCl \quad (B)$$
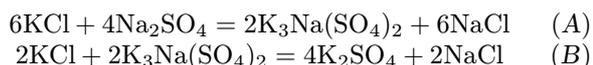
According to patents *WO* 16899 and *WO* 16900 [5, 6] the process of KCl conversion with Na_2SO_4 is carried out at 25 °C. In the first stage, the saturated solutions of Na_2SO_4, glaserite, and NaCl, or NaCl, KCl, and glaserite are formed apart from $K_3Na(SO_4)_2$. Fur-

---

thermore, at the second reaction stage both potassium sulphate and saturated solution of KCl are produced. Next, $Na_2SO_4 \cdot 10H_2O$ and sodium chloride are separated at 0 ℃ from the mother liquor delivered from the 1st stage and during the hot separation, respectively. However, there is also a possibility to separate NaCl from the mother liquor only. Consistent with *RU* 2161125, the mother liquor from the 1st stage is subjected to vaporization in solar ponds [7]. Subsequently, NaCl is separated from glaserite and KCl by means of crystallization and flotation. The two latter compounds are then recycled to the second stage of the process. As described elsewhere [8], both $NaHCO_3$ and K_2SO_4 could be simultaneously obtained from Na_2SO_4 and NH_4HCO_3, whereas, during the proposed procedure K_2SO_4 is formed due to the reaction between indirectly formed ammonium sulphate and potassium chloride.

A single-stage method for the potassium sulphate preparation from sodium sulphate and potassium carbonate was described in *RU* 2154026 [9]. A different procedure for the preparation of potassium sulphate is described in [10]. Substrates employed in this method are K_2SO_4 and the solution containing NaCl, Na_2SO_4, and KCl at the temperature ranging from 5 ℃ to 50 ℃. In this procedure, both K_2SO_4 and the mother liquor are obtained. The latter is merged with a mixture of both KCl and NaCl. A proper amount of the mixture allows obtaining of pure crystalline KCl and the solution nearly saturated with reference to both KCl and NaCl.

The aim of our research was to develop a single-stage method for obtaining potassium sulphate from sodium sulphate (a by-product from the manufacturing of trimethylolpropane [11]) and potassium chloride. Taking into account earlier research, a two-stage method for the production of potassium sulphate as fertilizer was developed. Potassium sulphate was prepared using potassium chloride and sodium sulphate as reagents [12]. The latter compound was a by-product formed during the manufacture of sodium dichromate.

EXPERIMENTAL

The reagent grade sodium sulphate, the waste sodium sulphate (61.3 mass % Na_2SO_4, 2.1 mass % C, 35.5 mass % H_2O) and potassium salt (98.1 mass % KCl) were used as raw materials. Experiments were carried out in laboratory thermostated shaker at 20—25 ℃. The reaction mixture was shaken with 150 cycles per minute and the amplitude was 8 mm. During experiments, both the mixture composition and the total content of salts were changed. Mole ratios of the mixture components $n(K_2SO_4) : n(Na_2SO_4) : n(KCl) : n(NaCl)$ of $(0—2) : 1 : (2—8) : (0—2)$, and the total salts content of 27—50 % in the initial mixture were used. The mixture was prepared either by adding solid Na_2SO_4, NaCl, and K_2SO_4 to KCl solution, or by combining solid K_2SO_4, KCl, and NaCl with the solution of sodium sulphate.

Mother solution formed during the conversion process was subjected to evaporation and fractional crystallization of salts. Both, degree of the liquid phase evaporation and the crystallization temperature were changed. Due to the variation of evaporation degree, solids in the mother solution were concentrated to 30—70 mass %. The two crystallization steps were performed at 2—10 ℃ and 100—110 ℃, respectively.

Both solid and liquid phases were analyzed in order to estimate the content of individual components. Content of potassium and sodium was measured with the flame-emission photometry [13]. Chloride and sulphate anions contents were estimated with the use of potentiometric and gravimetric (as barium sulphate) methods, respectively [14]. The X-ray diffraction analysis was employed to identify the crystalline phases in the products and to determine the conversion of sodium sulphate to potassium sulphate [15].

RESULTS AND DISCUSSION

Reaction of potassium chloride with anhydrous sodium sulphate in the presence of crystalline nuclei of the product (K_2SO_4) was investigated. Regarding the reaction stoichiometry, the process was carried out at a high excess of potassium chloride (mole ratio $n(Na_2SO_4) : n(KCl)$ of 1 : 8—18).

$$Na_2SO_4 + 2KCl = K_2SO_4 + 2NaCl \qquad (C)$$

As shown in Table 1, high conversion of sodium sulphate to potassium sulphate (above 96—99 %) was achieved using initial mole ratios of $n(Na_2SO_4) : n(KCl)$ about 1 : 6 to 1 : 10. At the same time mole ratio of $n(K_2SO_4)$ to $n(Na_2SO_4)$ was higher than 2 : 1. After replacing anhydrous sodium sulphate with hydrated one ($Na_2SO_4 \cdot H_2O$), conversion of Na_2SO_4 to K_2SO_4 increased to 98—99 %. Moreover, much lower amount of recycled crystalline product in the starting mixture was needed. Possibly, it was caused by a higher solubility of hydrated sodium sulphate in comparison with anhydrous one. Thus, also procedure used for the initial mixture preparation was changed. Hence, opposite to the previous method (solid Na_2SO_4 and K_2SO_4 were added to KCl solution), potassium salts were dosed to the solution of sodium sulphate. Then, neither conversion of Na_2SO_4 to K_2SO_4 nor properties of obtained products depended on the level of sodium sulphate hydration.

Furthermore, both the amount of recycled product and the excess of KCl introduced (mole ratio $n(K_2SO_4) : n(Na_2SO_4) : n(KCl) = 0—0.5 : 1 : 2—8$) were lowered. It was found (Fig. 1) that the excess of potassium chloride (reaction (C)) influences negatively sodium content in the separated phase (de-

Table 1. The Influence of Reagents Mole Ratio on the Degree of Na_2SO_4 Conversion to K_2SO_4

m_r*	Salt content/%	w/mass %			α/%
		Na_2SO_4	K_2SO_4	Glaserite	
0.33 : 1 : 8	30	4.00	73.00	23.01	77.65
0.5 : 1 : 18	27	1.68	31.32	67.00	44.12
0.75 : 1 : 8	30	1.23	21.89	76.88	26.69
0.75 : 1 : 12	30	1.59	71.38	27.02	74.40
0.75 : 1 : 18	30	3.24	20.03	76.73	25.01
1 : 1 : 18	27	0.91	63.72	35.38	69.70
1 : 1 : 18	30	2.33	55.96	41.70	58.72
2 : 1 : 6	30	3.62	43.60	52.79	45.53
2 : 1 : 10	30	1.56	60.22	38.22	62.46
2 : 1 : 10	40	3.01	45.58	51.41	41.35
2 : 1 : 8	30	0.00	95.50	4.50	95.88
2 : 1 : 8	40	3.57	52.31	44.12	50.31
2 : 1 : 18	27	0.00	58.62	41.38	62.07
3 : 1 : 8	30	0.00	98.65	1.35	98.75
3 : 1 : 8	40	1.63	45.02	53.35	40.49

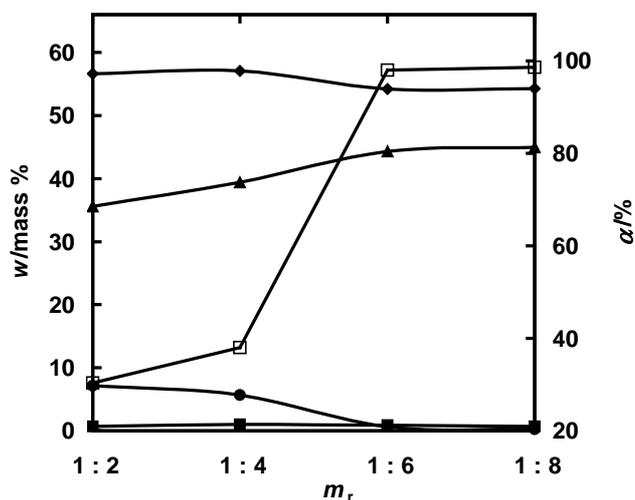*$n(K_2SO_4) : n(Na_2SO_4) : n(KCl)$.

Fig. 1. Influence of the initial mixture composition (total salts content of 30 mass %) on the composition of solid phases and the conversion of Na_2SO_4 to K_2SO_4: SO_4^{2-} (◆), K^+ (▲), Na^+ (●), Cl^- (■), and conversion (□).

Fig. 2. Influence of the total salts content ($n(K_2SO_4)$: $n(Na_2SO_4)$: $n(KCl)$ = 0.5 : 1 : 8) on the composition of solid phases and the conversion of Na_2SO_4 to K_2SO_4: SO_4^{2-} (◆), K^+ (▲), Na^+ (●), Cl^- (■), and conversion (□).

crease from about 8.2 mass % to 0.2 mass % of Na^+) and positively the corresponding potassium content (increase from 33.2 mass % to 44.8 mass % of K^+). This fact should be attributed to a gradual increase of sodium sulphate conversion not only to glaserite (reaction (*A*)) but also to potassium sulphate.

Influence of the initial salts content (27—50 mass %) on the conversion of sodium sulphate to potassium sulphate (mole ratio $n(K_2SO_4)$: $n(Na_2SO_4)$: $n(KCl)$ = 0—0.5 : 1 : 8) is illustrated in Fig. 2. By increasing the total salt concentrations, the amount of chlorides in the resulting mixture increased rapidly (*ca.* 0.2—32 mass %); meanwhile, the increase of sodium ion content was less steep (*ca.* 0.15—3.7 mass % of Na^+). At the same time, the content of sul-
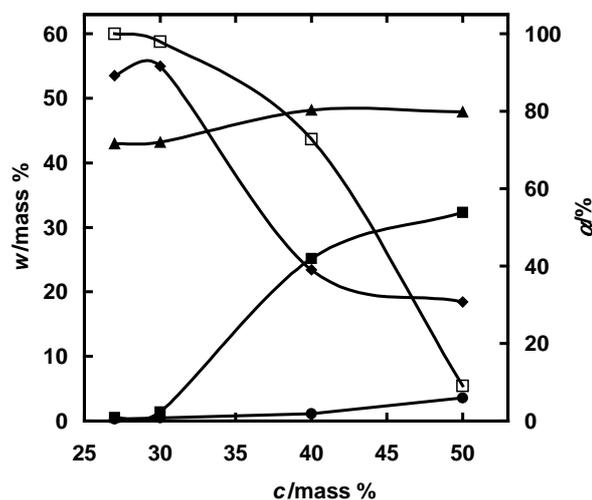
phate anions decreased from 55.2 mass % to 18 mass %. Thus, the amount of potassium sulphate obtained by crystallization is lowered and the content of undesirable glaserite and potassium chloride increased.

Investigated process was assumed to be wasteless. Therefore, separation of NaCl as a by-product from the mother liquor containing also glaserite and potassium chloride was required. On the other hand, the remaining salts, contaminated with traces of sodium chloride, should be recycled in order to maximize the sodium sulphate to potassium sulphate yield. Then, the influence of excess NaCl amount, with respect to the stoichiometry, on the reaction (*C*) conversion was determined.

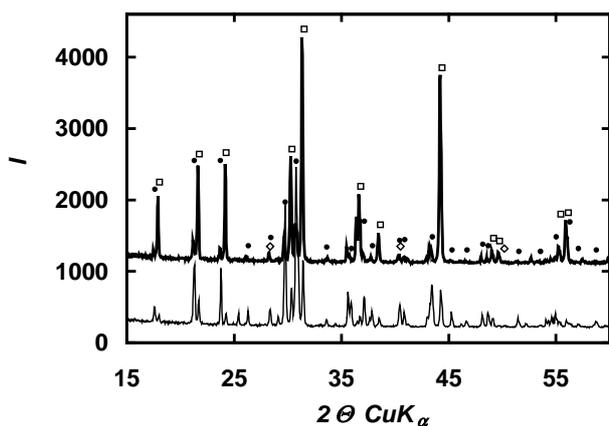Two series of experiments with different mole ra-

Fig. 3. Comparison of X-ray diffractograms of solid products obtained from the initial mixture ($n(Na_2SO_4) : n(KCl)$ of 1 : 6) at $n(K_2SO_4) : n(NaCl)$ mole ratio of 1 : 1 (thin line) and 1 : 4 (thick line). Diffraction peaks of $K_3Na(SO_4)_2$ (□), K_2SO_4 (●), and KCl (◇).

Fig. 4. Flow sheet of the one-stage production of potassium sulphate from sodium sulphate.

tios (1 : 6 or 1 : 8) of $n(Na_2SO_4) : n(KCl)$ were carried out. With increasing content of NaCl in the initial mixture, also glaserite content in the product rose gradually, reaching the value comparable with that obtained for lower initial mole ratios of raw materials $n(KCl) : n(Na_2SO_4)$ and $n(K_2SO_4) : n(Na_2SO_4)$. Depending on the mixture composition conversion of Na_2SO_4 to K_2SO_4 varied from 31 % to 99 %. However, at high mole ratios of $n(NaCl) : n(K_2SO_4)$, in spite of high potassium chloride content, potassium sulphate undergone reaction with sodium chloride to form glaserite. In Fig. 3 X-ray diffractograms of the products obtained from the initial mixtures comprising $n(Na_2SO_4)$ to $n(KCl)$ mole ratio of 1 : 6 and two different $n(K_2SO_4) : n(NaCl)$ mole ratios of 1 : 1 and 1 : 4 are compared. In the product obtained in the second case (higher fraction of NaCl in the reaction mixture) glaserite was the main phase, whereas K_2SO_4 was the main phase in the first case. The presence of small amounts of KCl was found in both products. A phase corresponding to NaCl was not identified.

During the process raw potassium sulphate and mother liquor containing 10—12.4 mass % of K^+, 2.9—3.7 mass % of Na^+, 1.2—2.4 mass % of SO_4^{2-}, and 10—12 mass % of Cl^-, was produced. In order to increase raw material utilization, mother liquor was evaporated and subjected to a two-stage fractional crystallization. Variation of solubilities of NaCl, KCl, K_2SO_4, and $K_3Na(SO_4)_2$ with temperature [16, 17] was used to discriminate an appropriate crystallization temperature. It was found that mother liquor concentrated to about 40 mass % of solids by evaporation and submitted to crystallization at 2 °C yielded solid phase containing mainly KCl and $K_3Na(SO_4)_2$ (including traces of NaCl). After a subsequent solvent evaporation (to 60 mass % of solid) and crystallization at 110 °C, raw sodium chloride (containing mainly
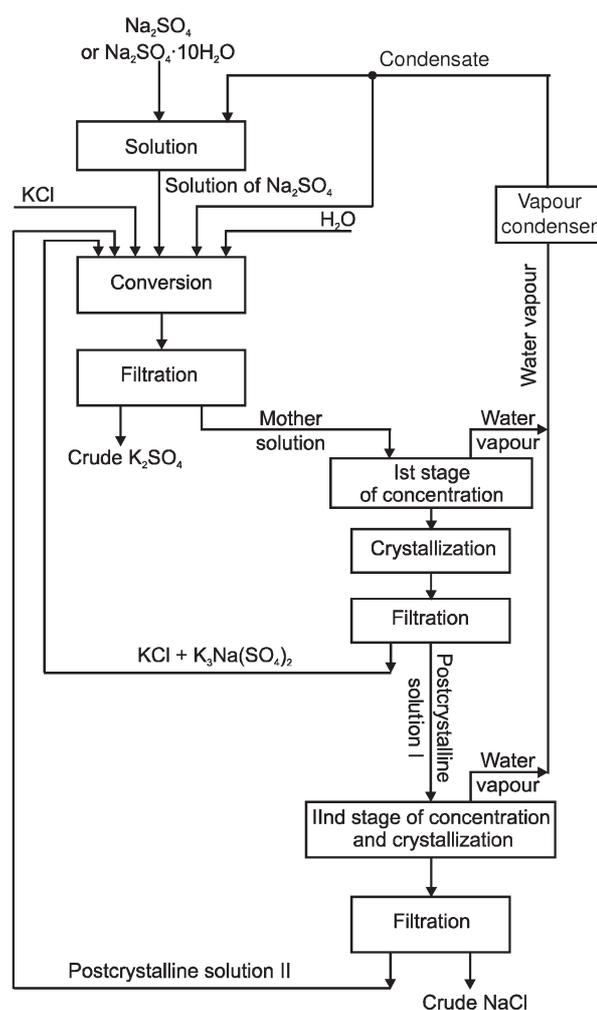
NaCl with traces of KCl and $K_3Na(SO_4)_2$) as well as final post-crystallization liquor was obtained. Recirculation of both the post-crystallization liquor and the mixture of potassium salts from the first crystallization stage was proposed (Fig. 4).

Finally, reagent-purity Na_2SO_4 was replaced with sodium sulphate produced during the manufacture of trimethylolpropane. About 2 mass % of carbon in this substrate indicated the presence of organic phase entrapped in crystals of Na_2SO_4. Based on the previous investigation, the process of potassium sulphate preparation was examined. After six production cycles (including separation of potassium sulphate as well as post-crystallization liquor and potassium salts recirculation), neither the content of chlorides nor sodium was increased in the main product. Moreover, no increase in the content of both potassium and sulphate anions was noticed in the by-product using a number of successive recycles. Obtained raw potassium sulphate contained 94—98 mass % of K_2SO_4 comprising: 43—44 mass % of K^+, 0.15—0.30 mass % of Na^+,

53.4—54.6 mass % of SO_4^{2-}, 0.5—2 mass % of Cl^-, and 0.6 mass % of C. The raw sodium chloride (92—93 mass % of NaCl) contained 2.1—3.3 mass % of K^+, 33.4—37.1 mass % of Na^+, 1.2—3.6 mass % of SO_4^{2-}, 60—63 mass % of Cl^-, and 0.2 mass % of C. It was confirmed that the degree of sodium chloride separation at these conditions ranged from 40 % to 45 %.

A single-step method for the preparation of potassium sulphate from potassium chloride and either anhydrous or hydrated sodium sulphate was developed [18]. Sulphates used for K_2SO_4 production can be of natural as well as of anthropogenic origin. The obtained potassium sulphate can be used for the production of multi-component fertilizers. Hence, it should not contain heavy metals, the amount of which in fertilizers is limited [19]. Therefore, the use of raw materials for K_2SO_4 production is limited to sources free of the above-mentioned impurities.

SYMBOLS

c	concentration of salts	mass %
I	intensity	
m_r	mole ratio	
x	mole fraction	mole %
T	temperature	°C
w	content	mass %
α	conversion of Na_2SO_4 to K_2SO_4	%

REFERENCES

1. Anonymous, Let us put knowledge into practice. *Fert. Int.* **392**, 20 (2003).
2. Anonymous, Potash alternatives. *Phosph. Potass.* **219,** 26 (1999).
3. Anonymous, Making chloride-free potash fertilizers. *Phosph. Potass.* **156,** 27 (1988).
4. Kostick, D. S., Sodium sulfate. *U.S. Geological Survey, Mineral Commodity Summaries,* p. 156, 2002.
5. Co-production of potassium sulphate and sodium sulphate. *WO* 16899 (1996).
6. Co-production of potassium sulphate, sodium sulphate and sodium chloride. *WO* 16900 (1996).
7. Safragin, Yu. S., Buksha, Yu. V., Rutkovskaya, T. I., Timofeeva, V. I., Titkov, S. N., Terent'eva, G. I., and Vybornova, G. Yu., Method of production of potassium sulphate. *RU* 2161125 (2000).
8. Method of formulating alkali metal salts. *WO* 21887 (2000).
9. Method of preparing potassium sulphate. *RU* 2154026 (2000).
10. Process for the utilization of waste sodium sulphate. *DE* 4340839 (1994).
11. Terlak, K., Method for production of trimethylolpropane. *PL* 174671 (1998).
12. Grzmil, B. and Zienkiewicz, M., *Chemistry for Agriculture 2*, 205 (2002).
13. Szczepaniak, W., *Instrumental Methods in Chemical Analysis*, p. 160. Scientific Publishers, Warsaw, 1997.
14. Struszyński, M., *Quantitative and Technical Analysis,* Vol. *2*, p. 282. Scientific Publisher NPS, Warsaw, 1954**.**
15. Chung, F. H. and Smith, D. K., *Industrial Application of X-Ray Diffraction,* p. 21. Dekker, New York—Basel, 2000.
16. Pozin, M., *Technology of Mineral Salts.* Scientific Publishers, Warsaw, 1953.
17. *Physicochemical Handbook.* Scientific Publishers, Warsaw, 1974.
18. Grzmil, B., Kic, B., Kałucki, K., and Czerniawska, B., The Preparation Method of Potassium Sulphate. *Bulletin of Patent Office* **794**, 24 (2004).
19. *Directive (UE) No. 2003/2003 of the European Parliament and of the Council Regarding the Fertilizers,* Brussels, 2003.