

SHORT COMMUNICATION

Production of potassium sulfate from potassium hydrosulfate solutions using alcohols[‡]

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Potassium sulfate is used to produce multicomponent fertilizers, free of chlorides. The desalting out of potassium sulfate from an aqueous solution of potassium hydrosulfate was conducted using 40 mass %, 45 mass %, or 50 mass % aqueous solutions of either methanol or propan-2-ol. Composition of the resultant precipitate was analyzed using chemical methods and XRD analysis. The results of the XRD analysis revealed that the main precipitate phase is K_2SO_4 . Small amounts of $K_5H_3(SO_4)_4$ were detected when the desalting out was carried out from 2.5 M $KHSO_4$ solution using 40 mass % and 50 mass % methanol solution. When the amount of potassium bisulfate in the solution increased to 3.5 M and 3.8 M, the main phase consisted of $K_3H(SO_4)_2$. Generally, the desalting out process using propan-2-ol caused the formation of $K_3H(SO_4)_2$. Potassium sulfate was obtained only by desalting out the 2.5 M $KHSO_4$ solution using 50 mass % aqueous propan-2-ol.

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Potassium is one of the basic nutrients for plants. It is found in soil in quantities insufficient to produce optimum quality crops and, therefore, it must be added to soil as an essential component of all fertilizers. In agriculture, complex fertilizers almost always contain potassium chloride as a potash constituent (Khliisa et al., 2004, Abu-Eishah et al., 2000). However, for such crop plants as potatoes, tomatoes and tobacco, which are sensitive to chlorides, it is advisable to use potassium sulfate. Potassium sulfate is recommended to be used as a fertilizer instead of potassium chloride because it has the following distinct advantages (Abu-Eishah et al., 2000, Jannet et al., 2004, Mullin et al., 1989):

- It is a special two-component fertilizer (K+S) containing 50 mass % K_2O and 18 mass % S.
- It contains a very low amount of chlorine.
- It has a low salt index, so it is better suited for fertilizing the saline-sensitive crops.

– It possesses excellent physical properties and it is usually recommended for the high-quality crops cultivation.

In the world, K_2SO_4 is produced from KCl 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 sulfate can be formed at high temperature, about 600–700 °C. K_2SO_4 can also be obtained by acidulation of KCl at lower temperature. Under such conditions potassium hydrosulfate is formed (Giambra, 2005, Zisner et al., 1996, Efraim et al., 1996).

The paper presents the results of experiments on desalting out K_2SO_4 from solution containing $KHSO_4$ using an aqueous alcohol solution. Production of pure K_2SO_4 from the respective hydrogen sulfate describes the following reaction (Taboada et al., 2003)

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Table 1. Initial composition of solutions used for K₂SO₄ precipitation

| Experiment No. | <i>m/g</i> | | <i>c</i> (KHSO ₄)/M | <i>w</i> _{alcohol} */% |
|----------------|-------------------|------------------|---------------------------------|---------------------------------|
| | KHSO ₄ | H ₂ O | | |
| 1 | 6.808 | 47 | 1 | 40, 45, 50 |
| 2 | 17.02 | 32 | 2.5 | 40, 50 |
| 3 | 23.828 | 26 | 3.5 | 40, 50 |
| 4 | 25.87 | 22 | 3.8 | 40, 45, 50 |

*Methanol or propan-2-ol.



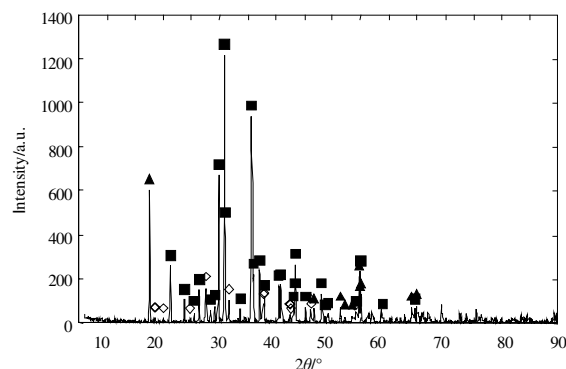
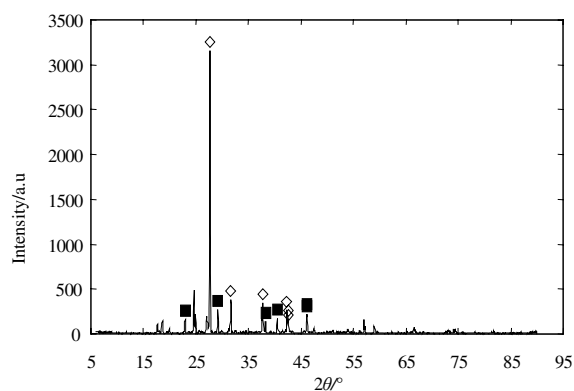
Precipitation of K₂SO₄ from the aqueous solution of potassium hydrogen sulfate by desalting out using a solvent was carried out in magnetically stirred glass beakers (200 cm³). Solutions of KHSO₄ in distilled water with various concentrations (1 M to 3.8 M) were used for this purpose. The amounts of KHSO₄ and solvent employed in precipitation experiments are presented in Table 1. Alcohol (methanol or propan-2-ol) from a burette was instilled to 50 cm³ of solution of hydrogen sulfate in order to obtain the required concentration. During all experiments the temperature of approximately 20 °C was maintained.

The addition of alcohol to the hydrogen sulfate solution causes the formation of a white precipitate. When the whole amount of alcohol was added, the stirrer was switched off and the liquor was left for 120 min. The precipitate was then filtered off using vacuum, dried at 105 °C, weighted, and analyzed. The solid phases were characterized by means of chemical analysis and the X-ray diffraction method (X'Pert PRO, Philips with Cu α lamp). The concentration of K⁺ ions was analyzed using the flame photometer FLAPHO 40, whereas the concentration of SO₄^{2−} was deduced on the basis of the amount of BaSO₄ formed by precipitation with 10 % BaCl₂ solution (Hermanowicz et al., 1996). The concentration of H⁺ was determined by titration. The concentrations of K⁺, SO₄^{2−}, and H⁺ were also studied in the mother liquor obtained after the precipitate separation. The desalting out coefficient of potassium salt was determined according to equation

$$N = \frac{m_K}{m_P} \quad (2)$$

where *m_P* and *m_K* represent the amounts of KHSO₄ used and precipitate formed during the desalting out process, respectively.

Figs. 1–4 present the X-ray diffraction patterns of the precipitates prepared by the above-mentioned method. It was found that both the amount of alcohol added and the concentration of potassium bisulfate in the solution influence the precipitate composition. The saturation concentration of KHSO₄ in water at 293 K is 51.4 g per 100 g H₂O (Handbook of Chemistry and Physics, 1974). K₂SO₄ is less soluble in water

**Fig. 1.** X-ray diffraction pattern of the precipitate from the 1 M KHSO₄ solution and 40 % methanol containing KHSO₄ (▲), K₃H(SO₄)₂ (◇), and K₂SO₄ (■).**Fig. 2.** X-ray diffraction pattern of the precipitate from the 3.8 M KHSO₄ solution and 40 % propan-2-ol containing K₂SO₄ (■) and K₃H(SO₄)₂ (◇).

than KHSO₄ and, moreover, the presence of alcohol decreases its solubility in water. The X-ray diffraction analysis showed that the main phase in the precipitate is K₂SO₄, when formed from the solution containing 1 M KHSO₄ and 40 mass % of methanol. The precipitate also contained K₃H(SO₄)₂ and a small amount of KHSO₄ (Fig. 1). A study of the mother solution left after the separation of the solid phase showed that a part of potassium hydrogen sulfate remains unreacted. Concentrations from 0.975 g dm^{−3} to 1.189 g dm^{−3} and from 2.106 g dm^{−3} to 2.631 g dm^{−3} were found in the mother solutions for K⁺ and SO₄^{2−}, re-

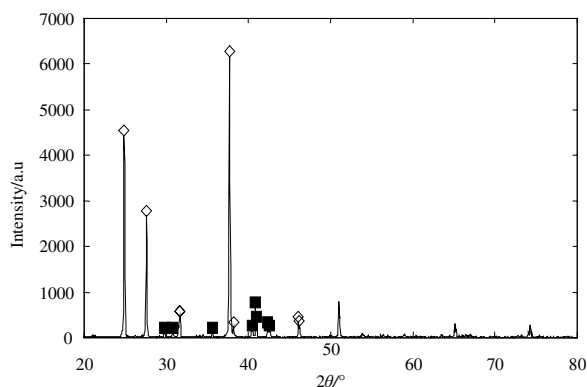


Fig. 3. X-ray diffraction pattern of the precipitate from the 2.5 M KHSO_4 solution and 40 % methanol containing $\text{K}_3\text{H}(\text{SO}_4)_2$ (\diamond) and K_2SO_4 (\blacksquare).

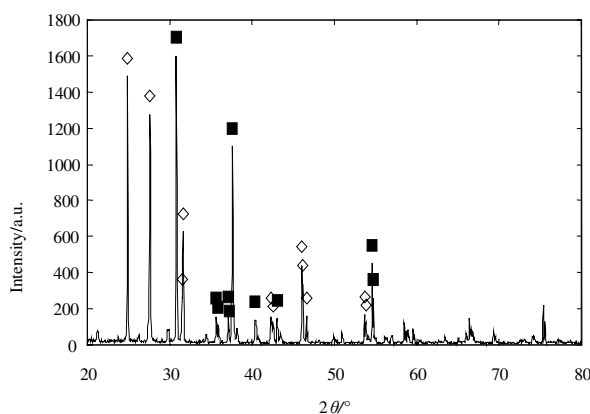


Fig. 4. X-ray diffraction pattern of the precipitate from the 3.5 M KHSO_4 solution and 40 % propan-2-ol containing $\text{K}_3\text{H}(\text{SO}_4)_2$ (\diamond) and K_2SO_4 (\blacksquare).

spectively. An increase of methanol concentration to 45 mass % and 50 mass % resulted in an increased of the conversion of potassium hydrogen sulfate. It can be stated that the increase of methanol amount in the solution, increases the desalting out coefficient of potassium salt (Fig. 5). The XRD analysis showed that K_2SO_4 remains the main component of the solid phase, while traces of KHSO_4 and $\text{K}_3\text{H}(\text{SO}_4)_2$ could also be found in the precipitate.

An increase of the KHSO_4 concentration in the initial mixture to 2.5 M and desalting out using the same concentrations of alcohol caused a decrease of the amount of potassium hydrogen sulfate in the precipitate. K_2SO_4 was the main component of the product with a small admixture of $\text{K}_3\text{H}(\text{SO}_4)_2$ (Fig. 6). An increase of the initial concentration of KHSO_4 to 3.8 M and desalting out using 40 mass % methanol caused an increase of desalting out coefficient of potassium salt from 46.7 % to 86.6 %. On the other hand, a change in the solid phase composition was observed. The precipitate obtained by desalting out the 3.5 M KHSO_4

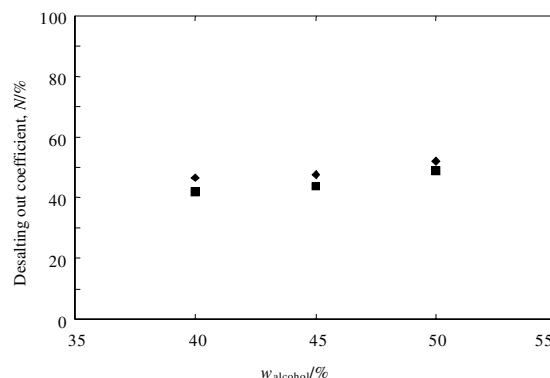


Fig. 5. Dependence of the desalting out coefficient of potassium salt on the amount of methanol (\diamond) and propan-2-ol (\blacksquare) added to 50 cm³ of 1 M KHSO_4 solution.

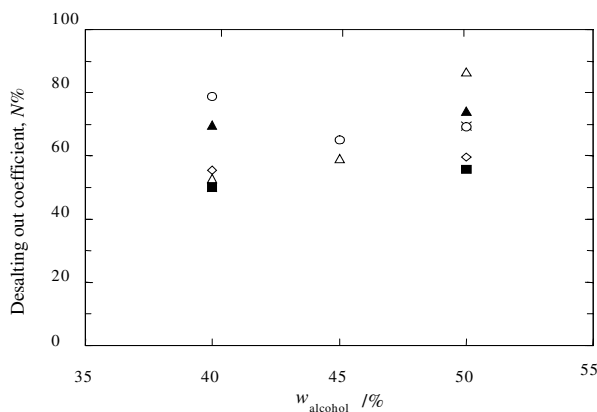


Fig. 6. Dependence of the desalting out coefficient of potassium salt on the alcohol concentration (\diamond – methanol and 2.5 M KHSO_4 ; \blacksquare – isopropanol and 2.5 M KHSO_4 ; \times – methanol and 3.8 M KHSO_4 ; \blacktriangle – methanol and 3.5 M KHSO_4 ; \triangle – isopropanol and 3.5 M KHSO_4 ; \circ – isopropanol and 3.8 M KHSO_4).

solution was a mixture of KHSO_4 and $\text{K}_5\text{H}_3(\text{SO}_4)_4$. At even higher concentration of KHSO_4 in the solution (3.8 M) the supersaturation state was achieved for $\text{K}_3\text{H}(\text{SO}_4)_2$ and the respective precipitate contained mainly $\text{K}_3\text{H}(\text{SO}_4)_2$.

The tests of desalting out K_2SO_4 from a solution of potassium hydrosulfate using propan-2-ol as a solvent were also conducted. The results of these experiments are shown in Figs. 3 and 4. An addition of propan-2-ol to a solution of KHSO_4 showed that K_2SO_4 is the main precipitate constituent. However, a comparison of the results obtained for the same conditions using 40 mass % of methanol showed that in the presence of propan-2-ol, the precipitate is free of potassium hydrogen sulfate. Analyzing the mother solution obtained after the precipitate separation was found that the application of propan-2-ol in higher concentration results in an increase of the K^+ ions concentration from 0.267 g dm⁻³ to 1.539 g dm⁻³. The sulfates concen-

tration was changed from 3.70 g dm^{-3} to 1.91 g dm^{-3} . The desalting out coefficient of the potassium salt obtained using propan-2-ol increased, for higher initial concentrations of KHSO_4 in the solution, to 48.9 % compared to the value of 41.8 % observed for the solution of 1 M KHSO_4 and 40 mass % of propan-2-ol. However, the values of the desalting out coefficient were smaller in comparison to the results obtained for methanol. The resultant precipitate consisted mainly of $\text{K}_3\text{H}(\text{SO}_4)_2$ as shown in Fig. 4.

It was found that methanol is a better desalting out medium for the potassium sulfate production than propan-2-ol, i.e. 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 recycle.

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