VERSITA

Preparation of potassium nitrate from potassium chloride and magnesium nitrate in a laboratory scale using industrial raw materials

Jana Jurišová[a], Pavel Fellner[a], Vladimír Danielik[a],
Marek Lencsés[b], Milan Králik[b], Rastislav Šípoš[a]

[a]*Institute of Inorganic Chemistry, Technology and Materials,*
Faculty of Chemical and Food Technology STU in Bratislava,
Radlinského 9, 812 37 Bratislava, Slovak Republic
[b]*VUCHT, a.s., Nobelova 34, 836 03 Bratislava, Slovak Republic*
*jana.jurisova@stuba.sk*

Abstract: Preparation of potassium nitrate from magnesium nitrate and potassium chloride was investigated. Prepared potassium nitrate contains less than 0.5 % chlorides and it can be applied as environmentally friendly fertilizer in hydroponic systems. After filtration out potassium nitrate crystals from the reciprocal system K^+, $Mg^{2+}//Cl^-$, $NO_3^- - H_2O$, the mother liquor still contains reasonable amount of potassium cations. By evaporation of the mother liquor, carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) with admixture of $MgCl_2 \cdot 6H_2O$ crystallizes out. Decomposition of carnallite with cold water makes it possible to separate potassium chloride from this compound. When this KCl is returned back to the process of KNO_3 making, utilization of potassium as high as 97 % can be achieved.

Keywords: potassium nitrate, magnesium nitrate, carnallite

Introduction

Pure chemicals and their mixtures are increasingly applied in environmentally friendly plant growing, especially in irrigation and hydroponic systems. Pure magnesium nitrate, calcium nitrate and potassium nitrate represent important components used for these purposes.

Depending on available raw materials, different methods for production of KNO_3 have been proposed. Some of them were actualized in industrial measure. For example, KCl reacts with HNO_3 at the temperature of 75 °C according to the following reaction scheme (Phosphorus and Potassium 1965):

$$3\ KCl + 4\ HNO_3 = 3\ KNO_3 + Cl_2 + NOCl + 2\ H_2O \quad (1)$$
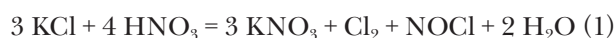
In the next step, NOCl is oxidized with nitric acid at 150 °C

$$2\ NOCl + 4\ HNO_3 = Cl_2 + 6\ NO_2 + 2\ H_2O \quad (2)$$

NO_2 is oxidized and used again for the production of nitric acid and chlorine can be used for another purpose. To avoid corrosion problems and oxidation of NOCl the company Israel Mining Industries carries out the reaction between KCl and HNO_3 at low temperatures:

$$KCl + HNO_3 = KNO_3 + HCl \quad (3)$$

In this case HCl has to be removed from the reaction mixture, which is done with organic solvent (Phosphorus and Potassium 1969).

Several methods based on the conversion of KCl with another nitrates were studied. Some of them were carried out in industrial measure. General reaction scheme is as follows:

$$K^+(aq) + Cl^-(aq) + M^+(aq) + NO_3^-(aq) =$$
$$= M^+(aq) + Cl^-(aq) + KNO_3(s) \quad (4)$$
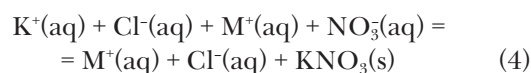
where M^+ can be Na^+, Ca^{2+}, or as in the case discussed in this paper Mg^{2+}.

When K_2SO_4 is used instead of KCl as source of potassium, KNO_3 can be prepared by the reaction

$$K_2SO_4 + Ca(NO_3)_2 = 2\ KNO_3 + CaSO_4 \quad (5)$$

Each of these methods has advantages and disadvantages, the main problems being purity of prepared KNO_3, treatment of wastes and, of course, price of the used technology.

In this work we will discuss in detail the conversion of KCl with $Mg(NO_3)_2$:

$$2\ KCl + Mg(NO_3)_2 = 2\ KNO_3 + MgCl_2 \quad (6)$$
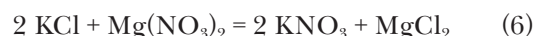
Patent literature describes preparation of starting solutions for crystallization of KNO_3 (Germany Patent 374.095 (1923); 365.587 (1923); 374.096 (1923); 394.464 (1924); 399.465 (1924); 401.979 (1924); 403.996 (1924); 403.997 (1924)) and the conditions for removing $MgCl_2$ from the solution, usually as carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$ (Germany Patent 414.597 (1927); 413.300 (1925); 413.299 (1925); 405.579 (1924)). It would be of great advantage if

potassium from carnallite could also be used for preparation of KNO_3. This would substantially increase utilization of potassium which is valuable constituent of fertilizers.

For quantitative evaluation of reaction (6), reliable equilibrium data for the reciprocal system K^+, $Mg^{2+}//Cl^-$, NO_3^- – H_2O are needed. Phase diagram of the system K^+, $Mg^{2+}//Cl^-$, NO_3^- – H_2O for the temperature of 5 °C was published by Žúžiová et al. 1988. Matveeva and Kudryashova 2009 studied this system at 25 °C and 50 °C. Equilibrium data at 20 °C, 40 °C and 60 °C are available only in an internal report (VÚAgT 1973). For illustration phase diagram of the reciprocal system K^+, $Mg^{2+}//Cl^-$, NO_3^- – H_2O obtained at the temperature of 20 °C is presented in Fig. 1 (VÚAgT 1973). (Potassium chloride is denoted as K_2Cl_2 because of charge equality of two potassium cations with Mg^{2+} cation. This formalism makes the phase diagram more symmetric.)

For industrial application the phase equilibria at higher temperatures up to 90 °C are desirable. Prediction of equilibria at higher temperatures could limit a number of necessary experimental measurements. For the purpose of KNO_3 production, only the section $MgCl_2$ – KNO_3 were thermodynamically treated for consistency and prediction. This topic will be discussed in detail in paper (Danielik et al. to be published). In this paper we will present the results obtained at preparation of potassium nitrate in laboratory scale from raw materials that are expected to be used in industry. Purity of final product (KNO_3), especially the content of chlorides, is of primary importance. Thus the influence of rate of crystallization, washing of crystals, etc. is discussed in detail.

Experimental

Chemicals used

As has been mentioned in the introduction, industrial raw materials were used for preparation of KNO_3. KCl (supplier: Kalij — White Russia) has following composition (wt. %):

KCl — 94.6 %; $MgCl_2$ — 1.2 %; NaCl — 1.8 %; $CaCl_2$ — 0.4 %; sand 2 %.

Composition of magnesite (supplier SMZ Jelšava, Slovakia) is as follows (wt. %):

$MgCO_3$ — 85.7 %; $CaCO_3$ — 7.20 %; $FeCO_3$ — 4.36; SiO_2 — 1.93 %; $MnCO_3$ — 0.11 %; moisture 0.7 %.

Preparation of $Mg(NO_3)_2$ solution

2 kg of raw magnesium carbonate (diameter from 50 to 90 % of particles is in the range 0.063–0.250 mm) is added under mixing to 5 kg of nitric acid (60 %) until concentration of the nitric acid drops to 2–4 %. Because of reaction heat, temperature of the solution increases from ca 30 °C up to ca 110 °C. Rate of addition of magnesite is determined by foam formation. Rest of the acid is neutralized by the addition of MgO powder until pH of the solution reaches 6.6–7.0. This solution is diluted by distilled water and filtered at the temperature of 50–80 °C.
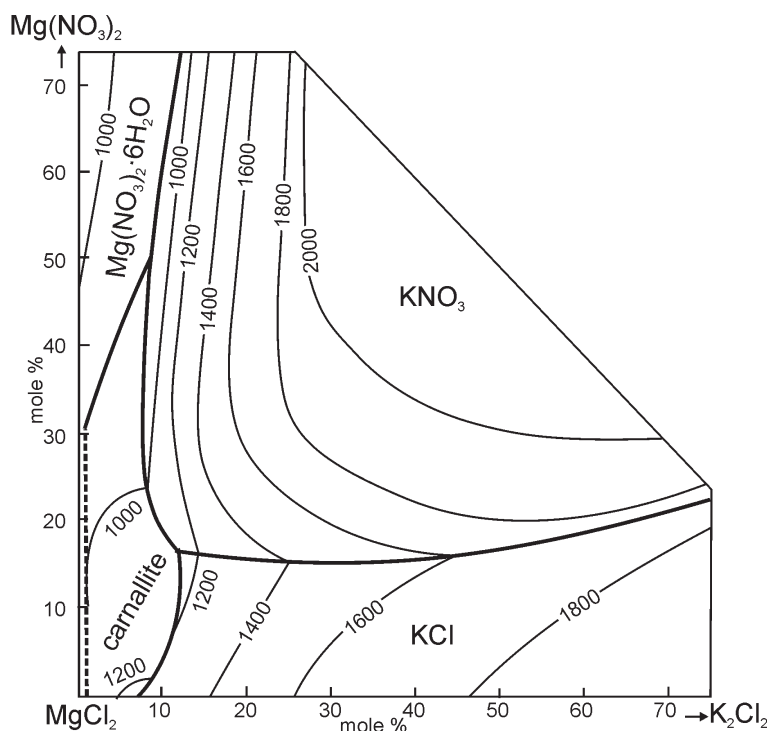

Fig. 1. Phase diagram of the system K^+, $Mg^{2+}//Cl^-$, NO_3^- – H_2O at the temperature of 20 °C with the areas of crystallization of components (VÚAgT 1973).

Analysis of raw materials and of KNO₃

Analysis of raw materials and of KNO₃

Magnesium and calcium are determined by complexometric titration with aqueous solution of sodium salt of EDTA at pH = 10. Erichrome black T is used as indicator.

Determination of NO_3^-. Nitrate anion oxidizes $FeSO_4$ in the presence of H_2SO_4 at elevated temperature to $Fe_2(SO_4)_3$. Surplus of $FeSO_4$ is titrated with 0.05 M $KMnO_4$ solution.

Chloride anions were determined either by ion chromatography or by argentometry.

Preparation of KNO₃

Mother liquor for crystallization of KNO_3 was prepared in the following way. 350 g of $Mg(NO_3)_2$ solution (40.7 wt. % $Mg(NO_3)_2$) was mixed with 158 g of KCl (technical grade) and 148 g of deionized water in 1000 ml beaker. The beaker was covered with a lid to prevent evaporation. The mixture was heated up to 96 °C. When salts were dissolved, solid impurities originating from KCl were filtered out at the temperature higher that 90 °C in order to prevent crystallization of potassium nitrate. Mass of solid impurities was ca 2 g. Then the solution was cooled to 10 °C. The amount of KNO_3 crystals obtained by filtration from this solution was washed with 171 g of deionized water. Temperature of washing deionized water was also 10 °C. Washing of KNO_3 crystals was carried out in a closed vessel which made it possible to use intensive mixing. The crystals of KNO_3 were filtered out and dried at 60 °C.

Solution remaining after washing of KNO_3 crystals (ca 210 g) was used in the next experiment for preparation of the reaction mixture instead of water. Mother liquor remaining after filtration of KNO_3 was concentrated by evaporation of water. The amount of evaporated water was that required for washing of KNO_3 crystals (and required in the next step for preparation of the solution (see Fig. 2).

Scheme for preparation of KNO_3 with proposed recycling streams is depicted in Fig. 2.

KNO_3 crystals were characterized also by SEM (Tesla BS 300 equipped with digital unit Tescan).

Results and Discussion

Maximal yield of potassium nitrate can be estimated on the basis of phase diagram of the reciprocal system K^+, Mg^{2+}//Cl^-, NO_3^- – H_2O. It follows that maximum utilization of potassium chloride can be 86.6 %. This yield is achieved when the saturated mother liquor is prepared from pure $Mg(NO_3)_2$ and KCl and the solution is cooled to 10 °C. Of course, when raw materials containing impurities are used, this has to be taken into account.

Crucial requirement on prepared potassium nitrate is its purity. The amount of chlorides should not exceed ca 0.5 wt. %. Purity of KNO_3 crystals is influenced not only by the presence of impurities in the solution but also by washing of the crystals. It depends also on the kinetics of crystal growth which can be influenced by the rate of cooling and by mixing of the mother solution.
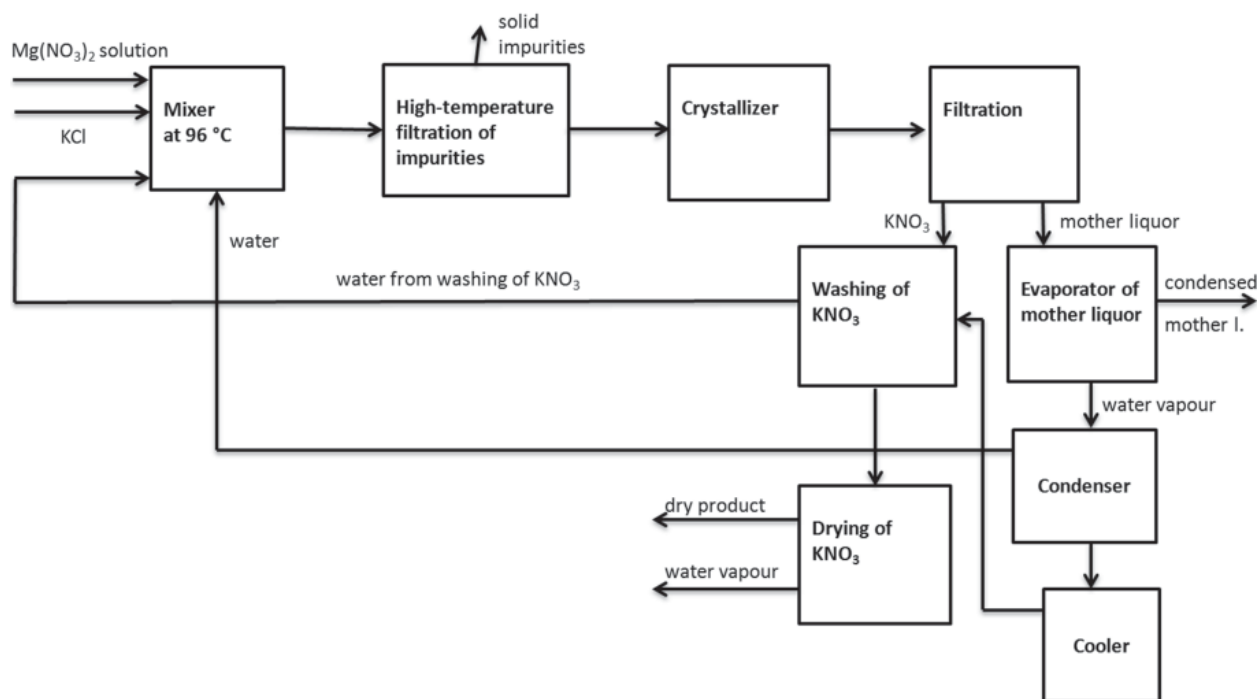

Fig. 2. Scheme of production of KNO_3 by conversion reaction of KCl and $Mg(NO_3)_2$.

Two series of experiments were carried out:

A. Crystallization of KNO_3 without mixing of the mother liquor
B. Crystallization with mixing

Series A

In this series of experiments, crystallization of KNO_3 proceeded without mixing. After removal of solid impurities by filtering, the beaker containing saturated solution was cooled down in the mixture of water with ice. When the temperature of the solution reached 10 °C, KNO_3 crystals were filtered out using a Büchner funnel. The results are summarized in Table 1.

Series B

In this series, the preparation of KNO_3 was carried out in a similar way as in series A. The only difference was in cooling which was now carried out under mixing by an impeller stirrer. All data related to these experiments are summarized in Table 2. It can be seen that we could obtain product with content of chlorides as low as 0.2 % at high yield (84 %) of potassium nitrate. Crystals of KNO_3 obtained in this way are smaller and more homogeneous as the crystals obtained without mixing. Appearance of the crystals can be seen on Fig. 3.

Decomposition of carnallite

When solid potassium nitrate is removed from the system, the solution still contains reasonable amount of potassium ions. By evaporation of water from this solution (this water is returned back to the process) we obtain after cooling to 25 °C solid phase consisting of carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), KNO_3, and small amount of $MgCl_2 \cdot 6H_2O$. In the next we will denote this mixture of crystals as "raw carnallite". Carnallite makes 94 % of the solid phase, i.e. of "raw carnallite". Decomposition of this material (this is also known as "processing of carnallite") yields solid KCl and solution containing $MgCl_2$ and KCl (and small amount of nitrates). This is a well established process (see for example Ullmann's encyclopedia of Industrial Chemistry).

The process of decomposition of "raw carnallite" is illustrated in Fig. 4. Result of our experiments is as follows. When we added 42.5 ml of distilled water to 100 g of "raw carnallite" we obtained 19.7 g of KCl which is returned back to the process of preparation of KNO_3. Using this procedure, utilization of potassium from KCl for KNO_3 production increases up to 97 %. Work on the treatment of the residual solid phase containing ca 25 % of carnallite and ca 74 % of $MgCl_2 \cdot 6H_2O$ (the rest being nitrates) is under progress.
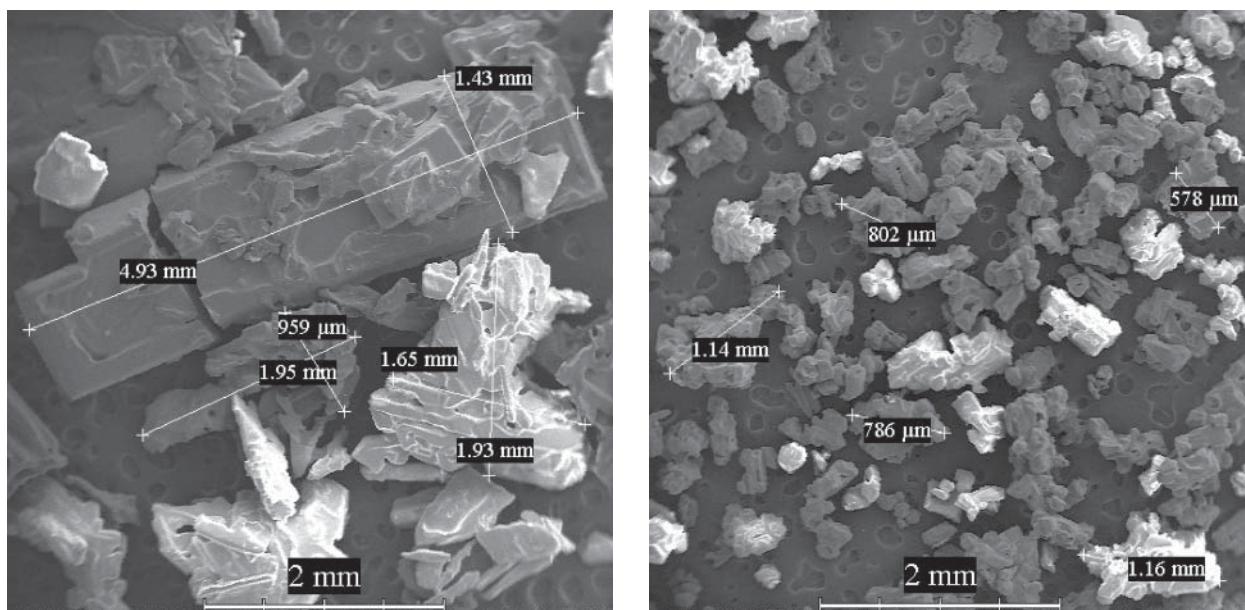
References

Danielik V, Jurišová J and Fellner P to be published in Chemical Papers.

Tab. 1. Summary of results, series A.

No.	1	2	3	4
Weighed-in	158g KCl	158 g KCl	158 g KCl	158 g KCl
	350 g $Mg(NO_3)_2$ solution	350 g $Mg(NO_3)_2$ solution	350 g $Mg(NO_3)_2$ solution	350 g $Mg(NO_3)_2$ solution
	148 g deion. water	203g of washing solution from No.1.	208 g washing solution from No. 2.	209 g washing solution from No. 3
Solid impurities	1.66 g	1.13 g	2.48 g	1.92 g
Mass of dry KNO_3	144 g	169 g	167 g	167 g
Content of chlorides, wt. %	0.49	0.57	0.62	0.61

Tab. 2. Summary of results, series B.

No.	1	2	3
Weighed-in	158 g KCl	158 g KCl	158 g KCl
	350 g $Mg(NO_3)_2$ solution	350 g $Mg(NO_3)_2$ solution	350 g $Mg(NO_3)_2$ solution
	148 g water	209 g washing solution from No. 1	214 g washing solution from No. 2
Impurities	3.18 g	0.64 g	1.72 g
Mass of dry KNO_3	133 g	157 g	159
Content of chlorides, wt. %	0.22	0.23	0.20

A.   B.

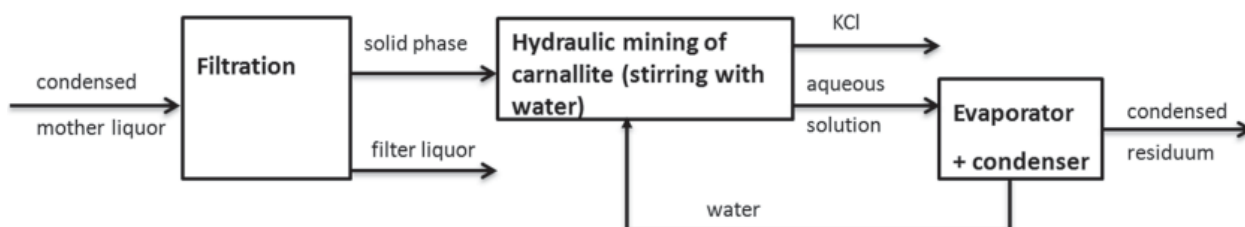**Fig. 3.** Pictures of crystals of potassium nitrate obtained in series A and B, respectively.

Fig. 4. Scheme of processing of the secondary product (condensed mother liquor)
from the evaporator (see also Fig. 1).

Germany Patent 374.095 (1923).
Germany Patent 365.587 (1923).
Germany Patent 374.096 (1923).
Germany Patent 394.464 (1924).
Germany Patent 399.465 (1924).
Germany Patent 401.979 (1924).
Germany Patent 403.996 (1924).
Germany Patent 403.997 (1924).
Germany Patent 414.597 (1927).
Germany Patent 413.300 (1925).
Germany Patent 413.299 (1925).
Germany Patent 405.579 (1924).

Internal report VÚAgT (1973) Bratislava.
Matveeva KR, Kudryashova OS (2009) Russian Journal of Inorganic Chemistry 54 (12) 2079–2082.
Phosphorus and Potassium (1965) 19, 31.
Phosphorus and Potassium (1969) 41, 40.
Ullmann's encyclopedia of Industrial Chemistry, Potassium Compounds, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, p. 22, 2005, DOI: 10.1002/14356007.a22 039.
Žúžiová A, Khandl V, Plančík M (1988) Chemický průmysl 38/63 (12) 643–646.