(54) Titre : PROCEDE DE PRODUCTION DE KNO₃ A PARTIR DE POLYHALITE
(54) Title: POLYHALITE IMI PROCESS FOR KNO₃ PRODUCTION

(57) Abrégé/Abstract:
A process for producing KNO₃ from polyhalite is disclosed. In a preferred embodiment, the process comprises steps of (a) contacting polyhalite with HNO₃; (b) adding Ca(OH)₂ to the solution, thereby precipitating as CaSO₄ at least part of the sulfate
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(57) Abrégé(suite)/Abstract(continued):

present in said solution; (c) precipitating as Mg(OH)2 at least part of the Mg2+ remaining in said solution by further addition of Ca(OH)2 to the remaining solution; (d) concentrating the solution, thereby precipitating as a sulfate compound at least part of the sulfate remaining in solution; (e) separating at least part of the NaCl from the solution remaining; and (f) crystallizing as solid KNO3 at least part of the K+ and NO3- contained in the solution. The process enables direct conversion of polyhalite to KNO3 of purity exceeding 98.5% and that is essentially free of magnesium and sulfate impurities.
POLYHALITE IMI PROCESS FOR KNO₃ PRODUCTION

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POLYHALITE IMI PROCESS FOR KNO₃ PRODUCTION

REFERENCE TO RELATED PUBLICATION

[01] This application claims priority from U.S. provisional application 61/220,230, dated 25 June 2009, which is hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION
This invention concerns methods for production of KNO₃, in particular, methods that use polyhalite as the starting material.

BACKGROUND OF THE INVENTION
Potassium nitrate (KNO₃) is a commercially important chemical with uses from explosives to fertilizers. Polyhalite (K₂SO₄•MgSO₄•2CaSO₄•2H₂O) is a widely-distributed and readily available source of potassium. Reaction of polyhalite with acids (e.g. HNO₃) is known in the literature as a means of producing crude salt mixtures containing "complex mineral fertilizer." For example, U.S. Pat. No. 4,246,019 discloses a method for production of a mixture containing 53.54% KNO₃, 39.87% Mg(NO₃)₂, 5.48% CaSO₄, and 1.01% H₂O from the reaction of polyhalite with HNO₃. Russian Pat. No. 2,276,123 discloses a method for production of a solution containing a mixture of K₂SO₄, MgSO₄ and NH₄NO₃ from reaction of polyhalite with HNO₃ followed by neutralization with ammonia. Thus the processes described in the literature allow to produce a solution containing a mixture of substances, including potassium and magnesium nitrates, as well as gypsum that had not been separated in early stages of the process.

Several well-known processes, such as the Southwest Potash and IMI processes, are known for the production of KNO₃ by reaction of KCl with HNO₃ (Ullman's Agrochemicals, vol. 1; Weinheim: Wiley-VCH, 2007, pp. 334 – 336). Production of essentially pure KNO₃ directly from the reaction of polyhalite with strong acid remains unknown, however. Thus, there remains a long-felt need for a process that can produce essentially pure KNO₃ from polyhalite without the complications of known processes such as production of complicated product mixtures and necessity of neutralization with ammonia.
SUMMARY OF THE INVENTION

The process disclosed in the present invention produces KNO₃ from polyhalite with almost total recovery, without any necessity for preliminary thermal treatment and without the necessity for washing out of NaCl from the polyhalite. The separation of NaCl from the KNO₃ is effected by the different temperature dependences of the solubility of the two substances: the solubility of NaCl changes very little with temperature, while that of KNO₃ strongly increases with increasing temperature. In the process herein disclosed, Mg is recovered as Mg(OH)₂, which is precipitated with lime. The Mg(OH)₂ thus recovered can be used directly as a slurry with water, dried or transformed into Mg salts such as MgSO₄·H₂O.

It is therefore an object of the present invention to disclose a process for producing KNO₃ wherein the starting material for the process is polyhalite.

It is a further object of the present invention to disclose a process for producing KNO₃ from polyhalite, comprising steps of (a) contacting polyhalite with a substance comprising NO₃⁻; (b) adding at least one inorganic base to the solution obtained in the step of contacting polyhalite with HNO₃, thereby precipitating as a solid at least part of the sulfate present in said solution; (c) precipitating as Mg(OH)₂ at least part of the Mg²⁺ remaining in said solution by adding at least one basic compound to the remaining solution; (d) concentrating the solution obtained after said step of precipitating at least part of the Mg²⁺ remaining in said solution; (e) precipitating at least part of the NaCl derived from said polyhalite, if any, from the solution obtained after said step of concentrating the solution obtained after said step of precipitating at least part of the Mg²⁺ remaining in said solution; (f) separating said precipitated NaCl, if any, from the reaction stream, and (g) separating as solid KNO₃ at least part of the K⁺ and NO₃⁻ contained in the solution remaining after the step of precipitating at least part of the NaCl derived from said polyhalite. It is within the essence of the invention wherein said process is adapted to produce commercially usable KNO₃ from polyhalite.

It is a further object of this invention to disclose such a process, further including an additional step of washing said polyhalite prior to said step of contacting polyhalite with a substance comprising NO₃⁻, thereby removing at least a part of the NaCl contained within said polyhalite.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of contacting polyhalite with a substance comprising NO₃⁻ takes place at a temperature between about 60 °C and about 90 °C.
It is a further object of this invention to disclose such a process as defined in any of the above, wherein said substance comprising NO₃⁻ is chosen from the group consisting of (a) HNO₃; (b) Ca(NO₃)₂; (c) any combination of the above.

It is a further object of this invention to disclose such a process, wherein said substance comprising NO₃⁻ is HNO₃, and further wherein said step of contacting polyhalite with a substance containing NO₃⁻ further includes an additional step of contacting polyhalite with a quantity of HNO₃ sufficient that the amount of HNO₃ in the solution thus obtained is at least 0.5% (w/w).

It is a further object of this invention to disclose such a process, wherein said substance comprising NO₃⁻ is HNO₃, and further wherein said step of contacting polyhalite with a substance containing NO₃⁻ further includes an additional step of contacting polyhalite with a quantity of HNO₃ sufficient that the amount of HNO₃ in the solution thus obtained is at least 5% (w/w).

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of contacting polyhalite with a substance comprising NO₃⁻ further includes an additional step of contacting polyhalite with 60% HNO₃.

It is a further object of this invention to disclose such a process as defined in any of the above, further including an additional step of recycling into the reaction vessel at least part of the solution remaining after said step of separating solid KNO₃.

It is a further object of this invention to disclose such a process, wherein at least a part of said substance comprising NO₃⁻ is obtained from said solution recycled into said reaction vessel.

It is a further object of this invention to disclose such a process as defined in any of the above, further including an additional step removing from the reaction stream at least part of the solid produced during said step of contacting polyhalite with HNO₃.

It is a further object of this invention to disclose such a process, further including an additional step of removing by filtration at least part of the solid produced during said step of contacting polyhalite with HNO₃.

It is a further object of this invention to disclose such a process, further including an additional step of washing said solid.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of adding at least one inorganic base to the solution obtained in the
step of contacting polyhalite with a substance comprising NO$_3^-$ further includes an additional step of adding at least one inorganic base chosen from the group consisting of Ca(OH)$_2$, CaCO$_3$, and CaO.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of adding at least one inorganic base to the solution obtained in the step of contacting polyhalite with a substance comprising NO$_3^-$ further includes an additional step of adding sufficient inorganic base to reduce substantially the SO$_4^{2-}$ content of said solution.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of adding at least one inorganic base to the solution obtained in the step of contacting polyhalite with a substance comprising NO$_3^-$ further includes an additional step of adding sufficient inorganic base to reduce the SO$_4^{2-}$ content of said solution by at least 85%.

It is a further object of this invention to disclose such a process, wherein said inorganic base is chosen from the group consisting of (a) basic Ca compounds; (b) basic Ba compounds; (c) any combination of the above.

It is a further object of this invention to disclose such a process as defined in any of the above, further including an additional step of removing from the reaction stream at least part of the insoluble sulfate produced during said step of contacting polyhalite with HNO$_3$.

It is a further object of this invention to disclose such a process as defined in any of the above, further including an additional step of separating by filtration at least part of the insoluble sulfate produced during said step of contacting polyhalite with HNO$_3$.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of precipitating as Mg(OH)$_2$ at least part of the Mg$^{2+}$ remaining in said solution further comprises an additional step of adding a sufficient amount of at least one basic Ca compound to precipitate more than 50% of the Mg$^{2+}$ remaining in said solution as Mg(OH)$_2$.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of precipitating as Mg(OH)$_2$ at least part of the Mg$^{2+}$ remaining in said solution further comprises an additional step of adding a sufficient amount of at least one basic Ca compound to precipitate more than 85% of the Mg$^{2+}$ remaining in said solution as Mg(OH)$_2$. 

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It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of precipitating as Mg(OH)$_2$ at least part of the Mg$^{2+}$ remaining in said solution further comprises an additional step of adding at least one basic Ca compound chosen from the group consisting of Ca(OH)$_2$ and CaO.

It is a further object of this invention to disclose such a process as defined in any of the above, further including an additional step of removing from the reaction stream at least part of said Mg(OH)$_2$ obtained in said step of precipitating as Mg(OH)$_2$ at least part of the Mg$^{2+}$ remaining in said solution.

It is a further object of this invention to disclose such a process, further including an additional step of washing said Mg(OH)$_2$.

It is a further object of this invention to disclose such a process, wherein said Mg(OH)$_2$ is at least 92% pure.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of concentrating the solution remaining after said step of precipitating at least part of the Mg$^{2+}$ remaining in said solution further comprises a step chosen from the group consisting of (a) using a multiple effect evaporator to concentrated said solution and (b) concentrating said solution by mechanical vapor recompression.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of precipitating at least part of the NaCl further includes an additional step of precipitating NaCl by evaporative crystallization.

It is a further object of this invention to disclose such a process, wherein said step of precipitating NaCl by evaporative crystallization occurs at a temperature exceeding about 60°C.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of separating as solid KNO$_3$ at least part of the K$^+$ and NO$_3^-$ contained in the solution remaining after said step of adding a basic Ca compound further includes an additional step of crystallizing KNO$_3$ from said solution.

It is a further object of this invention to disclose such a process, wherein said step of crystallizing KNO$_3$ from said solution further includes an additional step of cooling said solution in order to affect crystallization of KNO$_3$.
It is a further object of this invention to disclose such a process, wherein said step of cooling said solution includes a further step of cooling said solution to a temperature below 40 °C.

It is a further object of this invention to disclose such a process as defined in any of the above, further including an additional step of purifying said KNO₃ obtained in said step of separating KNO₃.

It is a further object of this invention to disclose such a process, wherein said step of purifying said KNO₃ further includes an additional step of purifying said KNO₃ by at least one method chosen from the group consisting of (a) washing said KNO₃; (b) pulping with a substantially pure KNO₃ solution; and (c) recrystallization.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein the purity of said KNO₃ exceeds 98.5%.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of precipitating at least part of the Mg²⁺ is carried out prior to said step of separating KNO₃.

It is a further object of this invention to disclose such a process as defined in any of the above, wherein said step of precipitating at least part of the Mg²⁺ is carried out subsequent to said step of separating KNO₃.

BRIEF DESCRIPTION OF THE FIGURE

FIG. 1 shows a schematic flowchart of the process herein disclosed.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is described hereinafter with reference to the drawings and examples, in which preferred embodiments are described. For the purposes of explanation, specific details are set forth in order to provide a thorough understanding of the invention. It will be apparent to one skilled in the art that there are other embodiments of the invention that differ in details without affecting the essential nature thereof. Therefore the invention is not limited by that which is illustrated in the figures and described in the specification, but only as indicated in the accompanying claims, with the proper scope determined only by the broadest interpretation of said claims.
In the detailed description that follows, formulas indicating water of hydration are given according to conventional literature practice. As such, no claims are made regarding the specific level of hydration of the compounds (including those for which no water of hydration is indicated explicitly), and the invention herein disclosed is not limited to the specific levels of hydration given.

The fundamental chemistry involved in the process herein disclosed can be summarized as follows:

\[ K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O + 2HNO_3 + 4H_2O + Ca(OH)_2 \ [ + Ca(NO_3)_2 \] \longrightarrow \]

\[ 2KNO_3 + Mg(NO_3)_2 + 4(CaSO_4 \cdot 2H_2O) \]

The Mg(NO_3)_2 produced is precipitated as Mg(OH)_2 by further reaction with Ca(OH)_2:

\[ Mg(NO_3)_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca(NO_3)_2 \]

In the present invention, in contrast to methods known in the art, nitrate ion and calcium ion are added in separate independent steps of the process. In some embodiments of the process, Ca(NO_3)_2 recovered from later stages of the process is recycled and reacted with the polyhalite.

In a preferred embodiment of the invention herein disclosed, the following series of steps is employed to produce a commercial grade of KNO_3 from the reaction of polyhalite with HNO_3. The various "stages" are listed with reference to the schematic flowchart given in FIG. 1 for a preferred embodiment 10 of the invention herein disclosed.

In some embodiments of the invention, NaCl is washed from the polyhalite. This step is entirely optional; there is no requirement to wash out the NaCl from the polyhalite, nor is there any need for preliminary thermal treatment of the polyhalite.

In Stage 1 of the process (1010), polyhalite 101 is contacted with a substance comprising NO_3\^- 102. In preferred embodiments, substance 102 is HNO_3; in most preferred embodiments, the HNO_3 is provided in 60% concentration. In preferred embodiments of the invention, a sufficient amount of 60% HNO_3 is added such that concentration of HNO_3 in the resulting solution (i.e. including the polyhalite) is at least 5% (w/w). In preferred embodiments of the invention, the polyhalite and HNO_3 are brought into contact at a temperature of between about 60 °C and about 90 °C. In other embodiments of the invention, temperatures outside of the range used in preferred embodiments are used. In other embodiments, substance 102 may comprise another nitrate salt such as Ca(NO_3)_2, or a
mixture of a nitrate salt and HNO₃. In typical embodiments in which Ca(NO₃)₂ is used, it is added at the beginning of stage 1 in addition to or instead of the HNO₃ added at the beginning of the stage and the Ca compound added at the end of this stage, described below.

In preferred embodiments of the invention, at least part of the solution (210) obtained in stage 5 (described below) is recycled into the reaction vessel in which the contact between polyhalite and the substance comprising NO₃⁻ takes place.

The reaction mixture is then brought into contact with a base (in preferred embodiments, a Ca(OH)₂ slurry (105)); in preferred embodiments, sufficient slurry is added to bring the pH to substantially neutral. Addition of the Ca(OH)₂ slurry thereby yields a solution comprising primarily K⁺, Mg²⁺, Ca²⁺, Na⁺, NO₃⁻, and Cl⁻, along with solid CaSO₄ (gypsum). In preferred embodiments, sufficient base is added to precipitate at least 85% of the SO₄²⁻ present in the solution.

In preferred embodiments of the invention, solid gypsum precipitated during the reaction between the polyhalite and the HNO₃ is filtered and washed with wash water 103 (in preferred embodiments, by counter-current washing on a filter 1015) in order to reduce the nitrate content. The mother liquor (106) is transferred to stage 2, while the wet gypsum after washing (201) is discharged from the system. The wash filtrate 104 is then returned to the reaction vessel in which stage 1 takes place.

In Stage 2 of the process (1020), additional Ca(OH)₂ slurry (105) is added to the solution obtained in Stage 1 (106) after removal of solid gypsum in order to precipitate the major part of the Mg²⁺ contained in the solution as Mg(OH)₂ (202); in preferred embodiments, sufficient Ca(OH)₂ is added to precipitate at least 50% of the Mg²⁺ present. The Mg(OH)₂ is washed (1025) and removed. After precipitation of Mg(OH)₂, a solution comprising primarily Ca²⁺, K⁺, Na⁺, NO₃⁻, Cl⁻ and residual Mg²⁺ remains. In some embodiments, this stage is carried out after Stage 5 (described below) on the solutions to be recycled in stage 1. The chemical purity of the Mg(OH)₂ produced is dependent on the purity of the CaO or Ca(OH)₂ used. In preferred embodiments, Mg(OH)₂ with a purity exceeding 92% is obtained.

The process then proceeds to Stage 3 (1030), in which the solution obtained in Stage 2 is concentrated. In preferred embodiments, the concentration is effected by evaporation using any technique known in the art, e.g., a multiple effect evaporator or by mechanical vapor recompression. In a preferred embodiment, at least part of the residual CaSO₄ thus precipitated is separated from the supernatant solution at the exit of the vessel in which the
concentration takes place. The evaporation can be also carried out by solar evaporation in an evaporation pond and thus the calcium sulfate precipitated can be left on the bottom of the pond.

The process then continues to **Stage 4 (1040)**, in which NaCl (203) and a small part of the CaSO₄ (204) present in the solution are partially separated from the solution remaining after **Stage 3** by crystallization in an evaporative crystallizer at a temperature exceeding 60 °C. The solids are separated (in preferred embodiments, by filtration 1045) and removed.

In **Stage 5** of the process (1050), KNO₃ is crystallized from the solution by cooling the solution remaining from **Stage 4**. The crystallization can be carried out by any technique known in the art, e.g., in a cooling crystallizer of the various types existing, including cooling disc crystallizer. In typical embodiments of the invention, the purity of the white KNO₃ product obtained after washing in the tests exceeds 98.5%. In typical embodiments of the invention, the main impurities are Ca (<0.2%), Cl⁻ (<1000 ppm); Na (~500 ppm); SO₄²⁻ (~200 ppm); Mg (~10 ppm); and Sr (~10 ppm). The KNO₃ thus produced can be further purified by any technique known in the art, for example, by repulping with a pure KNO₃ solution or by recrystallization.

The solution 210 remaining from **Stage 5** is recycled to the vessel in which **Stage 1** takes place. The Ca(NO₃)₂ contained in the solution remaining from **Stage 5** reacts with the sulfate in the solution in stage 1 to precipitate gypsum.

**EXAMPLE 1**

Polyhalite (unwashed, crushed and screened to -0.5mm, 400 g) was added to a stirred mixture of nitric acid (59%, 146.7 g) and recycled solution (1090 g, made from combining mother liquor from KNO₃ crystallization presented in Example 3 and gypsum wash water from a previous batch). The concentration of the nitric acid is modified by dilution with wash water from previous runs in order to maintain a constant nitrate concentration of 15-16% in the final filtrate. The reaction mixture was heated to 65 °C and stirred for 3 h. After that time, milk of lime (169.4 g, 30% in water) was added dropwise via pump over a 1 h period to the hot mixture in order to neutralize the acidity of the slurry. When the mixture reached pH of 5.5-6.5 the addition was stopped and the mixture was filtered while hot under vacuum. The gypsum cake (700g, 60.8% solids) was then washed with water (3 x 350g) so that the nitrate content of the cake was satisfactorily low. The wet, washed gypsum (575.6g, 73.9% solids)
was then dried overnight in an oven at 60 °C yielding 425.5g of gypsum (CaSO₄·2H₂O > 98.5%, K < 0.4%, Mg < 0.2%, NO₃⁻ < 100 ppm). The filtrate (1094.7 g, K = 4.7%, Mg = 1.5%, Ca = 0.6%, SO₄²⁻ = 0.3%, NO₃⁻ = 15.5%) was used as the basis for the Mg(OH)₂ separation step (see Example 2 below) while the wash water was combined with the recycled solution for the next batch.

EXAMPLE 2
A sample of solution obtained after completion of the reaction presented in Example 1 above (720 – 900 g of solution were treated at a temperature of 60 -- 70°C with 15% solution of milk of lime (300 g). As a result of this treatment, the Mg concentration decreased from 1.5% to less than 0.2%. The solids precipitated were settled and, afterwards, filtered and washed. The dry solids contained more than 92% Mg(OH)₂. The main impurities were Ca (<5%), SO₄²⁻ (2%), NO₃⁻ (0.2%) and Cl⁻ (0.05%).

EXAMPLE 3
A sample of the solution of remaining after the precipitation of Mg(OH)₂ described in Example 2 above, comprising (concentrations on w/w basis relative to the total solution) 2.2% Ca, 4.4% K, 1.9% Na, 0.01% Mg, 13.3% NO₃⁻, 3.1% Cl⁻, and 0.08% SO₄²⁻ was concentrated by evaporation at a temperature exceeding 80 °C. The total concentration of dissolved salts increased by >80% as a result of the concentration. The NaCl thus crystallized was separated at a temperature exceeding 80 °C and its purity after washing exceeded 98%.

The remaining solution was then cooled down to a temperature <40 °C, leading to precipitation of KNO₃, which was then separated from the mother liquor and washed. The purity of the KNO₃ obtained exceeded 99.5%, while the concentration of dissolved salts in the mother solution to be recycled to the reaction was in the range of 55 – 60%.
CLAIMS

The following set of claims replaces all prior listings.

We claim:

1. A process for producing KNO₃ of at least 98% purity, wherein the starting material for said process is polyhalite and said process comprises:
   a. contacting polyhalite with a substance comprising NO₃⁻;
   b. adding at least one inorganic base to the solution obtained in the step of contacting polyhalite with HNO₃, thereby precipitating as a solid at least part of the sulfate present in said solution;
   c. precipitating as Mg(OH)₂ at least part of the Mg²⁺ remaining in said solution by adding at least one basic compound to the remaining solution;
   d. concentrating the solution obtained after said step of precipitating at least part of the Mg²⁺ remaining in said solution;
   e. precipitating at least part of the NaCl derived from said polyhalite, if any, from the solution obtained after said step of concentrating the solution obtained after said step of precipitating at least part of the Mg²⁺ remaining in said solution;
   f. separating said precipitated NaCl, if any, from the reaction stream, and,
   g. separating as solid KNO₃ at least part of the K⁺ and NO₃⁻ contained in the solution remaining after the step of precipitating at least part of the NaCl derived from said polyhalite.

2. The process according to claim 1, further including an additional step of washing said polyhalite prior to said step of contacting polyhalite with a substance comprising NO₃⁻, thereby removing at least a part of the NaCl contained within said polyhalite.

3. The process according to claim 1, wherein said step of contacting polyhalite with a substance comprising NO₃⁻ takes place at a temperature between about 60 °C and about 90 °C.

4. The process according to claim 1, wherein said substance comprising NO₃⁻ is chosen from the group consisting of (a) HNO₃; (b) Ca(NO₃)₂; (c) any combination of the above.

5. The process according to claim 4, wherein said substance comprising NO₃⁻ is HNO₃, and further wherein said step of contacting polyhalite with a substance containing NO₃⁻ further includes an

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additional step of contacting polyhalite with a quantity of HNO₃ sufficient that the amount of HNO₃ in the solution thus obtained is at least 0.5% (w/w).

6. The process according to claim 4, wherein said substance comprising NO₃⁻ is HNO₃, and further wherein said step of contacting polyhalite with a substance containing NO₃⁻ further includes an additional step of contacting polyhalite with a quantity of HNO₃ sufficient that the amount of HNO₃ in the solution thus obtained is at least 5% (w/w).

7. The process according to claim 1, wherein said step of contacting polyhalite with a substance comprising NO₃⁻ further includes an additional step of contacting polyhalite with 60% HNO₃.

8. The process according to claim 1, further including an additional step of recycling into the reaction vessel at least part of the solution remaining after said step of separating solid KNO₃.

9. The process according to claim 8, wherein at least a part of said substance comprising NO₃⁻ is obtained from said solution recycled into said reaction vessel.

10. The process of claim 1, further including an additional step removing from the reaction stream at least part of the solid produced during said step of contacting polyhalite with HNO₃.

11. The process according to claim 10, further including an additional step of removing by filtration at least part of the solid produced during said step of contacting polyhalite with HNO₃.

12. The process according to claim 10, further including an additional step of washing said solid.

13. The process according to claim 1, wherein said step of adding at least one inorganic base to the solution obtained in the step of contacting polyhalite with a substance comprising NO₃⁻ further includes an additional step of adding at least one inorganic base chosen from the group consisting of Ca(OH)₂, CaCO₃, and CaO.

14. The process of claim 1, wherein said step of adding at least one inorganic base to the solution obtained in the step of contacting polyhalite with a substance comprising NO₃⁻ further includes an additional step of adding sufficient inorganic base to reduce substantially the SO₄²⁻ content of said solution.

15. The process of claim 14, wherein said step of adding at least one inorganic base to the solution obtained in the step of contacting polyhalite with a substance comprising NO₃⁻ further includes
an additional step of adding sufficient inorganic base to reduce the $\text{SO}_4^{2-}$ content of said solution by at least 85%.

16. The process of claim 14, wherein said inorganic base is chosen from the group consisting of (a) basic Ca compounds; (b) basic Ba compounds; (c) any combination of the above.

17. The process according to claim 1, further including an additional step of removing from the reaction stream at least part of the insoluble sulfate produced during said step of contacting polyhalite with HNO$_3$.

18. The process according to claim 1, further including an additional step of separating by filtration at least part of the insoluble sulfate produced during said step of contacting polyhalite with HNO$_3$.

19. The process according to claim 1, wherein said step of precipitating as Mg(OH)$_2$ at least part of the Mg$^{2+}$ remaining in said solution further comprises an additional step of adding a sufficient amount of at least one basic Ca compound to precipitate more than 50% of the Mg$^{2+}$ remaining in said solution as Mg(OH)$_2$.

20. The process according to claim 1, wherein said step of precipitating as Mg(OH)$_2$ at least part of the Mg$^{2+}$ remaining in said solution further comprises an additional step of adding a sufficient amount of at least one basic Ca compound to precipitate more than 85% of the Mg$^{2+}$ remaining in said solution as Mg(OH)$_2$.

21. The process according to claim 1, wherein said step of precipitating as Mg(OH)$_2$ at least part of the Mg$^{2+}$ remaining in said solution further comprises an additional step of adding at least one basic Ca compound chosen from the group consisting of Ca(OH)$_2$ and CaO.

22. The process of claim 1, further including an additional step of recovering from the reaction stream at least part of said Mg(OH)$_2$ obtained in said step of precipitating as Mg(OH)$_2$ at least part of the Mg$^{2+}$ remaining in said solution.

23. The process of claim 22, further including an additional step of washing the Mg(OH)$_2$ recovered from the reaction stream.

24. The process of claim 22, wherein said recovered Mg(OH)$_2$ is at least 92% pure.
25. The process according to claim 1, wherein said step of concentrating the solution remaining after said step of precipitating at least part of the Mg\(^{2+}\) remaining in said solution further comprises a step chosen from the group consisting of (a) using a multiple effect evaporator to concentrated said solution and (b) concentrating said solution by mechanical vapor recompression.

26. The process according to claim 1, wherein said step of precipitating at least part of the NaCl further includes an additional step of precipitating NaCl by evaporative crystallization.

27. The process according to claim 26, wherein said step of precipitating NaCl by evaporative crystallization occurs at a temperature exceeding about 60 °C.

28. The process according to claim 1, wherein said step of separating as solid KNO\(_3\) at least part of the K\(^+\) and NO\(_3^-\) contained in the solution remaining after said step of adding a basic Ca compound further includes an additional step of crystallizing KNO\(_3\) from said solution.

29. The process of claim 28, wherein said step of crystallizing KNO\(_3\) from said solution further includes an additional step of cooling said solution in order to affect crystallization of KNO\(_3\).

30. The process of claim 29, wherein said step of cooling said solution includes a further step of cooling said solution to a temperature below 40 °C.

31. The process according to claim 1, further including an additional step of purifying said KNO\(_3\) obtained in said step of separating KNO\(_3\).

32. The process according to claim 31, wherein said step of purifying said KNO\(_3\) further includes an additional step of purifying said KNO\(_3\) by at least one method chosen from the group consisting of (a) washing said KNO\(_3\); (b) pulping with a substantially pure KNO\(_3\) solution; and (c) recrystallization.

33. The process according to claim 1, wherein the purity of said KNO\(_3\) is greater than 99%.

34. The process according to claim 1, wherein said step of precipitating at least part of the Mg\(^{2+}\) is carried out prior to said step of separating KNO\(_3\).

35. The process according to claim 1, wherein said step of precipitating at least part of the Mg\(^{2+}\) is carried out subsequent to said step of separating KNO\(_3\).