Potassium Nitrate

The third most widely used potassium salt in agriculture is potassium nitrate. An ore containing sodium nitrate, potassium nitrate, some chloride and sulfate is mined in Chile; for the production of KNO₃ the ore is leached and part of the sodium nitrate is crystallized and removed. Potassium chloride is added to the brine and the resulting sodium chloride is separated. Cooling to 5°C crystallizes the potassium nitrate which is then recovered with centrifuges. Residual brine is concentrated by solar evaporation to remove salt and sodium sulfate more KCl is added and KNO₃ is again crystallized. KCl or K₂SO₄ may also be used in fractional crystallization processes with NH₄NO₃ or Ca(NO₃)₂ to produce potassium nitrate. Low temperature reaction of potash with nitric acid with solvent extraction of the coproduct hydrochloric acid can also be used to produce KNO₃. The HCl is reextracted from the solvent with water and then distilled as about a 20% HCl solution. The solvent is recycled to the first extraction stage.

Nitric acid reacts with potassium chloride at low temperature according to the equation:

\[ \text{KCl} + \text{HNO}_3 \rightarrow \text{KNO}_3 + \text{HCL} \]

Potassium chloride and a stoichiometric quantity of chilled 60% -70% nitric acid are fed into the first reactor at 5°C -10°C. Recycled brine and solvent are added to the reactor. In the presence of the solvent, the reaction goes almost to completion. During the process potassium nitrate crystallizes from solution. Solid product is separated in a decanter and directed to a centrifuge and dryer. It can be sold in the powder form or melted and prilled. The hydrochloric acid and the unreacted nitric acid are dissolved in the liquid phase. Obviously both nitric acid and hydrochloric acid are soluble in the solvent, but distribution coefficients differ sufficiently for the hydrochloric acid to be removed in a countercurrent liquid extraction system by water. The extraction is carried out in the mixer-settler extraction system vessels the remaining nitric acid and solvent are recycled through a refrigeration unit to the first reactor. The water is stripped from the solvent, which is also recycled. The low concentration hydrochloric acid is evaporated in a multiple effect evaporated to a concentrated of 22%. This acid is used in another plant to produce phosphoric acid by a hydrochloric acid attack.
In another process the same reactants are used except at a higher temperature to take advantage of the oxidizing power of nitric acid. In a complex process with exotic corrosion-resistant equipment, chlorine is produced as a byproduct is given figure15.10

Potassium chloride is slurried with 65% nitric acid, which has been previously chilled to prevent a reaction occurring before the slurry is fed into reactor. In the reactor, which operates at about 75°C, whereupon the reaction takes place, according to the following equation:

\[
3\text{KCl} + 4\text{HNO}_3 \rightarrow \text{3KNO}_3 + \text{Cl}_2 + \text{NOCl} + 2\text{H}_2\text{O}
\]
Approximately 90% of the chlorine is removed in gaseous form. Because of the extreme corrosiveness prevailing in the reactor, this vessel, which is in fact an agitated autoclave, has to be fabricated from titanium and lined with acid-resistant brick.

The solution from the reactor flows to the chloride stripping column where it is heated with more nitric acid vapor to its boiling point of about 150°C. This treatment takes the reaction to completion and gives rise to a stripped solution containing less than 10 ppmw of chlorine. If this degree of completion is to be obtained, it is necessary to maintain an excess of nitric acid corresponding to a concentration of 55% in the solution.

The gaseous mixture containing nitrosyl chloride and chlorine from the agitated reactor is oxidized in the gas reactor by using hot nitric acid at a concentration of at least 80% at 150°C.

Water formed in the oxidation is condensed and fed to the primary reactor. The chlorine and nitrogen dioxide are separated into liquid products; the chlorine is fed to storage while the nitrogen dioxide is oxidized with air and absorbed in water to produce to produce 65% nitric acid.
This oxidation step is characterized by the following chemical equation:

$$2\text{NO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{HNO}_3$$

The overall reaction through the process is given by:

$$2\text{KCl} + 2\text{HNO}_3 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{KNO}_3 + \text{Cl}_2 + \text{H}_2\text{O}$$

In the gas section of the process, two distillation columns are used to separate the pure chlorine from pure nitrogen dioxide. Chlorine is removed from the top of the first column and nitrogen dioxide from the bottom of the second column while in the wet section the potassium nitrate-nitric acid solution is concentrated in the acid distillation column. It has been practical to concentrate the solution up to 81% nitric acid; the weak acid vapors in the overhead fraction are subsequently concentrated to about 62% HNO₃ in a second distillation column. Bottoms from the first acid distillation column are fed to a battery of vacuum crystallizers where potassium nitrate is precipitated and separated by a centrifuge. The product is dried and may be stored directly or melted and prilled at 340°-350°C in a 35-ft (10.7-m) tower. Either technical grade (99.3%) or agriculture grade (99%) potassium nitrate may be produced.

**Compound Fertilizers**

Potash is often applied in mixtures with other nutrients to provide the specific fertilizers needed by crops or soil and to allow placement in one application. To meet this need most fertilizer dealers have modest blending equipment, but to prevent segregation the fertilizers must be in the granular or coarse form.

**Chemical Grade Potash**

About 4%-5% of potash production is used in industrial applications. The industrial potash (chemical grade) has a different purity from fertilizer grade potash. The composition of chemical grade potash is given. Product is shipped in bags or in bulk form in modified hopper cars called spargers (in slurry form) or solution cars (in liquid form).
Chemical-grade potash has the following consumption pattern:

- Detergents and soaps: 35%-30%
- Glass and ceramics: 25%-28%
- Textiles and dyes: 20%-22%
- Chemicals and drugs: 13%-15%
- Other: 7%-5%

Most of the chemical grade potash is used for production of potassium hydroxide. Potassium hydroxide (KOH) and its derivative potassium carbonate are the next largest industrial potassium compounds. The KOH is made by the electrolysis of KCL in installations similar to caustic soda/chlorine production. The main use of caustic potash is in the manufacture of liquid soaps; textile operations; production of grease, catalysts, alkaline batteries electro polishing and rubber production.

Several other potassium compounds have a limited use in agriculture but much wider use in industrial or commercial applications. Potassium phosphate, for instance, is used in some high analysis, low salt content fertilizer mixtures. It is not yet a large tonnage fertilizer but several companies over the years have announced plans to produce it for that purpose. Potash is reacted with sulfuric Acid, and the HCl is removed at the KHSO₄ stage. This salt is then reacted with more H₂SO₄ and phosphate rock [Ca₃(PO₄)₂] usually to produce the more easily crystallized monopotassium phosphate (KH₂PO₄). However, the yields are low because of K losses with many of the impurities in the rock and the process is corrosive and complex. By far the widest use of potassium phosphate has been as an additive to heavy duty detergent, predominantly as low molecular weight polymers created by fusing various KOH and H₃PO₄ mixtures.

Potassium carbonate is used primarily in the glass manufacture eg., of television and similar display tubes. Potassium carbonate solution (0-0-30 grade) is marketed in the United States as a specialty liquid fertilizer. Potassium carbonate is produced by carbonating KOH with CO₂. Some potassium carbonate is further carbonated to produce KHCO₃ (potassium bicarbonate), which is used largely in the food and pharmaceutical industries.