Potassium Sulfate

Potassium sulfate is the second largest tonnage potassium compound and it is also used primarily as a fertilizer. The sulfate or other nonchloride forms of potassium are preferred for certain crops that do not tolerate the chloride ion well, e.g., tobacco and some fruits and vegetables. Nonchloride potash sources are also needed in areas where chloride accumulate or in areas of very intensive agriculture, potassium sulfate may be preferred because of its sulfur content where soils are deficient in both potassium and sulfur.

Potassium Sulfate Production

Mannheim Process – Historically potassium sulfate has been made primarily from KCL and sulfuric acid (and a small amount from KCL and SO₂) when the byproduct HCL was the dominant product. However, over the year the HCL market has had more competition and “natural” K₂SO₄ with lower capital and operating coasts has begun to dominate its production in some countries with natural complex salts.

The Mannheim process was originally developed from sodium sulfate production by reacting NaCl with sulfuric acid. Replacing NaCl with KCl produces potassium sulfate. The reaction is two-stage:

a. Exothermic reaction
   \[ \text{KCl} + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{HCl} \]

b. Endothermic reaction
   \[ \text{KHSO}_2 + \text{KCl} \rightarrow \text{K}_2\text{SO}_4 + \text{HCl} \]
The potassium chloride reacts during slow mixing in the heated Mannheim furnace with sulfuric acid, producing gaseous HCl and K₂SO₄. The furnace is heated by natural gas or fuel oil. The product K₂SO₄ is cooled in a cooling drum. Lump material from the cooler is crushed and finished or can be compacted and granulated as with KCl.
The HCl gas is cooled in a graphite in a graphite heat exchanger and absorbed in water in two stages to produce 30% hydrochloride acid as a byproduct. The process gives an excellent quality that contains over 50% K₂O and less than 1% chlorine. Emissions are well controlled.

**Recovery of Potassium Sulfate From Natural Complex Salts** – The chief natural complex salts that are the source of the potassium sulfate are:

- Kainite (KCl • MgSO₄ • 3H₂O)
- Langbeinite (K₂SO₄ • 3MgSO₄)
- Carpathian polmineral ores

The natural process involves the initial conversion with recycled K₂SO₄ end liquor “mined” kainite or langbeinite to form an intermediate product schoenite. All processes are based on intercrystalline reactions of ion exchange.

The Process comprises four basic units:

- Preparation of the ore and flotation;
- Production of schoenite and its recovery;
- Leaching of the schoenite to potassium sulfate;

The kainite is repulped with recycled brine, screened, and directed to ball mills and hydroclassifiers. Overflows go to a thicker and main filter and underflows to flotation and filtration. Float material, after filtration, is combined with the solid fraction from the main filter and directed to the schoenite reactors and separating cyclones. After a two step hydroseparation, centrifugation, and filtration, schoenite is directed to the leaching reactors. After decomposition of the schoenite, product is directed to final centrifuges and a dryer; the overflows are cooled and crystallized. After additional thickening, the product is centrifuged and dried. The
product specification ensures that the K₂O content is not lower than 50% and the chlorine content is less than 1%.

In the recovery unit, italkali forms syngenite to moderately increase the recovery of schoenite from the plant end liquor. The brine from the schoenite filter is reacted with main flow to be leaching reactors.

Other processes involve adding sylvite to kainite, langbeinite kieserite, etc. The schoenite intermediate can be formed kieserite, etc. the schoenite intermediate can be formed by reacting KCl with mined kieserite or the epsomite. Where solar or plant evaporation can be done economically, the yields can be further improved by evaporating the schoenite or glaserite end liquor and recycling the salts.

A complex process can production of potassium sulfate from ores can been implemented on an industrial scale. The naturals ores are composed of calcium sulfate anhydride, epsomite, halite, kainite, kieserite, langbeinite, polyhalite, sylvite and clay. The treatment of such an ore requires permanent analytical services and the development of a large number and for the kind of salts intended to be produced, additional sylvite must be added in varying amounts to maintain the right proportions for crystal formation. The basic process concept is to produce schoenite from all available salts. The remaining products or processes are subjugated to his basic process.

The Carpathian ore contains about 9% potassium and 15% clay. The ore is leached with hot synthetic kainite solution in a dissolution chamber. The langbeinite, polyhalite and halite remain undissolved chamber containing salts and clay is directed to a Dorr-Oliver settler where clay is settled and directed to a washer and discarded. The solution is crystallized at the proper cation and anion proportions to produce crystalline schoenite. To avoid crystalline of potassium chloride and sodium chloride, the saturated solution of potassium and magnesium sulfates is added to the Dorr-Oliver settler. The slurry of schoenite is filtered and crystals are leached with water to produces K₂SO₄ crystals, which are centrifuged and recycled and a liquor of potassium
and magnesium sulfates. Also liquid phase from filter is recycled and added to the schoenite liquor from vacuum crystallization. Part of the schoenite liquor is evaporated to produce crystalline sodium sulfate and discard the magnesium chloride liquid end products. The slurry from the evaporation unit is recycled as “synthetic kainite”. This process permits the use of the Carpathian ores to produce several commercially valuable products such as potassium sulfate, potassium-magnesium sulfate, potassium chloride, sodium sulfate and magnesium chloride liquors. Neither the economic evaluation of the process nor any of the consumption figures has been published.

Fig. 2 Potassium Sulfate Process from Langbeinite
The production of potassium sulfate from langbeinite is possible with a large amount of muriate of potash is possible with a large amount of nitrate of potash by mixing langbeinite and sylvite.

The langbeinite ore is separated from sylvite and halite by selective washing, froth flotation, or heavy media separation. The commercial langbeinite used in the process must pulverized in ball mills, and fine powder is mixed with a solution of the muriate of potash. The muriate of potash is dissolved and clarified in a separate unit. The reaction in the presence of water yield potassium sulfate in a crystalline form and brine. Crystals are centrifuged or filtered, dried in a rotary dryer, sized and finished. The finished methods either produce coarse material or granulated product. The mixed salts are added to the sulfate reactor the liquor is discard as a waste.