INTRODUCTION

Potassium sulfate (K₂SO₄) also called sulfate of potash, arcanite, or archaically known as potash of sulfur is a non-flammable white crystalline salt which is soluble in water. The chemical is commonly used in fertilizers, providing both potassium and sulfur.

It is known since 14th century, and was studied by Glauber, Boyle and Tachenius. In the 17th century, it was named arcanuni or sal duplicatum, as it was a combination of an acid salt with an alkaline salt. It was also known as vitriolic tartar and Glaser’s salt or sal polychrestum Glaseri after its first used in medicine by Christopher Glaser.

Potassium sulfate contains 48 to 54% potassium (as K₂O) and supplies 17-20 % of sulfate. Potassium sulfate is the second largest tonnage of potassium compound and is primarily used as a fertilizer.

Potassium sulfate can be made either by the Mannheim process where potassium chloride is reacted with sulfuric acid, or, made from natural complex salts like kainite or langbeinite.

MANUFACTURE

Potassium sulfate can be manufacture by two processes

1. Mannheim process
2. Recovery from natural complex salts

1. **Mannheim process**

   **Raw materials**
   
   Potassium chloride
   Sulfuric acid

   **Reaction**
   
   \[
   \text{KCl} + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{HCl} \\
   \text{KHSO}_4 + \text{KCl} \rightarrow \text{K}_2\text{SO}_4 + \text{HCl}
   \]
The Mannheim process was originally developed for sodium sulfate production. For making potassium sulfate, sodium chloride is replaced with potassium chloride.

Potassium chloride reacts with sulfuric acid during the slow mixing of the ingredients in the gas heated Mannheim furnace consisting of cast iron muffle with rotating plough which helps to agitate the mixture. Hydrochloric acid produced during the reaction is cooled and absorbed into water to produce 33% hydrochloric acid as a byproduct. The precipitated potassium sulfate fertilizer is cooled, filtered and the lumps are crushed and granulated.

Potassium sulfate is twice as costly as potassium chloride. Granulation adds further to its cost. Potassium sulfate contains over 50% potassium (as K₂O) and less than 1% chlorine.
2. **Recovery from natural complex salts**

Potassium sulfate occurs naturally as complex salts. The basic reactions leading to potassium sulfate from kainite are by transformation of kainite to schoenite followed by water leaching.

**Natural resources**

The mineral form of potassium sulfate, arcanite, is relatively rare. Natural resources of potassium sulfate are minerals abundant in the Stassfurt salt. These are co-crystallizations of potassium sulfate and sulfates of magnesium calcium and sodium.

The minerals of potassium sulfate are

- Kainite, $\text{MgSO}_4 \cdot \text{KCl} \cdot \text{H}_2\text{O}$
- Schönite, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
- Leonite, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$
- Langbeinite, $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$
- Glaserite, $\text{K}_3\text{Na} \cdot \text{SO}_4 \cdot 2$
- Polyhalite, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Minerals like kainite, from which potassium sulfate can be separated, because the corresponding salt is less soluble in water. Kainite $\text{MgSO}_4 \cdot \text{KCl} \cdot \text{H}_2\text{O}$ can be combined with a solution of potassium chloride to produce potassium sulfate.

Process of recovery of potassium sulfate from kainite consists of four basic elements, and they are

- Preparation of the ore and floatation
- Production of schoenite and its recovery
- Leaching of schoenite to potassium sulfate
- Liquor treatment

Other processes involve addition of sylvite to kainite, langbeinite or kieserite. The reactions are as follows

- Mixing of kainite with sylvite
- Mixing of sylvite with kieserite and other magnesium salts

A Russian Kalush plant method of potassium sulfate production uses potash ores as the starting material. 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 and are discarded. The overflow from the dissolution chamber is directed to a Dorr Oliver
settler where clay is settled and directed to a washer and discarded. The slurry of schoenite is filtered and the crystals, leached with water, to produce potassium sulfate crystals.

Potassium sulfate from langbeinite is produced by mixing large amounts of muriate of potash, sylvite and langbeinite.

\[4\text{KCl} + \text{K}_2\text{SO}_4.2\text{MgSO}_4 \rightarrow 3\text{K}_2\text{SO}_4 + 2\text{MgCl}_2\]
\[2\text{KCl} + 2(\text{K}_2\text{SO}_4.2\text{MgSO}_4) \rightarrow 3(\text{K}_2\text{SO}_4.\text{MgSO}_4) + \text{MgCl}_2\]

The langbeinite ore is separated from sylvite and Halite by selective washing, froth floatation and heavy media separation. Langbeinite must be powdered and mixed with potassium chloride solution to get crystalline potassium sulfate and brine. The crystals are centrifuged or filtered, dried and classified to the required size.

**Handling and storage**

The crystalline potassium sulfate is free flowing and does not normally pose any problem in handling and storage. It is imported as bulk cargo and transported to NPK fertilizer mixing plants and dealers in bulk or in bags. It is stored in bulk in closed storage yards.

**PROPERTIES**

- Molecular formula: $\text{K}_2\text{SO}_4$
- Molecular weight: 174.26 gm/mole
- Appearance: white solid
- Odour: Odourless
- Boiling point: 1689°C
- Melting point: 1069°C
- Density: 2.66 gm/ml
- Solubility: Soluble in water, slightly soluble in glycerol, insoluble in acetone, alcohol, CS₂

**USES**

Potassium sulfate is used as fertilizer particularly in chloride sensitive crops like tobacco, grapes and potato which require chloride free potassium fertilizers. These three crops, being major crops, account for about 7% of the total potash consumption. For best results, potassium sulfate should contain at least 50% potash by weight.

- Used as a flash reducer in artillery propellant charges.
- It reduces muzzle flash, flareback and blast overpressure
- The crude salt is also used in the manufacture of glass.