Potassic fertilizers –Manufacturing process and properties of Muriate of Potash and sulphate of potash

Potassic Fertilizers:

The Latin / German word for the element with symbol K is'' Kalium''. It is derived from the Arab word ''el-kali'' means ash (Potash in English, Potassic in French).

The term potash generally refers to any salt used to provide fertilizer potassium. In early days, potassium carbonate was produced from solutions leached form wood ashes evaporated in iron pots, hence term potash meaning "pot ashes".

The crude potassium salts (K-minerals with impurities) were found in the processes of drying up of sea water in former ocean basins which occur largely during the permian period some 200 million years ago .The sea water salts crystallized in the order of solubility i.e., (common salt) NaCl, strata are overlain by K-minerals. In course of time they were covered by many geological strata and converted to a hard rock. Crude potassium salts are thus natural sea water minerals.

Potassium content of earth crust is 2.40 %, whereas the content of phoshorus is only 0.11%. Potassium reserves are large. The large deposits of potassium salts are in North America (Canada, USA), USSR, West Germany, East Germany and France in that order. The important potash minerals of the world occurring as deposits and their chemical composition are given

S.NO.	Mineral	Chemical formula	Approx.	
			Content of K (%)	
1	Carnallite	KCl MgCl ₂ 6H ₂ O	14.1	
		KCl Mg SO ₄		
2	Kainite	3H ₂ O	15.7	
3	Langbeinite	K ₂ SO ₄ 2 Mg SO ₄	18.8	
4	Nitre	KNO ₃	38.6	
5	Polyhalite	K ₂ SO ₄ MgSO ₄ 2CaSO ₄	12.9	
		$2H_2O$		
6	Sylvite	KCl	52.4	
7	Sylvinite	KCl NaCl	29.4	

Principal	l potash	minerals	of	the	world
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All the fertilizers potassium viz., KCl and K₂SO₄ used in India is imported as on today. Recently Geological Survey of India has reported the occurrence of K-deposits in Leh (Jammu and Kashmir) and Bikanir (Rajasthan) which await commercial exploitation. Potassium schoenite a double salt of K₂SO₄ and Mg SO₄ obtain from salt bitterns is recently being produced on a pilot scale at Bhavanagar (Gujarat).

Manufacturing processes of potassium fertilizers

Two types of potassium fertilizers are widely produced in India

1. Potassium chloride (Muriate of potash)

2. Potassium sulphate (Sulphate of potash)

1. POTASSIUM CHLORIDE (KCl)/ [MOP]:

Potassium chloride is popularly known as muriate of potash [MOP]. The term muriate is derived from muriatic acid, a common name for hydrochloric acid (HCl)). It is the most important K-fertilizer used directly or in conjunction with P and N fertilizers.

Raw materials:

1. Sylvinite (or) brine

Unlike phosphate rock, K mineral salts do not require heat or strong acid treatment as they are water soluble. Potassium chloride is recovered, from sylvinite adopting either of the two processes viz.,

1. Crystallization process

2. Flotation process

1. Crystallization process:

Principle:

Crystallization process employed in separating potassium chloride from sodium chloride (Sylvinite: KCl .NaCl) is largely dependent on their different solubilities in hot (100 0 C) and cold (20 0 C) water. The solubility of KCl increases rapidly with a rise in temperature whereas the solubility of NaCl varies very slightly.

Cool brine (20 0 C) saturated with both the slats is heated to (100 0 C) and passes over the finely ground sylvinite ore, when KCl rich brine solution is obtained. It is cooled by vacuum evaporation which produces KCl crystals, which are centrifuged, washed, dried and packed. The filtrate (brine rich NaCl) is recycled for treating fresh ore.

2. Flotation process:

Separation of potassium chloride from its ore by mineral flotation is widely practiced all over the world relative to the crystallization process.

Principle:

Flotation is a separation process in which a solid treated with a selective agent is suspended in an aerated aqueous liquid. The treated solid adheres to the bubbles of air, and the froth is floated off the suspension. Non floating material is removed as pulp. The sylvinite ore is a mixture of interlocked crystals of potassium chloride and sodium chloride plus small quantities of clay and other impurities.

Raw material:

2. Sylvinite ore

Sylvinite ore is ground to a particle size of 10 mesh

- 1. Pulped in a saturated NaCl-KCl brine and scrubbed (Centrifuge) to disperse clay and other impurities.
- 2. The resultant slurry is thus deslimed in spiral classifiers to remove finely divided clay slimes.
- 3. Deslilming or removal of clay is the most important step since these material consume large quantities of flotation reagents.
- 4. The deslimed slurry relatively free of clay is treated with binding agents such as starch or mannogalactan gums.
- 5. The reagents used for sylvinite flotation is a mixture of primary aliphatic amine salts derived from beef tallow, which selectively film the sylvinite particle so that they will float.
- 6. The conditioned slurry is carried to flotation cells where air is drawn into the slurry.
- 7. The air bubbles attach themselves to the reagent treated sylvinite particle in the pulp causing them to float to the surface as froth, which is mechanically skimmed off by paddles.
- 8. The concentrate rich in KCl is further purified by sending it to cleaner cells to remove residual NaCl.
- 9. The MOP is separated from brine by centrifuging and drying in rotary driers, screened to a desirable particle size and finally sent for product storage.

Physical properties of MOP:

- 1. MOP in pure form is white crystalline salt. However, colour ranges from white to red based on the impurities present in K minerals and methods of refinement.
- 2. It has a solubility of 37 grams per 100 grams of water at 30 ^oC.
- 3. The crystalline MOP is not very hygroscopic ,flows freely and does not cake
- 4. Has specific gravity is 1.98.

Chemical properties of MOP:

- 1. MOP contains 58% by weight of K₂O and about 47 % chloride.
- 2. MOP is neutral in reaction and does not produce acidity and alkalinity on soil application.

2. POTASSIUM SULPHATE (K2SO4) /[SOP]:

The entire potassium sulphate fertilizer used in India is imported and it is more expensive than MOP.

Raw materials:

The manufacturing process is of two types viz.,

1. Langbeinite process

2. Mannheim furnace process

1. Langbeinite process:

The ore Langbeinite is a double sulphate of potassium and magnesium (K₂SO₄ 2Mg SO₄).

In this process Langbeinite is ground and dissolved in water and concentrated solution of KCl (brine) is added ,when the potassium sulphate precipitates and is separated by centrifuging. The wet material is dried, screened and sent to storage. The chemical reaction involved is

 $K_2SO_4 \ 2Mg \ SO_4 + 4KCl \rightarrow 3 \ K_2SO_4 + 2MgCl_2$

2. Mannheim furnace process:

In this process, potassium chloride (KCl) is reacted with sulphuric acid in a special furnace provided with rotary plough to form potassium bisulphate (KHSO₄) in exothermic reaction and to form potassium sulphate in endothermic reaction. HCl gas is evolved as a by product which is cooled and absorbed in water. Reactions that occur are-

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

 $KCl + KHSO_4 \rightarrow K_2SO_4 + HCl \rightarrow [Endothermic reaction]$

Physical properties of SOP

- 1. Potassium sulphate [SOP] is a white crystalline salt, less hygroscopic as compared to MOP and free flowing.
- 2. It has specific gravity of 2.66 and has a solubility of 13 g/100 grams of water at 30 0 C.

Chemical properties of SOP:

- 1. SOP contains 48 % K2 O and 18 % S by weight.
- 2. Like MOP, it is also neutral salt providing neither acidity nor alkalinity on soil application.
- 3. The SOP is widely desirable .The chloride content of KCl effects the burning quality of tobacco. Never use KCl (MOP) on tobacco crop.

Mode of action of K fertilizers in soils or reactions of fertilizers in soils

- 1. Water soluble and as such act rapidly
- 2. In the soil K-fertilizers first enters the soil solution, but most of it directly absorbed on the complex and stored as loosely bound K and easily available to plants.