

12. Potassic fertilizers – manufacturing of KCl, K₂SO₄ and Schoenite

Potassium found to occur very commonly in the combined form as naturally occurring minerals. Common soil forming rocks like granite and gneiss are found to have about 3% K. For many years, K has been considered as important plant nutrient element. The Chinese were the pioneers among the various farmers who used K for agricultural purposes. The mineral deposits were not discovered and used as fertilizers until eighteenth century. The first product to be used as K manure was the wood ash and the practice of using wood ash existed for centuries.

In olden days, the wood ash was primarily used to get the potassium salts. The wood was burnt and the resultant ash was leached in mud pots to get the salt mixture containing chlorides, SO₄ and CO₃ of K, Ca and Mg. (Pot + ash = Potash). It would be advantageous and more correct to use P and K to refer to P and K, instead of P₂O₅ and K₂O in the fertilizer technology i.e.,

$$\% K = \% K_2O \times 0.83 \text{ and } \% \text{ of } K_2O = \% K \times 1.2)$$

Source of potassium

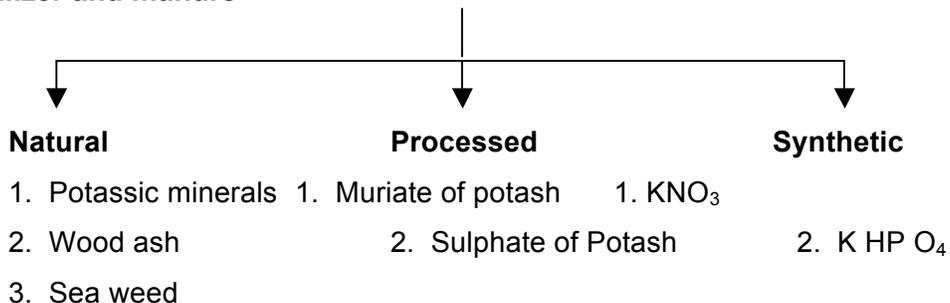
The following are the main sources of K.

1. Mineral deposits
2. Industrial by products
- and 3. Synthetic K salts

Classification of potassic fertilizers

Potassic fertilizer are classified broadly into chlorides and non- chlorides. The following are the most important K containing materials. Wood ash, tobacco stems, wool waste, flue dust, by products from sugar and alcohol industry. Sea weed, sea water, K minerals, processed fertilizer like muriate and SO₄ of potash and synthetic fertilizers.

K Fertilizer and manure



A. Organic K fertilizer Sources

1.Wood ash

Use of wood ash as K fertilizer has been there for centuries. Wood twigs and branches are burnt to get the ash. Sawdust is also used. The burnt material will contain

varying amounts at K_2O from 5 to 25%. Since wood ash is highly alkaline it should not be applied to germinating crops.

2. Tobacco stem

In the manufacture of cigarette, cigar and chewing tobacco, there results considerable wastes consisting of mainly the stems and midribs of the leaves. This waste material is collected, ground and sold as manure. Tobacco stem contains 4 to 10% K_2O and 2 to 3% N. It is found to be a valuable conditioner and adds bulk to the fertilizer mixtures.

3. Wool waste

Before the raw wool could be used for spinning, it must be treated for the removal of 'suint' which is the dried sweat of sheep. This 'suint' consists largely of K salts and contains 1.5 to 5.0 % K_2O .

4. Flue dust

It is a by product from the steel and cement industry. For melting the iron a mixture of iron ore, coal, coke and limestone are introduced into a blast furnace. When ignited, due to tremendous heat, the K contained in the iron ore volatilizes and when the gases containing volatilized K are burnt, the K dust will settle in the flue through which the gases pass and from time to time the dust accumulated will be collected and used. This will have 3 to 18% K_2O as Cl , SO_4 and CO_3 of K.

In the same way in cement manufacture also the raw materials used are found to have appreciable amount of K and this volatilized during the cement manufacture. The flue dust obtained from this is found to have 3 to 13% K_2O . The dust can be used as a straight fertilizer.

5. Sea weeds

This is referred to as the poor mans manure. It contains a high amount of K_2O varying with species of weeds. Out of many varieties 'kelp' is found to occur extensively throughout the world. The Sea weeds ash is found to have more than 25% K_2O .

6. Sea water

It contains an inexhaustible amount of K. It contains 0.04 % K, 0.14% Mg, 0.05 % Ca and 1.14 % Na.

B. Potassic minerals

There are as many as 50 minerals that are found to contain K but all of them are not economically important. The K containing minerals are roughly classified into

1. Minerals highly soluble in water occurring in brines or salt deposit

Sylvinite	-	KCl (Sylvite)
Carnallite	_	KCl. MgCl ₂ . 6 H ₂ O
Langbeinite	-	K ₂ SO ₄ . MgSO ₄
Kainite	-	KCl. MgSO ₄ . 3 H ₂ O

2. Minerals less soluble in water.

Polyhalite	-	K ₂ SO ₄ . Mg SO ₄ . 2 CaSO ₄ . 2 H ₂ O
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3. Minerals insoluble in water

Glauconite	-	KFeSi ₂ O ₆ . 2 H ₂ O
Feldspars	-	orthoclase - KAlSi ₃ O ₈
Micas	-	Muscovite and biotite.

The following are commercially used for the manufacture of potassic fertilizers.

1. Sylvinite - KCl - contains 63.1 % K₂O
2. Carnallite _ KCl. MgCl₂. 6 H₂O - contains 17% K₂O
3. Kainite - KCl. MgSO₄. 3H₂O - contains 18.9% K₂O
4. Langbeinite - K₂SO₄. 2MgSO₄ – contains 26.6% K₂O
5. Polyhalite - K₂SO₄. MgSO₄. 2CaSO₄. 2H₂O – contains 15% K₂O

The deposits are found to occur at a depth of 650 to 2,500 feet below the earth's surface.

Processed K Fertilizers

1. Muriate of potash (KCl)

KCl is commercially manufactured using any one of the minerals; 1. Sylvinite or sylvite and 2. Carnallite . There are two main steps involved in the manufacture of this fertilizer.

1. Mining of the K mineral
2. Separation of the main ingredient and purifying.

Mining

The deposits are found to occur usually from 650 to 2,500 feet below the earth's surface. Many methods of mining are employed out of which the room and pillar method of mining is found to be familiar. After a mine shaft is sunk to a point slightly below the level of the ore body a large tunnel is driven on both sides of the shaft. At right angles to this tunnel the ore is mined in larger rooms about 25 to 50 feet wide and 300 feet long. The ore is brought over to the surface by electrically operating elevators and machineries.

Purification

This involves the following process: 1. Grinding 2. Lixiviation or converting the ore into solution form 3. Crystallization 4. Separation, drying etc.

Grinding

The potassic ore, after mining and bringing over to the factory site, is ground to fine size and screened to get only the ore of required size.

Solutioning

The ore is dissolved in hot water and to that is added the NaCl solution (brine) for obtaining a mixture of KCl + NaCl. The temperature of the mixture is increased by which more and more of sylvinite will dissolve and the solubility of NaCl will stop after a stage. This is continued till a saturated solution of KCl is obtained.

Crystallization

The saturated solution containing both KCl and NaCl is suddenly cooled in a vacuum and the KCl separates out as crystals while NaCl remains in the solution.

Separation

Crystallized KCl can be separated out by mechanical means and it is dried, powdered and used. The above process is called the crystallization method and the principle involved is the differential solubility of KCl and NaCl in cold and hot solution. When KCl is mixed with NaCl it is much more soluble in hot water than in cold water, whereas NaCl is somewhat more soluble in cold water than in hot water. By increasing the temperature, therefore, the solubility of KCl increases while that of NaCl remains virtually constant.

Floatation method

Floatation is a metallurgical process in which small quantities of special reagents are added to the pulp to coat or film some of the minerals selectively with respect to other minerals present. When the reagent added pulp is agitated in a mechanical cell in such a manner that air is drawn into the pulp to create a frothing action or condition, the finely divided air bubbles attach themselves to the reagent filmed particles and float them to the surface of the cell, where the froth rich with the selected mineral may be skimmed off. Some are found to be very effective to NaCl that is present in sylvinite.

First, after grinding and passing through the screen, the desired sized sylvinite mineral is dissolved in water to get a pulp and the reagent is added to the pulp. The reagent will form a coating or film round the NaCl molecules and this reagent added pulp is allowed to pass through a series of floatation cells in which air is introduced at the

bottom in such a manner as to form a small bubble froth that attaches to NaCl. The commonly used reagents are (1) Sulphonated aliphatic alcohols of KCl and (2) 20% of mono-n-octadecyl- amines neutralized with acetic acid and a 0.5% solution of this is used for NaCl.

It is found that at least 90% of the potassic fertilizers consumed is in the form of muriate of potash. It contains 48 to 62% K₂O and 35 to 47% Cl. The commercial product is either granular or powdery having white or red colour.

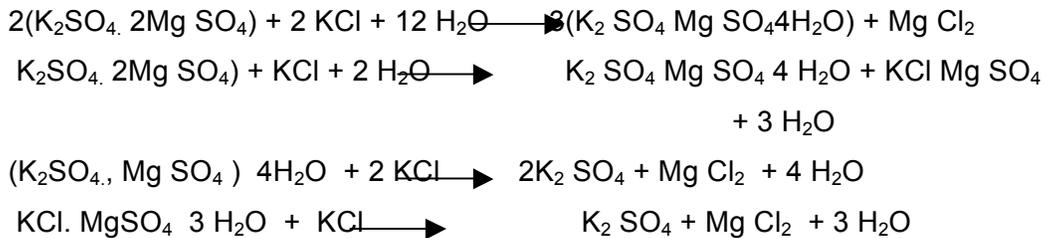
2. Potassium sulphate – K₂SO₄

This is manufactured from kainite (KCl. Mg SO₄, 3H₂O) or langbeinite (K₂ SO₄, Mg SO₄), the latter being commonly used. The raw materials required are the mineral langbeinite and KCl



The MgCl₂ is rejected. The KCl is used in the form of a mother liquor obtained from KCl manufacturing process.

The method is found to be efficient only in the presence of a proper ratio between K₂SO₄ and MgSO₄ of the raw material and to maintain a proper ratio, KCl or Kainite is added. The reactions are found to take place in different ways



Langbeinite, ground to pass through a 200 mesh sieve and the mother liquor from the KCl process is mixed and then the salts are recycled with water and fresh quantity of langbeinite. The reactions are allowed to take place in interconnected tanks and the crystallized K₂SO₄ is separated out by means of centrifuge. The used K₂SO₄ is separated out by means of centrifuge. The wet K₂SO₄ is dried and conveyed to storage place. It contains 48% K₂O. Only limited quantities of K₂SO₄ are manufactured, as the cost of manufacture is more, but is preferred for those crops where quality is desired or where chlorine toxicity will result when K Cl is used.

3. Potassium Magnesium sulphate

In U.S.A. it is manufactured by mere washing of langbeinite (K₂SO₄, Mg SO₄) to remove the impurities and is sold under the name sulphate of potassium and magnesium. It contains 18.5% MgO and 22.6% K₂O. Since, the langbeinite is soluble in

water; the washing is done very easily. In Germany, it is prepared by dissolving $MgSO_4$ and adding KCl to it.



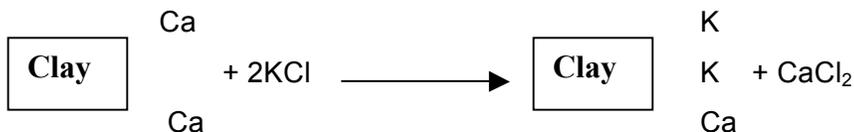
Manure salts

The ground and partially processed potassium mineral is sold under the name manure salt or mine run potassium salt. Various grades are available in different counties; Carnalite of 9-12 % K_2O and other salts of 12-15 % K_2O , 18-22% K_2O , 28-32 % K_2O , 38-42 % K_2O are also marketed and used on a limited scale.

The muck, peat, sandy, lateritic and laterite soils are deficient in K and response will be more in these soils for K fertilizers. Clayey soils are found to give poor response for K fertilizers. Potassic fertilizers can be added to these soils in which heavy feeders of K are grown such as tuber crops, coconut, arecanut, banana etc. The vegetables are found to respond well to K application.

Reactions of potassic fertilizers in the soil

Application of any potassic fertilizer does not change the pH of the soil. When a potassium salt is applied to a soil it is immediately dissolved and undergoes ionization. A portion of K^+ ions remains in the soil solution, another portion gets adsorbed to clay complex by CEC reactions and a third portion is converted into unavailable form.



Hence, in the soil the K will be in the solution, exchangeable and fixed forms. The solution form is readily available and the exchangeable form is slowly and steadily available to plants. The fixed K is unavailable but always in any soil there is a constant equilibrium among these three forms and hence mostly exists no deficiency of K . A small quantity of K is fixed by clays like illite, and this fixation of K depends upon the type of clay, temperature, wetting and drying and soil pH. In this case the fixation is beneficial as it reduces leaching loss and the availability of K will be there for a long time.

Factor affecting K fixation in soils

1. Nature of Colloids

The ability of various soil colloids to fix K varies widely. Kaolinite fixes little, while montmorillonite and illite fix more.

2. Wetting and Drying

When soils containing exchangeable K are alternatively wetted and dried, a large portion of exchangeable K is converted to the less available form.

This has been explained by assuming an entrapment of K ions between contracting structural units when the soil dries some release of the ions thus held occurs upon rewetting but the liberation is slow.

3. Influence of lime

Soils with high degree of base saturation lose less of their exchangeable K by leaching than the soils with a low degree of base saturation. Liming is the common means by which the base saturation of soils is increased and so liming decreased the loss of exchangeable K. The K ions are more readily replaced by calcium.

Application

The K fertilizers are usually applied before the crop is planted or sown, that is the basal dressing. Since the applied K is not lost from the soil either by leaching or by fixation, K fertilizers can be applied well in advance but it is preferable to apply only just before planting. Top dressing with K fertilizers can also be done for vegetables and other crop.