06. Manufacturing of ammonium sulphate, ammonium nitrate and ammonium chloride

Ammoinum sulphate

$(NH_4)_2\ SO_4$ is one of the important fertilizers produced in India. It contains about 21% N and 24% S and has been traditionally been very popular in various parts of the country. It is a white crystaline salt having good keeping quality in dry conditions.

Production capacity

The total installed capacity in the country is about one million tones of $(NH_4)_2\ SO_4$

Raw materials / sources

The raw materials required to produce $(NH_4)_2SO_4$ are

- H_2SO_4 for its recovery from coke oven plants.
- NH_3 and H_2SO_4 for neutralization process.
- Gypsum (natural or by product from H_3PO_4 plants) and NH_3 for process using gypsum route.

Method of manufacture

The following methods are used for producing $(NH_4)_2\ SO_4$.

(i) Recovery from coke-ovens

The coke-oven gas (obtained when coal is heated to make coke) contains about 1% NH_3 by volume. The gas is cooled and passed into saturators containing weak H_2SO_4 so as to form $(NH_4)_2SO_4$ crystals which is then recovered, centrifuged, washed and dried. This process is used in the steel plants where large coke- oven batteries are in operation.

(ii) Direct neutralization

Gaseous ammonia is directly neutralized with H_2SO_4 to produce $(NH_4)_2SO_4$.

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

The neutralizer reactor and the crystallizer are interconnected so that the heat released during neutralization is used to evaporate water in the slurry. The crystallizer is designed to produce uniformly sized crystals.

Amorphous $(NH_4)_2\ SO_4$ is prepared by reacting gaseous NH_3 and H_2SO_4 in spray towers. The heat of reaction removes all the water present and the dry, fine product is continuously removed from the base of the tower. This product is suitable for making dry-mixed and granular fertilizers, FCI (Sindri), FACT (Alwaye) use the direct neutralization process.

In the manufacture of some granular NPK fertilizers, $(NH_4)_2SO_4$ is formed directly with other ammonium salts. E.g. in the 16 – 20 – 0 grade product made by FACT, a

mixture of H_3PO_4 and H_2SO_4 is neutralized with NH_3 to form a slurry of $(NH_4)\ PO_4$ and $(NH_4)_2\ SO_4$, which is then granulated.

(iii) Gypsum process

NH_3 gas is absorbed in water and then converted to $(NH_4)_2CO_3$ by absorbing CO_2. The $(NH_4)_2CO_3$ is reacted with gypsum ($CaSO_4.\ 6\ H_2O$) to produce $(NH_4)_2SO_4$ and $CaCO_3$.

$$Ca\ SO_4\ 2H_2O + (NH_4)_2CO_3 \longrightarrow (NH_4)_2\ SO_4 + CaCO_3 + 2H_2O$$

$CaCO_3$ is removed by filtration $(NH_4)_2SO_4$ solution is evaporated, crystallized, centrifuged and dried. Naturally occurring gypsum, or by product gypsum from H_3PO_4 plants can be used for this process. $CaCO_3$ produced can be used for cement manufacture FCI (Sindri), FACT (Alwaye), EID-parry (Ennore), and GSFC (Baroda), produce $(NH_4)_2\ SO_4$ from $Ca\ SO_4$.

(iv) Byproduct

$(NH_4)_2SO_4$ from caprolactum plants $(NH_4)_2SO_4$ solution is formed during the manufacture of caprolactum (the starting material for Nylon- 6). The solution is concentrated and $(NH_4)_2SO_4$ is recovered by crystallization, centrifuging and drying. GSFC (Baroda) has commissioned a 20,000 t p a caprolactum plant which will produce about 80,000 tonnes of $(NH_4)_2\ SO_4$ per year.

Specification as per FCO

- Moisture % by weight. Max	1.0
- NH_4 – N % by weight Min	20.6
- Free acidity as H_2SO_4 % by weight max	0.025
- Arsenic (As $As_2\ O_3$) % by weight max	0.01

Handling storage and packing

Crystalline $(NH_4)_2\ SO_4$ is free flowing and does not normally pose any problem in handling and storage. However, it generally contains some powdered material which causes caking especially under high humidity.

Due to its susceptibility to caking and slight acidity $(NH_4)_2SO_4$ is normally bagged in polyethylene lined gunny bags or high density polyethylene (HDPE) woven sacks.

Properties

- It is a white crystalline salt and to some extent hygroscopic
- It has good storage quality
- It is very soluble in water and so called as quick acting fertiliser
- It should not be used along with alkaline materials

- It is physiologically acidic in nature

Reactions in soil

$(NH_4)_2\ SO_4 \longrightarrow 2\ NH4^{+} + SO4^{-}$

Soil colloid $Ca^{++} + (NH_4)_2\ SO_4 \longrightarrow$ Soil colloid $H_4^{+} + CaSO_4$ (soluble)

Ammonia gas is evolved when ammonium sulphate reacts with alkaline materials

When lime and ammonium sulphate is used together in the soil, ammonia gas is produced

Ammonium chloride (NH_4 Cl) 26% N

This is sometimes called nitrate of ammonia. It is commercially prepared by combining ammonia with HCl and the resultant product, NH_4Cl is found to have very good physical condition. Though this fertilizer has not been used extensively as straight fertilizer, it is preferred in preparing many fertilizer mixtures because of its good physical properties. This fertilizer is also obtained as a by product of the Solvay process of making $(Na)_2\ CO_3$.

The commercial sample is a white, crystalline salt containing 26% N in the NH_4 form. The fertilizer is suitable for many crops except for those, which are sensitive to high chlorine content. This is physiologically acidic fertilizer.

Manufacture

Sodium chloride is treated with ammonia and carbon dioxide to form ammonium chloride and sodium bicarbonate. The resulting ammonium chloride is then separated

$NaCl + CO_2 + NH_3 + H_2O \rightleftharpoons NH_4Cl + NaHCO_3$

Ammonium chloride is also obtained as a byproduct of soda ash (Na_2CO_3) and manufactured as Solvays process. It is prepared by reacting calcium chloride with ammonium carbonate. Ammonium chloride is obtained by double decomposition between ammonium sulphate and sodium chloride at 1300^0 C

Ammonium nitrate ($NH_4\ NO_3$) – 33% N

This is mainly manufactured by passing NH_3 gas into HNO_3 and then isolating the product in a solid form suitable for use as fertilizer. The equipment should be stainless steel or other special alloys.

$HNO_3 + NH_3 \longrightarrow NH_4\ NO_3 + \text{Heat}$

$NH_4\ NO_3$ is continuously produced with the aid of a neutralization tower. NH_3 gas is introduced near the bottom of the tower, while air is added at a higher point to cool the

solution and carry off the water vapor. The solution containing about 80% of $NH_4 NO_3$ is with drawn and converted to crystals or pellets as the case may be.

Pure $NH_4 NO_3$ is a white crystalline salt having 33% of N, one half of which is in the NH_4 form and the other half in the NO_3 form. It is readily soluble in water and completely utilized by crops and hence no residues are left in the soil. It is highly hygroscopic and cakes up very soon. But, when the crystal is coated with about 5% of a conditioning agent like clay etc, it is found to have good physical properties. It is an excellent fertilizer both for direct application to the soil and for use in mixtures. It is an economical source of fertilizer N, suited to a wide range of crops, soils and climatic conditions. Its NO_3 content contributes to rapid crop response while the NH_4- N makes it more resistant to leaching losses than other materials carrying their entire N in the NO_3 form.