

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

Ammonium sulphate

(NH₄)₂ SO₄ 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 crystalline salt having good keeping quality in dry conditions.

Production capacity

The total installed capacity in the country is about one million tones of (NH₄)₂ SO₄

Raw materials / sources

The raw materials required to produce (NH₄)₂SO₄ are

- H₂SO₄ for its recovery from coke oven plants.
- NH₃ and H₂SO₄ for neutralization process.
- Gypsum (natural or by product from H₃PO₄ plants) and NH₃ for process using gypsum route.

Method of manufacture

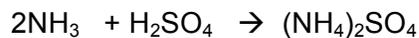
The following methods are used for producing (NH₄)₂ SO₄.

(i) Recovery from coke-ovens

The coke-oven gas (obtained when coal is heated to make coke) contains about 1% NH₃ by volume. The gas is cooled and passed into saturators containing weak H₂SO₄ so as to form (NH₄)₂SO₄ 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 H₂SO₄ to produce (NH₄)₂SO₄.



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 (NH₄)₂ SO₄ is prepared by reacting gaseous NH₃ and H₂SO₄ 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, (NH₄)₂SO₄ 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 $(\text{NH}_4)\text{PO}_4$ and $(\text{NH}_4)_2\text{SO}_4$, which is then granulated.

(iii) Gypsum process

NH_3 gas is absorbed in water and then converted to $(\text{NH}_4)_2\text{CO}_3$ by absorbing CO_2 . The $(\text{NH}_4)_2\text{CO}_3$ is reacted with gypsum ($\text{CaSO}_4 \cdot 6\text{H}_2\text{O}$) to produce $(\text{NH}_4)_2\text{SO}_4$ and CaCO_3 .



CaCO_3 is removed by filtration $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ from CaSO_4 .

(iv) Byproduct

$(\text{NH}_4)_2\text{SO}_4$ from caprolactum plants $(\text{NH}_4)_2\text{SO}_4$ solution is formed during the manufacture of caprolactum (the starting material for Nylon- 6). The solution is concentrated and $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ per year.

Specification as per FCO

- Moisture % by weight. Max	1.0
- $\text{NH}_4 - \text{N}$ % by weight Min	20.6
- Free acidity as H_2SO_4 % by weight max	0.025
- Arsenic (As_2O_3) % by weight max	0.01

Handling storage and packing

Crystalline $(\text{NH}_4)_2\text{SO}_4$ 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.

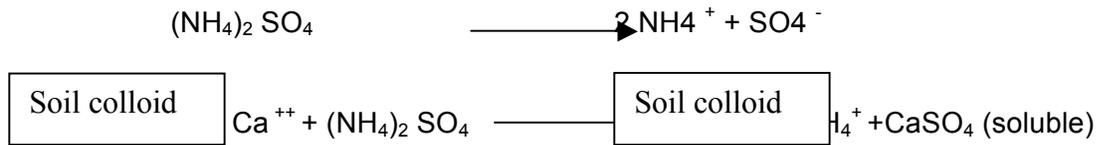
Due to its susceptibility to caking and slight acidity $(\text{NH}_4)_2\text{SO}_4$ is normally bagged in polyethylene lined gunny bags or high density polyethylene (HDPE) woven sacks.

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



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 (NH₄ Cl) 26% N

This is sometimes called nitrate of ammonia. It is commercially prepared by combining ammonia with HCl and the resultant product, NH₄Cl 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 CO₃.

The commercial sample is a white, crystalline salt containing 26% N in the NH₄ 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



Ammonium chloride is also obtained as a byproduct of soda ash (Na₂CO₃) and manufactured as Solvay's 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 1300⁰ C

Ammonium nitrate (NH₄ NO₃) – 33% N

This is mainly manufactured by passing NH₃ gas into HNO₃ and then isolating the product in a solid form suitable for use as fertilizer. The equipment should be stainless steel or other special alloys.



NH₄ NO₃ is continuously produced with the aid of a neutralization tower. NH₃ 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 $\text{NH}_4 \text{NO}_3$ is with drawn and converted to crystals or pellets as the case may be.

Pure $\text{NH}_4 \text{NO}_3$ 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.