Lecture 12

Ammonium chloride

Ammonium chloride ride is used fertilization either such or in a variety of compound fertilizers. Examples are:

18-22-0 (ammonium phosphate chloride)
16-0-20 (ammonium-potassium chloride)
14-14-14
12-18-14

Ammonium chloride is used in other grades of compound fertilizers in combination with urea or ammonium sulfate. Advantages of ammonium chloride are that it has a higher concentration than ammonium sulfate and a somewhat lower cost per unit of N (in Japan). It has some agronomic advantages for rice; nitrification is less rapid than with urea or ammonium sulfate and, therefore N losses are lower and yields are higher.

Although ammonium chloride is best known as a rice fertilizer, it has been successfully tested and used on other crops such as wheat, barley, sugarcane, maize, fiber crops, and sorghum in a variety of climatic conditions.

Ammonium chloride is as highly acid-forming as ammonium sulfate per unit of N, which can be a disadvantage. Other disadvantages are its low N content compared with urea or ammonium nitrate and the high chloride content, which can be harmful on some crops or soils. Nevertheless, it is possible that ammonium chloride fertilizer could become a useful outlet for surplus chlorine or byproduct hydrochloric acid that arises from time to time. Another ruse full feature of ammonium chloride is that it can be applied to rice with safety in the presence of certain fungi, which would reduce ammonium sulfate to toxic sulfides.

Properties of ammonium chloride- The properties of ammonium chloride are given in table.
Commercial form, storage, and transportation- The fertilizer-grade product contains 25% N. The product can be in the form of either crystals or granules. Coarse crystalline or granular forms are preferred for direct application, whereas fine crystals can be used in compound fertilizers.

Raw Materials- principal raw materials are common salt (NaCl0 and anhydrous ammonia in the case of the dual-salt process or anhydrous ammonia and hydrochloric acid (HCl) for the direct-neutralization method. To take advantage of byproduct CO₂, it is advisable to install the dual-salt process at a site where anhydrous ammonia is produced. For the direct

Table 8.29. Properties of Ammonium chloride

<table>
<thead>
<tr>
<th>Formula</th>
<th>NH₄Cl</th>
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<tbody>
<tr>
<td>Molecular weight</td>
<td>53.5</td>
</tr>
<tr>
<td>Nitrogen content</td>
<td>26%</td>
</tr>
<tr>
<td>Color</td>
<td>white</td>
</tr>
<tr>
<td>Density of solid, 20°C</td>
<td>1.526</td>
</tr>
</tbody>
</table>

Solubility, g/100g of water at:

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.4</td>
</tr>
<tr>
<td>20</td>
<td>37.2</td>
</tr>
<tr>
<td>40</td>
<td>45.8</td>
</tr>
<tr>
<td>60</td>
<td>55.3</td>
</tr>
<tr>
<td>80</td>
<td>65.6</td>
</tr>
<tr>
<td>100</td>
<td>77.3</td>
</tr>
</tbody>
</table>
115.6 (boiling point) 87.3

Effect of heat: Ammonium chloride begins to dissociate at 350°C and sublimes at 520°C.

Crystal relative humidity

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Relative Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>79.2</td>
</tr>
<tr>
<td>30°C</td>
<td>77.5</td>
</tr>
</tbody>
</table>

Neutralization method, byproduct HCl may be used, e.g., byproduct HCl from the production of potassium sulfate by the Mannheim process.

Production Methods- Several methods for producing ammonium chloride are used: the order of importance is follows:

1. The dual-salt process, whereby ammonium chloride and sodium carbonate are produced simultaneously.

2. Direct neutralization of ammonia with hydrochloric acid.

The Dual-Salt Process- Most ammonium chloride used in India, China, and Japan for fertilizer purposes is produced by the dual-salt process as shown.

In this method, ammonium chloride is salted out by the addition of solid, washed sodium chloride rather than decomposition by lime liquor to recover ammonium carbonate:

\[
2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3
\]

Additional carbonation produces ammonium bicarbonate:

\[
(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3
\]

The addition of sodium chloride yields sodium bicarbonate and ammonium chloride:
\[
\text{NH}_4\text{HCO}_3 + \text{NaCl} \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl}
\]

The sodium bicarbonate is separated by centrifuging or filtration and calcined to produce sodium carbonate and \(\text{CO}_2\); the latter is recycled to the system.

**The Direct-neutralization Method** - Ammonium chloride of high purity can be made by the direct reaction between anhydrous ammonia vapor and hydrochloric acid gas, according to the reaction

\[
\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}
\]

The reaction is exothermic (42,000 cal/g-mole). In most cases, neutralization is undertaken at reduced pressures of 250-300 mm of mercury in one or more rubber-lined steel vacuum reaction vessels protected with an additional inner lining of inert brick. Concentrated hydrochloric acid gas is passed through an aspirator, wherein it is diluted with air to about 20% concentration and enters the reaction vessel via a vertical sparger tube. According to preference, ammonia gas is introduced either by a second sparger or by tangential nozzles in the base of the reaction vessel. Agitation is provided by the large volume of air entering the reactor with the hydrochloric acid vapor; thus, the need for a mechanical agitator with its additional power requirements and maintenance problems is avoided.

Similarly, operation under vacuum not only provides excellent cooling but simultaneously prevents escape of noxious vapors and eliminates the need for hydrochloric acid-vapor blowers, plus their attendant cost and maintenance charges. A reduced pressure of 250-330 mm of mercury and a corresponding slurry temperature of 75°-80°C represent typical operating conditions.

Mother liquor the centrifuge is pumped back to the saturator(s) via a storage tank. Saturator off gases must be well scrubbed before entering the vacuum pump or ejector unit to prevent corrosion and to eliminate air pollution. A two-stage scrubbing system is usually employed and may consist of a direct, barometric scrubber condenser followed by a wetted,
packed tower. Liquor from the scrubber-condenser is returned to the mother liquor tank and is evaporated in the saturator, thus providing a means of temperature control and recovery.

As with other processes involving reactions between hydrochloric acid (or chlorides) and ammonia, traces of free chlorine in the acid feed can lead to disastrous explosions caused by the formation of nitrogen trichloride in the saturator. Hence, adequate safety precautions must be installed whereby the HCl gas feed is monitored and the flow discontinued when chlorine is detected. This can be accomplished by such means as bypassing a small stream of gas through a photocell-calorimeter unit containing potassium iodide or using a modern continuous gas analyzer of the absorption or chromatographic type.

After separation and drying, the crystalline ammonium chloride is bagged as quickly as possible to minimize subsequent storage and application difficulties.