8.5.2 Triple Superphosphates

8.5.2.1 General

Triple superphosphate, also known as double, treble, or concentrated superphosphate, is a fertilizer material with a phosphorus content of over 40 percent, measured as phosphorus pentoxide ($P_2O_5$). Triple superphosphate is produced in only 6 fertilizer facilities in the U. S. In 1989, there were an estimated 3.2 million megagrams (Mg) (3.5 million tons) of triple superphosphate produced. Production rates from the various facilities range from 23 to 92 Mg (25 to 100 tons) per hour.

8.5.2.2 Process Description

Two processes have been used to produce triple superphosphate: run-of-the-pile (ROP-TSP) and granular (GTSP). At this time, no facilities in the U. S. are currently producing ROP-TSP, but a process description is given.

The ROP-TSP material is essentially a pulverized mass of variable particle size produced in a manner similar to normal superphosphate. Wet-process phosphoric acid (50 to 55 percent $P_2O_5$) is reacted with ground phosphate rock in a cone mixer. The resultant slurry begins to solidify on a slow moving conveyor en route to the curing area. At the point of discharge from the den, the material passes through a rotary mechanical cutter that breaks up the solid mass. Coarse ROP-TSP product is sent to a storage pile and cured for 3 to 5 weeks. The product is then mined from the storage pile to be crushed, screened, and shipped in bulk.

GTSP yields larger, more uniform particles with improved storage and handling properties. Most of this material is made with the Dorr-Oliver slurry granulation process, illustrated in Figure 8.5.2-1. In this process, ground phosphate rock or limestone is reacted with phosphoric acid in 1 or 2 reactors in series. The phosphoric acid used in this process is appreciably lower in concentration (40 percent $P_2O_5$) than that used to manufacture ROP-TSP product. The lower strength acid maintains the slurry in a fluid state during a mixing period of 1 to 2 hours. A small sidestream of slurry is continuously removed and distributed onto dried, recycled fines, where it coats the granule surfaces and builds up its size.

Pugmills and rotating drum granulators have been used in the granulation process. Only 1 pugmill is currently operating in the U. S. A pugmill is composed of a U-shaped trough carrying twin counter-rotating shafts, upon which are mounted strong blades or paddles. The blades agitate, shear, and knead the liquified mix and transport the material along the trough. The basic rotary drum granulator consists of an open-ended, slightly inclined rotary cylinder, with retaining rings at each end and a scraper or cutter mounted inside the drum shell. A rolling bed of dry material is maintained in the unit while the slurry is introduced through distributor pipes set lengthwise in the drum under the bed. Slurry-wetted granules are then discharged onto a rotary dryer, where excess water is evaporated and the chemical reaction is accelerated to completion by the dryer heat. Dried granules are then sized on vibrating screens. Oversize particles are crushed and recirculated to the screen, and undersize particles are recycled to the granulator. Product-size granules are cooled in a countercurrent rotary drum, then sent to a storage pile for curing. After a curing period of 3 to 5 days, granules are removed from storage, screened, bagged, and shipped.
Figure 8.5.2-1. Dorr-Oliver process for granular triple superphosphate production.\(^1\)
8.5.2.3 Emissions And Controls

Controlled emission factors for the production of GTSP are given in Table 8.5.2-1. Units are expressed in terms of kilograms per megagrams (kg/Mg) and pounds per ton (lb/ton). Emission factors for ROP-TSP are not given since it is not being produced currently in the U. S.

Table 8.5.2-1 (Metric And English Units). CONTROLLED EMISSION FACTORS FOR THE PRODUCTION OF TRIPLE SUPERPHOSPHATES

EMISSION FACTOR RATING: E

<table>
<thead>
<tr>
<th>Granular Triple Superphosphate Process</th>
<th>Pollutant</th>
<th>Controlled Emission Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kg/Mg Of Product</td>
</tr>
<tr>
<td>Rock unloading&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Particulate&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>PM-10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.04</td>
</tr>
<tr>
<td>Rock feeding&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Particulate&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>PM-10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.01</td>
</tr>
<tr>
<td>Reactor, granulator, dryer, cooler, and screens&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Particulate&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Fluoride&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>PM-10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.04</td>
</tr>
<tr>
<td>Curing building&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Particulate&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Fluoride&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>PM-10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.08</td>
</tr>
</tbody>
</table>

<sup>a</sup> Factors are for emissions from baghouses with an estimated collection efficiency of 99%. PM-10 = particulate matter with a diameter of less than 10 micrometers.

<sup>b</sup> Reference 1, pp. 77-80, 168, 170-171.

<sup>c</sup> Based on Aerometric Information Retrieval System (AIRS) Listing For Criteria Air Pollutants.

<sup>d</sup> Factors are for emissions from wet scrubbers with an estimated 97% control efficiency.

Sources of particulate emissions include the reactor, granulator, dryer, screens, cooler, mills, and transfer conveyors. Additional emissions of particulate result from the unloading, grinding, storage, and transfer of ground phosphate rock. One facility uses limestone, which is received in granulated form and does not require additional milling.

Emissions of fluorine compounds and dust particles occur during the production of GTSP triple superphosphate. Silicon tetrafluoride (SiF<sub>4</sub>) and hydrogen fluoride (HF) are released by the acidulation reaction and they evolve from the reactors, den, granulator, and dryer. Evolution of fluoride is essentially finished in the dryer and there is little fluoride evolved from the storage pile in the curing building.

At a typical plant, baghouses are used to control the fine rock particles generated by the rock grinding and handling activities. Emissions from the reactor, den, and granulator are controlled by scrubbing the effluent gas with recycled gypsum pond water in cyclonic scrubbers. Emissions from...
the dryer, cooler, screens, mills, product transfer systems, and storage building are sent to a cyclone separator for removal of a portion of the dust before going to wet scrubbers to remove fluorides.

Particulate emissions from ground rock unloading, storage, and transfer systems are controlled by baghouse collectors. These baghouse cloth filters have reported efficiencies of over 99 percent. Collected solids are recycled to the process. Emissions of SiF₄, HF, and particulate from the production area and curing building are controlled by scrubbing the offgases with recycled water. Exahusts from the dryer, cooler, screens, mills, and curing building are sent first to a cyclone separator and then to a wet scrubber. Tailgas wet scrubbers perform final cleanup of the plant offgases.

Gaseous SiF₄ in the presence of moisture reacts to form gelatinous silica, which has the tendency to plug scrubber packings. Therefore, the use of conventional packed countercurrent scrubbers and other contacting devices with small gas passages for emissions control is not feasible. Scrubber types that can be used are: (1) spray tower, (2) cyclone, (3) venturi, (4) impingement, (5) jet ejector, and (6) spray-crossflow packed.

The effectiveness of abatement systems for the removal of fluoride and particulate varies from plant to plant, depending on a number of factors. The effectiveness of fluorine abatement is determined by: (1) inlet fluorine concentration, (2) outlet or saturated gas temperature, (3) composition and temperature of the scrubbing liquid, (4) scrubber type and transfer units, and (5) effectiveness of entrainment separation. Control efficiency is enhanced by increasing the number of scrubbing stages in series and by using a fresh water scrub in the final stage. Reported efficiencies for fluoride control range from less than 90 percent to over 99 percent, depending on inlet fluoride concentrations and the system employed. An efficiency of 98 percent for particulate control is achievable.

The particulate and fluoride emission factors are identical to the previous revisions, but have been downgraded to "E" quality because no documented, up-to-date source tests were available and previous emission factors could not be validated from the references which were given. The PM-10 emission factors have been added to the table, but were derived from the AIRS data base, which also has an "E" rating. No additional or recent data were found concerning fluoride emissions from gypsum ponds. A number of hazardous air pollutants (HAP) have been identified by SPECIATE as being present in the phosphate fertilizer manufacturing process. Some HAPs identified include hexane, methyl alcohol, formaldehyde, methyl ethyl ketone, benzene, toluene, and styrene. Heavy metals such as lead and mercury are present in the phosphate rock. The phosphate rock is mildly radioactive due to the presence of some radionuclides. No emission factors are included for these HAPs, heavy metals, or radionuclides due to the lack of sufficient data.

References For Section 8.5.2

