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Triple Superphosphate

by

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TRIPLE SUPERPHOSPHATE[1]

Introduction

Triple superphosphate, also known in the trade as double, treble or concentrated superphosphate, is produced by reacting phosphate rock[a] with phosphoric acid, or with a mixture of phosphoric and sulfuric acids in which phosphoric acid preponderates. The phosphoric pentoxide (P_2O_5) content of the acid ranges up to about 55%; the available P_2O_5 in the superphosphate runs 40 to 49% with the bulk of production in the range 45 to 47%. Wet-process phosphoric acid, which is produced by treating phosphate rock with an excess of sulfuric acid, is commonly used, and usually contains 1 to 5% of sulfuric acid.

The major chemical component of concentrated superphosphate is monocalcium phosphate monohydrate ($CaH_4P_2O_8.H_2O$). However, there are other constituents, as shown in the following tabulation of analyses, of commercial concentrated superphosphate made from wet-process phosphoric acid.

Components:	Percent
$Ca(H_2PO_4)_2.H_2O$ or $CaH_4P_2O_8.H_2O$	63-73
$CaSO_4$	3-6
$CaHPO_4$, and Al phosphates	13-18
Silica, fluosilicates, unreacted rock, organic matter	5-10
Free moisture	3-6

The chemical composition of the reactants, rock and acid, as well as the physical characteristics of the rock, affect the type and amounts of compounds formed; for example, if furnace-type phosphoric acid is used, sulfate is practically eliminated and the content of the other impurities is reduced. Other factors influencing the quality of the product and the proportions of components in the product include the ratio of reactants, the reaction temperature, the degree of mixing, and the curing temperature.

There are currently (1990) only six fertilizer facilities that have the capability of producing triple superphosphate in the United States. One of the plants is located in North Carolina, four in Florida, and one in Idaho.[2]

All use phosphate rock mined and beneficiated near their facilities, except the plant in Idaho that uses limestone. In 1989, there was an estimated 3.5 million tons of triple superphosphate produced.[3]

Process Description

The two principal types of triple superphosphate are run-of-the-pile (ROP) and granular; at this time, no facilities are producing ROP triple, but a description of the process is presented for information purposes. ROP is essentially a pulverized mass of variable particle size produced in a manner similar to normal superphosphate. Phosphoric acid (50% P_2O_5) is reacted with ground phosphate rock in a cone mixer. The resultant slurry begins to solidify on a slow moving conveyer (den) 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 product is sent to a storage pile and cured for a period of 3 to 5 weeks. The final product is then mined from the "pile" in the curing shed, and then crushed, screened, and shipped.

Granular triple superphosphate yields larger, more uniform particles with improved storage and handling properties. In this process, shown in Figure GTS-1, ground phosphate rock (67-73% BPL,[a] 85%-200 mesh) or limestone (-50 mesh) is reacted with phosphoric acid in one or two reactors in series. The phosphoric acid used in this process is appreciably lower in concentration (40% P_2O_5) than that used to manufacture ROP product. The lower strength acid helps maintain the slurry in a fluid state during a mixing period that ranges from 10-15 minutes to up to 2 hours. A thin slurry is continuously removed and distributed onto dried, recycled fines in the granulator where it coats the granule surfaces and builds up size.

Pugmills and rotating drum granulators have been used in the granulation process. Currently there is only one pugmill operating in the U.S. The remainder of the producers use drum granulators. 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 or spray nozzles above the bed. Slurry-wetted granules then discharge to a rotary dryer, where excess water is evaporated. Evaporation of water essentially stops the chemical reaction. Dried granules are then sized on vibrating screens. Oversize particles are crushed and recirculated to the screen; undersize particles are recycled to the granulator. Product size granules are cooled and sent to a storage pile. After a curing period of 3 to 5 days, granules are removed from storage, screened, and shipped.

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[a] BPL, bone phosphate of lime. BPL x 0.4576 = % P_2O_5.

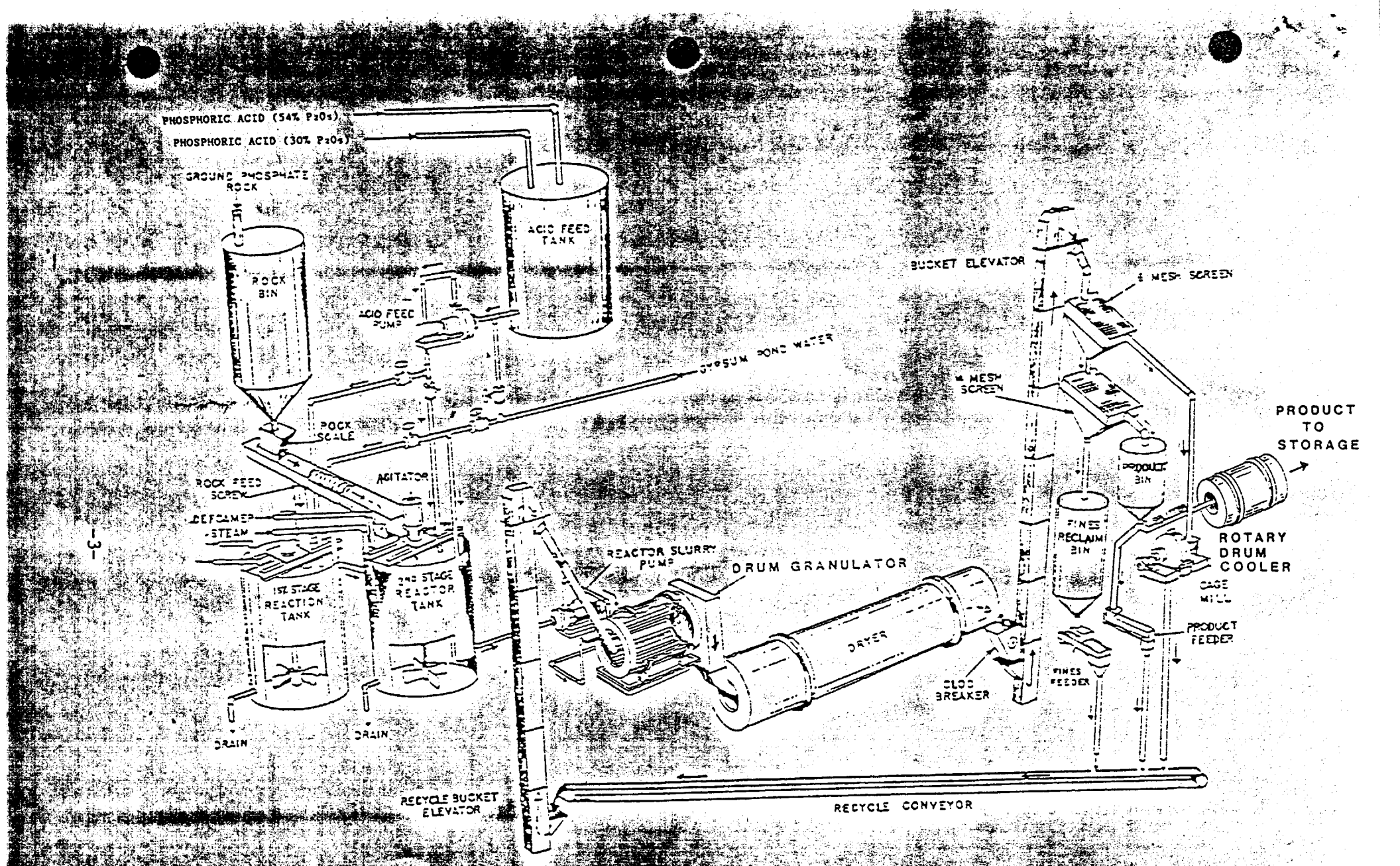

Figure GTS-1
Slurry Process for Granular Triple Superphosphate

The granular product contains about 45-47% P_2O_5 in an available form. Production rates from the various facilities range from about 25 to 100 tons per hour.

Air Emission Characteristics

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. The limestone is received already ground and no further milling is necessary.

Emission of fluorine compounds and dust particles occur during the production of granular triple superphosphate. Silicon tetrafluoride and hydrogen fluoride are released by the acidulation reaction 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.

Air Pollution Control Measures

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, screens, mills, product transfer systems and storage buildings are sent to a cyclone separator for removal of a portion of the dust before going to wet scrubbers to remove fluorides. In some instances, where little particulate is present, cyclonic separators are used to remove both the particulate and fluorides.

Emission factors for the production of granular triple superphosphate are given in Table TS-1. The fluoride emission factors are the maximum allowable emissions based on Federal regulations; in Florida and Idaho, more stringent regulations have been adopted and these are shown also. There are no current Federal emission limits for particulates, but state regulations are given for the three states that have triple manufacturing facilities.

Baghouse collectors (cloth filters) have reported efficiencies of over 99%. Collected solids are recycled to the process. Emissions of silicon tetrafluoride, hydrogen fluoride, and particulate from the production area and curing building are controlled by scrubbing the offgases with recycled water. Exhausts from the dryer, screens, mills, and curing building are sent first to a cyclone separator and then to a wet scrubber. Tail gas wet scrubbers are installed to handle final clean-up of the plant offgases.

Gaseous silicon tetrafluoride in the presence of moisture reacts to form gelatinous silica, which has the tendency to plug scrubber packings. The use of conventional packed countercurrent scrubbers and other contracting devices

Table TS-1
Allowable Emissions From Triple Superphosphate Production Facilities

Process	Emission Point	Maximum Allowable Emissions: Fluoride	Maximum Allowable Emissions: Particulates
Granular Triple Superphosphate from Phosphate rock and H_3PO_4	Manufacturing facility (reactors, granulators, dryers, screens, and mills)	Federal Regulations[a] 0.2 lb/ton P_2O_5 fed 0.1 kg/MT P_2O_5 fed	none
		NC Regulations same as Federal Regulations	Varies with production rate i.e. @ 50 T/hr = 31 lb/hr; @ 100 T/hr = 38 lb/hr
		FL Regulations 0.15 lb/ton P_2O_5 fed	E = 17.3 P0.16 when P (Production rate, T/hr) > 30 tons/hr E = emissions, lbs/hr
	Storage facilities (storage for curing piles conveyors, elevators, screens and mills)	Federal Regulations[a] 0.0005 lb/hr ton P_2O_5 stored 0.00025 kg/MT P_2O_5 stored	none
		NC Regulations Same as Federal Regulations	Included in manufacturing facility rate.
		FL Regulations 0.05 lb/ton P_2O_5 fed	Included in manufacturing facility rate.
Granular triple superphosphate from limestone and H_3PO_4	Manufacturing facility (reactors, granulators, dryers, screens, and mills)	ID Regulations 1.7 lbs./hr	Site specific
	Storage facilities (Storage for curing piles conveyors, elevators, screens and mills)	ID Regulations 0.036 lbs/hr	Site specific

[a] Source: Federal regulations (for facilities that commence construction or modifications after 10/22/74) 40FR33155 August 6, 1975.

with small gas passages for emissions control is therefore limited. Scrubber types that can be used are (1) spray tower, (2) cyclonic, (3) venturi, (4) impingement, (5) jet ejector, and (6) spray-crossflow packed.

Air pollution control equipment varies with particular plant designs. The effectiveness of abatement systems for the removal of fluoride and particulate also 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% to over 99%, depending on inlet fluoride concentrations and the system employed. An efficiency of 98% for particulate control is achievable.

In routine operation, all of the facilities are reported to meet or produce less emissions than is allowable by the appropriate Federal or state regulations.

Key Words
Triple superphosphate, concentrated superphosphate, phosphoric acid, phosphate rock, monocalcium phosphate

References for Section on Triple Superphosphate

1. Portions of this chapter were edited from AP-42, U.S. EPA's Emission Factors Handbook, Vol 1, Chapter 6.10.2 and U.S. Department of Agriculture & Tennessee Valley Authority, Superphosphate: Its History, Chemistry, and Manufacture, December 1964.

2. One facility currently uses limestone instead of phosphate rock to minimize fluorine evolution. Details are presented in U.S. Patent No. 410163, dated July 18, 1978, by Larry Bierman and Bary Long.

3. North American Fertilizer Capacity Data, TVA/NFDC 89/1, Circular Z-243.

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