TVA

Tennessee Valley Authority, Post Office Box 1010, Muscle Shoals, Alabama 35660

February 24, 1992

Mr. John Hamilton
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Dear Mr. Hamilton:

Enclosed are copies of the chapters on normal and triple superphosphate that I revised and updated for the Air and Waste Management Association in 1991. Information for this revision was obtained from National Fertilizer and Environmental Research Center (NFERC), International Fertilizer Development Center, and industry sources. It is my understanding that Pacific Environmental Services has a contract with EPA to update the AP-42 air emissions manual and that the chapters I send you may be included in the updated AP-42. You indicated that if the information sent to you is used, recognition that the information was obtained from TVA's NFDC would be given and that a draft of what you intend to publish would be sent to TVA prior to publication.

For your information, chapters on ammonium nitrate, urea, and ammonium phosphate have also been updated.

If you have any questions, please do not hesitate to contact me.

Sincerely,

Horace C. Mann

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Enclosure

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Normal Superphosphate

by

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With assistance from authorities at
International Fertilizer Development Center
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and
TVA's NFERC

NORMAL SUPERPHOSPHATE[1]

Introduction

The solid product obtained by treating natural phosphates with sulfuric acid alone is often designated simply as superphosphate. However, precise technology requires its differentiation from other materials in the superphosphate category. Definitions used for this purpose include the adjectives regular, standard, ordinary, single, or normal superphosphate. The term normal superphosphate is now generally used in statistical publication of the United States Government. As defined by the Bureau of the Census, normal superphosphate (prepared with the aid of sulfuric acid alone) contains not more than 22% of available P_2O_5. In the United States, the superphosphate manufacturer needs to achieve a minimum of about 15% P_2O_5[2] in his marketed product. There are currently only about eight fertilizer facilities producing normal superphosphates in the United States with an estimated total production of about 300,000 tons per year.

The raw materials generally used for production of normal superphosphate are ground phosphate rock and sulfuric acid. The phosphate rock now comes mainly from either the Florida or western phosphate fields; the rock can either be ground at the mining site or at the manufacturing site. Rock for superphosphate manufacture is for the most part produced by beneficiation of mined ore.

Important characteristics of rock introduced into the superphosphate manufacturing cycle are those that govern its performance in processing. The most important index of this quality is grade usually expressed as BPL.[a] The most skilled operator can use phosphate rock that runs no lower than 68-70% BPL; in a reasonably efficient operation, rock running 75-76% BPL will yield a superphosphate containing 20% available P_2O_5 or more. A factor closely related to grade is the content of iron and aluminum in the phosphate rock. Amounts of Al_2O_3 plus Fe_2O_3 greater than about 5% cannot be tolerated because of the extreme stickiness imparted to the superphosphate. Another widely recognized index of quality is fineness of the phosphate rock. The finer the rock the more rapid is its reaction with the sulfuric acid.

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

The two general types of sulfuric acid used in superphosphate manufacture are virgin and spent acid. Virgin acid is produced from elemental sulfur, pyrites, and industrial gases. Spent acid is derived as a waste product in sundry industries that use large quantities of sulfuric acid in processing a great variety of products. Problems using spent acid are unusual color, unfamiliar odor, and toxicity to crops in the normal superphosphate made using this acid.

The major chemical compounds present in normal superphosphate are (1) calcium sulfate ($CaSO_4$) with 0, 0.5, or 2 moles of hydration water; and (2) monocalcium phosphate, monohydrate ($CaH_4P_2O_8 \cdot H_2O$). Minor components consist of dicalcium phosphate, calcium iron phosphate, calcium aluminum phosphate, and such inert materials as silicon, fluosilicate salts, unreacted rock, organic matter, and phosphates of other metals present in the rock. Apatite is the major constituent of the phosphate rock that reacts with the sulfuric acid to form these chemical compounds.

As in any manufacturing process, the main operating objective is to make an acceptable product at as low a cost as possible. The principal factors affecting acceptability of the product in superphosphate manufacture are:

1. Physical condition which is affected adversely by high moisture and free acid content;

2. Content of available phosphate when the product is sold on a guaranteed minimum analysis basis. It is desirable to have as high a phosphate content as possible, and it is helpful to the user to have a fairly uniform available P_2O_5 content from shipment to shipment.

3. Ammoniating characteristics; the product should be sufficiently porous and reactive to allow good ammoniation when it is used in making mixed fertilizer.

4. Graininess. There appears to be a growing demand, here and abroad, for a grainy rather than a powdery product. Aside from the improvement in physical condition, this makes the product more acceptable for the various uses to which nongranular superphosphate is put.

Considerable emphasis is placed on efficient use of raw materials, especially in regard to getting high conversion of phosphate to the available (citrate soluble) form. Finding the ratio of acid to rock that gives a good product at the lowest overall raw material cost is an important operating objective. The main process variables in manufacture of superphosphate are acid temperature and concentration, and acid-rock ratio. Particle size of rock is important also, as are the grade and type of rock and acid used.

Process Description

The term "normal superphosphate" is used to designate a fertilizer material containing 15-21% P_2O_5. It is prepared by reacting ground phosphate rock with 65-75% percent sulfuric acid. Rock and acid are mixed in a reaction vessel, held in an enclosed area (den) while the reaction goes to partial completion (approximately 30 minutes), and transferred to a storage pile where the reaction continues. Following storage for "curing", the product is most often used as a raw material in the production of granular fertilizers. It can also be granulated for sale as granular superphosphate. To produce granular normal superphosphate, cured superphosphate is fed through a clod breaker and sent to a rotary drum granulator where steam, water, and acid may be added to aid in granulation. The material then passes through a rotary dryer, a rotary cooler, screened to specification, and sent to storage for sale as bulk or bagged product. A generalized flow diagram of the process for the production of normal superphosphate is shown in Figure NSP-1.

Air Emission Characteristics

Sources of emissions at a normal superphosphate plant include rock unloading and feeding, mixer (reactor), den, curing building, and fertilizer handling operations. Rock unloading, handling and feeding generate particulate emissions of phosphate rock dust. The mixer, den, and curing building emit gaseous fluorides (HF and SiF_4) and particulates composed of fluoride and phosphate material. Fertilizer handling operations release fertilizer dust. Emission factors for the production of normal superphosphate are presented in Table 6.10.1-1. These emission factors are averages based on source test data from controlled phosphate fertilizer plants in Florida.

Air Pollution Control Measures

At a typical normal superphosphate plant, the emissions from the rock unloading, handling, and feeding operations are controlled by a baghouse. The mixer and den emissions are controlled by a wet scrubber. The emissions from the curing building and fertilizer handling operations normally are not controlled.

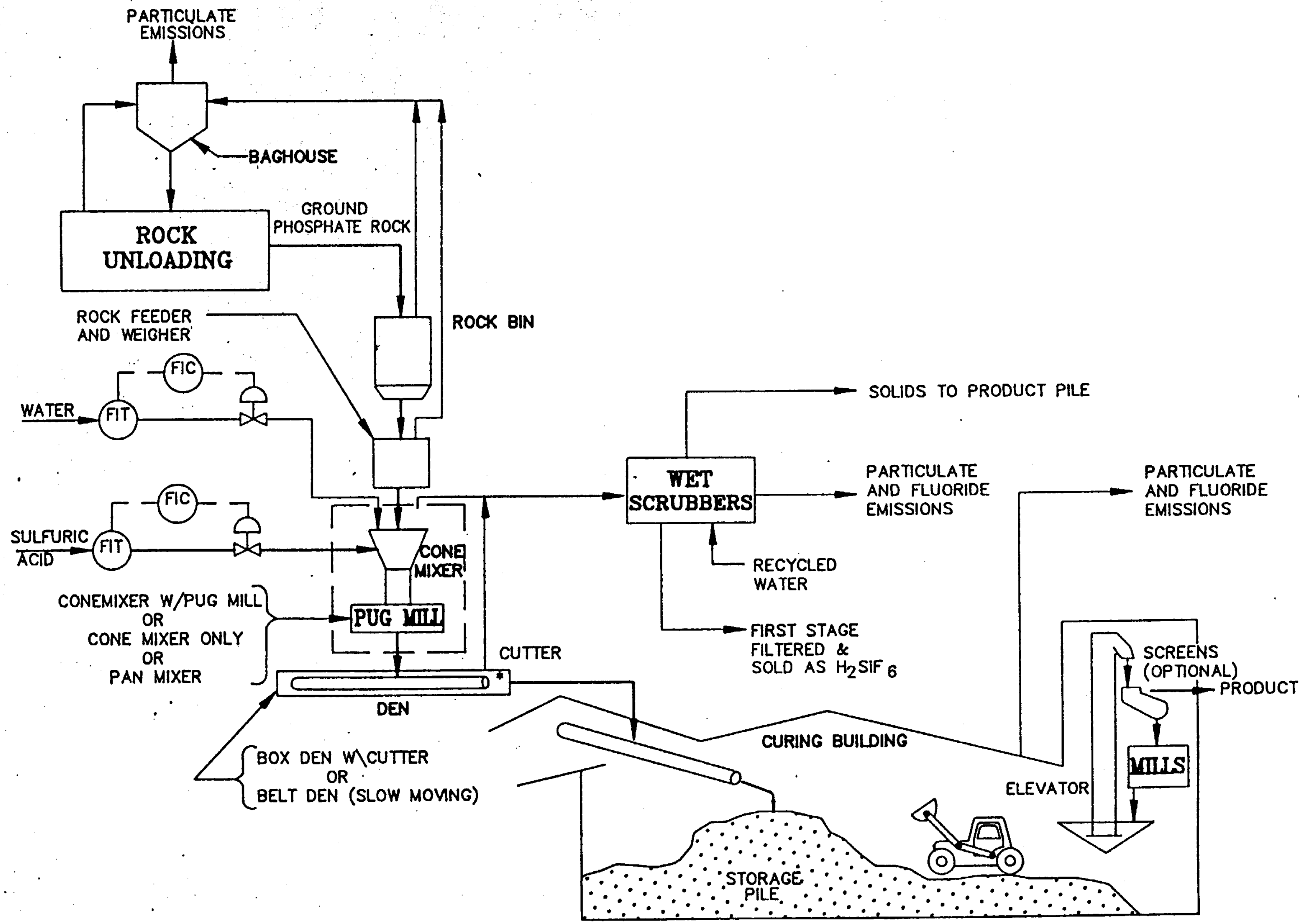

FIGURE NSP-1

NORMAL SUPERPHOSPHATE PROCESS FLOW DIAGRAM

Table 6.10.1-1. Emission Factors for the Production of Normal Superphosphate (See Ref. 1, Page 6)

Emission point	Pollutant	Emission factor lb/ton P_2O_5	Emission factor kg/MT P_2O_5
Rock unloading[a]	Particulate	0.56	0.28
Rock feeding[a]	Particulate	0.11	0.06
Mixer and den[b]	Particulate	0.52	0.26
	Fluoride	0.20	0.10
Curing building[c]	Particulate	7.20	3.60
	Fluoride	3.80	1.90

[a] Factors are for emissions from baghouse with an estimated collection efficiency of 99%.
[b] Factors are for emissions from wet scrubbers with a reported 97% control efficiency.
[c] Uncontrolled.

Particulate emissions from ground rock unloading, storage, and transfer systems are controlled by baghouse collectors. These cloth filters have reported efficiencies of over 99%. Collected solids are recycled to the process.

Silicon tetrafluoride and hydrogen fluoride emissions, and particulate from the mixer, den, and curing building are controlled by scrubbing the offgases with recycled water. 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 contacting devices with small gas passages for emissions control is therefore limited. Scrubber types that can be used are cyclonic, venturi, impingement, jet ejector, and spray crossflow packed. Spray towers also find use as precontactors for fluorine removal at relatively high concentration levels (greater than 3,000 ppm, or 4.67 g/m³).

Air pollution control techniques vary with particular plant designs. The effectiveness of abatement systems in 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. The scrubbed fluorides are collected as hydrofluosilicic (H_2SiF_6) acid and are sold for municipal water fluoridation. An efficiency of 98% for particulate control is achievable.

Key Words

Normal superphosphate, phosphate rock, sulfuric acid, fertilizer, den, mixer, scrubber, fluoride, particulate.

References for Section on Normal Superphosphate

1. Portions of this chapter were edited from AP-42, U.S. EPA's Emission Factors Handbook, Vol 1, Chapter 6.10.1 and U.S. Department of Agriculture & Tennessee Valley Authority, Superphosphate: Its History, Chemistry, and Manufacture, December 1964.

2. North Carolina requires 18% P_2O_5 minimum; the Official Journal of the European Communities lists 16% P_2O_5 as the minimum for normal superphosphate.

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