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Air Pollution Emissions and Control Technology: Nitrogen and Phosphate Fertilizer Industries

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Canada

AIR POLLUTION EMISSIONS AND CONTROL TECHNOLOGY: NITROGEN AND PHOSPHATE FERTILIZER INDUSTRIES

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ABSTRACT

The Canadian nitrogen and phosphate fertilizer and fertilizer precursor industries are examined; the air contaminant emissions from these industries are estimated and an overview of the technology available to control these emissions is presented.

Data were obtained primarily from a 1977 Environment Canada questionnaire. Nitrogen oxides, suphur dioxide, ammonia and fluoride are the atmospheric contaminants of most concern originating from this industry.

RÉSUMÉ

On fait l'étude des industries qui fabriquent des engrais au phosphate et à l'azote et de celles qui produisent les matières premières pour les engrais. On a estimé leurs émissions de contaminants atmosphériques et on présente un aperçu des techniques qui peuvent être employées pour réduire ces émissions.

Les données proviennent surtout d'une enquête par questionnaire faite en 1977 par Environnement Canada. Les polluants atmosphériques les plus à craindre sont les oxydes d'azote, le dioxyde de soufre, l'ammoniac et les fluorures.

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1 INTRODUCTION

1.1 Scope

This study pertains to air pollution control in the nitrogen and phosphate fertilizer industries, including fertilizer intermediates, in Canada. Discussed are the size and location of plants, the products and processes, the magnitude and nature of the air pollutant emissions, and emission control technology.

1.2 Purpose

The purpose of this report is to provide an overview of the Canadian fertilizer and precursor industries from an air contaminant emission viewpoint. It is intended to provide a synopsis of environmental, technical and atmospheric emission information for the provinces, the industry and other interested parties. In addition this report is intended to assist in the development of federal briefs, state-of-the-art reviews, and other documents related to air pollutant emissions from the fertilizer industries.

1.3 Information Sources

Information was obtained through a literature search, an industry questionnaire survey and plant visits. U.S. Environmental Protection Agency publications, the Atmospheric Emission Questionnaire completed by the Canadian fertilizer industry for Environment Canada in 1978, the fertilizer guidelines prepared by the Alberta Department of the Environment, and information from a seminar sponsored by Environment Canada and the Canadian Fertilizer Institute in November 1978 were most useful. The Canadian Fertilizer Institute assisted in many ways, including the arrangement of plant tours and the review of this study.

2 INDUSTRY DESCRIPTION

2.1 History and Growth

The first Canadian fertilizer plant commenced operation in 1869 (1) at Brockville, Ontario, for the manufacture of superphosphate. Since that time, the industry has undergone major changes and expansions as crop acreages expanded and crop production became more intensive. The first phase of rapid growth was from 1926 to the immediate post-war years. In the 1950s the production growth rate dropped considerably, but the 1960s saw a sharp rise in production and consumption. The average production growth rate in Canada throughout the 1960s was 10.8% annually. Combined output of nitrogen and P_2O_5 equivalent increased from 412 000 tonnes in 1959/60 to 1 030 000 tonnes in 1968/69 (2), making Canada a major producer of fertilizers.

By 1969, however, there was an unanticipated decline in fertilizer sales in North America as well as a marked reduction in exports to developing countries. This reduced demand for fertilizers lasted until 1972 (3), a period during which most manufacturing plants were operating at 50-60% of design capacity. In 1973 there was a pronounced upswing in demand for fertilizers in North America; Western Canada increased consumption by 36.5% (4), as high grain prices spurred farmers to expand crop acreages and optimize fertilizer inputs. This increase, together with the occurrence of world-wide fertilizer shortages, was responsible for an expansion of Canadian production capacity. The combined production capacity of nitrogen and P_2O_5 equivalent increased to about 4 million tonnes in 1977.

There is a worldwide trend towards increased use of nitrogen with consumption of nitrogenous fertilizers being more than either phosphorus- or potassium-based ones (5). For example, in 1970, on a world-wide basis, 26 million tonnes of nitrogen, 17 million tonnes of phosphate expressed as P_2O_5 equivalent and 14 million tonnes of potassium expressed as K_2O were applied to the soil. By 1980 production had increased as follows; nitrogen to 62 million tonnes, phosphate to 34 million tonnes and potassium to 26 million tonnes. In Canada, the use of nitrogen has been increasing steadily; however, phosphate fertilizer is still being consumed in large quantities. The consumption of potash, in relation to the other two nutrients, is smaller and its utilization differs between Eastern and Western Canada. In the West, soils generally contain sufficient potash. However, in Eastern Canada, this is not the case and potash is added in substantial quantities.

2.2 Summary of the Total Canadian Annual Emissions

Table 1 summarizes the air pollutant emissions from the Canadian fertilizer industry, based primarily on questionnaire data (6); however, when data from this source were not available, emission factors were used.

TABLE 1 SUMMARY OF AIR CONTAMINANT EMISSIONS (TONNES) FROM ALL FERTILIZER AND PRECURSOR PROCESSES IN CANADA, 1977

Source	Nitrogen Oxides (As NO_2)	Ammonia	Urea Dust	Fluoride	Phosphate Rock Dust	Sulphur Dioxide
Ammonia	7 200*					
Nitric Acid	6 400					
Ammonium Nitrate		1 270				
Urea		8 000	350			
Normal Superphosphate				7		
Triple Superphosphate				11		
Phosphoric Acid				119		
Ammonium Phosphate				625		
Phosphate Rock Handling					335	
Gypsum Pond Emissions				407*		
Sulphuric Acid						31 500
TOTAL	13 600	9 270	350	1 169	335	31 500

* Based on emission factors.

3 NITROGEN FERTILIZER INDUSTRY

3.1 General

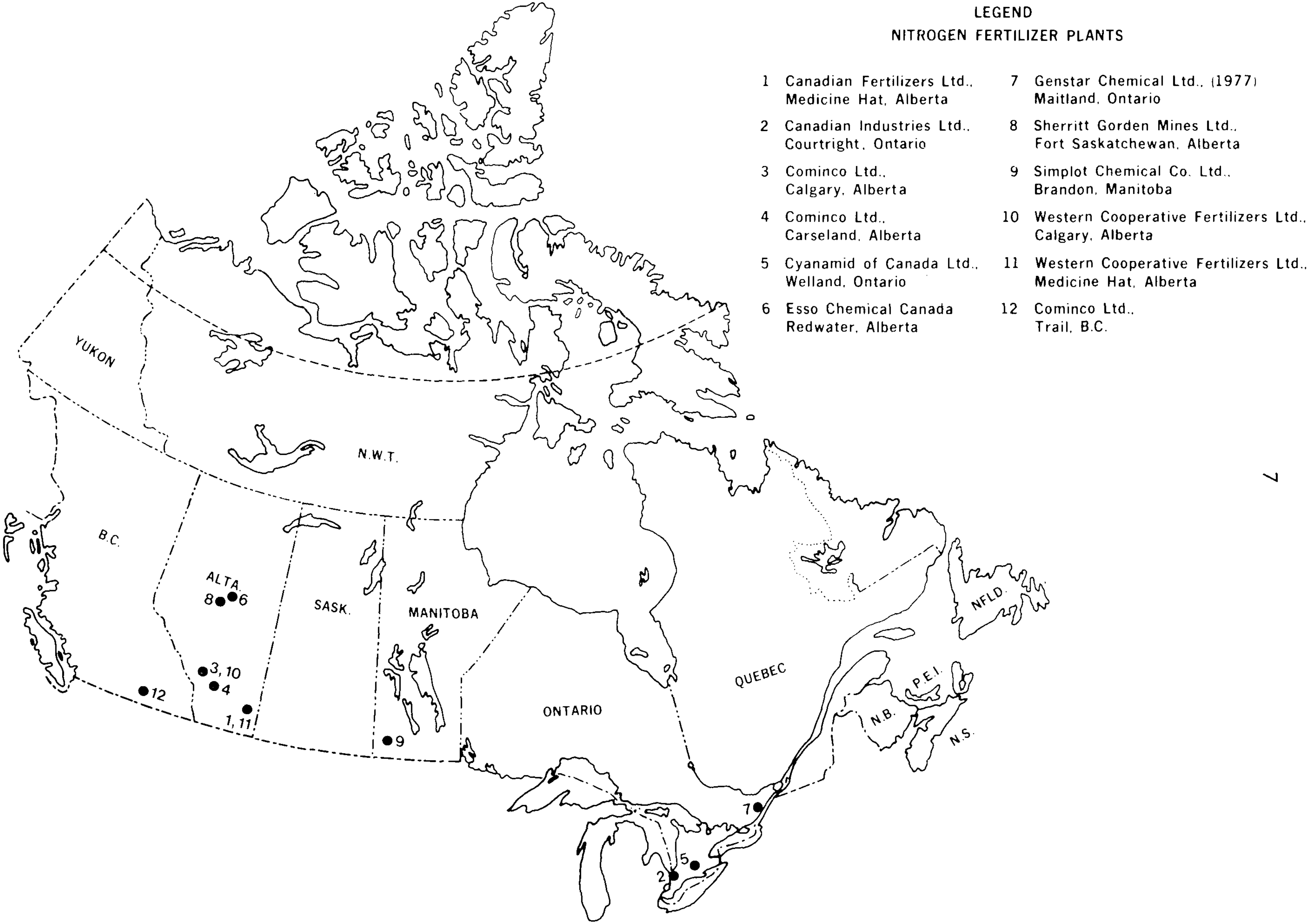
There are twelve nitrogen fertilizer complexes in Canada: seven in Alberta, three in Ontario, and one in each of Manitoba and British Columbia.

The production of ammonia, ammonium nitrate and urea fertilizers is covered in this report as well as the precursor nitric acid which is reacted with ammonia to produce ammonium nitrate. The capacity and location of Canadian nitrogen fertilizer plants in 1977 are given in Table 2 and Figure 1(6).

TABLE 2 LOCATION AND PRODUCTION CAPACITY OF NITROGEN FERTILIZER MANUFACTURING PLANTS IN CANADA, 1977*

Company	Plant Location	Ammonia	Ammonium Nitrate	Urea	Nitrogen Solution	Nitric Acid
Canadian Fertilizers Limited	Medicine Hat, Alberta	2265	-	1359		
Canadian Industries Limited (1977)	Courtright, Ontario	898	378	219	-	378
Cominco Limited	Calgary, Alta.	306	167	216	-	132
	Carseland, Alta.	1041	-	1358	-	-
	Trail, B.C.	186	-	-	-	-
Cyanamid of Canada Limited	Welland, Ontario	632	586	271	-	452
Esso Chemical Canada	Redwater, Alberta	682	687	-	-	517
Genstar Chemical Limited (1977)	Maitland, Ontario	224	498	134	235	860
Sherritt Gordon Mines Limited	Fort Saskatchewan, Alberta	457	-	370	-	-
Simplot Chemical Co. Ltd.	Brandon, Manitoba	271	271	90	227	224
Western Co-operative Fertilizers Ltd.	Calgary, Alberta	178	268	-	-	189
Western Co-operative Fertilizers Ltd.	Medicine Hat, Alberta	186	181	-	-	150
	TOTAL	7326	3036	4017	462	2902

*Name plate capacity, tonnes per day.
*Production figures for the materials and mixtures are not additive as some of the former are used in making the latter.



LEGEND
NITROGEN FERTILIZER PLANTS

1 Canadian Fertilizers Ltd.,
Medicine Hat, Alberta

2 Canadian Industries Ltd.,
Courtright, Ontario

3 Cominco Ltd.,
Calgary, Alberta

4 Cominco Ltd.,
Carseland, Alberta

5 Cyanamid of Canada Ltd.,
Welland, Ontario

6 Esso Chemical Canada
Redwater, Alberta

7 Genstar Chemical Ltd., (1977)
Maitland, Ontario

8 Sherritt Gorden Mines Ltd.,
Fort Saskatchewan, Alberta

9 Simplot Chemical Co. Ltd.,
Brandon, Manitoba

10 Western Cooperative Fertilizers Ltd.,
Calgary, Alberta

11 Western Cooperative Fertilizers Ltd.,
Medicine Hat, Alberta

12 Cominco Ltd.,
Trail, B.C.

FIGURE 1 NITROGEN FERTILIZER PLANT LOCATIONS

4 AMMONIA

4.1 General

Of the inorganic chemicals produced in Canada, ammonia is second only to sulphuric acid in terms of tonnage and it could overtake the latter if the expansion anticipated takes place. Anhydrous ammonia can either be applied directly to the soil or used as an intermediate in the manufacture of various fertilizers.

Ammonia is manufactured in 12 plants across Canada with a combined daily production capacity of about 7 325 tonnes. It is expected that most of the expansion will take place in Alberta owing to its vast reserves of natural gas. In keeping with current industrial trends, plant designs will essentially be large capacity to ensure substantially reduced production costs. Production capacities of 1000 tonnes/day ammonia or more are now common throughout the world and new Canadian plants will most likely be of similar size.

4.2 Process Description

Ammonia is produced in Canada exclusively by the Haber-Bosch Process which involves the reaction between nitrogen and hydrogen in a converter at high temperature and pressure in the presence of a catalyst (7):

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

Ammonia production is accomplished in two stages. The first involves the preparation of ammonia synthesis gas (nitrogen and hydrogen in stoichiometric proportion) with the second involving their catalytic conversion to ammonia.

Atmospheric nitrogen is readily available, but obtaining hydrogen is a major step for the industry. In Canada, almost all of the hydrogen is obtained from the steam reforming of natural gas, although there are more than a dozen alternative processes in use throughout the world.

Production of ammonia synthesis gas requires six major steps:

1. Removal of sulphur impurities from the natural gas;
2. Catalytic reaction of natural gas with steam to form hydrogen and carbon monoxide (primary reformer);

3. Catalytic reaction of the gas from the primary reformer with air to provide the nitrogen required to make the synthesis gas, and reduce the unwanted oxygen with hydrogen (secondary reformer);
4. Shift reaction of carbon monoxide and steam at high and low temperature to form carbon dioxide and hydrogen;
5. Removal of the carbon dioxide;
6. Removal of carbon monoxide by reacting it with hydrogen to form methane in the methanator.

This mixture containing the stoichiometric ratio of nitrogen and hydrogen is compressed between 2 000 and 3 000 psi and sent to the converter where the catalytic reaction takes place at 340-650°C to form ammonia.

The product gas stream is cooled to condense the ammonia which is removed in a liquid/gas separator. Conversion is low and the unreacted gases are recirculated to the converter. To prevent build-up of inert material in the recirculating stream, a small quantity of purge gas is continuously bled from the system. A typical process flow sheet for ammonia manufacture is presented in Figure 2.

4.3 Air Contaminant Emissions and Controls

The emission of most concern is purge gas which contains the impurities vented from the synthesis loop to prevent build-up. This gas contains methane, ammonia, hydrogen, argon and other impurities with ammonia being the contaminant of most concern.

Emissions are controlled by one or more of the following techniques:

(1) Incineration in boilers and/or reformers;
(2) Scrubbing with water, sulphuric acid or other suitable media;
(3) Use as fuel for a nitric acid tail-gas combustion unit;
(4) Scrubbing the feed-stock hydrogen with liquid nitrogen which reportedly eliminates the necessity of purging the product stream.

Emergency ammonia releases are flared or vented through a tall stack.

4.4 Survey of Emissions

A survey of the nitrogen fertilizer industry, including ammonia manufacture, was completed by Environment Canada in 1978 by means of a joint air-water questionnaire.

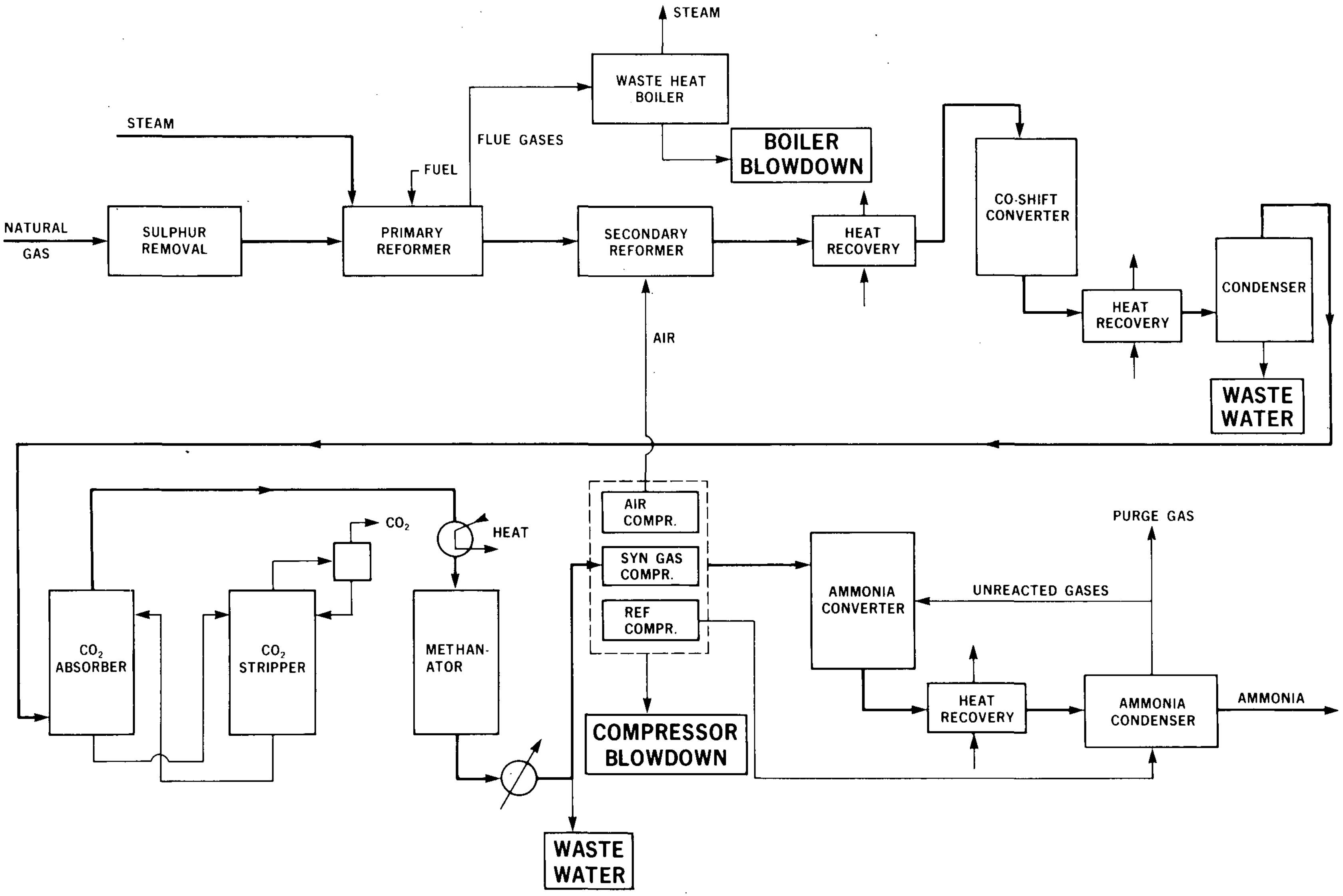


FIGURE 2 PROCESS FLOW SHEET AMMONIA PRODUCTION

Seven of the twelve plants manufacturing ammonia reported using the purge gas as fuel at boilers and reformers within the ammonia plant. Each of the following three utilized a different method to control purge gas emissions, as follows:

(1) Scrubbing with water;
(2) Using it as fuel at a nitric acid plant;
(3) Scrubbing the hydrogen produced from natural gas with liquid nitrogen, thereby reportedly eliminating the need to purge the synthesis gas.

One plant stated emissions were nil and provided no further information; another did not complete the questionnaire.

Vent gases from storage tanks were reported as being refrigerated, condensed and sent back to storage under normal conditions. Under emergency situations, the ammonia is either vented through a tall stack or incinerated.

Emission data provided by these questionnaires were insufficient to estimate a nationwide emission total. Consequently, an emission factor for nitrogen oxides, expressed as equivalent nitrogen dioxide, of 2.7 kg per tonne of ammonia produced, was used (8). Based on this factor, nationwide annual emissions of nitrogen oxides were 7 200 tonnes.

5 PRODUCTION OF NITRIC ACID AS AN INTERMEDIATE

5.1 General

Nitric acid is an important intermediate in the fertilizer industry. It can either be used for the manufacture of ammonium nitrate or for the acidulation of phosphate rock. About 75% of the nitric acid produced in the world is used in the fertilizer industry, 15% in explosives manufacture and the remainder in the plastics and resin industries (9).

5.2 Process Description

All major commercial processes for the manufacture of nitric acid at concentrations between 50 and 70% use the same basic process but employ different operating conditions (10). Basically a modern nitric acid process proceeds in two stages:

(i) Ammonia is oxidized with air in a catalytic converter containing a pad of platinum-rhodium gauzes. A rapid exothermic reaction takes place at 800-960°C and nitric oxide is produced.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1)$$

The heat of reaction is recovered in waste heat boilers. Gases leaving the boilers are cooled and most of the water is condensed out. The condensate, a dilute solution of nitric acid, is used in the absorption tower.

(ii) The gases pass into the absorption tower together with air and water. The nitric oxide reacts with oxygen homogeneously in the gas phase to form nitrogen dioxide, which is then absorbed in water.

$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (3)$$

The nitric oxide produced by Reaction (3) in the liquid phase is reoxidized to nitrogen dioxide in the spaces between the trays in the absorption column.

Figure 3 is a representative flow sheet of a nitric acid process.

The presence of NO_x in the tail gas from nitric acid plants is a major environmental problem The type of NO_x abatement technique that can be employed depends to a large extent on the operating pressure. There are six commercially available

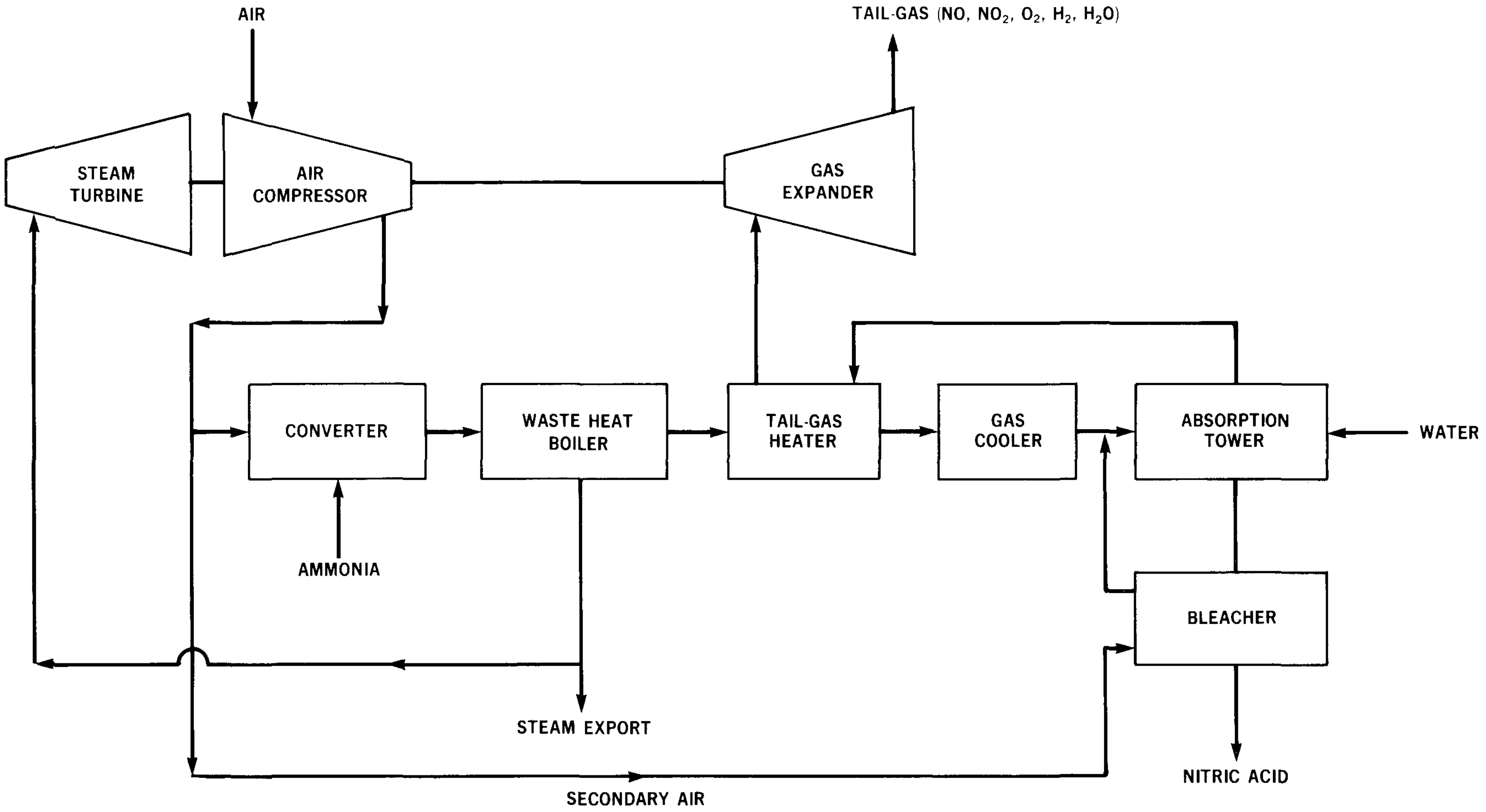


FIGURE 3 PROCESS FLOW SHEET NITRIC ACID PRODUCTION

processes for NO_x abatement which are briefly described subsequently. All of these processes successfully abate the NO_x in the tail-gas streams to a level of 200 ppm or less. By comparison, nitric acid plants with no abatement techniques emitted 2 000 to 5 000 ppm NO_x in the tail-gas stream.

5.3 Sources of Pollution

The only continuous source of pollution from a nitric acid plant is the tail gas which contains NO_x.

The composition of the tail gas depends on the efficiency of the absorption system. Older atmospheric-pressure plants frequently used absorption in an alkaline solution. All modern processes carry out absorption at not less than 3 atmospheres. Typical tail-gas composition before treatment is:

NO, NO_2 (NO_x)	800 - 3000 ppm by volume
Oxygen	2 - 3.5% by volume
Water	1%
Nitrogen	Balance

With a concentration of 1000 ppm in the tail gas, the emission of nitrogen oxides, calculated as NO_2, is about 7 kg/tonne of 100% acid produced. Part of the emission is in the form of nitrogen dioxide which if present at greater than 50 ppm gives rise to a characteristic reddish-brown plume.

5.4 Emissions and Controls

5.4.1 **General.** Various technologies have been developed for treating tail gas from nitric acid plants. The six commercially applied NO_x-abatement techniques are described below, namely: extended absorption, catalytic reduction, selective catalytic reduction, the Masar process, the Purasiv N process and the Goodpasture Chemical Abatement process.

5.4.2 **Extended Absorption.** The concentration of NO_x leaving the absorber is reduced by increasing the residence time in the absorber. This is achieved in existing plants by installing an additional absorber. In new plants the absorber is considerably larger than in the earlier nitric acid plants. In some cases NO_x abatement is achieved by additional cooling as well as extended absorption, and in some instances a combination of extended absorption and catalytic combustion is used. Emissions as low as 1.5 kilograms of NO_x per tonne of 100% nitric acid produced (200 ppm NO_x expressed as NO_2) are possible with this process (11).

5.4.3 **Catalytic Reduction.** The tail gas leaving the absorber is heated and passed over a platinum or palladium catalyst. Fuel is introduced to react with the oxygen in the tail gas, and then excess fuel reacts with the NO_x to form N_2(12). The energy of combustion is recovered in an expansion turbine and boiler downstream of the catalytic combustor. An emission level of 200 ppm NO_x or less is achievable with this process (13).

5.4.4 **Selective Catalytic Reduction.** The tail gas leaving the absorber is heated and mixed with ammonia upstream. Ammonia and nitrogen oxides are preferentially absorbed on the catalyst, reacting within the pores to form nitrogen and water. An emission level of 200 ppm NO_x or less is possible with this process (14).

5.4.5 **The Masar Process.** The tail gas is cooled, and scrubbed with chilled water in the first section of the Masar absorber. In the second section it is scrubbed with urea solution which is converted to ammonium nitrate. Final scrubbing of the tail gas is performed with process water. An emission level of 200 ppm NO_x or less is possible (15).

5.4.6 **The Purasiv N Process.** Chilled tail gas from the absorber is passed through an adsorber vessel containing a molecular sieve adsorbent/catalyst in which NO is converted to NO_2 and the NO_2 is selectively adsorbed. An emission level of less than 50 ppm can be reached; this is equivalent to 0.375 kg of NO_x (as NO_2) per tonne of 100% nitric acid produced (16).

5.4.7 **Goodpasture Chemical Abatement.** This method of abatement employs four stages of absorption and reaction in a liquid/gas scrubber. The gas is first scrubbed with acidic ammonium nitrate generating free nitric acid. In the second stage the scrubbing medium is a basic ammonium nitrate solution. Scrubbing then takes place with water in a venturi scrubber, and finally in a packed bed again with water. An emission level of 200 ppm NO_x is possible (17). There is, however, some concern regarding the safety aspects of this process (18).

5.4.8 **Survey of Emissions.** Information from the industry questionnaire survey and other sources indicate that eight plants produce nitric acid in connection with the fertilizer industry in Canada.

Six plants utilize catalytic reduction to convert NO_x to N_2. One uses extended absorption, with the tail gas going to ammonia production, and one scrubs the tail gas with ammonia to produce ammonium nitrate.

Six plants report NO_x emissions as equivalent NO_2 at less than 6 kg per tonne of 100% nitric acid produced and two report emissions in excess of 20 kg per tonne.

The annual atmospheric emissions of nitrogen oxides (expressed as equivalent NO_2) in Canada in 1977 total 6400 tonnes (6).

6 AMMONIUM NITRATE

6.1 General

Pure ammonium nitrate contains 35 percent nitrogen; fertilizer grades contain at least 33.5 percent nitrogen.

Ammonium nitrate is very hygroscopic and requires a coating of clay, diatomaceous earth, or other conditioning agent to prevent caking. It is also extremely hazardous when mixed with organic compounds as exemplified in the manufacture of explosives.

Ammonium nitrate may be applied directly to the soil or used as an ingredient in granulating mixtures or in the preparation of liquid fertilizers.

6.2 Process Description

The production of ammonium nitrate liquor involves intimately mixing and reacting nitric acid and ammonia:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

This reaction is done in a neutralizer and takes place very rapidly with the generation of a considerable amount of heat. The nitric acid fed to the neutralizer contains water and the heat generated in the reaction generates steam which is condensed or vented to the atmosphere.

In many fertilizer plants the ammonium nitrate neutralizer is a convenient sink for tail gases containing ammonia from other units. The most common tail gas is the partial recycle urea plant off-gas which contains both ammonia and carbon dioxide.

In an atmospheric neutralizer the ammonium nitrate liquor is produced at a concentration near 83%. This liquor has to be further concentrated before granular ammonium nitrate can be produced.

Concentration can be achieved in either a vacuum evaporator or an air-swept evaporator. After concentration it is prilled or granulated. Since none of the Canadian plants reported granulating the ammonium nitrate, it will not be discussed further.

In the process of producing prilled ammonium nitrate, the liquor is concentrated to a melt containing approximately 99.8% ammonium nitrate (95% for low-density prills) and then sprayed, generally through shower heads, from the top of a tall tower. As the droplets fall down the tower they are cooled by a countercurrent stream of air, the air being exhausted to the atmosphere by a set of fans mounted at the top of the tower.

The prills are collected at the base of the tower on a conveyer belt and are cooled, screened and coated before being conveyed to storage. Figure 4 is a typical process flow sheet.

6.3 Emissions and Controls

6.3.1 General. Ammonium nitrate, nitric acid and ammonia fumes are the emissions of concern from this process. The neutralizer, evaporator and prilling tower are the principal sources. A synopsis of the types of emissions and their control is presented.

The dangers of combustion and explosion resulting from ammonium nitrate being incorrectly handled are well known, and this gives rise to considerable problems in designing an ammonium nitrate plant. The least hazardous conditions are often not those that minimize pollution and some compromise must be reached. Decomposition of ammonium nitrate is catalyzed by the presence of chlorides, organic materials and some metals. It is therefore dangerous to recycle spilled material.

6.3.2 The Neutralizer. The major source of pollution from neutralizers is the tail-gas stream which consists mainly of steam but may contain CO_2 if the off gas from the urea plant is fed to the neutralizer.

The tail gas contains very small particles of ammonium nitrate, nitric acid vapour and ammonia fumes. The consequence of these contaminants is that the particulate can act as nuclei in conjunction with condensing steam causing a very dense smog. In addition nitric acid and ammonium nitrate emissions are quite corrosive to surrounding structures and equipment. In some instances the steam in the tail gas is used as a heating medium. The resulting condensate is contaminated and is used where possible in liquid fertilizer formulations in the fines-dissolving tank and in the scrubbers.

Ammonium nitrate emissions from conventional neutralizers without scrubbers range from 1.3 to 1.8 kg/tonne of product for those plants that do not utilize the urea off-gas. On a kg/tonne of 100% ammonium nitrate produced basis, nitric acid emissions range from 0.1 to 0.15 and when operating on the basic side, ammonia losses range from 1.5 to 2.5 (19).

One approach for reducing emission problems has been to redesign the neutralizer to provide greater residence time, more intimate mixing, and lower exit velocity.

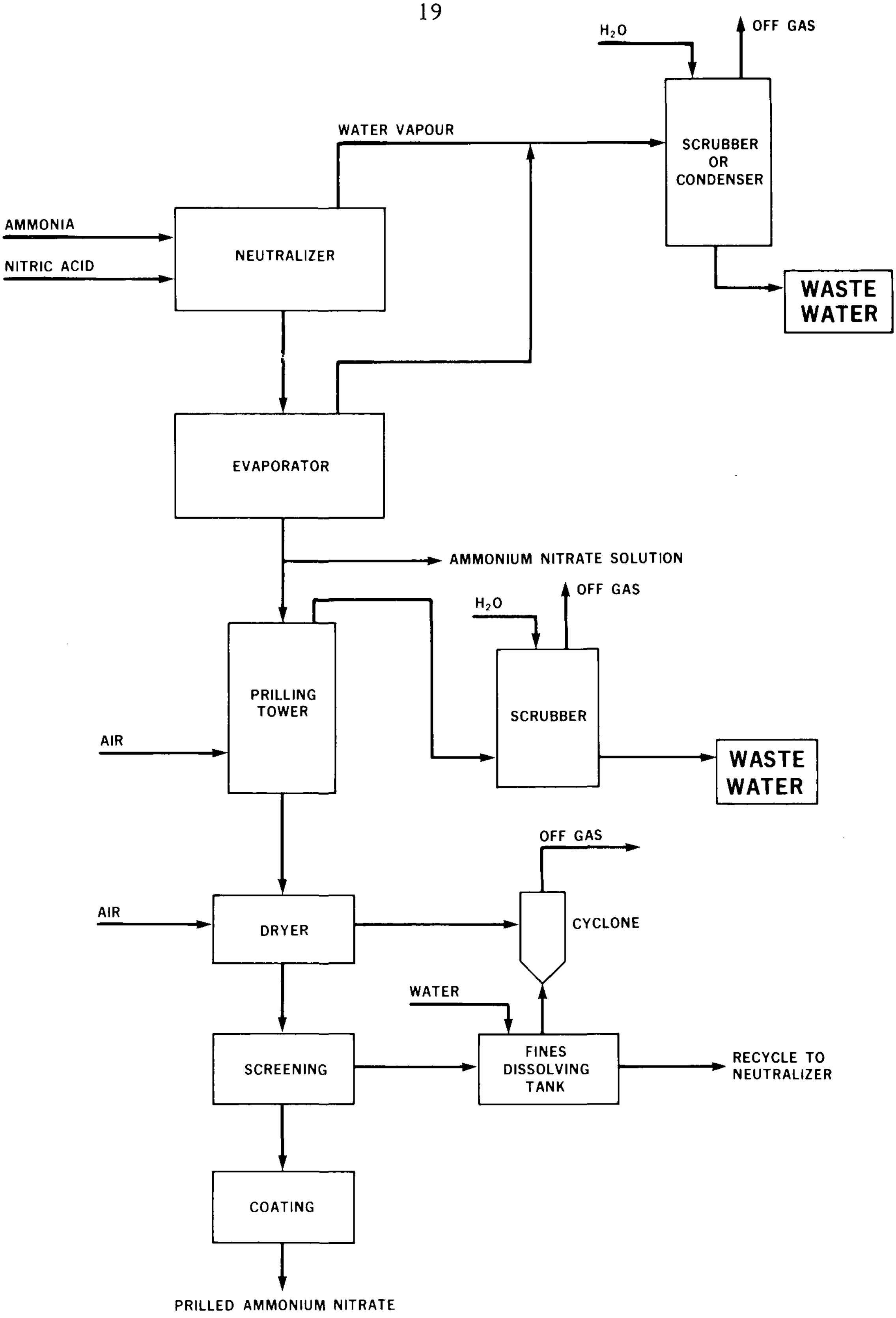


FIGURE 4 PROCESS FLOW SHEET AMMONIUM NITRATE PLANT

In the United States many companies have chosen to eliminate only the ammonium nitrate particulates by installing high-efficiency fibre filters which virtually eliminate the particulate emissions but which do not affect the nitric acid or ammonia vapour emissions.

In other cases the system chosen has been a combination of absorption and filtration. The tail gas is first passed through a packed bed scrubber where it is contacted with acidic 50% ammonium nitrate liquor. Here most of the nitric acid or ammonia is removed. The tail gas leaving the scrubber passes through a high-efficiency fibre filter to remove particulates and mist. Using these techniques, total emissions, i.e. particulates, nitric acid and ammonia, can be reduced to 70 kg/day or less on a 500-tonne/day neutralizer (20).

6.3.3 The Evaporator. Two types of evaporators are used, vacuum and air-swept. In the case of a vacuum evaporator the overhead condensate is contaminated with ammonium nitrate. This stream is most conveniently disposed of in the production of liquid fertilizer solutions or as a make-up feed to the nitric acid plant absorber. The tail gas leaving an air-swept evaporator contains both particulate matter and ammonia fumes. It generally passes through a venturi scrubber and final clean-up can be incorporated as part of a prilling tower emission control system.

6.3.4 The Prilling Tower. There are three contributions to the emissions from the prilling tower:

1. Carryover of prills (ammonium nitrate dust);
2. Ammonium nitrate fume;
3. Ammonia.

Dust emissions from a prilling tower can be kept to low levels by using a low air velocity in the tower. When the tower is fully loaded the carryover of dust must be balanced against the degree of cooling required to solidify the prills. If the tower is only slightly loaded it will be possible to decrease the air velocity.

Ammonium nitrate fume consists of small solid particles, generally less than 5 µm in diameter, formed by evaporation and subsequent condensation or by chemical decomposition and subsequent recombination in the air. It can appear as a dense blue smoke, but in a well-designed plant it should be no more than a faint bluish haze.

The evolution of both ammonia and fume depends upon melt pH, melt temperature and the air velocity over the surface of the melt. The optimum pH at which the total loss in terms of nitrogen is minimized is about 4.5, but there is a tendency to operate at a higher pH to give a less visible plume at the expense of increased ammonia losses. In industrial areas where there are appreciable amounts of sulphur dioxide in the atmosphere the ammonia may be more serious than is apparent because of the tendency to form ammonium sulphate which can cause mist formation.

The prilling temperature frequently employed is 180-185°C, but it is possible to reduce the temperature slightly below this level, with a resultant reduction of emissions by a factor of about two. The emissions can also be reduced by lowering the velocity past the surface of the liquid droplets. This can be done by withdrawing some air at a point below the spray nozzles. Finally overall emissions are affected by the mechanical design of the top of the tower.

By careful design of the equipment, taking into account the principles discussed, and with the use of accurate process control it should be possible to reduce the losses due to ammonia and ammonium nitrate fume to less than 0.05% of production. At present this is the control procedure used by most plants in Canada.

Pollution abatement by add-on control in this particular case is extremely difficult in view of the large air flow involved as well as the small size of the particles. The first step in the solution of the problem was the development of the Cooperative Farm Chemicals Association shroud (21). The basis of the operation of the shroud is that the pollutants (micro prills, ammonia, and nitric acid fumes) are formed at the prill nozzles. This contaminated air, which represents only a portion of the total air flow, is drawn off and treated. Figure 5 shows a typical shroud or collection duct system.

The next step in abatement is to treat the air stream collected from the shroud in a set of high-efficiency fibre filters which are irrigated to wash off insolubles as well as the ammonium nitrate.

The alternative to the method of abatement described, is to collect the full air flow from the prill tower and treat it in the same manner.

Prior to the abatement techniques described here, emissions from a 500-tonne /day ammonium nitrate prill tower were in the range of 3 tonnes/day. Installation of the Cooperative Farm Chemicals Association shroud and filter system can reduce emissions to 170 kg/day (about 94% control efficiency), and the opacity can be as low as 10% (22).

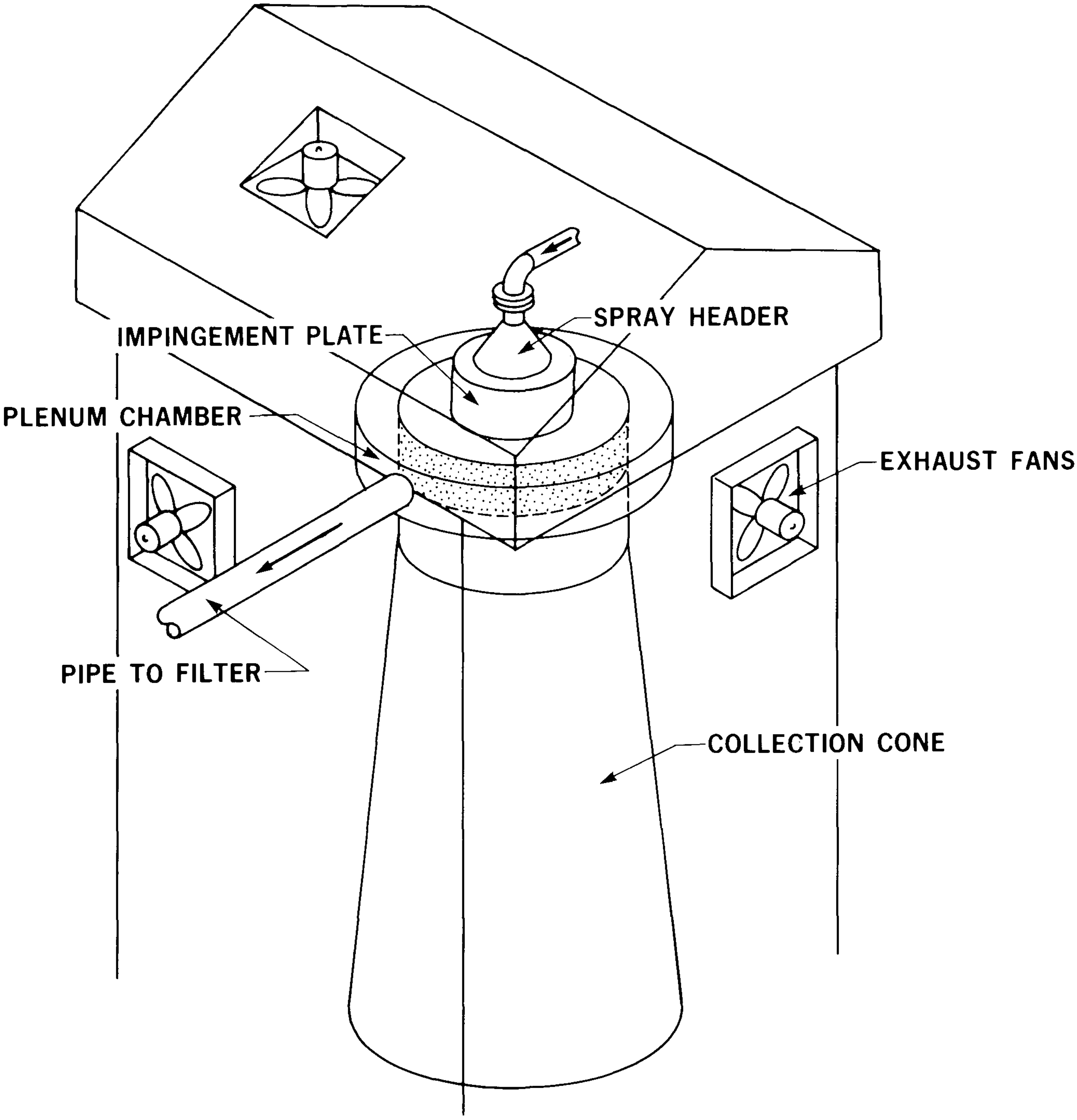


FIGURE 5 PRILL TOWER DUST COLLECTION DUCT

6.3.5 Coolers and Dryers. Air streams from coolers and dryers can contain large quantities of ammonium nitrate dust. Wet scrubbers are used to recover the ammonium nitrate and return it to the neutralizer. The scrubbing medium is a solution of ammonium nitrate. Recovery in this way is economical and effective.

6.3.6 Survey of Emissions. Eight companies in Canada produce ammonium nitrate. The major emission sources of ammonia and ammonium nitrate are the neutralizer, the evaporator and the prilling tower. There were no nitric acid vapour emissions reported probably because the equipment was operated under basic conditions.

Neutralizer emissions were reported as being controlled by a scrubber (one plant), scrubbing followed by condensation (one plant), demisting (one plant), condensation (four plants) and venting to the atmosphere (one plant). Reported ammonia emissions were in the range of zero to 1.0 kg of ammonia per tonne of ammonium nitrate produced with the average being 0.5. Particulate emission data were not considered sufficient to warrant inclusion.

Evaporator emissions were reported as being controlled by scrubbing (three plants), scrubbing followed by a total condenser (one plant), condensation (one plant), and discharging the gases to a stack (three plants). While all plants reported the type of control, many did not report on the magnitude of emissions; those that did reported emissions of ammonia between 0.1 and 0.9 kg of ammonia per tonne of ammonium nitrate produced with the average being about 0.5. Particulate emission data were not considered sufficient to warrant inclusion.

The prill tower discharge air, contaminated with ammonia, ammonium nitrate fume and dust, is vented directly to the atmosphere. Reported ammonium nitrate dust emissions ranged from 0.6 to 4.5 kg per tonne of product, the average being 3.0. In terms of kilograms of particulate per 1000 kilograms of flue gas, the reported high and low values were 0.3 and 0.03 with the average being 0.12. Reported ammonia emissions ranged from 0.1 to 0.4 kg per tonne of product with the average being 0.2. Subsequently one plant has installed a Cooperative Farm Chemicals Association shroud. However, emission data on this control device are not available.

Table 3 summarizes the annual estimated emissions associated with ammonium nitrate fertilizer manufacture. Insufficient data were reported on particulate emissions from neutralizers and evaporators to enable the calculation of emission factors, however, on the basis of the information collected, these emissions are considered insignificant.

TABLE 3 AMMONIUM NITRATE FERTILIZER MANUFACTURE IN CANADA, ESTIMATED ANNUAL EMISSIONS (TONNES), 1977

	Ammonia	Particulate
Neutralizer	480	*
Evaporator	590	*
Prilling Tower	200	2 700
Total	1 270	2 700

* Information not available.

7 UREA

7.1 General

Urea, as a granular fertilizer, has been markedly increasing in popularity in recent years due chiefly to its high nitrogen content (45%) and its ease of handling and shipping. It can be applied directly to the soil or alternatively used for preparation of granulated or bulk-blend mixtures. Eight fertilizer companies produce urea with individual production ranging between 29 000 and 436 000 tonnes per year (1977). Total production amounts to 1 183 000 tonnes per year.

7.2 Process Description

Urea is a major source of fertilizer nitrogen and is also used in the plastics and organic chemical industries.

Urea production is based on the reaction of ammonia and carbon dioxide to form ammonium carbamate which is subsequently dehydrated. Since both ammonia and carbon dioxide are obtained from an ammonia plant (carbon dioxide as a by-product), Canadian urea plants are invariably located adjacent to the ammonia installations.

The chemical reactions involved in urea production are:

$$CO_2 + 2NH_3 \rightleftarrows NH_4\,CO_2\,NH_2$$

(Ammonium Carbamate)

$$NH_4\,CO_2\,NH_2 \rightleftarrows NH_2\,CO\,NH_2 + H_2O$$

(Urea)

Although the process chemistry, as shown above, is straightforward, the actual process itself is complex. The following process description is presented as a brief overview.

The carbamate formation reaction is strongly exothermic, proceeding almost to completion. Ammonium carbamate dehydration is endothermic and proceeds to 40-60% completion. The net effect of the above two reactions is a large heat release and external cooling must be provided. Both reactions are reversible and the equilibrium conditions are dictated by pressure, temperature and concentration of the raw materials and products. By increasing the temperature, urea formation increases but the pressure has to be increased concomitantly because urea is only formed in the liquid phase. Since pressure increases markedly with temperature, the reactor temperature is rarely above

210°C. Depending on the particular process being used, the operating temperature varies between 170 and 210°C and the pressure between 135 and 400 atmospheres.

The ammonia and carbon dioxide fed into a reactor generates a product stream of urea, ammonium carbamate and water. The carbamate is subsequently converted to urea, which is recovered as a marketable product and the unreacted gases are either recycled or removed. Several alternatives are employed for carrying out these reactions:

1) <u>No Recycle</u>

No recycling of the unreacted ammonia and carbon dioxide is employed. Off-gas ammonia is used in the production of other fertilizer products or intermediates (nitric acid, ammonium nitrate, etc.) while the carbon dioxide is vented.

2) <u>Partial Recycle</u>

A portion of the unreacted ammonia is recycled to the reactor.

3) <u>Total Recycle</u>

Both unreacted gases are recycled to the reactor.

The stream exiting from the reactor is sent to a stripper where the pressure is reduced from 200 to approximately 20 atmospheres. The ammonia, carbon dioxide and water vapour are released from solution and a portion of the carbamate is dehydrated. The stripper solution goes to a decomposer to dehydrate the remaining carbamate. The 75-80% urea solution, formed at this stage, can be sold as such or solidified. Prilling or granulation are used as solidification techniques in Canada.

The solution, from the decomposer, goes to a concentrator to increase the urea concentration to greater than 98%. This urea stream is then contacted with cold air in a tower to form urea prills which are further cooled, screened, coated and packed for storage or alternatively it is sent to a granulator.

Figure 6 is a flow sheet of a representative process which uses total recycle and a prilling tower.

7.3 Emissions, Sources and Magnitude

Storage tanks and prilling towers are usually vented directly to the atmosphere; other emission sources are usually treated by scrubbing or condensation. The following list refers to emissions originating from a typical total recycle process:

i) Ammonia scrubber - ammonia, water vapour;

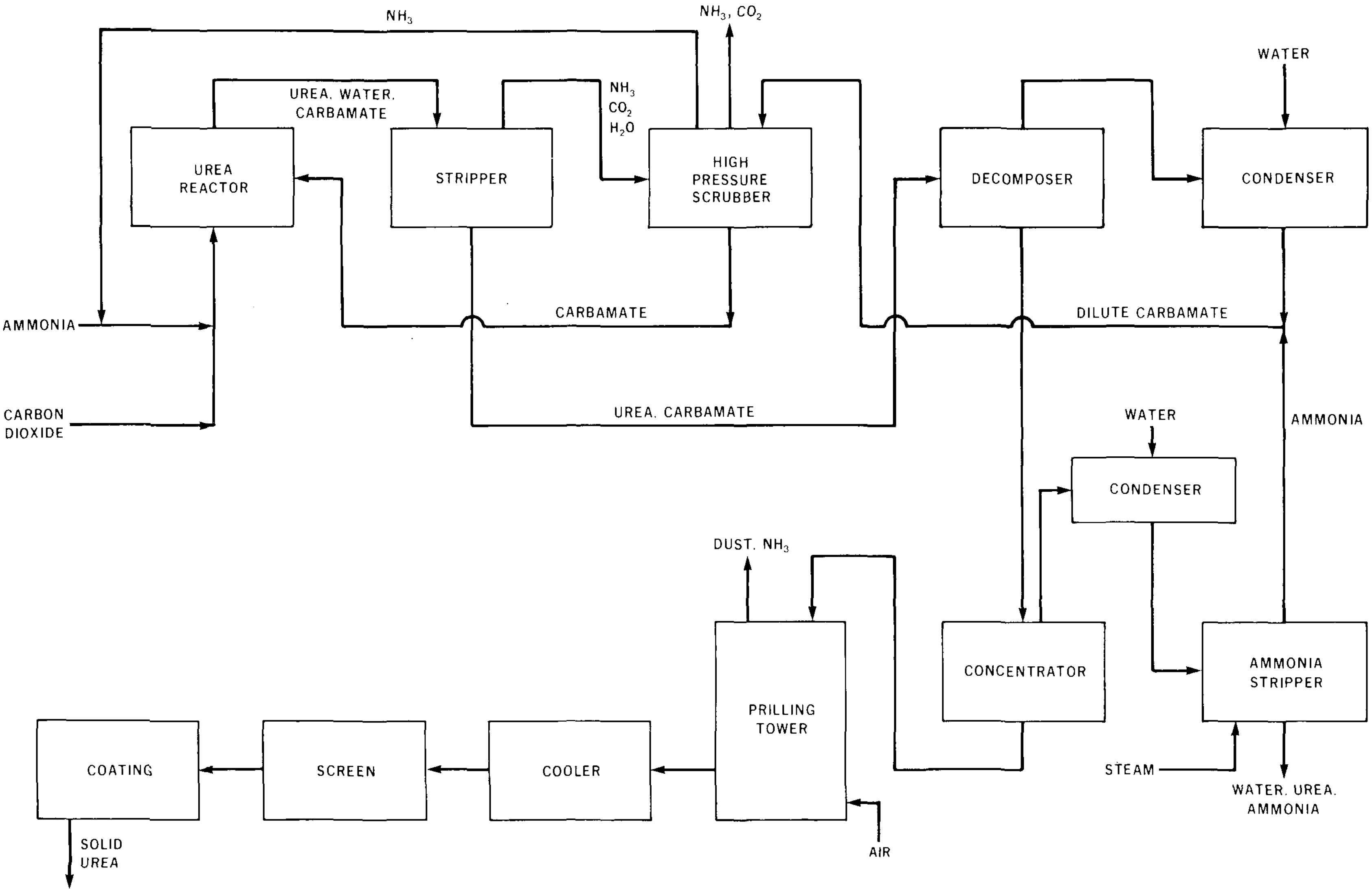


FIGURE 6 PROCESS FLOWSHEET UREA PRODUCTION: TOTAL RECYCLE AND PRILLING TOWER

ii) Condensers - water vapour or ejector steam, ammonia;
iii) Storage tanks - water vapour, ammonia;
iv) Prill tower - dust, ammonia;
v) Granulation scrubber - particulates, ammonia, water vapour.

The complexity of the process is such that not all of the emission sources can be presented in the schematic diagram.

7.4 Survey of Emissions

Eight urea producers responded to the Environment Canada questionnaire. The emissions of most concern in urea production are ammonia and urea dust.

Three of the eight plants use granulators to solidify the urea. All three use scrubbers as a form of control. Ammonia and urea emissions averaged 3.58 and 0.08 kg per tonne of urea produced, respectively. Particulate emissions were reported to average 0.01 kg per 1000 kg of flue gas.

The remaining five plants use prilling towers. Questionnaire information indicates that pollution control is limited to the basic design of the tower, i.e. the air exiting from the tower is vented directly to the atmosphere. Reported particulate and ammonia emissions averaged 0.88 and 0.53 kg/tonne of urea produced respectively. In terms of kilograms of particulate matter per 1000 kilograms of air, reported emissions ranged from 0.06 to 0.18 with the average being 0.13.

Other emissions originating from such sources as scrubber vents and evaporators were not reported in sufficient quantity to warrant inclusion.

The annual nationwide emissions are estimated at 8 000 tonnes of ammonia and 350 tonnes of particulate urea. The ammonia emissions refer to the total emissions from all sources, while the particulate urea refers only to those emissions from granulation and prilling. Insufficient data were reported on particulate emissions from other sources to enable calculation of emission factors; however, on the basis of the information collected, these emissions are considered insignificant.

8 PHOSPHATE FERTILIZER INDUSTRY

8.1 General

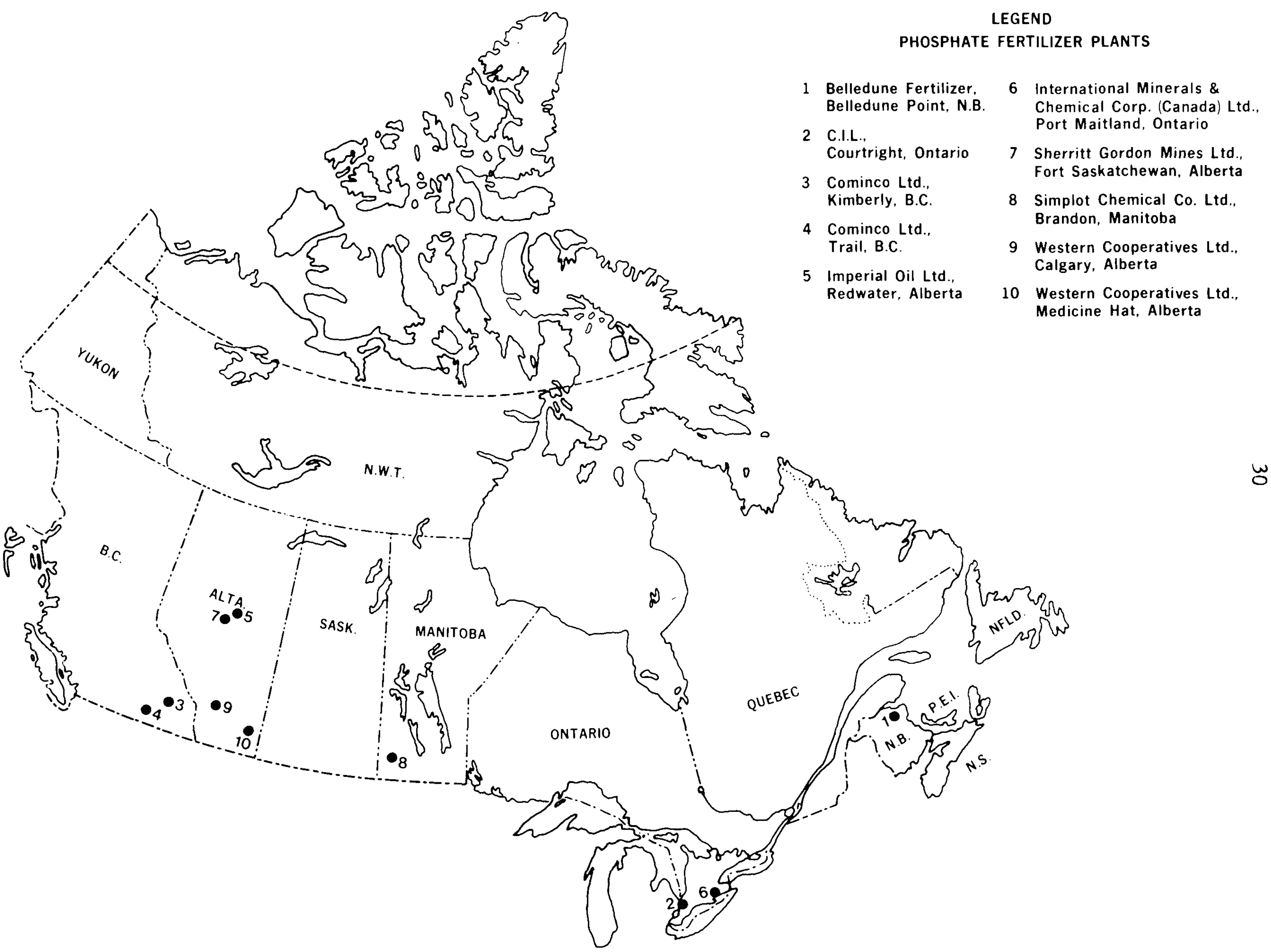
The phosphate rock used in the Canadian fertilizer industry is obtained from either Florida or the mid-western states. In general, this rock has the composition, $CaX_2 \cdot 3Ca_3(PO_4)_2$ (X-halogen or hydroxyl group) and contains 3-4% fluorine. The phosphate in the rock is almost completely insoluble in water. Since plant growth requires soluble phosphate in its soil environment, the rock, must be converted to this form.

Figure 7 indicates the location of phosphate manufacturing plants in Canada. Table 4 (6) lists the plants and their capacities, and Table 5 (6) summarizes Canadian production capacity according to the phosphate product manufactured.

Phosphate rock can be converted into a variety of products for fertilizer applications. In this study the production of the following fertilizers and intermediates is reviewed:

1. Normal superphosphate;
2. Triple superphosphate;
3. Ammonium phosphate;
4. Sulphuric acid (intermediate);
5. Phosphoric acid (intermediate).

Most terms used are self-explanatory. However, the term P_2O_5 equivalent arises frequently and seems to cause some confusion. To determine the P_2O_5 equivalent content of a substance, the quantity of phosphorous present is multiplied by the stoichiometric equivalent factor, 2.2914.



LEGEND
PHOSPHATE FERTILIZER PLANTS

1 Belledune Fertilizer, Belledune Point, N.B.
2 C.I.L., Courtright, Ontario
3 Cominco Ltd., Kimberly, B.C.
4 Cominco Ltd., Trail, B.C.
5 Imperial Oil Ltd., Redwater, Alberta
6 International Minerals & Chemical Corp. (Canada) Ltd., Port Maitland, Ontario
7 Sherritt Gordon Mines Ltd., Fort Saskatchewan, Alberta
8 Simplot Chemical Co. Ltd., Brandon, Manitoba
9 Western Cooperatives Ltd., Calgary, Alberta
10 Western Cooperatives Ltd., Medicine Hat, Alberta

FIGURE 7 PHOSPHATE FERTILIZER PLANT LOCATIONS

TABLE 4 SUMMARY OF PHOSPHATE FERTILIZER MANUFACTURING PLANTS IN CANADA (1977) DAILY RATED PRODUCTION CAPACITY (TONNES)*

Company	Plant Location	Normal or Triple Superphosphate	Ammonium** Phosphate	Phosphoric Acid	Sulphuric Acid
Belledune Fertilizer	Belledune Point, New Brunswick	-	898	449	-
C.I.L.	Courtright, Ontario	-	638	317	-
Cominco Limited	Kimberley, B.C.	-	539	317	802
	Trail, B.C.	-	632	235	1200
Imperial Oil Limited	Redwater, Alberta	-	1473	706	1789
International Minerals & Chemical Corporation (Canada) Ltd.	Port Maitland, Ontario	638	-	400	608
Sherritt Gordon Mines Limited	Fort Saskatchewan, Alberta	-	498	153	649
Simplot Chemical Company Limited	Brandon, Manitoba	-	649	-	-
Western Co-operative Fertilizers Limited	Calgary, Alberta	-	797	542	1295
Western Co-operative Fertilizers Limited	Medicine Hat, Alberta	-	636	235	561

* Phosphoric acid is P_2O_5 equivalent, sulphuric acid is 100% equivalent; the remaining fertilizers are total weight. Name plate capacity.

** Exact composition unknown, roughly 11% Nitrogen, 48% P_2O_5 equivalent.

TABLE 5 PRODUCTION CAPACITY OF PHOSPHATE FERTILIZER PLANTS IN CANADA (6)

	Daily Production Capacity (tonnes) 1977	
Phosphoric Acid	3354	(P_2O_5 Equivalent)
Normal or Triple Superphosphate	638	(Total Weight)
Ammonium Phosphate	6760	(Total Weight)

9 POLLUTION CONTROL IN THE PHOSPHATE FERTILIZER INDUSTRY

The emissions of most concern in the phosphate fertilizer industry are gaseous fluorides. Scrubbers are used to remove them. It has been found that a scrubber that effectively controls gaseous fluoride emissions will effectively control particulate fluoride.

Baghouses are used in the control of particulate emissions resulting from phosphate rock handling (see section 14).

While scrubber efficiency will vary considerably depending on the conditions, scrubbers, as they are used in the fertilizer industry, are capable of a high degree of efficiency; in some cases 98% and more of the fluorides can be removed. The exit concentrations of fluorides from well-run scrubbers do not vary greatly, but due to the large variation in the volumes of gases, the emissions in terms of weight of fluoride per tonne of product can differ substantially. Table 6 (23), which is based on data from the U.S. Environmental Protection Agency, indicates the range of conditions found in the American phosphate fertilizer industry for plants employing state-of-the-art technology; similar emissions may be expected from equivalent Canadian plants. Fluoride is emitted from phosphate fertilizer processes as colourless, gaseous silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF). In this report the fluoride referred to is the weight of the fluorine and does not include the chemically combined elements.

TABLE 6 EMISSIONS IN AND OUT OF CONTROL DEVICE

Process	Typical Gas Flow (m^3/tonne)	Inlet Gas Concentration (kg/m^3)	Emissions (kg/m^3)	(kg/tonne P_2O_5)
Wet-Process Phosphoric Acid	1 550	4.5×10^{-5} - 2.2×10^{-4}	2.2×10^{-6} -4.5×10^{-6}	5×10^{-3} -0.01
Diammonium Phosphate	9 300	1.1×10^{-5}(a)	2.2×10^{-6} 0.02	
Run-Of-Pile Triple Superphosphate(e) and ROP-TSP Storage(e)	11 000	7×10^{-4} - 1.3×10^{-3}	6.8×10^{-6} -1.3×10^{-5}	0.1 -0.15
Granular Triple Superphosphate	14 000	4.5×10^{-5}	2.2×10^{-6} - 6.8×10^{-6}	0.025 -0.125
Granular Triple Superphosphate Storage	1(b)	2.3×10^{-6} - 6.8×10^{-6}	1.8×10^{-6} - 2.2×10^{-6}	1.5×10^{-4}-2.5×10^{-4}(d)
	0.1 - 0.3(c)	2.3×10^{-6} - 6.8×10^{-6}	1.8×10^{-6} - 2.2×10^{-6}	1.5×10^{-4}-2.5×10^{-4}(d)

(a) Gas concentration into packed scrubber

(b) kg/tonne P_2O_5 (emission factor based on tonnes of product stored in the building during testing)

(c) kg/tonne P_2O_5 (emission factor based on the capacity of the building)

(d) kg/hour per tonne P_2O_5 stored

(e) Emissions from these two sources are frequently treated in a common control device.

10 NORMAL SUPERPHOSPHATE

10.1 General

Single or normal superphosphate, obtained from the acidulation of phosphate rock, contains 18-22% phosphorous as P_2O_5 equivalent. Only the International Minerals & Chemical Corporation (Canada) Limited plant at Port Maitland, Ontario produces normal superphosphate.

10.2 Process Description

By acidulation in a pug mixer the insoluble tricalcium phosphate is converted into water soluble calcium phosphate and gypsum, according to the following simplified reaction:

$$Ca_3(PO_4)_2 \quad + \quad 2H_2SO_4 \quad \rightarrow \quad Ca(H_2PO_4)_2 \quad + \quad 2CaSO_4$$

Solidification is achieved in a Broadfield den, an enclosed slatted steel conveyor into which the acid and rock mixture is discharged and allowed to set. The solid material is broken off by a cutter at the discharge end and conveyed to a curing area. During the curing stage the superphosphate hardens and must be broken loose, crushed, and screened and then granulated.

Normal raw material requirements are 0.64 tonnes of phosphate rock (32% P_2O_5) and 0.36 tonnes sulphuric acid (100% basis) for every tonne of 20% superphosphate produced (24).

Representative flow sheets for producing run-of-pile and granular superphosphate are presented in Figures 8 and 9, respectively.

10.3 Emissions and Control Technology

10.3.1 General. When phosphate rock is acidulated, hydrogen fluoride is produced which reacts with the silicon dioxide present to produce silicon tetrafluoride, the major gaseous emission, in accordance with the following equations:

$$CaF_2 \cdot 3Ca_3(PO)_2 + 7H_2SO_4 \rightarrow 3\ Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF$$

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

Overall fluoride emissions can vary between 10% and 50% of the fluoride in the rock. Assuming a fluorine content of 3.5% in the rock, between 2 and 11 kg of fluorine will be released per tonne of product.

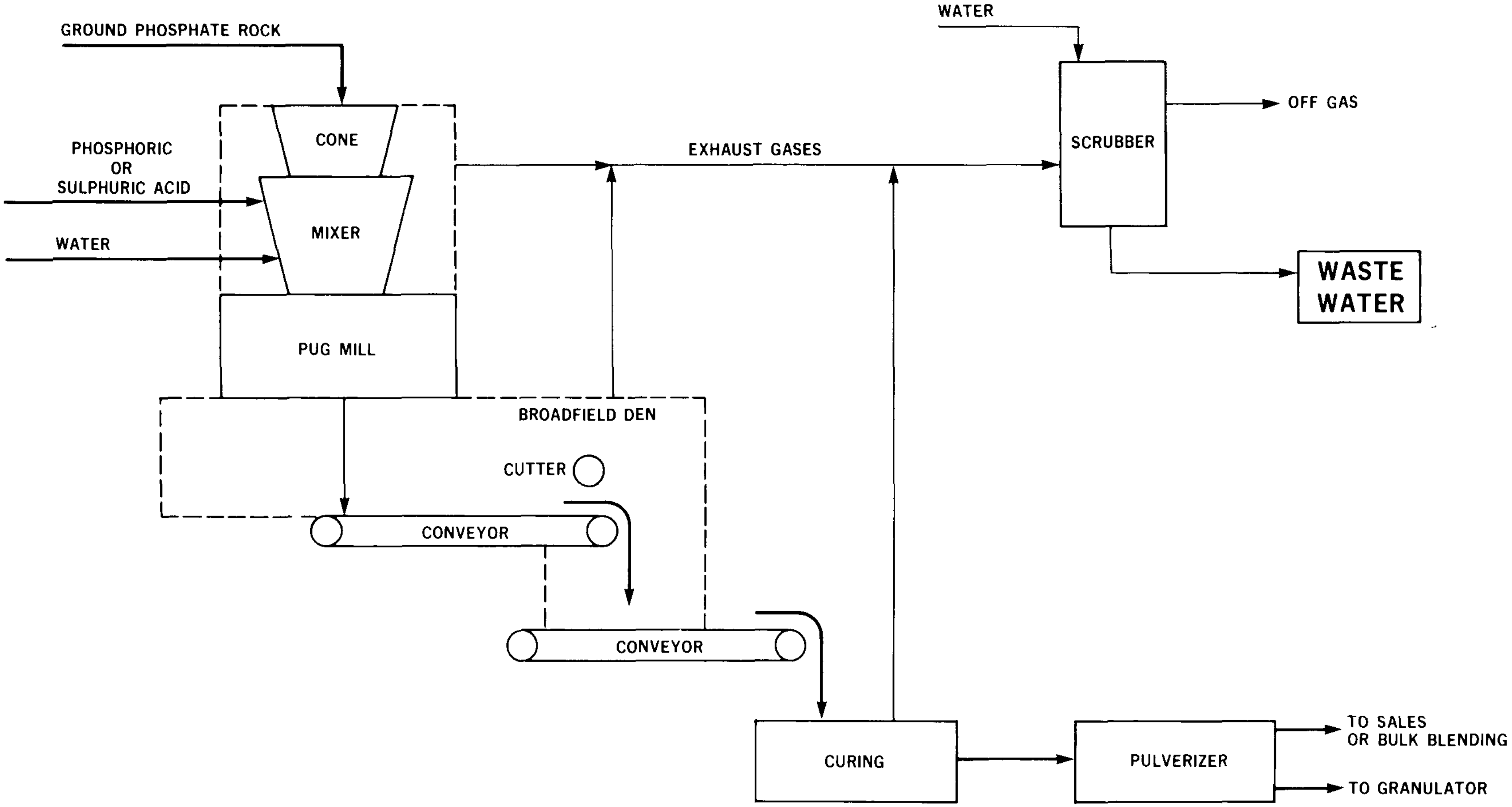


FIGURE 8 PROCESS FLOW SHEET SUPERPHOSPHATE PRODUCTION

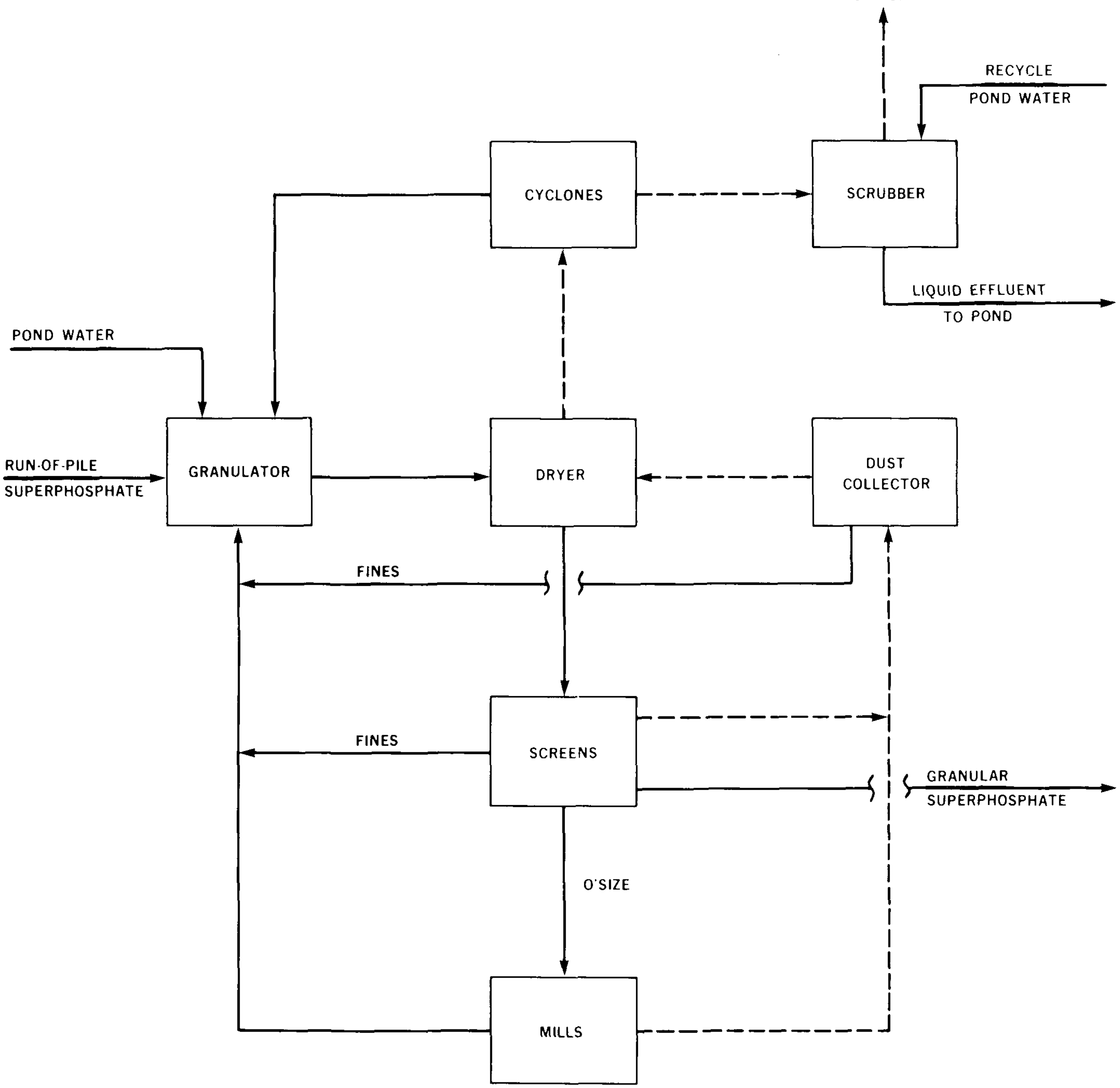


FIGURE 9 PROCESS FLOW SHEET GRANULAR SUPERPHOSPHATE PRODUCTION

10.3.2 Phosphate Rock Preparation Facilities. Phosphate rock preparation for normal superphosphate production is identical to rock preparation for all other phosphate processes. Section 14 discusses the emissions and control technology for this part of the process.

10.3.3 Mixer (Reactor) and Den. The fluoride concentration in the off-gas streams from the mixer or reactor and den is relatively high, e.g., a concentration range of 1100-8300 mg/m^3 has been quoted for a den making 11 tonnes/hour of single superphosphate. These streams are usually combined and scrubbed in a single scrubber system.

10.3.4 Granulator and Dryer. The run-of-pile material is sent to a granulator and then to a dryer. The off gases from the dryer are sent to cyclones to remove the particulate and then on to a scrubber. The small quantity of particulate remaining is removed by the scrubber.

10.3.5 Screens, Mills and Belt Transfer Points. Dust from these sources is usually removed by a vacuum collection system and the gas is then exhausted through a scrubber to remove any fluoride present.

10.3.6 Storage Pile (Curing). About 3% of the fluorine which was originally present in the phosphate rock is emitted over a period of 4-6 weeks. Natural circulation of air is used for ventilation and fluoride concentrations are low. Usually no attempt is made to control this source of air pollution. In Florida it has been found that uncontrolled emissions from a curing building are 0.7-1.4 kg of fluoride per tonne of product manufactured. The daily emissions ranged from 90 to 1600 kg (25). Concentrations of fluoride in the atmosphere varied between 34 to 68 mg/m^3 at the surface of the pile and 5100 to 7650 mg/m^3 in the centre of the pile. Air-flow quantities were 5700-17 100 m^3/min and the concentration of fluoride in the off gas was 105-525 mg/m^3 (26).

10.3.7 Survey of Emissions (6). Only one plant in Canada produces normal superphosphate. Emissions from rock preparation, i.e. grinding, are sent to a cyclone and then to a baghouse dust collector. Resultant emissions are very low.

Off gases from the mixing and denning operations are scrubbed with recycle pond water in a multi-stage venturi scrubber followed by a highly irrigated packed scrubber. The liquid effluent is recycled to the pond system. Emissions were reported as being controlled to 0.0002 kg of fluoride per tonne of product (6).

Exhaust gases from the granulator and dryer are passed through a cyclone prior to being scrubbed in a two-stage cyclonic scrubber. Product fines from the cyclones are recirculated to the granulator. The water supply for the scrubbers is recycled pond water with the scrubber effluent being returned to the pond system. Emissions were reported as 0.04 kg of fluoride per tonne of product from this treatment system.

Dust from the screens, mills and belt transfer points is exhausted through a baghouse dust removal system and then on through the scrubber used on the granulator.

Air naturally circulates through the run-of-pile storage building and exits to the atmosphere untreated. Data on these emissions are not available.

The total annual fluoride emissions from mixing, denning, granulating and drying are estimated at 7 tonnes per year.

11 TRIPLE SUPERPHOSPHATE

11.1 General

Triple or concentrated superphosphate is the product obtained when phosphate rock is treated with phosphoric acid. The product generally averages 46% P_2O_5 equivalent but it can vary from 44 to 52% depending on the purity of the reactants and the efficiency of the process.

This fertilizer can be applied directly to the soil or used in either granulating mixtures or formulating bulk blends. The most common phosphate fertilizer is diammonium phosphate (DAP) but significant tonnages of normal superphosphate, monoammonium phosphate (MAP) and triple superphosphate are also produced. Only the International Minerals & Chemical Corporation (Canada) Limited plant located at Port Maitland, Ontario produced triple superphosphate in Canada during 1977.

11.2 Process Description

The production process for triple superphosphate is similar to that for producing normal superphosphate. The lone producer in Canada alternates the equipment between both processes. The reactions are as follows:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF$$

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

As in the case of normal superphosphate production the process involves four main steps:

1. Mixing of rock and acid;
2. Permitting the mix to assume a solid form;
3. Curing the material;
4. Crushing and granulating.

Normal raw material requirements are 0.42 tonnes of phosphate rock (34% P_2O_5 content) and 0.35 tonnes of P_2O_5 as phosphoric acid per tonne of 46% superphosphate produced, regardless of the process (27). Globally, most operators use 70 to 75% H_3PO_4.

The acidulation and curing parts of the process are identical to those for normal superphosphate production, with the exception that phosphoric acid replaces sulphuric acid. (Figures 8 and 9).

11.3 Emissions and Control Technology

11.3.1 General. As in the case of normal superphosphate manufacture, hydrogen fluoride is produced which reacts with the silicon dioxide present to produce silicon tetrafluoride, the major gaseous emission. Fluoride evolution ranges between 32% and 40% of the fluoride in the rock, or 5-6 kg/tonne of product. Typical fluoride distribution in triple superphosphate manufacture is summarized in Table 7.

TABLE 7 FLUORIDE DISTRIBUTION IN TRIPLE SUPERPHOSPHATE MANUFACTURING

Source	% of the F in rock	kg/tonne product
Mixer, Den and Conveyor Emissions	32	5
Storage Pile (Curing) Emissions	3	0.5
In Product	65	10

11.3.2 Phosphate Rock Preparation Facilities. Phosphate rock preparation for triple superphosphate production is identical to rock preparation for all other phosphate processes. Section 14 discusses the emissions and control technology for this part of the process.

11.3.3 Reactor, Den, Conveyors, Granulators and Dryers. Emissions of fluorides from these sources are estimated at 0.08 kg of fluoride per tonne of P_2O_5 produced with a control level of 99% for plants in the United States in 1972 (28). Wet scrubbers are used to reduce emissions to this level. In the case of the dryers the dust is removed before scrubbing.

11.3.4 Storage Pile (Curing). Tests by the U.S. Environmental Protection Agency at two storage buildings containing granular triple superphosphate indicated that emissions at one averaged 1.8×10^{-4} kg of fluoride per tonne of P_2O_5 in storage while at the other emissions ranged from 0.5×10^{-4} to 1.8×10^{-4} kg of fluoride per tonne of P_2O_5 in storage. Both were controlled with scrubbers using pond water (29).

11.3.5 Survey of Emissions (6). The emissions of most concern from this process are fluorides. In the single Canadian plant the off gases from the mixer and den are scrubbed in a multi-stage venturi scrubber followed by a highly irrigated packed system. The scrubbing medium is pond water. The resulting emissions were reported as 0.0009 kg of fluoride per tonne of product.

The exhaust gases from the granulator and dryer are withdrawn through a cyclone to remove the dust before being scrubbed in a two-stage cyclonic scrubber. The medium for all scrubbers is the pond water which is recycled. Resulting emissions are reported as 0.05 kg per tonne of product granulated.

Dust from the screens, mills and belt transfer points is exhausted through a baghouse dust collector before the air stream is scrubbed in the two-stage scrubber used on the granulator. The emissions are included in those described in the preceding paragraph.

Emissions from storage or curing were reported as 30 kg of fluoride per day. The addition of a small amount of sodium hydroxide to phosphoric acid prior to its reaction with the rock to form the triple superphosphate reduces significantly the quantity of fluoride that would otherwise be emitted. International Minerals & Chemical Corporation (Canada) Limited has been issued a patent on this process modification (Canadian Patent No. 827,594, Nov. 18, 1969).

The combined annual fluoride emissions from the above sources are approximately 11 tonnes.

12 PHOSPHORIC ACID (INTERMEDIATE)

12.1 General

Phosphoric acid, an intermediate in the fertilizer industry, is used to acidulate phosphate rock to produce triple superphosphate or alternatively it is used to neutralize ammonia to produce ammonium phosphate.

Nine companies in Canada produce phosphoric acid as an intermediate in the fertilizer industry. The total tonnage of P_2O_5 equivalent is about 1 200 000 tonnes per year.

12.2 Process Description

When phosphate rock is treated with sulphuric acid, either normal superphosphate or phosphoric acid is produced depending on the quantity of sulphuric acid added. To produce phosphoric acid, additional sulphuric acid is added and the calcium sulphate is removed as waste. The term "wet process" is used exclusively to describe this method of phosphoric acid production. In the digestion process, sulphuric acid and finely ground phosphate rock, usually averaging 30 to 34% P_2O_5 equivalent, are continuously fed into a slurry composed of reactants, products, and enough recycled weak phosphoric acid to maintain fluidity. Completely reacted slurry is continuously drawn off, filtered and washed to remove waste gypsum. The principal reaction can be represented by the following equation:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 10H_2SO_4 \rightarrow 6H_3PO_4 + 10CaSO_4 + 2HF$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

The reaction takes place very rapidly but a retention period of five to eight hours is necessary to allow for gypsum crystal growth.

Individual operators choose different processes, each of which is generally named after the designer and calls for different equipment, arrangement and techniques. All systems follow the basic process outlined above and aim for the highest concentration of acid with the maximum P_2O_5 recovery and complete separation of gypsum and other products at lowest unit cost. Basic differences are in the reaction and filtering systems. Some plants have multiple-tank reactors employing one or two stages of reaction while others contain single-tank reactors; both types have mechanical agitators. Tilting-pan filters have been the most popular installation in recently built plants. Rotary drum vacuum filters with either internal or external bath and travelling belt filters are also used.

Raw material consumption differs according to the P_2O_5 content of the rock. Common requirements are about 3.1 tonnes of 34% P_2O_5 phosphate rock and 2.6 tonnes of 100% sulphuric acid per tonne of P_2O_5 equivalent produced (30). Normal procedure calls for a sulphuric acid concentration of 55 to 60%. About 4.5 tonnes of waste calcium sulphate (gypsum) must be disposed of for every tonne of P_2O_5 equivalent manufactured.

A flow sheet of the process is presented in Figure 10.

12.3 Emissions and Control Technology

12.3.1 General. Rock dust emissions and control methods are common to all phosphate processes and are discussed in section 14. Fluoride in the phosphate rock is attacked by sulphuric acid to produce hydrogen fluoride (HF), which reacts with silica to form silicon tetrafluoride (SiF_4) and fluosilicic acid. Hydrogen fluoride and silicon tetrafluoride together with dust containing fluorides from the digester, filter and concentrator areas are scrubbed, usually with pond water, prior to venting to the atmosphere. The phosphate rock contains about 3.5 to 4% fluorine and about one half of this fluorine is volatilized in the processing (31). Most of this is recovered in scrubbers.

Figure 11 indicates that, typically, 0.93 kg of fluorine is volatilized (as HF, SiF_4, etc.) by acid attack on 100 kg of the rock. A substantial quantity is volatilized when concentrating the acid. The remaining fluoride goes to either the gypsum pond or with the product acid.

12.3.2 Digester (Reactor). The digester is the largest emission source of gaseous fluorides and rock dust. Tests in the United States have measured gaseous fluoride emissions between 0.019 to 1.0 kg per tonne of acid produced (32). As much as 5.5 kg of particulate per tonne of acid is generated at this source (32).

Exit gases are treated in a scrubber which usually scrubs emissions from the reactor, filter and miscellaneous sources as well. Scrubber outlet emissions for these combined sources were measured by the Environmental Protection Agency for five plants and were found to range from 0.0008 to 0.03 kg per tonne of P_2O_5 input (33).

12.3.3 Filters. Data collected by the Environmental Protection Agency indicate that gaseous fluoride emissions originating at the filter range from 0.005 to 0.03 kg/tonne of P_2O_5 produced (34). Control technology is described in section 12.3.2.

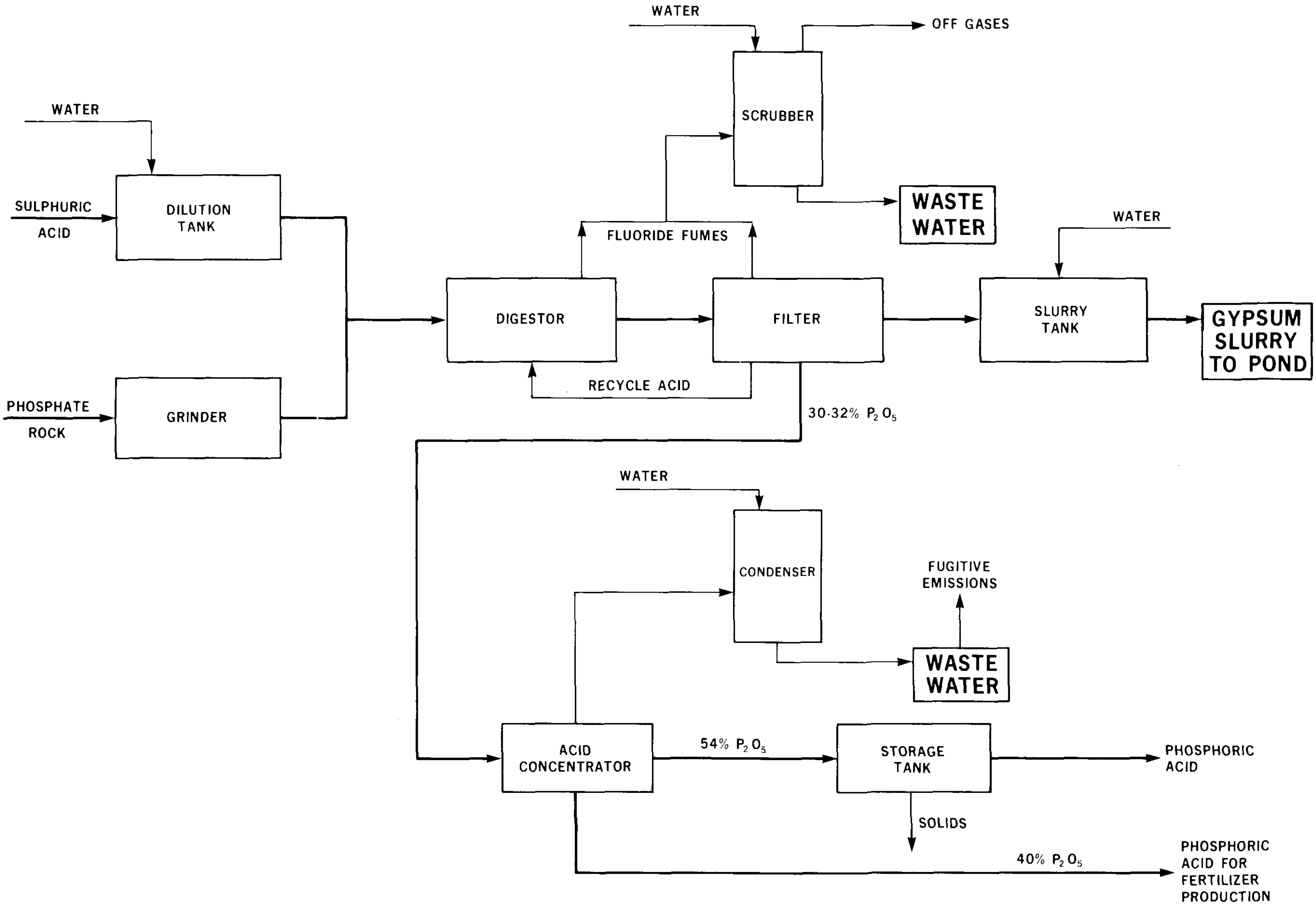


FIGURE 10 PROCESS FLOW SHEET WET PROCESS PHOSPHORIC ACID PRODUCTION

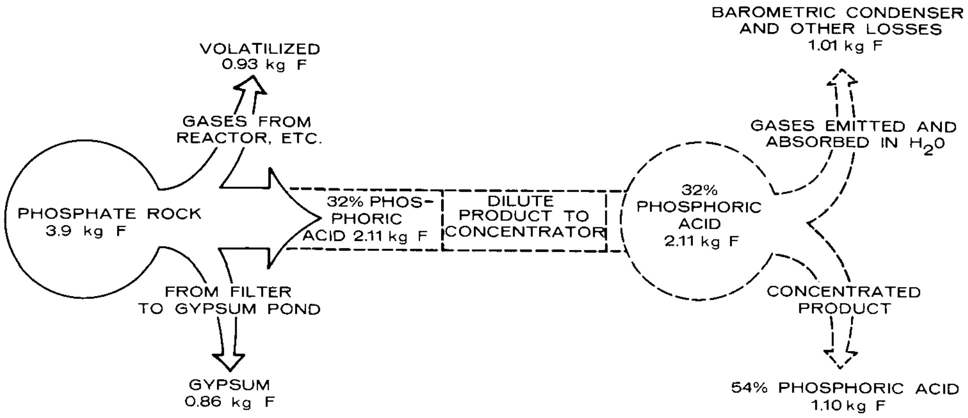


FIGURE 11 TYPICAL MATERIAL BALANCE OF FLUORINE IN MANUFACTURE OF WET PROCESS PHOSPHORIC ACID (31)

12.3.4 Evaporation. It has been estimated that 20 to 40% of the fluorine originally present in the rock is emitted during concentration of the acid (35). The fluoride is dissolved and entrained in the water from the barometric condenser, which is used to keep a vacuum on the evaporator, and is a source of fluoride emission. This emission can be controlled by the scrubber described in section 12.3.2.

12.3.5 Fugitive Emission Sources. Fugitive emission sources include sumps, phosphoric acid tanks, and acid splitter boxes; the magnitude of the emissions is not known.

12.3.6 Survey of Emissions (6). In the nine fertilizer plants in Canada manufacturing phosphoric acid as an intermediate, individual plant production ranges from 54 000 to 219 000 tonnes of P_2O_5 equivalent per year.

Five of the nine plants combine the emissions and treat them in a cross-flow packed scrubber, a treatment that the Environmental Protection Agency recommends as the best technology. Reported emissions ranged from 0.002 to 0.04 kg of fluoride per tonne of P_2O_5 equivalent produced with the average being 0.01.

The remaining four use a number of different types of scrubbers. Some plants use more than one scrubber. Impinger, cross-flow, venturi, packed and barometric scrubbers were reported. Reported emissions from these four ranged from 0.02 to 0.7 kg of fluoride per tonne of P_2O_5 equivalent produced with the average being 0.4.

Most scrubbers use recycled pond water as the scrubbing medium. However, one uses sea water, while another uses both ammonia plant waste water and raw water.

The annual fluoride emissions from the aforementioned sources in Canada in 1977 are estimated at 119 tonnes based on questionnaire data.

13 AMMONIUM PHOSPHATE PRODUCTION

13.1 General

There have been fluctuations in the production of ammonium phosphate fertilizers in Canada; however, production has increased substantially, for example, from about 400 000 tonnes in 1967 to 1 500 000 tonnes in 1977.

The main advantages of these fertilizers are:

1. High strength;
2. Phosphate in readily soluble form;
3. Low production and transportation costs;
4. Ease of storage and handling;
5. Ease of formulation with other fertilizers.

These phosphates are manufactured by the neutralization of phosphoric acid with ammonia under controlled conditions. Depending on these conditions, either monoammonium phosphate (MAP) or diammonium phosphate (DAP) are produced. The chemical reactions involved are:

$$H_3PO_4 + NH_3 \rightarrow NH_4 \cdot H_2PO_4$$
$$NH_4H_2PO_4 + NH_3 \rightarrow (NH_4)_2HPO_4$$

13.2 Process Description

Phosphoric acid (greater than 30% P_2O_5) is reacted with ammonia in predetermined proportions in a neutralizer. The reaction is exothermic and water is continually evaporated. The resultant slurry is fed to a granulator, where fines from recycle provide the nuclei for the production of granular fertilizers.

Additional ammonia or other fertilizers can be fed to the granulator to achieve the product with the desired nutrient ratios. The granular DAP (or MAP) flows to a dryer, then to screening for recycle of undersize and oversize particles to the granulator; the oversize are crushed prior to being recycled. The product-size material is cooled prior to storage.

Figure 12 represents a typical process flow sheet.

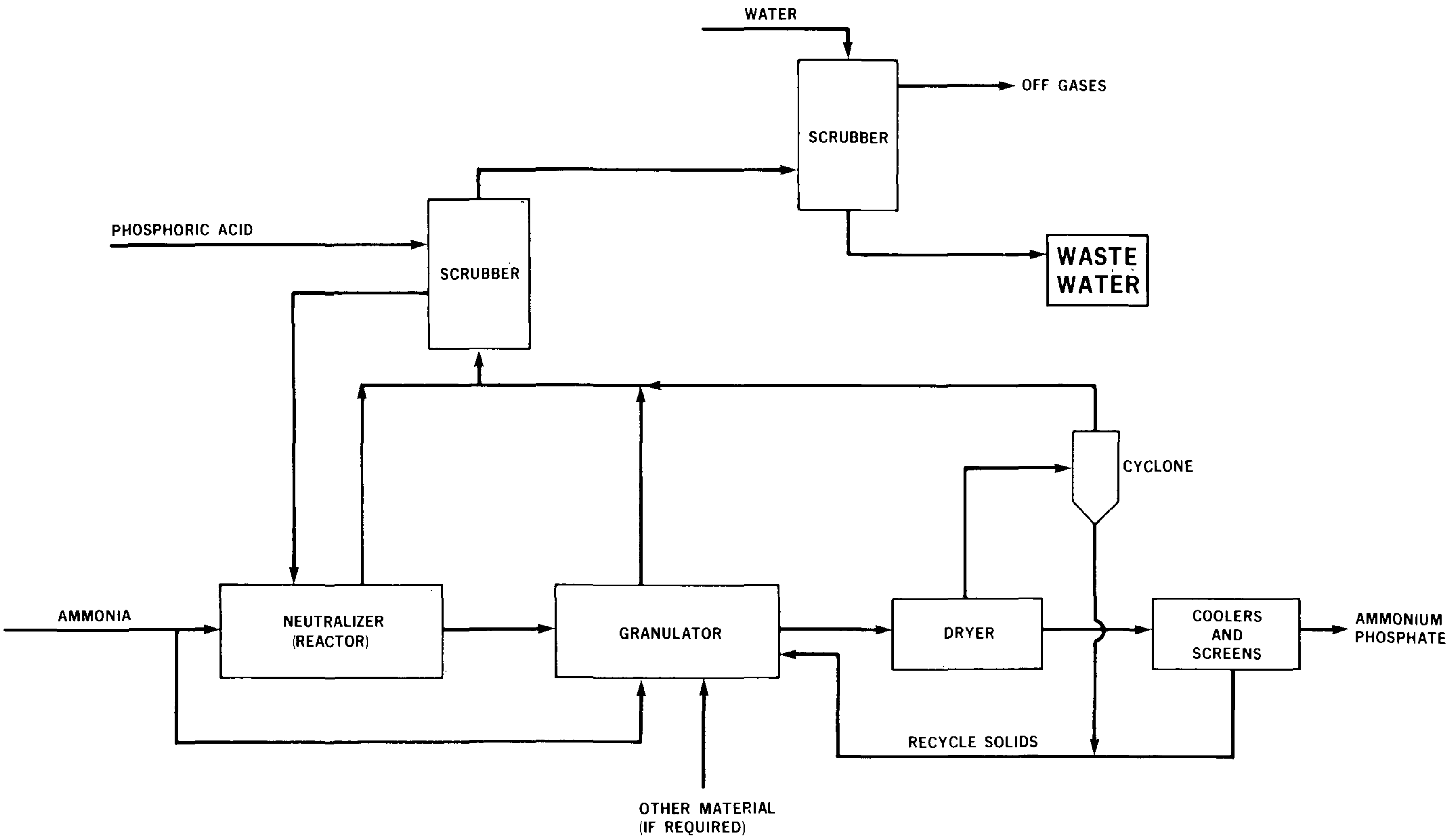


FIGURE 12 PROCESS FLOW SHEET AMMONIUM PHOSPHATE PRODUCTION

13.3 Emissions and Control Technology

The sources of emissions of most concern are the reactor, the granulator, the dryer, the cooler and the screens. Fluorides, ammonia and particulate ammonium phosphate are the contaminants of concern.

Best technology emission control for ammonium phosphate production consists of scrubbing the emissions from the granulator and reactor with phosphoric acid to remove the ammonia followed by a second scrubber which uses pond or rain water to remove fluorides that have been stripped from the phosphoric acid in the first scrubber. The effluent from the first scrubber is used as feed for the reactor while the effluent from the second goes to a settling pond.

A poorly controlled diammonium phosphate plant can release up to 0.5 kg of fluoride per tonne of product whereas a well-controlled plant using the previously discussed technology can reduce emissions to below 0.06 kg of fluoride per tonne of product (36). Experimental data on emissions from monoammonium phosphate production are not available but should not differ significantly from the above.

Particulate emissions originating at the dryer, cooler and screens are normally treated by cyclones to remove the particulate and then treated in a scrubbing system (Figure 12).

13.4 Survey of Emissions and Control Technology

Nine Canadian phosphate fertilizer producers reported manufacturing ammonium phosphate (6). Reactor emissions are generally controlled by scrubbing, the only exception being a plant that has two reactors, one of which sends emissions directly to a stack. Phosphoric acid and pond water are the primary scrubbing media used. The phosphoric acid is sent to the reactor and the pond water is recycled to the pond. One plant uses raw water as the scrubbing medium.

Although the questionnaire responses were not complete with regard to the types of scrubbers used, the following were mentioned: venturi, spray tower and impinger.

Following the reaction between ammonia and phosphoric acid, the slurry is granulated. For this purpose, five plants use a granulator where recycled fines provide nuclei for the formation of granular material, three use a blunger (a tank with rotating agitators) and one uses a pug mill (horizontal shafts with paddles). Most plants treat emissions from these sources in common with the emissions from the reactor, described previously. The plant with the separate treatment system uses two impinger scrubbers in series. Raw water is the scrubbing medium, with the effluent from the first going back to the reactor and from the second to the sewer.

Emissions from dryers, coolers, and screens are sent through cyclones, where most of the particulates are removed. Next, these streams, normally combined, are scrubbed, usually with phosphoric acid with the effluent going to the reactor. Particulate remaining after the cyclones is removed in the scrubber.

After treatment many of the emissions are vented to a common stack. Questionnaire data were frequently presented as measured at a stack where these emissions have been combined. Since emissions from individual sources are not known, the total from the plant is presented below.

The breakdown for the nine plants is complicated by the fact that one plant has dual reactors, only one of which treats emissions. The average of the emissions from this plant is 2.76 kg of fluoride per tonne of product. Emissions from one other plant were not reported. The seven remaining plants reported fluoride emissions ranging between 0.02 and 0.6 kg per tonne of product with the average being 0.14.

Estimated total fluoride emissions into the atmosphere in Canada from the above mentioned sources are 625 tonnes annually.

14 PHOSPHATE ROCK HANDLING

14.1 General

Phosphate rock is used in the preparation of normal superphosphate, triple superphosphate and phosphoric acid. It must be finely ground in order to react readily with the acid. The dust given off in grinding must be controlled due to the value of the product and the necessity for good housekeeping.

14.2 Emissions and Control Technology

Several methods are available to the industry to control the dust emissions mentioned above, including wet scrubbing and electrostatic precipitation but the method used almost universally is fabric filtration (baghouses), usually preceded by a cyclone to remove the larger particles. Fabric filters are capable of removing in excess of 99.8% of particulates in most cases.

14.3 Survey of Emissions and Control Technology

Nine Canadian phosphate fertilizer producers reported handling phosphate rock (6).

Eight of the nine plants, use baghouses to control emissions associated with rock preparation and handling. One uses a wet impinger scrubber. Collected fines in all cases are recycled to the process. One phosphate fertilizer producer purchases phosphoric acid and consequently does not handle phosphate rock.

Although all plants described their pollution abatement equipment, many did not have data on actual emissions. Reported rock dust emissions on a kilogram per tonne of rock purchased basis varied between 0.03 and 0.5 with the average being 0.14. In terms of kilograms per 1000 kilograms of air handled, reported rock dust emissions ranged from 0.05 to 0.18 with the average being 0.13.

Total rock dust emissions in Canada, based on the above data, amount to 335 tonnes/year.

15 GYPSUM POND EMISSIONS

15.1 General

In the production of phosphoric acid, an intermediate in the phosphate fertilizer industry, large quantities of gypsum are produced which must be disposed of. The gypsum also contains significant quantities of fluoride ion. In Europe this waste is almost always disposed of at sea. In Canada most plants use gypsum ponds. Most of the fluoride present precipitates; however, a significant quantity, about 0.5 g F/kg P_2O_5 equivalent produced, is emitted to the atmosphere (37).

Fluoride evolution from the ponds can be made negligible by raising the pH of the pond by liming (38).

15.2 Survey of Canadian Plants

Nine fertilizer plants produce phosphoric acid as an intermediate in Canada. Seven of the nine use settling ponds. One plant sends the waste stream to the sea, the other removes part of the fluoride present as a by-product and discharges the gypsum and remaining fluoride to a river.

The smallest pond reported had a surface area of 0.04 km^2 (9.8 acres), the largest 1.5 km^2 (370 acres) with the average being 0.73 km^2 (178 acres).

Fluoride emissions from gypsum ponds in the United States were found to range from 11 to 1000 kg F per km^2 per day (0.1 to 10 lb per acre per day) with an average value of 220 kg F per km^2 per day (37). Based on this emission factor, total fluoride emissions in Canada from gypsum settling ponds are estimated to be 407 tonnes per year.

16 SULPHURIC ACID

16.1 General

Sulphuric acid is a very important intermediate in the manufacture of phosphate fertilizers. Its manufacture in Canada dates back to 1867; the first heavy chemical plant in Canada was a sulphuric acid plant in London, Ontario operated by the Canada Chemical Co. It has many uses, but the greatest single use is in the manufacture of fertilizer which accounts for about 40% of the sulphuric acid manufactured.

16.2 Single Absorption Process

Sulphur, in molten form, is sprayed into a dry air stream in a burner and is oxidized to sulphur dioxide. The reaction is exothermic and the heat released raises the temperature of the exiting gases to 1800-2000°F. The waste heat from this stream is captured in a heat-exchanger boiler to generate steam either for in-plant needs or for sale to outside users.

After heat recovery, the gas stream flows to a four-stage catalytic converter for conversion to sulphur trioxide (SO_3). This reaction is exothermic and intermediary cooling is generally required between each stage with the heat recovered for steam production where possible.

The gas stream, containing SO_3, is then introduced into the bottom of an upward flow absorber to contact a downward flow stream of 98-99% sulphuric acid. On hydrolysis of the SO_3, heat is released so the enriched acid stream is chilled in a cooler and then sent to tank storage.

The acid is then either recycled to the absorption tower or diluted to 93% acid before being sent to a drying tower. The excess acid is stored in acid tanks. A simplified process flow sheet is shown in Figure 13. An efficiency of 95 to 98% can be expected for the conversion of sulphur dioxide to sulphur trioxide with this process (39).

16.3 Double Absorption Process

The novel feature of this process is the intermediate removal of SO_3 by absorption in H_2SO_4 from the partially reacted gas stream followed by another stage of catalytic oxidation. By removing SO_3, overall conversions of 99.7% (40) can be obtained compared to a previous standard of 95% to 98% conversion. Other parts of the plant are similar to the older single absorption process. New plants will most likely employ this technology.

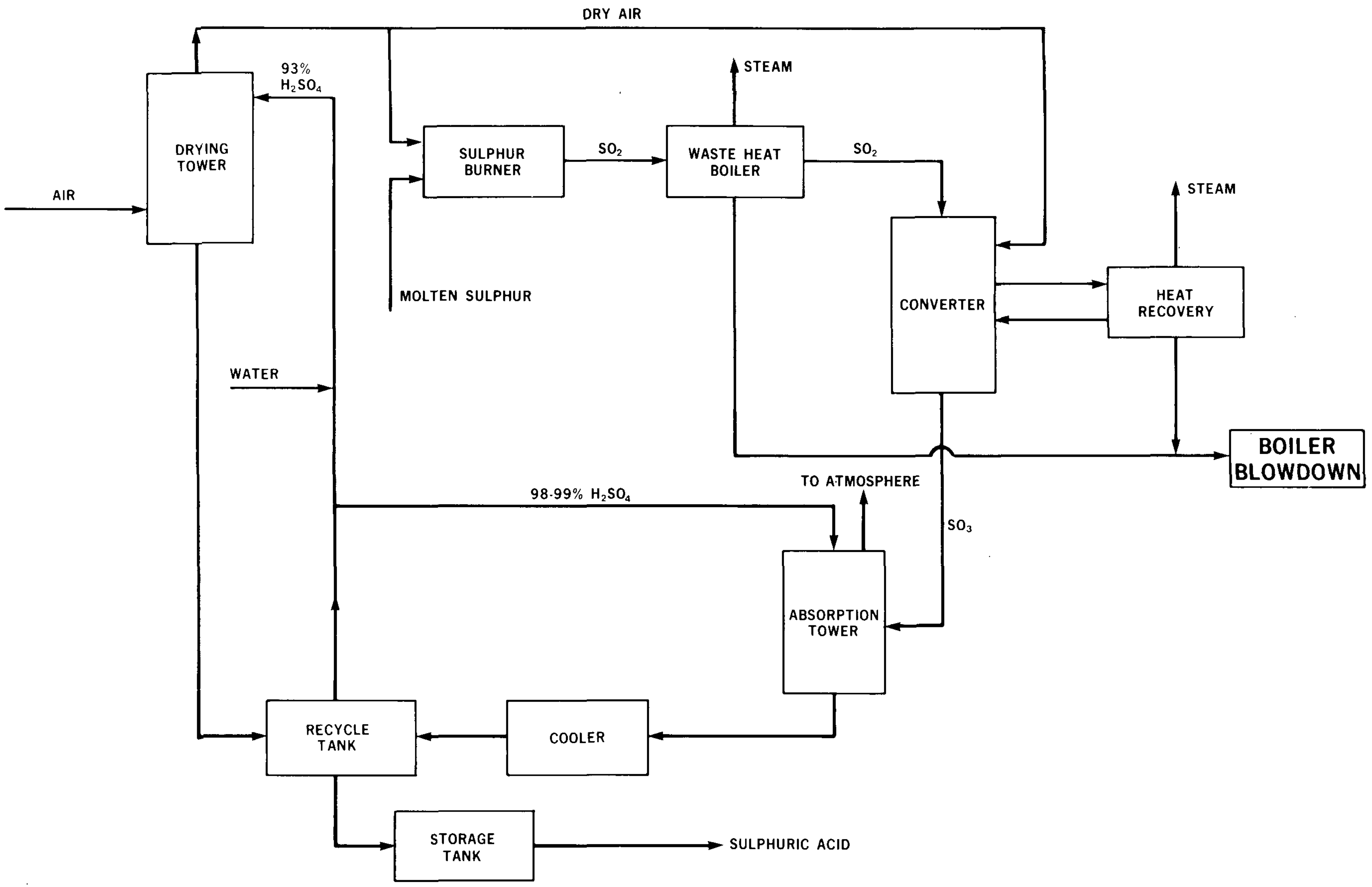


FIGURE 13 PROCESS FLOW SHEET SULPHURIC ACID PRODUCTION

16.4 Emissions

16.4.1 General. The subsequent descriptions deal with the single absorption process as almost all of the sulphuric acid manufactured by the fertilizer companies in Canada use this process. The major emission source is the waste gas from the absorber exit stack. This gas contains predominantly nitrogen and oxygen but also unreacted sulphur dioxide and unabsorbed sulphur trioxide as well as sulphuric acid mist and spray. Trace amounts of nitrogen oxides may also be present.

16.4.2 Emission Sources, Composition and Magnitude

Absorber Exit Stack

Sulphur dioxide in the stack gas results from the incomplete conversion of sulphur dioxide to sulphur trioxide in the catalytic converter. In the United States, tests showed that sulphur dioxide concentrations in absorber stack gas, range from 0.13 to 0.54% by volume; the mean for 33 tests was 0.26% (41) and the average SO_2 emission rate was 2000 kg/100 tonnes of acid produced.

A second pollutant emitted from the absorber exit stack is sulphuric acid mist. Acid mist is formed as a result of the presence of water vapour in the process gases fed to the converter. The drying towers in most contact plants are able to dry the air to a moisture content of about 106 mg/standard m^3. The remaining moisture combines with the sulphur trioxide after the converter, when the temperature falls below the dew point of sulphuric acid. The acid mist so formed is very difficult to remove in the absorber and much of it escapes.

In sulphur-burning plants, mist may also be formed from water resulting from the combustion of hydrocarbon impurities in the sulphur. In some instances, where the sulphur has a high organic content, appreciably more mist may be formed from combustion of organic matter in sulphur than from moisture in the dried air.

During plant startups and shutdowns emissions may be higher. These emissions result from low temperatures in the catalyst chamber and absorber, conditions under which neither the catalyst nor the absorber tower work efficiently. If the catalyst and the absorber tower are preheated, these emissions can be kept to a minimum.

Other Sources

Losses of solid sulphur during unloading and from outdoor storage piles by wind are appreciable, usually from 1 to 2% of the sulphur delivered. However, any dust settles rapidly within a short distance. If sulphur is purchased in a molten form all such losses are eliminated.

Most of the process equipment in a contact plant is under low pressure, usually less than 40 kilopascal gage (6 psig). Because of an obnoxious odour, any leakage of sulphur dioxide or sulphur trioxide from process equipment is very noticeable. Also sulphur trioxide leaks can be easily seen because of the white mist that forms in the presence of atmospheric moisture.

16.5 Emission Reduction by Optimizing Process Parameters

16.5.1 Sulphur Dioxide. The emission of sulphur dioxide to the atmosphere is related primarily to the efficiency of conversion of sulphur dioxide to sulphur trioxide. If conversion efficiency is high, sulphur dioxide emissions are low. To maintain a high conversion efficiency, the following operational parameters must be optimized:

1. The concentration of sulphur dioxide in the gases entering the converter and the ratio of oxygen to sulphur dioxide particularly in the last converter stage;
2. The number of catalyst converter stages;
3. The volume and distribution of catalyst in various converter stages;
4. The catalyst efficiency;
5. The uniformity of gas composition;
6. The impurities in the entering gas;
7. The temperature control at various points in the converter.

16.5.2 Sulphuric Acid Mist. Although acid mist emission is a very small proportion of the overall acid plant yield, it is, nevertheless, worthy of consideration due to its tendency to form a very visible plume. There are many operational parameters that effect the rate of mist formation. By optimizing these parameters, mist formation can be substantially reduced. The parameters to be optimized include:

1. The concentration and temperature of the absorbing acid;
2. The amount and concentration of the oleum if produced;
3. The organic matter content in the raw materials of a sulphur-burning plant;

4. The moisture content of sulphur dioxide entering the converter;
5. The cooling of sulphur trioxide leaving the converter;
6. The quantity of nitrogen oxides present which results from excessive temperatures in the combustion chamber and impurities in the raw materials;
7. The rate of acid circulation and uniformity of distribution;
8. The efficiency of the 98% sulphuric acid absorber.

Of all readily controllable factors, the most important is probably the concentration and temperature of the sulphuric acid absorber.

16.5.3 Sulphuric Acid Spray. Acid spray is normally not a problem. If it does occur the problem is usually caused by the failure of demister elements, operating appreciably above design rate, or poor design.

16.6 Emission Reduction by Use of Control Equipment

16.6.1 Sulphur Dioxide. Plants are usually designed to minimize acid gas emissions to the atmosphere. Since addition of auxiliary equipment increases capital expenditures and operating costs, some plants today operate with no recovery equipment.

Data from two plants in the United States, utilizing the ammonia scrubbing process developed by Cominco, indicate this process reduces SO_2 concentrations in exit gases to about 0.08% by volume for single-stage units or about 0.03% by volume for two-stage units (42).

Although this process is efficient at removing SO_2, it is inefficient at removal of acid mist. The ammonia scrubbing equipment is normally fitted with mist removal equipment.

Scrubbing with fresh or salt water may remove one half to two thirds of the SO_2, but may present problems in the use or disposal of the resulting solution.

The Wellman-Lord, a chemical absorption, regenerative process designed to remove SO_2 from stack gases, can be used on sulphuric acid plants. The chemical absorption takes place in the gas-handling train where a sodium sulphite-bisulphite solution contacts the gas in a trayed or packed absorber. The SO_2 reacts with sodium sulphite to give sodium bisulphite and 90 to 95% of the sulphur dioxide reacts. The sodium bisulphite-rich solution discharged from the absorber is then transferred to the chemical plant for regeneration. The clean, saturated gas exiting from the absorber can be exhausted directly to the atmosphere or reheated for esthetic value to eliminate the water vapour plume (43).

16.6.2 Sulphuric Acid Mist and Spray. There are a number of devices available to remove sulphuric acid mist and spray. Efficiencies of over 90% are available with any of them; however, this does not guarantee that an invisible plume will result unless there are few particles less than 3 µm. The following paragraphs describe the equipment now in use in the United States (44).

Wire-Mesh Mist Eliminators

The wire-mesh eliminator is the lowest-cost device that effectively removes particles larger than 3 microns in diameter. The eliminator is commonly constructed with two beds in series and operates with pressure drops of 0.25 to 0.75 kPa. Efficiencies in excess of 92% can be reached with this system (44).

Fibre Mist Eliminators

High-efficiency glass-fibre mist eliminators are capable of operating with acid-mist collection efficiencies of over 99%. Pressure drops vary usually between 1.2 and 2.5 kPa (45).

Ceramic Filters

The ceramic filter, a German device, is reported to operate with highly efficient acid-mist collection at constant tail-gas flow rates. The pressure drop is about 2.4 kPa. High maintenance costs and inflexibility in handling varying gas volumes are two of its main disadvantages.

16.7 Survey of Emissions (6)

Nine of the ten Canadian phosphate fertilizer producers use sulphuric acid as a precursor in the production of fertilizer. One of the nine purchases the acid. Three of the remaining eight obtain their sulphuric acid as a by-product from a pollution control process at an adjoining metallurgical complex as internal product transfer. The remaining five produce their own acid.

Only three plants provided acid mist data. Based on this limited data, a rough estimate of the acid mist emissions from all plants is 350 tonnes/year.

Reported sulphur dioxide emissions in terms of kilograms per tonne of 100% acid produced ranged from 2.5 to 28.6 with the average being 13.7. Total sulphur dioxide emissions associated with the sulphuric acid in the nine Canadian phosphate fertilizer plants that use it, are estimated at 31 500 tonnes per year based on questionnaire data.

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