

**EP**

**Group I, Phase II**

**Developmental Document for  
Effluent Limitations Guidelines and  
New Source Performance Standards  
for the**

**OTHER NON-FERTILIZER  
PHOSPHATE CHEMICALS**

**Segment of the  
PHOSPHATE  
MANUFACTURING  
Point Source Category**



**UNITED STATES ENVIRONMENTAL  
PROTECTION AGENCY**

**JUNE 1976**



DEVELOPMENT DOCUMENT FOR  
EFFLUENT LIMITATIONS GUIDELINES  
AND NEW SOURCE PERFORMANCE STANDARDS  
FOR THE  
OTHER NON-FERTILIZER PHOSPHATE  
CHEMICALS SEGMENT OF THE  
PHOSPHATE MANUFACTURING  
POINT SOURCE CATEGORY

Russell E. Train  
Administrator

Andrew W. Breidenbach  
Assistant Administrator for Water  
and Hazardous Materials

Eckardt C. Beck  
Deputy Assistant Administrator for  
Water Planning and Standards



Robert B. Schaffer  
Director, Effluent Guidelines Division

Chester E. Rhines  
Project Officer

June 1976

Effluent Guidelines Division  
Office of Water and Hazardous Materials  
U.S. Environmental Protection Agency  
Washington, D.C. 20460



## ABSTRACT

A study was carried out on the non-fertilizer phosphate chemical segment of the phosphate manufacturing point source category for the purpose of developing effluent limitation guidelines, federal standards of performance, and pretreatment standards. This was done to implement sections 304, 306, and 307 of the Federal Water Pollution Control Acts Amendments of 1972.

The study included a detailed and extensive exemplary plant survey, contacts with consultants and government officials, and literature search.

The industry survey involved data gathering, sample collection and analysis, and personal visitation with responsible plant operating personnel to obtain first-hand information on treatment technology in commercial use and technology in development and pilot plant stages.

The three main outputs from the study were: industry subcategorization, recommendations on effluent guidelines, and definition of treatment technology. The non-fertilizer phosphate chemicals consisted of three subcategories which were considered separately for more meaningful separation and division of waste water treatment, and subsequent development of effluent guidelines. These subcategories are defluorinated phosphate rock, defluorinated phosphoric acid and sodium phosphates. Notice of interim final effluent limitations guidelines has been drafted for existing sources for both best practicable control technology currently available, and for best available technology economically achievable. Notice of proposed standards of performance for new sources and notice of pretreatment standards for existing sources and for new sources has, likewise, been drafted for each subcategory (FR 40, 4102 and FR 40, 4110, January 27, 1975). The interim final regulations have been amended and promulgated for existing and new sources in the Federal Register notice associated with this document. Pretreatment standards are being reserved at this time.

Treatment technologies such as in-process or end-of-process add on units are available singly or in combination to meet the recommended effluent guidelines.



## Index

TITLE PAGE

ABSTRACT

TABLE OF CONTENTS		<u>Page</u>
Section I	Conclusions	1
Section II	Recommendations	5
Section III	Introduction	9
Section IV	Industry Subcategorization	21
Section V	Waste Characterization	23
Section VI	Selection of Pollutant Parameters	45
Section VII	Control and Treatment Technology	57
Section VIII	Cost, Energy and Non-Water Quality Aspects	71
Section IX	Best Practicable Control Technology Currently Available, Final Guidelines and Limitations	79
Section X	Best Available Technology Economically Achievable, Final Guidelines and Limitations	89
Section XI	New Source Performance Standards and Pretreatment Standards	93
Section XII	Acknowledgments	99
Section XIII	References	101
Section XIV	Glossary	105





FIGURES		<u>Page</u>
III-1	Defluorinated Phosphate Rock Plant Locations	17
III-2	Defluorinated Phosphoric Acid Plant Locations	18
III-3	Sodium Phosphates Plant Locations	19
V-1	Defluorinated Phosphate Rock Fluid Bed Process	24
V-2	Defluorinated Phosphoric Acid Vacuum Process	33
V-3	Defluorinated Phosphoric Acid Submerged Combustion	34
V-4	Defluorinated Phosphoric Acid Aeration Type	35
V-5	Sodium Phosphate Process from Wet Process Phosphoric Acid	40
VII-1	Contaminated (Pond) Water Treatment	64



TABLES		<u>Page</u>
VIII-1	Water Effluent Treatment Costs	73
VIII-2	Summarized Estimated Wastewater Treatment Costs of Phosphate Manufacturing Plants	74
XIV-1	Metric Conversion Table	106



## SECTION I

### CONCLUSION

This study was conducted for the purpose of extending effluent limitations guidelines and standards of performance to all the major chemical products of the Phosphate Manufacturing Point Source Category, and was directed at products neither covered in the Phase I phosphate manufacture study, nor included among the fertilizer phosphate products. The Phase I phosphate study covered the production of phosphorus, and products derived from phosphorus. This Phase II study covers phosphate chemicals produced by the defluorination of phosphate rock, the defluorination of phosphoric acid, and the sodium phosphates produced from wet process phosphoric acid. The subcategories previously established for the Phosphate Manufacturing Point Source Category were:

The Phosphorus Derived Chemicals Segment

Subpart A - Phosphorus Production Subcategory

Subpart B - Phosphorus Consuming Subcategory

Subpart C - Phosphate Subcategory.

The Other Non-Fertilizer Phosphate Chemicals Segment, now added, include:

Subpart D - Defluorinated Phosphate Rock Subcategory

Subpart E - Defluorinated Phosphoric Acid Subcategory

Subpart F - Sodium Phosphates Subcategory

The study of Subparts A, B and C (Phase I) has been completed and regulations published in the Federal Register, Title 40, Part 422, page 6580, February 20, 1974. This Phase II study deals only with Subparts D, E, and F.

The major waste water pollutant problems for Subparts D, E and F processes of phosphate chemicals manufacture are much closer associated with the fertilizer phosphate industry problems than with Subpart A, B and C phosphate manufacturing problems. The phosphoric acid raw material utilized for making defluorinated phosphoric acid, for making sodium phosphates, and used as a reagent in

defluorination of rock, is exclusively produced by the wet phosphoric acid process. The purification processes carried on constantly in this segment create fluoride waste water problems. Residues from salt purification processes contain phosphate residues along with salt contaminants that create problems if recycled indefinitely, and require blowdown. The contaminated water recycle pond, heart of the fertilizer phosphate waste water treatment system, provides the best known means of dealing with most of these components. Fluorides, sulfates and phosphates are precipitated by lime treatment. Under favorable water balance circumstances, operation is without discharge of process waste water. The radium 226 problem is similar to that in the fertilizer phosphate industry. Radium 226 can be and is controlled by an adequately alkaline coagulation reaction and effective clarification while carrying out the double lime effluent treatment process. Extremely rigorous controls are essential to prevent flow into ground water through channels left open by improper lagoon lining operations. Dikes must be built and maintained in a manner that eliminates failure. Dike failures have occurred in the slime ponds of phosphate mining operations and in phosphate manufacturing operations, recirculation and reuse ponds. Dike failure is a serious potential hazard from contaminated water ponds. Dike failure leads to massive pollution by at least 5 highly objectionable pollutants, radium 226, fluoride, acidic wastes, phosphate and suspended solids. Recommendations that drastically reduce the dike failure hazard are provided in this development document.

The information on fertilizer phosphates in the Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the basic fertilizer chemicals segment of the fertilizer point source category is fully as important as the information gathered in this study for dealing with the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Practicable treatment is available to these manufacturing operations only through utilization of the recirculation and reuse lagoon developed for waste water treatment in wet phosphoric acid manufacture.

In the defluorinated phosphate rock and defluorinated phosphoric acid processes the techniques and treatment technologies do exist and are commercially practiced to achieve essentially no process waste water effluent discharge to navigable waters. The exception to this situation would be an adventitious condition such as abnormal rainfall accumulation. Under such a condition treatment technology does exist to treat contaminated

process waste waters for reduction of contaminants on a commercially demonstrated basis to the effluent limitation guideline levels.

In the sodium phosphates process, technology does exist to continuously treat the process waste water effluent to commercially demonstrated levels that meet the promulgated effluent limitation guideline levels.

In-process modifications and end-of-process plant waste water treatment technologies are in current industrial use to enable new non-fertilizer phosphate chemicals manufacturing plants to meet the promulgated new source standards.





## SECTION II

### RECOMMENDATIONS

These amendments to the phosphate manufacturing point source category are being introduced to include the defluorinated phosphate rock subcategory (Subpart D), the defluorinated phosphoric acid subcategory (Subpart E) and the sodium phosphates subcategory (Subpart F).

Final effluent limitations have been written for existing sources, covering both best practicable control technology currently available (BPCTCA), and best available technology economically achievable (BATEA). New source performance standards (NSPS) have also been promulgated. Pretreatment has been reserved.

The regulations are about to appear in the Federal Register; the Federal Register presents the regulations in official form.

#### Defluorinated Phosphate Rock and Defluorinated Phosphoric Acid Subcategories

The effluent guidelines limitations written for the defluorinated rock and the defluorinated acid subcategories include specifications on the capacity of the recirculation and reuse lagoon. The lagoon must maintain reserve capacity to retain the heaviest expected 24 hour rainfall for a 10 year (or 25 year) period. The treated effluent that may be discharged in periods of excessive rainfall must meet specified concentration limits. The surge capacity must hold the heaviest expected 10 year 24 hour rainfall for BPCTCA, and the heaviest expected 25 year 24 hour rainfall for BATEA and NSPS. The guidelines written for the sodium phosphates subcategory are based on weight units of pollutant per weight unit of product.

Concentrations of pollutant components permitted in process wastewater discharges for BPCTCA, BATEA and NSPS:

#### Effluent Characteristic

#### Effluent Limitations

Maximum for  
any one day

Average of daily  
values for thirty  
consecutive days  
shall not exceed

(Metric units, mg/l)

Total phosphorus (as P)	105	35
Fluoride	75	25
TSS	150	50
pH	Within the range 6.0 to 9.5	

The total suspended solid limitation set forth in this paragraph shall be waived for process wastewater from a calcium sulfate storage pile runoff facility, operated separately or in combination with a water recirculation system, which is chemically treated and then clarified or settled to meet the other pollutant limitations set forth in this paragraph.

Concentration of pollutants discharged in contaminated non-process wastewater shall not exceed the values listed in the following table:

<u>Effluent Characteristic</u>		<u>Effluent Limitations</u>
	Maximum for any one day	Average of daily values for thirty consecutive days <u>shall not exceed</u>
		mg/l
Total phosphorus (as P)	105	35
Fluoride	75	25
pH	Within the range 6.0 to 9.5	

Pretreatment standards are reserved.

#### Sodium Phosphates Subcategory

The following limitations establish the quantity or quality of pollutants or pollutant properties controlled by final regulations for best practicable control technology currently available:

<u>Effluent Characteristic</u>		<u>Effluent Limitations</u>
	Maximum for any one day	Average of daily values for thirty consecutive days

		<u>shall not exceed</u>
	(Metric units, kg/kkg of product)	
	(English units, lb/1000 lb of product)	
TSS	0.50	0.25
Total phosphorus (as P)	0.80	0.40
Fluoride	0.30	0.15
pH	Within the range 6.0 to 9.5	

The following limitations establish the quantity or quality of pollutants or pollutant properties controlled by final regulations for best available control technology economically achievable and for new source performance standards:

<u>Effluent Characteristic</u>	<u>Maximum for any one day</u>	<u>Effluent Limitations</u>
		Average of daily values for thirty consecutive days <u>shall not exceed</u>
	(Metric units, kg/kkg of product)	
	(English units, lb/1000 lb of product)	
TSS	0.35	0.18
Total phosphorus (as P)	0.56	0.28
Fluoride	0.21	0.11
pH	Within the range 6.0 to 9.5	

Pretreatment standards are reserved.



## SECTION III

### INTRODUCTION

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administration pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works. These are to be based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) of the Act. Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, processes and regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the fertilizer manufacturing category of point sources.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b) (1) (a) of the Act, to propose regulations establishing Federal Standards of performances for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources

within the fertilizer manufactuirng category of point sources, which included within the list published January 16, 1973.

The effluent limitations guidelines and standards of performance proposed in this report were developed from operating data, sampling, and information gathered from six plants. These plants represent a very high percentage of the total number of the industrial units in two of the three study processes. The methods and procedures used in the accumulation of the overall information are described in the following paragraphs.

#### Summary of Methods Used for Development of the Effluent Limitations Guidelines and Standards of Performance

The effluent limitations guidelines and standards of performance proposed herein were developed in the following manner. The point source category was first studied for the purpose of determining whether separate limitations and standards are appropriate for different segments within the category. This analysis included a determination of whether differences in raw material used, product produced, manufacturing process employed, age, size, waste water constituents, and other factors require development of separate limitations and standards for different segments of the point source category.

The raw waste characteristics for each such segment were then identified. This included an analysis of (1) the source flow and volume of water used in the process employed and the sources of waste and waste waters in the plant; and (2) the constituents (including thermal) of all waste waters, including toxic constituents and other constituents which result in taste, odor, and color in the water or unfavorable influence on aquatic organisms. The constituents of the waste waters which should be subject to effluent limitations guidelines and standards of performance were identified.

The range of control and treatment technologies existing within each segment was identified. This included an identification of each distinct control and treatment technology, including both inplant and end-of-process technologies, which are existent or capable of being designed for each segment. It also included an identification in terms of the amount of constituents (including thermal) and the effluent level resulting from the application of each of the treatment and control technologies. The problems, limitations and reliability of

each were also identified. In addition, the nonwater impact of these technologies upon other pollution problems, including air, solid waste, noise and radiation were also identified. The energy requirements of each control and treatment technology was identified as well as the cost of the application of such technologies.

The information, as outlined above, was then evaluated in order to determine what levels of technology constituted the "best practicable control technology currently available", the "best available demonstrated control technology, processes, operating methods, or other alternatives". In identifying such technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects of the application of various types of control techniques, process changes, nonwater quality environmental impact (including energy requirements), and other factors.

#### Delineation of Study

The industry is characterized by a relatively small number of plants. Only 1 plant exists for the sodium phosphate subcategory. Some of the plants did not cooperate with the study because of trade secret factors. Fortunately, the technology developed for the phosphorus derived segment of phosphate manufacturing, and for the phosphate subcategory of fertilizer manufacturing is extremely well suited for handling the waste water problems of this segment of the industry. The background technology has been utilized extensively in establishing standards for the industry.

The effluent limitations guidelines and standards of performance proposed in this report were developed from operating data, sampling, and information gathered from 6 plants. The methods and procedures used in the accumulation of that data is described in the following paragraphs.

Identification and categorization of the 3 processes covered in this report were made during the preparation of the Phase I portion of the industry report on Phosphorus Derived Chemicals. These are:

Defluorinated Phosphate Rock (Subpart D)

Defluorinated Phosphoric Acid (Subpart E)

Sodium Phosphates (Subpart F)

(produced from wet process phosphoric acid)

#### Basis for Definition of Technology Levels

The validated data and samples described in the foregoing pages were the primary basis for choosing the levels of technology which were considered to be the "best practicable control technology currently available", the "best available technology economically achievable", and the "best available demonstrated control technology, process operating methods, or other alternatives". This selection of the separate technologies, of necessity, required consideration of such additional factors as evaluation of the engineering and operational problems associated with the technology, effect on existing processes, total cost of the technology in relation to the effluent reduction that would be realized, energy requirements and cost, the range of control variations on contaminant concentration and/or quantity, and non-water quality environmental impact. Information regarding the influence of these diverse factors was obtained from a number of sources. These sources include government research information, published literature, trade organization publications, United States process patents, and qualified consultants. Final levels were set after extensive discussions between legal and technical divisions.

#### Implementation

The value of a study such as this is entirely dependent upon the quality of the data from which it is made. Particular attention was, therefore, directed to selecting criteria for determining the commercial installations to be visited and from which to collect information.

In this Phase II phosphate study the selection of individual plants for participation in the survey required a minimum of consideration after the initial U. S. industry plant identification. Two of the three processes had less than five total U. S. operating plants. The third process represented a slightly larger number of operating plants, eleven, and was found to have essentially identical water usage, water management and effluent treatment characteristics as one of the Phase I Phosphate Fertilizer Industry processes.

Because of the relatively few plants involved in each of the Phase II processes, the consideration of exemplary plant selection for the survey was not used. For one process, all U. S. plants were included. For another, all except one U. S. plant were included. For the third process, its close relationship to a similar Phase I process necessitated that



only two plants representing each of the two different process variations in industrial use be included in the survey. Full consideration of exemplary plants has now been covered in cost studies.

Contact was then made with each of the plants selected in the separate processes to establish a time for a screening visit. The screening visit had the objective of informing the plant manager on the purpose and intent of the study. Information acquired during the visit was used to determine whether that particular plant was to be included in the study or whether other plants and/or conditions better exemplified industry standards. The plants included in the survey were found to have good effluent monitoring programs in effect and were maintaining comprehensive records. Study covered the important fluoride, suspended solids, phosphate, radium 226, and pH parameters. In some cases the plant records did not necessarily isolate the liquid streams to and from the specific process unit involved in the survey but did provide valuable information on water management control.

A comparative evaluation was made of the various plants visited. This evaluation was based upon the criteria used in the Phase I study. It consisted of the following points:

1. Discharge Effluent Quantities

Installations with low effluent quantities including some plants operating with no discharge of process waste water.

2. Effluent Contaminant Level

Installations with low effluent contaminant concentrations and quantities.

3. Effluent Treatment Method and Effectiveness

Installations utilizing the best currently available treatment methods, and control equipment.

4. Water Management Practice

Installations with utilization of good management practices such as main water re-use, planning for seasonal rainfall variations, in-plant water segregation and proximity of cooling towers to operating units where airborne contamination can occur.

## 5. Land Utilization

Consideration of land area involved in waste water effluent control system with the most acceptable being those with the least area.

## 6. Air Pollution Control

Consideration given to those plants with the most comprehensive and effective air pollution control. In turn liquid effluent from such plants may represent the most serious waste water effluent condition. Major air pollution problems considered were fluorine, sulfur dioxide and radon 222.

## 7. Geographic Location

Consideration given to those facilities in close proximity to sensitive vegetation, and with high population density. Land availability and local and state restrictions and standards were considered. The greatest attention was directed to rainfall and evaporation conditions in the area.

## 8. Management Operating Philosophy

Plants whose management insists upon effective equipment maintenance and housekeeping practices.

## 9. Diversity of Processes

On the basis that other criteria are met, then consideration was given to installations having a multiplicity of processes.

Each above criterion was assigned a range of numerical values to allow a comparative evaluation of the different plants visited in each process category.

## Sampling Collection and Validation of Data

The most important item in a study of this nature is to obtain data representative of a given process under all conditions of operation and range of production rates. Steps and procedures used in selecting data, stream sampling, and sample analysis were all designed to accomplish this goal to the best possible degree.

An important step toward this objective was the assignment of only highly experienced operating personnel to the field

work. Three persons were used. The fertilizer plant operating experience of these three people ranged from a minimum of 16 years to 24 years. With such operational knowledge it was possible to expeditiously select data, identify specific process streams for sampling, and conduct sampling under readily discernible plant operating conditions. The points considered and identified in all data collection, sampling, and validation were:

1. Segregation of process effluent streams so that only an identifiable single process and/or piece of equipment was represented.
2. Collection of data and samples at different states of process conditions such as normal steady state, plant washout when such a procedure is followed on a routine basis, upset process condition, operation at above/below plant design rate, and during shutdown conditions if effluent flow occurs.
3. Evaluation of the effect, if any, of seasonal rainfall, particularly on non-point source effluent and ponds.
4. Establishment of the existence of flow measurement devices and/or other means of quantitatively measuring effluent flows.
5. Making positive identity of the type, frequency, and handling of the samples represented by collected data - i.e., such items as grab, composite, or continuous type; shift, daily or weekly frequency, etc. All samples collected by the contractor were composite samples.
6. Validation of data through determination of plant laboratory analytical procedures used for sample analysis, check samples analyzed by independent laboratories, and/or DPG sampling under known and defined process conditions with sample analysis by an accredited commercial laboratory, was completed at each plant. A total of 6 plants were visited and data were collected at each plant.

#### GENERAL DESCRIPTION OF THE INDUSTRY

The segment of the U.S. phosphate industry included in this Phase II survey includes phosphate manufacturing processes which utilize phosphate rock or wet process phosphoric acid as basic raw materials. Phosphate products manufactured from these processes are utilized as animal feed

ingredients, fertilizer intermediates, and high quality sodium phosphate salts.

One of the phosphate processes is the defluorination of phosphate rock. During the early stages of World War II bone meal for use as an animal feed supplement came into short supply. This short supply situation spurred activity for finding an alternate source and/or process to satisfy this material so important to the production of animal foodstuffs. Bone meal supplies two important animal mineral requirements, namely calcium and phosphorus. Lack of adequate levels of these ingredients can result in such animal disorders as aphosphorosis, rickets or infertility.

Materials which can furnish these calcium and phosphorus ingredients can be derived from two general sources. The natural occurring type materials used for these minerals are such items as bonemeal, meatmeal and fishmeal. An alternate source was through processing phosphate rock. The problem with phosphate rock as a direct source lay in the need to reduce the 3 to 4 percent fluorine content in the rock to a level which was not harmful to animals upon ingestion.

The outcome of this animal feed supplement supply problem was that three methods were developed and put into commercial operation. Over the past years process and equipment improvements have gradually proven one process to have the better overall commercial values. This process is described in detail on the following pages of this section and is the process used at the three plants included in the survey.

The estimated annual U.S. production of defluorinated phosphate rock for recent years is indicated below.

<u>Estimated Annual U.S. Production</u>						
Thousands of kkg (tons)						
Defluorinated Rock						
18% P Content						
<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>
373 (410)	394 (435)	380 (430)	394 (435)	444 (490)	485 (535)	485 (535)

Plant site locations for U.S. plants are indicated on Figure III-1.

A second phosphate process included in the study is the defluorination of wet process phosphoric acid. Acid defluorination is accomplished commercially by two methods.

DEFLUORINATED PHOSPHATE ROCK

PLANT LOCATIONS

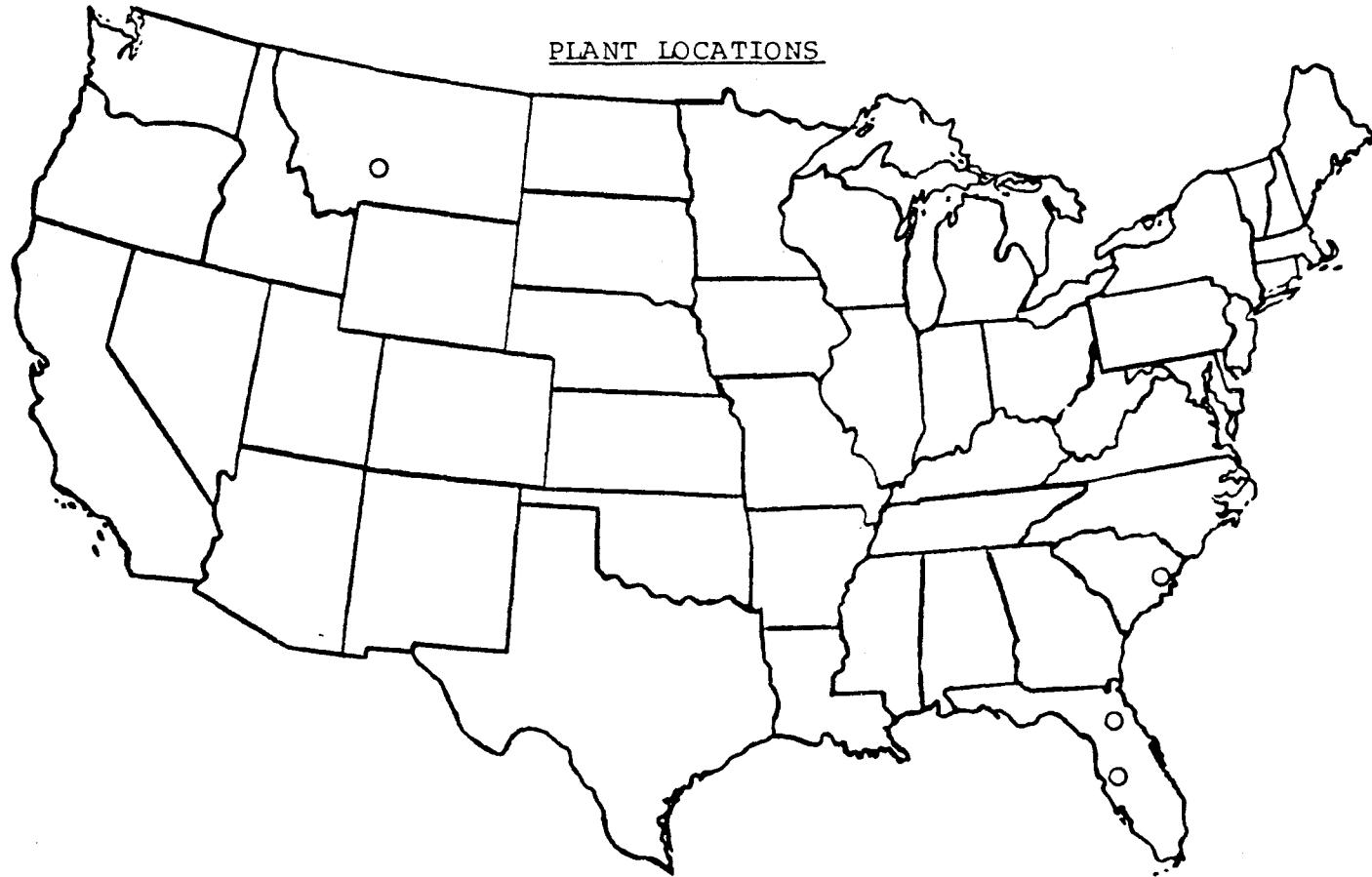


FIGURE III-1

DEFLUORINATED PHOSPHORIC ACID

PLANT LOCATIONS



FIGURE III-2

SODIUM PHOSPHATES

PLANT LOCATIONS

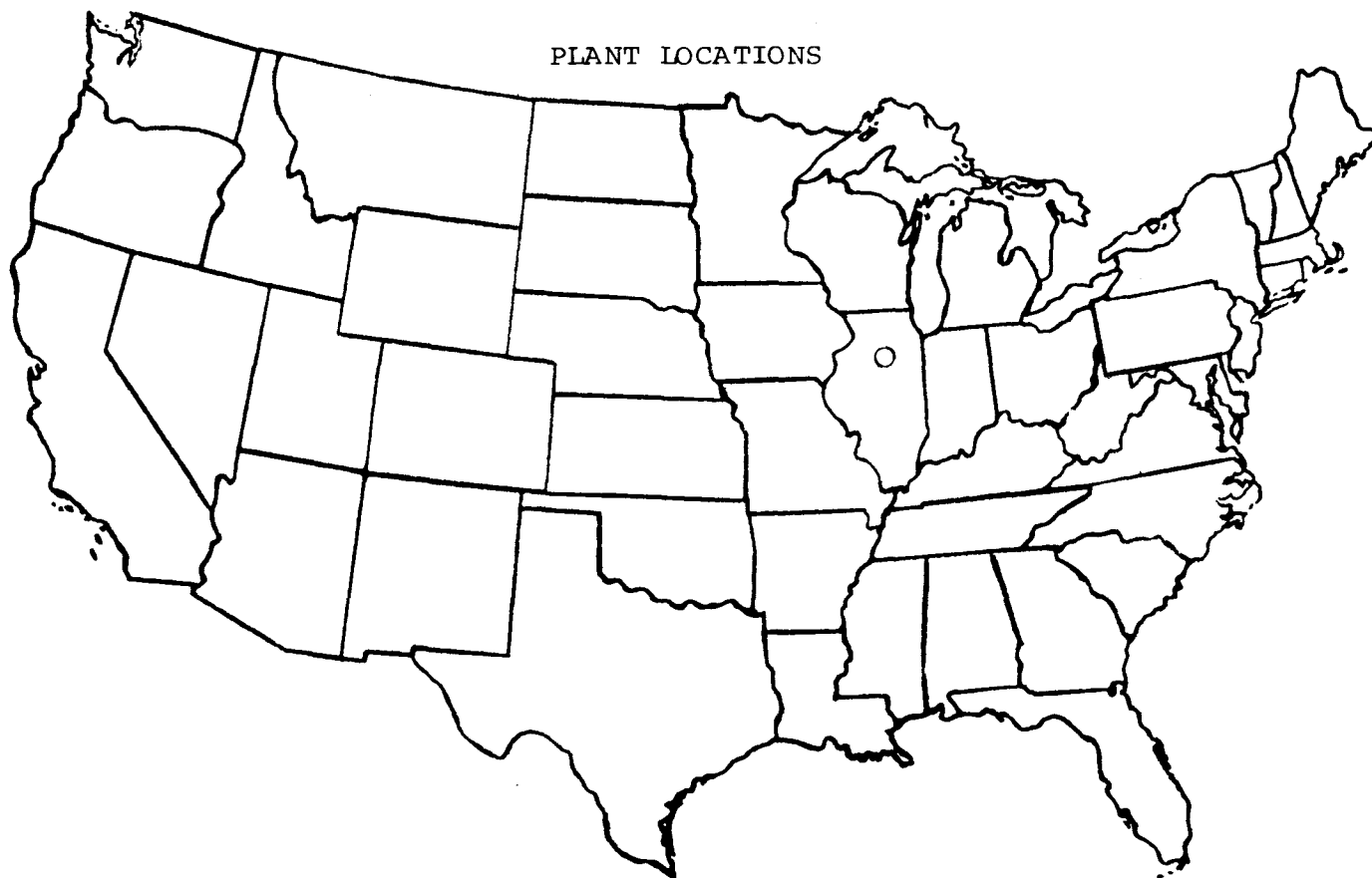


FIGURE III-3

The method in most common use is the manufacture of superphosphoric acid. This process essentially involves the concentration of phosphoric acid from a 52-54%  $P_{2O_5}$  concentration level to a 68-72%  $P_{2O_5}$  level. In the process of evaporating water from the acid, fluorine is also removed. The degree of fluorine removal is dependent upon the initial fluorine level and the final phosphoric acid concentration. In most cases the fluorine removal is sufficient to permit use of the concentrated phosphoric acid for manufacture of animal feed supplements.

Two types of phosphoric acid evaporators are used to produce superphosphoric acid. One type uses the principle of acid circulation in a vessel maintained at sub-atmospheric pressure. This is the type most prominent in the United States. A second type uses the principle commonly referred to as submerged combustion. In this type hot gases directly from a fuel fired combustion chamber are bubbled through the acid.

The second method of acid defluorination in commercial use is the combination of the addition of an additive to the acid which in turn facilitates fluorine removal by aeration.

Defluorinated acid has several end uses. A large percentage of the defluorinated acid is mixed with limestone to produce dicalcium phosphate for animal feed supplement use. Increasingly greater quantities are being used for liquid fertilizer production. This use, however, does not require low fluorine content acid. There is also an increasing use of superphosphoric acid as an intermediate in the production of dry mixed fertilizer. The advantage in this latter usage is a combination of reducing fluorine evolution from the manufacturing process and savings on raw material freight costs.

The current annual U.S. production of defluorinated phosphoric acid is estimated at 760,000 kkg (835,000 tons)  $P_{2O_5}$ . Plant site locations for U.S. plants are indicated on Figure III-2.

The third phosphate process included in the survey is the production of high quality sodium phosphate salts. Conventionally, high purity phosphoric acid as produced from thermal or electric furnace operations is used as the raw material for such compounds. Wet process acid is however, used by one U.S. manufacturer to produce these compounds primarily for use as intermediates in the production of cleaning compounds. The plant site location map for this type unit is indicated as Figure III-3.



## SECTION IV

### INDUSTRY SUBCATEGORIZATION

The subcategorization developed for this segment of the phosphate industry was largely determined in the course of the Phase I phosphate study and the Phase I fertilizer phosphate study. Phosphoric acid derived from phosphorus is a much purer product than the wet process acid of the fertilizer industry. Human food grade calcium phosphates, most reagent chemical quality phosphate compounds and sodium tripolyphosphate are made from phosphorus derived acid.

A comparative list of the impurities and physical characteristics of furnace acid and wet process acid are indicated in the following table.

<u>Impurities</u>	<u>Furnace Acid</u>	<u>Wet Process Acid</u>
	<u>Weight Percent</u>	
F	0.007	0.6 - 1.0
SO <sub>3</sub>	0.003	2.7
Al <sub>2</sub> O <sub>3</sub>	0.001	0.9
Fe <sub>2</sub> O <sub>3</sub>	0.0007	1.2
Water Insolubles	-	0.8
Total Impurities	0.012	6.2 - 6.6
Density kg/l (lb/gal) @ 27°C (80°F)	1.57 (13.1)	1.72 (14.3)
Viscosity, cp	18	85
Color	Colorless	Pale green to dark brown

Although the phosphate compounds of highest purity requirements are made from phosphorus derived acid, a substantial demand developed for products of adequate quality for many uses, but cheaper than the furnace acid derived materials. Major products in this area are calcium phosphates for animal feed, defluorinated phosphoric acid and sodium phosphates. The industry supplied this demand through defluorination of phosphate rock, and defluorination of phosphoric acid. The sodium phosphate demand is supplied by products derived from the purification of wet process phosphoric acid, derived from calcined rock.

Within this group of chemicals, the defluorination of phosphate rock is carried out by dry calcining, which distinguishes it sharply from the remaining products derived through defluorinating liquid phosphoric acid. The most favorable water balance within the segment is held by this defluorinated rock process. Substantial evaporation loss occurs in stack washing to control fluoride emission. The water used for stack washing picks up substantial fluorine pollution, much the same as the scrubber water for fertilizer phosphate plant acid. The major problem is best handled by recirculation through a contaminated water pond type of recycle system.

Water is collected from the defluorination of phosphoric acid. This is water driven from the acid by heat, aided by air streams and/or vacuum. This water contains the fluoride contaminant common to phosphoric acid production. The defluorination processes in use are accompanied by the formation of dehydrated and polymer forms of phosphate from the orthophosphate in rock and in wet process acid. These phosphate varieties have high calcium salt solubility; this introduces a treatment problem lacking in fertilizer phosphate production if the defluorinated products get to the waste water.

Sodium phosphates are produced from conventional wet process phosphoric acid, which has been derived from calcined rock. The calcining improves product color through destruction of organic components. The production of sodium phosphates is associated with waste water problems similar to the fertilizer phosphate problems. The conversion of rock to phosphoric acid is by the usual fertilizer phosphate process. The purification steps conducted in phosphate salt manufacture required the blowdown of process water with fluorine, sulphate and phosphate waste water components, as well as other salts and solids.

Conventional wet acid production is carried out prior to production of both defluorinated acids and the sodium salts. These plants have typical wet acid problems. As a result of these considerations, and factors developed in the following sections on manufacturing technology and waste water characteristics, 3 subcategories have been established for this segment of phosphate manufacturing:

Subpart D - The Defluorinated Phosphate Rock Subcategory

Subpart E - The Defluorinated Phosphoric Acid Subcategory

Subpart F - The Sodium Phosphates Subcategory.

## SECTION V

### WASTE CHARACTERIZATION

The technical aspects of the manufacturing processes are described in this section, along with identification of water usage, and the development of waste water flow.

#### DEFLUORINATED PHOSPHATE ROCK - PROCESS DESCRIPTION

##### General

As mentioned earlier in Section III, the early World War II shortage of bonemeal produced the necessary incentive to find an alternate source of animal feed supplement. The two ingredients required were calcium and phosphorus and these two elements were prominently present in apatite type phosphate rock. The one natural apatite rock ingredient which prevented its use as an animal feed material was the relatively high (3.0 - 4.0%) fluorine content. Basically the problem was to find an economical means of defluorinating the rock and still have an end product which would be palatably acceptable to primarily cows, chickens and pigs. Three general methods were developed to defluorinate the phosphate rock.

One method involved treatment of normal superphosphate-produced by mixing phosphate rock with sulfuric acid. Reaction of the phosphate rock and sulfuric breaks the chemical bond that holds the fluorine in the fluorapatite lattice. This superphosphate is then subjected to temperatures which volatilize essentially all the fluorine. The mono and dicalcium phosphate compounds in the material are converted to alpha and beta tricalcium phosphate during the heat treatment.

A second method involves treating a prescribed mixture of phosphate rock and silica in an oil fired shaft furnace. This also volatilizes the fluorine and yields a fused tricalcium phosphate mass. The hot mass is quenched in water immediately upon exit from the furnace. Chemical composition of the product is approximately 28% phosphorus pentoxide and 0.4% fluorine.

The third method is described as the calcination of phosphate rock without fusion. It has demonstrated the most favorable commercial characteristics and has become the most prominent U.S. defluorination process. There have been several significant modifications to this process since its

DEFLUORINATED PHOSPHATE ROCK  
FLUID BED PROCESS

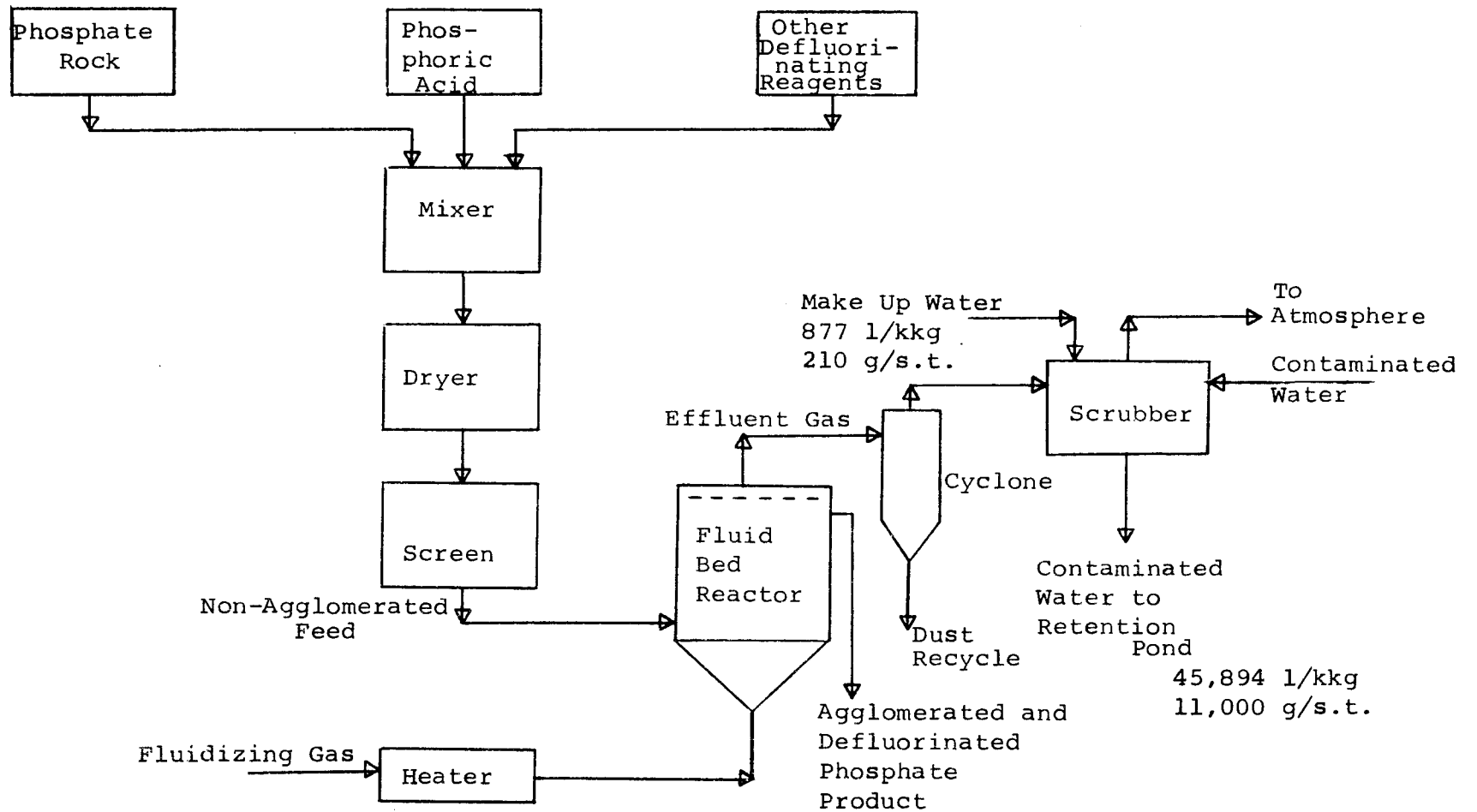


Figure V-I

initial commercial operation in 1944. Initially the process utilized a mixture of phosphate rock and silica as a feed material. The silica used was sand that is a by-product from phosphate rock beneficiation. Ratio of silica to phosphate rock was an important criterium in the defluorination process. This charge of silica and phosphate was then introduced to a rotary kiln. In the interim years these two original steps - use of silica ratio and rotary kiln - have been modified. Silica has been partially replaced with sodium compounds and the rotary kiln has been replaced by a fluid bed reactor. Not all U.S. production units utilize both of these modifications but both are practiced by the major producers. A more detailed process description of the process using both these modifications is presented on the following pages.

The defluorination of phosphate rock as practiced at U.S. commercial production plants is a process on which there is a limited amount of published information available. Plant visits included only guarded technical discussions and limited plant observations. One of the primary reasons for these practices is the protection of trade secret information. U.S. patents were therefore the major source of process information.

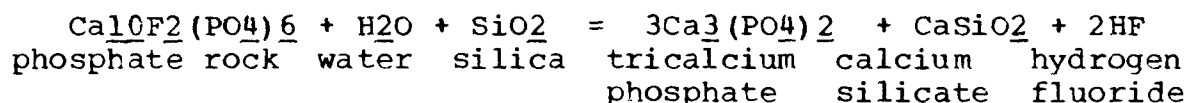
The fluorapatite type of phosphate rock is the primary raw material. Phosphate content of the rock is typically 35%  $P_2O_5$ . Other raw materials used in lesser amounts but very critical to the process include sodium containing reagents, wet process phosphoric acid and silica. The quantity, point of addition of these materials to the process, and how they are mixed with the phosphate rock constitute some of the know-how involved to realize a workable process and a consistent product quality. These raw materials are added in specific quantities or ratios dependent upon the feed phosphate rock analysis.

The sodium containing reagent is commonly soda ash (sodium carbonate) which has a  $Na_2O$  content of approximately 58% or over 98%  $Na_2CO_3$ . The wet phosphoric acid reagent concentration used is 45-54%  $P_2O_5$ . Silica addition is in the form of sand and is dependent on the silica present in the basic phosphate rock feed. As previously mentioned the point of addition and how these materials are mixed together either as a physical mixture or agglomerated into nodular form is one of the trade secrets. The above described mixture or charge is then fed into either a rotary kiln or a fluid bed reactor. In the case of a fluid bed reactor, it is desirable that the charge be nodular and dried prior to being fed into the reactor. This is in consideration of the

fluid bed characteristics of effecting particle classification and loss in the exhaust gas. In the kiln or fluid bed reactor, temperature control and retention time are the process variables which require close control. Reaction temperatures are maintained in the 1205 - 1366°C (2200-2700°F) range with the rotary kiln requiring the upper portion of the range.

Retention time ranges from 30 to 90 minutes with the fluid bed reactor generally requiring the lesser time.

The state of the charge in the kiln or fluid bed reactor is highly dependent upon the ratio of the raw materials added to the phosphate rock. That is, whether the fluorine is evolved in a minimal time period or in sufficient quantity and/or whether the charge fuses into an unmanageable mass that rings or solidifies in the unit. Another critical factor in these units is that water vapor content be maintained at a sufficiently high percentage to effect the required fluorine evolution. The equation representative of the chemical reaction and fluorine release in the kilns and fluid bed reactors cited in preceding text is:



The reaction is actually much more complex. Dehydration, not hydrolysis, occurs in the kiln. The product phosphates are primarily in the poly or dehydrated form. Hydrolysis of silicon fluoride to silica and hydrofluoric acid occurs on water scrubbing of the tail gas.

From the kiln or fluid bed reactor the defluorinated product is quickly quenched with air or water. This is necessary to maintain the product in the alpha rather than beta tricalcium phosphate form. The alpha form is the high solubility material most desirable in the final product. From this point the product is crushed and sized for storage or shipment.

#### Defluorinated Phosphate Rock - Waste Water Characterization

As previously mentioned, the detail and amount of specific information on water usage and effluents received and verified in this survey was minimal. There were two general reasons for this situation. One was that none of the plants had operable flow metering equipment. A second reason is the point already mentioned - that of reluctance to give

technical data and free access to the plant operating area due to the many items regarded as trade secrets. From a practical standpoint such information in this case would serve only as background data and a better understanding of the overall process water balance. On those items which are important to the study such as water management practices, effluent analyses, and permission to conduct sampling of inlet and outlet effluents there was excellent industry cooperation and information input.

The following types of water usage and effluents were identified.

- A. Contaminated Process Waste Water from Stack Scrubbing and Reuse Pond
- B. Water Supply
- C. Spills and Leaks
- D. Non-Point Source Discharges

Each of the above listed items are further identified below as to flow and contaminant content under their respective headings.

A. Contaminated Process Waste Water from Stack Scrubbing (Recycle and Reuse Pond)

The greatest single process wastewater source is from water used in scrubbing contaminants from the gaseous effluent streams. This has an instantaneous water requirement is of appreciable magnitude and process conditions do permit use of recirculated contaminated water for this service. The quality of this contaminated water is similar to that in fertilizer process circulation systems. The waste water volume is not normally dependent on the rainfall and evaporation conditions prevalent at the plant site. Most plants are on complete recycle. Evaporation losses are so great that excessive wastewater accumulations will require treatment and discharge only in periods of excessive rainfall.

Complete recycle does not eliminate the need for lime treatment. Hydrofluoric acid is released constantly in the high temperature calcining process, along with sulfurous and sulfuric acids derived from fuel. Each plant must take measures

to control the accumulation of acid to prevent excessive air pollution. Air pollution control is achieved by adding lime to the recirculating wastewater at the stack, adding lime to the pond, or by constantly liming a portion of the recirculating pond water, removing the calcium fluoride, the calcium sulfate and the calcium phosphate precipitates, and returning the supernatant fraction to the pond. Solid wastes are always formed by the measures essential to control air pollution. The wastewater composition may be unusual at sites where manufacture of products other than defluorinated rock is carried out and the wastewater from these products discharged into the recycle and cooling pond. system. A water analysis obtained from a Plant B sample during the survey is typical of contaminated water used in defluorinated phosphate rock process units.

#### Contaminated Water Constituents

<u>Parameter</u>	<u>Concentration</u>
pH	1.65
Total Suspended Solids	16.00 mg/l
Total Solids	2,267.00 mg/l
Chloride (Cl)	101.00 mg/l
Sulfate (SO <sub>4</sub> )	350.00 mg/l
Calcium (Ca)	40.00 mg/l
Magnesium (Mg)	12.00 mg/l
Aluminum (Al)	58.00 mg/l
Iron (Fe)	8.30 mg/l
Fluorine (F)	1,930.00 mg/l
Arsenic (As)	0.38 mg/l
Zinc (Zn)	5.20 mg/l
Phosphorus (P)	600.00 mg/l
BOD <sub>5</sub>	3.00 mg/l
COD	48.00 mg/l
Color	#120 (after filter)
Turbidity	45.00 Jackson Candle Units

The following figures indicate a representative water usage. These figures will vary within reasonable limits between plants and at different seasons of the year but are representative of the magnitude of usage required in the process.

l/kkg

(gal/ton)



B. Water Supply

Water supply water is defined as essentially uncontaminated water from such sources as wells, commercial or municipal water systems, and impoundment areas for natural rainfall or runoff. Such water is added to the process for such reasons as process functions where contaminated water use is prohibited due to process requirements, make-up water to the contaminated water system and equipment, or area wash downs. The following figures indicate the usage range.

l/kg

(gal/ton)

877

(210)

C. Leaks and Spills

Various sources of contaminated non-process wastewater have been established by the definition of "contaminated non-process wastewater" that appears in the regulations pertaining to defluorinated phosphate rock manufacture:

The term "contaminated non-process wastewater" shall mean any water including precipitation runoff, which during manufacturing or processing, comes into incidental contact with any raw material, intermediate product, finished product, by-product or waste product by means of (1) precipitation runoff, (2) accidental spills, (3) accidental leaks caused by the failure of process equipment and which are repaired or the discharge of pollutants therefrom contained or terminated within the shortest reasonable time which shall not exceed 24 hours after discovery or when discovery should reasonably have been made, whichever is earliest, and (4) discharges from safety showers and related personal safety equipment, and from equipment washings for the purpose of safe entry, inspection and maintenance; provided that all reasonable measures have been taken to prevent, reduce, eliminate and control to the maximum extent feasible such contact and provided further that all reasonable measures have been taken that will mitigate the effects of such contact once it has occurred.

While an allowance has been made for the discharge of treated contaminated non-process wastewater, it is the responsibility of every manufacturer to exercise diligence in repairing leaks or in correcting other conditions that create contaminated non-process wastewater, so that contamination is held to the lowest possible level.

Many manufacturers have demonstrated that spurious contamination from leaks and spills and other sources can be kept at a very low level. Continuous analysis of pH, conductivity or total organic carbon is being conducted on large cooling water streams so that serious leaks are almost immediately detected. Corrective measures are put into action immediately on detection. In many circumstances, the system salvages products of sufficient value to more than pay for the monitoring system. Good housekeeping practices, efficient operation and prompt maintenance will minimize contamination of water from leaks and spills. Techniques for achieving control and prevention of such losses are described in "Guidelines for Chemical Plants in the Prevention, Control and Reporting of Spills" by the Manufacturing Chemists Association, 1972.

Shipping losses were excluded from the data base and regulations. These losses are equally amenable to control and prevention as leaks and spills. Good housekeeping, prompt and regular maintenance, and careful operations will tend to minimize losses from shipping operations.

#### D. Non-Point Source Discharge

The origin of this discharge is dry materials - both raw material and product - which dust over the plant area usually emitted from conveying equipment. These materials are then solubized or sluiced by rain or melting snow into the plant drainage system.

### DEFLUORINATED PHOSPHORIC ACID - PROCESS DESCRIPTION

#### General

Defluorinated phosphoric acid is to a degree a bit misleading to persons associated with the fertilizer industry. The reason being that acid defluorination is

inherently included in the process of evaporating commercial wet process 54% P<sub>2</sub>O<sub>5</sub> phosphoric acid to the superphosphoric acid (68-72% P<sub>2</sub>O<sub>5</sub>) concentration level. To fertilizer people therefore, the principal U. S. defluorinated acid process is better known as a superphosphoric acid unit. Two different type superphosphoric units are in commercial use in the U. S.

Another method of defluorinating wet process phosphoric acid has come into commercial use in the past few years. This process also uses commercial wet process 54% P<sub>2</sub>O<sub>5</sub> phosphoric acid as the raw material. In this process an additive is mixed with the phosphoric acid to aid in the release and volatilization of fluorine from the liquid. The mechanism for fluorine removal from the acid is aeration.

Defluorinated phosphoric acid is used primarily as a raw material for production of mixed fertilizer goods - both dry and liquid types. It is also mixed with limestone in the manufacture of dicalcium phosphate for use as an animal feed supplement. Approximately 67% of the estimated U. S. 835,000 annual tons P<sub>2</sub>O<sub>5</sub> quantity of defluorinated acid is used in fertilizer manufacture and 33% in the production of dicalcium phosphate. The degree of defluorination required to meet animal feed regulations is that the P to F ratio be at least 100 to 1.

#### DEFLUORINATED ACID - VACUUM TYPE EVAPORATION

The vacuum type evaporation method for defluorination of wet process phosphoric acid is essentially identical to the procedure and equipment used to produce 54% P<sub>2</sub>O<sub>5</sub> phosphoric acid from 26-30% P<sub>2</sub>O<sub>5</sub> strength acid.

Concentration of 54% P<sub>2</sub>O<sub>5</sub> acid to a 68-72% P<sub>2</sub>O<sub>5</sub> strength is performed in vessels which use high pressure (450-550 psig) steam or externally heated Dowtherm solution as the heat energy source for evaporation of water from the acid. These units effect evaporation by circulating acid at a high volume rate consecutively through a shell and tube heat exchanger and a flash chamber under low absolute (vacuum) pressure conditions. In the heat exchanger, steam or Dowtherm solution is applied to the shell side and acid flows through tubes. Acid flow through the tubes is of the wetted wall type rather than full tube flow. The flash chamber serves to provide a large liquid surface area where water vapor is released without significant acid entrainment loss. Fluorine removal from the acid occurs concurrently with the water vapor release. Both of these gases pass to a

barometric condenser and are absorbed in the condenser water. Dependent upon the quality of superphosphoric acid being produced (e.a. 30 or 50-60% conversion to polyphosphates), either a single unit or a series of two units may be used to accomplish the evaporation and/or defluorination required.

#### DEFLUORINATED ACID - SUBMERGED COMBUSTION

A second method of phosphoric acid defluorination is by the direct contact of hot combustion gases with the acid. In this method a combustion chamber fitted with one or more fuel oil or gas burners is mounted directly on top of an acid containment chamber. Pressurized hot gases from the fuel combustion are bubbled through the acid to an immersion depth of up to approximately 46 cm (18 inches). Acid in the containment chamber is maintained at a constant level by control of the low concentration feed acid flow. The production of evaporated and defluorinated product acid from the unit is continuous and is controlled by acid boiling point or temperature.

Gases (evaporated water, stripped hydrogen fluoride and silicon tetrafluoride) from the evaporation chamber flow to a series of gas cleaning and absorption equipment. First, entrained phosphoric acid is recovered from the gas stream and re-introduced to the unit or to the phosphoric acid plant. Following acid removal, the gases pass to a multi-stage direct contact condenser system where a high percentage of the contaminants are removed before exhaust to the atmosphere. Water can be used in all or only the final stages of the condenser system as a condensing and scrubbing medium.

#### DEFLUORINATED ACID - AERATION

This method of defluorinating phosphoric acid is the most recent proprietary method to come into commercial use. Relatively small quantities of diatomaceous silica or spray dried silica gel with high surface area characteristics are mixed with commercial 54%  $P_2O_5$  phosphoric acid. This silica material addition serves to supply sufficient silica for conversion of the minor quantity of hydrogen fluoride (HF) present in the impure phosphoric acid to fluosilicic acid ( $H_2SiF_6$ ). Fluosilicic acid at an adequate temperature in turn breaks down to  $SiF_4$  and by simple aeration is stripped from the heated mixture. The gaseous effluent stream is maintained above its dew point until it enters the gas

DEFLUORINATED PHOSPHORIC ACID - VACUUM PROCESS  
(Super Phosphoric)

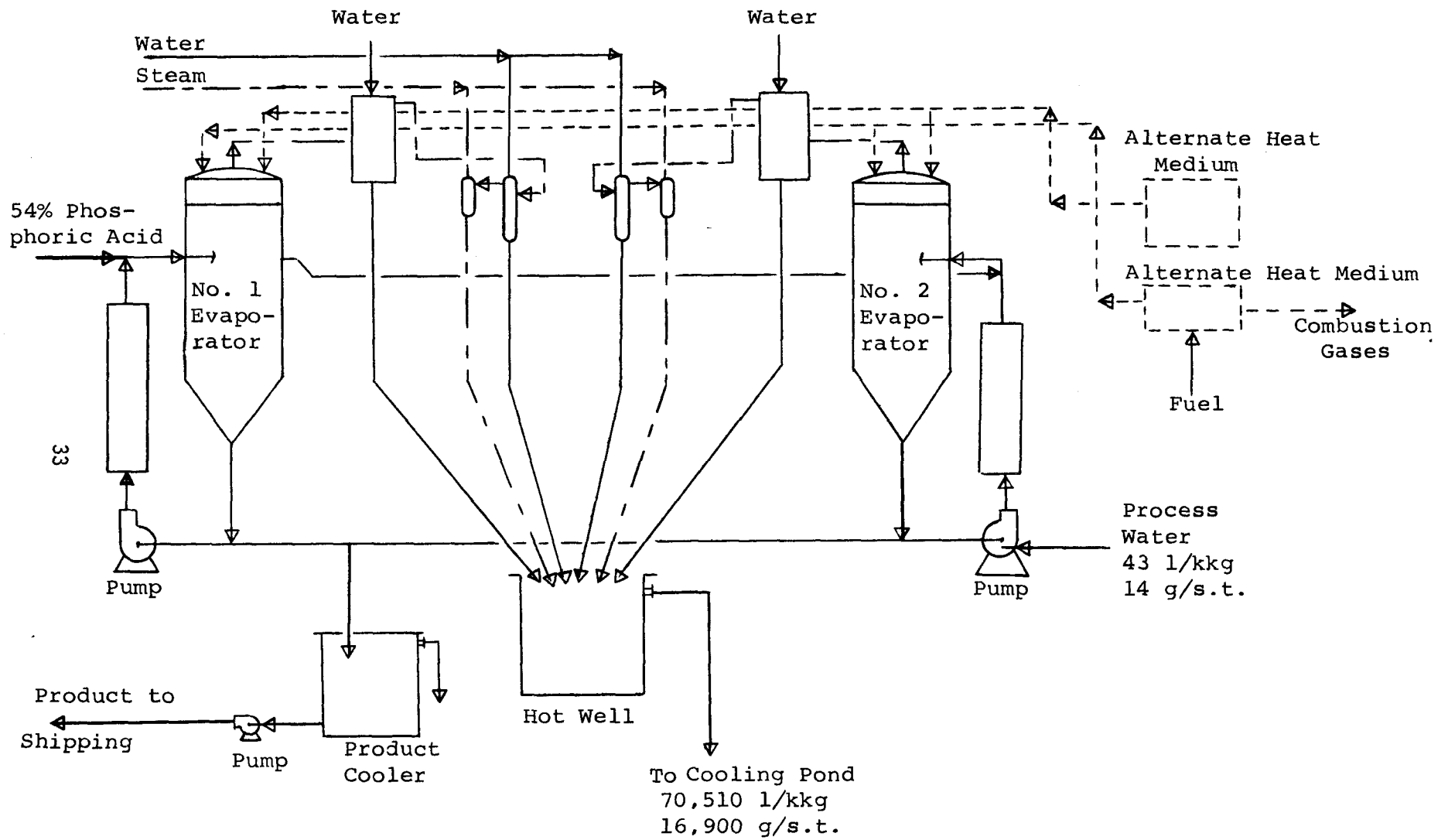


Figure V-2

DEFLUORINATED PHOSPHORIC ACID  
(Submerged Combustion)

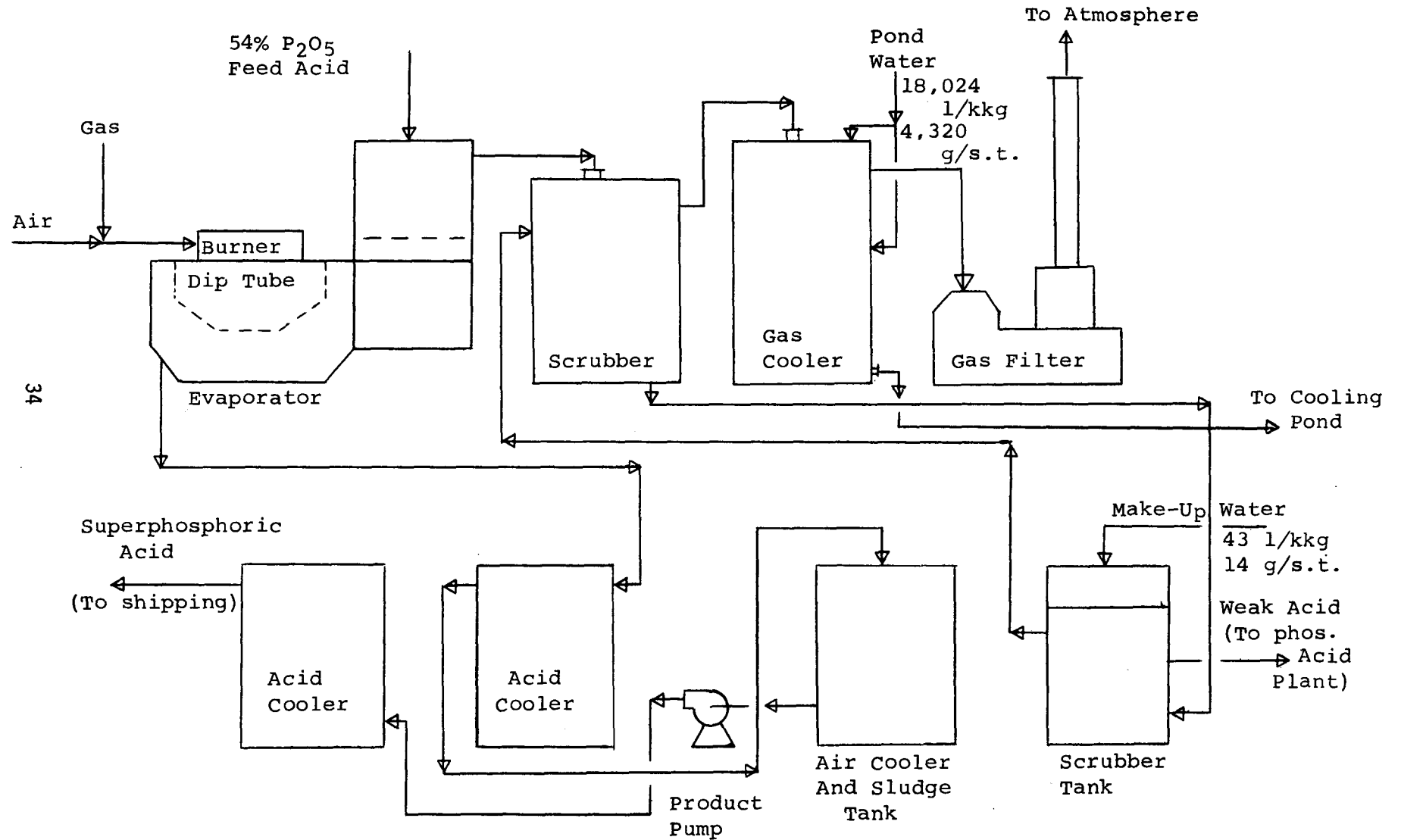


Figure V-3

DEFLUORINATED ACID - AERATION TYPE

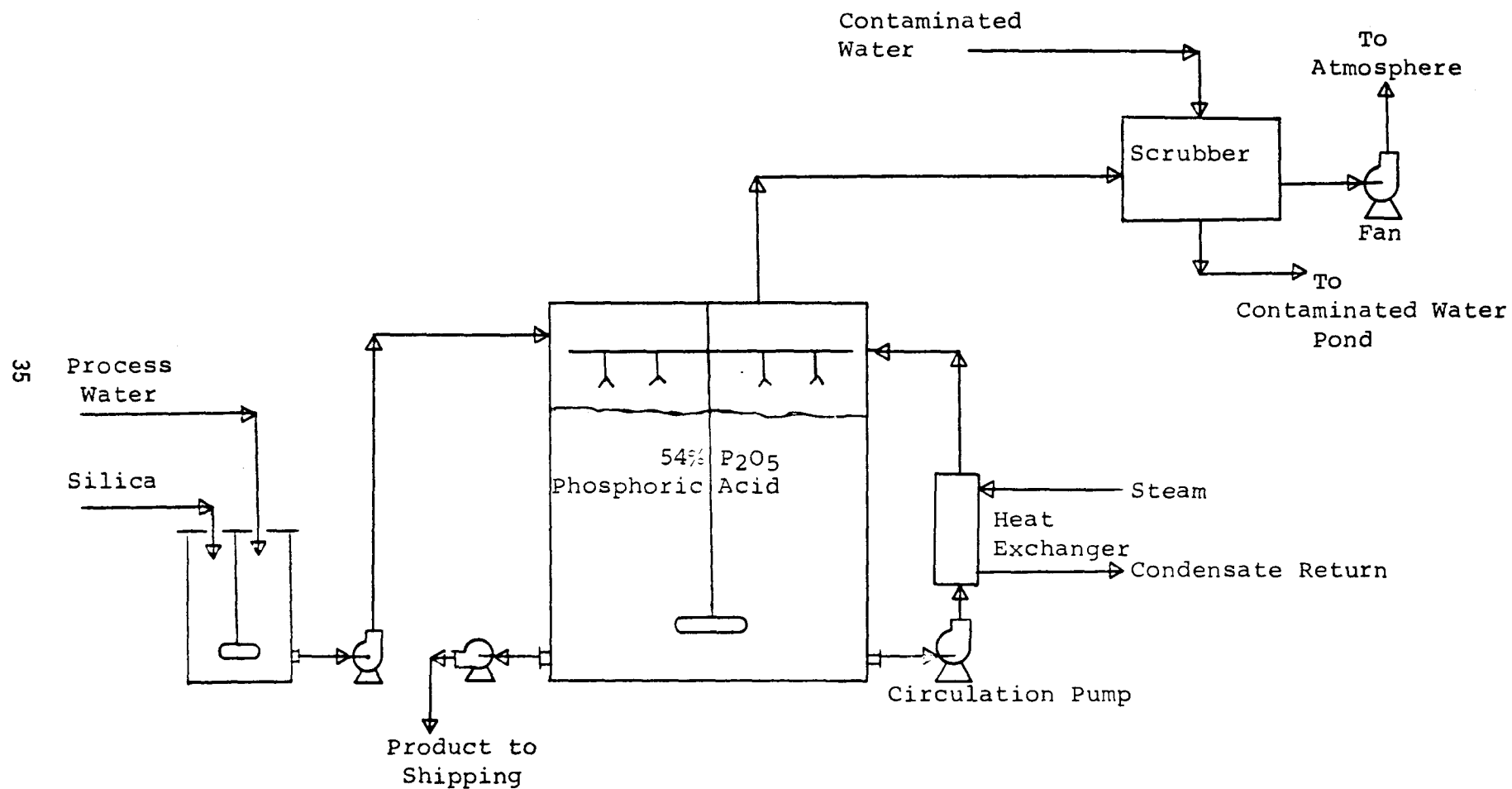


Figure V - 4

scrubbing unit. At this point the gas stream is contacted with water to remove contaminants before release to the atmosphere. Phosphoric acid (54% P<sub>2</sub>O<sub>5</sub>) can be defluorinated to a weight ratio of 100 to 1 or better P to F by this method.

#### Defluorinated Phosphoric Acid - Waste Characterization

Information on water usage and effluents was obtained on two of the three defluorination methods described, namely, Defluorinated Acid - Vacuum Type Evaporation and Defluorinated Acid - Submerged Combustion. No commercial operating data or sampling information was obtained on the Defluorinated Acid - Aeration method. This method of defluorination has been commercial for a relatively short time and patent protection had not yet been granted either the original inventor or the licensee on his additional modifications. As a result of this situation no detailed information was attainable on this process. It is known however, that the method's usage is confined to removal of air contaminants from the gaseous effluent stream and possibly a minor quantity of process water for seal water use. Both of these usages will qualitatively and quantitatively be equal to or less than those indicated for the other two methods.

The following types of water usage and effluents were identified:

- A. Contaminated Process Waste Water from Tail Gas or Stack Scrubbing Operation (Recycle and Reuse Pond)
- B. Water Supply
- C. Leaks and Spills

Various sources of contaminated non-process wastewater have been established by the definition of "contaminated non-process wastewater" that appears in the regulations pertaining to defluorinated phosphoric acid manufacture:

The term "contaminated non-process wastewater" shall mean any water including precipitation runoff, which during manufacturing or processing, comes into incidental contact with any raw material, intermediate product, finished product, by-product or waste product by means of (1) precipitation runoff, (2) accidental spills, (3) accidental leaks caused by the failure of process equipment and which are repaired or the discharge of pollutants therefrom contained or terminated within the shortest reasonable time which shall not exceed 24 hours after discovery or when



discovery should reasonably have been made, whichever is earliest, and (4) discharges from safety showers and related personal safety equipment, and from equipment washings for the purpose of safe entry, inspection and maintenance; provided that all reasonable measures have been taken to prevent, reduce, eliminate and control to the maximum extent feasible such contact and provided further that all reasonable measures have been taken that will mitigate the effects of such contact once it has occurred.

While an allowance has been made for the discharge of treated contaminated non-process wastewater, it is the responsibility of every manufacturer to exercise diligence in repairing leaks or in correcting other conditions that create contaminated non-process wastewater, so that contamination is held to the lowest possible level.

Many manufacturers have demonstrated that spurious contamination from leaks and spills and other sources can be kept at a very low level. Continuous analysis of pH, conductivity or total organic carbon is being conducted on large cooling water streams so that serious leaks are almost immediately detected. Corrective measures are put into action immediately on detection. In many circumstances, the system salvages products of sufficient value to more than pay for the monitoring system. Good housekeeping practices, efficient operation and prompt maintenance will minimize contamination of water from leaks and spills. Techniques for achieving control and prevention of such losses are described in "Guidelines for Chemical Plants in the Prevention, Control and Reporting of Spills" by the Manufacturing Chemists Association, 1972.

Shipping losses were excluded from the data base and regulations. These losses are equally amenable to control and prevention as leaks and spills. Good housekeeping, prompt and regular maintenance, and careful operations will tend to minimize losses from shipping operations.

#### A. Contaminated Water

The only significant water usage in these defluorinated acid methods is for use in scrubbing contaminants from the gas effluent streams. The scrubber equipment may be in the form of either a barometric condenser or the more conventional gas scrubber type. In either case, the instantaneous water requirement is of appreciable magnitude. As in the defluorinated phosphate rock, the process conditions do permit use of contaminated water for this service. Water quality similar to that

prevailing in wet process phosphoric acid recycle systems. A common recycle system is utilized at some plants for wet acid and for defluorinated acid production. Wastewater volume is dependent on rainfall and evaporation conditions at plant site. The amount of acid collected in the wastewater at a defluorinated acid plant is determined by the amount of hydrofluoric acid removed from the raw product wet phosphoric acid, and the phosphoric and sulfuric acids entrained and separated in the fluoride removal process. A water analysis obtained from a Plant D sample during the survey is typical of contaminated water used in defluorinated acid process units.

#### Contaminated Water Constituents

<u>Parameter</u>	<u>Concentration</u>
pH	1.29
Total Suspended Solids	30.00 mg/l
Total Solids	28,810.00 mg/l
Chloride (Cl)	65.00 mg/l
Sulfate (SO <sub>4</sub> )	4,770.00 mg/l
Calcium (Ca)	1,700.00 mg/l
Magnesium (Mg)	106.00 mg/l
Aluminum (Al)	260.00 mg/l
Iron (Fe)	180.00 mg/l
Fluorine (F)	967.00 mg/l
Arsenic (As)	0.83 mg/l
Zinc (Zn)	5.30 mg/l
Total Phosphorus (P)	5,590.00 mg/l
BOD <sub>5</sub>	15.00 mg/l
COD	306.00 mg/l
Color	#120 (after filter) *
Turbidity	45 Jackson Candle Units

\* Unit of color - potassium chloroplatinate

The following figures indicate a representative water usage. These figures will vary within reasonable limits between plants and at different seasons of the year but are representative of the magnitude required in the process.

<u>Method</u>	<u>l/kkg</u>	<u>(gal/ton)</u>
Defluorinated Acid - Vacuum Type Evaporation	70,510	16,900

Defluorinated Acid -	18,024	4,320
Submerged Combustion		

## B. Water Supply

Water supply water is defined as uncontaminated water from such sources as wells and commercial or municipal water systems. The water is used for pump seal water. Usage figures are listed below:

<u>Method</u>	<u>l/kkg</u>	<u>(gal/ton)</u>
All Methods	43	14

## C. Spills and Leaks

Spills and leaks are collected as part of process efficiency and housekeeping. Sources of this water are pump seals and plant wash up. The quantity is minor and/or periodic.

### SODIUM PHOSPHATE - PROCESS DESCRIPTION

#### General

The high quality standards set by detergent manufacturers for their products necessitates that an essentially pure sodium phosphate solution be used as a raw material. This high purity standard has greatly limited the use of wet process phosphoric acid as a phosphate source for this industry. One U. S. manufacturer however, does commercially purify wet process acid to the degree necessary to allow its use in the manufacture of sodium phosphate compounds for detergent manufacture.

Wet process acid contains an appreciable number and quantity of impurities which must be removed to achieve the acceptable detergent purity requirements. The more significant impurities to be removed include excess sulfuric acid, sodium fluosilicate, iron phosphate, aluminum phosphate and calcium sulfate. Many of the process procedures and techniques used for removal of these impurities are regarded to be trade secrets.

#### Sodium Phosphates - Process Description

Removal of impurities from the wet process acid used in this process begins with the phosphate rock used in the acid

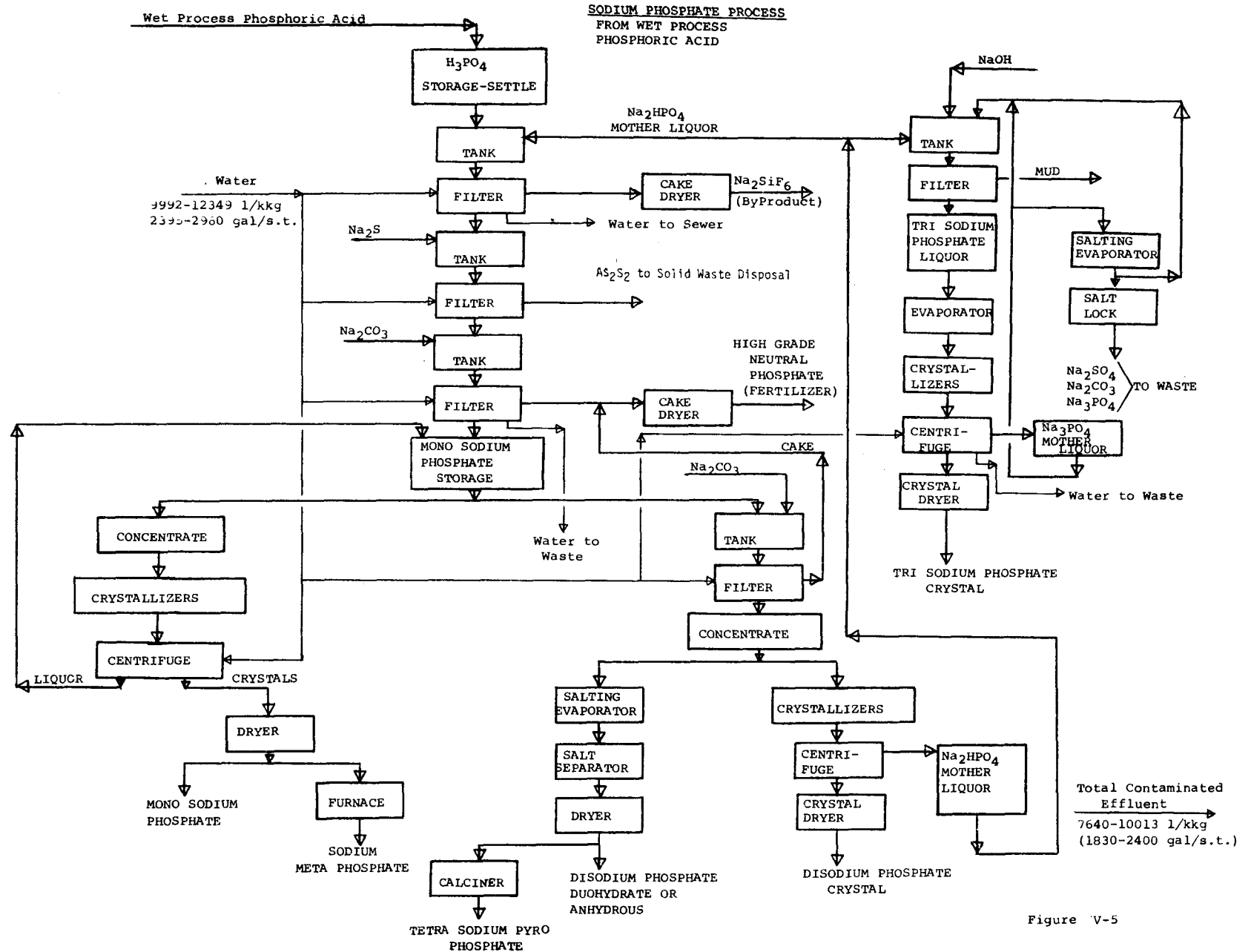


Figure V-5

manufacture. Calcined phosphate rock is used in the acidulation step to yield a nearly colorless acid to start the purification steps. Rock calcination destroys the organic matter inherent in mined rock. It is organic matter which causes the brown coloration that normally characterizes wet process phosphoric acid.

After the initial 20-25%  $P_2O_5$  acid is produced, the acid is treated in a series of separate neutralization steps to individually remove the various acid impurities. The first partial neutralization with recycled sodium phosphate liquor is designed to remove the fluosilicates. In this step granular sodium fluosilicate is precipitated and removed from the acid solution by filtration. This precipitate has commercial value as 98-99% sodium silicofluoride ( $Na_2SiF_6$ ).

The next step consists of adding sodium sulfide to the remaining solution to precipitate the minor quantity of arsenic present. Concurrently with this precipitation, barium carbonate can be added to remove the excess sulfate present as barium sulfate. Barium carbonate is not used at the plant producing sodium phosphates at the present time. Precipitates are now removed by another filtration step. The quantity of precipitate is small and is disposed of as solid waste. Local landfill authorities should be notified of the arsenic component.

At this point the partially neutralized acid still contains iron and aluminum phosphates, and some residual fluorine. A second neutralization is now made with soda ash to an approximate 4.0 pH level. This induces precipitation of essentially all the remaining impurities. These precipitated impurities are both quite voluminous and difficult to separate from the remaining solution. Special techniques of heating, agitation, and retention are necessary to adequately condition the slurry so that a filtration separation of the impurities can be made. These impurities contain a relatively high quantity of  $P_2O_5$  (40-50%) and have value as a fertilizer material. Following this neutralization step, the remaining solution is sufficiently pure for the production of monosodium phosphate.

Monosodium phosphate is crystallized from the purified solution by concentrating the solution in an evaporator. The monosodium crystals, with further dehydration, neutralization and crystallization, can be converted to such other compounds as sodium meta phosphate, disodium phosphate, and tri-sodium phosphate. The several chemical

equations and steps involved in this process are indicated on the process flowsheet.

Water effluents from these different processes are from spills and leaks, filtration washes, and gas scrubber liquors.

#### Sodium Phosphates - Waste Characterization

The survey of this process was limited by the same type of conditions and for the same reason which existed in the defluorinated phosphate rock process. This was that many of the various unit operations are considered trade secret and therefore plant access was necessarily limited to observations of effluent streams external to the process buildings. As previously stated, from a practical standpoint this restricted access takes nothing away from the value of the study other than background information and a better understanding of the overall process water balance. On those items which were basic and important to the study, the industry cooperation and response to information requests was excellent. The installed process effluent measurement and monitoring facilities were found to be well developed and maintained.

The following types of water usage and effluents were identified.

- A. Water Supply
- B. Contaminated Effluent
- C. Spills and Leaks
- D. Non-Point Source Discharges

Each of the above listed items are further identified below as to flow and contaminant content.

##### A. Water Supply

Water supply is defined as uncontaminated water from wells. The water is used for pump seal water and in various product filtration and washing procedures. Usage figures are listed below.

<u>kg</u>	<u>(gal/ton)</u>
9,992-12,349	2,395-2,960

##### B. Contaminated Effluent

This effluent is essentially the used process water with impurities that were added from the process function in which it was used. An effluent analysis typical of an effluent sample from Plant E is listed below.

#### Contaminated Water Constituents

<u>Parameter</u>	<u>Concentration</u>	
pH	7.8	
Total Suspended Solids	460	mg/l
Total Solids	2,100	mg/l
Chloride (Cl)	90	mg/l
Sulfate (SO <sub>4</sub> )	240	mg/l
Calcium (Ca)	95	mg/l
Fluorine (F)	15.0	mg/l
Total Phosphorus (P)	250	mg/l
BOD <sub>5</sub>	31.0	mg/l
COD	55.0	mg/l
Temperature	78°F	

The following figures represent the range of water effluent quantities found.

<u>l/kg</u>	<u>(gal/ton)</u>
7,640-10,013	1,830-2,400

#### C. Leaks and Spills

Many manufacturers have demonstrated that spurious contamination from leaks and spills and other sources can be kept at a very low level. Continuous analysis of pH, conductivity or total organic carbon is being conducted on large cooling water streams so that serious leaks are almost immediately detected. Corrective measures are put into action immediately on detection. In many circumstances, the system salvages products of sufficient value to more than pay for the monitoring system. Good housekeeping practices, efficient operation and prompt maintenance will minimize contamination of water from leaks and spills. Techniques for achieving control and prevention of such losses are described in "Guidelines for Chemical Plants in the Prevention, Control and Reporting of Spills" by the Manufacturing Chemists Association, 1972.

Shipping losses were excluded from the data base and regulations. These losses are equally amenable to control and prevention as leaks and spills. Good

housekeeping, prompt and regular maintenance, and careful operations will tend to minimize losses from shipping operations.

No special allowance has been made for discharge of cooling water and other non-process wastewater that becomes contaminated by spills and leaks or incidental contact with raw materials, reagents or products. The contaminated process wastewater allowances are adequate to take care of these incidental sources of water contamination. It is the responsibility of the manufacturer to exercise diligence in repairing leaks or correcting other conditions that create contaminated non-process wastewater so that contamination is held to the lowest possible level.

#### D. Non-Point Source Discharge

The origin of this discharge is primarily dry product which dusts over the plant area from conveying equipment. This product is periodically solubilized by rain or melting snow and collected by the plant waste sewer system. In this process the non-point discharge is considered to be a significant periodic influence on the plant effluent contaminant level.

#### RAW WASTE LOADS

The raw waste loads are summarized below:

##### Defluorinated Phosphate Rock

Flow:	46,000 l/kg	(11,000 gal/ton)
Total Phosphorus (P)	600	mg/l
Fluoride (F)	1,930	mg/l
TSS	16	mg/l
pH	1.65	

##### Defluorinated Phosphoric Acid

Flow:	Vacuum Type Evaporation	70,500 l/kg	(16,900 gal/ton)
	Submerged Combustion	18,000 l/kg	(4,300 gal/ton)
Total Phosphorus (P)	5,590	mg/l	
Fluoride (F)	967	mg/l	
TSS	30	mg/l	
pH	1.29		

##### Sodium Phosphates

Flow:	7,600 - 10,000 l/kg	(1,830 - 2,400 gal/ton)
Total Phosphorus (P)	250	mg/l
Fluoride (F)	15	mg/l
TSS	460	mg/l
pH	7.8	



## SECTION VI

### SELECTION OF POLLUTANT PARAMETERS

#### General

The selection of pollutant parameters was a necessary early step of the study. Collection of meaningful data and sampling was dependent on knowing what fertilizer process contaminants are important so far as degradation of natural water resources are concerned.

The general criteria considered and reviewed in the selection of pollutant parameters included:

- quality of the plant intake water
- products manufactured
- raw materials used
- environmental harmfulness of the compounds or elements included in process effluent streams

#### Other Non-Fertilizer Phosphate Chemicals

Effluent waste waters from the three processes included in this survey are similar to those associated with the phosphate fertilizer industry. The primary factors and contaminants to be controlled to achievable levels are: suspended solids, pH, phosphorus and fluorides.

Radium 226 is considered to be a very important raw waste load component. Radium 226 coprecipitates with most sedimentary fractions, particularly at a reasonably high pH level. The pH 6.0 to 9.5 range set for effluent discharges, along with the limitations as suspended solids, deals effectively with the effluent problem. The Environmental Protection Agency has ongoing studies and is initiating new studies on the problem of radium-226 in recycle pond waters. Such studies indicate that double lime treatment to a pH range of 6.0 to 9.5 is required to achieve optimum removal of radium-226. Additional information obtained from these studies will be evaluated, and where appropriate, current effluent guidelines may be amended. Procedures currently proposed are judged to be adequate and provide for rigorous control of radium-226. A more detailed discussion of this problem can be found in references N and O.

Secondary parameters which should be monitored but do not warrant definitive guidelines are: temperature, total dissolved solids, chemical oxygen demand (COD), arsenic, and cadmium. The prime reason for not setting guidelines for these secondary parameters is that treatment for the primary parameters will effect removal of also the secondary ones. A considered additional reason is that insufficient data exists from which to establish responsible guidelines.

Selection of these parameters is justified by the fact that best available technology economically achievable as well as best demonstrated technology is in current commercial use.

#### Rationale for Selection of Parameters

##### Temperature

Temperature is one of the most important and influential water quality characteristics. Temperature determines those species that may be present; it activates the hatching of young, regulates their activity, and stimulates or suppresses their growth and development; it attracts, and may kill when the water becomes too hot or becomes chilled too suddenly. Colder water generally suppresses development. Warmer water generally accelerates activity and may be a primary cause of aquatic plant nuisances when other environmental factors are suitable.

Temperature is a prime regulator of natural processes within the water environment. It governs physiological functions in organisms and, acting directly or indirectly in combination with other water quality constituents, it affects aquatic life with each change. These effects include chemical reaction rates, enzymatic functions, molecular movements, and molecular exchanges between membranes within and between the physiological systems and the organs of an animal.

Chemical reaction rates vary with temperature and generally increase as the temperature is increased. The solubility of gases in water varies with temperature. Dissolved oxygen is decreased by the decay or decomposition of dissolved organic substances and the decay rate increases as the temperature of the water increases reaching a maximum at about 30°C (86°F). The temperature of stream water, even during summer, is below the optimum for pollution-associated bacteria. Increasing the water temperature increases the bacterial multiplication rate when the environment is favorable and the food supply is abundant.

Reproduction cycles may be changed significantly by increased temperature because this function takes place under restricted temperature ranges. Spawning may not occur at all because temperatures are too high. Thus, a fish population may exist in a heated area only by continued immigration. Disregarding the decreased reproductive potential, water temperatures need not reach lethal levels to decimate a species. Temperatures that favor competitors, predators, parasites, and disease can destroy a species at levels far below those that are lethal.

Fish food organisms are altered severely when temperatures approach or exceed 90°F. Predominant algal species change, primary production is decreased, and bottom associated organisms may be depleted or altered drastically in numbers and distribution. Increased water temperatures may cause aquatic plant nuisances when other environmental factors are favorable.

Synergistic actions of pollutants are more severe at higher water temperatures. Given amounts of domestic sewage, refinery wastes, oils, tars, insecticides, detergents, and fertilizers more rapidly deplete oxygen in water at higher temperatures, and the respective toxicities are likewise increased.

When water temperatures increase, the predominant algal species may change from diatoms to green algae, and finally at high temperatures to blue-green algae, because of species temperature preferentials. Blue-green algae can cause serious odor problems. The number and distribution of benthic organisms decreases as water temperatures increase above 90°F, which is close to the tolerance limit for the population. This could seriously affect certain fish that depend on benthic organisms as a food source.

The cost of fish being attracted to heated water in winter months may be considerable, due to fish mortalities that may result when the fish return to the cooler water.

Rising temperatures stimulate the decomposition of sludge, formation of sludge gas, multiplication of saprophytic bacteria and fungi (particularly in the presence of organic wastes), and the consumption of oxygen by putrefactive processes, thus affecting the esthetic value of a water course.

In general, marine water temperatures do not change as rapidly or range as widely as those of freshwaters. Marine and estuarine fishes, therefore, are less tolerant of

temperature variation. Although this limited tolerance is greater in estuarine than in open water marine species, temperature changes are more important to those fishes in estuaries and bays than to those in open marine areas, because of the nursery and replenishment functions of the estuary that can be adversely affected by extreme temperature changes.

#### Acidity and Alkalinity - pH

Although not a specific pollutant, pH is related to the acidity or alkalinity of a waste water stream. It is not a linear or direct measure of either, however, it may properly be used as a surrogate to control both excess acidity and excess alkalinity in water. The term pH is used to describe the hydrogen ion - hydroxyl ion balance in water. Technically, pH is the hydrogen ion concentration or activity present in a given solution. pH numbers are the negative logarithm of the hydrogen ion concentration. A pH of 7 generally indicates neutrality or a balance between free hydrogen and free hydroxyl ions. Solutions with a pH above 7 indicate that the solution is alkaline, while a pH below 7 indicates that the solution is acid.

Knowledge of the pH of water or waste water is useful in determining necessary measures for corrosion control, pollution control, and disinfection. Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and such corrosion can add constituents to drinking water such as iron, copper, zinc, cadmium, and lead. Low pH waters not only tend to dissolve metals from structures and fixtures but also tend to redissolve or leach metals from sludges and bottom sediments. The hydrogen ion concentration can affect the "taste" of the water and at a low pH, water tastes "sour".

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity\* to aquatic life of many materials is increased by changes in the water pH. For example, metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. Similarly, the toxicity of ammonia is a function of pH. The bactericidal effect of chlorine in most cases is less as the pH increases, and it is economically advantageous to keep the pH close to 7.

---

\*The term toxic or toxicity is used herein in the normal scientific sense of the word and not as a specialized term referring to section 307(a) of the Act.

Acidity is defined as the quantitative ability of a water to neutralize hydroxyl ions. It is usually expressed as the calcium carbonate equivalent of the hydroxyl ions neutralized. Acidity should not be confused with pH value. Acidity is the quantity of hydrogen ions which may be released to react with or neutralize hydroxyl ions while pH is a measure of the free hydrogen ions in a solution at the instant the pH measurement is made. A property of many chemicals, called buffering, may hold hydrogen ions in a solution from being in the free state and being measured as pH. The bond of most buffers is rather weak and hydrogen ions tend to be released from the buffer as needed to maintain a fixed pH value.

Highly acid waters are corrosive to metals, concrete and living organisms, exhibiting the pollutional characteristics outlined above for low pH waters. Depending on buffering capacity, water may have a higher total acidity at pH values of 6.0 than other waters with a pH value of 4.0.

Alkalinity: Alkalinity is defined as the ability of a water to neutralize hydrogen ions. It is usually expressed as the calcium carbonate equivalent of the hydrogen ions neutralized.

Alkalinity is commonly caused by the presence of carbonates, bicarbonates, hydroxides and to a lesser extent by borates, silicates, phosphates and organic substances. Because of the nature of the chemicals causing alkalinity, and the buffering capacity of carbon dioxide in water, very high pH values are seldom found in natural waters.

Excess alkalinity as exhibited in a high pH value may make water corrosive to certain metals, detrimental to most natural organic materials and toxic to living organisms.

Ammonia is more lethal with a higher pH. The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

#### Total Suspended Solids

Suspended solids include both organic and inorganic materials. The inorganic compounds include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, and animal and vegetable waste products. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids.

Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Suspended solids in water interfere with many industrial processes, cause foaming in boilers and incrustations on equipment exposed to such water, especially as the temperature rises. They are undesirable in process water used in the manufacture of steel, in the textile industry, in laundries, in dyeing, and in cooling systems.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often damaging to the life in water. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a food source for sludgeworms and associated organisms.

Disregarding any toxic effect attributable to substances leached out by water, suspended solids may kill fish and shellfish by causing abrasive injuries and by clogging the gills and respiratory passages of various aquatic fauna. Indirectly, suspended solids are inimical to aquatic life because they screen out light, and they promote and maintain the development of noxious conditions through oxygen depletion. This results in the killing of fish and fish food organisms. Suspended solids also reduce the recreational value of the water.

Turbidity: Turbidity of water is related to the amount of suspended and colloidal matter contained in the water. It affects the clearness and penetration of light. The degree of turbidity is only an expression of one effect of suspended solids upon the character of the water. Turbidity can reduce the effectiveness of chlorination and can result in difficulties in meeting BOD and suspended solids limitations. Turbidity is an indirect measure of suspended solids.

## Fluorides

Fluorine is the most reactive of the nonmetals and is never found free in nature. It is a constituent of fluorite or fluorspar, calcium fluoride, cryolite, and sodium aluminum fluoride. Due to their origins, fluorides in high concentrations are not a common constituent of natural surface waters; however, they may occur in hazardous concentrations in ground waters.

Fluoride can be found in plating rinses and in glass etching rinse waters. Fluorides are also used as a flux in the manufacture of steel, for preserving wood and mucilages, as a disinfectant and in insecticides.

Fluorides in sufficient quantities are toxic to humans with doses of 250 to 450 mg giving severe symptoms and 4.0 grams causing death. A concentration of 0.5 g/kg of body weight has been reported as a fatal dosage.

There are numerous articles describing the effects of fluoride-bearing waters on dental enamel of children; these studies lead to the generalization that water containing less than 0.9 to 1.0 mg/l of fluoride will seldom cause mottled enamel in children, and for adults, concentrations less than 3 or 4 mg/l are not likely to cause endemic cumulative fluorosis and skeletal effects. Abundant literature is also available describing the advantages of maintaining 0.8 to 1.5 mg/l of fluoride ion in drinking water to aid in the reduction of dental decay, especially among children. The recommended maximum levels of fluoride in public water supply sources range from 1.4 to 2.4 mg/l.

Fluorides may be harmful in certain industries, particularly those involved in the production of food, beverages, pharmaceutical, and medicines. Fluorides found in irrigation waters in high concentrations (up to 360 mg/l) have caused damage to certain plants exposed to these waters. Chronic fluoride poisoning of livestock has been observed in areas where water contained 10 to 15 mg/l fluoride. Concentrations of 30 - 50 mg/l of fluoride in the total ration of dairy cows is considered the upper safe limit. Fluoride from waters apparently does not accumulate in soft tissue to a significant degree and it is transferred to a very small extent into the milk and to a somewhat greater degree into eggs. Data for fresh water indicate that fluorides are toxic to fish at concentrations higher than 1.5 mg/l.

## Phosphorus

Phosphorus occurs in natural waters and in waste waters in the form of various types of phosphate. These forms are commonly classified into orthophosphates, condensed phosphates (pyro-, meta-, and polyphosphorus), and organically bound phosphates. These may occur in the soluble form, in particles of detritus or in the bodies of aquatic organisms.

The various forms of phosphates find their way into waste waters from a variety of industrial, residential, and commercial sources. Small amounts of certain condensed phosphates are added to some water supplies in the course of potable water treatment. Large quantities of the same compounds may be added when the water is used for laundering or other cleaning since these materials are major constituents of many commercial cleaning preparations. Phosphate coating of metals is another major source of phosphates in certain industrial effluents.

The increasing problem of the growth of algae in streams and lakes appears to be associated with the increasing presence of certain dissolved nutrients, chief among which is phosphorus. Phosphorus is an element which is essential to the growth of organisms and it can often be the nutrient that limits the aquatic growth that a body of water can support. In instances where phosphorous is a growth limiting nutrient, the discharge of sewage, agricultural drainage or certain industrial wastes to a receiving water may stimulate the growth, in nuisance quantities, of photosynthetic aquatic microorganisms and macroorganisms.

The increase in organic matter production by algae and plants in a lake undergoing eutrophication has ramifications throughout the aquatic ecosystem. Greater demand is placed on the dissolved oxygen in the water as the organic matter decomposes at the termination of the life cycles. Because of this process, the deeper waters of the lake may become entirely depleted of oxygen, thereby, destroying fish habitats and leading to the elimination of desirable species. The settling of particulate matter from the productive upper layers changes the character of the bottom mud, also leading to the replacement of certain species by less desirable organisms. Of great importance is the fact that nutrients inadvertently introduced to a lake are, for the most part, trapped there and recycled in accelerated biological processes. Consequently, the damage done to a lake in a relatively short time requires a many fold increase in time for recovery of the lake.



When a plant population is stimulated in production and attains a nuisance status, a large number of associated liabilities are immediately apparent. Dense populations of pond weeds make swimming dangerous. Boating and water skiing and sometimes fishing may be eliminated because of the mass of vegetation that serves as a physical impediment to such activities. Plant populations have been associated with stunted fish populations and with poor fishing. Plant nuisances emit vile stench, impart tastes and odors to water supplies, reduce the efficiency of industrial and municipal water treatment, impair aesthetic beauty, reduce or restrict resort trade, lower waterfront property values, cause skin rashes to man during water contact, and serve as a desired substrate and breeding ground for flies.

Phosphorus in the elemental form is particularly toxic, and subject to bioaccumulation in much the same way as mercury. Colloidal elemental phosphorus will poison marine fish (causing skin tissue breakdown and discoloration). Also phosphorus is capable of being concentrated and will accumulate in organs and soft tissues. Experiments have shown that marine fish will concentrate phosphorus from water containing as little as 1 ug/l.

### Radioactivity

Ionizing radiation, when absorbed in living tissue in quantities substantially above that of natural background levels, is recognized as injurious. It is necessary, therefore, to prevent excessive levels of radiation from reaching any living organism humans, fishes, and invertebrates. Beyond the obvious fact that radioactive wastes emit ionizing radiation, they are also similar in many respects to other chemical wastes. Man's senses cannot detect radiation unless it is present in massive amounts.

Plants and animals, to be of any significance in the cycling of radionuclides in the aquatic environment, must accumulate the radionuclide, retain it, be eaten by another organism, and be digestible. However, even if an organism accumulates and retains a radionuclide and is not eaten before it dies, the radionuclide will enter the "biological cycle" through organisms that decompose the dead organic material into its elemental components. Plants and animals that become radioactive in this biological cycle can thus pose a health hazard when eaten by man.

Aquatic life may receive radiation from radionuclides present in the water and substrate and also from radionuclides that may accumulate within their tissues.

Humans can acquire radionuclides through many different pathways. Among the most important are through drinking contaminated water, and eating fish and shellfish that have concentrated nuclides from the water. Where fish or other fresh or marine products that have accumulated radioactive materials are used as food by humans, the concentrations of the nuclides in the water must be further restricted, to provide assurance that the total intake of radionuclides from all sources will not exceed the recommended levels.

In order to prevent unacceptable doses of radiation from reaching humans, fish, and other important organisms, the concentrations of radionuclides in water, both fresh and marine, must be restricted.

#### Radium-226

Radium-226 is one of the most hazardous radioisotopes of the uranium decay scheme, when present in water. The human body preferentially utilizes radium in lieu of calcium when present in food or drink. Plants and animals concentrate radium, leading to a multiplier effect up the food web.

Radium-226 decays by alpha emission into radon-222, a radioactive gas with a half life of 3.8 days. The decay products of radon-222, in turn, are particulates which can be adsorbed onto respirable particles of dust. Radon and its decay products has been implicated in an increased incidence of lung cancer in those workers exposed to high levels (Bureau of Mines, 1971). Heating or grinding of phosphate rock would liberate radon and its decay products to the surrounding atmosphere.

It is generally agreed that unlike other materials, there is no threshold value for radiation exposure. Accordingly, the Federal Radiation Council has repeatedly stated that all radiochemical material releases are to be kept to the minimum practicably obtainable. The Council states "It should be general practice to reduce exposure to radiation, and positive efforts should be carried out to fulfill the sense of these recommendations. It is basic that exposure to radiation should result from a real determination of its necessity (Federal Radiation Council, 1960)."

## METHODS OF ANALYSIS

The methods of analysis to be used for quantitative determination are given in the Federal Register 40 CFR 136 for the following parameters pertinent to this study:

Alkalinity (and Acidity)  
fluoride  
oxygen demand, chemical  
total phosphorus (as P)  
solids, total  
suspended nonfilterable solids, total  
temperature



## SECTION VII

### CONTROL AND TREATMENT TECHNOLOGY

The factors and contaminants in non-fertilizer phosphate chemical process effluent streams have for the most part been well identified and well known for many years. As a consequence considerable effort has been expended to correct or minimize the majority of those which are particularly detrimental to natural water receiving bodies. Much of this work has been directed at correcting the source of the contamination or an in-process improvement rather than an end-of-pipe type of treatment. A large part of the motivation for such improvement has been economics - that is, improved operating efficiency and costs. Such improvements are just plain good business and justify capital expenditure required to achieve them.

With an appreciation of the above mentioned facts, the following criteria were established as bases for investigating treatment technology.

- A determine the extent of existing waste water control and treatment technology
- A determine the availability of applicable waste water control and treatment technology regardless of whether it be intra-industry transfer technology
- A determine the degree of treatment cost reasonability

Based upon these stated criteria the effort was made to factually investigate overall treatment technologies dealing with each of the primary factors and contaminants listed in Section VI.

Process technology does exist both for containment and for treatment and reduction of the and contaminants present in the non-fertilizer phosphate chemical wastewaters as defined in Section VI. These processes have been divided into two separate technologies to make them better adaptable to all the processes. For example, in two of the processes it is very possible that both technologies need to be used and therefore be considered as a single treatment method. In another process however it would be somewhat impractical to consider using more than one of the technologies although they are closely inter-related. These two technologies are therefore described separately even though it is recognized that they may be essentially integral in some cases.

### Containment and Cooling Pond

The above title provides a reasonably precise description of this technology. The pond retains sufficient wastewater to meet the high demand for cooling water, particularly for stack and tail gas scrubbing operations. The pond surface provides cooling. An indication of the land area used for this purpose is shown by the fact that survey plant A utilizes approximately 0.11 hectare (0.26 acre) per daily production ton. This figure also includes area adequate to provide collection of excessive rainfall until normal conditions can be restored.

Acids are collected in the wastewater during the manufacturing operations. Insufficient basic substances are present to neutralize these acids. Lime neutralization is provided in some manner at each plant to prevent excessive air pollution by stack or tail gases. Lime may be applied to the wastewater pumped to the stack, directly to the pond in a clarifier treating a fraction of the pond recycle water. The clarifier removes sulfate fluoride and phosphate as precipitate. The neutralized supernatant fraction is returned to the pond. One plant manufactures sodium fluosilicate from the fluoride derived from the distillation process.

### Factors in Pond Construction and Management that Provide Pond Reliability and Efficiency of Operation

#### A. Prevention of Dike Failure

Dike failure has been by far the greatest cause of navigable water contamination from phosphate mining operations. Many slime pond dike failures have occurred. These have caused massive contamination of surface waters. Dike failures have also been reported for containment and cooling ponds.

A potential hazard, therefore, exists from gyp-pond and recirculation cooling pond dikes, although these are generally much smaller structures than the slime pond dikes. Gypsum derived from total manufacturing and waste water treatment practices is the only dike material readily available at many sites. It is not an ideal material for construction of dams. A dam constructed entirely of gypsum has a uniform and relatively high permeability. Water seeps through the structure. Saturation is maintained in much of the dam mass unless special provision is made for drainage of the toe. Some States maintain a degree of regulation of dikes. The State of Illinois requires some underdrainage of gyp-pond dikes at Joliet, Illinois.

A saturated dam is weakened in a number of ways. Piping occurs in the outer toe. The water in the dam buoys the structural material, reducing the dikes effective weight. Granular materials saturated with water will become momentarily fluid if an earthquake or a shock wave of any type sets up a tremor.

Hazardous conditions are common in pond dams. The contractors diagram of a typical dam, supplied with this study, indicates, no provision of underdrainage. The lack of specifications that make dikes safe, and/or the lack of enforcement of these specifications can lead to dike failures.

A gyp-pond or recirculation pond dike must be constructed in a manner that maintains effective drainage in the outer half of the dike. If gypsum is the sole material in the dike, a farm tile (or other equally effective) underdrainage system should be provided in the toe of the dike. The tile lines must be close enough together, located below sufficiently permeable liner materials and sloped adequately. The tile field must remain operational and drain effectively throughout the entire period of waste water containment. The engineering details of any new gyp-pond utilized for treating the waste water in the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing should be based on sound engineering fundamentals and should be in compliance with applicable local, State or federal regulations.

In the event of declining efficiency of a drainage system, relief wells should be provided to maintain the drainage function.

Both a relief well system or a farm tile underdrainage system leading to an underground sump have many advantages over the open ditches commonly utilized to catch seepage. The underground systems permit return of seepage without lowering the outer edge of the dam. This strongly favors dike safety. The ditch alone provides none of the underdrainage required to make the dam safe.

An inherent advantage of the underground sump or relief well system is that seepage can be returned to the lagoon free of outer slope rain run-off water. A ditch is not essential to collect this runoff water where a sound underdrain seepage control system is provided.

Planting the dam slopes with low plants can be utilized to improve the water balance and to stabilize the dam surface.

Tall plants that reduce wind velocity over the pond surface must be avoided. Wind is an aid to cooling.

The U.S. Department of Interior, Bureau of Reclamation, book "Design of Small Dams" (Reference L) presents discussions and diagrams of toe draining systems, with a horizontal drainage blanket, an underground drainage trench, and an underground pipe conduit leading to an outfall. This system can readily replace the open seepage interceptive ditch in common use. The intercepted seepage can be pumped back to the pond from an underground sump. This system does not return runoff from outer slopes to the lagoon.

The reliability of a properly installed underground drainage system is extremely high. A soundly designed system assures a safe dam for its full service life.

If some local factor introduces a reliability problem two control measures should be considered:

1. Install a conduit to the top altitude of the drain system for periodic drain pipe flushing to prevent plugging.
2. Install a vertical permeable pipe at the center of the dam, through which the phreatic line may be measured. The design engineer should specify the maximum safe height of this phreatic line for each dam. Various instruments can be installed in the dike to monitor the height of the phreatic line. These must be of fully established reliability.

#### B. Control of Seepage

A pond, to be acceptable for use in waste water treatment, must have an interceptor system that collects and returns seepage, or should be provided with a liner that prevents significant percolation, and that blocks flow to groundwater through underground channels. Furthermore, any waste water seepage must have no dissolving action on underlying layers. It is particularly important to prevent acidic waste water seepage through limestone formations. Some liming may be required, particularly at start-up, to protect limestone layers, to provide sediment for plugging of the bottom liner, and to prevent seepage of fluoride, radium-226 and phosphate components.

Relief wells, underdrainage or other provision must be made to prevent upflow of groundwater into the lagoon. Upflow into a lagoon normally breaches the liner and permits flow



of waste water through existent channels to groundwater when lagoon hydrostatic pressure exceeds the groundwater pressure.

Groundwater monitoring by means of wells in the percolation area should be installed whenever the lagoon is provided with a liner of questionable impermeability. The addition of lime to bottom sediments in lagoons will lead to neutralization of waste water seeping into ground water. The use of lime will also provide sedimentary conditions that tend to block seepage.

The liming of pond water can be utilized to aid both air pollution control and to reduce loss of waste water pollutants by seepage.

#### C. Deposits of Objectionable Substances at Phosphate Manufacturing Plants

Various deposits of objectionable waste water components occur in ponds or landfill areas. Examples of these are calcium fluoride, radium-226, arsenic and sulfide. Local State and EPA authorities with jurisdiction over this landfill problem should be notified of the deposits and the control measures required should then be established. It is vital that percolating water does not carry these substances into ground water or into surface waters.

#### D. Ponds in Regions with Severe Cold Seasons

The cooling problem for a reuse and cooling pond varies drastically from summer to winter seasons in cold climates. It is essential to install conduits underground, or otherwise protect from freezing. Provision must be made for isolation of a pond with a limited surface area for winter operation. The heat discharged to the pond in normal operation will then prevent troublesome freezing incidents. The winter pond must be deep enough to remain operable after a plant shutdown. A defluorinated rock plant has been operating a recycle pond in Montana. No difficulty has been reported.

National standards are not being proposed for recirculation and reuse ponds. Some State and local authorities have set standards. Monitoring should cover the factors that control loss of waste water to surface and ground waters, and local authorities should be notified of conditions threatening navigable and ground waters with pollution.

## Contaminated (Pond) Water Treatment

This technology is identical to that treatment technology designated as gypsum pond (contaminated) water treatment in the phosphate fertilizer section of the development document for the Basic Fertilizer Chemicals Manufacturing Industry.

The Containment and Cooling Pond technology described above is intended to function as a no discharge closed loop system the majority of the time. This "no discharge" situation is however dependent upon the quantity of rainfall it can accept before its water storage capacity is exceeded. Once the storage area approaches capacity it is necessary to begin treating the contaminated water for subsequent discharge to natural drainage areas. Similarly, in those processes in which a containment pond is impractical it may be necessary to continuously treat the contaminated process effluent water. This technology in part or as a whole is capable of treating the contaminated effluent of either the containment pond or the process effluent streams.

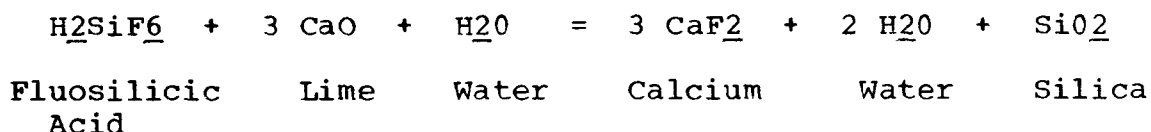
### Process Description

Contaminated water can be treated effectively for control of the pollution parameters identified in Section VI, namely suspended solids, pH, phosphate, radium-226, and fluorides. The treatment described is by means of either single or two-stage lime neutralization procedure. In the Sodium Phosphate process there are indications that only single liming is required for removal of the impurities.

Normally two stages of liming or neutralization are necessary to effect an efficient removal of the fluoride and phosphate contaminants. Fluorides are present in the water principally as fluosilicic acid with small amounts of soluble salts as sodium and potassium fluosilicates and hydrofluoric acid. Phosphorus is present principally as orthophosphoric acid with some minor amounts of soluble calcium orthophosphates in the conventional wet phosphoric acid production process. Polyphosphates that require special pretreatment prior to lime sedimentation may be present in lagoons accepting waste water from defluorination processes, and from the manufacture of defluorinated (poly) phosphates.

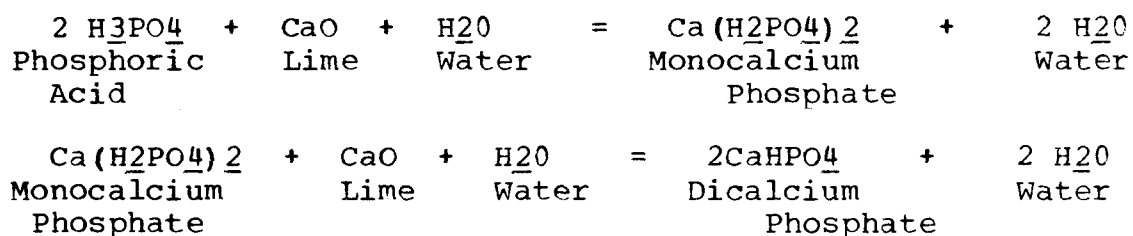
The first treatment stage provides sufficient neutralization to raise the contaminated water containing up to 9,000 mg/l F and up to 6,500 mg/l P from pH 1-2 to pH 3.5-4.0. The resultant treatment effectiveness is, to a significant degree, dependent upon the mixing efficiency at the point of

lime addition and the constancy of the pH control. At a pH level of 3.5 to 4.0, the fluorides will precipitate principally as calcium fluoride ( $\text{CaF}_2$ ) as shown by the following chemical equation.



This mixture is then held in a quiescent area to allow the particulate  $\text{CaF}_2$  to settle.

Equipment used for neutralization ranges from crude manual distribution of lime with localized agitation to a well engineered lime control system with a compartmented mixer. Similarly the quiescent areas range from a pond to a controlled, settling rate thickener or settler. The partially neutralized water following separation from the  $\text{CaF}_2$ , (pH 3.5-4.0) now contains 30-60 mg/l F and up to 5,500 mg/l P. This water is again treated with lime sufficient to increase the pH level to 6.0 or above. At this pH level calcium compounds, primarily dicalcium phosphate plus additional quantities of  $\text{CaF}_2$  precipitate from solution. The primary reactions are shown by the following chemical equation:



As before, this mixture is retained in a quiescent area to allow the  $\text{CaHPO}_4$  and minor amounts of  $\text{CaF}_2$  to settle.

After settlement, the clear, neutralized water will contain 15-30 mg/l F and 30-60 mg/l P at a pH of 6-8. The reduction of the P value is strongly dependent upon the final pH level and quality of the neutralization facilities, particularly mixing efficiency. Neutralization to pH levels of 9-11 will reduce P values to 15-30 mg/l or less. Figure VII-1 shows a sketch of a well designed "double lime" treatment facility. Plants B, C and D all practice some degree of liming.

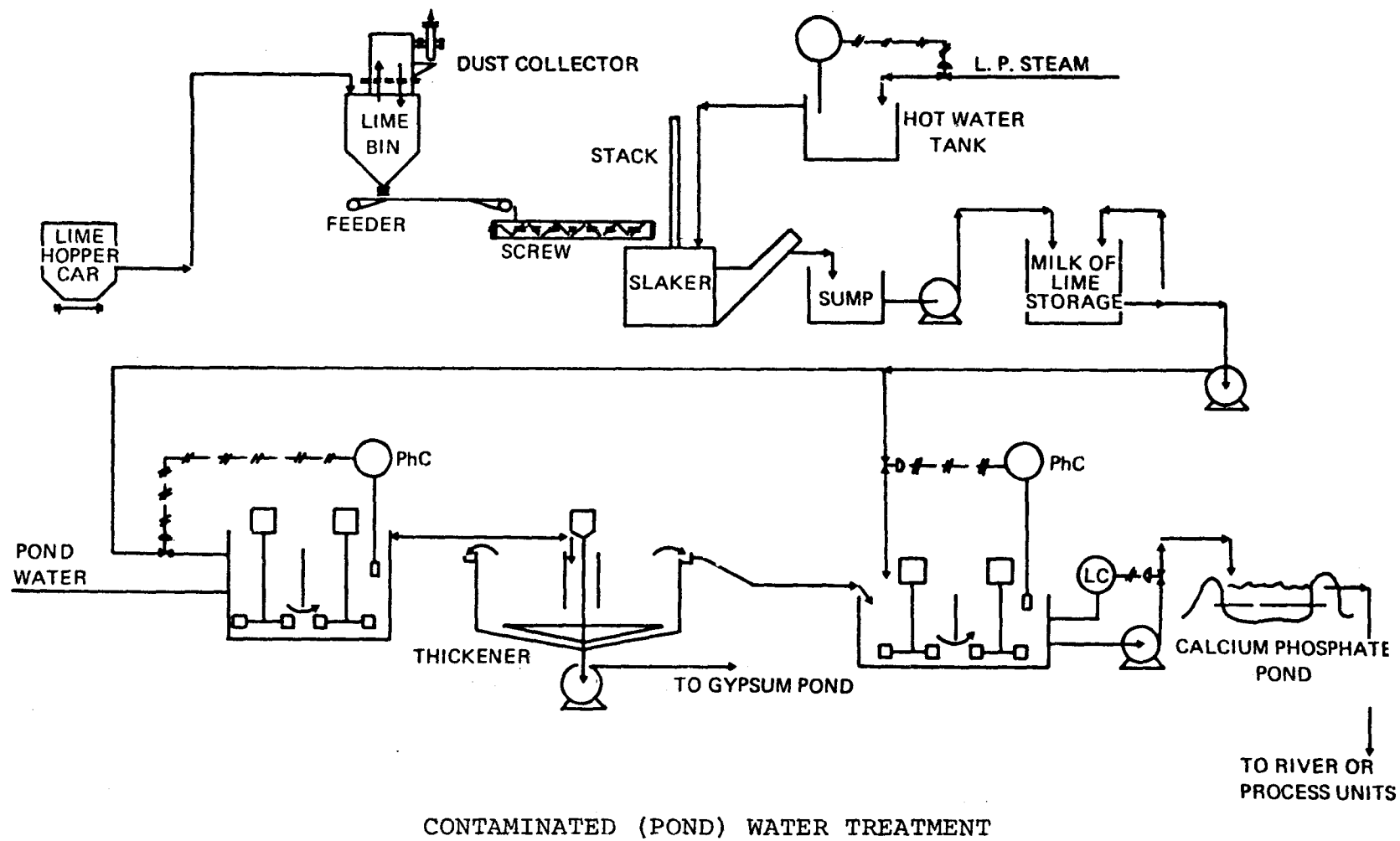


FIGURE VII-1

A number of pollutants may cause interference with lime precipitation. Silicates are normal components of most recycle ponds and exert an interfering action through formation of fluosilicates. Some boron compounds will complex fluorine and interfere with precipitation. Borax has a chelating action on calcium ion and therefore, like many other chelating agents, has an interfering action on lime precipitation. Spurious contaminants that interfere with lime precipitation must be excluded from recycle ponds if satisfactory lime precipitation is to be maintained.

Some special precautions are essential at a plant producing sodium phosphates. All meta, tetra, pyro and polyphosphate waste water in spills should be diverted to the reuse pond. These phosphates will not precipitate satisfactorily in the lime treatment process and will interfere with the removal of fluoride and suspended solids.

Polyphosphate in waste water will exert a desirable anti-fouling action if diverted to the cooling water stream from the reuse lagoon. Furthermore, the compound will hydrolyze and precipitate in the lagoon.

Domestic waste, unless completely bio-oxidized, has undesirable effects in sodium phosphate plant effluent. The amino acids and other organic components interfere with both precipitation and flocculation. The high calcium level of the recycle pond is lacking in the waste water stream from the sodium phosphate plant. Lime and/or calcium salts may be required for acceptable removal of P and F pollutants. Adequate precipitant reagent use must be supported by effective clarification for control of F, P and SS.

In some circumstances it may be desirable to strip carbon dioxide from the waste stream before lime treatment so that carbonate does not compete with phosphate in the precipitation reaction.

The sodium phosphates subcategory manufacturing process utilizes a series of salting out processes for separating various crystallized products. The resultant waste water streams contain a variety of contaminants that cannot be recycled in the process without degenerating product quality. The manufacturing processes isolate some of the potential waste water pollutants from the waste stream. Sodium silicofluoride is precipitated out and sold as a byproduct; this process disposes of most of the troublesome fluoride problem. Radium 226 is segregated into various sediment fractions. Arsenic is separated as sulfide precipitate. Sedimentation occurs in the waste streams from

the sodium phosphate processes and the sediments are removed by clarification. The technical details of these processes have not been fully disclosed by the manufacturer.

A recirculation pond is available on the site for handling difficult waste water streams to the same extent that this lagoon system is available for defluorinated rock and acid waste water.

Modified forms of phosphate create a unique treatment problem at defluorination plants. Phosphoric acid and/or phosphate salts undergo polymerization and molecular rearrangement reactions when subjected to severe dehydration treatment. The acid defluorination treatments applied are predominantly operated with application of heat and a gas stripping action. These heating and/or stripping actions induce a substantial degree of molecular conversion in the defluorinated acids. The conversion is particularly high in super-acid grades concentrated to a high  $P_{2O_5}$  content. Likewise, the high temperatures applied for rock defluorination convert the raw orthophosphate rock to polyphosphates.

These modified phosphates differ sharply from orthophosphates in solubility. Calcium orthophosphates have extremely low solubility in moderately alkaline solutions; the calcium salts of the modified phosphates have appreciable solubility. In fact, these modified phosphates are applied extensively as chelating agents to combat calcium induced hardness. These modified phosphates are relatively stable at ambient temperatures. The half life varies from compound to compound and is poorly defined; this half life is commonly taken to be about 2 days in acidic waters, but is several weeks in neutral or alkaline waters.

These modified phosphates enter the process waste water from various sources. Stack washing introduces some dust from rock defluorination. Spray carryover to barometric condenser water is a common source of contamination in acid defluorination. Spills and leaks carry polyphosphates into waste water in all the subcategories. Rain run-off from drying, packaging, loading and shipping areas carry these modified phosphates into the waste water stream.

It is vitally important that waste water bearing these modified phosphates be excluded from streams flowing to lime treatment facilities; this is especially objectionable without impoundment. The calcium salts of these modified phosphates are much more soluble than the calcium orthophosphate salts. Satisfactory phosphate precipitation

will not occur on lime treatment. Furthermore, polyphosphates exert an objectionable interference action on clarification processes. And still further, the soluble calcium salts of molecular species other than orthophosphate act as individual agents in the calcium precipitation process. Thus, a system with only orthophosphate will remain saturated with calcium orthophosphate. The mixed system will remain saturated with calcium orthophosphate and with each component calcium phosphate. The sum of the phosphate components in solution will be higher than the orthophosphate component alone.

Where waste water contamination does occur with these modified phosphates, the resultant waste streams, should be directed to a special holding pond, along with acidic wastes that speed hydrolysis. Completing of hydrolysis can be promoted further by discharge into the contaminated water recirculation pond. The modified phosphates continue the hydrolysis to orthophosphate in the recirculation lagoon. This factor adds another plus value to the desirability of the recirculation and reuse lagoon at a phosphate facility with defluorination processes. The holding is especially beneficial at the typical low pH levels prevailing in typical contaminated water ponds. Acidity hastens hydrolysis to the orthophosphate form.

A unique condition prevails in the waste water discharge from the single plant producing sodium phosphates. This stream also contains the domestic waste discharge from the septic tanks accepting the plant's domestic sewage. An efficient aerobic bio-oxidation step applied to this waste water would destroy most of the organic substances that interfere with sedimentation; furthermore, this bio-oxidation process will catalyze the hydrolysis of polyphosphates present in the waste water to orthophosphate. Bio-oxidation may be the most practicable means of converting any polyphosphates present to orthophosphate in this situation. The waste stream is neutral; hydrolysis of polyphosphates will be extremely slow unless bio-catalytic action is induced in the system. Many microorganisms produce enzymes that catalyze the hydrolysis of polyphosphates. Reference P brings out the observation that no problem was encountered in precipitating phosphates in domestic waste water following bio-oxidation of the waste water.

It must be recognized that pH alone does not indicate the total effectiveness of the precipitating reagent. The calcium content in the pond water will also be a factor and will vary widely. The sulfate ion competes for the calcium

ion; a high sulfate content will tend to reduce the calcium content of a pond and create a condition relatively unfavorable for fluoride and phosphate precipitation. The pH change induced by lime addition, gives a general indication of the precipitation potential in the system. A pH rise from lime addition is accompanied by a rise in soluble calcium content. In normal circumstances, lime to pH 6.0 will be adequate for precipitating fluorine and phosphate to meet required limitations, but lime will have to be added, as required, if fluoride and phosphate limitations are not met.

Soluble iron and aluminum compounds are present at high concentrations in many ponds. The iron and aluminum cations exert a strong influence on phosphate precipitation.

Strong winds interfere with sedimentation in lagoons. A covered terminal sedimentation basin, or a covered final segment of a sedimentation basin will be indispensable for attaining satisfactory suspended solids removal under many conditions. A cover is particularly beneficial in periods of cold weather. Temperature inversion currents cause severe disturbance of sedimentation in open basins in cold weather. Inlet and outlet arrangements are critical. Poorly designed inlets and outlets permit excessive short circuiting. Arrangements that direct flow tangentially are vastly superior to arrangements that direct flow from inlet toward outlet structure.

#### Monitoring Treatment After Rainfall Breaches the Required Freeboard of a Lagoon

The authority monitoring a lagoon should specify a treatment rate for the waste water breaching the required freeboard high enough to restore the required freeboard in a reasonable time period. If treatment is delayed, or conducted at an unreasonably slow rate, overflow will occur from rains considerably below the heaviest expected rainfall in a 10 or 25 year period.

Personnel concerned with monitoring recirculation and cooling water lagoons may find it prudent to define several stages of freeboard that relate to control of surge capacity and to hazard of breaching the lagoons capacity:

- A. The spillway level capacity, as established by the elevation of the spillway, should be clearly defined.



- B. A crest should be provided around the pond above the spillway elevation. This is essential to prevent breaching of the structure by wave action in windy weather. The height of this crest should be related to wind problems at the lagoon site.
- C. A maximum permissible operating level to avoid breaching in periods of excessive rainfall should be established. This is now set by the regulation. Operational experience should be recorded to provide data for reconsideration if excessive breaching is noted in operation under the promulgated regulations.

#### Control of Unusual Discharges to Pond

Monitoring authorities should require a report on all waste water streams discharged to the recirculation and reuse pond. Problems may arise at plants discharging waste water from processes other than phosphate manufacturing or fertilizer phosphate production. Ponds should also be managed and located in a manner that limits ammonia and organic compound intrusion.

The recirculation and reuse pond will have considerable capacity to absorb noncontact cooling water that has become contaminated by leaks and process waste waters from ancillary phosphate manufacturing operations at most sites; however, the situation at a point source should be monitored to make certain that the point source is not utilizing the pond as a device for evading regulations on waste water discharges from unrelated manufacturing operations.

Many objectionable metals are kept under control by the sedimentation processes in the pond and by the terminal lime treatment process. The presence of ammonia and of some organic compounds interfere seriously with these treatment processes. Particular care should be taken around plants producing ammonia and other nitrogenous fertilizers; drying towers and other facilities losing ammonia gas to the atmosphere are particularly troublesome sources of contamination. Domestic wastes interfere with metal precipitation processes and with flocculation and clarification processes.

The pH range was extended from the proposed 9.0 top limit to 9.5 because of the difficulty experienced at some plants in meeting the suspended solids, phosphate and fluoride limitations on liming to the proposed 9.0 pH limit.

No suspended solids limitation was set in discharge of treated contaminated non-process wastewater. The major volume is cooling water with no significant content of suspended solids.

## SECTION VIII

### COST, ENERGY AND NON-WATER QUALITY ASPECT

#### General

The costs - capital and operating - have been estimated for the two treatment technologies described in Section VII. These costs are given as August 1971 dollar values. In the case of the costs indicated for Containment and Cooling Pond technology, there is additional explanation made on what they represent and how they might be used. The costs indicated for the Contaminated (Pond) Water Treatment technology are based on a specific treatment capacity such as would be found at a moderate size production unit. The following paragraphs provide identification of the cost elements used in this section and indicated on Table VIII-1.

#### Cost Elements

##### Investment

This is the capital cost associated with the engineering; site preparation; construction and installation; and such other costs required to place the technology in operation. It does not include production loss or profits loss that may be encountered from tying the new facilities into the existing plant operations.

##### Interest

This cost is based on the assumption that the capital expenditure was borrowed at a 7.5% annual interest rate.

##### Depreciation

The nature and service life expected of this type equipment were the bases for selection of an assumed ten year straight line depreciation.

##### Operating and Maintenance Costs

The items included in this cost element are operating supplies, replacement parts, insurance, taxes, operating labor and maintenance labor.

##### Energy

This item is the power costs to operate the mechanical equipment. Electrical energy is assumed at the cost of 10 mils per KWH.

#### Total Annual Costs

An accumulation of the various cost items described above.

#### Installation and Operation of Technologies

##### Containment and Cooling Pond

The cost of this technology is difficult to estimate due to the need of a specific design for each individual plant. Pond size is a function of many items including the water temperature (cooling) required for process, the economics of land availability, provision for rainfall, and geographical location. The indicated investment cost is that to establish a 10' high dike around one (1) acre. This cost also assumes that the dike will be established from earth at the site and strictly by large earth-moving equipment - no transportation of earth to the site. Cost of earth moving has been estimated at \$1.50 per cubic yard.

It can be stated that a minimum containment and cooling pond for a moderate size plant would be 10 - 20 acres.

Construction time is estimated at 80 hours per acre.

There would be no interruption of plant operation during construction.

##### Contaminated (Pond) Water Treatment

This is the same technology and costs estimated for Pond Water Treatment in the phosphate fertilizer section of the Basic Fertilizer Chemicals Survey.

Time required for engineering, procurement, and construction is 15 - 18 months.

There would be no interruption of plant operation during construction.

Start-up and initial operation would require approximately 24 hours of continuous operation to establish stabilized conditions.

Table VIII-1 cites 1971 cost figures derived from the original contract study. These figures have been expanded

TABLE VIII-1  
WATER EFFLUENT TREATMENT COSTS

					ANNUAL COST				
					Depreciation	Operating & Maintenance Cost Excluding Energy	Energy Cost	Total Annual Costs	
	Refer to Figure Number for Reference	Investment	Interest on Money						
Containment and Cooling Pond	-	① 13,983 per acre							
Contaminated (Pond) Water Treatment	VIII-1	349,000	26,222	34,960	13,990	\$0.05/1000 Gallons Treated	See Note Below ②		

- ① Based on preparation of a 10' high dike around the perimeter of a one acre area.
- ② Raw material cost \$1.40 per 1000 gallons treated; all other costs equal \$0.50 per 1000 gallons treated; total overall cost equal \$1.90 per 1000 gallons treated.

TABLE VIII-2

SUMMARIZED ESTIMATED WASTEWATER TREATMENT COSTS OF PHOSPHATE MANUFACTURING PLANTS  
(Costs Per Model Plant) \*

Subcategory and Plant Size	BPCTCA		BATEA and NSPS (a)	
	Capital Costs,\$	O&M Costs,\$	Capital Costs,\$	O&M Costs,\$ (b)
Defluorinated Phosphate Rock				
Medium (175,000 ton/yr)	77,000	7,200	155,000	9,600
Large (310,000 ton/yr)	100,000	10,840	220,000	11,300
Defluorinated Phosphoric Acid				
Small (193,000 ton/yr)	574,000	120,900	--- (c)	--- (c)
Large (720,000 ton/yr)	1,249,000	431,700	--- (c)	--- (c)
Sodium Phosphates				
Average (140,000 ton/yr)	548,000	120,100	--- (c)	--- (c)

(a) Incremental costs after achieving BPCTCA

(b) Does not include taxes, interest, or depreciation

(c) No additional costs to meet BATEA

\* Derived from Reference T. Investment costs are on a June, 1973 basis and operation and maintenance costs on a November, 1973 basis.

to cover the entire industry in the Economic Analysis of Proposed Effluent Guidelines, EPA, September, 1974 and revised in the economic analysis study conducted for promulgation. Table VIII-2 presents an independent study result derived from Reference T.

No cost estimate was made for BAT practice for the Sodium Phosphates Subcategory. It was the opinion of the review committee that the BAT standards can be easily achieved. The plant was building an expanded lagoon system for the wet process phosphoric acid plant and for hydrofluoric acid manufacture. This lagoon will be available to handle difficult streams from the sodium phosphate plant. Cost increase from BPT to BAT should be less than five percent.

The 1.3 area factor originally utilized in calculating rainfall accumulation in lagoons is no longer utilized. This factor did not appear in the contractor's original cost estimates. There is no reason to include it now. There is no change in wastewater flow due to the change in the guidelines.

Our contractor did not include seepage interceptor ditches or underdrainage systems for lagoons. These costs need not be added. The problem is State and non-point source and not handled by Effluent Guidelines.

#### Air Pollution Control

Air pollution control poses a serious problem in the industry, particularly in the defluorinated phosphate rock subcategory. The fluoride expelled from the rock on heating would cause an extremely serious air pollution situation without the stack scrubbing applied in the industry. The EPA air pollution control authorities are initiating studies to determine the status of the air pollution problem, and the relationship to the water pollution problem.

Defluorinated phosphate rock plants and submerged combustion defluorinated phosphoric plants lose much water by evaporation, and have no normal need to discharge wastewater from their recirculation and cooling ponds. However, all of these must lime treat at some place to control the pH to prevent excessive air emission of fluoride.

Information must also be gathered on radon-222 and the radioactive breakdown solid substances derived from radon-222. Radon-222 is an inert gas with a very short half life. Exposure of human beings to these radioactive products must be held to safe levels. Hopefully, more definite

information will soon be available on how to deal with this problem. The use of solid wastes, particularly gypsum, for home construction is inadvisable unless found to be free of radioactive component hazard.

### Solid Wastes

Many solids residues are left as solid wastes.

The proper management of solid wastes resulting from air pollution control systems must be practiced. Air pollution control technologies generate many different amounts and types of solid wastes and liquid concentrates through the removal of pollutants from air emissions. These substances vary greatly in their chemical and physical composition and may be either hazardous or non-hazardous. A variety of techniques may be employed to dispose of these substances depending on the degree of hazard.

If thermal processing is the choice for disposal, provisions must be made to ensure no re-entry of the pollutants into the atmosphere. Consideration should also be given to recovery of materials of value in the wastes.

For those waste materials considered to be non-hazardous where land disposal is the choice for disposal, practices similar to proper sanitary landfill technology may be followed. The principles set forth in the EPA's Land Disposal of Solid Wastes Guidelines (40 CFR 241) may be used as guidance for acceptable land disposal techniques.

For those waste materials considered to be hazardous, disposal may require special precautions. In order to ensure long-term protection of public health and the environment, special preparations and pretreatment may be required prior to disposal. If land disposal is to be practiced, these sites must not allow movement of pollutants such as fluoride and radium-226 to either ground or surface water. Sites should be selected that have natural soil and geological conditions to prevent such contamination or, if such conditions do not exist, artificial means (e.g., liners) should be provided to ensure long-term protection of the environment from hazardous materials. Where appropriate, the location of solid hazardous materials disposal sites should be permanently recorded in the appropriate office of the legal jurisdiction in which the site is located.



### Pretreatment

No manufacturer in these subcategories is known to discharge wastewater to a publicly owned treatment plant. Pretreatment standards have been reserved for the present time because of ongoing studies with incomplete administrative decisions.



SECTION IX  
BEST PRACTICABLE CONTROL TECHNOLOGY  
CURRENTLY AVAILABLE

Introduction

The effluent limitations which must be achieved by July 1, 1977 are based on the degree of effluent reduction attainable through the application of the best practicable control technology currently available. For the non-fertilizer phosphate chemicals manufacturing industry, this level of technology is based on the best existing performance by exemplary plants of various sizes, ages and chemical processes within each of the industry's categories. In some cases where no truly exemplary plants were surveyed, this level of technology is based upon state-of-the-art unit operations commonly employed in the chemical industry.

Best practicable control technologies currently available in the non-fertilizer phosphate chemicals industry involve both in-process techniques and end-of-process treatment.

Based upon the information contained in Section III through VIII of this report, the following determinations were made on the degree of effluent reduction attainable by application of the best practicable control technology currently available in the individual process of the non-fertilizer phosphate chemical industry. Each process is presented separately in the following paragraphs.

Specialized Definitions

(a) Except as provided below, the general definitions, abbreviations and methods of analysis set forth in 40 CFR 401 shall apply to this subpart.

(b) The term "process waste water" means any water which, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, by-product, or waste product. The term "process waste water" does not include contaminated non-process waste water, as defined below.

(c) The term, "contaminated non-process wastewater" shall mean any water including precipitation runoff which, during manufacturing or processing, comes into incidental contact with any raw material, intermediate product, finished product, by-product or waste product by means of

(1) precipitation runoff (2) accidental spills (3)

accidental leaks caused by the failure of process equipment and which are repaired or the discharge of pollutants therefrom contained or terminated within the shortest reasonable time which shall not exceed 24 hours after discovery or when discovery should reasonably have been made, whichever is earliest, and (4) discharges from safety showers and related personal safety equipment, and from equipment washings for the purpose of safe entry, inspection and maintenance; provided that all reasonable measures have been taken to prevent, reduce, eliminate and control to the maximum extent feasible such contact and provided further that all reasonable measures have been taken that will mitigate the effects of such contact once it has occurred.

(d) The term "ten year 24 hour rainfall event" shall mean the maximum precipitation event with a probable recurrence interval of once in 10 years as defined by the National Weather Service in technical paper no. 40, "Rainfall Frequency Atlas of the United States," May, 1961, and subsequent amendments or equivalent regional or State rainfall probability information developed therefrom.

(e) The term "25 year 24 hour rainfall event" shall mean the maximum precipitation event with a probable recurrence interval of once in 25 years as defined by the National Weather Service in technical paper no. 40, "Rainfall Frequency Atlas of the United States," May, 1961, and subsequent amendments or equivalent regional or State rainfall probability information developed therefrom.

(a), above, applies to all three subcategories; (b), (c), (d) and (e) apply to the defluorinated phosphate rock and the defluorinated phosphoric acid subcategories.

#### Subpart D - Defluorinated Phosphate Rock Subcategory

The provisions of this subpart are applicable to discharges resulting from the defluorination of phosphate rock by application of high temperature treatment along with wet process phosphoric acid, silica and other reagents.

In establishing the limitations set forth in this section, EPA took into account all information it was able to collect, develop and solicit with respect to factors (such as age and size of plant, raw materials, manufacturing processes, products produced, treatment technology available, energy requirements and costs) which can affect the industry subcategorization and effluent levels established. It is, however, possible that data which would affect these limitations have not been available and, as a result, these limitations should be adjusted for certain plants in this industry. An individual discharger or other

interested person may submit evidence to the Regional Administrator (or to the State, if the State has the authority to issue NPDES permits) that factors relating to the equipment or facilities involved, the process applied, or other such factors related to such discharger are fundamentally different from the factors considered in the establishment of the guidelines. On the basis of such evidence or other available information, the Regional Administrator (or the State) will make a written finding that such factors are or are not fundamentally different for that facility compared to those specified in the Development Document. If such fundamentally different factors are found to exist, the Regional Administrator or the State shall establish for the discharger effluent limitations in the NPDES permit either more or less stringent than the limitations established herein, to the extent dictated by such fundamentally different factors. Such limitations must be approved by the Administrator of the Environmental Protection Agency. The Administrator may approve or disapprove such limitations, specify other limitations, or initiate proceedings to revise these regulations.

The following limitations establish the quantity or quality of pollutants or pollutant properties, which may be discharged by a point source subject to the provisions of this subpart after application of the best practicable control technology currently available.

(a) Subject to the provisions of paragraphs (b), (c) and (d) below:

The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of the best practicable control technology currently available: there shall be no discharge of process wastewater pollutants to navigable waters.

(b) Process waste water pollutants from a cooling water recirculation system designed, constructed and operated to maintain a surge capacity equal to the runoff from the 10-year, 24-hour rainfall event may be discharged, after treatment to the standards set forth in subparagraph (c) below, whenever chronic or catastrophic precipitation events cause the water level in the pond to rise into the surge capacity. Process waste water must be treated and discharged whenever the water level equals or exceeds the mid point of the surge capacity.

(c) The concentration of pollutants discharged in process wastewater pursuant to the limitations of paragraph

(b) shall not exceed the values listed in the following table:

<u>Effluent Characteristic</u>	<u>Maximum for Any 1 Day</u>	<u>Average of Daily Values for 30 Consecutive Days Shall Not Exceed</u>
	mg/l	
Total Phosphorus(P)	105	35
Fluoride	75	25
TSS	150	50
pH	Within the range 6.0 to 9.5	

The total suspended solid limitation set forth in this paragraph shall be waived for process wastewater from a calcium sulfate storage pile runoff facility, operated separately or in combination with a water recirculation system, which is chemically treated and then clarified or settled to meet the other pollutant limitations set forth in this paragraph.

(d) The concentration of pollutants discharged in contaminated non-process wastewater shall not exceed the values listed in the following table:

<u>Effluent Characteristic</u>	<u>Maximum for Any 1 Day</u>	<u>Average of Daily Values for 30 Consecutive Days Shall Not Exceed</u>
	mg/l	
Total Phosphorus(P)	105	35
Fluoride	75	25
pH	Within the range 6.0 to 9.5	

#### Rationale for Best Practicable Control Technology Currently Available

The criteria used for selection of the technology was information obtained at three of the four total operating plants in the U.S. Two of the three plants (survey plants A and B) have the Containment and Cooling Pond Technology in service and to date have never found it necessary to treat or discharge water to navigable waters. Survey Plant C stated plans of installing this technology in the near future.

The proposed limitations are based on composite (not grab) sampling and years of historical effluent data. These

limitations represent values which are being achieved by the better exemplary plants surveyed.

The volume of process waste water that may be discharged is determined by the rainfall-evaporation circumstances at the site, and by the definitions and regulations pertaining to the structure of the recirculation and reuse pond. Process waste water discharge is not necessary at some sites. Plants that discharge process waste water normally do this only in periods of heavy rainfall.

Discharged effluent must be lime treated. This is a relatively costly operation. Diligent water conservation and reuse practices have proven to be the most economical means to handle the waste water problem.

#### Subpart E - Defluorinated Phosphoric Acid Subcategory

The provisions of this subpart are applicable to discharges resulting from the defluorination of phosphoric acid. Wet process phosphoric acid is dehydrated by application of heat and other processing aids such as vacuum and air stripping. The acid is concentrated up to 70-73 percent  $P_{2O_5}$  in the defluorination process.

The technology described as Containment and Cooling Pond is defined as the best practicable control technology currently available. This technology confines all process waste waters to the plant area. Recirculation of these contaminated process waters to the process together with good water management practices essentially eliminate the need for treatment or discharge of treated contaminated process water to navigable waters. In the event of a need for emergency type discharge, then the Contaminated (Pond) Water treatment technology or a facsimile of it would also be indicated.

The following limitations establish the quantity or quality of pollutants or pollutant properties, which may be discharged by a point source subject to the provisions of this subpart after application of the best practicable control technology currently available:

(a) Subject to the provisions of paragraphs (b), (c) and (d) below:

The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application

of the best practicable control technology currently available: there shall be no discharge of process wastewater pollutants to navigable waters.

(b) Process waste water pollutants from a cooling water recirculation system designed, constructed and operated to maintain a surge capacity equal to the runoff from the 10-year, 24-hour rainfall event may be discharged, after treatment to the standards set forth in subparagraph (c) below, whenever chronic or catastrophic precipitation events cause the water level in the pond to rise into the surge capacity. Process waste water must be treated and discharged whenever the water level equals or exceeds the mid point of the surge capacity.

(c) The concentration of pollutants discharged in process wastewater pursuant to the limitations of paragraph (b) shall not exceed the values listed in the following table:

<u>Effluent Characteristic</u>	<u>Maximum for Any 1 Day</u>	<u>Average of Daily Values for 30 Consecutive Days Shall Not Exceed</u>
	mg/l	
Total Phosphorus(P)	105	35
Fluoride	75	25
TSS	150	50
pH	Within the range 6.0 to 9.5	

The total suspended solid limitation set forth in this paragraph shall be waived for process wastewater from a calcium sulfate storage pile runoff facility, operated separately or in combination with a water recirculation system, which is chemically treated and then clarified or settled to meet the other pollutant limitations set forth in this paragraph.

(d) The concentration of pollutants discharged in contaminated non-process wastewater shall not exceed the values listed in the following table:

<u>Effluent Characteristic</u>	<u>Maximum for Any 1 Day</u>	<u>Average of Daily Values for 30 Consecutive Days Shall Not Exceed</u>
	mg/l	
Total Phosphorus(P)	105	35
Fluoride	75	25
pH	Within the range 6.0 to 9.5	



## Rationale for Best Practicable Control Technology Currently Available

The criteria used for selection of the technology was information obtained at three of the four total operating plants in the U.S. Two of the three plants (survey plants A and B) have the Containment and Cooling Pond Technology in service and to date have never found it necessary to treat or discharge water to navigable waters. Survey Plant C stated plans of installing this technology in the near future.

The proposed limitations are based on composite (not grab) sampling and years of historical effluent data. These limitations represent values which are being achieved by the better exemplary plants surveyed.

The volume of process waste water that may be discharged is determined by the rainfall-evaporation circumstances at the site, and by the definitions and regulations pertaining to the structure of the recirculation and reuse pond. Process waste water discharge is not necessary at some sites. Plants that discharge process waste water normally do this only in periods of heavy rainfall.

Discharged effluent must be lime treated. This is a relatively costly operation. Diligent water conservation and reuse practices have proven to be the most economical means to handle the waste water problem.

### Subpart F - Sodium Phosphates Subcategory

The provisions of this subpart are applicable to discharges resulting from the manufacture of purified sodium phosphates from wet process phosphoric acid.

The technology described as Contaminated (Pond) Water Treatment is defined as the best practicable control technology currently available, and/or in-process technology - whichever will achieve the same results. Process waste water is also continuously treated and discharged to navigable waters. A lagoon recirculation system is in use for treatment of the process waste water from production of the raw product acid required for sodium phosphates manufacture, and can be utilized for disposal of troublesome waste water streams.

The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source



parameters within limits that would not initiate the need for additional treatment facilities. That is, the guidelines proposed coincide with contaminant levels attainable at the proposed pH 6.0 to 9.5 treatment range. This pH range permits direct discharge of clarified effluent, without neutralization. All waste streams that bear any of the dehydrated products, metaphosphate through polyphosphate, can be diverted to the recirculation pond when flow to the clarifier is sufficient to cause a discharge violation. These modified phosphates create problems in the usual clarification process. The treatment system will require a hydrolytic process that converts phosphate components to the orthophosphate form if significant quantities of polyphosphate waste water components are in the stream undergoing lime precipitation and clarification. These processes are discussed in Section VII.



## SECTION X

### BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

The effluent limitations which must be achieved by July 1, 1983, are based on the degree of effluent reduction attainable through application of the best available technology economically achievable. This level of technology was based on the very best control and treatment technology employed by a specific point source within the industrial category and on sound, established waste water management and treatment processes.

Specialized definitions are the same as for the best practicable control technology currently available except that the surge capacity must hold the heaviest 25-year-24-hour rainfall instead of the 10-year event rainfall.

#### Subpart D - Defluorinated Phosphate Rock Subcategory

The following limitations establish the quantity or quality of pollutants or pollutant properties, which may be discharged by a point source subject to the provisions of this subpart after application of the best available technology economically achievable:

(a) Subject to the provisions of paragraphs (b), (c) and (d) below:

The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of the best available technology economically achievable: there shall be no discharge of process wastewater pollutants to navigable waters.

(b) Process waste water pollutants from a cooling water recirculation system designed, constructed and operated to maintain a surge capacity equal to the runoff from the 25-year, 24-hour rainfall event may be discharged, after treatment to the standards set forth in subparagraph (c) below, whenever chronic or catastrophic precipitation events cause the water level in the pond to rise into the surge capacity. Process waste water must be treated and discharged whenever the water level equals or exceeds the mid point of the surge capacity.

(c) The concentration of pollutants discharged in process wastewater pursuant to the limitations of paragraph (b) shall not exceed the values listed in the following table:

<u>Effluent Characteristic</u>	<u>Maximum for Any 1 Day</u>	<u>Average of Daily Values for 30 Consecutive Days Shall Not Exceed</u>
	mg/l	
Total Phosphorus(P)	105	35
Fluoride	75	25
TSS	150	50
pH	Within the range 6.0 to 9.5	

The total suspended solid limitation set forth in this paragraph shall be waived for process wastewater from a calcium sulfate storage pile runoff facility, operated separately or in combination with a water recirculation system, which is chemically treated and then clarified or settled to meet the other pollutant limitations set forth in this paragraph.

(d) The concentration of pollutants discharged in contaminated non-process wastewater shall not exceed the values listed in the following table:

<u>Effluent Characteristic</u>	<u>Maximum for Any 1 Day</u>	<u>Average of Daily Values for 30 Consecutive Days Shall Not Exceed</u>
	mg/l	
Total Phosphorus(P)	105	35
Fluoride	75	25
pH	Within the range 6.0 to 9.5	

#### Rationale for the Best Available Technology Economically Achievable

The rationale is identical to that for best practicable control technology currently available, except that a greater freeboard is required for retention of heavier rains. The required technology to achieve BATEA has been established at exemplary plants.

#### Subpart E - Defluorinated Phosphoric Acid Subcategory

The following limitations establish the quantity or quality of pollutants or pollutant properties, which may be discharged by a point source subject to the provisions of this subpart after application of the best available technology economically achievable:

(a) Subject to the provisions of paragraphs (b), (c) and (d) below:

The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of the best available technology economically achievable: there shall be no discharge of process wastewater pollutants to navigable waters.

(b) Process waste water pollutants from a cooling water recirculation system designed, constructed and operated to maintain a surge capacity equal to the runoff from the 25-year, 24-hour rainfall event may be discharged, after treatment to the standards set forth in subparagraph (c) below, whenever chronic or catastrophic precipitation events cause the water level in the pond to rise into the surge capacity. Process waste water must be treated and discharged whenever the water level equals or exceeds the mid point of the surge capacity.

(c) The concentration of pollutants discharged in process wastewater pursuant to the limitations of paragraph (b) shall not exceed the values listed in the following table:

<u>Effluent</u> <u>Characteristic</u>	<u>Maximum for</u> <u>Any 1 Day</u>	<u>Average of Daily</u> <u>Values for 30</u> <u>Consecutive Days</u> <u>Shall Not Exceed</u>
	mg/l	
Total Phosphorus (P)	105	35
Fluoride	75	25
TSS	150	50
pH	Within the range 6.0 to 9.5	

The total suspended solid limitation set forth in this paragraph shall be waived for process wastewater from a calcium sulfate storage pile runoff facility, operated separately or in combination with a water recirculation system, which is chemically treated and then clarified or settled to meet the other pollutant limitations set forth in this paragraph.

(d) The concentration of pollutants discharged in contaminated non-process wastewater shall not exceed the values listed in the following table:

<u>Effluent</u>	<u>Maximum for</u>	<u>Average of Daily</u> <u>Values for 30</u> <u>Consecutive Days</u>
-----------------	--------------------	--

<u>Characteristic</u>	<u>Any 1 Day</u>	<u>Shall Not Exceed</u>
	mg/l	
Total Phosphorus (P)	105	35
Fluoride	75	25
pH	Within the range 6.0 to 9.5	

The rationale is identical to that for BPCTCA except that a greater freeboard is required for retention of heavier rains. The required technology has been established at exemplary plants.

#### Subpart F - Sodium Phosphates Subcategory

The best available treatment economically achievable includes the use of the contaminated water pond and continuous lime treatment of some waste water streams.

The best available treatment economically achievable standards for the sodium phosphates subcategory are set at 70 percent of the discharge levels for suspended solids, fluoride and phosphate waste water components proposed for the best practicable control technology currently available. It is the opinion of the Environmental Protection Agency staff and its advisors that this reduction can be readily achieved. Improvements of this order and greater are common in fertilizer phosphate plants facing the need for improved water conservation practices to avoid excessive costly lime treatment. The recirculation lagoon is available to handle waste streams that present difficult treatment problems.

The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of the best available technology economically achievable:

<u>Effluent Characteristic</u>	<u>Effluent Limitations</u>
	Maximum for any one day
	Average of daily values for thirty consecutive days <u>shall not exceed</u>

(Metric units, kg/kg or lb/1000 lb of product)

TSS	0.35	0.18
Total phosphorus (as P)	0.56	0.28
Fluoride	0.21	0.11
pH	Within the range 6.0 to 9.5.	



## SECTION XI

### NEW SOURCE PERFORMANCE STANDARDS AND PRETREATMENT STANDARDS

#### New Source Performance Standards

This level of technology is to be achieved by new sources. The term "new source" is defined in the Act to mean "any source, the construction of which is commenced after publication of proposed regulations prescribing a standard of performance." New source performance standards are to be evaluated by adding to the consideration underlying the identification of best practicable control technology currently available, a determination of what higher levels of pollution control are available through the use of improved production processes and/or treatment techniques. Thus, in addition to considering the best in-plant and end-of-process control technology, new source performance standards are to be based upon an analysis of how the level of effluent may be reduced by changing the production process itself. Alternative processes, operating methods or other alternatives are to be considered. However, the end result of the analysis identifies effluent standards which would reflect levels of control achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology which must be employed. A further determination which was to be made for new source performance standards is whether a standard permitting no discharge of pollutants is practicable.

The following factors were to be considered with respect to production processes which were analyzed in assessing new source performance standards:

- a. The type of process employed and process changes.
- b. Operating methods.
- c. Batch as opposed to continuous operations.
- d. Use of alternative raw materials and mixes of raw materials.
- e. Use of dry rather than wet processes (including substitution of recoverable solvents for water).

f. Recovery of pollutants as by-products.

Subpart D - Defluorinated Phosphate Rock Subcategory

The following effluent limitations establish the quantity or quality of pollutants or pollutant properties, which may be discharged by a point source subject to the provisions of this subpart after application of the standards of performance for new sources.

(a) Subject to the provisions of paragraphs (b), (c) and (d) below:

The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of new source performance standards: there shall be no discharge of process wastewater pollutants to navigable waters.

(b) Process waste water pollutants from a cooling water recirculation system designed, constructed and operated to maintain a surge capacity equal to the runoff from the 25-year, 24-hour rainfall event may be discharged, after treatment to the standards set forth in subparagraph (c) below, whenever chronic or catastrophic precipitation events cause the water level in the pond to rise into the surge capacity. Process waste water must be treated and discharged whenever the water level equals or exceeds the mid point of the surge capacity.

(c) The concentration of pollutants discharged in process wastewater pursuant to the limitations of paragraph (b) shall not exceed the values listed in the following table:

<u>Effluent</u> <u>Characteristic</u>	<u>Maximum for</u> <u>Any 1 Day</u>	<u>Average of Daily</u> <u>Values for 30</u> <u>Consecutive Days</u> <u>Shall Not Exceed</u>
		mg/l
Total Phosphorus (P)	105	35
Fluoride	75	25
TSS	150	50
pH	Within the range 6.0 to 9.5	

The total suspended solid limitation set forth in this paragraph shall be waived for process wastewater from a calcium sulfate storage pile runoff facility, operated separately or in combination with a water recirculation system, which is chemically treated and then clarified or

settled to meet the other pollutant limitations set forth in this paragraph.

(d) The concentration of pollutants discharged in contaminated non-process wastewater shall not exceed the values listed in the following table:

<u>Effluent Characteristic</u>	<u>Maximum for Any 1 Day</u>	<u>Average of Daily Values for 30 Consecutive Days Shall Not Exceed</u>
	mg/l	
Total Phosphorus(P)	105	35
Fluoride	75	25
pH	Within the range 6.0 to 9.5	

#### Subpart E - Defluorinated Phosphoric Acid Subcategory

The following limitations and guidelines establish the quantity or quality of pollutants or pollutant properties, which may be discharged by a point source subject to the provisions of this subpart after application of the standards of performance for new sources:

(a) Subject to the provisions of paragraphs (b), (c) and (d) below:

The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of the standards of performance for new sources: there shall be no discharge of process wastewater pollutants to navigable waters.

(b) Process waste water pollutants from a cooling water recirculation system designed, constructed and operated to maintain a surge capacity equal to the runoff from the 25-year, 24-hour rainfall event may be discharged, after treatment to the standards set forth in subparagraph (c) below, whenever chronic or catastrophic precipitation events cause the water level in the pond to rise into the surge capacity. Process waste water must be treated and discharged whenever the water level equals or exceeds the mid point of the surge capacity.

(c) The concentration of pollutants discharged in process wastewater pursuant to the limitations of paragraph (b) shall not exceed the values listed in the following table:

Average of Daily  
Values for 30

<u>Effluent Characteristic</u>	<u>Maximum for Any 1 Day</u>	<u>Consecutive Days Shall Not Exceed</u>
	mg/l	
Total Phosphorus (P)	105	35
Fluoride	75	25
TSS	150	50
pH	Within the range 6.0 to 9.5	

The total suspended solid limitation set forth in this paragraph shall be waived for process wastewater from a calcium sulfate storage pile runoff facility, operated separately or in combination with a water recirculation system, which is chemically treated and then clarified or settled to meet the other pollutant limitations set forth in this paragraph.

(d) The concentration of pollutants discharged in contaminated non-process wastewater shall not exceed the values listed in the following table:

<u>Effluent Characteristic</u>	<u>Maximum for Any 1 Day</u>	<u>Average of Daily Values for 30 Consecutive Days Shall Not Exceed</u>
	mg/l	
Total Phosphorus (P)	105	35
Fluoride	75	25
pH	Within the range 6.0 to 9.5	

#### Subpart F - Sodium Phosphates Subcategory

Performance standards for new sources are the same as for best available technology economically achievable:

The following standards of performance establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a new source subject to the provisions of this subpart:

<u>Pollutant or Pollutant Property</u>	<u>Effluent Limitations</u>
<u>Maximum for any one day</u>	<u>Average of daily values for thirty consecutive days shall not exceed</u>

(Metric units, kg/kg of product)

(English units, lb/1000 lb of product)

TSS	0.35	0.18
Total phosphorus	0.56	0.28
(as P)		
Fluoride	0.21	0.11
pH	Within the range 6.0 to 9.5	

#### Pretreatment Standards for Existing and New Sources

All pretreatment standards are reserved for the present time because of ongoing studies and incomplete administrative decisions.



## SECTION XII

### ACKNOWLEDGMENT

This report was prepared by the Environmental Protection Agency on the basis of a comprehensive study performed by Davy Powergas, Inc., under contract no. 68-01-1508, model #2. Mr. R. W. Heinz, Project Manager, prepared the original (contractor's) report. Mr. Heinz was assisted in the preparation of this report, by the following personnel: Mr. D. W. Ross, Mr. Charles T. Harding, Mr. Gerald T. Fields, Mr. N. V. Fry, Mr. George Telatnik, Mr. Jack Frost, Mr. E. Singler, and Mr. H. Honey.

This study was initiated under the supervision and guidance of Elwood E. Martin. The final phases of the study were supervised by Chester E. Rhines, with extensive transition assistance from Mr. Martin.

Overall guidance and excellent assistance was provided by the author's associates in the Effluent Guidelines Division, particularly Messrs. Allen Cywin, Director, Ernst P. Hall, Deputy Director, and Walter J. Hunt, Branch Chief.

The cooperation of manufacturers who offered their plants for survey and contributed pertinent data is greatly appreciated. The operations and the plants visited were the property of the following companies:

Borden Chemical Company, Plant City, Fla.

Occidental Chemical Co., Houston, Tex.

Olin Corporation, Stamford, Conn.

J. R. Simplot Co., Pocatello, Idaho

Thornton Laboratory, Tampa, Fla.

The members of the working group/steering committee who participated in the internal EPA review are:

Mr. Walter J. Hunt, Chairman, Effluent Guidelines  
Division

Dr. Chester E. Rhines, Project Officer,  
Effluent Guidelines Division

Mr. Elwood Martin, Effluent Guidelines Division

Mr. Lamar Miller, Effluent Guidelines Division

Dr. Robert Swank, NERC, Corvallis (Athens)

Mr. Paul Desrosiers, ORM, Headquarters

Mr. Louis W. DuPuis, Economic Analysis Section

Dr. Edmund Lomasney, Region IV

Mr. James Rouse, NFIC, Denver

Acknowledgement and appreciation is also given to Ms. Kaye Starr, Ms. Nancy Zrubek, Ms. Brenda Holmone, Ms. Alice Thompson, and Ms. Ernestine Christian of the Effluent Guidelines Division secretarial staff and to the secretarial staff of Davy Powergas, Inc., for their efforts in the typing of drafts, necessary revisions, and the final preparation of this and the contractor's draft document.



## SECTION XIII

### REFERENCES

- A. Phosphoric Acid, Phosphates and Phosphatic Fertilizers by William Henry Waggaman, University Microfilms, Inc., Ann Arbor, PP. 233-236, original volume copyright 1927, 1952, by Reinhold Publishing Corporation, Library of Congress Card Number 52-9791.
- B. Defluorination of Phosphate Rock by Clinton A. Hollingsworth, Lakeland, Florida, assignor to Smith-Douglas Company, Inc., Norfolk, Va., United States Patent Office Number 2,995,437, Patented Aug. 8, 1961.
- C. Method of Defluorinating Phosphate Rock in a Fluid Bed Reactor by Clinton A. Hollingsworth and John H. Snyder, Lakeland, Fla., assignors to the Borden Company, New York, N.Y., a corporation of New Jersey, United States Patent Office Number 3,364,008, Patented January 16, 1968.
- D. Method of Agglomerating Phosphate Material by Clinton A. Hollingsworth and Jack F. Lewis, Lakeland, Fla., assignors, by mesne assignments, to The Borden Company, United States Patent Office, Number 3,189,433, Patented June 15, 1965.
- E. Chemical Economics Handbook, Stanford Research Institute, Phosphorus and Compounds, 762.2030 A, 762.2030 B, 762.2030 C, December 1969.
- F. Phosphorus and Its Compounds, John R. Van Wager, Interscience Publishers, Inc., New York (1961) Library of Congress Card No. 58-10100.
- G. 1972 Fertilizer Summary Data, Norman L. Hargett, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama.
- H. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Phosphorus Derived Chemicals Segment of the Phosphate Manufacturing Point Source Category, United States Environmental Protection Agency, EPA 440/1-74/006, January, 1974.
- I. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Basic Fertilizer Manufacturing Point Source Category, United

States Environmental Protection Agency, EPA 440/174-011-a, March, 1974.

- J. Engineering Field Manual for Conservation Practices, U.S. Department of Agriculture, Soil Conservation Service Section I, 1969 and Section 2, 1971.
- K. Earth Manual, U.S. Department of the Interior, Bureau of Reclamation, First Edition, Denver, Colorado, July, 1940 (a new edition is being printed).
- L. Design of Small Dams, U.S. Department of the Interior, Bureau of Reclamation, Second Edition, 1973.
- M. Those Nasty Phosphatic Clay Ponds, Environmental Science and Technology, page 312, April, 1974.
- N. Reconnaissance Study of Radiochemical Pollution from Phosphate Rock Mining and Milling, National Field Investigations Center-Denver, Denver, Colorado, Revised May, 1974.
- O. Interim Radium-226 Effluent Guidance for Phosphate Chemicals and Phosphate Fertilizer Manufacturing, Statement of Considerations - August 5, 1974, Criteria and Standards Division, Office of Radiation Programs, Environmental Protection Agency, Washington, D.C. 20460.
- P. Black & Veatch, Consulting Engineers, Process Design Manual for Phosphorus Removal, U.S. Environmental Protection Agency Program 17010 GNP, Contract 14-12-936 (October 1971).
- Q. "Water Quality Criteria 1972," National Academy of Sciences and National Academy of Engineering for the Environmental Protection Agency, Washington, D.C. 1972 (U.S. Govt. Printing Office Stock No. 5501-00520).
- R. R.E. Kirk and D.F. Othmer, Encyclopedia of Chemical Technology, Interscience, N.Y., 1966.
- S. EPA Report, Suspect Carcinogens in Water Supplies, by Office of R & D, April, 1975.
- T. Final Report on "Cost of Implementation and Capabilities of Available Technology to Comply with P.L. 92-500", Industry Category 18, Phosphate Manufacturing for National Commission on Water Quality, R.A. Ewing,

Battelle's Columbus Laboratories with assistance from Burgess & Niple, Ltd., July 3, 1975.

- U. Technical Note ORP/CSD-75-3 Radioactivity Distribution in Phosphate Products, By-Products, Effluents, and Wastes, The U.S. EPA, Office of Radiation Programs, August, 1975.
- V. Technical Note, ORP/CSD-75-4 Preliminary Findings, Radon Daughter Levels in Structures Constructed on Reclaimed Florida Phosphate Land, U.S. EPA, Office of Radiation Programs, September, 1975.



## SECTION XIV

### GLOSSARY

#### Apatite

A natural calcium phosphate usually containing fluorine occurring as phosphate rock.

#### DPG

Davy Powergas

#### Gyp-pond

This term is widely used at fertilizer phosphate plants to indicate the pond receiving waste water and acting as a recirculation, cooling and water reuse pond. Many plants have ponds with a variety of functions such as receiving the calcium sulfate residue from acid treatment of rock, receiving calcium fluoride from first stage of lime precipitation, receiving calcium phosphate and calcium fluoride sediment from second stage of lime precipitation, recirculation of stack washing and tail gas scrubber water and simultaneously removing heat and sediment, and deposition of troublesome solids, as arsenic sulfide. Local authorities will have to determine specific pond uses in order to establish essential solid waste control and groundwater pollution control measures.

#### kkq

1,000 kilograms

#### l

liter

#### Process Waste Water

The term "process waste water" means any water which, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, by-product, or waste product.

#### Ton

All uses of term "ton" imply short ton equal to 2,000 pounds.

TABLE XIV-1  
METRIC TABLE  
CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)		by		TO OBTAIN (METRIC UNITS)	
ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT	
acre	ac	0.405	ha	hectares	
acre - feet	ac ft	1233.5	cu m	cubic meters	
British Thermal Unit	BTU	0.252	kg cal	kilogram - calories	
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/kilogram	
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute	
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute	
cubic feet	cu ft	0.028	cu m	cubic meters	
cubic feet	cu ft	28.32	l	liters	
cubic inches	cu in	16.39	cu cm	cubic centimeters	
degree Fahrenheit	°F	0.555(°F-32)*	°C	degree Centigrade	
feet	ft	0.3048	m	meters	
gallon	gal	3.785	l	liters	
gallon/minute	gpm	0.0631	l/sec	liters/second	
horsepower	hp	0.7457	kw	kilowatts	
inches	in	2.54	cm	centimeters	
inches of mercury	in Hg	0.03342	atm	atmospheres	
pounds	lb	0.454	kg	kilograms	
million gallons/day	mgd	3,785	cu m/day	cubic meters/day	
mile	mi	1.609	km	kilometer	
pound/square inch (gauge)	psig	(0.06805 psig +1)*	atm	atmospheres (absolute)	
square feet	sq ft	0.0929	sq m	square meters	
square inches	sq in	6.452	sq cm	square centimeters	
ton (short)	ton	0.907	kkg	metric ton (1000 kilograms)	
yard	yd	0.9144	m	meter	

\* Actual conversion, not a multiplier



U.S. ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460  
WH 552

POSTAGE AND FEES PAID  
ENVIRONMENTAL PROTECTION AGENCY  
EPA-335

