

Best Available Techniques
for Pollution Prevention and Control
in the European Fertilizer Industry

Booklet No. 4 of 8:

PRODUCTION OF PHOSPHORIC ACID

2000

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European Fertilizer Manufacturers' Association

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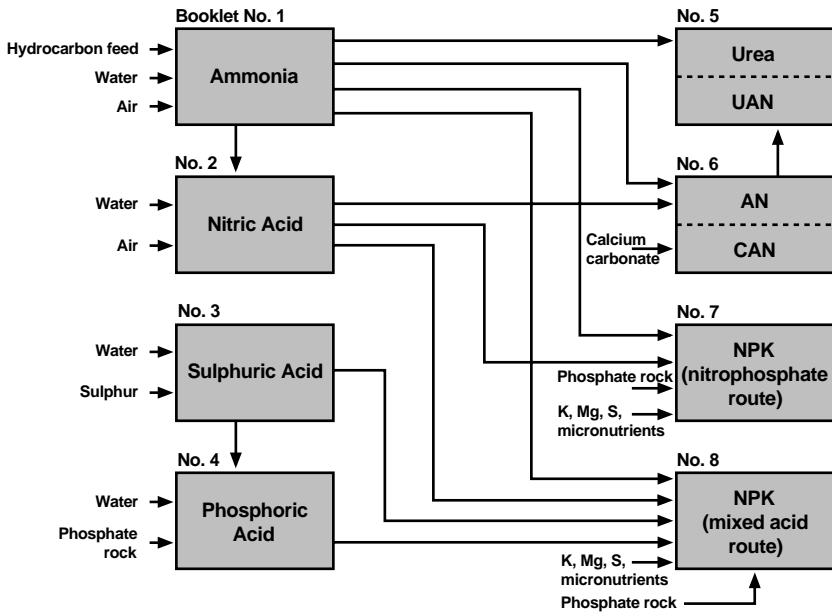
Booklet No. 4 of 8:

**PRODUCTION OF PHOSPHORIC
ACID**

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EFMA's BAT Booklets



CONTENTS

PREFACE	4
DEFINITIONS	6
1. INTRODUCTION	7
2. DESCRIPTION OF PRODUCTION PROCESSES	7
2.1 Raw Materials for Phosphoric Acid Production	7
2.2 Principles of the Process	10
2.3 Production Processes	12
2.4 Emission Abatement	24
2.5 Gypsum Disposal	27
3. DESCRIPTION OF STORAGE AND TRANSFER EQUIPMENT	28
3.1 Raw Materials Storage	28
3.2 Phosphoric Acid Storage	29
4. ENVIRONMENTAL DATA	29
4.1 Input Requirements	29
4.2 Output Production	30
4.3 Emissions and Wastes	30
4.4 Environmental Hazards Associated with Emissions and Wastes	31
5. EMISSION MONITORING	32
5.1 Fluoride	32
5.2 Gypsum	32
5.3 Radioactivity	33
6. MAJOR HAZARDS	33
7. OCCUPATIONAL HEALTH & SAFETY	33
8. SUMMARY OF BAT EMISSION LEVELS	34
8.1 Achievable Emission Levels for New Plants	34
8.2 Achievable Emission Levels for Existing Plants	34
8.3 Cost of Pollution Control Measures	35
9. REFERENCES	35
GLOSSARY OF TERMS	36
APPENDIX 1 Emission Monitoring in Phosphoric Acid Plants	39
APPENDIX 2 General Product Information on Phosphoric Acid	42

PREFACE

In 1995, the European Fertilizer Manufacturers Association (EFMA) prepared eight Booklets on Best Available Techniques (BAT) in response to the proposed EU Directive on integrated pollution prevention and control (IPPC Directive). These booklets were reviewed and updated in 1999 by EFMA experts drawn from member companies. They cover the production processes of the following products:-

No. 1 Ammonia

No. 2 Nitric Acid

No. 3 Sulphuric Acid
(updated in collaboration with ESA)

No. 4 Phosphoric Acid

No. 5 Urea and Urea Ammonium Nitrate (UAN)

No. 6 Ammonium Nitrate (AN) and Calcium Ammonium Nitrate (CAN)

No. 7 NPK Compound Fertilizers by the Nitrophosphate Route

No. 8 NPK Compound Fertilizers by the Mixed Acid Route

The Booklets reflect industry perceptions of what techniques are generally considered to be feasible and present achievable emission levels associated with the manufacturing of the products listed above. The Booklets do not aim to create an exhaustive list of BAT but they highlight those most widely used and accepted. They have been prepared in order to share knowledge about BAT between the fertilizer manufacturers, as well as with the regulatory authorities.

The Booklets use the same definition of BAT as that given in the IPPC Directive 96/61 EC of 1996. BAT covers both the technology used and the management practices necessary to operate a plant efficiently and safely. The EFMA Booklets focus primarily on the technological processes, since good management is considered to be independent of the process route. The industry recognises, however, that good operational practices are vital for effective environmental management and that the principles of Responsible Care should be adhered to by all companies in the fertilizer business.

The Booklets give two sets of BAT emission levels:-

- For existing production units where pollution prevention is usually obtained by revamps or end-of-pipe solutions
- For new plants where pollution prevention is integrated in the process design

The emission levels refer to emissions during normal operations of typical sized plants. Other levels may be more appropriate for smaller or larger units and higher emissions may occur in start-up and shut-down operations and in emergencies.

Only the more significant types of emissions are covered and the emission levels given in the Booklets do not include fugitive emissions and emissions due to rainwater. Furthermore, the Booklets do not cover noise, heat emissions and visual impacts.

The emission levels are given both in concentration values (ppm, mg.m⁻³ or mg.l⁻¹) and in load values (emission per tonne of product). It should be noted that there is not necessarily a direct link between the concentration values and the load values. EFMA recommends that the given emission levels should be used as reference levels for the establishment of regulatory authorisations. Deviations should be allowed as governed by:-

- **Local environmental requirements**, given that the global and inter-regional environments are not adversely affected
- **Practicalities and costs of achieving BAT**
- **Production constraints** given by product range, energy source and availability of raw materials

If authorisation is given to exceed these BAT emission levels, the reasons for the deviation should be documented locally.

Existing plants should be given ample time to comply with BAT emission levels and care should be taken to reflect the technological differences between new and existing plants when issuing regulatory authorisations, as discussed in these BAT Booklets.

A wide variety of methods exist for monitoring emissions. The Booklets provide examples of methods currently available. The emission levels given in the Booklets are subject to some variance, depending on the method chosen and the precision of the analysis. It is important when issuing regulatory authorisations, to identify the monitoring method(s) to be applied. Differences in national practices may give rise to differing results as the methods are not internationally standardised. The given emission levels should not, therefore, be considered as absolute but as references which are independent of the methods used.

EFMA would also advocate a further development for the authorisation of fertilizer plants. The plants can be complex, with the integration of several production processes and they can be located close to other industries. Thus there should be a shift away from authorisation governed by concentration values of single point emission sources. It would be better to define maximum allowable load values from an entire operation, eg from a total site area. However, this implies that emissions from single units should be allowed to exceed the values in the BAT Booklets, provided that the total load from the whole complex is comparable with that which can be deduced from the BAT Booklets. This approach will enable plant management to find the most cost-effective environmental solutions and would be to the benefit of our common environment.

Finally, it should be emphasised that each individual member company of EFMA is responsible for deciding how to apply the guiding principles of the Booklets.

Brussels, April 2000

DEFINITIONS

The following definitions are taken from Council directive 96/61/EC of 1996 on Integrated Pollution Prevention and Control:-

“Best Available Techniques” mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing, in principle, the basis for emission limit values designed to prevent or, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole:-

“Techniques” include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned.

“Available” techniques mean those developed on a scale which allows implementation in the relevant industrial sector under economically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator.

“Best” means most effective in achieving a high general level of protection for the environment as a whole.

1. INTRODUCTION

Processes with different raw materials are used in the manufacture of phosphoric acid. The process is known as “thermal” when the raw material is elemental phosphorus. This process has been abandoned because of the amount of energy which is needed. The processes that use phosphated minerals which are decomposed with an acid, are known as “wet processes” and they are the only economic alternative way to produce phosphoric acid.

There are three possible subgroups of wet processes depending on the acid that is used for the acidulation. This may be nitric, hydrochloric or sulphuric but this Booklet is concerned only with processes using the sulphuric acid route since this is the process normally used in the production of fertilizers in Europe.

There are three types of sulphuric acid process, according to the condition of the calcium sulphate produced, since it can be obtained in the form of anhydrite, hemihydrate or dihydrate. Finally, there are the processes that obtain a determined final grade in one stage and those that do so in several stages.

In Europe the more current processes are the following:-

- Dihydrate process
- Hemihydrate process
- Di-Hemihydrate process (double-stage)
- Hemi-Dihydrate process (single-stage)
- Hemi-Dihydrate process (double-stage)

Different processes are needed because of different rocks and gypsum disposal systems.

The storage and transfer of phosphoric acid is the same for all the acids and does not depend on the method of production.

2. DESCRIPTION OF PRODUCTION PROCESSES

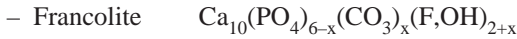
2.1 Raw Materials for Phosphoric Acid Production

Bones used to be the principal natural source of phosphorus but phosphoric acid today is produced from phosphatic ores mined in various parts of the world.

Phosphate ores are of two major geological origins:-

- Igneous as found in Kola, South Africa, Brazil, etc.
- Sedimentary as found in Morocco, Algeria, Jordan U.S.A., etc.

The phosphate minerals in both types of ore are of the apatite group, of which the most commonly encountered variants are:-



Fluorapatite predominates in igneous phosphate rocks and francolite predominates in sedimentary phosphate rocks.

The most easily mined phosphate deposits are found in the great sedimentary basins. These sedimentary deposits are generally associated with matter derived from living creatures and thus contain organic compounds. These phosphates are interposed with sedimentary strata of the waste materials interpenetrated by gangue minerals and thus sedimentary phosphate ores have differing compositions within the same source.

Most phosphate ores have to be concentrated or beneficiated before they can be used or sold on the international phosphate market. Different techniques may be used at the beneficiation stage, to treat the same ore for removal of the gangue and associated impurities. This gives rise to further variations in the finished ore concentrate product. Phosphoric acid technology, having to rely on raw materials of great variety, has to readapt itself constantly.

Table 1 shows the variation in chemical analysis of various phosphate rocks.

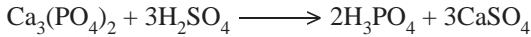
Table 1

	CEI Russia*	S.AFRICA Phalaborwa*	MOROCCO Khouribga	USA Florida	SENEGAL	TOGO
Grade (nominal)						
% BPL	84	80	73	75	80	80
	Composition(%wt)					
P ₂ O ₅	38.9	36.8	33.4	34.3	36.7	36.7
CaO	50.5	52.1	50.6	49.8	50.0	51.2
SiO ₂	1.1	2.6	1.9	3.7	5.0	4.5
F	3.3	2.2	4.0	3.9	3.7	3.8
CO ₂	0.2	3.5	4.5	3.1	1.8	1.6
Al ₂ O ₃	0.4	0.2	0.4	1.1	1.1	1.0
Fe ₂ O ₃	0.3	0.3	0.2	1.1	0.9	1.0
MgO	0.1	1.1	0.3	0.3	0.1	0.1
Na ₂ O	0.4	0.1	0.7	0.5	0.3	0.2
K ₂ O	0.5	0.1	0.1	0.1	0.1	0.1
Organics		0.1	0.3	0.5		
Organ. C	0.1			0.2	0.4	0.1
SO ₃	0.1	0.2	1.6	0.1		0.3
Cl			0.1			0.1
SrO	2.9	0.3	0.1			
	Trace elements (ppm)					
Rare earth metals	6,200	4,800	900	600		
U ₃ O ₈	11	134	185	101	124	
As	10	13	13	11	18	12
Cd	1.2	1.3	15	9	53	53
Cr	19	1	200	60	6	
Cu	37	102	40	13		
Hg	33	0.1	0.1	0.02	0.2	0.6
Ni	2	2	35	28		
Pb		11	10	17	5	
Zn	20	6	200-400	70		

* Igneous

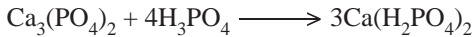
2.2 Principles of the Process

The basic chemistry of the wet process is exceedingly simple. The tricalcium phosphate in the phosphate rock is converted by reaction with concentrated sulphuric acid into phosphoric acid and the insoluble salt calcium sulphate.



The insoluble calcium sulphate is then separated from the phosphoric acid, most usually by filtration.

The reaction between phosphate rock and sulphuric acid is self-limiting because an insoluble layer of calcium sulphate forms on the surface of the particles of the rock. This problem is kept to a minimum by initially keeping the rock in contact with recirculated phosphoric acid to convert it as far as possible to the soluble monocalcium phosphate and then precipitating calcium sulphate with sulphuric acid.



Calcium sulphate exists in a number of different crystal forms depending particularly on the prevailing conditions of temperature, P_2O_5 concentration and free sulphate content (see Figures 1 and 2).

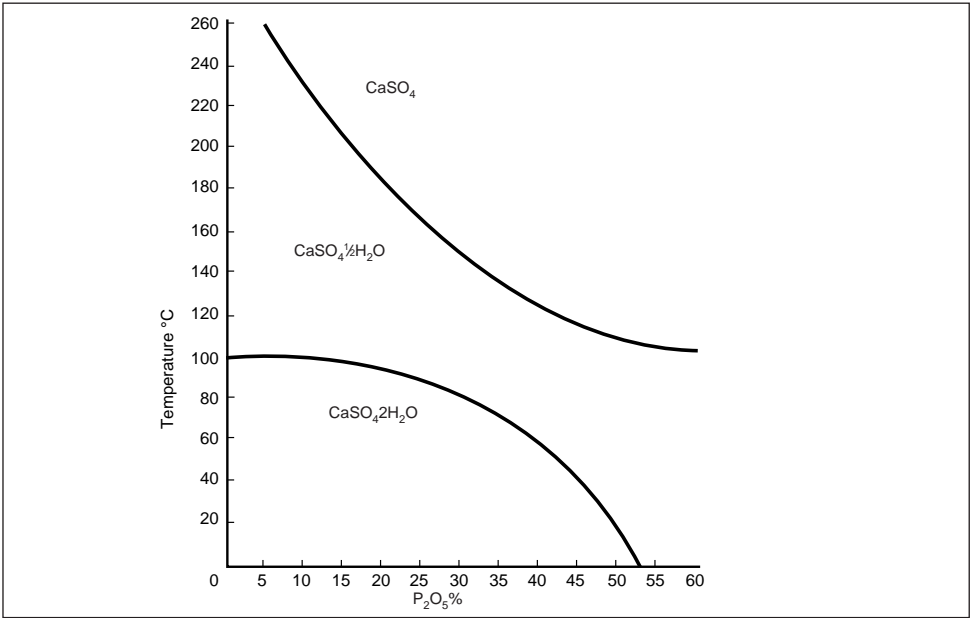


Figure 1 – Dependence of Calcium Sulphate Hydrate Crystallisation on Temperature and P_2O_5 .

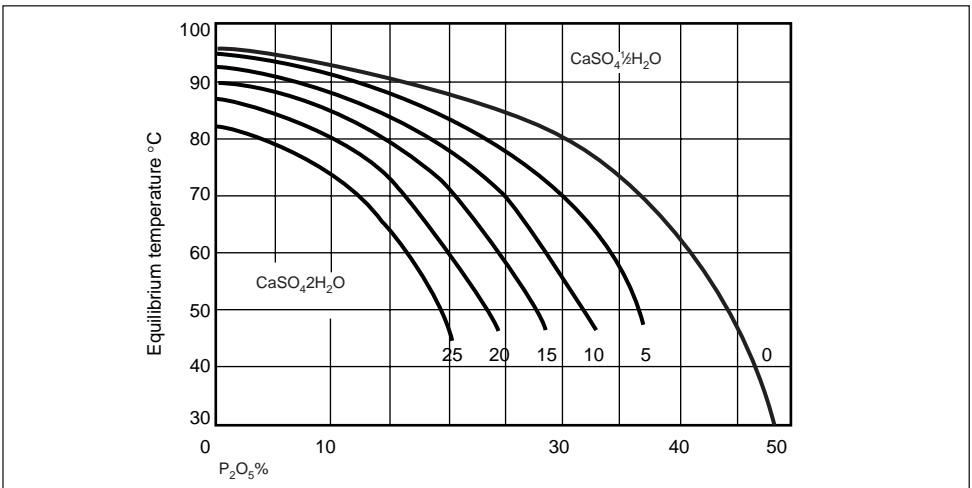


Figure 2 – Dependence of Calcium Sulphate Dihydrate/ α – Hemihydrate Equilibrium on Sulphuric Acid Concentration.

The operating conditions are generally selected so that the calcium sulphate will be precipitated in either the dihydrate or the hemihydrate form, 26-32% P_2O_5 at 70-80°C for dihydrate precipitation and 40-52% P_2O_5 at 90-110°C for hemihydrate precipitation.

There are many impurities in phosphate rock, the amounts and proportions of which are very variable. The ill effects of some are manifested in the reaction system, whereas others are predominantly seen in the filtration or in the properties of the product acid.

Fluorine is present in most phosphate rocks to the extent of 2-4% by weight. This element is liberated during acidulation, initially as hydrogen fluoride but in the presence of silica this readily reacts to form fluosilicic acid, H_2SiF_6 . Other components such as magnesium and aluminium can also react with HF to form compounds ($MgSiF_6$ and H_3AlF_6). A proportion of the fluorine is evolved as vapour, depending on the reaction conditions and the rest remains in the acidic medium. Some of this remainder may be precipitated by interaction with other impurities sufficiently quickly to be removed in the filter and a further proportion may subsequently contribute to sludge formation in the product acid. More volatile fluorine compounds will appear in the vapours exhausted from the evaporators when the acid from the filter is concentrated.

Emphasis must also be placed on another group of impurities such as arsenic, cadmium, copper, lead, nickel, zinc and mercury, which are present in most phosphate rocks and which may pass into the acid during acidulation. Phosphate rocks contain naturally-occurring uranium and the radioactive components of the uranium decay series are associated with the phosphate material. The uranium goes into the product acid solution and any radium is co-precipitated with the phosphogypsum. The amount of uranium is practically nil in some phosphate rocks.

Impurities such as iron, aluminium, sodium, potassium, chlorine, etc have some influence during the production of phosphoric acid and on the quality of the acid produced.

2.3 Production Processes

Five process routes are discussed in this section and these represent the principal process routes which are available.

2.3.1 Dihydrate process

This is the most diffused process and the advantages of dihydrate systems are:-

- There is no phosphate rock quality limitation
- On-line time is high
- Operating temperatures are low
- Start-up and shut-down are easy
- Wet rock can be used (saving drying costs)

The disadvantages are:-

- Relatively weak product acid (26-32% P_2O_5)
- High energy consumption in the acid concentration stage
- 4-6% P_2O_5 losses, most of them co-crystallised with the calcium sulphate

The dihydrate process comprises four stages: grinding, reaction, filtration and concentration and these are represented in Figure 3.

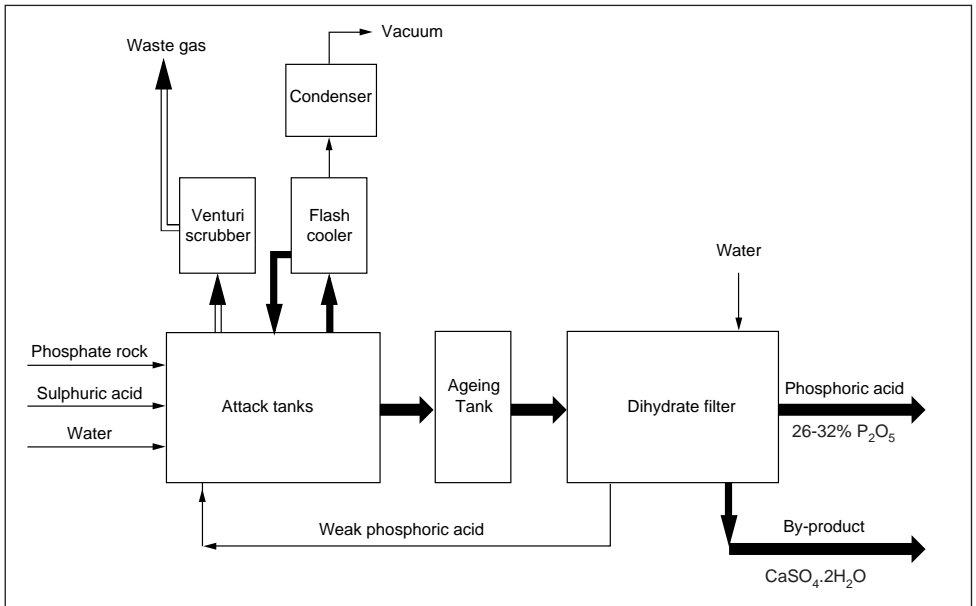


Figure 3 – Dihydrate Process.

Grinding

Some grades of commercial rock do not need grinding, their particle size distribution being acceptable for a dihydrate reaction section (60-70% less than $150\mu\text{m}$). Most other phosphate rocks need particle size reduction, generally by ball or rod mills. Both mills can operate with wet or dry rock.

Reaction

The tricalcium phosphate is converted by reaction with concentrated sulphuric acid into phosphoric acid and insoluble calcium sulphate. The reactor maintains an agitated reaction volume in circulation. The reaction system consists of a series of separate agitated reactors

but in the interests of economy of materials and space, the multi-vessel reaction system is replaced by a single tank in some processes. Some of these single tanks may be divided into compartments which are virtually separate reactors.

The operating conditions for dihydrate precipitation are 26-32% P_2O_5 and 70-80°C (see Figure 1). This temperature is controlled by passing the slurry through a flash cooler, which also de-gasses the slurry and makes it easier to pump. The temperature can also be controlled by using an air circulating cooler.

Filtration

This stage separates the phosphoric acid from the calcium sulphate dihydrate. Five tonnes of gypsum are generated for every tonne (P_2O_5) of product acid produced. The filter medium must move in sequence through the various stages for continuous operation. The initial separation must be followed by at least two stages of washing, to ensure a satisfactory recovery of soluble P_2O_5 . It is only possible to achieve the desired degree of separation at a reasonable rate if the filtration is either pressure or vacuum assisted and in practice vacuum is always used. The remaining liquid must be removed from the filter cake as far as possible at the end of the washing sequence. The cake must then be discharged and the cloth efficiently washed to clear it of any remaining solids which might otherwise build up and impair filtration in subsequent cycles. The vacuum must be released during the discharge of the cake and it is beneficial to blow air through in the reverse direction at this point to help dislodge the solids.

The filtrate and washings must be kept separate from one another and have to be separated from air under vacuum conditions and then delivered under atmospheric pressure, as product, or for return to the process. The pressure difference is usually maintained by delivering the filtrates below the surface of the liquid in barometric tanks placed at a level sufficiently below the separators for the head of liquid to balance the vacuum.

The most common filtration equipment is of three basic types: tilting pan, rotary table or travelling belt.

Concentration

There is a long history of direct contact concentrators, in which evaporation is effected by bringing the acid into intimate contact with hot combustion gas from a burner, enabling equipment walls to be made of materials and in thicknesses which are suitable for efficient indirect heat transfer. Various patterns of direct-fired concentrator have been devised. Currently, almost all evaporators that are being built today for this service are of the forced circulation design as shown in Figure 4.

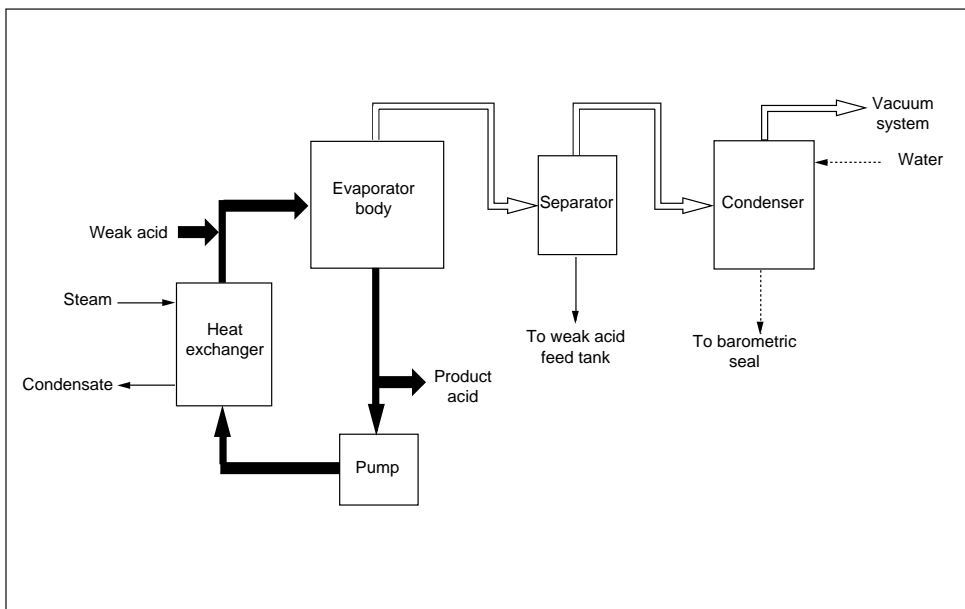


Figure 4 – Phosphoric Acid Concentration. Feed Circulation System.

The forced circulation evaporator consists of a heat exchanger, vapour or flash chamber, condenser, vacuum pump, acid circulating pump and circulation piping. A fluosilicic acid scrubber is usually included in the forced circulation evaporator system. All the evaporators in this service are generally of the single-effect design because of the corrosive nature of phosphoric acid and the very high boiling point elevation. The heat exchangers are fabricated from graphite or stainless steel with the rest of the equipment made from rubber-lined steel.

All equipment designs will be made using the best practices of engineering available. More than one evaporator may be used, with the acid passing in sequence through each, depending on the degree of concentration required.

2.3.2 Hemihydrate (HH) process

Operating conditions are selected in this process so that the calcium sulphate is precipitated in the hemihydrate form. It is possible to produce 40-52% P_2O_5 acid directly, with consequent valuable savings in energy requirements. Figure 5 shows a simplified flow diagram of a HH process. The stages are similar to those of the dihydrate process but grinding may be unnecessary.

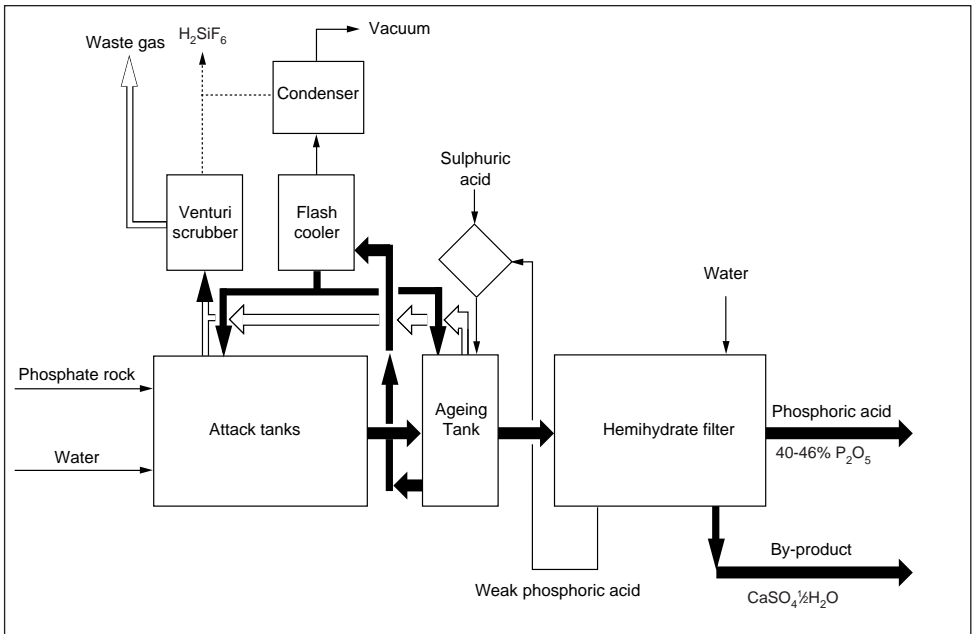


Figure 5 – Hemihydrate Process.

The main advantages of this process, apart from the reduction or elimination of evaporation heat requirement, are:-

Capital savings.

Purer acid.

Acid from the HH process tends to contain substantially less free sulphate and suspended solids and lower levels of aluminium and fluorine than evaporated dihydrate process acid of the same strength.

Lower rock grinding requirements.

A satisfactory rate of reaction can be achieved from much coarser rock than in the dihydrate process, because of the more severe reaction conditions in the HH process.

The disadvantages of HH systems are:-

Filtration rate.

Hemihydrate crystals tend to be small and less well formed than dihydrate crystals and thus hemihydrate slurries tend to be more difficult to filter than dihydrate slurries unless crystal habit modifiers are used to suppress excessive nucleation. With a good HH process however, there is no need to use crystal habit modifiers. There are examples of phosphate rocks that produce hemihydrate crystals achieving higher filtration rates than obtained with dihydrate crystals.

Phosphate losses.

Water balance considerations restrict the amount of wash water that can be used. At the same time, the amounts of both soluble and insoluble P_2O_5 remaining in the filter cake are greater because of the higher P_2O_5 concentration of the slurry being filtered. Nevertheless the simplicity of the HH plant and the absence of silicofluoride and chucrovite scaling in the HH filter, may compensate for the higher insoluble P_2O_5 loss via HH cake.

Scaling.

Hemihydrate is not a stable form of calcium sulphate and there is a tendency for it to revert to gypsum even before the acid has been filtered off. The conditions are even more in favour of rehydration during washing. In a good HH plant there is no conversion in the reactor battery. A small quantity of anti-scale agent may be required in a single-stage HH plant filter to avoid scaling.

Filter cake impurity.

The cake is more acidic than gypsum filter cake because of the extra P_2O_5 losses and it also contains more fluorine and cadmium.

Corrosion.

The demands on susceptible items of equipment, particularly agitators and slurry pumps, are increased because of the higher temperature (100°C) and acid concentration (40-50% P_2O_5) compared to a dihydrate plant.

2.3.3 Recrystallisation processes

The best P_2O_5 recovery efficiencies that generally can be expected in the single-stage dihydrate and hemihydrate processes considered so far, are 94-96% and 90-94% respectively. The P_2O_5 losses are retained in the filter cake and this can create problems with disposal or use of the by-product gypsum. Some of this loss of P_2O_5 passes into solution and can be recovered when the calcium sulphate is finally separated, if the calcium sulphate is made to recrystallise to its other hydrate. This not only raises the overall efficiency of the process but also gives a much cleaner calcium sulphate.

Several processes have been developed but there are only three basic routes:-

- Acidulate under hemihydrate conditions; recrystallise to dihydrate without intermediate hemihydrate separation; separate product. (Hemihydrate recrystallisation (HRC) process)
- Acidulate under hemihydrate conditions; separate product; recrystallise hemihydrate to dihydrate; filter and return liquors to process. (Hemi-dihydrate (HDH) process)
- Acidulate under dihydrate conditions; separate product; recrystallise hemihydrate; filter and return liquors to process (Dihydrate-Hemihydrate (DH/HH) process)

2.3.3.1 HRC process

The flow diagram of this process resembles that of the multiple reactor dihydrate process (see Figure 3) with the exception that the attack reactor operates under hemihydrate conditions, while succeeding reactors operate under conditions favouring the rehydration of hemihydrate to gypsum. This is encouraged by seed dihydrate crystals recycled in the slurry from the filter feed. The product acid is no more concentrated than that obtained from dihydrate but the gypsum is much purer. A flow diagram for this process is shown in Figure 6.

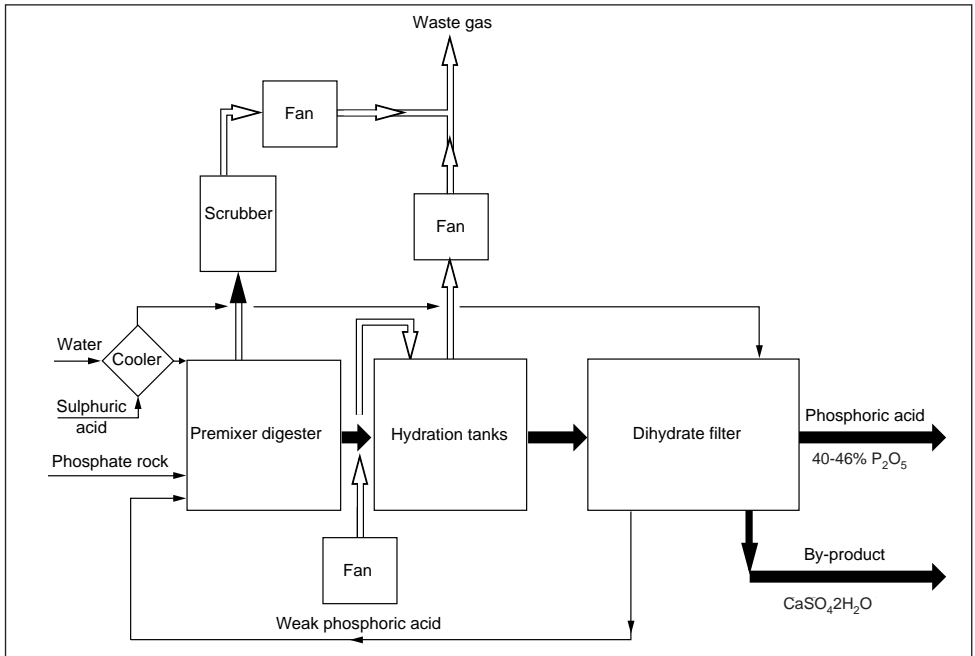


Figure 6 – Hemihydrate Recrystallisation Process.

2.3.3.2 HDH process

It is possible to obtain 40-52% P_2O_5 acid directly, by acidulating under hemihydrate conditions and separating the hemihydrate before recrystallising, in this process. The additional filter and the other equipment required, add to the capital cost of the plant but enable savings to be made on evaporation equipment. A flow diagram for this process is shown in Figure 7.

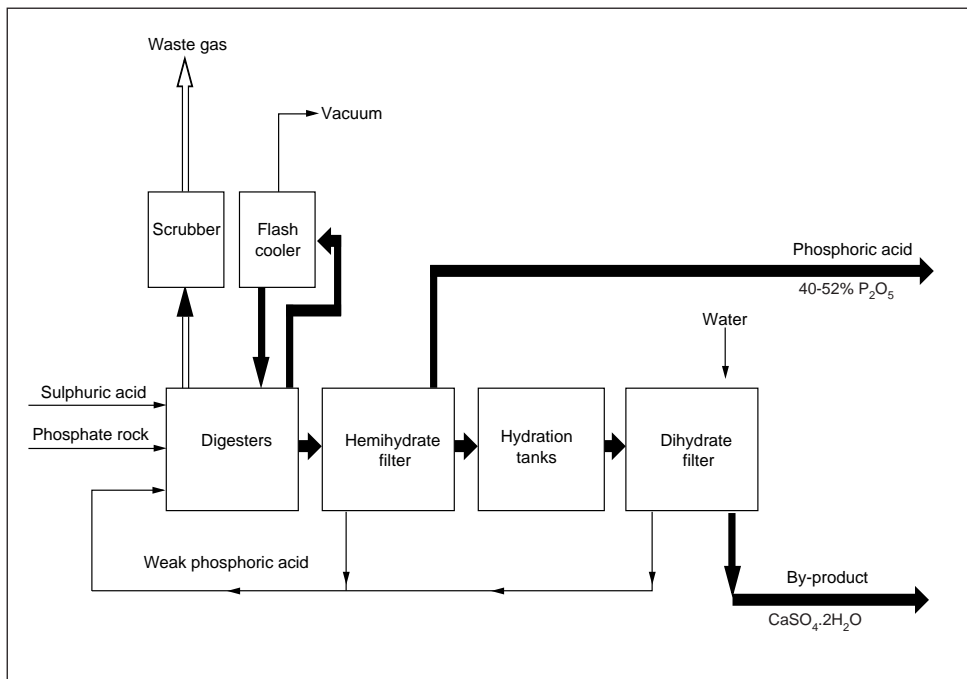


Figure 7 – Hemihydrate Process.

2.3.3.3 DH/HH process

In this process, although the reaction runs under dihydrate conditions, it is not desirable to effect a very high degree of P_2O_5 recovery during the separation of the acid from the dihydrate. The succeeding dehydration stage requires around 20-30% P_2O_5 and 10-20% sulphuric acid. The strength of the product acid is 32-35% P_2O_5 . A flow diagram for this process is shown in Figure 8.

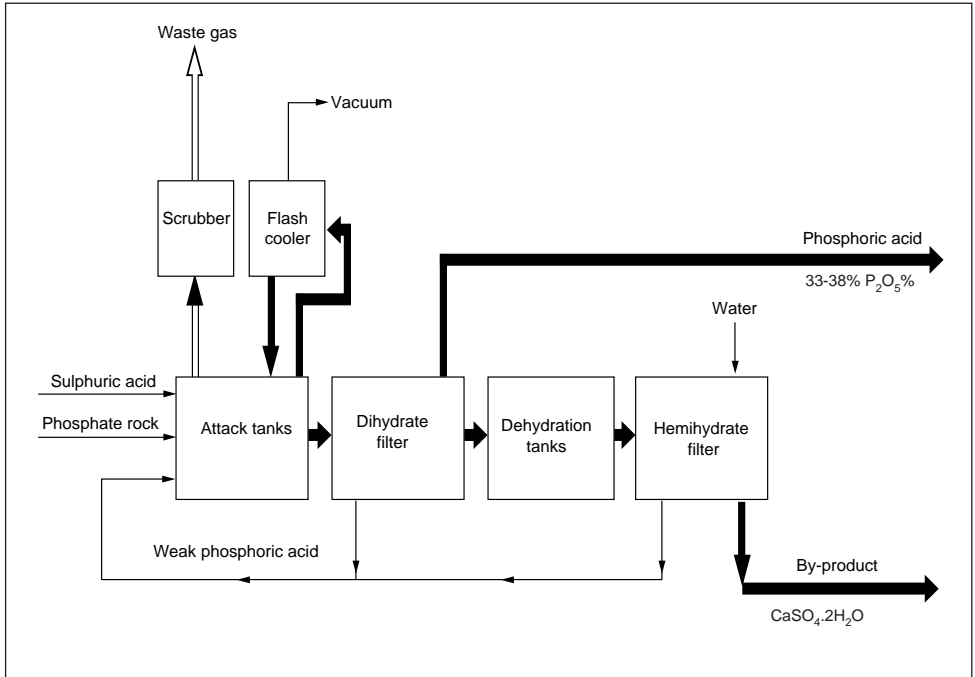


Figure 8 – Dihemihydrate Process.

2.3.4 Repulping process

A further optimisation of the HRC process can be obtained by re-slurrying and washing the gypsum, followed by a second filtration step in the so called “Repulping Process”. Most of the free acid which is not removed in the first filtration step, can be removed in this process and the efficiency can be improved by up to 1% (depending on the amount of free acid).

The gypsum from the first filter is re-slurried in a tank and then pumped to a second filter where the gypsum is de-watered. The gypsum is then washed with the fresh water coming into the plant. The liquid obtained from the second filter is used on the first filter to wash the gypsum. The repulp process is in fact an additional step in the counter-current washing of the gypsum using the water that enters the plant. The flow diagram for a repulping process is shown in Figure 9.

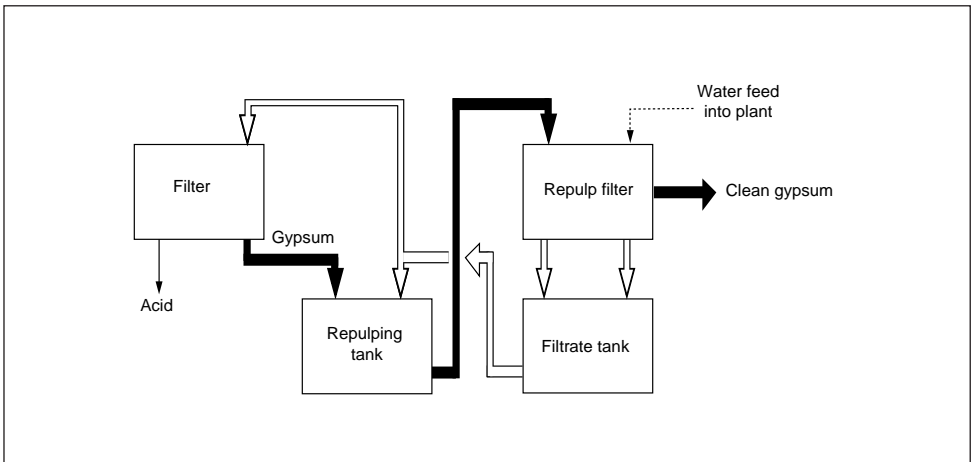


Figure 9 – Repulp Process.

Table 2, mostly taken from Reference [1], shows the advantages and disadvantages of the different processes.

Table 2

ADVANTAGES

Dihydrate Process

Single stage filtration.
Simple design.
Flexibility of rock source.
Proven process.
Ease of operation/shut-down.
Requires lower grades of materials of construction.
Wet rock grinding possible.
Low maintenance cost and high operating factors.
Easy transport of gypsum slurry.

Hemihydrate Process

Single-stage filtration.
Produces strong acid directly 40-48% P_2O_5 .
No intermediate storage if acid is produced at user's strength.
Uses coarse rock.
Ease of operation.

HRC Process

Single stage filtration.
Proven process with sedimentary rock.
Produces a pure gypsum.
Higher P_2O_5 efficiency (97%).
Slightly higher acid strength (30-32% P_2O_5).
Lower sulphuric acid consumption.
Lower filter area.

DISADVANTAGES

Produces acid at 26-32% P_2O_5 .
Normally requires steam for evaporation.
Acid has high levels of F and Al.
 P_2O_5 efficiency 94-96%.
May require rock grinding.
Requires weak acid storage and evaporation.

Limited number of rocks processed industrially.
Large filter area required for 48% P_2O_5 acid.
High lattice loss, low P_2O_5 efficiency (90-94%).
Produces impure hemihydrate.
Tight water balance.
Requires higher grade alloys.
Care required in design and shut-down.

Requires a fine rock grind.
Requires sulphuric acid dilution.
Large recrystallisation volume required.
May dissolve more partially soluble impurities.
Requires 32% acid storage and evaporation.
Post-precipitation before and after evaporation.
Requires sophisticated materials of construction.

ADVANTAGES

HDH Process

Produces strong acid directly (40-52% P_2O_5).

Produces purer acid (low SO_4 , Al, F).

Limited post-precipitation.

Uses coarse rock.

Low sulphuric acid consumption.

High P_2O_5 efficiency (98.5%).

Produces a purer gypsum.

DH/HH Process

Flexible as to rock source.

Proven process.

Produces a pure hemihydrate.

High P_2O_5 efficiency (98%).

Higher acid strength (32-36% P_2O_5).

Lower sulphuric acid consumption.

Gypsum may be used directly for plasterboard, plaster or as a cement retarder, after the addition of lime and natural rehydration in a storage pile.

Additional techniques: Repulping Process

Pure gypsum.

High efficiency.

DISADVANTAGES

Two-stage filtration, lower utilisation.

Limited number of rocks processed industrially.

Care required in design and shut-down.

High recrystallisation volume.

High capital cost.

Two stage filtration, lower utilisation.

High capital cost.

Requires steam for conversion.

Requires 35% acid storage and evaporators.

Rock slurry feed unacceptable.

Requires final re-hydration of hemihydrate to gypsum.

Normally, requires rock grinding.

Care required in design and shut-down.

Requires sophisticated materials of construction.

High capital cost.

2.4 Emission Abatement

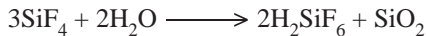
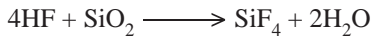
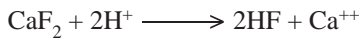
The gaseous and liquid effluents from all the processes need treatment to eliminate or at least to reduce, the contaminants.

The fluorine contained in the phosphate rock (2-4%) is distributed between the product acid, the gypsum cake and the vapours evolved from the reactor (and the evaporator if the acid needs to be concentrated).

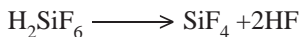
A typical fluorine distribution in the dihydrate and hemihydrate processes is:-

	Dihydrate process %	Hemihydrate process %
Acid	15	12
Phosphogypsum	43	50
Reactor off-gas	5	8
Flash cooler vapour	2	30
Concentrator vapour	35	—

The fluorine is liberated as hydrogen fluoride during the acidulation of phosphate rock. In the presence of silica this reacts readily to form fluosilicic acid via silicon tetrafluoride.



The fluosilicic acid may decompose under the influence of heat to give volatile silicon tetrafluoride and hydrogen fluoride.



The heat of reaction evolved during acidulation in a dihydrate process, is generally less than that required to cause this decomposition. The majority of the fluorine compounds will be evolved when weak phosphoric acid (26-32% P_2O_5) is concentrated. Conditions of higher temperature and reduced pressure exist in vacuum evaporators, thus causing the decomposition of fluosilicic acid.

Most of the fluorine is evolved during acidulation in the hemihydrate processes. Fluoride from the reaction will leave the reactor with the vacuum cooler condenser water or with the cooling air, depending on the cooling system, (flash cooler or air circulating cooler). In the first case, most of the released fluoride will be absorbed by the condenser water. In the second case, effluent gas washing must be installed.

In dihydrate processes, when flash coolers are used to control the temperature, it is usual to remove the fluoride from the gas evolved during acidulation and from the gas evolved during concentration, in separate systems. The fluoride scrubbing system is placed ahead of the condenser that follows the concentrator to avoid producing large quantities of highly contaminated water.

In hemihydrate processes, more fluoride is evolved during acidulation and may be removed from the gas from the reactor and the gas leaving the vacuum coolers that are commonly used.

2.4.1 Gas scrubbing systems

A number of different scrubbing systems have been used for removing fluoride. These can vary both in the scrubbing liquor and in the type of scrubber used. The most widely used scrubber is the void spray tower operating at atmospheric pressure but others, such as packed bed, cross-flow venturi and cyclonic column scrubbers have been extensively employed.

A product containing up to 22% fluosilicic acid is recovered in the fluoride recovery system at atmospheric pressure and the removal efficiency is better than 99% (90% with one absorber). Silica is removed from the acid by filtration. Fresh water, recycled pond water, sea water and dilute fluosilicic acid have all been used as scrubbing liquor.

Gas from the evaporator flash chamber is first fed through an entrainment separator if a system operating under vacuum is used. Essentially, this removes any P_2O_5 values from the gas. Only one scrubbing stage is generally used and 17-23% fluosilicic acid is obtained with a recovery efficiency of about 83-86%.

Systems operating under vacuum normally use a direct contact condenser in which most of the remaining fluoride is absorbed. An indirect condensation system has been developed to prevent the spillage of water which is contaminated with fluoride, for cases where certain phosphates are used and where a low cooling water temperature is feasible. These two systems are shown in Figures 10 and 11. The water required for condensing is recycled in the condenser but is cooled by a heat exchanger fed from an independent water supply. These two water loops are independent and ensure that there are no fluorine compounds in the effluent.

The scrubber liquor can be disposed of after neutralisation with lime or limestone to precipitate fluorine as solid calcium fluoride, if the fluorine is not to be recovered. Often, however, the fluorine can be used and in these cases a dilute solution of fluosilicic acid is used as the scrubbing liquor. The required concentration is maintained by removing a portion of liquor, which is then filtered to remove solid contaminants.

The fluosilicic acid is used mainly for the manufacture of aluminium fluoride and cryolite but is also used for the production of other fluorine compounds.

It is possible to recycle the fluosilicic acid into the phosphoric acid process and use it for acidulating rock. This slightly reduces the sulphuric acid requirement and solves the waste disposal problem as well. However it may produce compounds which are difficult to filter and lead to problems during the gypsum filtration.

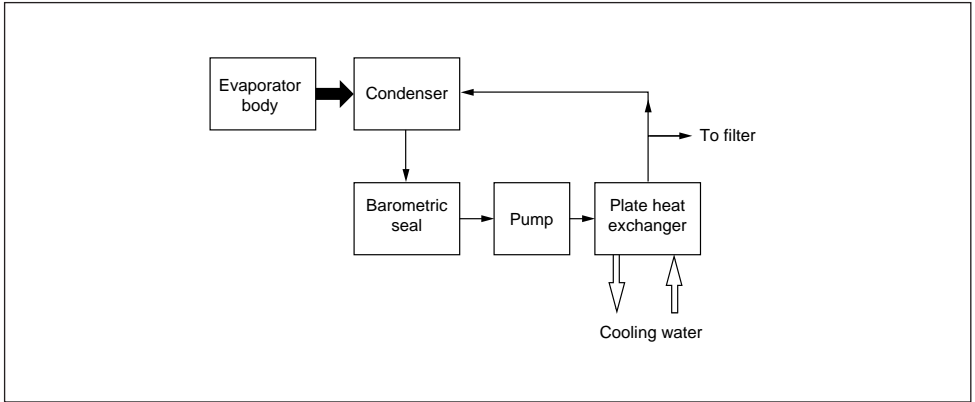


Figure 10 – Indirect Cooling Flowsheet.

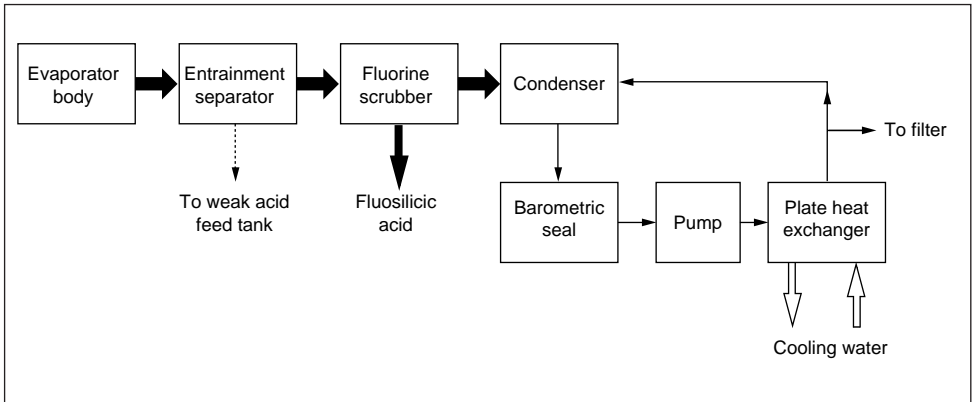


Figure 11 – Fluorine Recovery and Indirect Cooling Flowsheet.

2.5 Gypsum Disposal

Around 5 tonnes of gypsum are generated per tonne of P_2O_5 produced as phosphoric acid. This represents a serious disposal problem with the individual phosphoric acid production units of over $1,000t.d^{-1}$ capacity now being built.

Two methods can be used to dispose of gypsum:-

- Disposal to land
- Disposal into water

By-product gypsum contains four types of impurity that are considered to be potentially harmful:-

- Residual acidity (P_2O_5)
- Fluorine compounds
(These are only harmful if disposal is into fresh water because disposal into sea water results in the formation of insoluble calcium fluoride.)
- Undesirable trace elements
- Radioactivity

2.5.1 Disposal to water

The gypsum can be pumped through an outfall into the sea at coastal sites and estuaries. Disposal into rivers is no longer practised, as it is not a good environmental option. Disposal of gypsum into the sea has the advantage that gypsum is more soluble in sea water than in fresh water. However, some of the impurities in the gypsum should be controlled. Clean gypsum itself ($CaSO_4$) is soluble and is not harmful to the environment.

A phosphoric acid plant with high efficiency is essential for this method of disposal and only “clean” phosphates can be used in the plant if the pollution is to be kept within local environmental quality standards.

2.5.2 Disposal on land

Disposal on land, under proper conditions, is the best environmental option although it is not possible everywhere because it requires space and certain soil qualities where the gypsum stack is situated.

Dry gypsum from the filter in some plants is transported by belt conveyors to the gypsum storage pile. The pile area is completely surrounded by a ditch which collects the run-off water including any rain water.

In other plants the filter cake is slurried with recycled pond water and pumped to special storage areas where the phosphogypsum eventually dries in stacks. The area receiving the phosphogypsum slurry is sub-divided into smaller areas, with each section being used in rotation. Slurry is discharged on top of the storage pile and the phosphogypsum rapidly settles out of solution. Clear water runs off and drains to the adjacent cooling ponds. The water is recycled within the system to ensure that the contaminants are kept within the plant. The phosphogypsum stack is completely surrounded by a ditch which can contain not only this water but also rain water and any that might spill accidentally.

The more important considerations in the design and construction of phosphogypsum disposal areas are:-

Site selection.

The height of the stacks depends on the engineering properties of the underlying soil and its load bearing strength, if there are no legal restrictions.

Cooling ponds.

The cooling pond surfaces will have to be adapted to local climatic conditions and the water balance in the plant.

Percolation control.

The process water associated with phosphogypsum is highly acidic and contains high levels of contaminants. Some of the following options may be necessary to prevent this water reaching the surrounding ground water system:-

- Seepage collection ditches
- Intercept wells
- Natural barriers
- Lining systems (natural or synthetic)
- Fixing of soluble P_2O_5 and trace elements by neutralisation

2.5.3 Use as saleable products

The alternative to disposing of phosphogypsum is to make use of it in some way. However the basic problem with this is that the consumption rate for these uses is normally many times smaller than the production rate of the by-product.

3. DESCRIPTION OF STORAGE AND TRANSFER EQUIPMENT

3.1 Raw Materials Storage

3.1.1 Sulphuric acid

Reference should be made to EFMA BAT Booklet No 3 which covers the production of sulphuric acid.

3.1.2 Phosphate rock

Phosphate rock is generally loaded by crane from the ship and is transported to storage by belt conveyor or lorry. The unloading, handling and storage of these powdered materials should be carried out so as to minimise the emission of dust.

3.2 Phosphoric Acid Storage

Phosphoric acid is most commonly stored in rubber-lined steel tanks, although stainless steel, polyester and polyethylene-lined concrete are also used. The types of rubber linings used include neoprene, butyl and natural rubber.

Heating and insulation are not required in storage or during shipment since the impurities in wet-process acid promote supercooling and reduce the tendency for crystallisation.

Merchant grade acid is usually shipped with a guaranteed solids content of less than 1%. Storage tanks are normally equipped with some means of keeping the solids in suspension to avoid loss of product and costly cleaning of the tank.

Methods of agitation commonly used are:-

- Air injection
- Agitation from the top
- Jet mixing
- Agitation from the side
- Pump circulation and heating

Leak-floors are provided underneath vulnerable equipment to prevent contamination of the soil from acid leaks. Any leaks or spills flow to special pits from where the fluid is pumped back into the system. Most acid storage tanks are banded.

4. ENVIRONMENTAL DATA

4.1 Input Requirements

The specific consumption of phosphate rock and sulphuric acid depends mainly on the composition of the rock used and the overall efficiency of the process. Phosphate rock usage is about $2.6-3.5t.t^{-1}$ P_2O_5 produced.

The consumption of process water depends mainly on the concentration of the weak acid obtained in the filter and whether the condensed water in the evaporation loop is returned to the process or not. Consumption is about $4-7m^3.t^{-1}$ of P_2O_5 .

Cooling water is used in the reaction and concentration stages and during condensation of the vapours from the evaporators. Consumption of cooling water depends on the process used and is about $100-150m^3.t^{-1}$ of P_2O_5 produced as concentrated acid.

A phosphoric acid plant requires electric power and steam. The power consumption depends on whether the process requires the grinding of the phosphate rock or not.

Consumption is about 120-180kWh.t⁻¹ P₂O₅. Steam is used mainly for concentration at about 0.5-2.2t.t⁻¹ P₂O₅ concentrated.

When the phosphoric acid plant is linked to a sulphuric acid plant, the high pressure steam that is produced in the waste heat recovery boiler is normally used to produce electric power and the low pressure exhaust steam is used for phosphoric acid vacuum concentration. In addition it may be possible to reduce the steam consumption for concentration by using the waste heat originating in other parts of the sulphuric acid plant. This may be recovered as heated water and used to concentrate weak acid to intermediate concentrations.

4.2 Output Production

The main product is phosphoric acid with a commercial concentration of 52-54% P₂O₅. The production capacity of this type of plant reaches 1,200t.d⁻¹ P₂O₅ depending on the process used.

Fluosilicic acid with a concentration of 20-25% H₂SiF₆ is obtained as a by-product. The quantity of 100% fluosilicic acid produced depends on the composition of the phosphate rock used but is normally in the range 20-30kg.t⁻¹ P₂O₅ produced.

4.3 Emissions and Wastes

4.3.1 Emissions into air

The main emissions from the process are gaseous fluorides. 10-15% of the fluorine contained in the phosphate rock is released during the acidulation and filtration stages and the gaseous emissions must be scrubbed. The final result is an emission containing less than 10mg.Nm⁻³ as fluorine. Recovery of fluorine from the reactor battery in a HH process is much more difficult than from evaporators due to the relatively high SiF₄ content of the gas which causes precipitation of SiO₂ in the scrubber.

The secondary emission is dust originating from the unloading, handling and grinding of phosphate rock.

4.3.2 Emissions into water

The fluorine released from the reactor and evaporators can be recovered as a commercial by-product (fluosilicic acid 20-25%). The remainder passes to the condenser, producing a liquid effluent that contains mainly fluoride and a small amount of phosphoric acid. There is no liquid effluent from a plant with a closed-loop system because it is recycled to the process. New plants will be of the closed-loop type. Existing plants should reduce effluent as far as possible aiming to attain the level of new plants and any residual effluent will be treated before disposal.

The water used for the transport of phosphogypsum can be recirculated into the process after settling and thus there should be no liquid effluent containing undesirable elements such as Al, Ni, Cd, Pb, As, etc., as well as fluorides and phosphoric acid. In the case of disposal of gypsum slurry to a coastal area or estuary, such disposal should be limited and

the slurry shall be treated, if necessary, before disposal, to minimise the environmental impact. Besides this, the disposal area shall be monitored.

The run-off from phosphogypsum stacks will require treatment for several years after the acid plant has ceased production.

4.3.3 Solid wastes

Around 5 tonnes of phosphogypsum are generated per tonne of P_2O_5 produced. This phosphogypsum contains some of the trace elements from the phosphate rock, including cadmium and some radioactive elements. The percentage of these elements that is transferred from the phosphate rock to the phosphogypsum depends on the type of process and the rock used. The remainder of the trace elements pass to the intermediate and finished fertilizer products.

4.4 Environmental Hazards Associated with Emissions and Wastes

Wet-process phosphoric acid production may affect the environment in several ways:-

4.4.1 Fluoride emissions into air

The effect of fluorides emitted either as silicon tetrafluoride or hydrogen fluoride is more marked on vegetation than living creatures due to their accumulation in plants.

4.4.2 Dust emissions into air

The dust resulting from handling and grinding phosphate rock contains 3-4% water-insoluble fluoride. This dust is of little concern except for occasional effects on animals. The fluorides are not a problem with respect to plants and human beings but the dust is a troublesome nuisance.

4.4.3 Contamination of water

Disposal of phosphogypsum and its associated process water, including acidity, dissolved metals and radionuclides may give problems when the phosphogypsum is dumped on land. Hazards can be avoided by means of a lining system, collection ditches in the area, a recycle system for the water used for gypsum disposal and transport and appropriate monitoring. Any excess of contaminated water should be treated with lime before being disposed of. The most serious effect of discharging improperly treated pond wastes is the rapid change in pH, which can affect most species of fish, aquatic life and vegetation.

Phosphogypsum disposal into water is not the best environmental option. In the case of existing units having such a disposal, the environmental impact will depend to a great extent on the disposal pre-treatment, the amount disposed, the location of the outlet and the existing status of the receiving body. Impact monitoring shall be carried out systematically. The effect on sea water will be less because the fluoride, which is one of the major impurities in phosphogypsum, will precipitate as calcium fluoride at the pH value of sea water, the calcium originating from dissolved calcium sulphate or other sea water components.

4.4.4 Radionucleides

Potential pathways for exposure of humans to radionucleides include:-

- Direct irradiation from gamma radiation
- Airborne emissions of radon and dust (radioactive and non-radioactive)

Phosphate rock, phosphogypsum and the effluents produced from a phosphoric acid plant have a lower radioactivity than the exemption values given in the Directive 96/26/ EURATOM and are therefore excluded from reporting.

5. EMISSION MONITORING

A description of available methods for monitoring emissions is given in Appendix 1.

Emissions that should be monitored are:-

5.1 Fluoride

The frequency of measurements of fluoride emissions into the atmosphere from the stacks depends on local conditions and on the capacity and characteristics of the receiver. Emissions should be measured at least once every two weeks.

Equipment for the continuous monitoring of fluoride emissions is available and suitable for phosphoric acid plants and should be installed in all new plants. Emission monitors should be capable of recording the data for future reference. Emission monitor records should be retained and the competent authorities should consider the appropriate statistical analysis or reports which should be required.

A very important aspect of monitoring is regular observation by plant operators to detect abnormalities in the operation process and this should be taken into account by the competent authorities.

5.2 Gypsum

Typical parameters and frequencies of monitoring of disposals for phosphogypsum disposal on land with recirculation of the water, are:-

P	Daily
F ⁻	Daily
Ground water quality	Quarterly

Typical parameters and frequencies of monitoring of wet disposals for phosphogypsum disposal to sea or estuary, or for wet disposal to land without recirculation of the water, are:-

Flow	Continuous
pH or P	Continuous
F ⁻	Daily
Al	Once every two weeks
Trace elements (Cd, Hg, Zn, Cr, Ni, Pb, As)	Once every two weeks

5.3 Radioactivity

No monitoring is required as the phosphoric acid industry is excluded from the requirements of Directive 96/26/EURATOM. (See 4.4.4 above) However, some local legislation may require it.

6. MAJOR HAZARDS

Major hazards in phosphoric acid installations are not expected provided the the design of all the equipment has been made using the best engineering knowledge available.

The chance of an acid spill from storage tanks is very small, with the highest risk being a leak from the tank because of corrosion. Corrosion with phosphoric acid is a relatively slow process and starts with a small hole in the tank. Normally the leak will be seen and the tank emptied before a significant spillage can take place. The risk is minimised if the tank is adequately banded; the recommended BAT for new installations.

There is a risk of the loading pipe cracking during phosphoric acid loading and this could lead to a significant uncontrolled spillage. Pumping equipment should be available for emptying the pipes.

The most important considerations in the design and construction of phosphogypsum disposal systems have been mentioned in 2.5.2.

7. OCCUPATIONAL HEALTH & SAFETY

Phosphoric acid is a corrosive liquid of low toxicity that may cause burns on skin and eye contact and irritation in the respiratory tract. Prolonged contact may be necessary before some individuals notice burning or irritation of the skin. Sustained skin contact with phosphoric acid may cause dermatitis at the site of contact.

Ingestion may cause burns in the digestive zone. Inhalation of spray may cause irritation in the respiratory tract and can cause lung oedema.

Phosphoric acid is not explosive or flammable but in contact with ferrous metals less resistant than type 316 stainless steel, it liberates hydrogen gas which is explosive in the range 4-75% by volume of hydrogen in air. Contact with strong caustic substances must be avoided as the reaction is exothermic and produces splashes. A dangerously high concentration of fluoride gases often builds up in phosphoric acid storage tanks.

Workers handling phosphoric acid should be well informed by supervision of the hazards involved and should be instructed in safety procedures.

Suitable protective clothing, goggles and masks should be worn as required. Workers should be shown the location of first aid and safety equipment, such as showers, eye baths, or other emergency sources of water and instructed in their use.

Full health and safety information is given in Safety Data Sheets which must be available and updated. General product information on phosphoric acid is given in Appendix 2.

8. SUMMARY OF BAT EMISSION LEVELS

The following emission levels relate to steady-state production. Peaks may occur during the unsteady transient conditions of start-up and shut-down, particularly if the latter is unplanned.

8.1 Achievable Emission Levels for New Plants

The following emission levels can be reached with a modern plant.

8.1.1 Emissions into air

Emissions from the stack:-

Fluoride	5mg.Nm ⁻³ (40g.t ⁻¹ P ₂ O ₅)
Dust/particulates	50mg.Nm ⁻³

Emissions from gypsum piles and pond areas:-

No detectable effect on the environment is normally found from fluoride emissions in cases of worldwide wet and dry gypsum stacking and no standard measurement techniques or limits exist.

8.1.2 Emissions into water

New plants must ensure total recycle of both the process water and the water used for the transport and disposal of phosphogypsum.

8.1.3 Solid wastes

In new plants the phosphogypsum should be disposed of to land. The system should be designed to prevent any contaminated water from reaching the surrounding ground water system.

8.2 Achievable Emission Levels for Existing Plants

8.2.1 Emissions into air

Emissions from the stacks.

Fluoride	30mg.Nm ⁻³
Dust/particulates	150mg.Nm ⁻³

8.2.2 Emissions into water

Most existing plants with open-loop systems in reactors and evaporators can be converted to closed-loop type so process water disposal is eliminated. Should this not be entirely possible, the highest limitation in disposal is to be sought and the effluent treated.

Similarly water used for the transport and disposal of phosphogypsum shall be kept in a closed loop to the greatest possible extent compatible with the permitted gypsum disposal.

8.2.3 Solid wastes

For existing plants where water disposal has been practised in the past, such disposal in the future will be limited to 10-20% of the gypsum provided that the disposal of the gypsum is demonstrated as being acceptable to the receiving water.

The choice between storing the gypsum on land or disposal into the sea (if re-use is not possible) depends on the local situation and the impurity levels in the gypsum. When disposal into the sea is the only available option, a plant with a proven, high phosphate efficiency (above 97%) and an appropriate rock phosphate should be used to keep the contamination within acceptable limits.

Environmental monitoring shall be carried out systematically to ensure that no harm is caused to the receiving medium and the effluent treated if necessary.

8.3 Cost of Pollution Control Measures

The investment costs to install the equipment needed to achieve BAT emission levels in an existing 100,000t.y⁻¹ P₂O₅ plant are:-

– Closed-loop in reaction and filtration sections	0.4 million EUR
– Closed-loop in concentration section	0.5 million EUR
TOTAL	0.9 million EUR

The value of a phosphoric acid plant with this capacity is about 16 million EUR and thus the investment in these closed-loops represents about 5.4% of the total investment.

The annual operating costs of these systems is estimated to be 0.11 million EUR which is about 0.8% of the annual operating costs of the plant (14 million EUR).

The investment for disposal of the phosphogypsum to land with the transport water being recycled depends on the distances involved and the height and surface of the pile. The initial investment is estimated to be about 1.3 million EUR which represents about 8% of the phosphoric acid plant investment.

The annual operating costs of phosphogypsum storage and water recycling is estimated to be 0.6 million EUR or approximately 3.9% of the total operating costs of the plant.

The cost of closing a gypsum stack depends on the site but is estimated to be 6.4 million EUR.

The overall cost of gypsum ponds can range from 3-17 EUR.t⁻¹ P₂O₅.y⁻¹.

9. REFERENCES

- 1 Phosphates and Phosphoric Acid. Section 2.1.2 Edited by Pierre Becker. Published by Marcel Decker.

GLOSSARY

The following abbreviations occur frequently throughout the series of Booklets but without necessarily appearing in each Booklet:-

ACGIH	American Conference of Governmental Industrial Hygienists
AFNOR	Association Française de Normalisation (France)
AN	Ammonium Nitrate
AQS	Air Quality Standard
AS	Ammonium Sulphate
BAT	Best Available Techniques
BATNEEC	Best Available Technology Not Entailing Excessive Cost
BOD	Biological Oxygen Demand
BPL	Basic Phosphate of Lime (Bone Phosphate of Lime)
BS	British Standard
CAN	Calcium Ammonium Nitrate
CEFCIC	Conseil Européen de l'Industrie Chimique (European Chemical Industry Council)
COD	Chemical Oxygen Demand
DAP	Di-Ammonium Phosphate
DIN	Deutsches Institut für Normung (Germany)
EEC	European Economic Community
EFMA	European Fertilizer Manufacturers Association
ELV	Emission Limit Value
ESA	European Sulphuric Acid Association
EU	European Union (Formerly, European Community, EC)
IFA	International Fertilizer Industry Association
IMDG	International Maritime Dangerous Goods (Code)
IPC	Integrated Pollution Control
IPPC	Integrated Pollution Prevention and Control
ISO	International Standards Organisation (International Organisation for Standardisation)
MAP	Mono-Ammonium Phosphate
MOP	Muriate of Potash (Potassium Chloride)
NK	Compound fertilizer containing Nitrogen and Potash
NP	Compound fertilizer containing Nitrogen and Phosphate
NPK	Compound fertilizer containing Nitrogen, Phosphate and Potash
NS	Fertilizer containing Nitrogen and Sulphur
OEL	Occupational Exposure Limit
SSP	Single Super-Phosphate
STEL	Short Term Exposure Limit
TLV	Threshold Limit Value
TSP	Triple Super-Phosphate
TWA	Time Weighted Average
UAN	Urea Ammonium Nitrate (Solution)

CHEMICAL SYMBOLS

The following chemical symbols may be used where appropriate in the text.

C	Carbon
CaCO ₃	Calcium Carbonate
Cd	Cadmium
CH ₃ OH	Methanol
CH ₄	Methane
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
F	Fluorine
F ⁻	Fluoride
H (H ₂)	Hydrogen
H ₂ O	Water
H ₂ S	Hydrogen Sulphide
H ₂ SiF ₆	Hydrofluorosilicic Acid (Hexafluorosilicic Acid)
H ₂ SO ₄	Sulphuric Acid
H ₃ PO ₄	Phosphoric Acid
HNO ₃	Nitric Acid
K	Potassium
KCl	Potassium Chloride (Muriate of Potash) (“Potash”)
K ₂ O	Potassium Oxide
N (N ₂)	Nitrogen
N ₂ O	Dinitrogen Monoxide (Nitrous Oxide)
NH ₃	Ammonia
NH ₄ -N	Ammoniacal Nitrogen
NH ₄ NO ₃	Ammonium Nitrate
NO	Nitrogen Monoxide (Nitric Oxide or Nitrogen Oxide)
NO ₂	Nitrogen Dioxide
NO ₃ -N	Nitric Nitrogen
NO _x	Oxides of Nitrogen (Excluding Nitrous Oxide)
O (O ₂)	Oxygen
P	Phosphorus
P ₂ O ₅	Phosphorus Pentoxide
S	Sulphur
SO ₂	Sulphur Dioxide
SO ₃	Sulphur Trioxide

UNITS

Units have been standardised as far as possible and these are abbreviated as follows:-

bar	Unit of pressure (equivalent to one atmosphere)
GJ	Giga Joule
kg	Kilogramme
kg.h ⁻¹	Kilogrammes per hour
kWh	Kilowatt hour (1,000kWh = 3.6GJ)
l	Litre (liquid volume)
m	Metre
m ³	Cubic Metre (liquid or solid volume)
mg	Milligramme
mg.l ⁻¹	Milligrammes per litre
MJ	Mega Joule
µm	Micrometre
Nm ³	Normal cubic metre (gas volume)
ppb	Parts per billion
ppm	Parts per million
ppmv	Parts per million by volume
t	Tonnes (Metric Tons)
t.d ⁻¹	Tonnes per day
t.y ⁻¹	Tonnes per year
°C	Degree Celsius
K	Degree Kelvin

APPENDIX 1 EMISSION MONITORING IN PHOSPHORIC ACID PLANTS

1. Introduction

Monitoring of emissions plays an important part in environmental management. It can be beneficial in some instances to perform continuous monitoring. This can lead to rapid detection and recognition of irregular conditions and can give the operating staff the possibility to correct and restore the optimum standard operating conditions as quickly as possible. Emission monitoring by regular spot checking in other cases will suffice to survey the status and performance of equipment and to record the emission level.

In general, the frequency of monitoring depends on the type of process and the process equipment installed, the stability of the process and the reliability of the analytical method. The frequency will need to be balanced with a reasonable cost of monitoring.

A typical extractive gas sampling system for emissions would need to be iso-kinetic to ensure the accurate collection of particulates.

Iso-kinetic sampling is subject to a variety of national standards and appropriate methods will generally need to be agreed with the regulatory authorities. Typically, they consist of combined air flow measurement and extraction sampling equipment that can be controlled to maintain the same velocity in the sampling nozzle as is present in the duct. These can be combined to give mass emissions.

National standards for gas sampling exist and the appropriate method should be adopted.

Manual methods may be necessary or accepted by the authorities in certain cases and for situations where no continuous method is available.

Typical methods for monitoring emissions into water rely on flow-proportioned sample collection or high frequency spot sampling together with analysis and continuous flow measurement.

The use of trained staff is essential. Methods available for monitoring the emissions given in Chapter 8 of this Booklet are briefly described below.

2. Emissions into Air

2.1 On Line Methods

Commonly used methods for the determination of fluoride in solutions from the gas sampling system are colorimetric and ion selective electrode methods.

Colorimetric methods include the zirconium SPADNS (sulpho phenyl azo dihydroxy naphthalene disulphonic acid) method as the most widely used. Fluoride reacts with zirconium lake dye to produce a colourless complex for spectrophotometric determination.

A fluoride selective electrode using a lanthanum fluoride membrane may be used.

2.2 Manual Methods

In addition to the methods outlined in 2.1 a volumetric method may be used which relies on the titration of fluoride ion against lanthanum nitrates to an end point determined by coloration of an indicator dye such as Alizarin Red S or Eriochrome Cyanine R.

3. Emissions into Water

Phosphogypsum disposed into the sea or estuary will require flow measurement and flow proportional sampling or high frequency sampling with on-line analysis applied as follows:-

Flow	–	Ultrasonic
pH	–	Applicable national standard for pH electrodes
F ⁻	–	See 2.1 above
P ₂ O ₅ or P	–	Spectrophotometry

The P₂O₅ or P is measured by reaction with acidic molybdate reagents to form a reduced phosphomolybdenum blue complex whose concentration is measured spectrophotometrically.

Trace elements in samples accumulated from flow proportional sampling systems are analysed by inductively coupled plasma or atomic absorption. Some or all of the following may be required to be analysed:-

As, Cd, Cr, Hg, Ni, Pb and Zn.

Frequency would need to be agreed with national authorities and may be weekly to quarterly. Inductively coupled plasma emission spectroscopy relies on sample injection into a plasma formed by the ionisation of argon. The sample is injected as an aerosol and the resulting plasma analysed at a point when the background radiation is free of argon lines and well suited for spectroscopic analysis.

Atomic absorption takes place when an atom in the vapour phase absorbs a photo of visible or ultraviolet light. One of the outer electrons of the atom is raised to an excited energy level. The wavelength at which absorption takes place is characteristic of the element and the degree of absorption is a function of the concentration of atoms in the vapour phase.

4. Emission to Land

4.1 Water Recirculation

The discharge will need to be monitored for flow and flow proportional samples or high frequency sampling with on-line analysis applied as follows:-

Flow	–	Ultrasonic
P ₂ O ₅ or P	–	See 3.1 above
F ⁻	–	See 2.1 above

Ground water quality should be monitored at vulnerable locations to detect any contamination from the land-based gypsum disposal. Ground water contamination would need to be agreed with authorities.

4.2 No Water Recirculation

See 3.1 and 3.2 above and comments in 4.1 regarding ground water assessment.

APPENDIX 2 GENERAL PRODUCT INFORMATION ON PHOSPHORIC ACID

1. Identification

Chemical name	: Orthophosphoric acid
Commonly used synonyms	: Phosphoric acid, 40-60% Merchant grade acid
C.A.S. Registry number	: 7664-38-2
EINECS Number	: 231-633-2
EINECS Name	: Orthophosphoric acid
Molecular formula	: H_3PO_4

3. Hazards to Man and the Environment

To man

Phosphoric acid is corrosive to all parts of the body.

Contact with the skin can cause redness and burns.

Splashes in the eyes cause irritation and burns.

Acid mists may cause throat and lung irritation.

To the environment

Phosphoric acid is harmful to aquatic life.

3. Physical and Chemical Properties

Appearance	: Brownish/greenish viscous liquid
Odour	: Slight acid odour
pH (no dilution)	: < 1
Freezing point	: $-17.5^{\circ}C$ (75%)
Boiling point	: $133^{\circ}C$ (75%)
Auto-ignition temperature	: Not applicable
Vapour pressure	: 267Pa at $20^{\circ}C$
Solubility in water	: Miscible in all proportions
Density	: $1.58g.cm^{-3}$ at $15.5^{\circ}C$ (75%)

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