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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

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MANUFACTURE OF PHOSPHORIC ACID.

by MONTECATINI Soc. Gen. per l'Industria Mineraria e Chimica. (June, 1949).

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Summary.

This report deals very briefly with some methods for the preparation of soluble phosphates from phosphatic minerals.

The production of phosphoric acid through the action of sulphuric acid on phosphate rock is studied in greater detail.

General remarks.

Phosphoric acid is used in the preparation of concentrated superphosphate, diammonium phosphate and various industrial technical products.

The following table shows the Italian production of the various forms of phosphorus compounds employed in industry and agriculture.

Production of Phosphorus Derivatives in Italy.

(metric tons)

	1947	1948
Mono-ammonium phosphate	73.6	-
Di-ammonium " (pure)	168.6	72.3
" " (fertiliser)	1,079.0	6,873.0 *
Mono-sodium ")	92.0	47.7
Di-sodium ")	2,860.0	1,663.0
Tri-sodium ")		
Sodium pyrophosphate	?	73.6
Phosphorus trichloride	62.2	48.8
" pentachloride	1.1	0.8
" oxychloride	18.0	10.1
Phosphoric acid 84%	171.0	130.0
Phosphorus sesquisulphide	69.0	70.0
Zinc phosphide	47.0	30.0
Dicalcium phosphate, pharmaceutical	?	12.7
" " zootechnical	?	251.6

* During 1948 the Montecatini Company had a plant under construction for an annual capacity of 300,000 tons of diammonium phosphate.

Phosphoric acid is obtained by treating phosphate rock according to one of the following processes:

Wet Process: by the action on phosphate rock of sulphuric, nitric or hydrochloric acids, or by a mixture of sulphuric and nitric acids.

Pyrolytic process: burning the phosphate rock in an electric furnace, condensing the released phosphorus vapours, burning the phosphorus in air and hydrating the phosphoric anhydride to phosphoric acid; or by treating a mixture of coke and phosphate rock in a blast furnace. The phosphoric anhydride obtained by burning the distilled phosphorus in the atmosphere, combines with water to form phosphoric acid.

The treatment of the mineral with HCL or HNO₃ will not separate the phosphoric acid as the calcium salts of these acids are soluble and therefore not easy to separate from the H₃PO₄. More precisely:

- treatment with HCL gives place to dicalcium phosphate, which depending upon its purity, is used as a fertiliser or in zootechnology;
- treatment with HNO₃ yields only calcium nitrate and a mixed fertiliser by the addition of NH₃.
- treatment with H₂SO₄ and HNO₃ gives also a mixed fertiliser with the help of NH₃.

Needless to say treatment with H₂SO₄ is by far the most important of all and on this we will dwell for a moment.

In the U.S.A. pyrolytic processes are widespread but in Italy they have not found any application at all in the manufacture of fertilisers.

The high cost of maintenance and the heavy consumption of electric power precludes the use of such processes at the present time in our country, so we will not waste time in considering it.

Processing by sulphuric acid.

(a) Mineral employed and its grinding:

Use is generally made of a mineral rich in tricalcium phosphate and containing little gangue so as to avoid waste of sulphuric acid in attacking the gangue and consequent dilution of the resulting phosphoric acid. Minerals employed in Italy are Russian apatite and Morocco phosphate: the first contains about 86% of tricalcium phosphate and 1% of CaCO₃ the second about 75 - 77% of tricalcium phosphate and 9% of CaCO₃.

The Morocco rock is not ground so fine as in the preparation of superphosphate a simple disintegration being enough.

Often the apatite is delivered as a sufficiently fine powder.

(b) Concentration of the sulphuric acid:

The concentration of the acid is important. It has been found that the best concentration is between 63 and 66% of H₂SO₄. An acid which is too weak dilutes the phosphoric acid produced, whilst an acid which is too concentrated causes an excessive heat and an insufficient attack of the mineral.

Generally phosphoric acid with 3 to 6% of free sulphuric acid should be obtained. It is not advisable to use more sulphuric acid as, apart from being an unnecessary expense, it would react with a greater quantity of calcium which would be found as an impurity in the resultant phosphoric acid.

(c) Treatment:

Sulphuric acid with weak phosphoric acid are brought to react upon the phosphatic mineral in suitable vessels provided with agitators. The action on the apatite is slow, with little foam, the greater part of the fluorine remaining unreacted upon. With Morocco phosphate the action is violent with a much greater quantity of foam, the fluorine being mostly expelled in the form of HF and SiF_4 .

Usually the action takes place at about 60 - 65° C without recourse to heating in consequence of the heat developed by the reaction. In these conditions of temperature the calcium sulphate precipitates in the form of dihydrate. The crystals must be of as large dimensions as possible in order to permit a satisfactory separation of the gypsum from the phosphoric acid; this can best be done by treating the mineral with the required quantity of free phosphoric acid sulphuric acids; the precipitate must be allowed to remain for some time in its liquor for the formation of sufficiently large crystals. In industrial processes, the size of these crystals rarely exceeds 0.12 mm as they are largely in the form of needles; it is necessary, therefore, to avoid rough handling as breakages will cause difficulties in subsequent separation.

Iron, aluminium, magnesium, sodium and other metallic impurities contained in the phosphate rock in the form of oxides, silicates, phosphates, etc. react and become partly soluble during the action and therefore traces of them can be found in the phosphoric acid produced.

Calcium chloride, which is present in small quantities in apatite, is decomposed by the sulphuric acid to form hydrochloric acid.

Organic substances are partly burnt and partly dissolved.

During the action, besides the precipitation of the gypsum, gases have also been produced (consisting chiefly of H_2O , CO_2 , SiF_4 , HCl , nitrogen oxides, in the case of using chamber sulphuric acid, and also HF) which, being poisonous and obnoxious, must be removed.

Expressed as a ratio between P_2O_5 carried into solution and the insoluble P_2O_5 contents of the mineral, the commercial yield of the treatment is about 97%.

(d) Separation of phosphoric acid from gypsum:

When the action is complete, the liquor must be separated from gypsum which has to be washed so as to contain but slight traces of phosphoric acid. This method, used in the Montecatini plant is represented schematically in the attached flow sheet.

This plant has clarifiers placed in series and three drum rotary filters each of which has 15 m² of filtering surface.

The plant has a capacity of 30 tons a day of P_2O_5 and possesses the following features:

- concentration of the phosphoric acid to 45% in weight of H_2PO_4 this being also the theoretical limit;
- conversion efficiency 96%
- filtration efficiency 98%
- P_2O_5 contained in the dry cake discharged from the last filter: 0.36%

In addition to drum filters, other manufacturers use:

- drum filters with reversible elements;
- plain ring filters;
- belt filters;
- basin filters.

Filters of the continuous type permit multiple counter current washing of the filters themselves.

According to facts appearing in technical publications, the results should be:

- a plain filter of a filtering surface of 17 m^2 will be capable of handling 30 tons per day of P_2O_5 as a 30% phosphoric acid. The washing yield will be about 95%.
- a belt filter has a useful filtering surface of 5 m^2 and is capable of producing 10 tons a day of P_2O_5 with a washing yield of about 96%. The resultant phosphoric acid has a concentration of 38 - 40% in weight of H_3PO_4 .

As we see from these figures, the results of washing with such filters would be less favourable than those normally achieved in the Montecatini Company plant.

(e) Concentration of the phosphoric acid:

The phosphoric acid obtained after separation from the gypsum does not have sufficient concentration for some subsequent uses; moreover it contains various impurities in solution. Here, for example, is an analysis:

H_3PO_4	44.5%	in weight
H_2SO_4	4.0%	"
HF	1.1%	"
Fe, Al, Mg phosphates	2.3%	"
CaSO_4	1.2%	"

Concentration of the acid is effected by tube evaporators or in towers by blowing warm air. During the concentration HF and fluorine compounds are evolved, whilst gypsum and phosphate are precipitated; both have a tendency to form deposits. For this reason the evaporators must be frequently cleaned.

The procedure of blowing air, which is mostly free from this trouble, consists of passing the acid into a cement vessel lined with lead. These vessels have many nozzles blowing hot air (about 250°C). The hot air may come from the cooling of the pyrites furnace arms or from elsewhere. Forced draught is effected by means of 250 mm Hg fans.

The system of tower concentration consists of circulating the phosphoric acid in an acid-proof brick lined tower with a diameter of 3 metres and a height of about 10 metres; to this acid is added continually the manufactured 25% P_2O_5 phosphoric acid in order to obtain a concentration of about 49%; hot air about 400°C produced in a suitable furnace, is blown into the bottom of the tower.

The acid concentrates up to about 50% and a part is bled off.

By adopting a strong circulation the gypsum will not be precipitated in the tower, but will be deposited instead into a suitable basin for decantation of the bled off acid.

In the Montecatini process, the phosphoric acid when required for the manufacture of diammonium phosphate, is saturated with NH_3 until mono-ammonium phosphate is obtained. During such reaction there is also a purification due to the precipitation of the various impurities in the form of fluorides. The mono-ammonium phosphate is subsequently concentrated by means of multiple effect evaporation; no incrustations take place on the heating surfaces. The concentrated mono-ammonium phosphate then becomes saturated with NH_3 until diammonium phosphate is obtained.

(f) Materials used:

The vessels in which the treatment is carried out are constructed with steel plates lined with lead to a thickness of 5 mm and with acid-proof stoneware.

All piping to and from and between each reaction vessel is in antimonial lead.

The settling tanks are of reinforced concrete lined with lead and the arms of the agitators are of Oregon pine wood.

The pumps extracting the sludges from the settlers are made with hard lead and have spherical lead valves lined with rubber.

The metal parts of the filters coming in contact with raw cold phosphoric acid are of stainless steel (18% Cr, 8% Ni, 2% Mo) which has proved to be resistant in such conditions; the stainless steel 18 - 8 without molybdenum is attacked fairly rapidly; in some cases lead is used but this also corrodes in time.

The filtering material is made with nitrated cotton, Vinyon (Polyvinyl c ride acetate), Vinyon N.

Normal Vinyon can be employed up to 55° C; beyond this temperature the material contracts and becomes rigid. Vinyon N can be used up to 90° C.

Notes on processing by hydrochloric acid.

Hydrochloric acid is employed when it is available as a by-product as in the case in some countries where large plants recover the hydrochloric acid, by-product of the potassium sulphate process.

In Italy we have only a small plant for the degreasing and degelatinising of bones with very diluted HCL to get dicalcium phosphate for zootechnological and pharmaceutical purposes.

The method is well known: the slow action of the hydrochloric acid gives a phosphochloro-calcium solution from which, by means of milk of lime, dicalcium phosphate is precipitated.

This is separated by filtration and centrifugal action and is dried at a temperature below 70° C.

A good drier is of the rotary type with vertical axis with many floors; the dicalcium falls in countercurrent with the air at about 50 - 70° C.

Notes on processing by nitric acid.

The attack of phosphate rock is effected with 62% nitric acid; 65 - 70% of the calcium nitrate thus formed is separated by means of cooling to 4° C and centrifugal action. It contains about 15% N₂ and 1% P₂O₅.

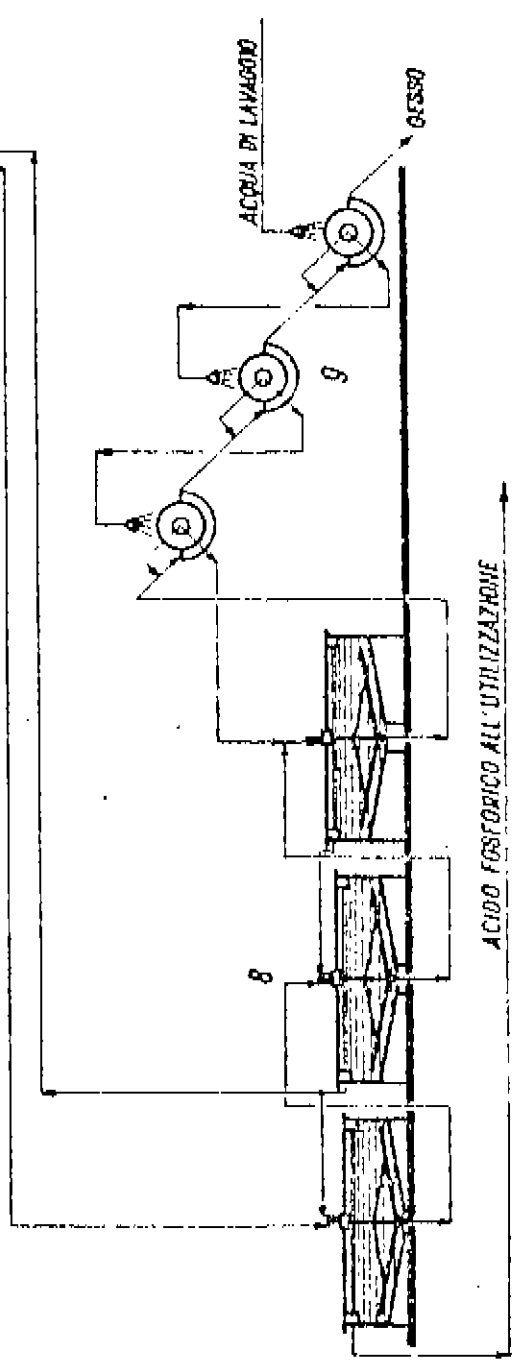
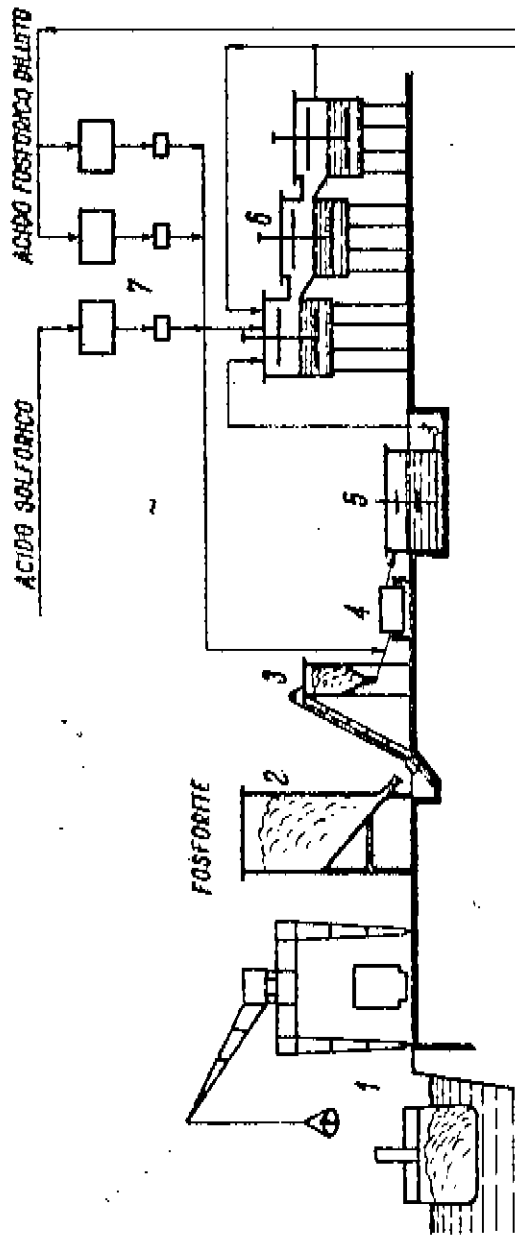
The residual liquor from crystallisation contains the remaining calcium nitrate free phosphoric acid and a certain percentage of free nitric acid, saturated with NH₃.

The product contains:

20% P ₂ O ₅
10% nitric N
10% ammoniacal N.

This method we have mentioned is interesting as being different from the other wet processes inasmuch as there are no waste products such as gypsum and calcium chloride.

The Mont catini Company has made a long study of this problem but up to now only a pilot plant has been built.



1. ARRIVO E SCARICO FOSFORITE.
2. SILEO.
3. ALIMENTATORE.
4. ATTACCO.
5. VASCA DI ATTESA.
6. REATTORI.
7. POSATORI DEGLI ACIDI.
8. SEPARATORI.
9. FILTRI.

FABBRICAZIONE DELL'ACIDO FOSFORICO