

ISMA* Technical Meetings

Paris, France

25-27 September 1951

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

RAC

THE INTERNATIONAL SUPERPHOSPHATE MANUFACTURERS' ASSOCIATION

AGRICULTURAL COMMITTEE
1, AVENUE FRANKLIN D. ROOSEVELT
PARIS (8^e)
TEL. BALZAC 57-25

SECRETARY:
R. M. COLLINS

CENTRAL OFFICE
32 OLD QUEEN STREET
LONDON, S.W.1.
TEL. WHITEHALL 7282

LE 288

September 1951

TECHNICAL MEETINGS 1951.

Paper No. D. 13. CONFIDENTIAL

This paper will be presented at the Technical Meetings in Paris on September 25th and 27th, 1951. It must not be published prior to that date and, in any case, it must not be published without the permission of the author.

ON THE FUTURE OF PHOSPHATIC FERTILISERS.

by Sven Nordengren, Landskrona, Sweden.

In 1939 the author took part in the writing of a paper called "Possible Development of the Superphosphate Industry". It was to have been presented at a meeting of the International Superphosphate Manufacturers' Association in Hamburg, but the meeting was cancelled owing to the outbreak of war. The paper was subsequently published in 1940. (1)

The paper called attention to the stable nature of the superphosphate industry. Although a century had elapsed since Liebig had suggested the treatment of bone meal with sulphuric acid and since Lawes had manufactured the first superphosphate on a technical scale, superphosphate still was being manufactured according to the original process and was maintaining its position as the principal phosphatic fertiliser. The reason for this was not far to seek: simplicity of operation and essential cheapness of the process.

The paper then proceeded to refer to the competitors of superphosphate known at that time: basic slag, the principal competitor, Rhénania phosphate and other phosphates belonging to this group, such as "Basi"- and "Supra-Phosphate" sold in France and Belgium and the Russian "Thermo-phosphate", further dicalcium phosphate and ammonium phosphate. It also called attention to the trials made in America and Germany with thermal processes and the calcium metaphosphate produced in the United States.

In view of this competition, said the paper, an improvement in the quality of superphosphate should be regarded as desirable. The effectiveness of superphosphate is very low, owing to the fixation of phosphoric acid in the soil. The paper pointed out that the effectiveness would be improved by granulation. A coating of the granules with a thin layer of dicalcium phosphate might prevent bag-rot and give the produce better physical properties without diminishing its fertilising effect. A reduction of the free phosphoric acid would be desirable. An improvement of the fertilising value would result in a better utilisation of all the other constituents of vegetation in the soil.

After a further 12 years, superphosphate is still the most important phosphatic fertiliser, with basic slag as its chief competitor. The West European (O.E.E.C.*) consumption of

*O.E.E.C. = Organisation for European Economic Cooperation.

phosphatic fertilisers was in 1948-49:

Superphosphate	43.2 %
Basic slag	31.5 "
Ground phosphate rock	3.9 "
Other straight phosphatic fertilisers	3.9 "
Mixed and compound, water soluble	13.5 "
" " " not water soluble	4.0 "
	<u>100.0 %</u>

At the same time the phosphatic fertiliser consumption has risen considerably during the last years. The consumption in West European (O.E.E.C.) countries in million metric tons P₂O₅ is:

Pro-war	1.65
1947-48	1.72
1948-49	2.03
1949-50	2.08
1950-51	2.31

It is considered probable that the demand will still increase.

An improvement in the quality of superphosphate can be noted in some countries where the product (ordinary or concentrated) is delivered in a granular form. About half the Swedish superphosphate consumption, being about 97% of the total phosphatic fertilisers in use, is covered by granular superphosphate. Also compound fertilisers are being granulated in many countries.

A new factor which hardly could be foreseen in 1939 now threatens the superphosphate industry: the world shortage of sulphur and sulphuric acid. There is considerably less sulphur imported into Europe from America and at the same time sulphuric acid is consumed in increasing quantities by other industries.

Alternatives to the use of sulphuric acid for treatment of phosphate rock.

In view of this shortage it will be interesting to study the present situation regarding other phosphatic fertilisers than those manufactured with the aid of sulphuric acid. The processes by which these phosphatic fertilisers are manufactured can be grouped in the following way:

- I. Basic slag process
- II. Nitric acid processes
- III. High temperature processes
- IV. Processes based on elementary phosphorus or phosphoric acid produced by thermal reduction.

I. Basic slag process.

The basic slag process naturally belongs to the high temperature processes, but owing to the importance of basic slag as a phosphatic fertiliser and also to its character as a by-product, it should be treated separately.

The world production of basic slag was 850,000 tons in 1938, but fell to 600,000 tons in 1948-49. An increase is wholly dependent on an increase in the Bessemer steel production. It is not to be expected that a deficit in superphosphate production can be made up by basic slag.

II. Nitric acid processes.

Sulphuric acid can be substituted by nitric acid. There is no great difficulty in breaking down phosphate rock by nitric acid, if the temperature is kept low by cooling. A product can be obtained containing mainly monocalcium phosphate and calcium nitrate. The author has tried to drive off nitric oxides by heating in order to re-make the nitric acid, but unfortunately all the fluorine remains as calcium fluoride in the resulting product, and in the heating process the apatite molecule is re-formed.

Consequently the final product must contain nitrogen as well as phosphate. The best known of these processes are the following:

Nitrophoska process.

This process was developed by the I.G. Farbenindustrie in Sondershausen, Germany, 1929. Phosphate rock was treated with nitric acid so that monocalcium phosphate and calcium nitrate were formed. Afterwards a solution of potassium sulphate was added, reacting with calcium nitrate to form potassium nitrate and calcium sulphate. The product consequently contained monocalcium phosphate, potassium nitrate and calcium sulphate. Sometimes ammonia was added.

Nitrophosphate process.

This process was developed at Toulouse. Ground phosphate is treated with nitric acid in such proportions that phosphoric acid and calcium nitrate are formed. Part of the calcium nitrate is separated in crystal form and the mother liquor is mixed with ammonium nitrate and neutralised with ammonia.

Norsk Hydro process.

Phosphate rock is treated with dilute nitric acid. After addition of ammonium nitrate and ammonium phosphate a product is obtained containing a double nitrate of calcium and ammonium, as well as mono-ammonium phosphate.

Dutch State Mines process.

Dr. M.H.R.J. Plusjé, Holland, has given an interesting exposé of the theory of this process and also a description of the process itself. (2) Phosphate rock is dissolved in about 50% HNO_3 . In this solution the molar ratio between CaO and P_2O_5 has the value 4 (the same as in the phosphate rock). By cooling the solution and crystallising and separating calcium nitrate-hydrate, the molar ratio of the solution is brought down to a little under 2. The solution is now neutralised with ammonia so that a suspension of solid dicalcium phosphate in a concentrated solution of ammonium nitrate is obtained. The mixture is concentrated, granulated, dried and cooled in the usual manner.

Undoubtedly, there are other processes of this kind besides those mentioned here. The object of this exposé is to show that the treatment of phosphate rock with nitric acid leads to compound fertilisers, and that the processes lack the simplicity of the superphosphate process.

III. High temperature processes.

There are two groups of such processes, one containing processes in which soda or sodium salts are used, the other in which solubility is attained by breaking down the apatite molecule at a very high temperature, water vapour being the main re-active matter.

The processes of the first group are all based on the work of I.G. Wäbergh, Stockholm, round 1900, who found that a citrate

soluble compound could be formed if phosphate rock was heated to 800-1000°C with about 40% soda ash. (3) The best known of these processes are the following:

Rhenania process.

Phosphate rock is sintered with soda ash and natural silicates at a temperature of 1200-1250°C. The product contains about 23% citrate soluble P_2O_5 . The annual output is said to be about 100,000 tons a year.

Roehling process.

Phosphate rock is treated together with soda slag derived from certain steel works at a temperature of 1250°C. The production is limited by the supply of such soda slag.

Lurgi process.

Phosphate rock is treated together with large quantities of sodium sulphate, derived from the iron industry, at 800°C. The product is citrate soluble. The molecule built up is said to have not only sodium but also sulphur tied to the phosphorus radicals. Also in this case the production is limited being based on a by-product.

The second group of high temperature processes are based on the work of K.D. Jacob and co-workers in the Bureau of Soils of the United States Department of Agriculture, who first pointed out the effect of water vapour on phosphate rock at temperatures round 1400-1500°C. (4).

T.V.A. process.

The Tennessee Valley Authority have developed a process for the defluorination of rock phosphate in an oil-heated shaft furnace. (5) Phosphate rock, containing a certain amount of silica, is fused at a temperature of about 1550°C, the combustion gases containing an adequate amount of water vapour. The product is quenched in order to maintain its tricalcium phosphate in the citric acid soluble alpha-form, and at the same time granulated by high-velocity water jets.

Coronet Process.

Coronet Phosphate Co., Florida, has developed a process for defluorination of phosphate rock without fusion in rotary kilns. (6) The material is treated at temperatures about 1550°C. Owing to a high content of silica the product is not fused. It is quenched by jets of water just before leaving the kiln.

Olivine Fusion Process.

It has been known for several years that, if olivine or other minerals containing magnesium are added to the phosphate rock, the breaking down of the apatite molecule, which is present in all rock phosphates, can be accomplished in a shorter time and at lower temperatures than if magnesium is absent. When magnesium is present, magnesium fluoride is formed, which reaction takes place more easily than the reaction through which hydrofluoric acid is being driven off. The fusion can be performed in an arc furnace.

IV. Processes based on elementary phosphorus or phosphoric acid produced by thermal reduction.

Phosphoric acid processes.

Elemental phosphorus can be obtained by the thermal reduction of phosphate rock in the presence of coke and a siliceous

flux in an electric or blast furnace. It is burned to produce phosphorus pentoxide which is hydrated to phosphoric acid.

This acid can be used for the production of concentrated superphosphates or ammonium phosphate.

Calcium metaphosphate process.

Phosphorus produced in an electric or blast furnace is burned to pentoxide which is forced up through a column of phosphate rock. (7) Phosphate rock and pentoxide react to form a slag mainly consisting of metaphosphate. Special methods of analysis are necessary to show plant solubility.

Other measures suggested to counteract shortage of superphosphate.

As seen above, many processes are available for the production of phosphatic fertilisers without the use of sulphuric acid. However, the bulk of superphosphate now produced and sold is so large that a decrease and even a stand-still in the production of superphosphate at the present time will seriously affect the possibility of meeting a yearly increasing demand for phosphatic fertilisers. Therefore, other measures have been suggested in order to make up the deficiency. Among other things, it has been recommended to increase the use of finely ground phosphate rock where soil and climatic conditions are suitable.

It is well known that humic acids in peaty soils have a dissolving effect on phosphate rock. It is, however, doubtful whether this effect will be noted in all acid soils. It may depend on the nature of the acidity. In neutral or alkaline soils, the soil liquid will have no dissolving effect and the ground phosphate will consequently give no apparent result. The plants themselves are unable to break up the strongly knitted molecule of the phosphate rock.

It has also been recommended to under-acidulate the superphosphate in order to save sulphuric acid (Kotka phosphate). The under-acidulated superphosphate consists of a mixture of ordinary superphosphate and grains of undisrupted phosphate rock. What has been stated above will apply also to these grains even if they are mixed with superphosphate. On neutral or alkaline soils the whole fertilising effect will be due to the superphosphate portion of the mixture.

It has further been recommended that in areas, where cheap power is available, phosphoric acid should be produced by electric processes and then used in the manufacture of concentrated superphosphate and/or ammonium phosphates. Undoubtedly, the right thing in such cases would be to use the Olivine fusion process, which is a simple one-phase process, tried out in large-scale trials not only in U.S.A. (Tennessee Valley) but also in Europe (Sweden). The product, coming from the electric furnace in a fused condition, should be quenched and can be given a sandy granular form by jets of water.

Position of the superphosphate industry.

The dominating position of the superphosphate industry in the field of phosphatic fertilisers is threatened as never before, in this case, owing to a possible chronic deficiency in sulphur or sulphur-bearing minerals.

There are considerable investments in the West European superphosphate industry. Taking the figures of 1950-51, 2.31 million tons P_2O_5 were sold in the O.E.C. countries. If half of this quantity was manufactured with the aid of sulphuric acid

and if further this quantity was calculated as 18% superphosphate, the yearly production would be about 6,5 million tons. New investments in the industry would now cost about £12 per ton of yearly production. Taking £6 as a conservative figure for all plants, new and old, the investments in the superphosphate industry including its sulphuric acid plants, would amount to about 39 million £ in the O.E.E.C. countries.

It should now be asked what measures the industry can take in order to retain its hegemony.

There seems to be only one answer to this question. Sulphur is used in making the product. This sulphur should be released and used again for the production of sulphuric acid.

This would involve the necessity of making phosphoric acid so that the calcium sulphate could be separated. The consequence would be a production of concentrated superphosphate, at least so far as would be necessitated by the lack of sulphur.

A production of concentrated superphosphate would partly relieve the industry of one of its present troubles: the lack of bags. In recent years, paper bags have been used in increasing quantities. They are now difficult to obtain and prices have risen considerably. Concentrated superphosphate would cut down the quantity required to about half, and transport and handling costs would also be reduced.

The recovery of sulphur from calcium sulphate has been the object of serious research for many years, for instance in England (I.C.I., Billingham) and in Germany (Lurgi). It has been combined with the making of cement, as certain additions are made to the calcium sulphate so that, after heating the reaction mass to such a temperature that SO_2 is liberated, the remaining solids will form a cement.

The missing link.

It is fairly well known how to make phosphoric acid containing 30% P_2O_5 . (8) This phosphoric acid can be concentrated to 45-50% P_2O_5 , after which concentrated superphosphate can be manufactured by letting the concentrated acid react with phosphate rock.

The manufacture of concentrated superphosphate can be performed in the ordinary superphosphate mixing units, which then will have a double capacity in tons of P_2O_5 . The concentrated superphosphate can be granulated in ordinary granulating plants.

Recently it was found possible to make phosphoric acid of a concentration up to 45%, in a direct way, according to the wet phosphoric acid anhydrite process. (9) There are specially constructed filters of the horizontal type suitable for filtering these concentrated acids without undue dilution. (10)

By centrifuging, the moisture of the calcium sulphate can be brought down to about 3%, so that comparatively small quantities of heat would be required for its drying.

However, the missing link is a process which will enable even small superphosphate plants to recover sulphur from the calcium sulphate left as a residue when phosphoric acid is manufactured. It should be a cheap process giving SO_2 -gas, not mixed with carbonic acid, so that the gas could be used in chamber plants. It would be better not to have this process combined with the production of cement, as it will be inconvenient to sell small quantities of such products.

If such a process could be invented, the superphosphate industry would undoubtedly keep its position as the leading producer of phosphatic fertilizers.

References:

- (1) Sven Nordengren and Hans Lohrecke, Lännskrona, Sweden:
Possible Development of the Superphosphate Industry,
Chemical Age, March 9th, 1940.
 - (2) M.H.R.J. Plusjé: Theory and practice in the treatment of
phosphate rock with nitric acid,
The Fertiliser Society, London, Proceedings No. 13, 1951.
 - (3) I.C. Wiborgh, Brit. Pat. 2678/1896.
 - (4) K.D. Jacobs: Fertiliser Technology Research in the United
States Department of Agriculture,
The Fertiliser Society, London, 1950.
 - (5) T. O. Hignett and T.N. Hubluch: Fused tricalcium phosphate,
production by defluorination
of rock phosphate in a shaft furnace,
Ind. and Eng. Chem. Vol.38, No.12, 1946.
 - (6) W.T. Whitney and C.A. Hollingsworth: Production of Defluorinated
Phosphate Rock,
Ind. and Eng. Chem. Vol.41, No.7.
 - (7) L.D. Yates, L.F. Roy and R.S. Moline: Improved Fertilizer
Plant Design,
Chem. Eng. No.6, 1951, p. 135.
 - (8) Sven Nordengren: The Double Superphosphate and wet Phosphoric
Acid Processes: their present state and
future possibilities,
Acta Polytechnica, Stockholm, 46 (1949).
 - (9) Sven Nordengren: Studies on the Production of strong Phosphoric
Acid according to the Wet Anhydrite Pro-
cess,
Acta Polytechnica, Stockholm, 1951.
 - (10) Sven Nordengren: The horizontal Filter, Mining Mag., London,
July 1949.
-