

# ISMA\* Technical Conference

**Wiesbaden, Germany  
11-15 September 1961**

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



THE INTERNATIONAL

# SUPERPHOSPHATE

MANUFACTURERS' ASSOCIATION

TECHNICAL COMMITTEE · COMITE DES TECHNICIENS

CONFIDENTIAL

LE/61/44

Received: 26th May, 1961

## TECHNICAL MEETINGS - WIESBADEN

This paper will be presented at the Technical Meetings in Wiesbaden from September 11th to 15th, 1961. It must not be published prior to that date, and in any case it must not be published without the permission of the author.

### THE VALUE OF HYDROCHLORIC ACID FOR THE FERTILIZER INDUSTRY

by Alfred Strauchen,  
Fertilizers & Chemicals Ltd.,  
Israel.

The phosphate-fertilizer industry is based largely on acid treatment of the phosphate-bearing ores.

The common mineral acids, sulphuric, nitric and phosphoric, play major roles in the fertilizer industry whereas hydrochloric acid has, as yet, a rather limited application.

There are five main factors which limit the use of hydrochloric acid:

1) the chlorine-ion has no fertilizer value and is rather undesirable in the soil. Many plants are sensitive to it. Plants that withstand chlorine as such, may also suffer because the very soluble chlorides raise the osmotic pressure around the roots of the crop, thus reducing the rate of water intake.

By contrast, the sulphate ion has some significance as a secondary plant nutrient, while nitrates and phosphates are of course primary plant nutrients.

2) Chloride has the same disadvantage as nitrate of forming a highly hygroscopic calcium salt. In practice for most formulations these salts must be avoided.

In contrast, calcium sulphate is not only non-hygroscopic, but has some value as a soil improver.

3) In the one well-known application of hydrochloric acid to the phosphate industry, namely the production of dicalcium phosphate, the product as water-insoluble is of rather limited application as a fertilizer. Agriculture generally prefers water-soluble phosphates as having the quickest effect on crop yields. The use of water-insoluble fertilizers is established mainly on acid soils and especially in tropical countries.

4) Hydrochloric acid is generally much more corrosive than the other acids. This drawback can, however, be largely overcome by judicious use of the newer materials of construction, particularly plastics and modified graphite.

5) Last but not least, the use of hydrochloric acid was considered from an economic point of view as commercially impracticable. But sulphuric acid, until now the cheapest acid available for industrial use, is slowly giving up its economic hegemony to hydrochloric acid.

During the last two decades the available quantity of cheap, by-product hydrochloric acid increased enormously. This trend may develop even further in the near future, e.g. by further development of chlorination processes, increase of alkali electrolysis, metaphosphate manufacture from chlorides, etc. Even today, various processes give trouble because of the disposal of by-product hydrochloric acid, which cannot be treated as simple effluent due to its highly corrosive and air-polluting nature.

On the other hand, the sulphur shortage which occurred some years ago, may again someday face the fertilizer industry - which is the largest sulphuric acid consumer - causing difficulties in obtaining enough sulphur to keep the production at its present maximum level. While sulphur is supplied by some countries only, chlorides are present nearly around the whole world.

A recent Israeli development for thermal decomposition of chlorides (1) may allow the production of cheap hydrochloric acid for wide industrial use, and has encouraged us to re-evaluate the use of HCl.

For these reasons it may be interesting to discuss some of the more recent uses of hydrochloric acid for the fertilizer industry.

Surprisingly enough, with the development of a process for phosphoric acid manufacture from phosphate rock and hydrochloric acid (2), all fertilizer materials based on water-soluble phosphates became available without the use of sulphuric acid, except for ordinary superphosphate.

Furthermore, uranium occurs in certain phosphates in small concentrations. In our century of atomic energy development, the search for uranium sources has been stimulated. Many processes using sulphuric or phosphoric acid give solid or semi-liquid phosphate products and in these cases the recovery of uranium is still an unsolved problem.

Using hydrochloric acid, all processes are based on phosphate ore dissolution and enable the recovery of uranium from the intermediate liquid phase.

Some uses of hydrochloric acid for phosphate ore treatment are discussed below.

### I. The enrichment of calcareous rock phosphate. (3)

Many deposits of phosphate ore being of marine, sedimentary origin, contain considerable quantities of calcite. These calcareous phosphates may be diluted with calcium carbonate below the limit of their utility. Such low-grade phosphate ores are excellently suited for enrichment with hydrochloric acid. Spent hydrochloric acid of a concentration from 5 to 10% may be used for this purpose.

The process described below is not a simple leaching. When leaching the calcium carbonate from a phosphate ore with hydrochloric acid even below 3% concentration, the phosphate is also attacked and considerable quantities of P<sub>2</sub>O<sub>5</sub> are lost to the waste calcium chloride-bearing liquor. In the process under consideration however, not only is all the P<sub>2</sub>O<sub>5</sub> recovered, but the nature of the product is also improved. This is due to the partial destruction of the apatite phosphate structure.

The process consists of:

- 1) Dissolution of a batch of calcareous phosphate ore in aqueous hydrochloric acid, in a quantity at least sufficient to convert the P<sub>2</sub>O<sub>5</sub> in the rock into mono-calcium phosphate.

2) To this mono-calcium phosphate/calcium chloride bearing liquor, another batch of calcareous phosphate rock is added; the calcium carbonate thus introduced with the phosphate acts as a precipitant for the dissolved phosphate.

For complete re-precipitation of the soluble phosphate a small final adjustment with milk of lime is made.

3) The mother liquor containing mainly calcium chloride is separated from the precipitate, which contains all the P2O5 introduced in the two phosphate batches.

The product consists of a blend of precipitated di- and tricalcium phosphate and unchanged apatite, and contains from 30% to 36% P2O5, depending on the quantity of phosphate used for re-precipitation.

From the operational point of view the process is even simpler than flotation and commercially depends mainly on the price of available spent hydrochloric acid.

## II. The production of feed grade dicalcium phosphate.

Although feed grade dicalcium phosphate, used as an additive to poultry and cattle feeds, is not a fertilizer, nevertheless it should be considered by the fertilizer manufacturer, because it is used by the same consumer - the farmer. Distinct from usual manufacturing processes for feed-grade dicalcium phosphate based on degreased bones or phosphoric acid, the process described starts straight from soft phosphate rock and hydrochloric acid. (4,5).

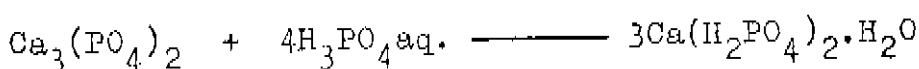
All phosphate ores in question, however, are contaminated with fluorine, which is a poison and accumulates in the animal body. The maximum fluorine allowed in animal feed-supplements is about 1:200 expressed as F to P2O5 ratio. On the average, the ratio of F/P2O5 is 1:10 in phosphate rock.

By selective phosphate rock decomposition with hydrochloric acid, nearly 95% P2O5 may be solubilised, accompanied only by about 10% of total fluorine originally present in the ore. This gives a F/P2O5 ratio of about 1:100, which is still too high. The excess of dissolved fluorine is removed by pre-treatment with milk of lime, which leads to a substantially defluorinated solution having a F/P2O5 ratio of between 1:250 and 1:1000. After separation of gangue and impurities, dicalcium phosphate is precipitated from the clear solution with milk of lime.

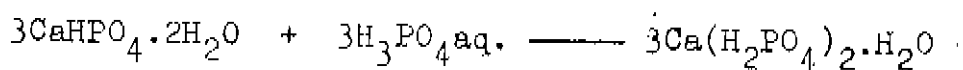
The feed-grade dicalcium phosphate produced from phosphate rock and hydrochloric acid is competitive even with a price of hydrochloric acid equal to that of the equivalent quantity of sulphuric acid.

## III. The production of fertilizer-grade dicalcium phosphate.

Although, as said before, there is a limited demand for fertilizer grade dicalcium phosphate for direct fertilization because of its water-insoluble character, nevertheless it may be considered a very valuable intermediate product for conversion to concentrated water-soluble phosphates. The reason is simple: phosphate is converted into triple superphosphate according to the following reaction:

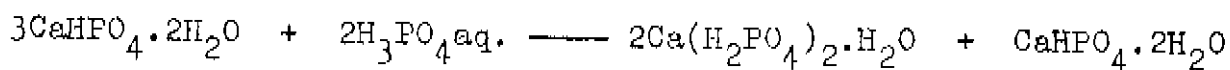


while dicalcium phosphate is converted into an equivalent monocalcium phosphate according to the reaction:



Comparing these two reactions it is quite evident that a 25% saving of phosphoric acid is effected, to say nothing of the considerable quantity of phosphoric acid required for the decomposition of the other constituents of phosphate rock. This saving is brought about by hydrochloric acid used in the early step of dicalcium phosphate preparation.

Water-soluble phosphates although acting quickly on plants are not utilized entirely, because a major part is lost by fixation in the soil. A more effective and prolonged effect could be achieved, according to many authors, with a fertilizer containing about two-thirds of its P<sub>2</sub>O<sub>5</sub> in water soluble form while the remaining one-third or less would also be available but released slowly. A fertilizer of this type may be readily obtained by re-acting 2 moles of phosphoric acid with 3 moles of dicalcium phosphate:



In this case, a saving of nearly 50% of phosphoric acid is effected as compared with common triple superphosphate.

Fertilizer grade dicalcium phosphate suitable for the above application may be prepared from soft phosphate rock and hydrochloric acid in a continuous process with or without continuous removal of gangue.

#### IV. Simultaneous production of feed and fertilizer-grade dicalcium phosphate (5).

Feed grade and fertilizer grade dicalcium phosphate may be simultaneously produced in a combined process, which also permits, without difficulty, the switch-over entirely from one product to another.

In this process the soft, calcareous phosphate rock is at first selectively decomposed with hydrochloric acid; in the second step the solution is defluorinated with calcium carbonate derived from another portion of phosphate; in a third step the solids are settled and the supernatant defluorinated solution separated; from this defluorinated P<sub>2</sub>O<sub>5</sub>-bearing solution, feed-grade dicalcium phosphate is produced; in a final step the separated solids suspended in the remainder of the mother liquor are treated with more hydrochloric acid for total decomposition and converted into fertilizer grade dicalcium phosphate.

#### V. Phosphoric acid from rock phosphate and hydrochloric acid (2).

Various processes have been suggested for the conversion of phosphate rock into free phosphoric acid by the use of hydrochloric acid. However, no known method has achieved a commercially acceptable recovery of phosphoric acid as such, because the phosphoric acid could not be separated from the aqueous reaction system which also contained calcium chloride.

A commercial process was developed in 1956 by the Research Department of the Israel Mining Industries. The process is based on the observation that free phosphoric acid and calcium chloride can be separated by distribution between two liquid phases, namely an aqueous phase and a suitable solvent phase.

The process consists of dissolving phosphate rock in aqueous hydrochloric acid. The free phosphoric acid is extracted from the aqueous reaction slurry into the solvent phase; the solvent-acid phase is separated from the aqueous calcium chloride phase, and aqueous phosphoric acid is recovered from the solvent phase by re-extracting with water. Suitable solvents for this process are aliphatic alcohols having three or more carbon atoms in the molecule especially the commercial readily available propanols, butanols, pentanols and mixtures thereof, as well as ketones and other polar solvents.

Phase separation can be carried out without filtration, because any fine suspension of gangue remaining after sedimentation and separation behaves as water-phase and makes it possible to subject the reaction slurry directly to solvent extraction. The phase separation is rapid and sharp, and hardly any solid matter passes into the solvent phase.

The extraction yield of P<sub>2</sub>O<sub>5</sub> from the raw phosphate is very efficient and achieves 96-98%. The phosphoric acid obtained is considerably purer than conventional wet process acid.

A demonstration plant for the process is being erected in Haifa and a plant has been licensed to a Japanese firm.

The attached simplified flow-diagram shows the main processing steps for the phosphoric acid manufacture from rock phosphate and hydrochloric acid.

#### Bibliography.

1. "Thermal decomposition of chlorides" J. Aman, Brit. Pat. 793,700 (1958), licensed to "NORDAC" Chem. Eng. Ltd. London.
  2. "Improvements in or relating to a process for the preparation of phosphoric acid", A. Banicl and R. Blumberg, Brit. Pat. 805,517 (1958).
  3. "Process for the enrichment of rock phosphate by treatment with hydrochloric acid", A. Strauchen, Israel Pat. 12856, (1959).
  4. "Process for the manufacture of feed-grade dicalcium phosphate" A. Strauchen, J. Bresslerman and R. Wardi, Isr. Pat. 12765 (1959).
  5. "Process for the manufacture of feed-grade dicalcium phosphate" A. Strauchen and J. Bresslerman, Isr. Pat. 13002 (1960)
  6. "Combined process for the manufacture of feed and fertilizer-grade dicalcium phosphate", A. Strauchen and J. Bresslerman, Isr. Pat. 12765 (1959).
-

PHOSPHORIC ACID  
FROM ROCK PHOSPHATE AND HYDROCHLORIC ACID

Simplified Flow Diagram

