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

THE MANUFACTURE OF MONOPOTASSIUM PHOSPHATE

By

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INTRODUCTION

The IMI process (Ref. 1) for the manufacture of monopotassium phosphate from potash and phosphoric acid, using novel technologies, was first announced at the ECAFE conference in India in 1963. At that time, the process did not attract too much attention, the main reason being that the present rapidly increasing demand for high purity, high analysis fertilizers had not yet made itself fully felt. In addition, although the process as disclosed then was fully viable, certain problems existed in connection with feed acid quality and equipment design.

The appearance on the fertilizer market of a pure, ballast-free potash fertilizer, namely potassium nitrate, at competitive prices has reawakened interest in other high-analysis, potassium-containing fertilizer materials.

At the time when the IMI process for monopotassium phosphate was first announced, there were only two sources of phosphoric acid available, namely thermal acid and wet process acid. The cost of thermal acid at the time was such as to put a fertilizer material based on its use completely out of court. While the process was perfectly feasible with wet process acid, it was germane to the process that all impurities and sludges present in the acid would report to the monopotassium phosphate product, reducing its grade. In the interim, other sources of phosphoric acid have become available such as the IMI hydrochloric acid-based phosphoric acid process, and the IMI Cleaning Process for phosphoric acid.*

The availability of high quality, low price phosphoric acid prompted IMI to undertake a reevaluation of the monopotassium phosphate process; this reevaluation was enhanced by the increased know-how gained by IMI

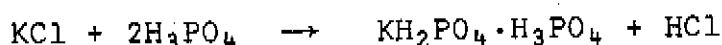
* Both these processes are described in "Phosphoric Acid" (A.V. Slack, ed.) Marcel Dekker Inc., New York (1968)

in the novel technologies incorporated into the process in the interim period.

It is therefore thought to be appropriate, at the present time, to focus attention on this process once again, since it offers a high-quality fertilizer material of known efficiency (Ref. 2) at a competitive cost.

PROCESS DESCRIPTION

The basis of the process is the reaction of phosphoric acid with potash to form a double salt according to the reaction



The double salt can be treated to give two possible potassium based fertilizers, namely monopotassium phosphate (MKP) or an equi-molecular mixture of monopotassium phosphate and monammonium phosphate (KPAP). In the former case, one mole of phosphoric acid will be recycled; in the latter case there is no recycle.

At ambient temperatures the reaction is negligible; it is accelerated by increased temperature, and its extent is increased by removal of the HCl co-product by vaporization, preferably under reduced partial vapour pressure. In addition, the reaction is endothermic. The lower limit for the reaction is 130°C, at which temperature HCl and water are vaporized and the reactants and product have a high miscibility range. The upper temperature limit is 160°C, above which considerable quantities of condensed phosphates are formed. It is therefore obvious that large quantities of heat (approximately 360 Kcal/Kg double salt) must be transformed between fairly narrow temperature limits.

The imposed temperature limitation, together with the considerable heat input requirement, postulates a very efficient heat transfer method. The condition of low HCl partial pressure may be fulfilled by vacuum operation, or dilution with inert gases or superheated steam; each of these alternatives poses its own problems in connection with the production of alkali phosphates. Happily, in the IMI process (Ref. 3) the two basic requirements are simultaneously fulfilled by use of a condensible heat carrier; this is normally a hydrocarbon fraction, whose boiling range is chosen to span the prescribed temperature regime. Very efficient heat transfer is obtained by the intimate mixing of heat carrier vapours with the reactants;

the process heat requirements are supplied by the latent heat of condensing vapours, while vapour entrainment of hydrogen chloride and water promotes the reaction.

In the process as presented schematically in Figure 1, the raw materials (and recycled phosphoric acid) are mixed together and fed to the reactor, where they are contacted with heat carrier vapour. This leads to full dissolution of the KCl in the H_3PO_4 so that the process presents no problems of solid-liquid contacting. The quantity of heat carrier vapours fed to the reaction is determined by

- a) the heat requirements of the reaction plus the heat of vaporization of volatile components
- b) the quantity of gas phase required for vapour entrainment of HCl under reduced partial vapour pressure.

The part of the heat carrier that condenses in the reactor is separated from the double salt by decantation; the remainder leaves the reactor as vapour entrainer for the HCl and H_2O vapours. Process-wise, the reaction may be carried out in one contact stage; for reasons of heat economy and reactor design, a semi-counter-current system of operation has advantages.

HCl - H_2O vapours are condensed as a 30% HCl solution, and separated from accompanying heat carrier; this is one product of the process. The double salt is separated from condensed heat carrier, and processed further by one of the following process alternatives:

- a) For production of MKP, the double salt is decomposed, giving MKP and H_3PO_4 , which is returned to the reaction. The decomposition can be carried out in several ways, of which decomposition by contact with a partially miscible solvent is preferred: this method minimizes the cost of recycling the separated H_3PO_4 . The double salt is dissolved in a recycle brine solution, and is contacted with a partially miscible solvent in a counter-current operation. Phosphoric acid is extracted into the solvent and MKP precipitates. The MKP crystals are separated from the mother liquor, which is returned as a recycle brine to the dissolution step. The extract is stripped of its phosphoric acid content with water in a counter-current liquid-liquid extraction operation, giving an aqueous phosphoric acid solution, and an acid-free solvent for return to the decomposition step. The aqueous phosphoric acid is stripped of its dissolved solvent content, concentrated to the required extent and recycled to the reaction step.

- b) For the production of KPAP, the double salt product of the reaction section is ammoniated using gaseous ammonia. The ammoniation may be carried out either directly on the double salt, or on a solution of the double salt. Direct ammoniation is technologically feasible, but poses some problems. Ammoniation in solution which can be combined with a crystallization or granulation operation to give a product of controlled particle size, is the preferred procedure. Physico-chemical characteristics of products are given in Table 1.

TECHNOLOGY AND EQUIPMENT.

The equipment used in implementing the process is straight-forward in concept; the reaction is carried out in one or more packed column reactors, while all liquid-liquid contacting operations are carried out in mixer-settlers. The other operations involved include solvent stripping and phosphoric acid concentration (both well-known operations) dissolution of double salt, separation of solids and product treatment, e.g. crystallization, granulation. For production of KPAP, ammoniation is carried out in a specially designed reactor. The rest of the plant consists of intermediate tanks, pumps, heat exchangers and a vaporizer for the heat carrier.

Corrosion problems are generally overcome by use of synthetic materials, either by themselves or for protection of structural metals. For certain applications, graphite or acid resistant ceramics may be used.

IMPLEMENTATION AND COSTING

The process has been successfully implemented on bench and pilot scales; extensive engineering studies, both theoretical and experimental, for the design of a full scale plant have been undertaken. The data are sufficient to undertake the engineering design of an industrial plant with full confidence. The process will produce MKP and KPAP in a wide range of combinations, from mainly MKP with a small amount of KPAP to 100% KPAP; optimum economic proportions for a particular case can readily be evaluated. Costing figures illustrating the process extremes, i.e. either full MKP or full KPAP, are given below for Israeli conditions.

Production level : 42,000 tpy P₂O₅

	<u>MKP</u>	<u>KPAP</u>
Fixed capital investment :	\$ 3,140,000	\$ 1,250,000
Operating cost, per ton product		
Capital cost (13% of FCI)* :	\$ 5,12	\$ 1,97
Electric power :	\$ 0,42	\$ 0,16
Fuel :	\$ 2,16	\$ 1,03
Cooling water :	\$ 0,72	\$ 0,16
Steam :	\$ 1,24	-
Labour and overhead :	\$ 4,13	\$ 4,03
Solvent losses :	\$ 0,55	-
<u>Total</u>	<u>\$14,34</u>	<u>\$ 7,35</u>
Per ton P ₂ O ₅ :	\$27,30	\$13,00

The above costing does not include a credit for the co-produced HCl.

* This includes maintenance, depreciation and insurance.

REFERENCES.

1. Alon, A., Conference on the Development of Fertilizer Industry in Asia and the Far East, Bombay 1963.
2. Waggaman, W.H., "Phosphoric Acid Phosphates and Phosphate Fertilizers" Reinhold, New York (1952) p. 354
3. Process for manufacture of mono alkali phosphates
IMI - Institute for Research and Development
Brit. Pat. 1080661, 13/12/1967.

DISCUSSION

DR. J. MIZRAHI (IMI Institute for Research and Development, Israel): I do not think that I have to explain to an audience such as this the advantages of potassium phosphate as an ingredient of compound fertilisers. This has been widely discussed in the past and the general agreement on the point is shown by the efforts made by many companies in recent years in the field of process development.

Therefore, the problem for fertiliser manufacturers is how to produce potassium phosphate in the most profitable way for their own market. This question can be subdivided into four parts:

- 1) The potassium phosphate must be marketed in such a way that its producer has a fair return for all the savings in transportation, handling, storage, distribution and field application, which result from the higher nutrient concentration of his product.
- 2) Whether the market is able and willing to pay an additional price for the fact that this is a chlorine-free potassium fertilizer, similar to the difference between K_2O in KCl and in K_2SO_4 . It is evident that there are such markets, though they may be limited. It is also evident that for other, larger markets, the chlorine represents only a ballast. In both cases, processes starting with K_2SO_4 as a source of K_2O cannot claim this up-grading value.
- 3) The next preoccupation is whether there is a market in the vicinity for the by-product HCl solution, either as a source of acid or as a source of chlorine for PVC (after dehydration, of course). If so, the selling of this by-product can cover a large part of the production cost of potassium phosphate. Such opportunities exist in most industrialised countries. If not, the HCl could be used to make more phosphoric acid or DCP.

- 4) The final consideration is the choice of the process or combination of processes for each case. Each process offered has been developed in a particular set of local circumstances, which may make it irrelevant in other locations.

The essential features of the IMI process, as regards its industrial implementation, derive from the fact that IMI, as a Research Institute, has no direct production involvement.

1. First, it completely separates the production of phosphoric acid from that of potassium phosphate. This was decided from the beginning as a matter of policy, for many reasons; for instance, the trend towards bigger and more efficient phosphoric acid plants, producing acid for a variety of uses or for sale; the trend towards having these plants near raw material sources while the final processing would be done near the markets, the rapid changes and diversification in phosphoric acid specifications, partly deriving from new sources of rock; the need for flexibility in the production pattern of large fertiliser complexes; the resistance of many experts to changes in operating conditions in existing phosphoric acid plants, etc.
2. The process starts with KCl as the cheapest form of K_2O and produces a concentrated HCl solution as a by-product.
3. The process can accept any source of acid as raw material, from Florida type wet phosphoric acid to liquid-fertilizer-grade clean acid. The grade of the product will be in accordance with the grade of the feed acid. Table 2 refers only to the pure products. However, recycle acid in the monopotassium process will be much purer than the feed acid and could be directed to other uses, (wholly or partly). The process can yield various proportions of mono-potassium phosphate and mono-potassium-mono-ammonium phosphate, KPAP, as designed.
4. Any degree of polymerisation of the phosphate product can be obtained in the KPAP process, by adjusting the operating conditions and in the MPP process, during the final drying operation.
5. It is also possible to change, within limits, the degree of ammoniation and the remaining chlorine

content, by adjusting operating parameters. In any case, the NPK ratio must be adjusted with the addition of other conventional components, before granulation or prilling.

6. The essentials of the processes were put forward some 10 years ago but in the meantime and in particular during the last 3 years, the details were extensively studied at IMI and the process now seems to us ready for industrial application.

MR. C. BELPAIRE (Produits Chimiques du Rupel, Belgium): The new and interesting paper just put before us provides further evidence of the interest aroused by monopotassium phosphate in the fertiliser world, and of the progress recently made in perfecting the manufacturing process.

To date, however, it must be acknowledged that potassium sulphate is the only potassic raw material available for the manufacture of chlorine-free fertilisers.

We note in specialised literature many methods of manufacture of MPP from a wide range of raw materials.

At the current stage of study, it seems that only two methods offer any possibility of application on an industrial scale. These are:

- 1) Reaction of phosphate rock and H_2SO_4 in the presence of potassium sulphate or disulphate.
- 2) Direct reaction of phosphoric acid on potassium chloride. The IMI process, which has just been described to us, and which uses the second method, may be distinguished from the others by its originality and the considerable purity of the MPP obtained. As we have no experience of the IMI process, we thought it worthwhile to compare it, according to our knowledge of it, with the process being studied by our company; both processes start from the same base reaction.

In this way, we bring out problems which we encountered, and which the authors will have met to a certain extent, and no doubt solved.

Let us consider first of all the stage of reaction. We know now that the reaction between phosphoric acid and potassium chloride has become feasible provided certain fundamental conditions are observed.

- 1) For consumption of raw materials, the mole ratio phosphoric acid/potassium chloride will be equal to or more than two.
- 2) The reaction temperature for a given pressure will be less than that at the start of polymerisation.

We carry out this reaction using unpurified wet process phosphoric acid under a vacuum of 700 mm mercury at temperatures not exceeding 115°C in the mass, while securing a KCl conversion yield in excess of 99%.

The reaction mixture is heated by indirect transmission. The main obstacle to the industrial use of this process is the choice of materials which will withstand this corrosive environment at the optimum reaction temperature.

We should note that 70% of the fluorine present in the original acid goes with the released HCl.

The Israeli researchers have found an ingenious method of resolving the problem of direct transfer of calories in the reactive mass through the use of a chemically inert heat carrier fluid, which has a boiling point higher than that of the HCl/H₂O mixture at the pressure concerned.

As for the second stage of manufacture, which involves breaking down the acid complex, several methods may be envisaged, giving as end products MPP and phosphoric acid, or a mixture of monoammonium and potassium phosphates, or MPP which has been rendered soluble in the presence of another insoluble phosphate, etc.....

We shall stick to the main subject of this paper, i.e. the possibility of obtaining MPP separately.

Previous studies have proved that it is possible, although very complicated, to precipitate the MPP from an aqueous acid mixture like that resulting from the reaction, in the absence of any organic solvent.

This precipitation is, however, impracticable if wet process phosphoric acid is used.

The authors found a solution to this problem by using a partially miscible solvent such as butanol, the function of which is to extract the released phosphoric acid from the complex salt, which has first been diluted

with an aqueous solution of MPP. We precipitate the MPP from a complex salt, which appears as a black, syrupy liquid, using a fully miscible solvent such as methanol. In the case of the IMI process, the following is obtained:

- a) an organo-phosphorus phase
- b) a recycled aqueous phase, which is basically a saturated solution of MPP
- c) a solid phase, which represents the end product, and contains 87% of fertilising substances.

In the second case (ours), we have:

- a) a single liquid phase basically consisting of alcohol and phosphoric acid. The phosphoric acid, which is then separated from the solvent by distillation of the latter, is obtained in a very pure state through a spontaneous process of refinement.
- b) a solid phase, formed by the MPP impregnated with impurities contained in the original acid. The content of fertilising elements is in the region of 75 to 80%. These impurities do not affect the filterability of the MPP, owing to the precipitation, which takes place in a non-aqueous medium.

What are the principal problems ?

- 1) Solvent losses
- 2) Sulphuric acid content of the original phosphoric acid: the ion SO_4 , which precipitates in the form of potassium disulphate together with the MPP and the other impurities basically found in the original acid, is responsible for the residual acidity of the fertiliser.

Without minimising the perseverance of the authors of this paper and taking into account the difficulties we are encountering, we should like to have answers to the following questions:

1. In view of the temperature of 130 to 160°C needed for the reaction and also in view of the release of hydrochloric acid, what materials are used for the construction of the reaction column or tank ?

In your experience, are these materials equally suited to cases where wet process technical phosphoric acid is used and to cases where a previously purified phosphoric acid is employed ?

2. The solvent used to break down the complex salt is partially miscible with water. I should like to ask, in this connection:
 - a) What is the quantity of solvent to be used per tonne of P_2O_5 , obtained in the form of MPP ?
 - b) What is the percentage representing the loss of solvent out of the total used ?
3.
 - a) As the yield on conversion of KCl is in the region of 95%, how is the potassium chloride which did not take part in the reaction eliminated from the manufacturing circuit, since the end product obtained is pure, according to the analytical data quoted on page 6 of the French text ?
 - b) What is the yield of K_2O and P_2O_5 of the MPP obtained ?
4. Since it is not necessary to produce so pure an MPP (87%) for solid fertilisers, I should like to ask whether the IMI process can be applied using at the outset a phosphoric acid obtained by sulphuric acid attack and, if so, what is the main difficulty and what is the percentage of fertilising matter in the product obtained ?

In conclusion, I should like to congratulate the authors of the IMI process on their remarkable work.

Finally, I should like to express the hope that all those who have investigated the problem of MPP may arrive at a form of open collaboration, so that the experience and knowledge acquired can be pooled with a view to the application of a general purpose process, i.e. one technically and above all economically valid in all conditions.

DR. MIZRAHI: I wish I could agree to Mr. Belpaire's proposition to collaborate for the formulation of a unique universal process. Unfortunately, it seems that in the present state of diversification of the fertiliser

industry, a plurality of processes is needed, each one having its own optimum field of application. The first section of the plant, producing double salt, can operate on various acid feeds; of course, there are differences which must reflect themselves in adequate design.

The question on construction material is of course a crucial one, to which, as you well know, there is no obvious answer in the traditional materials. We gave this question very serious attention and reached several acceptable solutions.

The double salt can be extracted in various ways. With pentanol, we have to circulate about 2.5 tons of solvent per ton of product. The solvent losses in these conditions are not economically significant. In this connection, I should explain that the remaining chloride in the double salt is also extracted by the pentanol (as HCl), together with the phosphoric acid, bringing therefore the HCl conversion to 100%. The HCl extracted is separated during the concentration of the phosphoric acid.

There are no losses of K_2O or P_2O_5 . However, since the brine is in a closed cycle, it is necessary, in order to avoid accumulation of minor components, to withdraw a small bleed stream (a few per cent) which is ammoniated and either marketed separately or mixed with the product.

Methanol is not a suitable solvent in our process since, during its distillation, the HCl present would generate an esterification reaction to methyl chloride. With pentanol, this esterification is negligible, in adequate conditions.

TABLE 1

Physico-chemical Characteristics of Products

	<u>MKP</u>	<u>KPAP</u>
Formula	: KH_2PO_4	KH_2PO_4 $\text{NH}_4\text{H}_2\text{PO}_4$
Molecular weight	: 136	251
Colour	: White	White
Crystal form	: Tetragonal	Tetragonal
N content	: -	5.6%
P content	: 22.8%	24.7%
P_2O_5 content	: 52.0%	56.8%
K content	: 29.0%	15.5%
K_2O content	: 35.0%	18.6%
Specific gravity at 20°C	: 2.3	1.9
Melting point °C	: 253	204*
Solubility in water, parts per 100 part H_2O	12.9 at 0°C 33 at 25°C 45.5 at 90°C	37 at 30°C*
Relative humidity of air in equilibrium with saturated solution of MPP, %	89 at 10°C 96.2 at 20°C 92.9 at 30°C 92.9 at 40°C	
Hygroscopicity number	: 3.8 at 20°C	Similar*
pH of saturated solution	: 4.5	4.5*

* IMI experimental data

Fig 1

MONOPOTASSIUM PHOSPHATE PROCESS
BLOCK DIAGRAM

showing alternative routes to MKP and KPAP

