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

SOME FACTORS AFFECTING THE CHOICE OF PHOSPHATE ROCKS FOR PHOSPHORIC ACID MANUFACTURE

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It is hardly necessary to point out that the major economic factors such as rock price, transport costs and sulphuric acid requirements, generally over-rule other factors associated with production problems, but situations can arise where marginal differences in price lead to an examination of the minor issues. There are generally one of two situations:-

- a) the choice of phosphate is fixed and the plant has to be designed and operated for a particular raw material, e.g. plants built on phosphate fields.
- b) the plant is in existence and a choice is to be made from a range of available phosphates.

Different plant outputs and processing costs can occur on the same extraction plant due to the behaviour of different raw materials. It is these factors which are the main concern of this paper.

The plant for extracting P₂O₅ from rock can be split into four main sections:-

1. Storing, handling and grinding plant.
2. Reaction and extraction.
3. Evaporation and storage.
4. Neutralisation, product, and byproduct formation.

Each section has its operating costs and the physical and chemical properties of the phosphate can play a vital role in determining the processing costs.

These four sections of the plant are examined in turn.

1. Handling, storing and grinding:

Variations in particle size, hardness and bulk density can bring about variations in handling and storage characteristics. The finer phosphates have lower angles of repose and tend to require more floor space for a given tonnage than the rougher denser phosphates. The

capacity of a given storage area can vary by 15 to 20% when different phosphates are used.

Phosphates of igneous origin are more expensive to grind, and their use causes high rates of wear on conveyors and handling equipment due to the hardness of the crystalline particles. The sedimentary phosphates are better in this respect, and give higher outputs from milling plant. However, even these "softer" rocks vary considerably, e.g. The hourly tonnage passing through a mill, to produce the same fineness, for several different rocks was as follows:-

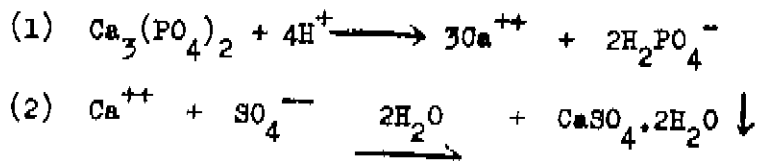
<u>Rock Source</u>	<u>Tons/hour.</u>	
Gafsa	20	} In each case grinding to a fineness of 85% passing 100 mesh.
Morocco	14	
Florida Pebble	10	
Nauru	8.5	

As power consumption and maintenance costs on handling and milling plant are approximately directly proportional to tonnage processed, the cost of preparing the rock for the extraction stage can add appreciably to the final product cost in some cases, and indeed the output of an otherwise adequate reaction system can be impeded by poor outputs from grinding plant, with an even greater increase in costs resulting.

2. Reaction and Extraction

In considering the reaction stages the main considerations are the physical and chemical composition of the phosphate and the reactions involved. More and more attention is being given to the role played by minor constituents in the process.

The main reaction can be written as two stages:-



Different phosphates produce different rates of reaction for stages (1) and (2).

Igneous phosphates are generally hard, crystalline particles which do not permit pore penetration and disintegration to occur from within. Stage (1) is generally slow and as a consequence stage (2) is retarded anyway. Rocks which are sedimentary usually all have fairly rapid rates of solution, but stage (2) may be fast or slow depending on the presence or otherwise of certain impurities or on reactor conditions. If stage (2) is very rapid, it may be necessary in multistage processes to introduce

the sulphuric acid feed closer to the point of rock entry, particularly with systems of fairly low magma recycle ratios (10/1 or less). If this is not done the subsequent crystallisation of gypsum deteriorates due to a high nucleation rate, and a high isomorphous loss of P₂O₅ also occurs within the gypsum lattice. Stage (1) may also be slowed down by raising the sulphate level of the system as a whole. Slower reacting igneous phosphates can be assisted by directing as much of the recycled weak phosphoric acid as possible to the point of rock entry. Sulphuric dilution requirements may minimise this method, and a useful alternative is to lower the free sulphate level slightly. It is worth perhaps pointing out that many phosphoric acid plants are designed in such a way that the operator cannot alter his technique unless he himself modifies the feeding arrangements. This is particularly true of sulphuric and recycled phosphoric acid feeds which can often only be added at one place. It would be interesting to know how many of the delegates here have had to alter feeding systems, and why.

If stage (1) of the reaction is slow, unattacked phosphate rock may appear in the byproduct gypsum. It is our experience however that the phosphates which are slow to dissolve bring about the least loss of P₂O₅ due to isomorphous replacement in the gypsum lattice, and even with the reputedly slow reacting igneous rocks the level of insoluble P₂O₅ lost in the gypsum may be lower than in the case of the faster reacting rocks. During the conference at Stockholm in 1959 an excellent paper on this subject was given by Fröchen and Becker. Too much emphasis has been placed in the literature on reactivity theory based on residence time distributions, and not enough on the physical chemical influences affecting overall extraction.

Graph 1 illustrates the reactivity of several phosphate rocks examined in our laboratories some years ago. A standard set of attack conditions was employed using a synthetic magma, and close sized rock fractions used. By assuming a spherical particle shape, the graph of radius v time for the degree of attack achieved was plotted. These graphs appeared to be almost linear, but because of the variation caused to both stages (1) and (2) by the presence of impurities, the real attack rate can only be determined by treating the rock particles with magma derived from the same rock source. Consequently no time scale has been given to graph 1 as the rates of reaction are relative only.

It is also interesting to compare the extraction efficiency for different phosphate rocks when operating the same plant under similar output and process conditions. For 4 different rocks we obtained the figures as follows:-

Rock	Extraction Efficiency (based on gypsum analysis)
Crystalline igneous	97.3) In each case operating a 240 m ³ reactor
Hard sedimentary	96.3) producing 65 tons output per day
Soft sedimentary (a)	96.0)
Soft sedimentary (b)	94.9)

Such differences naturally will lead to different extraction costs.

This aspect is of particular importance to the designer in calculating the ratio of filter area to reaction volume necessary. Low grade phosphates produce more gypsum per ton P₂O₅. M. Bigot of St. Gobain has presented several excellent papers to previous conferences on the uses of different rocks and on filter design. I wonder too how much consideration is given to crystal shape and chemical means of controlling it. Perhaps we may have some comments on these points from our friends from St. Gobain.

The reactions taking place in the extraction system decide the filterability and quality of the gypsum, which in turn determines the maximum plant output, both as regards tonnage and product acid strength. Different rocks can cause differences in production potential of up to 30% and lead to serious changes in factory profitability if phosphoric acid production becomes a restriction.

It is in this stage that the most important effect on plant costs and profitability occurs if maximum production is essential. A phosphate which enables a high output and high product strength to be achieved can help to compensate for dearer rock charges or freight costs. The capacity and hence cost of any evaporation equipment is similarly dependent on the reaction stage.

If a plant is such that the output required is less than its potential output, it is not operating at maximum efficiency anyway.

In addition to the desirability of producing maximum tonnages, it is also desirable to produce a given tonnage at the lowest hourly throughput possible - i.e. with the maximum operational time possible. This involves consideration of maintenance and operational problems in deciding shutdown frequencies and plant equipment scheduling and these are markedly affected by choice of phosphate.

It is known that the greater the hourly throughput of a given plant, then the poorer will be its extraction efficiency. Hence if a plant runs for 90% of the time it will produce a given tonnage with less usage of raw phosphate than a plant running for 80% of the time producing the same tonnage. The difference in extraction efficiency will be approximately 0.3% to 0.4% and this saving can counter the increased cost of maintenance effort required to attain this efficiency.

This is illustrated in graph 2.

The corrosion characteristics of a particular phosphoric acid and the rate at which the growth of scale interferes with pipelines, pumps, etc. largely determines the frequency of planned shutdowns. It has not been our policy to operate our plants using daily washing cycles, as operational efficiencies of 90% or more are virtually impossible with this technique. The installation of spare lines and regular changes of pumps, lines, filter cloths, etc. are employed. The differences between two different phosphates will indicate the variations in shutdown frequency necessary:-

With Nauru and Kola phosphates respectively the rates of deposition of scale on a particular pipeline under similar conditions of plant operation were:-

- (a) Nauru: 5 mm scale thickness in 6 weeks
- (b) Kola: 15 mm scale thickness in 10 days.

This means a difference in rate of scale formation of some 12 times. Much longer periods of running are possible with Nauru than with Kola, and our plant shuts down once per month for scheduled maintenance on Nauru, and once per week using Kola phosphate. Adopting these procedures we have been able to maintain a production efficiency of up to 95% on Nauru and 90% on Kola, exclusive of any annual shutdown.

The actual nature of the maintenance effort varies depending on the degree of scaling. High tendency for scale formation leads to a lower corrosion rate but higher labour costs, while rocks with a low scaling tendency are more corrosive and lead to greater replacement costs and a closer examination of materials of construction is required. Differences in scale formation can lead to alterations in evaporator running times and output.

By product considerations: in certain cases the subsequent uses of the acid to make other phosphate chemicals lead to considerations of impurities and colour and the methods and costs of removing these. As an example the output of silicofluorides from certain plants can be seriously affected by the different behaviour of the fluorine in the rock. The fate of the fluorine in 4 rocks is given:

Rock	% fluorine appearing in:-		
	(a) Acid product	(b) Gypsum	(c) Gaseous effluent
Nauru	23	75	2
Kola	73	15	12
Florida	52	45	3
Morocco	50	47	3

The fluorine balance can be altered by adding different materials, e.g. potassium, silica or sodium.

3. Evaporation and Storage:

Gypsum quality is of importance in by-product plaster manufacture, depending on the crystal nature and impurity levels. Differences in the fate of the fluorine vapours can lead to effluent and scrubbing problems and precipitation of impurities can cause chokage problems in unstirred storage vessels. The choice of cooling and scrubbing equipment can be affected by the tendency or otherwise of a given phosphate to form deposits, and indeed the choice of washing water can be affected. In two evaporation plants in this country where both sea water and fresh water were available, one plant was forced to use fresh water for scrubbing while the other was forced to use sea water. In one case the fluorine gases were largely HF due to a silica deficiency in the phosphate. The fresh water in the area contained appreciable quantities of calcium and hard insoluble calcium fluoride scale was formed. This was minimised by the use of sea water. In the other plant the silico-fluoride gases evolved caused chokage problems when combining with sodium ions in sea water, and in this case the use of fresh water, which was soft in this area, cured the problem.

The chokage of storage vessels can be minimised by stirring, and in cases where it is necessary to remove solids for the sake of subsequent processes, it is probably still advisable to stir the acid, allowing the sludge crystals an opportunity for growth. This would permit an easier separation of the acid and sludge external to the storage vessel. The use of thickeners leads to a smaller particle size as the absence of crystal surface in the supernatant acid can lead to continuous nucleation. There are serious difficulties associated with thickening equipment not often appreciated in the initial stages of design and operation. However, acids derived from phosphates high in silica, iron and aluminium almost certainly require stirring. The power cost of stirring large tanks is quite appreciable, and the cheapest solution in this case is probably to employ a large tank, with no stirrer for buffer insurance capacity, and a small tank of say 15 - 20 hours capacity fitted with a stirrer. The plant production would be fed into the small tank and the large vessel only brought into use to assist when required. In this way 80 - 90% of the plant production would never pass through the larger tank, which would not sludge up seriously and could be cleaned periodically. The power cost for stirring the small tank is much less than that required for a large tank. In addition to sludge deposition, storage tanks can suffer from growth of scale on the walls and again this can be minimised by stirring.

The potential sludge deposition of several phosphoric acids is shown in this table:-

Rock	g/litre of sludge deposited on standing and cooling
Nauru	2
Senegal	7.7
Morocco	11
Florida	12

(30% P2O5 Acid referred to in each case)

M. Michot of Prayon presented an excellent paper on precipitated impurities to the 1961 conference at Wiesbaden. I should like to hear comments on this problem, which causes difficulties to many of us, from our friends from Prayon.

4. Neutralisation:

P2O5 reversion problems.

This rather important item affecting costs depends in some cases on the method of payment for product P2O5 in fertilisers in different countries. In cases where water solubility of P2O5 is the criterion the presence in a phosphate rock of appreciable quantities of iron and aluminium can lead to the formation of insoluble phosphates on neutralisation. As far as the manufacturer is concerned, this represents a loss of P2O5 and also lowers product analysis. This loss can appreciably affect product costs and profitability as in some cases up to 10% of the P2O5 in a product may be given up in this way.

I have said nothing about the roles played by temperature, viscosity, or organic impurities. Not enough information has been published about the last two items, and I should be most interested to hear of experiences or data on these.

To summarise, the factors to be considered when choosing a phosphate rock are:-

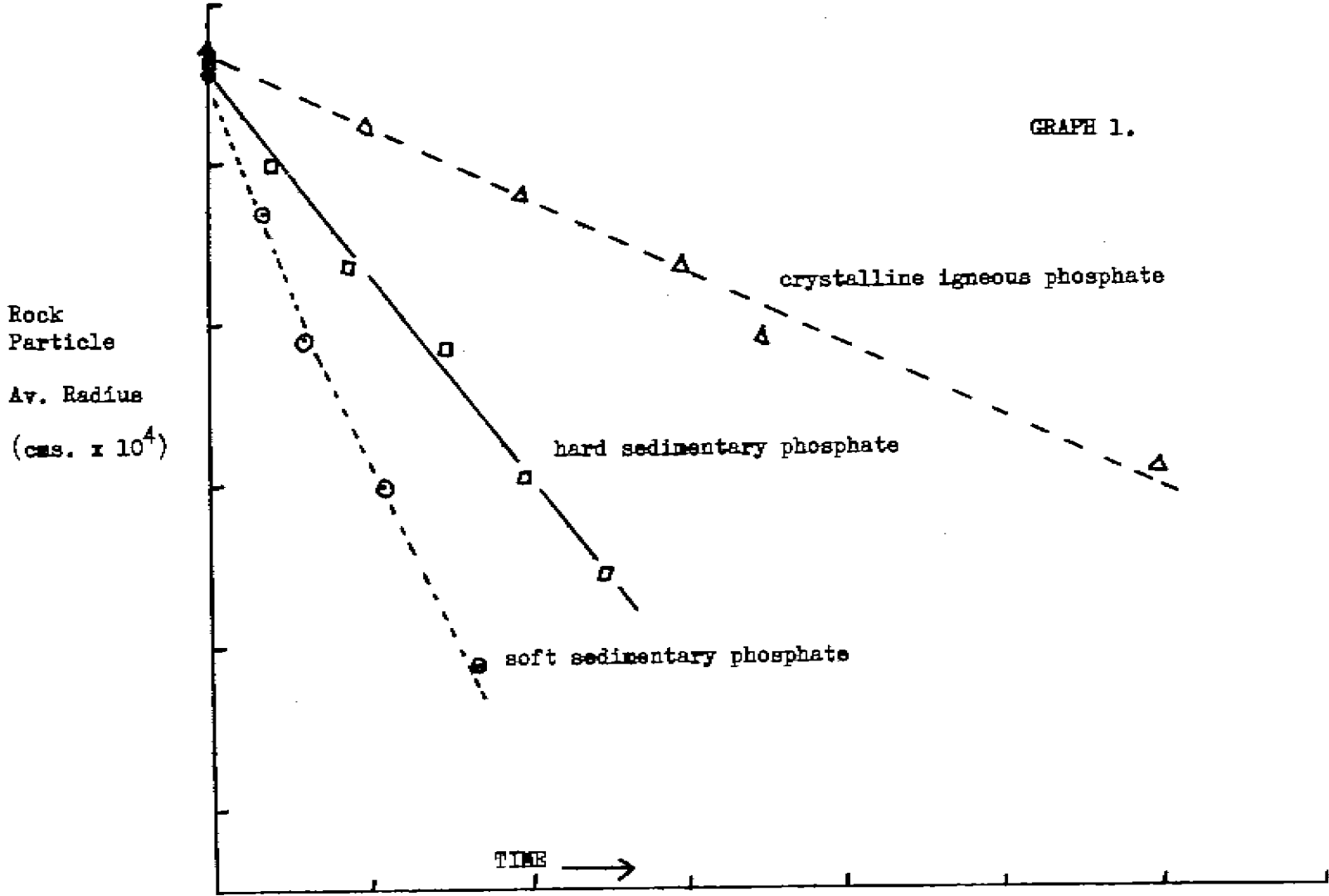
1. Unit cost of P2O5.
2. Cost of sulphuric acid needed to solubilise the P2O5.
3. Handling and grinding costs, and output restrictions, if any.
4. Extraction efficiency and output restrictions, if any.
5. Evaporation requirements and restrictions with particular reference to filterability, if any.
6. Maintenance and operational techniques and costs.
7. Loss of P2O5 due to reversion on subsequent treatment.

8. Byproduct problems and restrictions.

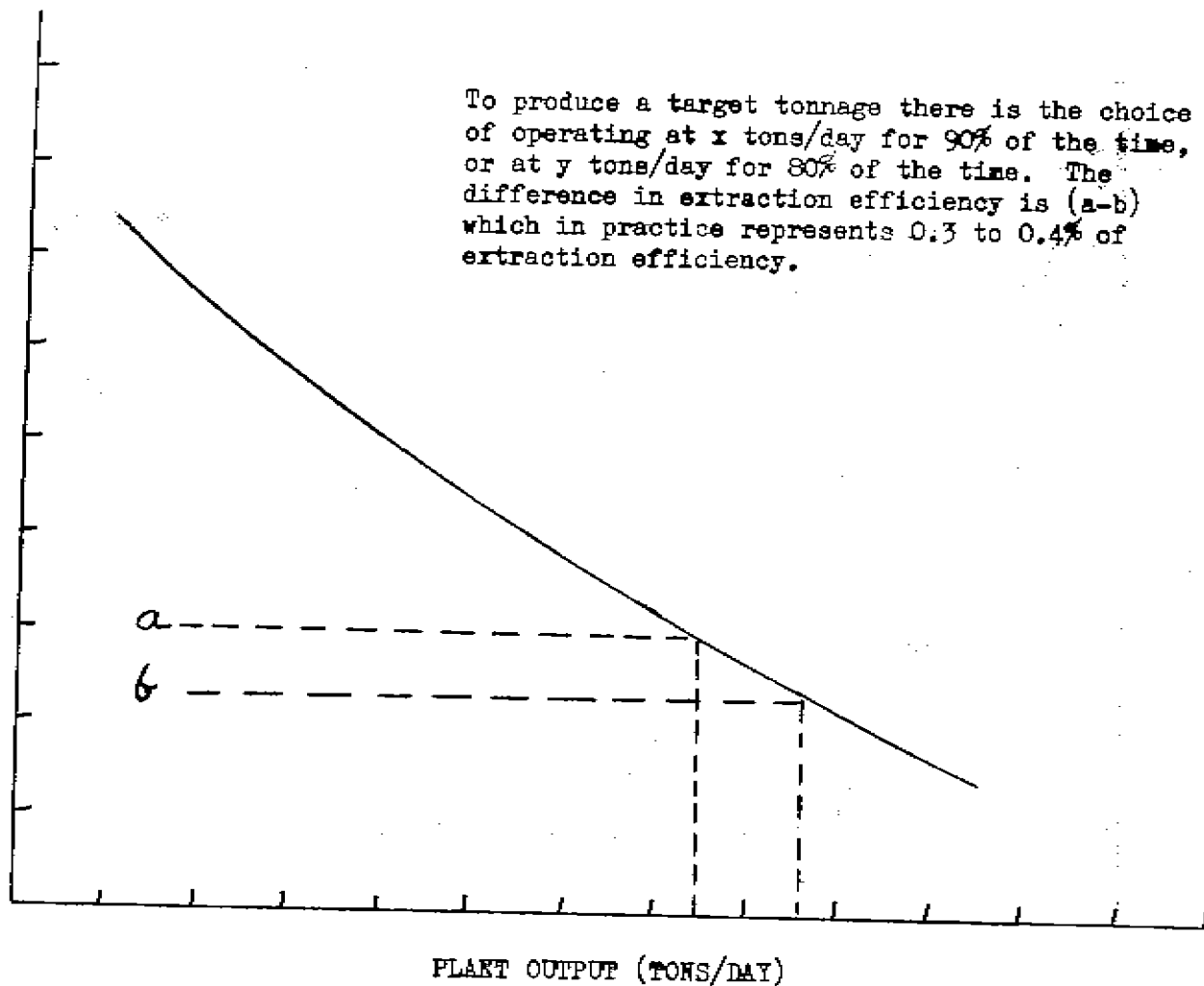
Generally in cases where a plant is operating well within its maximum capabilities, a wide range of phosphates can be processed, the major factors affecting costs being raw material prices including sulphuric acid, and any reversion losses. In cases where maximum output is essential, limitations caused by grinding, reaction conditions or product acid strength (i.e. evaporation costs) may well offset appreciable differences in rock costs unless it proves possible to combat bottlenecks by plant modifications or additions. Differences in unit cost of P₂O₅ of up to 25% can in some cases be countered by varying production conditions, and a detailed examination of these is essential. Some of the factors are difficult to evaluate unless prior experience exists or well planned research tests can make the necessary information available.

The author wishes to thank the directors of Scottish Agricultural Industries Limited for permission to give this paper.

GRAPH 1.



EXTRACTION
EFFICIENCY



GRAPH 2.