



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org



18636

Distr.
LIMITED

ID/WG.497/1(SPEC.)
28 November 1989

United Nations Industrial Development Organization

ENGLISH
ORIGINAL: FRENCH/ENGLISH

Expert Group Meeting on the Processing
and Utilization of Phosphates

Dakar, Senegal, 3-6 January 1990

20 SEP
1989
Dakar
UNIDO
Senegal

MANUFACTURE OF FERTILIZERS FROM LOW-GRADE PHOSPHATE ROCKS*

Prepared by

Armand L. Davister
UNIDO Consultant

3/10/89

* The views expressed in this paper are the author's and do not necessarily reflect the views of the Secretariat of UNIDO. This document has been translated from an unedited original.

V.89 61734 6593e

CONTENTS

	<u>Page</u>
INTRODUCTION	1
I. FERTILIZATION AND FERTILIZING MATERIALS	
II. INFLUENCE OF THE LOWERING OF THE GRADE OF PHOSPHATE ROCKS ON DIFFERENT LINES OF FERTILIZER MANUFACTURE	6
III. GEOLOGY OF PHOSPHATE ORE DEPOSITS	13
IV. BENEFICIATION OF LOW-GRADE PHOSPHATE ROCKS	15
V. NON-CONVENTIONAL FERTILIZERS FROM LOW-GRADE PHOSPHATE ROCKS	28
VI. CONCLUSIONS	47
<u>Annexes</u>	51

INTRODUCTION

This report is concerned with the production of fertilizers from rocks containing phosphates in medium or low concentrations. Hence these two introductory chapters.

I. FERTILIZATION AND FERTILIZING MATERIALS 1/

I.1. Why do we make phosphate fertilizers?

Natural soils are generally poor in phosphorus because of the amounts taken out by crops. The growing of crops breaks the almost closed phosphorus cycle characteristic of natural biocoenoses and quite quickly uses up the available phosphorus. As a result yields decline and soon become negligible. To prevent this from happening, it is necessary to put back at least as much phosphorus as has been taken out, and in fact even more, because the phosphate added as fertilizer also has to cover losses due to fixation and aging of the phosphates available in the ground. The role of phosphate fertilizers is thus to raise the phosphorus level in the soil to an acceptable level and keep it there.

I.2. Fertilizing means balancing the inputs

The ideas of soil balance, phosphate loss, leaching and fixing, on the one hand, and inputs and reserves available in the soil, on the other, have to be fully understood.

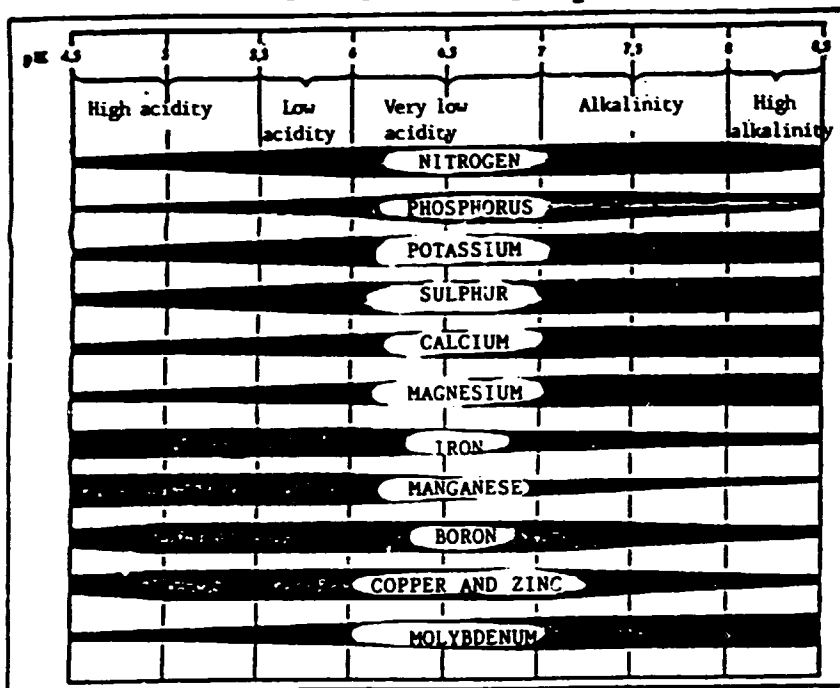
I.3. Low soil acidity is preferable to too high pH

Assimilation of the main nutrients used in agriculture depends largely on the pH of the soil in question.

1/ The following discussion is based on the booklet "Guide sur la fertilisation phosphatée" published by the International Fertilizer Association (IFA) and on articles in the review L'Agriculteur of 30 October 1988.

Table 1

Assimilation of nutrients as a function of soil pH
(pH expressed = pH H₂O)



Source: D. Soltner, Les bases de la production végétale, vol. 1: Le sol.

Note: The width of the black bands in the above table shows, for each nutrient in question, what is the optimum pH level for "availability" of the nutrient and how that level influences the dynamics of the nutrients.

I.4. The soil: a living environment with multiple interactions

The soil is a biological environment acted upon by many highly active micro-organisms, which affect the processes of humidification, mineralization and absorption of atmospheric nitrogen.

The nature of this living environment is not a matter of indifference. It ought to:

- Be well aerated, moderately humid, well structured;
- Have optimum pH;
- Be well supplied with calcium and magnesium.

It is thus the very opposite of inert: it reacts, depending upon its components, particularly its microbic and physico-chemical components.

I.5. Value of soil analysis

This gives the farmer the information he needs on the different parameters regulating the balances in the soil, determining a particular ion's tendency towards fixation or availability, of affecting the content of calcium, magnesium and micro-nutrients.

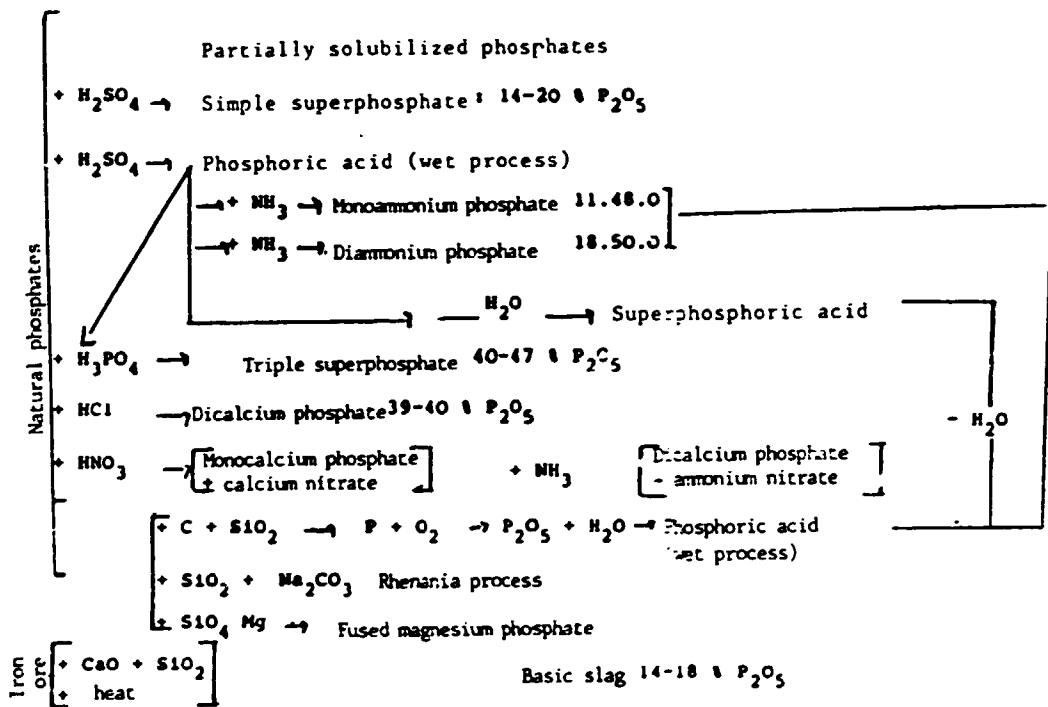
I.6. What are the aims of industrial phosphate processing?

In phosphate ores, the phosphorus occurs in forms that are insoluble and not available to the plant - essentially as fluorapatite. It is accompanied by impurities which are a nuisance because they are useless, heavy and unwanted, or even toxic.

The fertilizer industry therefore has to:

- (a) Get the phosphorus into a form where it will be available to the plant;
- (b) Eliminate the impurities (with or without recuperation).

The following table indicates the main types of phosphate fertilizer production.



MAIN PHOSPHATE FERTILIZERS

I.7. How soluble are phosphate fertilizers?

Commercially, in most countries, phosphate fertilizers are classified according to their solubility in different reagents:

I.7.1. Phosphates soluble in water

E.g. phosphoric acid, monocalcium and mono- and diammonium phosphates.

I.7.2. Phosphates soluble in ammonium citrate

E.g. dicalcium phosphate, Phospal (partly).

N.B. A distinction has to be made, however, between alkaline citrates (Joulie and Peterman) and neutral citrate, which also dissolves tricalcium phosphate in precipitation - present, for example, in superphosphates containing large amounts of ammonia.

I.7.3. Phosphates insoluble in the two reagents mentioned above, but soluble in relatively strong acids: e.g. some soft apatites.

Note: The solubility of a phosphate fertilizer does not by itself indicate how effective it will be, particularly in the medium and long term. Quite soon after they are dissolved in the soil, phosphates react with the soil's components, and it is the products thus formed that feed the plant.

I.8. Special role of phosphorus

Phosphorus is somewhat complicated to use because of the different forms in which it can be found.

The following table taken from Annales de Gembloux shows the many types of phosphate fertilizers that are commercially available. The variety of types should not really bother the user because what happens to the phosphorus once it gets into the soil is practically always the same - it dissociates into phosphoric ions. In the soil all these phosphoric ions will be subject to the same interactions and/or attacks of biological or physico-chemical origin.

Table 2

Main types of phosphate fertilizers

Type of fertilizer	Minimum grade required (P ₂ O ₅ %)	Solubility	Fineness (u)	Base equivalent
Superphosphate: Simple	16	Neutral ammonium citrate, 93 per cent water	-	-2
Concentrated	25			0
Triple	38			
Basic slag	10	2 per cent citric acid	75% at 360 96% at 630	+40 to +45
Dicalcium phosphate precipitate	38	Alkaline ammonium citrate (Peterman)	90% at 160 98% at 630	
Disaggregated phosphate	24	Alkaline ammonium citrate (Peterman)	75% at 160 96% at 630	
Alumino-calcium phosphate	30 of which 75	Mineral acids Alkaline ammonium citrate (Joulié)	90% at 160 98% at 630	-6
Soft natural phosphate	25 of which 55	Mineral acids Formic acid	90% at 63 99% at 125	+26
Partly solubilized soft natural phosphate	20 of which 40	Mineral acids Water	90% at 160 98% at 630	

Source: Annales de Gembloux - 3ème trimestre 86. Tendances actuelles en matière d'amendements et de fumure de fond.

It is not quite "all much of a muchness", however, since the different types of phosphate fertilizers differ in the speed with which they dissociate in the soil.

II. INFLUENCE OF THE LOWERING OF THE GRADE OF PHOSPHATE ROCKS ON DIFFERENT LINES OF FERTILIZER MANUFACTURE

II.1. Lowering of the grade of phosphate rock generally has all or some of the following consequences: 1/

Reduction in the concentrate's P_2O_5 content;

Problems created by the presence of greater quantities of cationic impurities such as Al, Mg, Fe, etc.;

Similar problems with anionic impurities such as Cl, CO_3 , etc.;

The effects of an increasing organic content;

A possible need to show imagination as to:

The quality of the fertilizers that can be produced from these phosphates;

The use of non-conventional procedures to process these phosphates into products whose phosphorus can be assimilated by plants;

The right production and distribution strategy for these new products (poor phosphates and fertilizers made from them).

II.2. The table reproduced on the next four pages summarizes the effects of different impurities present in phosphates on the production of some traditional phosphate fertilizers.

1/ This chapter is largely based on work done by a working group of the IFA Technical Committee.

INFLUENCE OF VARIOUS COMPONENTS TO P₂O₅ RATIOS
IN FERTILIZER INDUSTRY

	EFFECT(S) ON SOUGHT PRODUCT(S)					
	N-SUPER	TSP	WPA	MAP	DAP	WTRIP- PHOSPHATES
① 1. Effect of decreased rock BPL (the per se decrease due to the presence of higher inerts than "normal")	<ol style="list-style-type: none"> 1. decreased TP content of product 2. More power required for grinding/tP₂O₅. 3. Throughput reduction 4. Higher freight/tP₂O₅ in product. 5. Increased rock storage volume 	<ol style="list-style-type: none"> 1. ditto 2. ditto 3. ditto 4. ditto 5. ditto 11. In slurry process, added erosion 	<ol style="list-style-type: none"> 2. ditto 3. ditto 4. ditto 5. ditto 8. May have slight lowering of recovery. 10. Increased waste disposal requirements. 11. Higher pump & agitator erosion 	<ol style="list-style-type: none"> 6. No quality effect 	<ol style="list-style-type: none"> 6. ditto 7. ditto 	<ol style="list-style-type: none"> 1. ditto 3. ditto 4. ditto 5. ditto 9. Increased solid/liquid separation problems. 11. ditto 7. Disposal of inerts (or 1)
② 2. Effect of increase in CaO/P ₂ O ₅ ratio.	<ol style="list-style-type: none"> 1. Higher acid usage. 2. Decrease in product grade. 	<ol style="list-style-type: none"> 1. ditto 3. Grade may increase 	<ol style="list-style-type: none"> 1. ditto 4. Increased waste disposal 8. Throughput reduction 9. May lower recovery 			<ol style="list-style-type: none"> 1. ditto 5. Increased utility used. 6. Increased calcium nitrate production. 7. Loss of water solubility and 2 8-9 ditto

NITRIC PHOSPHATES

	N-SUPER	TSP	WPA	MAP	DAP	NITRIC PHOSPHATES
③ Effect of increase in Fe_2O_3/P_2O_5 ratio	<ul style="list-style-type: none"> 1. dilution 5. Rock may be harder to grind 7. Increased curing time 8. Sticky product 	<ul style="list-style-type: none"> 1. dilution 5. ditto 7. ditto 8. ditto 	<ul style="list-style-type: none"> 2. Sludge formation 3. Higher viscosity 5. ditto 	<ul style="list-style-type: none"> 4. IPA up, APA down 	<ul style="list-style-type: none"> 4. ditto 6. N/P₂O₅ ratio decreases 	<ul style="list-style-type: none"> 1. ditto 3. ditto 9. Loss of water solubility
④ Effect of increase in Al_2O_3/P_2O_5 ratio	<ul style="list-style-type: none"> 1. Sticky product 2. Grade reduction 12. Increased curing time 	<ul style="list-style-type: none"> 1. ditto 2. ditto 3. Loss of conversion 12. ditto 	<ul style="list-style-type: none"> 5. Higher viscosity 6. Changes in gypsum size and shape. 7. Reduces F evolution 8. Alters filter rate 9. Precludes making feed grade phosphates. 	<ul style="list-style-type: none"> 10. IPA up, APA down 2. ditto 	<ul style="list-style-type: none"> 10. ditto 11. N/P₂O₅ ratio decreases 2. ditto 	<ul style="list-style-type: none"> 2. ditto 4. Loss of water solubility 5. ditto
⑤ Effect of increase in H_2O/P_2O_5 ratio.	<ul style="list-style-type: none"> 1. Increased reactivity 2. Decreased grade 4. Physical condition and cure rate. 	<ul style="list-style-type: none"> 1. ditto 3. Grade may increase. 5. Foam(?) in slurry process 	<ul style="list-style-type: none"> 6. May require more foam control. 7. Higher viscosity 	<ul style="list-style-type: none"> 2. ditto 8. ditto 	<ul style="list-style-type: none"> 2. ditto 8. ditto 9. Decreased N/P ratio 	<ul style="list-style-type: none"> 2. ditto 7. ditto 8. Loss of water solubility

	N-SUPER	TSP	WPA	MAP	DAP	NITRIC PHOSPHATES
5. Effect of Increase in reactive silica/P ₂ O ₅ ratio	<ol style="list-style-type: none"> 1. Increased F evolution 2. Physical condition may improve 	<ol style="list-style-type: none"> 1. ditto 2. ditto 	<ol style="list-style-type: none"> 1. ditto 3. Effects gypsum characteristics. 4. May decrease filter scaling. 5. Changes solution viscosity. 6. Sludge formation may decrease. 8. May decrease corrosion. 	7. Slight grade improvement	7. ditto	<ol style="list-style-type: none"> 1. ditto (mixed acid system) 5. ditto
Effect of Increase in N ₂ O/P ₂ O ₅ ratio.	<ol style="list-style-type: none"> 1. Reduced F release 	<ol style="list-style-type: none"> 1. ditto 	<ol style="list-style-type: none"> 2. More filter scale. 3. Reduction in F release 4. Increased ralstonite type sludges 6. May decrease corrosion. 	5. Diluent	5. ditto	5. ditto
Effect of Increase in K ₂ O/P ₂ O ₅ ratio.	<ol style="list-style-type: none"> 1. Reduced F release 	<ol style="list-style-type: none"> 1. ditto 	<ol style="list-style-type: none"> 2. More filter scale. 3. Reduction in F release 4. Increased taranakite type sludges 6. Decreases corrosion 	5. Diluent	5. ditto	5. ditto (for NP grades)

	N-SUPER	TSP	WPA	MAP	DAP	NITRIC PHOSPHATES
1. Effect of increase in inorganic CO_2/P_2O_5 ratio. (10)	1. Increased reactivity 2. May decrease throughput	1. ditto 2. ditto 3. ditto (in slurry process)	2. ditto 3. Foam control may be required			2. ditto 3. ditto
1. Effect of increase of organic C/P_2O_5 ratio. (10)	1. Reactivity may be lowered	1. ditto 2. Foam control may be required	2. ditto 3. Throughput may decrease	2. ditto	2. ditto	2. ditto 3. ditto 4. NO_x release 5. Increased tendency to self-sustaining decomposition
Sulphides (11)	1. Risk of H_2S evolution	1. ditto 3. ditto (for slurry process)	1. ditto 3. Corrosion rate may increase			1. ditto 2. NO_x release
Chloride (12)		1. ditto (slurry process)	1. Corrosion rate increased			1. ditto 2. Safety problems during evaporation

Notes : Radio-activity and elements such as Pb, Hg, Cd, As under consideration by environmentalists do not appear to have any adverse effects on fertiliser manufacture.

II.3. Mineral elements essential for the plant

These are usually divided into:

(a) Plastic or macro-nutrients

C 40 to 50 per cent)	In all \approx 95 per cent of dry matter. They come from the air and water.
O 42 to 44 per cent)	
H 6 to 7 per cent)	

N: 1 to 3 per cent; P: 0.05 to 1 per cent; K: 0.3 to 3 per cent: major fertilizing elements

Ca: 0.5 to 3.5 per cent; S: 0.1 to 0.5 per cent; Mg: 0.03 to 0.8 per cent: secondary fertilizing elements.

Na: 0.01 to 3.5 per cent; Si: 0.005 to 1.35 per cent; Cl: 0.15 to 0.25 per cent.

It should also be noted that

N, P and S play a plastic role because they are the basic constituents of proteins and other fundamental substances in vegetable tissues;

K, Ca and Mg have an essential role in carrying and synthesizing various substances and maintain the cation-anion equilibrium within the plant.

(b) Micro-nutrients which represent no more than an insignificant part of the plant's weight - about 1 per cent, but which are nevertheless essential for the plant or for animals:

Fe, Mn, Cu, Zn, B, Mo, Co, Al, F, Se, Br, I.

II.4. Considerations relating to low-grade phosphates

The above list shows that the phosphate "impurities" referred to in section II.2 are sometimes elements needed by crops in large quantities, such as Ca, Mg and S.

But in recent decades the fashion for more and more concentrated fertilizers, generally produced by neutralization of phosphoric acid, has led to their being regarded as undesirable, either because they interfere with the technological processes (influence on gypsum filtration or the stability of liquid fertilizers) or that they dilute the final product simply by being there.

But if they are present in the ore in appreciable amounts and are complicated, expensive or even impossible to eliminate at the ore-beneficiation stage, that is not always a reason for rejecting the ore completely.

It cannot of course be used to supply a world-class unit producing concentrated fertilizers capable of competing in all international markets, but it may prove very useful for producing lower-grade fertilizers for local or regional use.

That brings to an end the introduction to this report. Its length, which the reader is asked to excuse, is justified by the need to establish precisely what the problem is.

Given the variety of people who will have to deal with the subject, it seemed essential to state the basic facts clearly. This will make it easier to grasp the choices that have to be made later with regard to processing techniques, whether for mechanical beneficiation or chemical or thermal processing of the ores.

STUDY

III. GEOLOGY OF PHOSPHATE ORE DEPOSITS

Without going into full details, a brief account of the three main aspects - deposit classification, prospecting, exploration - will help the reader understand the facts. ^{1/}

III.1. Deposit classification

There is a clear distinction between:

On the one hand, magmatic phosphates lodged in intrusive basic rocks such as carbonatite, nepheline syenite, etc. Morphologically, they appear as ring structures or lodes, as for example at Kola in the Soviet Union or Phalaborwa in South Africa. The minerals they contain are apatite, rutile, pyrochlore, sphene, calcite and nepheline.

On the other hand, sedimentary phosphates resulting from direct precipitation in a lagoon, as at Khouribga in Morocco, Metlaoui in Tunisia, Taïba in Senegal and the Togolese deposit. The apatite, present in the form of pseudo-oolithic phosphorites, is found together with calcite, dolomite, pyrites, opal and organic matter.

Note: Only apatite has been developed as a source for fertilizers. Lithium phosphates (amblygonite) are worked for lithium, rare-earth phosphates (monazite) for rare earth. Iron, manganese and aluminium phosphates are not worked. However, some aluminium phosphates may be the result of lateritic decay of a primary apatite, and recent attempts have been made to develop them (Gabon, Burundi). Aluminium phosphate from Thiès is sold as fertilizer after moderate calcining under the name of Phospal (see chapter V).

III.2. Prospecting

At the three stages of research, a distinction will again be made between:

Magmatic deposits

Large-scale research by remote sensing of rift-type lineaments or ring structures superimposed on stratifications, faults and relief.

Strategic research by mapping of associated oil-bearing deposits (nepheline syenite, ilmenite granite, etc.).

Regional research by mapping of geochemical anomalies in rare earths, titanium, uranium/thorium.

^{1/} This chapter, like the next one, is based essentially on contributions from the staff of Syres, a Liège University research group set up in association between the Laboratories of Applied Geology (Professor Dimanche) and Extractive Metallurgy (Professor Ek) for work aimed at developing natural mineral resources, including phosphates and in particular low-grade ores.

Sedimentary deposits

Large-scale research by mapping of cold sea currents and anomalies where such currents flow on top of warmer water (upwelling).

Strategic research by mapping of palaeo-shores.

Regional research by mapping of geochemical anomalies in uranium.

Local research by fine sedimentology of different lagoon deposits.

III.3. Exploration

This essentially comprises:

Grid surveys (kilometric, hectometric, decametric) with continuous coring, or better, immediate logging; the data are treated geostatistically by Fourier transforms to give regional maps of real anomalies.

Sampling by wells, trenches or ditches on the basis of the survey results. Only strict application of the scientific rules governing the above operations will allow a representative sample of the deposit to be obtained, justifying the operations to be carried out on it in order to establish its properties.

By chemical analysis: P₂O₅
CaO/MgO
Silica
Alumina
Fire waste
Iron and titanium oxides
Sulphur

By mineralogical analysis

Microscopic and/or X-ray diffraction methods to establish the types of phosphate, the types of carbonate, the amount of silica, organic matter and pyrites and the way they are found together.

If necessary, final analysis by electronic micro-probe to establish the reasons for any zone formation ("zoning") of phosphoritic pisoliths.

III.4. Considerations relating to the roles of the geological study

Before the ore-beneficiation study, it plays an essential role in making sure that the size of the deposit has been established and that the sample taken duly represents the quality.

Any error or omission in this process is liable to result in wasted effort or wrong conclusions, causing great financial losses whether the mistake is on the high or the low side.

During the beneficiation study, it is essential that the properties of the beneficiated products and the waste should be established by the methods described above so that the most appropriate techniques can be used at each stage in the preparation of the ore. Such collaboration between the two disciplines is the actual reason for the establishment of Syres (see annexes 1-6).

IV. BENEFICIATION OF LOW-GRADE PHOSPHATE ROCKS 1/

IV.1. Ore preparation

IV.1.1. Definitions

To define the terms used in ore preparation, one has first to explain the meaning of certain words as applied in this branch of industry. The definitions do not necessarily correspond to those accepted in other scientific or economic fields.

A mineral is a chemical compound which is solid at room temperature and has a definite crystalline structure. Its chemical composition is not always constant.

Mineral material is a number of minerals mixed up together as they occur in the earth's crust. By extension, petroleum and natural gas are also regarded as mineral material.

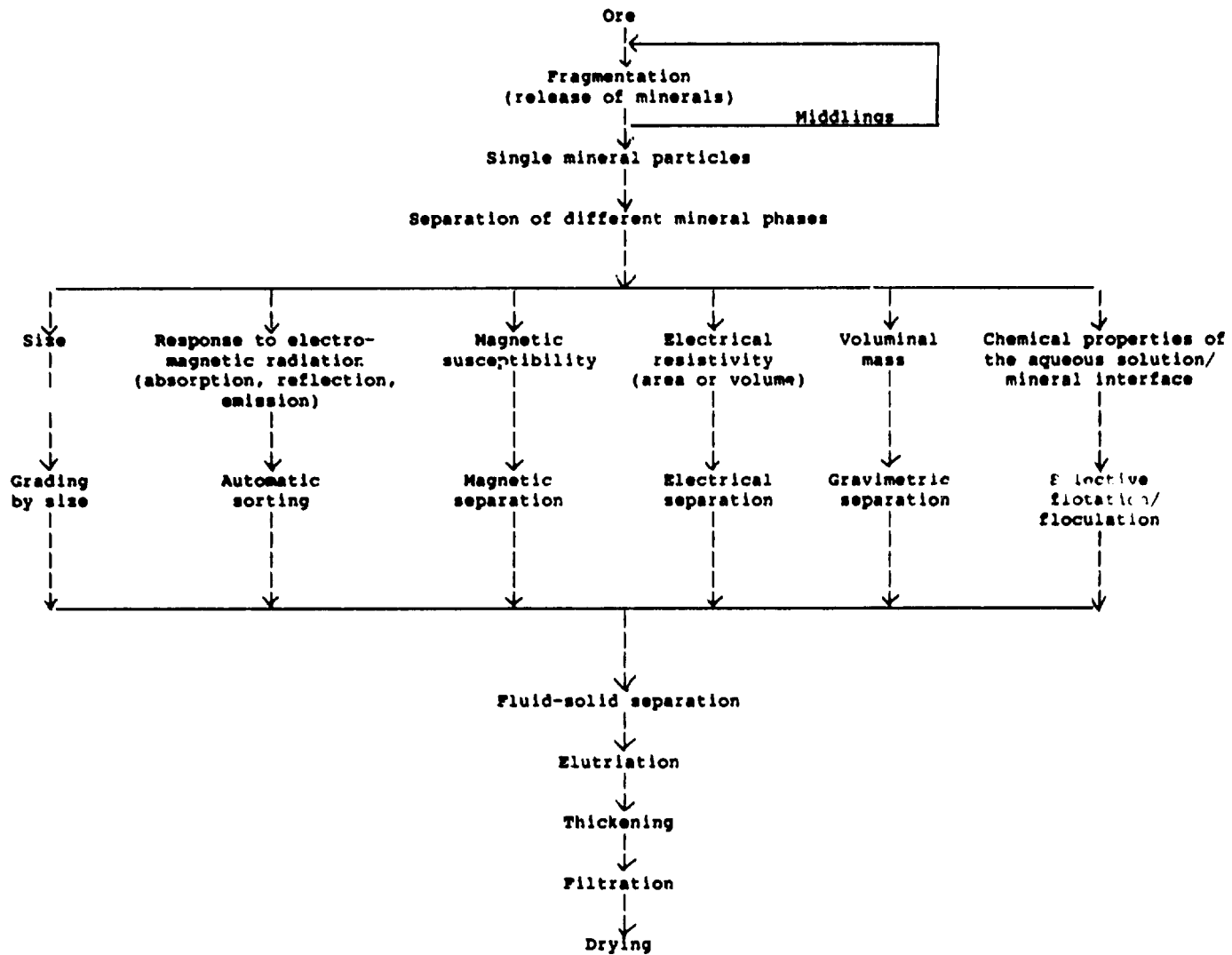
An ore is mineral material which is worth exploiting because its components include one or more particular minerals regarded as "useful". The criterion establishing that an ore is an ore is thus an economic one: mineral material does not become an ore unless the market value of the useful minerals it contains exceeds the cost of extracting them. Other minerals accompanying them that are not worth extracting are called deads or gangue. Their status as such is obviously not fixed in time or space. It will be found, for example, that constant impoverishment of deposits and improvements in technology mean that many of yesterday's deads are today's ores or will soon become so.

Ore preparation includes all processes carried out on the material from the mining of the ore to the final extraction of the commercial product.

It thus includes all the procedures for adjusting the granularity - grading, fragmentation, agglomeration - and all wet or dry processes for concentrating useful minerals without chemical modification of the materials (see figure 3 below).

1/ Like the last chapter, this one is based largely on information supplied by the Syres Natural Resources Research Group, which is a study and research association of Liège University.

Figure 3. Individual operations in ore preparation



IV.1.2. Objectives

It is exceptional for mineral materials to be usable without preparation, just as they are extracted from the soil or subsoil. Even for rich ores, such as some iron and manganese ores, for example, the blocks and pieces taken from the mine have to be reduced to a convenient size. But usually the useful materials are accompanied by dead matter, or gangue, without any value, in which they are even often scattered about in grains of varying fineness. For technical and economic reasons it is essential to separate the useful minerals from the greater part of their gangue before embarking on the operations that belong to metallurgy or industrial chemistry proper.

To process crude ore by pyrometallurgy would mean raising enormous masses of deads to a high temperature; fusing as slag they would then carry away a large proportion of the metals to be extracted. Hydrometallurgical processing would also mean considerable losses of metal and reagents in the solutions carried away by the considerable mass of gangue.

Similar considerations apply just as much to products of industrial chemistry.

The cost of transporting the material also plays an important role, as metallurgical or chemical units, unlike beneficiation plants, are often situated far away from the mines.

IV.1.3. Ore preparation processes

Ore preparation processes are of two main types:

1. Those to achieve the desired granularity;
2. Those to separate the gangue, with possible separation of various useful minerals between operations.

To these principal processes must be added subsidiary operations, such as deads removal, separation and recuperation of slime water, etc.

Granularity preparation comprises grading by size of the pieces, grains or particles and volumetric reduction by fragmentation or, on the contrary, agglomeration of fines.

Separation of all or some of the useful minerals by ore preparation processes is obviously only possible if they differ in some physical property.

This physical property may be appearance, colour, shininess, grain size, but usually it is specific gravity, magnetic susceptibility, electrical conductivity or ability to stick to air bubbles stabilized in froth.

Separations carried out during ore preparation always include removal of a considerable proportion of the gangue.

IV.1.4. Advantages of ore preparation

Perfect separation cannot be achieved with the ore preparation processes, even after many recyclings, and one has to be ready to get an impure concentrate if one does not want to lose much of the useful mineral or to lose metal in the waste if one wants the concentrate to be pure.

In addition, ores are getting lower and lower in grade and more and more complex. Extraction of the different kinds of minerals by isolating them as grains which only contain one mineral (a prerequisite for separating them from each other properly) entails a high degree of fragmentation, resulting in grains of such a size that they no longer lend themselves to simple mechanical concentration.

On the other hand, when it is feasible, mechanical concentration of ores by strictly physical means, in operations carried out at normal temperatures, is much more economical than any other system involving a change of physical state (fusion or volatilization) or chemical state (solution, calcination, oxidoreduction etc.).

IV.2. The need for physical beneficiation of low-grade ores*

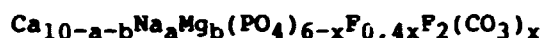
The primary source of phosphorus is fluorapatite $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$, whose P_2O_5 content is 42.2 per cent.

The poorer the phosphate, the more fluorapatite is diluted by other substances, which may occur in the ore in three different ways, namely: 1/

IV.2.1. In the apatite molecule itself

There are frequent substitutions: Mg, Sr, Na, Mn, Fe, Ba for Ca; OH, Cl and CO_3 for F; As and V for P; $\text{CO}_3 + \text{F}$ for PO_4 .

Carbonate or francolite apatites are usually found in sedimentary phosphates:



The value of x may range from 0 to 1.2; as it increases, the reactivity of the phosphate increases. In igneous phosphates, x is usually close to 0, which explains their low reactivity.

IV.2.2. In the endogangue

When phosphate elements of sedimentary origin are formed, impurities are incorporated in the shape of endogangue which does not form part of the apatite structure. It can consist of such varied elements as quartz, amorphous forms of silica such as chalcedony, different varieties of carbonates: calcite, dolomite and ankerite, sulphides (mainly pyrites), iron and aluminium oxides in various forms, together with organic material. These diluents may take the form of actual inclusions or of matter contained in the fissures of the apatite particles.

IV.2.3. In the exogangue

The exogangue consists of all mineral substances in the form of particles or crystals that are entirely separate from the phosphate material and from the cement surrounding them, when no on-site leaching has taken place. Ores are divided into those whose gangue is mainly siliceous, carbonate or aluminoferric.

* Paragraph IV.2 is illustrated in annexes 1 to 6.

1/ This information is taken from a lecture by B. Gaucherand, Director of CERMI-ALSTHOM, France.

With all these possible diluents, there is an obvious need in the case of low-grade phosphates, i.e. those having a P_2O_5 content of less than 20-25 per cent, to beneficiate them, in the first place by physical means (mechanical, hydraulic, aeraulic, magnetic) before subjecting them to chemical processing, during which the reactions may prove difficult to direct and control if the nature and volume of the diluents are unsuitable.

IV.3. Types of phosphate ore

IV.3.1. Phosphate ores can be classified according to the age of the formations to which they belong.

Ages of the major phosphate deposits

	<u>Age</u>	<u>Major deposits</u>
Miocene	10-20 m.y.	Florida, North Carolina, Baja California
Upper cretaceous, Eocene, Upper Jurassic	60-100 m.y.	Syria, Jordan, Israel, Egypt, Iraq, Algeria, Tunisia, Morocco, Senegal, Togo
Lower cretaceous	115-150 m.y.	Russian platform
Permian	230-270 m.y.	Western USA
Ordovician	440-480 m.y.	Tennessee, Estonia
Cambrian	530-570 m.y.	USSR (Karatau), Mongolian People's Republic (Hubsugal), South China (Yunan)
Proterozoic	570 m.y.	India (Udaipur)

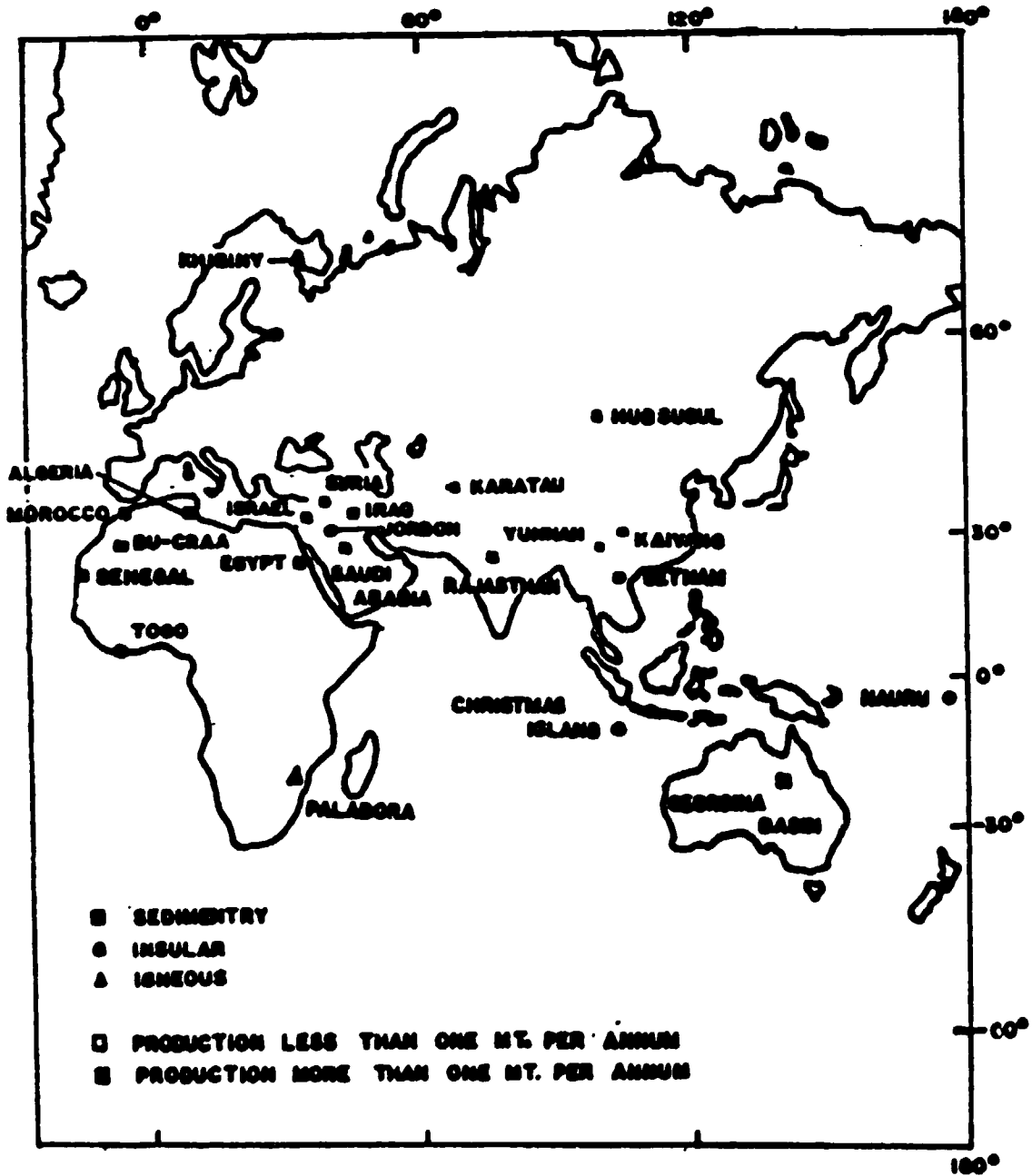
IV.3.2. A distinction is usually drawn between:

Ores of igneous origin

These are usually associated with alkaline or ultrabasic rocks, their chief constituent being well-crystallized hydroxy-fluorapatite. Although they are often very poor in P_2O_5 (averaging 4 per cent), their crystallinity, low rate of substitution and almost complete absence of inclusions make it possible to obtain the richest concentrates (35-39.5 per cent of P_2O_5).

Ores of sedimentary origin

Of marine origin, their chief phosphate constituent is francolite. The phosphate content varies widely according to the degree of substitution and the level of other components. The most viable are those in which atmospheric action and natural leaching have eliminated as many foreign bodies as possible.



DISTRIBUTION OF MAJOR PHOSPHATE DEPOSITS IN
AFRICA - ASIA & AUSTRALIA

(Modified after COOK)

IV.4. Industrial beneficiation processes

IV.4.1. Phosphates of igneous origin

IV.4.1.1. With siliceous gangue

The following plants may be cited:

- Kola (USSR) - 20 million tpy with 39 per cent P₂O₅
- Palabora (South Africa) - 2.75 million tpy with 36.5 per cent P₂O₅
- Siilinjärvi (Finland) - 0.6 million tpy with 31.5 per cent P₂O₅

This latter concentrate is obtained from one of the lowest-grade phosphate ores in the world (3.5 per cent P₂O₅), which is beneficiated by a factor close to 10.

Fraction µm	Flotation feed			Apatite concentrate				Tailings		
	Weight %	Assay % P ₂ O ₅	Distn. %	Weight %	Assay % P ₂ O ₅	Distn. %	Recovery %	Weight %	Assay % P ₂ O ₅	Distn. %
+315	9.4	0.5	1.4					10.3	0.3	6.1
315-200	10.1	2.0	5.8	5.4	37.7	6.0	85.7	9.8	0.3	5.7
200-125	13.0	3.3	12.3	11.5	37.1	12.6	91.7	13.7	0.3	8.1
125-90	12.5	3.9	14.0	12.1	34.9	12.5	93.1	11.8	0.3	6.9
90-75	7.1	4.8	9.8	7.0	38.9	8.0	94.5	5.8	0.3	3.4
75-40	12.4	4.5	16.1	15.1	37.1	16.5	94.1	14.0	0.3	8.3
40-0	35.5	4.0	40.8	48.9	30.8	44.4	79.8	34.6	0.9	61.5
Total	100.0	3.5	100.0	100.0	33.9	100.0	87.0	100.0	0.5	100.0

The composition of this phosphate is shown in figure 1 and table I below.

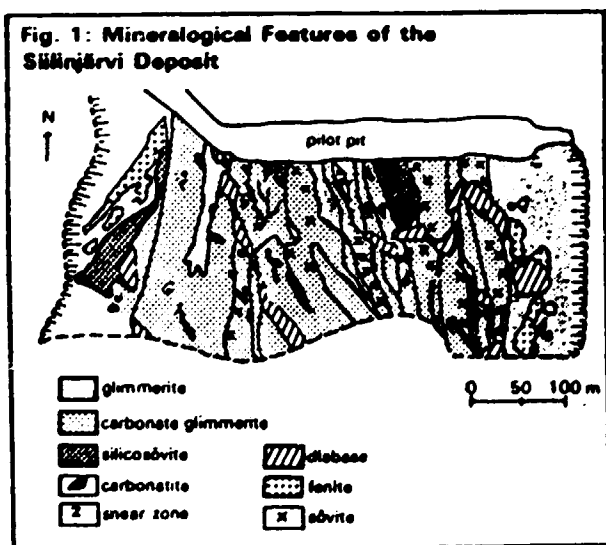


Table I
Compositions of the Main Minerals in
the Siilinjärvi Deposit
(wt-%)

Component	Apatite, Ca, F (PO ₄)	Calcite, CaCO ₃	Dolomite, (Ca, Mg)CO ₃	Phlogopite, (Mg, Na, Al)Fe silicates
CaO	55.8	53.0	30.1	0.1
SrO	1.2	0.8	0.3	—
BaO	—	(0.03)	0.1	—
P ₂ O ₅	41.5	—	—	(0.04)
F	2.7	—	—	1.1
CO ₂	0.3	43.9	46.4	—
Na ₂ O	0.4	—	—	0.1
K ₂ O	(0.02)	—	—	10.2
Al ₂ O ₃	0.1	—	—	9.8
Fe ₂ O ₃	(0.03)	—	—	4.7
FeO	—	0.4	2.8	5.5
MgO	0.1	1.6	19.4	24.3
SiO ₂	0.1	—	—	40.5

The flow sheets of the Siilinjarvi and Kola beneficiation plants are reproduced below:

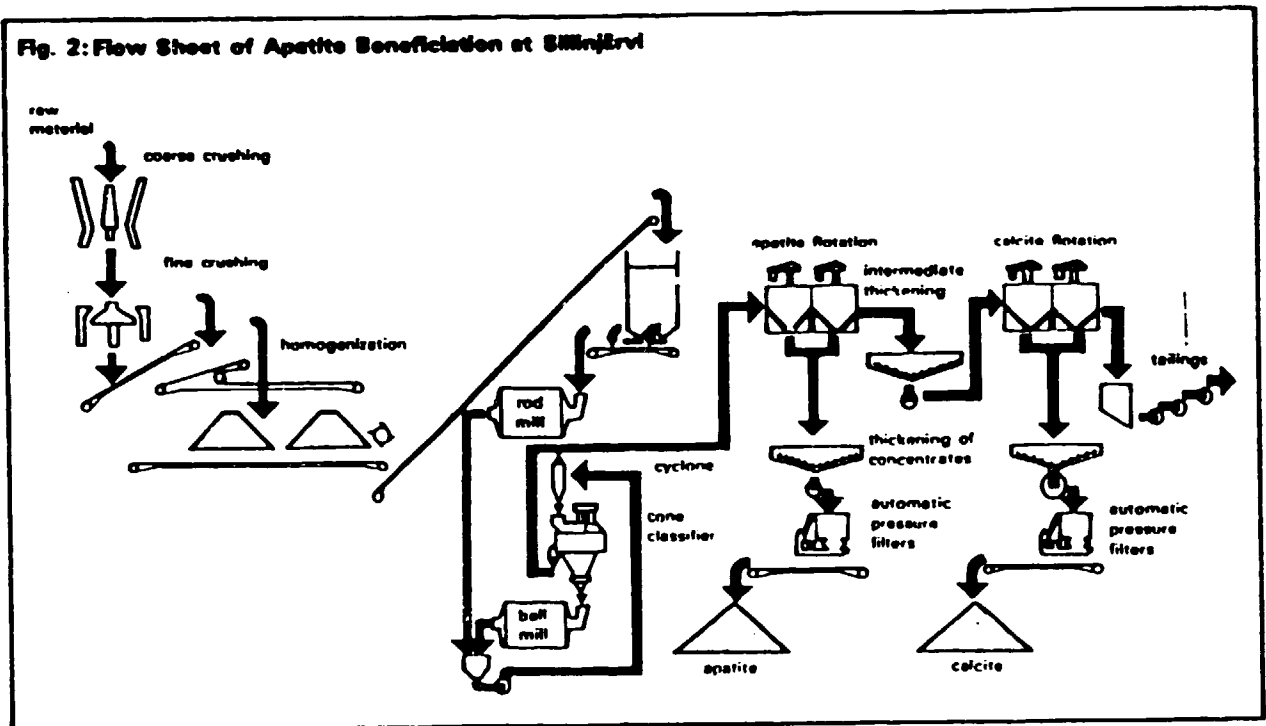
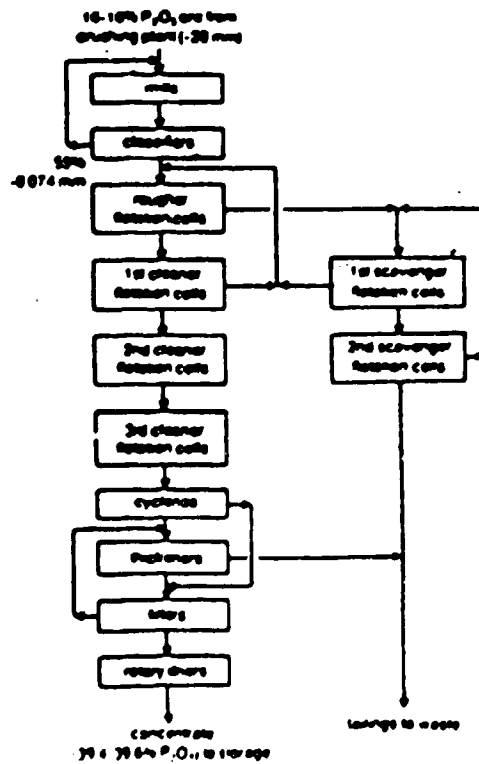
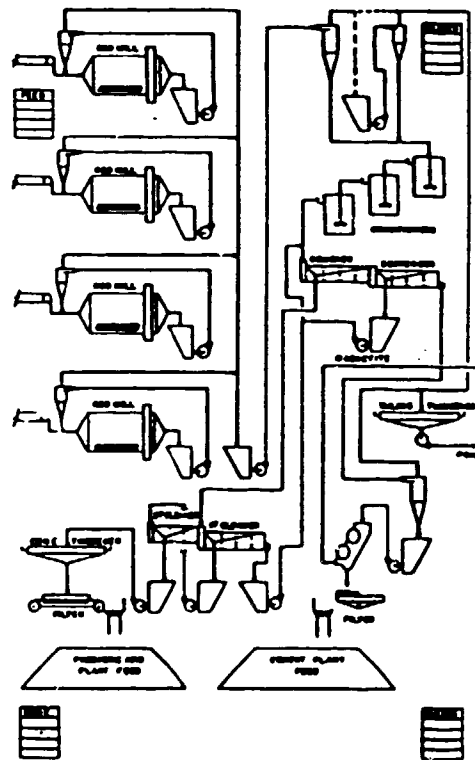


Figure 2: General scheme of treatment for phosphates from an igneous ore body, taken from the Kola complex, USSR.



IV.4.1.2. With carbonate gangue

Beneficiation of these ores is much more recent; it began in 1970 in Brazil, where there are at least three industrial plants - Jacupiranga, Araxa and Catalao - processing phosphates with calcareous gangue containing other minerals such as magnetite, barite, etc. These ores are found in "alkaline chimneys", in which apatite may occur in one or more of the ambient alkaline rocks. The Jacupiranga plant, which extracts apatite from unaltered carbonatite containing 80 per cent calcite and only 10 per cent apatite, is only equalled in complexity by the Siilinjärvi plant referred to above. The flow sheet includes crushing, washing, flotation, magnetic separation, second flotation, decantation and filtration.



JACUPIRANGA PLANT - CONCENTRATION PROCESS FLOWSHEET

It will therefore be no surprise to learn that beneficiation is much more expensive than the mine itself, which is really little more than a quarry. The following table gives a breakdown of the investment costs for the five Brazilian plants (total cost of the order of \$500 million for a combined production capacity of \pm 3,500,000 tons per year).

Table IV
Investment Costs
(1982 basis)

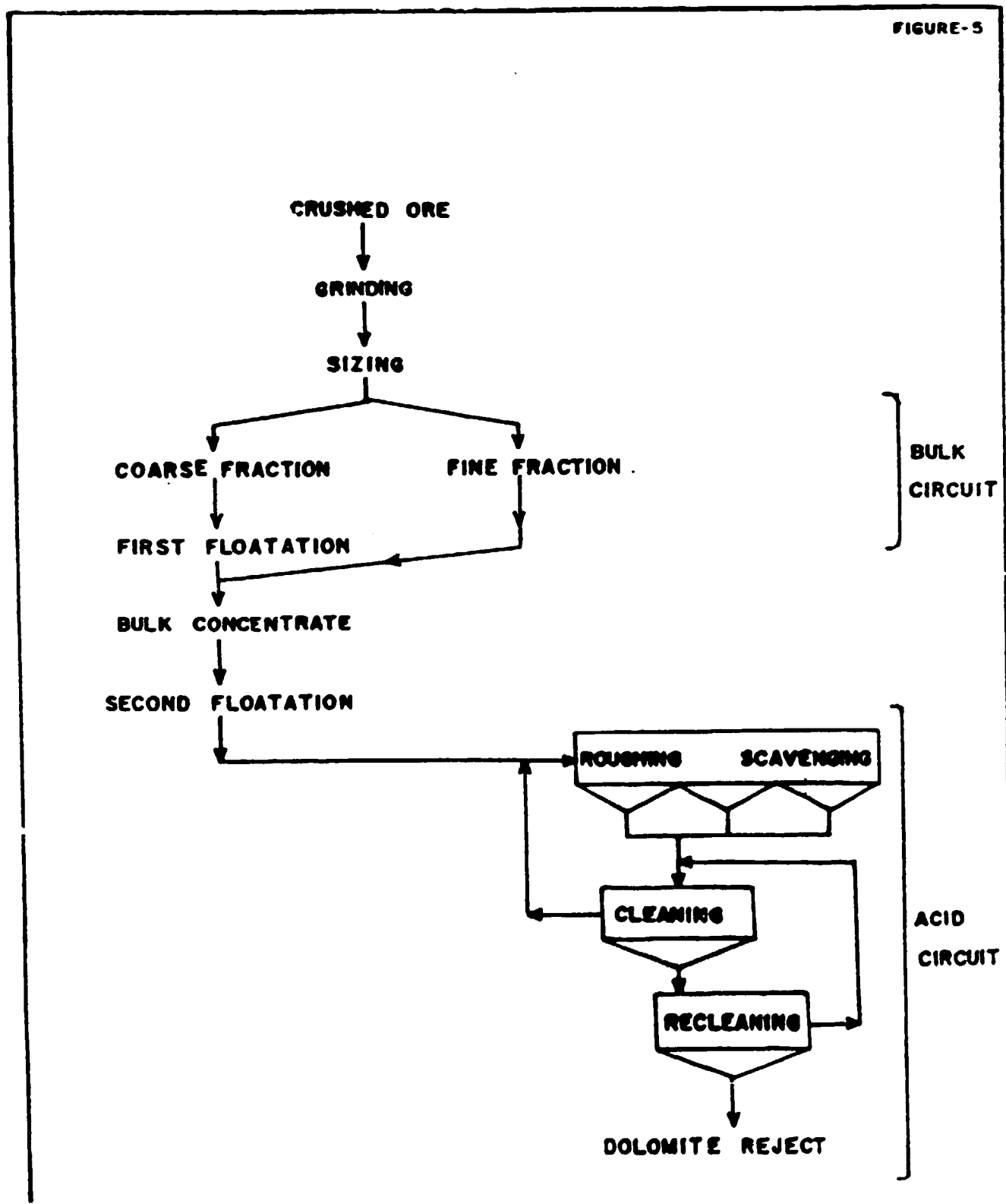
Specification	%
Mine	6.3
Crushing + storage	10.3
Concentration + reagents	18.2
Slurry pipeline	5.9
Water + tailings	4.9
Filtering + drying	7.3
Maintenance and utilities facilities	4.5
Infrastructure	7.0
Total for equipment and installation	64.4
Engineering and projects	12.6
Pre-operational expenses	13.7
Financing expenses	9.3
Total investment	100.0

While still rather high, the production cost is nevertheless acceptable at \$24 per ton in direct costs, to which depreciation of \$11 must be added (see details below).

Table VI
Specific Operating Costs
(US\$/tonne concentrate)

Variable costs		15.61
Ore	10.53	
Consumption Materials	1.72	
Electric Energy	2.97	
Royalties	0.39	
Fixed costs		9.59
Operating labour	1.42	
Maintenance labour	1.60	
Maintenance materials	2.23	
Indirect costs	4.34	
By-product credit		(1.41)
Total for moist concentrate		23.79
Oil fuel for drying		1.35
Total for dried concentrate		25.14
Depreciation		9.38
Overall production cost		34.52

that the most promising approach consisted in fine grinding (under 70 microns) followed by two-stage flotation, the first to remove the silica, the second to get rid of the magnesium (cf. the diagram below).



This circuit was tested on a 60-ton batch on a small-scale trial basis.

9.3. The important steps involved in this process were:

(a) Grinding the LGO to the fineness required for liberation of the main mineral constituents;

(b) Conditioning of the ground product with a fat acid salt as collector and reduction in the silica content by subjecting the ground product to flotation (silica depression) after it has been dislimed (the fine fraction of the ground product is not subject to flotation at this stage);

(c) Selective desorption of collector on phosphatic grains in the floated product and the fine fraction by action of phosphoric acid with sulphuric acid and removal of dolomite in froths. The non-floated product is the phosphate concentrate.

Since the process was entirely new, it was decided not to go straight into industrial production, but to proceed on a pilot basis by processing 200 tons per day, which gave the following results:

From Blocks	ORE TYPES TESTED		
	D	C	B
<u>Feed (Average)</u>			
P ₂ O ₅	16 - 17	18 - 20	11 - 13
SiO ₂	2 - 4	2 - 4	2 - 4
MgO	12 - 13	8 - 10	13 - 15
<u>Concentrate</u>			
P ₂ O ₅	34 - 36	34 - 36	34 - 36
SiO ₂	4 - 6	4 - 6	4 - 5
MgO	1.4	1.4	1.8-1.9

Calcination

When cheap energy is available, decarbonation by calcining followed by washing of the oxides is a useful method; it is usually done in a rotary kiln at a temperature of

This operation was chosen for the exploitation of the Djebel-Onk deposits in Algeria (fluidized bed calciner) and the Akashat deposits in Iraq (kiln). In Akashat the flow sheet consists of homogenization, crushing, screening, calcining (two rotary kilns of 6.0 x 6.6 x 145 m), quenching and washing. This plant processes 3.4 million tpy of crude with a 21 per cent P₂O₅ content to produce 1.6 million tpy of concentrate with a 31 per cent P₂O₅ content.

When all that is required is to eliminate the organic material, a fluidized bed calciner is perfectly adequate (Youssoufia, Morocco). Fuel consumption is in inverse proportion to the volume of organic material.

V. NON-CONVENTIONAL FERTILIZERS FROM LOW-GRADE PHOSPHATE ROCKS

The non-conventional phosphatic material that can be used for fertilizing purposes can be classified in three categories:

V-A: Materials for direct application (without chemical treatment):

1. Finely ground phosphate rock;
2. Phosphate rock after subjection to thermal treatment:
 - 2.1. Iron-aluminium phosphates calcined at low temperature,
 - 2.2. Phosphate rock calcined at high temperature;

V-B: Materials having undergone a simple chemical change:

3. Single superphosphate (SSP);
4. Under-acidulated derivatives:
 - 4.1. Single superphosphate + phosphate rock or Kotka superphosphate,
 - 4.2. Partially acidulated phosphate rock (PAPR);
5. Humifert;

V-C: Materials having undergone a biochemical transformation:

6. Composting;
7. Biosuper.

V.1. Finely ground phosphate rock

To the extent that a finely ground phosphate is effective in the function of supplying phosphorus to plants, it is - obviously - the cheapest of the phosphatic fertilizers since the only preparation required is the grinding of the rock.

However, as there is no conversion of the rock, its natural properties will fundamentally influence its fertilizing capability.

The reactivity of the phosphate present in the rock can be tested by means of reagents such as citric acid, formic acid and neutral and alkaline ammonium citrates.

It should be kept in mind that:

Ammonium citrates were developed in order to distinguish the soluble P_2O_5 of superphosphates and other fertilizers from apatitic P_2O_5 as it occurs in the rock;

Citric solubility was chosen in order to identify the soluble P_2O_5 in the basic slag;

Formic solubility was developed specifically to assess the P_2O_5 reactivity of phosphate rocks.

To gain an idea of the correlation between these different solubilities and the agronomic efficiency of the products, one may refer to table 1 below, devoted to United States phosphate rocks. 1/

Table 1

Solubility of phosphate rocks in various extractants
compared with agronomic efficiency a/

	Rock source					
	North Carolina	North Florida	Central Florida	Tennessee	Idaho	Missouri
Total P ₂ O ₅	30.5	32.4	32.7	30.7	32.5	34.7
	% of total P ₂ O ₅ extracted					
Ammonium citrate, pH 7 <u>b/</u> , <u>c/</u>	26.1	20.4	16.2	14.9	11.5	1.4
Citric acid, 2%	49.6	29.7	25.7	25.3	23.8	6.0
Formic acid, 2%	85.8	30.3	28.0	21.3	33.1	5.0
Ammonium citrate, pH 3 <u>b/</u>	81.1	48.4	42.3	31.5	27.9	5.3
	Relative agronomic efficiency, TSP = 100 <u>d/</u>					
Rice <u>e/</u>	84	46	37	6	24	0
Corn <u>f/</u>	77	41	34	10	33	1

a/ From unpublished co-operative studies by IFDC and TVA.

b/ Ammonium citrate solution concentration was equivalent to 185 g of citric acid per litre.

c/ Extracted 30 minutes at 65°C (AOAC method). All others extracted 1 hour at room temperature.

d/ Yield response expressed as percentage of response to TSP.

e/ Greenhouse experiment: Engelstad, O.P., A. Jugsujinda and S.K. De Datta. 1974. Soil Science Society of America Proceedings, 38:524-529.

f/ Greenhouse experiment: Khasawneh, F.D., TVA unpublished information.

Tables 2 and 3 hereafter incorporate, additionally, rocks from other countries, the best known for this type of use being the Tunisian Gafsa rock.

1/ The tables hereunder are taken from the Fertilizer Manual published by UNIDO in 1980, the preparation of which was directed by Travis P. Hignett, then Special Consultant to the International Fertilizer Development Center IFDC.

Table 2
Reactivity scales of the phosphate rocks
as measured by various methods

Rock source	Total P ₂ O ₅ in rock, %	Soluble P ₂ O ₅ , % of rock					Absolute citrate solubility % a/
		Neutral ammonium citrate		2%	2%	pH 3	
		1st	2nd	Citric acid	Formic acid	Ammonium citrate	
Huila, Colombia	20.9	0.8	3.4	5.2	6.2	10.5	12.2
Pesca, Colombia	19.8	1.9	1.9	7.0	5.3	8.5	9.7
Sechura, Peru	30.0	5.3	5.4	15.2	21.8	24.1	14.9
Gafsa, Tunisia	30.0	4.9	5.6	14.1	22.4	21.1	18.5
North Carolina	29.9	7.2	6.7	15.9	25.7	24.8	19.8
Central Florida	32.7	3.0	3.2	8.4	8.2	14.0	10.1
Tennessee	30.1	2.6	2.7	8.8	6.9	9.8	5.1

a/ Solubility of P₂O₅ in neutral ammonium citrate as determined by a method described in reference (4).

Table 3
Relative dry matter yield of crop response
to seven phosphate rocks

Rock sample	Relative dry matter yield, %		
	Guinea grass a/	Beans b/	Cassava b/
Huila	44	82	90
Pesca	30	60	88
Sechura	100	92	-
Gafsa	85	90	100
North Carolina	88	100	98
Central Florida	57	78	92
Tennessee	38	67	86
No P (check)	0	43	41

a/ Greenhouse experiment.

b/ Field experiment.

From the above one can deduce the correlation coefficients between reactivity and fertilization (see table 4 hereunder).

Table 4

Correlation of various reactivity scales of the phosphate rocks and the dry matter yields of guinea grass and beans

<u>Method of evaluation</u>	<u>Correlation coefficient, r</u>	
	<u>Guinea grass</u>	<u>Beans</u>
Neutral ammonium citrate <u>a/</u>	0.867	0.778
Neutral ammonium citrate <u>b/</u>	0.927	0.961
2% citric acid	0.921	0.774
2% formic acid	0.944	0.879
Ammonium citrate, pH 3	0.984	0.910
Absolute citrate solubility	0.811	0.874

a/ First extraction.

b/ Second extraction.

Moreover, in this case the field experiment with beans was continued over three harvests covering a period of 18 months. The results showed that the relative agronomic efficiency (RAE) of the ground phosphate rocks, as compared with triple superphosphate (TSP), increases with time.

	<u>RAE of phosphate rocks</u>		
	<u>High reactivity</u>	<u>Medium reactivity</u>	<u>Low reactivity</u>
1st crop	90	71	29
2nd crop	105	65	40
3rd crop	115	95	85
Total, 3 crops	105	77	51

As indicated in section I.9 above, the agronomic value of a fertilizer varies not only with its own reactivity, but also with the nature of the soil: pH, percentage of organic matter, type of soil and type of crop, developing a specific aggressivity for phosphate rock.

The main advantage of finely ground phosphate rock, applied directly, is its low cost (this may be less than 50 per cent of that of imported TSP), the low capital investment, the low requirement of skilled labour and the absence of chemical reagents.

An inconvenience noted is the dusty appearance of the product; this can be limited at the cost of an additional operation: granulation or, preferably, mini-granulation.

V.2. Phosphates having undergone thermal treatment

Half-way between the rustic technology of ground phosphates and the more sophisticated technology of conventional chemical fertilizers, thermal treatment may meet certain local fertilization needs if an appropriate ore and cheap energy are available locally.

V.2.1. Iron-aluminium phosphate rocks calcined at low temperature

As iron-aluminium phosphate rocks generally contain chemically bound water, their calcination in a kiln at low temperature (500-600°C) breaks up the basic molecule. The best known case is the Thiès ore in Senegal, which is industrially calcined to give a fertilizer named Phospal. Below will be found some explanations taken from the producer's information sheets.

V.2.1.1. Raw material

Phospal comes from an ore mined near Thiès, Senegal, where abundant reserves of a raw material with a constant phosphoric acid content have been located: over 100 million tons on a concession of 30,000 ha.

This ore is a double (calcium and aluminium) phosphate. Its formation is explained by the action of water in the ground on calcium phosphates deposited, at the beginning of the tertiary era, among clay sediments.

Mineralogists have distinguished complex crystalline phases such as pallite and pseudowavellite ($\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5, \text{H}_2\text{O}$).

The chemical analysis of the ore will be found hereunder.

COMPOSITION OF THE ORE

	<u>%</u>		<u>%</u>
Phosphoric acid (P_2O_5)	29.5	Total silica (SiO_2)	2.5
Alumina (Al_2O_3)	30.5	Titanium oxide (TiO_2)	1.5
Calcium oxide (CaO)	9	Fluorine (F_2)	0.8
Iron oxide (Fe_2O_3)	10	Chemically bound water	15.5
		Miscellaneous	0.7

Quantitative analysis carried out on the dried ore at 110°C.

V.2.1.2. Manufacture of Phospal

A. The crushed ore is calcined in a kiln. This results in fundamental changes in the rock's structure:

Physical changes: Dissociation of the complex and dense crystals of the ore, giving way to a new structure with smaller molecules whose ability to react with soil solutions is thus enhanced;

Chemical changes: The iron is taken out of the phosphatic molecule as free iron oxide, which gives Phospal its red ochre colour. In addition, the departure of the chemically bound water (initially 15.5 per cent) results in an increase in the P_2O_5 content.

These transformations have two consequences:

One is chemical: the phosphoric acid becomes largely soluble in ammonium citrate;

The other is agronomic: the fertilizing value is created.

The following results demonstrate the effect of the treatment of the ore (experiment on oats in a calcareous clay loam soil):

Harvest per vessel
(dry matter)

Reference without phosphoric acid	4 g
Same fineness (ore: 300 kg/ha)	5 g
(Phospal: 300 kg/ha)	24 g

B. To complete the manufacture, the calcined material is ground (100 mesh).

V.2.1.3. Characteristics of Phospal

Composition*

A. Principal and secondary constituents

P ₂ O ₅ (minimum)	34% (of which 26% is soluble in Joulie ammonium citrate)
Al ₂ O ₃	35%
CaO	10.4%
Fe ₂ O ₃	11.5%
SiO ₂	2.9%
TiO ₂	1.7%
MgO	0.3%
Loss on ignition and miscellaneous	4.2%

B. Oligo-elements

(a) Minor elements recognized as being useful: zinc, copper, manganese, molybdenum, cobalt, boron.

(b) Other trace elements: vanadium, chromium, nickel, lead, tin.

Only the phosphoric acid is guaranteed; the percentages of the other constituents, which may vary slightly, are given only for information.

V.2.2. Phosphates calcined at high temperature

A variety of phosphatic fertilizers can be prepared from low-grade rock by reactions taking place at high temperatures which destroy apatite structures and allow recombination of phosphate into more reactive compounds of higher solubility. Many of these substances have a long history of being used in agriculture but have been displaced in recent years by high-analysis fertilizers with water-soluble phosphate.

The best-known products of this type are defluorinated phosphate rock, basic slag, fused calcium-magnesium phosphate and Rhenania phosphate. Most of the above are prepared from phosphate rocks, alone or admixed with various inorganic reagents, and most of the apatite decomposition reactions are accompanied by the evolution of fluorine.

These compounds obtained at high temperatures are not to be confused with the calcined phosphates obtained from high-grade rock. The latter undergo a milder treatment at temperatures between 650°C and 1,000°C, which do not destroy the

* The information above concerns Phospal 34.

apatite structure. This basically promotes a phase transition from francolite-type apatites to the more stable and hence less reactive fluorapatite form.

While premium-grade phosphate rocks lack sufficient quantities of accessory minerals to promote a significant degree of apatite decomposition during calcination, low-grade phosphate rocks, on the other hand, which may contain as much as 30-40 per cent of accessory minerals, generally supply products that have greater reactivity than the original rock thanks to the presence of phosphate compounds formed during calcination.

Commercial thermal phosphate products are prepared from mixtures of phosphate rocks or concentrates and selected reagents in the stoichiometric proportions to yield specific products of a vitreous or crystalline nature.

The small group of possible reagents is listed hereunder.

Table 4

REACTANTS USED TO DECOMPOSE APATITES

<u>Silica and silicates</u>	<u>Phosphates</u>	<u>Halides</u>	<u>Alkali metals</u>	<u>Alkaline earths</u>
Quartz, opal <u>a/</u>	H ₃ PO ₄	Chlorides (Na,Ca,K,Mg) <u>a/</u>	Carbonates (Na,K)	CaCO ₃ , CaMg(CO ₃) ₂ <u>a/</u>
Feldspar	Alkali phosphates	KMgCl ₃ .6H ₂ O (carnallite) <u>a/</u>	Sulphates (Na,K,NH ₄)	CaSO ₄ .2H ₂ O (gypsum) <u>a/</u>
Olivine, serpentine <u>a/</u> (Mg silicate)	AlPO ₄ .nH ₂ O <u>a/</u>		Silicates (Na,K type) <u>a/</u>	Mg(Na,K) ₂ (SO ₄) ₂ .4H ₂ O <u>a/</u>
			Hydroxides (Na,K)	

a/ Denotes reactants that may occur in natural association with apatite in phosphate rocks.

Many traditional diluents of low-grade phosphates are found in this list; some types of low-grade phosphate rock may thus require little adjustment for the preparation of certain particular types of thermal phosphate, whereas they may be totally unusable for either direct application or chemical fertilizer manufacture.

The varieties of thermal phosphate products can be grouped on the basis of structural type and chemical composition as shown in the table below.

Table 5

Types of thermal phosphate products

<u>Idealized composition</u>	<u>Structural type</u>	<u>Reagents a/</u>
$(Ca.Mg)_3(PO_4)_2$ $Ca_4C(PC_4)_2$ $CaNaPO_4$ $CaKPO_4$	α, β -TCP; whitlockite; glasses Hilgenstockite; basic slags Crystalline "Rhenania" compounds	None Alkaline earths Alkalis
$Ca_7P_2Si_2O_{16}$ $(Ca,Mg)-P_2Si_2O_{16}$ $Ca_5Na_2(P,Si)_4O_{16}$	Nagelschmitite series of solid solutions	Silica, Mg silicates
$Ca_5P_2SiO_{12}$	Silicocarnotite series of solid solutions	Silica, silicates
$Ca_{2+n}(PnO_3)_n$ where $n \geq 2$	Polyphosphates	Phosphates
Ca_2ClPO_4	Chlorospodiosite	Halides

a/ Accessory mineral components in phosphate rock may supply part or all of the necessary reactants.

V.2.2.1. Defluorinated phosphates

There is a substantial production of defluorinated phosphates in Japan (about 100,000 tons/year).

Ground, high-grade rock is mixed with small proportions of calcium carbonate or sulphate and phosphoric acid. The mixture is calcined in a rotary kiln (diameter: 2.7 m; length: 45 m), and gives a product containing 38-42 per cent P_2O_5 of which over 90 per cent is soluble in 2 per cent citric acid and 85-90 per cent is soluble in neutral ammonium citrate solution. Practically all the fluorine is driven off and recovered in the form of sodium bifluoride ($NaHF_2$). The principal phosphate compound in the product is tricalcium phosphate. Requirements per ton of product containing 41-42 per cent total P_2O_5 are:

Phosphate rock (37% P_2O_5)	900 kg
Wet-process acid	95 kg of P_2O_5
Sodium carbonate	120 kg
Heavy fuel oil	200 kg

N.B. In the United States of America, this type of product is mainly used in animal feed.

V.2.2.2. Basic slag

This is a by-product of the steel industry. Iron made from high-phosphorus ore is converted to steel in a Thomas converter by oxidation in contact with a basic (high CaO) slag. It is mainly in western Europe that this product is obtained; the range of composition is:

P ₂ O ₅	15-20%
SiO ₂	4-6%
CaO	42-50%
MnO	3-6%
Al ₂ O ₃	0.5-2.5%
MgO	2-4%
Fe	9-13%

85-90 per cent of the P₂O₅ is soluble in 2 per cent citric acid; this P₂O₅ is present as calcium silicophosphates-silicocarnotite (5CaO-P₂O₅-SiO₂) and nagelschmitite (7CaO-P₂O₅-2SiO₂).

The consumption of agricultural-grade basic slag was still equivalent to 1.2 million tons of P₂O₅ in 1973. As a result of the use of low-phosphorus ores and changes in steelmaking processes, this quantity has decreased drastically; it amounted to less than 600,000 tons in 1977, and is practically nil at the present time.

This shows that the slag is regarded as a good fertilizer on acid soils; it is also still valued for its liming effect and micro-nutrient content.

It is applied in a finely ground state or granulated with potash.

V.2.2.3. Fused calcium magnesium phosphate (CMP)

The Tennessee Valley Authority (TVA) has developed a process in which a mixture of phosphate rock and olivine or serpentine (magnesium silicate) is fused in an electric furnace (850 kWh/ton). The molten product is quenched with water (10 tons of quench water, which may be recycled, is required per ton of product) and used in a finely divided state as a fertilizer. The product is a calcium magnesium phosphate glass containing 20 per cent P₂O₅ and 15 per cent K₂O. Over 90 per cent of the product is soluble in citric acid after grinding (70% finer than 150 microns).

The main compositions of the reagents used are:

Olivine	(Mg,Fe) ₂ SiO ₄
Serpentine	Mg ₃ H ₄ Si ₂ O ₉
Garnierite	(Mg,Ni) ₂ H ₂ SiO ₄
Magnesite	MgCO ₃

Greenhouse tests by the United States Department of Agriculture have shown that the product is, on the average, more effective than superphosphate when used on acid soils. It also has a liming value equivalent to 0.5-0.7 tons of calcium carbonate per ton of material, and the magnesium oxide content is available to growing plants. In some situations, the soil-soluble silica may be an advantage.

CMP is produced in several plants in Japan, where the annual production is 500,000 tons. It is also produced in Korea, Taiwan, China, Brazil and South Africa.

V.2.2.4. Rhenania phosphate

This is made by calcining a mixture of phosphate rock, sodium carbonate and silica in a rotary kiln, at 1,250°C. Enough sodium is used to form the compound CaNaPO_4 and enough silica to form Ca_2SiO_4 , with the excess calcium. Typical charge proportions are one part of sodium carbonate to three parts of phosphate rock plus enough silica to raise the SiO_2 content of the product to about 10 per cent.

The product contains 28-30% P_2O_5 which is nearly all soluble in neutral or alkaline ammonium citrate solution, even though most of the fluorine remains in the product.

It is used in pulverized form or granulated with potash.

The overall reaction is assumed to be:



Requirements per ton of 0-29-0 product are:

Phosphate rock, 38.7% P_2O_5	749 kg
Soda ash	289 kg
Sand, 97% SiO_2	77 kg
Electricity	36 kWh
Steam	10 kg
Fuel oil	66 kg

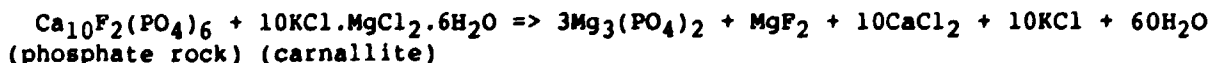
The product has been reported to be substantially more effective than superphosphate on several acid tropical soils in Costa Rica, Liberia, the Congo, Zaire and Malawi. This superiority is probably due to the product's alkalinity and resistance to fixation by the soil. The sodium and soil-soluble silica may also be beneficial.

V.2.2.5. Other products mentioned

Calcium metaphosphate: developed by TVA, which produced about 1 million tons. Dependence on elemental phosphorus made the cost prohibitive.

Chlorospodiosite, Ca_2ClPO_4 (33.7% P_2O_5): research has been conducted on this at TVA and IFDC, because its melting point is low (600°C as against 1,100-1,400°C for other salts). However, this product has not (yet?) reached the commercial production stage.

Magnesium phosphates: a pilot process has been developed by Israel Mining Industries (IMI).



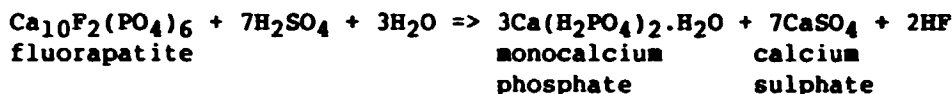
Much of the information used in the drafting of this chapter has been taken from the Fertilizer Manual already mentioned, and from the text of a lecture by Mr. Roy and Mr. McClellan of IFDC, whose source could not be found but which is less than five years old.

The reaction takes place at 400°C; the final product is washed with water to remove the calcium and potassium chlorides, and the remaining solid, consisting mainly of trimagnesium phosphate, is dried.

The final product is a first-class fertilizer, much too sophisticated to be of interest to us in considering the use of low-grade phosphates.

V.3. Single superphosphate (SSP)

Produced by reaction of the phosphate rock and sulphuric acid, without any separation of the reaction products:



The advantages of SSP are:

The process is simple, requiring little technological skill and capital investment;

The economies of scale are minor, so that small plants can be economical;

Since the plant is not expensive, it pays for itself even without continuous utilization; in fact, many SSP plants operate on a seasonal schedule;

The fertilizer effectiveness of SSP is unquestioned; in fact, it is a standard of comparison for other fertilizers;

SSP supplies two secondary elements, sulphur and calcium, which are sometimes deficient in the soil.

After reaction, the product is dumped in a den for a period from half an hour to a few hours to allow the solidification which results from the crystallization of monocalcium phosphate. Then it is excavated and sent to the curing pile for a few weeks to complete the reactions and so reduce the free acidity.

For many years, SSP was produced by batch-mixing methods (see figure 1 below). Most modern plants use continuous mixing and denning processes (see figure 2 below).

The operating requirements per ton of SSP are, for example:

626 kg phosphate rock
390 kg sulphuric acid
100 kg water
3 kWh electricity (plus rock grinding, at a rate of
7-25 kWh per ton of rock)
0.15 man-hours, operating labour
0.015 man-hours, supervision

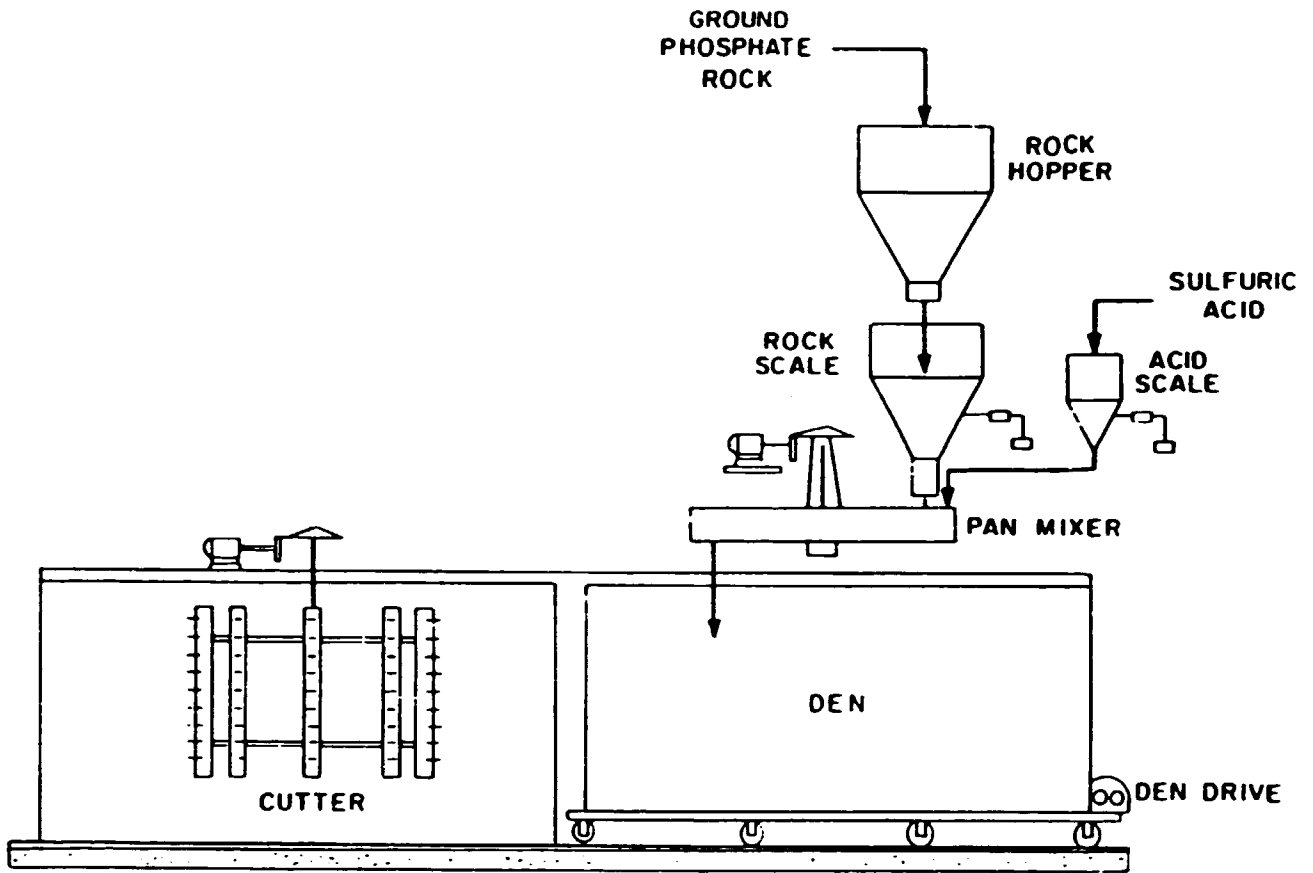


Figure 1. Batch Manufacture of Single Superphosphate.

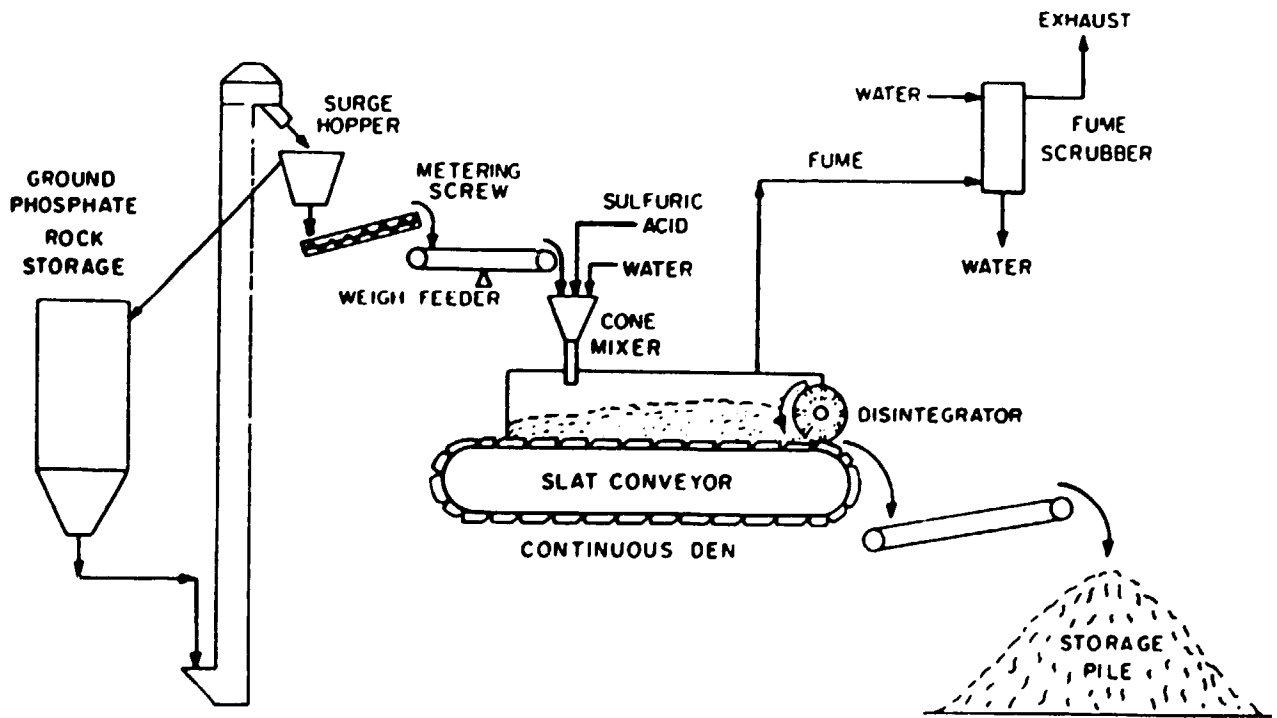


Figure 2. Continuous Manufacture of Single Superphosphate.

V.4. Under-acidulated derivatives

V.4.1. SSP + phosphate rock or Kotka superphosphate

The name comes from the city in Finland where the product was originally made.

Advantages: little curing is needed
the free acid content is low

The effectiveness of this product is equal to that of equivalent amounts of fully acidulated superphosphate plus raw phosphate rock applied separately.

A typical chemical composition, compared with those for superphosphates, is given in table I below.

Table I

Composition of single superphosphates

<u>Source of rock</u>	<u>Composition, % by weight</u>								
	<u>P₂O₅</u>		<u>Water soluble</u>	<u>Free acid</u>	<u>H₂O</u>	<u>CaO</u>	<u>SO₃</u>	<u>R₂O₃</u>	<u>F</u>
	<u>Total</u>	<u>Available</u>							
Florida	19.9	19.6	17.5	2.4	5.9	27.1	28.4	1.3	-
Florida (granular)	21.5	20.7	17.4	0.6	1.1	30.5	30.7	2.3	1.6
Morocco	19.8	-	18.8	2.0	8.4	-	-	-	-
Morocco	21.4	20.2	-	1.7	9.8	-	-	-	-
Ocean Island	22.8	-	20.8	4.6	10.6	-	-	-	-
Morocco and Kola (Kotka) <u>a/</u>	22.8	14.6 <u>b/</u>	14.5	1.3	8.9	-	-	-	-

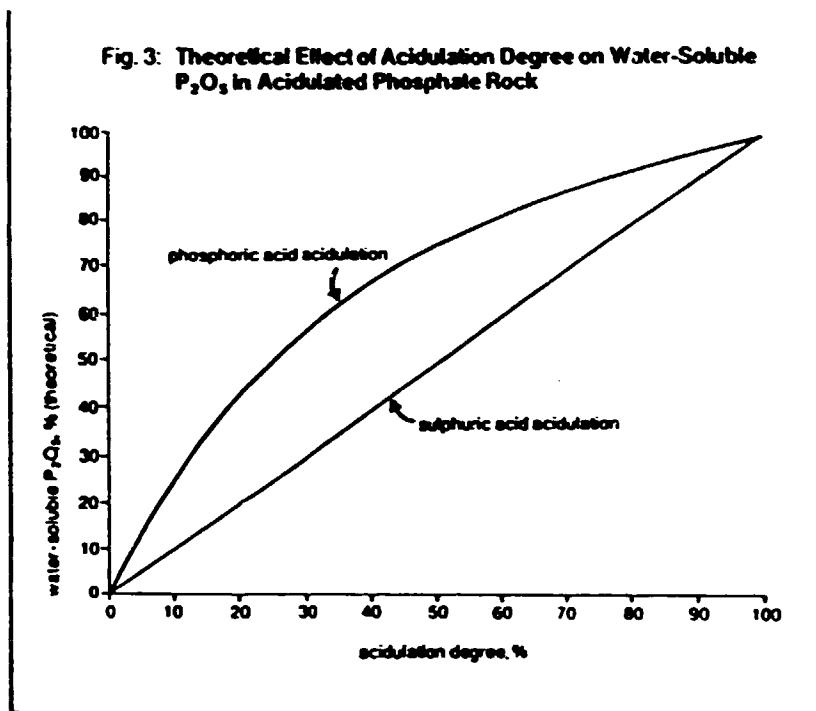
a/ Superphosphate plus additional phosphate rock.

b/ Alkaline citrate soluble.

V.4.2. Partially acidulated phosphate rock (PAPR)

Developed some 12 years ago by IFDC, this fertilizer has met with some success in several tropical countries.

When a phosphate rock cannot be directly applied owing to insufficient reactivity, partial acidulation, i.e. treatment by a fraction (expressed as a percentage) of the stoichiometric acid quantity, will improve solubility to a degree that is a function of the degree of acidulation.



The economical choice is to acidify using sulphuric acid, and there are two possible routes:

Production of a powdery product or "run-of-pile" (ROP), with or without post-granulation (see figure 4 below);

Single-step production of a granular product by a plant with combined acidulation-granulation (see figure 5 below).

Process variables

The behaviour of phosphates during acidulation can hardly be forecast because of the complexity of the reactions and the influence of associated compounds, so that preliminary testings are necessary to select the best operating conditions for each phosphate.

It will be noted that some rocks unsuitable for SSP manufacture may very well be suitable for partial acidulation. The latter is well adapted to low-grade ores.

This is the case for instance, according to IFDC, with the Kodjari rock in Burkina Faso; this sedimentary-type rock, containing high levels of silica, iron and aluminium, is very unreactive and quite unsuitable for SSP manufacture. Acidulation of this rock beyond 50 per cent results in a paste-like material and, moreover, the presence of iron and aluminium gives reaction products which decrease the availability of phosphorus (see tables II and III below). The lower the reactivity of the rock, the more diluted the acid must be (for example, 60-75 per cent as compared with 75-90 per cent for soft rocks), and the more limited is the acidulation possible before the point is reached where free acid makes the product sticky. It should also be noted that the powdery product, which has a curing time, accepts higher acidulation degrees than the one-step process. In addition, a decline in the solubility of the P_2O_5 takes place after several weeks or when too high temperatures are reached during drying (over $120^{\circ}C$). These properties are illustrated by tables II and III below.

Fig. 4: Run-of-Pile (ROP) Production Process for PAPR

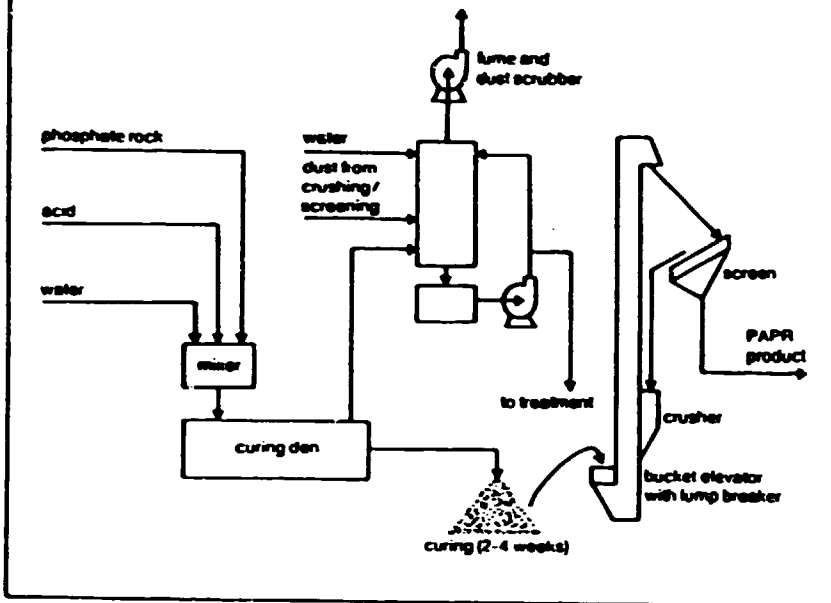


Fig. 5: Single-Step Acidulation/Granulation (SSAG) Process for PAPR

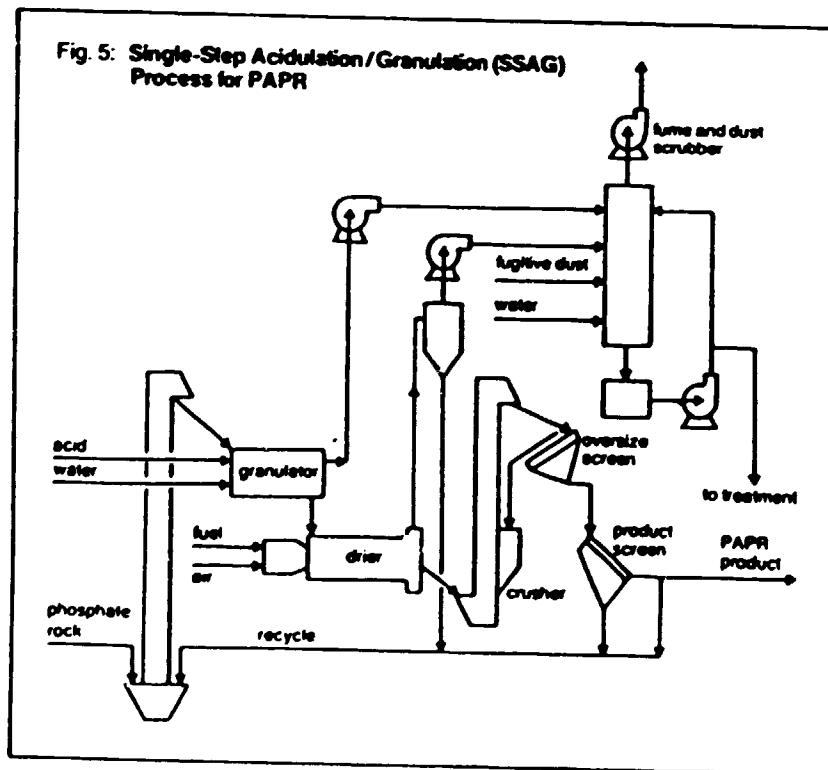


Table II

Maximum acidulation degree predicted for various phosphate rocks according to PAPER process

Source rock	Reactivity*	Predicted acidulation degree (%)	
		Run-of pile	Single step granular
Huila, Colombia	Medium	100	30
Kodjari, Burkina Faso	Low	60	40
Media Luna, Colombia	Low	100	70
Parc W, Niger	Low	100	60
Pesca, Colombia	Medium	100	30
Tahoua, Niger	Medium	60	40
Tilemsi Valley, Mali	Medium	70	50

* Low = Neutral ammonium citrate-soluble P₂O₅ 0-3%
 Medium = Neutral ammonium citrate-soluble P₂O₅ 3-6%

Table III

Influence of curing (aging) on P₂O₅ solubility in granular PAPER products

Product	Degree of acidulation (%)	Total	P ₂ O ₅ Solubility			Free acid (as P ₂ O ₅)	Free water	Fe ₂ O ₃	Al ₂ O ₃
			water-soluble	NAC-soluble†	Available				
Kodjari (Burkina Faso)									
Fresh*	50	18.0	6.5	3.0	9.5	na	na	3.1	4.0
Aged**	50	18.3	3.3	5.4	8.7	<0.1	2.0		
Tilemsi Valley (Mali)									
Fresh*	30	22.7	6.6	4.8	11.4	2.1	3.8	6.3	2.5
Aged**	30	23.1	2.6	5.7	8.3	<0.1	2.2		
Tahoua (Niger)									
Aged 1 day	50	22.6	6.5	2.9	9.4	1.1	1.3	10.3	2.1
Aged 1 week	50	22.4	6.6	3.3	9.9	0.9	1.8		
Aged 1 month	50	22.8	5.9	3.7	9.6	0.3	1.9		
Aged 3 months	50	22.4	4.7	4.0	8.7	0.1	na		
Aged 6 months	50	22.3	4.5	5.1	9.6	<0.1	1.6		

† Excludes water-soluble P₂O₅ fraction
 * Analyzed day of production
 ** Analyzed 3 weeks-12 months after production
 na Not available

V.5. Humifert

During the Global Preparatory Meeting held at Lomé, Togo, in February 1988, the Humifert process was presented; 1/ it is a simplified manufacture of binary NP fertilizer with humus. This new process is quite attractive and, if it can be successfully industrialized, it could provide an interesting solution in the case of some enclaved countries.

1/ Presentation by Mr. Besnard of SOPRECHIM.

V.5.1. What is the route proposed?

Considering, firstly, that phosphate dissolution can only be obtained economically by a reaction with an acid and, secondly, that many countries have phosphate resources but neither sulphur nor pyrites, SOFRECHIM has looked for the cheapest approach in terms of investment and of reagents. It turns out to be a simplified "nitric route".

For the nitric reaction, one needs a weight of ammonia about equal to the weight of sulphur that would be needed to dissolve a given weight of phosphate; drastically simplifying the operations required to produce high-grade fertilizers by this route, it is possible to imagine mini-plants suitable for operations in developing countries.

The simplification in question essentially concerns two points:

- (1) Manufacture in situ of the nitric acid required and the resulting elimination of the need for the absorption columns of conventional nitric acid plants;
- (2) Addition to the products reacted of an absorption medium based on organic matter which results both in an accelerated absorption of nitrous oxides and in the solidification of the slurry produced by the nitric reaction of the phosphates, which look like a wet compost.

As organic base, one can use agricultural wastes such as tree-tops, bagasse, straw (rice, cotton, etc.), peat or even lignite. The end product will have an N/P ratio which will be a function of the basic rock concentration and of the CaO/P₂O₅ ratio in the rock.

Starting from a 26 per cent P₂O₅ rock, the average composition will be around 5 per cent nitrogen and 14 per cent P₂O₅, water and citrate soluble, or altogether 19 per cent fertilizing materials (on dry matter).

This concentration compares with that of the "superphosphates" manufactured from similarly concentrated rocks which contain about 18 per cent P₂O₅, while in the fertilizer obtained through the nitric route there is some directly available nitric nitrogen besides a significant amount of P₂O₅.

V.5.2. Agronomic value of the Humifert fertilizer

Many comparative tests have shown the agronomic efficiency of the Humifert fertilizer.

The trials, carried out by various agronomic institutes, generally following the Standford and Kent method, compared the results obtained with the Humifert fertilizer and the results obtained with fertilizers manufactured from various phosphate rocks by classical routes.

For example, the following products were obtained with two completely different rocks:

	Case 1	Case 2
Ore:	Ancient	Recent
Content of P ₂ O ₅	27	31
CaO	34	46
SiO ₂	25	9
Fe ₂ O ₃ + Al ₂ O ₃	3	9.5

Relative quantity of dry organic matter produced under identical conditions with:

Humifert fertilizer	197	186
Nitric acid reaction fertilizer	185	173
Partially acidulated sulphuric reaction fertilizer	173	171
Reference without fertilizer	100	100

This fertilizer has the advantage of bringing to the soil organic materials which improve the soil's structure and which promote the absorption of mineral substances by the plants by keeping the metals (Fe, Al) as chelates, which avoids the degradation of the rock to the insoluble state. These organic materials also recycle a portion of the potassium taken away by the crops; this element would otherwise be lost.

V.6. Composting

The basic principle consists in submitting agricultural wastes (cassava, rice straw, etc.) to fermentation in order to produce organic acids (citric, lactic, oxalic, humic, etc.) which can be mixed and composted with phosphate rock and supply a product whose phosphate is more available. This technology would be accessible to the farmer alone or to small co-operatives; it would offer the advantage of increasing the availability of the phosphates from local rocks without importation of costly reagents.

V.7. Biosuper

Research carried out during this decade has shown that rock-sulphur, rock-pyrites and rock-urea mixtures give promising results under certain agro-climatic conditions. In addition, an increase in availability of sulphur to plants has been reported when the rock-sulphur mixture is inoculated with the sulphur-oxidizing bacterium Thiobacillus thiooxidans.

The product obtained, called "Biosuper", may constitute an effective way of utilizing indigenous phosphate rocks if the economics are favourable.

TAILPIECE

VI. CONCLUSIONS

VI.1. If an African country with access to the sea and substantial accessible phosphate resources wishes to process them with a view to expanding the range of its products on the international market, it must build a world-class chemical complex in order to be competitive.

This means a phosphoric acid plant with a capacity of at least 250,000 tons/year of P_2O_5 , at least a part of which should be processed into fertilizers (DAP or TSP) while the sulphuric acid required is supplied by a plant with a capacity of at least 700,000 tons/year of H_2SO_4 .

Under the best conditions as regards infrastructure and economic environment, this means an investment of not less than 250 million dollars which must incorporate the most modern technical features in order to be competitive both in terms of quality and in terms of price. This implies for the staff a "learning curve" which may last many years; the example below shows this.

Let us take the case of a young African engineer, freshly graduated, who is hired by the company. If one is in a country that is beginning to industrialize its economy, there is little chance that he will find there managers and assistants with a background in this type of industry. Experience shows that, in this case, the young engineer takes care of the most urgent needs by doing part of the work of his assistants, which is a good way of gaining experience and thus of learning what one must know in order to give orders to one's assistants. However, without sufficient guidance from the engineer's superiors, there is a danger that the result will be poor training and personal failure. If the same situation occurs too often at different hierarchical levels, there is even a risk of failure for the whole team and for the company.

It is found that the training of a normally gifted engineer beginning operations in an experienced environment takes about five years before he is able not only to understand the processes fully but also to manage his plants in the optimum way, and to keep cool when he goes adrift, in order to be able to take the right decisions. It is therefore important to give his African counterpart a similar training, all the more so as he must learn his job in a sophisticated technical environment, working with costly equipment which may be badly damaged if it is wrongly operated.

The transfer of technology must therefore be specially adapted and, in advance, it must incorporate:

The theoretical and practical training in similar industries of sufficient technical and administrative cadres;

The assistance of an adequate team (adequate in quantity, quality and personal characteristics) from the contractor or the licensing company for the physical reception, the commissioning and the obtaining of guaranteed performances;

Further guiding of the local staff by people:

recruited from outside for their know-how, experience and ability to teach by example and by word;

for a mission of long duration (several years if needed);

with the clearly defined objective, in addition to their technical mission proper, of training the person or people who will replace them and manage the operation subsequently.

The cost of these items, to which must be added on-site training, recycling courses and the lost income due to the slow build-up of the plant's capacity resulting from the lack of experience of the personnel, amounts to a sum which may vary between 25 per cent and 50 per cent of the investment if the problem is effectively tackled (if not, the cost will be much greater and there is even a substantial risk of a total write-off).

Although it does not represent a physical investment in equipment, this sum must be estimated in advance and its financing provided for in the same manner as, for example, the financing of the working capital.

In view of the very special nature of this investment, it would even be conceivable for it to be covered by a specially adapted financing formula. This would avoid giving the funding agencies a big surprise when, shortly after the commissioning of the plant, they are asked to share in a "recovery plan" which in fact has the purpose simply of covering foreseeable expenses that were not foreseen.

VI.2. Enclaved countries or areas having some phosphate resources cannot, of course, aim at investment on this scale. They will have to envisage processing technologies that are capable of supplying adequate fertilizers at costs below those of imported products.

Whatever the conditions, however, success will only be possible if, at every stage of the project, complete professionalism is displayed:

whether it is a matter of assessing the phosphate ore deposit in terms of both quality and quantity (see chapter III),

or of mining this deposit,

or of converting the ore into a phosphatic fertilizer

through beneficiation of the ore, if appropriate,
and/or an operation aimed at rendering the phosphorus soluble.

Although professionalism is essential, it is not sufficient; much integrity is also needed in the appraisal of the facts in order to ensure the harmonious progress of the project and avoid its being skewed by the influence of different interests.

This integrity must be based on great competence so that an independent judgement can be made on the quality of the information supplied and the pertinence of the suggested choices. Consequently, it will be desirable for the project's promoters to obtain the services of an independent expert who should be closely associated with the project so that he will involve himself personally in it.

Ideally, this expert should be a retired person with thorough experience of the industry concerned; this will qualify him from many points of view, i.e:

Availability since, having finished his main contract of employment, he will be free from all allegiances;

Experience acquired during a complete career which confers not only "know-how" and ability but also the coolness that allows a correct appraisal of the facts and the taking of wise decisions;

Work in an industrial environment less sophisticated than the present industrial environment; 30 or 40 years ago, small plants with simple technologies were still in operation, which would be much more manageable for populations that are just discovering industrialization;

A retired person has no career in view and is therefore naturally ready to help the rising generation.

In short, professionalism on the part of the consultants and the integrity of those in charge and their advisers must be supplemented by the complete assumption of responsibility for lucid organization of the transfer of technology, involving the three essential stages mentioned above, i.e. training, assistance and guidance.

VI.3. An example may aid comprehension.

Let us consider a new phosphate rock which it has been decided to convert into SSP or PAPR.

If one is in a milieu without any industrial tradition, with a limited market and an abundant workforce, there is no need to build a sophisticated plant; on the contrary, one will aim at a small capacity plant, rustic in its equipment and in its operation, and easy to maintain; its cost will consequently be limited - let us say around 10 million dollars.

The following, for example, will be recommended:

A batch-mixing process, which will allow simple volumetric metering of the stoichiometric proportions of raw materials.

Dumping of the reaction product in one or more fixed "dens" made from local materials - resinous wood is one of the best anti-acid materials!

Excavation by a drag-line, i.e. standard equipment, with a limited cost thanks to its mass production, easy to maintain and also available for other tasks when the plant is not in operation.

Such a unit can meet, competitively, local needs for the fertilizer produced since:

It is of low cost and can be paid for with a limited production;

Although of small size, it can meet local demand by seasonal operation;

Being simple in design and easy to operate, it does not call for a long "learning curve" and can thus be built and commissioned in a very short time.

VI.4. Comment 1

Some people consider that there is a conflict between meeting local needs through local mini-plants and the distribution of classical fertilizers by big plants aiming at the regional market.

This debate does not seem realistic!

Where the standard fertilizers can be supplied at a competitive cost, 1/ no mini-plant will be opened.

Where these standard fertilizers cannot be used, local production of lower-grade fertilizers with less solubility (slow release), containing more secondary and minor elements, can contribute to the intensification of agricultural production which, later on, will need more fertilizers and, having acquired resources through its development, will be able to supplement its fertilizer needs by buying standard fertilizers from large regional or world-class factories.

VI.5. Comment 2

There is no reason to despise the use of low-grade fertilizers if they provide an economic solution to local fertilization problems. The intensive use of basic slag in western Europe until 10 years ago is an example, and when its role decreased because the supply began to dry up, new low-cost products with limited solubility appeared, doubtless aiming at the same market segment.

VI.6. Comment 3

The prospects for non-conventional fertilizers in Africa will depend on various factors, including agro-climatic conditions, types of crop, the quality and availability of phosphatic ores and accessory materials, sources of energy and transport of raw materials and end products.

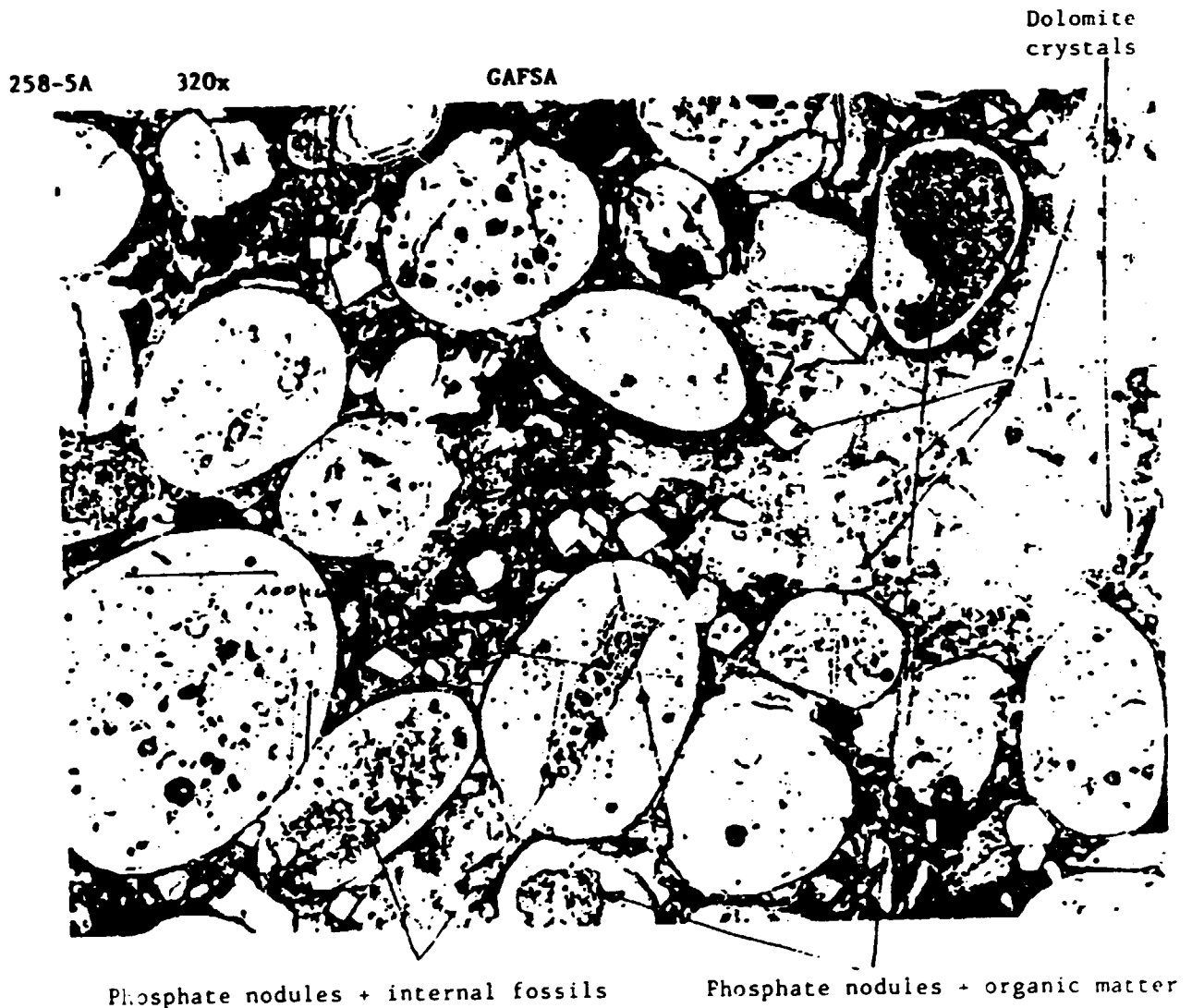
This latter point is basic as we are dealing with low-concentration products.

A decentralized production scheme with small, widely dispersed plants could help in keeping transport costs under control.

1/ A competitive cost taking into account the need per agricultural unit produced, after deduction of any assistance or subsidies, of whatever kind.

Annex 1

Microphotograph of a polished surface of Tunisian
Gafsa phosphate rock (by courtesy of Syres)



It will be noted that we have here a precipitation of phosphate as nodules in a marine environment with subsequent crystallization of the dolomite by reaction with other elements outside the ore deposit.

Annex 2

Microphotograph of a polished surface of Algerian Djebel Onk phosphate rock (by courtesy of Syres)

39-260

320X

DJEBEL ONK

Dolomite

Free quartz



Dolomite

Zoning

Many subidiomorphic grains of dolomite

As will be noted, there are important differences between this and the Gafsa rock, although the latter comes from a neighbouring deposit.

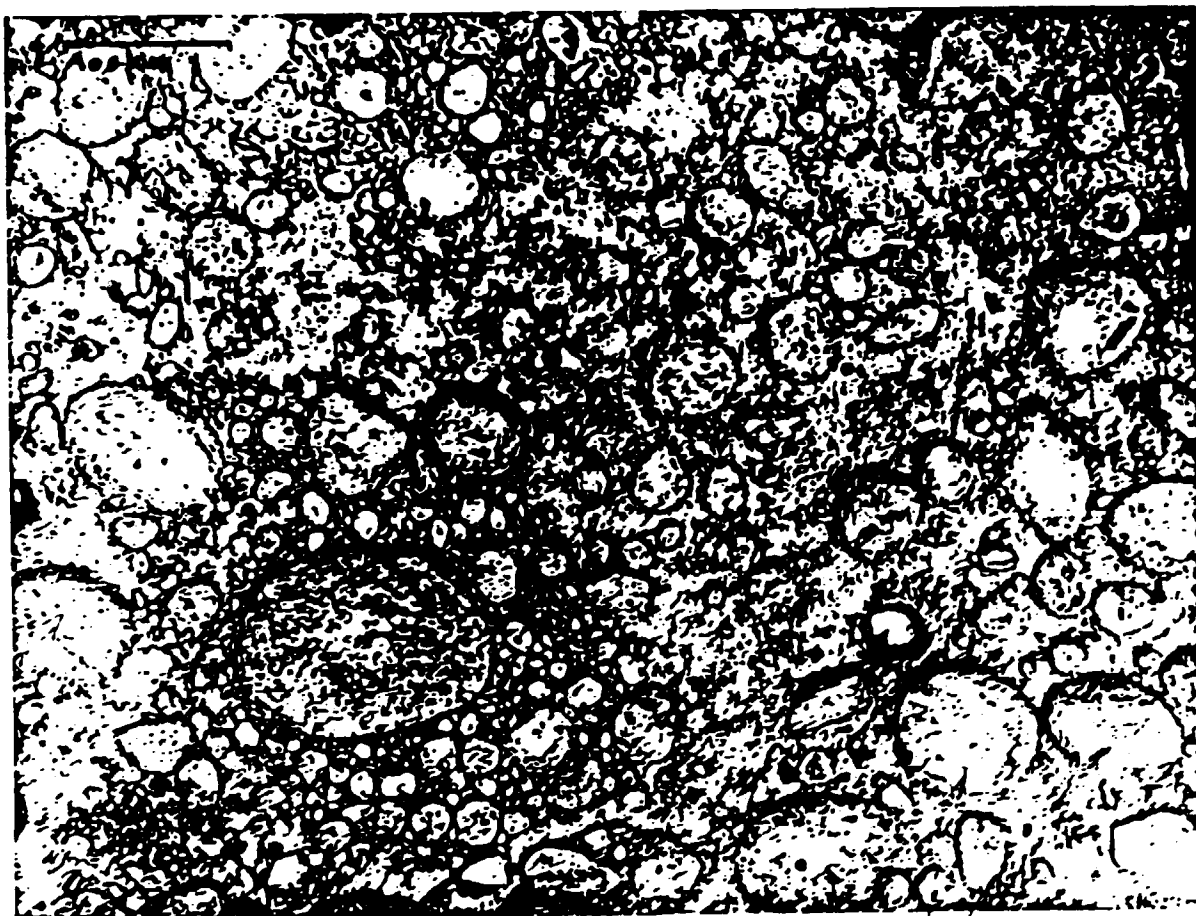
The many polishing scratches, and the presence of non-rolled quartz grains and many subidiomorphic grains of dolomite, suggest that it will be harder than Gafsa, and this is confirmed in practice.

Annex 3

Microphotograph of a polished surface of Moroccan Khouribga phosphate rock (by courtesy of Syres)

25^o - 14 320X

KHOURIBGA



Zoning

Very small grains
of phosphate

Free quartz

Zoning

The presence will be noted of a great number of very small phosphate grains, while the larger grains are generally highly "zoned", which implies radial alterations in the mineralogical composition.

Presence of free quartz.

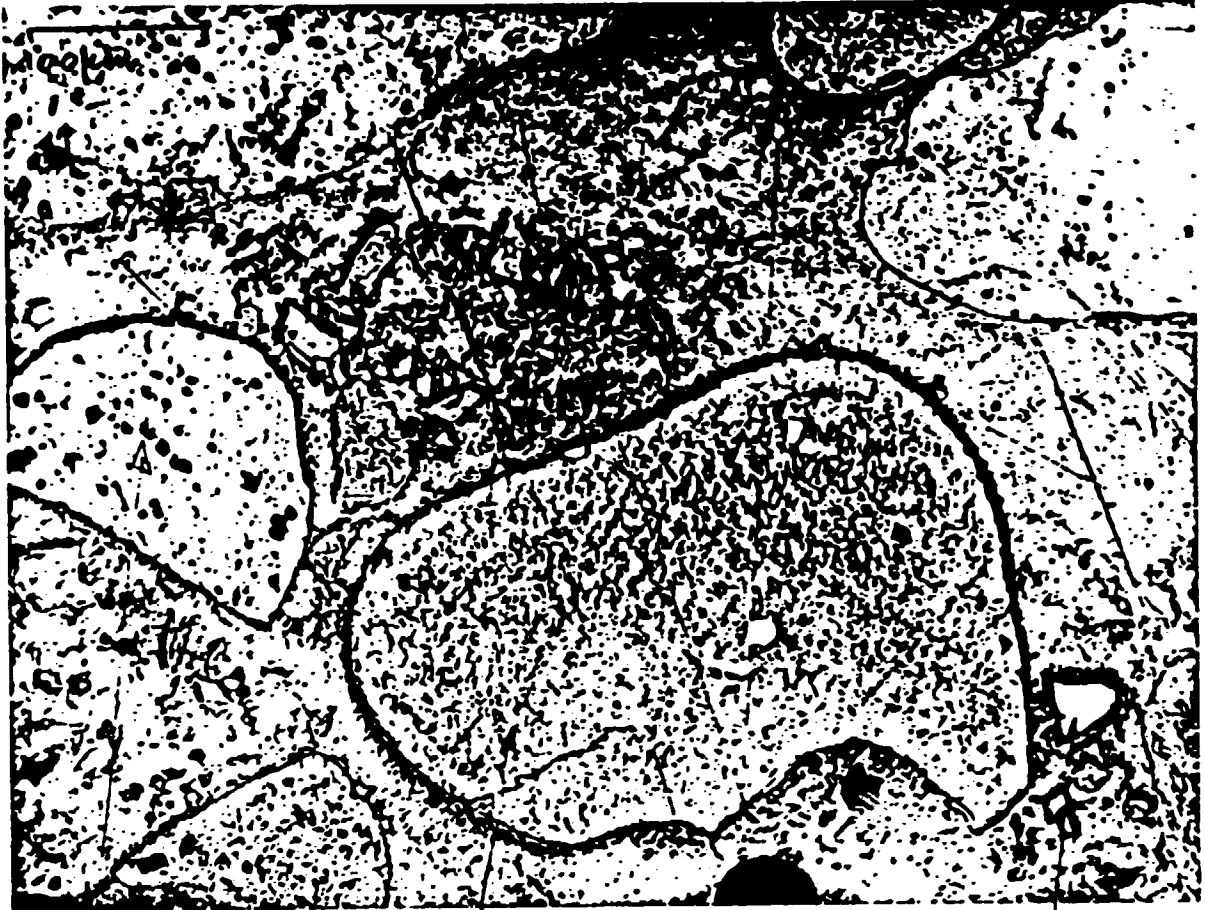
Annex 4

Microphotograph of a polished surface of Central Florida phosphate rock (by courtesy of Syres)

259-20A

320x

C. FLORIDA



Surface porous

Pyritized phosphate
grain (light and shiny
points = pyrites)

Free quartz

It will be noted that the size of the phosphate grains is much larger than in the Khouribga rock; this explains the greater hardness of the Florida rock in spite of a fairly porous surface.

Presence of free quartz and a noteworthy pyritized phosphate grain.

Annex 5

Microphotograph of a polished surface of Chinese Jiang-Chuan phosphate rock (by courtesy of Syres)

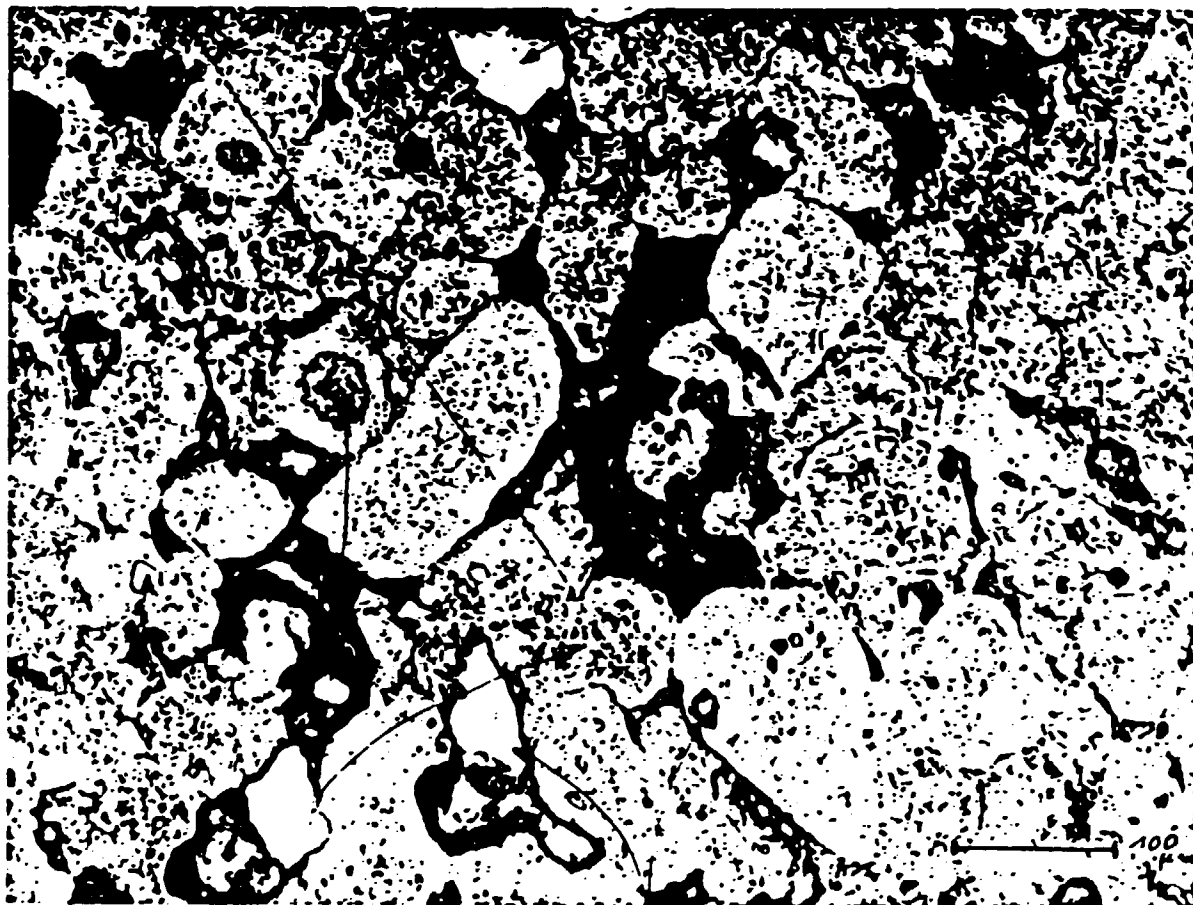
258-37A

320x

JIANG-CHUAN

Free quartz

9-87



It will be noted that this phosphate rock takes the form of rounded nodules with a very regular grain size (± 100 microns), which explains the large quantity of empty spaces (black areas with irregular outlines).

Also to be mentioned: the presence of quartz and pyrites;
the "zoning" of some phosphate nodules.

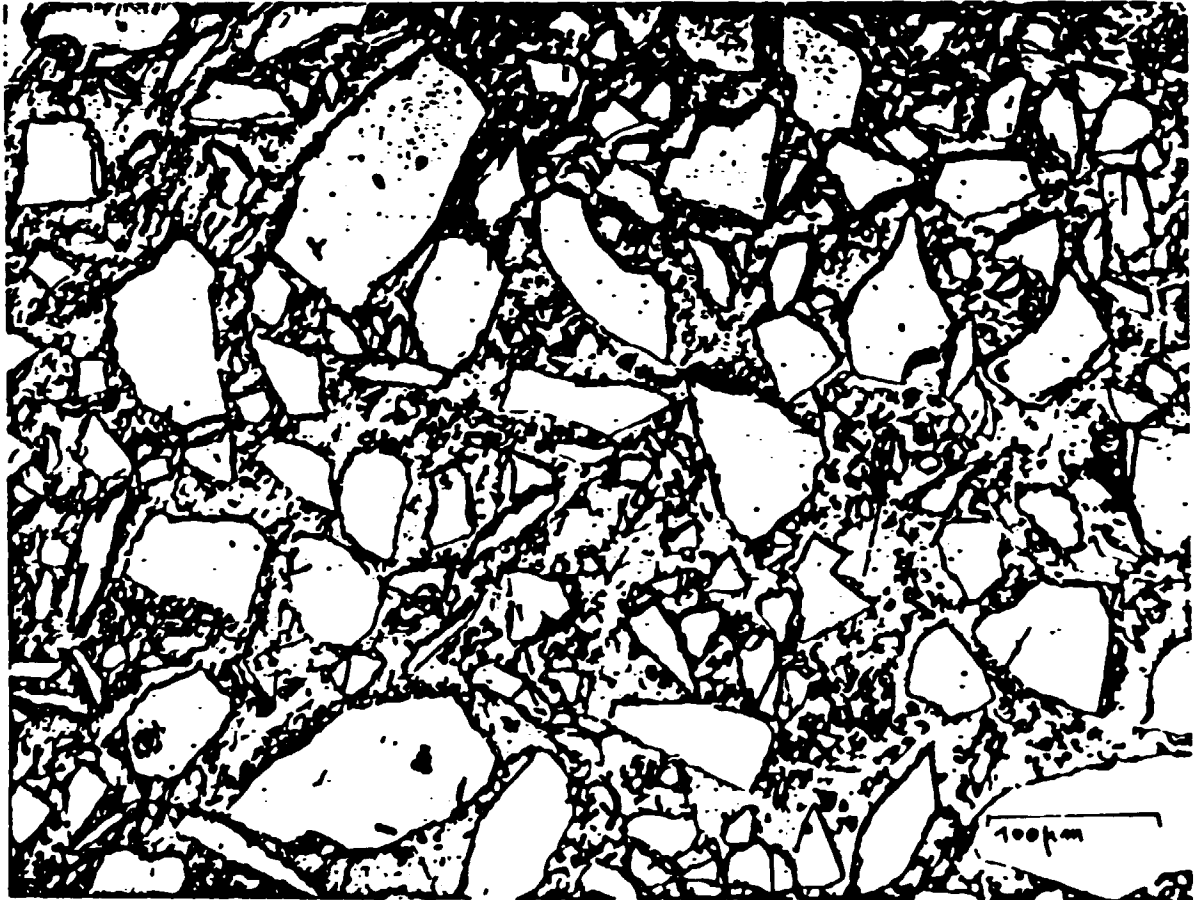
Annex 6

Microphotograph of a polished surface of Russian Kola phosphate rock (by courtesy of Syres)

259-15

320x

KOLA



The appearance of this ground magmatic phosphate rock is completely different from that of the preceding sedimentary phosphates.

It takes the form of angular fragments of apatite crystals without any trace of porosity, which indicates great hardness and low reactivity.