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

LAM-LAM PHOSPHATE (SENEGAL): THE USE OF A PHOSPHATE WITH A FERAL CONTENT
GREATER THAN 5% FOR THE PRODUCTION OF PHOSPHORIC ACID AND SUPERPHOSPHATES

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INTRODUCTION

In the various publications devoted to low grade PHOSPHATES or those with a high level of impurities, grades rich in iron and aluminium (or FERAL) are generally treated separately and as particularly difficult, even hopeless, cases. Even here, at ISMA, in 1976 a paper was given that considered an R_2O_3 content above a threshold of between 3 and 5% as critical, at least for the production of PHOSPHORIC ACID. Beyond that proportion, purification processes would have to be considered, some of which are well known, but costly, or else the production processes would have to be significantly modified. Such modifications would often involve alterations to the plants which it would clearly have been better to have anticipated at the design stage.

The present paper aims at relating the experience gained on production plants for PHOSPHORIC ACID and SINGLE and TRIPLE SUPERPHOSPHATE, which were designed for "high grade" phosphates (TAIBA or TOGO, for example), on replacing these PHOSPHATES by LAM-LAM rock (SENEGAL) containing 5% to 7% of FERAL.

Economic necessity has constrained the users first of all to undertake trials and then gradually to overcome all the obstacles encountered. In a context of rising prices for the richest grades of phosphates, and of international competition, competitiveness on the export market or even on local markets, required that the technical problems be solved in order to take advantage of a lower priced rock.

Following a description of the LAM-LAM rock, production of the three products will be studied, in the following order:

- PHOSPHORIC ACID
- SINGLE SUPERPHOSPHATE
- TRIPLE SUPERPHOSPHATE

1. Description of LAM-LAM PHOSPHATE

LAM-LAM is a phosphate of micro-crystalline or crystalline type with the chemical analysis overleaf (on crude sample).

Other physical characteristics

This PHOSPHATE flows poorly in the hopper, especially at a moisture content greater than 0.5%.

It binds together on conveyors; releases a great deal of dust when handled in the open air. Good results are obtained using pneumatic conveyors and by fluidisation.

It is friable and easy to grind, which can cause problems, as will be seen.

	<u>Mean</u>	<u>Max.</u>	<u>Min.</u>
P ₂ O ₅	34.5	35.5	33.3
CaO	47	50	45
Fe ₂ O ₃	1.5	2.0	1.0
Al ₂ O ₃	4.5	6.0	3.0
Total Feral	6.0	8.0	4.0
SiO ₂ + insoluble	5.5	7.0	4.0
F	3.5	4.0	2.5
CO ₂	1.0	1.2	0.9
H ₂ O	0.5	2.0	0.4

Particle size distributionCumulated oversize

2.0 mm	3 to 5%
1.0	5 to 10
0.800	8 to 15
0.630	10 to 20
0.315	20 to 30
0.250	25 to 40
0.160	40 to 50
0.100	45 to 65
0.080	50 to 85
0.040	65 to 90

Density: 0.9 to 1.2 according to packing.

2. Production of PHOSPHORIC ACID

LAM-LAM PHOSPHATE has been used since 1975 for the production of PHOSPHORIC ACID in the plant of the Société Industrielle d'Engrais au Sénégal, at M'BAO near DAKAR.

The plant was built in 1967 under licence from Pechiney Saint-Gobain (now Rhône-Poulenc), using the single tank dihydrate process with a Ucego filter. The plant was designed to produce 44 t/day of P₂O₅ from TAIBA phosphate and with minor modifications it has been possible to raise this to 75 t/day.

Some characteristics of the plant

- volume of the reactor (single) 90 m³
- filtration surface 8 m²
- phosphate feed not ground

The trials with LAM-LAM led to the adoption of the following parameters:

- H₂SO₄: 40 to 45 g/l
- temperature: 80 to 85°C
- acid concentration: 27%

The performances obtained are as follows:

- rate of production: 60 to 65 t/day
- gypsum analysis: (on dry product)
 - total P₂O₅: 1.5%
 - water soluble P₂O₅: 0.5
 - unattacked: 0.7
 - co-crystallised: 0.3
 - CaO: 39%

Particle size analysis

Oversize at 160:	3%
100:	12
80:	28
40:	67

- H₂SO₄ consumption: 2.6 t/t P₂O₅

- consumption of anti-foaming agent: 8 to 10 litres/24 hrs.

Concentration

The plant operates by flash evaporation under vacuum, with a vertical graphite heat exchanger. Also built under licence from Pechiney-Saint-Gobain to produce 44 t/day, it has been possible to raise its output to 70 t/day of 52% acid and 80 to 90 t/day of less concentrated acid for internal use by increasing the surface area of the heat exchanger.

In this case too, the changeover to LAM-LAM phosphate has not caused serious difficulties. It produces even less scale than Taiba. The greater viscosity of the acid is not inconvenient at this stage, but we have never exceeded 49% concentration, and we prefer to stay at 47-48%.

Characteristics of the acids obtained

	<u>Dilute</u>	<u>Concentrated</u>
P ₂ O ₅	27%	47%
Fe ₂ O ₃	0.8 to 1%	1.2 to 1.5%
Al ₂ O ₃	1.5 to 2%	2.5 to 3%
F	2 to 2.2%	1.8 to 2%
H ₂ SO ₄	40 to 45 g/l	80 to 100 g/l
Density	1300 to 1350	1700 to 1750

Utilisation of the acids

The acids are used as produced in the production of compound fertilizers at the M'Bao works. Granulation is excellent for all formulations, but we must admit that there is some under-formulation with high concentration compounds that do not incorporate a diluent, which is generally SSP. It should also be noted that in view of the difference in price, some customers prefer to agree to revise the grade requested. The M'Bao works has no phosphoric acid calcification plant and the only way to improve on the analysis is to leave the acid to decant in the storage tanks from which it is syphoned out.

3. Production of SUPERPHOSPHATES: (SIES at M'BAO, SENERAL, and ITALY)

Several works throughout the world use LAM-LAM phosphate to produce SINGLE SUPERPHOSPHATE (18-22% SSP), alone or in mixtures, in units as different as the BROADFIELD, KUHLMANN or SAINT-GOBAIN dens.

The M'BAO works also uses LAM-LAM to produce TRIPLE SUPERPHOSPHATE (45-47% TSP) in the same plant.

3.1. Single superphosphate31.2. In SENEGAL

- The plant, built in 1967 by PECHINEY-SAINT GOBAIN (now Rhône-Poulenc) consists of a cylindrical den (L = 8 m, diam. = 2.75 m),

preceded by a horizontal variable speed mixer. The 98% sulphuric acid is diluted in a graphite mixer cooled by sea water.

- the phosphate is ground in a MORITZ BG 12 roller grinder.
- the changeover to LAM-LAM phosphate has caused a certain number of problems that we will examine one by one in the order in which they occurred.

GRINDING LAM-LAM

Since the grinder was set for Taiba phosphate, the greater friability of LAM-LAM made it very difficult initially to operate, the grinder being alternately empty or, if the feed rate was increased, overloaded. The phosphate did not stay on the grinding ring and was entrained too quickly by the rising air flow. No setting of the pressure selector or the pressure of the rollers, or of the air flow was satisfactory.

The problem was finally solved by lowering the phosphate inlet to a few centimetres from the grinding ring and in particular by raising the external crown of the grinding ring, thus preventing it being swept by the air from the grinding chamber. The pressure of the rollers was also decreased.

In other works, problems of handling, phosphate grinding, and also of production of superphosphate were solved by mixing LAM-LAM with other phosphates having different and very often complementary properties; as the equipment at the M'Bao plant did not allow us to make such mixtures simply, that solution was rejected immediately.

The works considers that the problem of feeding the grinder is not solved properly and that the flow difficulties of the LAM-LAM will have to be overcome, probably by the use of air-chutes.

PRODUCTION OF SINGLE SUPERPHOSPHATE

- Fineness of the phosphate used: 70% passing through 80 microns (200 mesh)
- Dilution of the sulphuric acid to 70% (trials in progress to study the effect of greater dilution)
- In these conditions, a very rapid attack can be observed with the risk of binding up the mixer or blocking the entry to the den.
- The mixer has been pushed to its maximum speed. In addition, the point of introduction of acid and phosphate has been shifted towards the mixer outlet, the mixer now being used for no more than 2/3 of its length. This modification, carried out during the TSP trials, was retained for the single superphosphate.
- the superphosphate obtained at the outlet from the cylindrical den is slightly sticky, not well granulated and has the following characteristics

	<u>1st day</u>	<u>after granulation</u>
total P ₂ O ₅	22 - 23	21.9
citrate-soluble P ₂ O ₅	14 - 16	19.6
water-soluble P ₂ O ₅	12 - 14	15.1

	<u>1st day</u>	<u>after granulation</u>
free P ₂ O ₅	1 - 2	1.1
H ₂ O	7 - 10	1.6

- crushing strength: 2,000 to 3,000 g
- acidulation ratio: 0.61
- at M'BAO, no anti-foaming agent is used
- the granulation of this single superphosphate poses no problem, whether in straight fertilizer or in ternary compounds.

31.3. In ITALY: Fabbrica Cooperative Perfosfati, Cerea VERONA)

The first experience of using LAM-LAM phosphate in Italy was in 1975, when the price increases encouraged everyone to seek replacement raw materials, even if they had a higher content of impurities.

If we look at the chemical analysis of LAM-LAM phosphate we can anticipate two negative features of its use:

1. If we investigate the water and/or citrate solubility, the high Fe and Al content may dissuade us from using it for TSP production; for the production of SSP, such an impurity content would lead us to predict a greater consumption of H₂SO₄ which is not used to solubilise the P₂O₅.
2. The low carbonate content which leads, on the one hand, to a reduction in H₂SO₄ consumption, may, on the other, create technical problems in the reaction phase, owing to the inadequate porosity of the product formed, which in turn restricts the drying of the product in the den.

However, the LAM-LAM phosphate may have positive aspects owing to:

- the ease of grinding
- the high P₂O₅ content
- the lower consumption of H₂SO₄ resulting from the low carbonate content.

For this reason, it was decided to use LAM-LAM phosphate exclusively for SSP production, mixed with another phosphate preferably chosen from among those with a higher carbonate content. Mixtures with other phosphates of various origins (Morocco, Tunisia, Algeria, Jordan, Israel) were tried on the industrial scale, with ratios varying from (20% + 80%) to (80% + 20%). The best results appeared to be obtained with a 50% + 50% mixture.

It was recently decided to carry out a more thorough study in the laboratory to seek the optimum conditions as a function of water solubility, citrate solubility and H₂SO₄ consumption.

Analyses were made (after 1 day and after 15 days) on 20 different samples of SSP, obtained by combining 5 mixtures of phosphates with 4 values of the specific quantity of H₂SO₄ used for the reaction.

In order to eliminate the effect of the fineness of grind, the mixtures of phosphates were prepared from two phosphates previously ground to even fineness: 100% < 150 mesh, 70% < 200 mesh.

The five mixtures of phosphates obtained had the following composition (P_2O_5 on sample as produced):

A) 100% EL HASSA	31.85% P_2O_5
B) 75% EL HASSA + 25% LAM-LAM	32.47
C) 50% EL HASSA + 50% LAM-LAM	33.10
D) 25% EL HASSA + 75% LAM-LAM	33.72
E) 100% LAM-LAM	34.34

The specific quantities of H_2SO_4 used were:

0.5625 - 0.60 - 0.6375 - 0.675 kg H_2SO_4 /kg phosphate.

When the results were analysed the trials with LAM-LAM on its own and those with an H_2SO_4 consumption greater than 0.675 kg/kg of phosphate not suitable for industrial used, were excluded.

The trials with a consumption of 0.5625 and 0.6375 kg H_2SO_4 /kg of phosphate were regarded as confirming the trend, while the trials with a specific consumption of 0.60, which, on analysis after 15 days, all gave a ratio of water-soluble P_2O_5 /total P_2O_5 > 93%, were repeated.

The results with 0.60 kg H_2SO_4 /kg of phosphate for the four types of phosphate mixtures (A, B, C, D) taken into consideration were:

94%	≅ (citrate soluble P_2O_5) at 1 day	≅ 97%
97%	≅ (citrate soluble P_2O_5) at 15 days	≅ 99.30%
88%	≅ (water soluble P_2O_5) at 1 day	≅ 92%
92%	≅ (water-soluble P_2O_5) at 15 days	≅ 94%

In spite of the uncertainty of the analytical data, it appears that the following trends can be discerned:

- after one day: the percentage of citrate-soluble P_2O_5 increases with the increase in proportion of LAM-LAM
the percentage of water-soluble P_2O_5 increases with the increase in proportion of EL HASSA
- after 15 days: the type of phosphate has no effect on the percentage of citrate-soluble P_2O_5
the percentage of water-soluble P_2O_5 increases with the increase in proportion of EL HASSA.

Conclusions

- Mixtures of phosphates containing 50 to 75% of LAM-LAM phosphate can be suitable for use in the production of SSP with a high solubility in neutral ammonium citrate and a water solubility $\geq 93\%$.
- The specific consumption obtained is ≤ 0.60 kg H_2SO_4 /kg of phosphate. Taking account of the different P_2O_5 values of the different phosphate mixtures, those containing from 50 to 75% of LAM-LAM phosphate bring a reduction in H_2SO_4 consumption per unit of solubilised P_2O_5 , of 4% and 5.5% respectively.

COMMENT

Certain fertilizer users, particularly in Africa, tend towards a less

soluble form of P_2O_5 ; it is possible to under-acidify the LAM-LAM phosphate and to use it then unground, especially if the superphosphate is intended for the preparation of compounds. Advantage is taken of the natural presence of a quantity of fines (less than 80 microns) of between 50 and 85%. The use of surfactants is sometimes cited to improve the attack.

3.2. Triple Superphosphate

Once the problems of grinding were overcome, the production trials for Triple Superphosphate began in 1977, at the M'Bao works in Senegal. The plant is the same as for Single Superphosphate. The concentrated phosphoric acid can be heated in a graphite exchanger (using steam).

The first trials covered attacking LAM-LAM with phosphoric acid ex LAM-LAM. They were rapidly abandoned for the reasons below, but we propose to resume them as soon as the opportunity arises, since two changes have occurred since then:

- the quality of the phosphate has improved, the Feral content decreasing from 8 to 5/6%.
- the elevator situated at the outlet from the cylindrical den has been removed and replaced by inclined belt conveyors. The ease with which this piece of equipment - difficult and time-consuming to clean - clogged up, did not allow the slightest "stickiness", inevitable during trials.

We are only concerned here with the production of mixed TSP resulting from the attack of LAM-LAM by acid from Taiba phosphate.

The first trials in 1977 used a phosphate particularly rich in Feral. The production of crude superphosphate posed no insurmountable problems, but, in contrast, its granulation was practically impossible: the product "over-granulated" immediately and the granules obtained, which became increasingly large, were extremely hard: the grinders in the granulation plant went through several painful days... and this was irrespective of the age of the crude TSP, fresh or mature. The solution was rapidly found by adding a surfactant during the production of TSP, at the rate of a little less than 1 litre per tonne of phosphate.

This procedure was then adhered to in spite of the decrease in Feral content of the LAM-LAM. Below 6% of Feral, the opposite phenomenon occurred: the granules obtained had no mechanical strength (less than 800 g of crushing strength) and their despatch in bulk raised, in particular, serious unloading problems. Since the "cement" - the Feral - had decreased, its antidote, the surfactant, had to be decreased. We finally did away with it completely.

The last problem to be overcome was that of grade. Our plant now allows a large degree of over-acidification, and in spite of the slowness of the attack - after a quick start-up, as for Single Superphosphate, the product after maturation can have a content higher than 47% with a water-soluble fraction of 90%. But in spite of leaving out the surfactant, such a superphosphate does not have good mechanical strength. When this is required, in particular for transport of bulk product by sea and the use of TSP in bulk blending, we have two

alternatives:

- either to choose to add a cement: Phosphal or calcined and ground aluminium phosphate, also sold by the Société Sénégalaise des Phosphates de THIES, which the M'Bao works is familiar with, using it in certain compound fertilizers for the Senegal. A rate of 3% is enough to bring the crushing strength up above 1500 g, but at the expense of a large reduction in the water solubility, which is still accepted by some users.
- or to reduce the guaranteed analysis and to adopt a compromise between the chemical and mechanical properties.
- The superphosphate obtained in these last conditions has the following characteristics:

	<u>1st day</u>	<u>after granulation</u>
total P ₂ O ₅	45 - 46	46
citrate-soluble P ₂ O ₅	42 - 43	44
water-soluble P ₂ O ₅	39 - 40	40
free P ₂ O ₅	2 - 4	1
H ₂ O	10 - 12	< 3
Crushing strength	---	1500
Concentration of the Taiba acid used:	50 - 51%	
Temperature of the Taiba acid used:	75 - 80°C	

CONCLUSION

A Feral content greater than 5% is not an insuperable obstacle to the utilisation of a phosphate in the manufacture of phosphoric acid and superphosphates, even in an existing factory, not designed for them, if the phosphoric acid is used in situ. The presence of another phosphate - with a reactive acid - can also facilitate TSP production.

Producers must be sufficiently motivated - by the relative price of the phosphate - to accept long and difficult trials.

TA/80/2 Lam-Lam Phosphate (Senegal): the use of a phosphate with a feral content greater than 5% for the production of phosphoric acid and superphosphates by J. Le Page, SIES, Senegal, G. Menin, Fabbrica Perfosfati Cerea, Italy.

DISCUSSION : (Rapporteur J.D. Crerar, Fisons Ltd, United Kingdom)

In reply to a question by Mr. M. GAURON (Cofaz, France), M. LE PAGE said that during the manufacture of phosphoric acid, the loss of unattacked phosphate when using Lam-Lam rock was slightly less than for Taiba. This was probably as a result of the increased residence time since the production rate was 15% lower.

Mr. P. MORAILLON (GESA, France) asked about the method of determining particle size and the relative capacities for producing single superphosphate. Mr. LE PAGE stated that a dry screening method was used. There was no marked difference in superphosphate capacity when using Lam-Lam phosphate compared with Taiba.

In answer to a question from Mr. M. BARLOY (CERMI, France), Mr. LE PAGE confirmed that, although ground phosphate, with 70% minus 80 microns, was used for single superphosphate, there are certain applications for SSP where unground rock with 15-50% minus 80 microns could be used. Mr. BARLOY also raised the question about the need to pre-heat phosphoric acid for the production of triple superphosphate. Mr. LE PAGE had found the optimum pre-heat for Taiba to be 65° C, but, contrary to its high reactivity, a higher temperature was required for Lam-Lam phosphate. With a cold start, the phosphoric acid was pre-heated to 80° C and then reduced to around 70° C.

In reply to further questions by Mr. BARLOY, Mr. LE PAGE said that acetone extraction was used for determination of free P₂O₅. He also reported that little corrosion had been experienced despite operating the phosphoric acid reaction vessel at 80-85° C with a free H₂SO₄ content of 40-45 g/l. Lam-Lam phosphate gave a slight pickling effect but no greater overall corrosion rate than Taiba. One incident of rapid corrosion of pumps had been experienced but this had been due to the presence of KCl and acidic liquids in the plant, not an effect of the rock.

Mr. A. SINTE MAARTENSDIJK (UKF, Netherlands) asked for the viscosity of phosphoric acid produced from Lam-Lam phosphate. The viscosity had not been measured but was higher than for Taiba. This had limited the phosphoric acid strength to 47-48% P₂O₅ compared with 50-52% P₂O₅, but had never created a problem in the concentration units or granulation. Mr. SINTE MAARTENSDIJK suggested reducing the fineness of grinding in the manufacture of superphosphates to avoid problems of mixing and blockage. Mr. LE PAGE said that much work had been done on optimising the fineness of grind. For TSP the fineness had been reduced from 85% smaller than 200 microns for Taiba to 70% smaller than 200 microns for Lam-Lam phosphate. For SSP no grinding is required and slight under-acidulation is necessary to avoid problems in the den. Under-acidulated product is preferred by some customers, especially the Ivory Coast, this effecting a higher P₂O₅ retention under tropical conditions.

Mr. SINTE MAARTENDSDIJK suggested that the mechanical strength of granular TSP could be improved by addition of sulphuric acid to the phosphoric acid rather than adding a cement. Mr. LE PAGE thought this was a good idea which had not been tried through lack of mixing facilities, and he would try it.

Mr. M. ROCCA (Quimbrasil, Brazil) asked for details of the temperature and pressure under which samples had been stored during the 15 days curing time in laboratory studies. Since the work had been done in Italy, Mr. LE PAGE could not give immediate details but would reply in writing.

Mr. V. VANECEK (Research Institute of Inorganic Chemistry, Czechoslovakia) asked about the influence of high Al_2O_3 on the granulation of SSP. Mr. LE PAGE replied that granular SSP always had excellent mechanical properties with a crushing strength of about 2 kg. For granular TSP the crushing strength was normally 1.5 kg.

Mr de la CROIX (Coppée-Rust, Belgium) asked whether the characteristics of the phosphoric acid given on page 3 of the paper were for clarified or unclarified acid. Mr. LE PAGE replied that, since there were no facilities for clarifying acid, the information was for acid as made, he would let Mr. de la CROIX know the solids content in writing.

Mr. N. ROBINSON (Fisons Ltd, United Kingdom) pointed out that it could be very misleading to combine the concentration of aluminium and iron impurities to predict the performance of a phosphoric acid plant.

In reply to a question from Mr. N. ROBINSON, Mr. LE PAGE said that solids precipitated from phosphoric acid were removed or maintained in suspension and fed to the granulation process for low grade formulations. There was no sludge return to the phosphoric acid plant. He had no analysis of the solids.

In reply to Mr. B. NEVEU (APC, France), Mr. LE PAGE said SIES had not yet tried to transform gypsum from Lam-Lam phosphate into plaster.