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THE EFFECT OF PHOSPHATE ROCK IMPURITIES ON FINAL FERTILISER GRADE

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SUMMARY

The impurities present in phosphate rock influence not only the degree of difficulty in processing the rock, but also the analysis of the final fertilisers which can be produced. Solid fertilisers are sold on the basis of either total or available nutrient values and the particular legislation adopted by a country can have a profound effect upon the acceptability of the donor phosphate and upon the method of beneficiation and processing of the phosphate. In evaluating alternative routes from orebody to fertiliser, the objective should be to achieve minimum overall production and distribution cost whilst attaining the sometimes conflicting requirements of optimum utilisation of the phosphate reserve and maximum crop growth. In fact, crop growth as such is often taken out of the equation and replaced by legislative specification of fertiliser grade.

Even for projects based upon rock imported from another country, the above objectives are valid although economic analysis becomes more complex.

This paper describes several alternative routes from orebody to fertilisers, concentrating in particular on the relationship between phosphoric acid quality and DAP grade. Case history examples are presented.

INTRODUCTION

In considering the effect of rock grade on fertiliser analysis, it is appropriate to review the position in Florida over the last 20 years as this covers a period when considerable changes have taken place in an already established industry. This experience provides useful guidelines towards the effective exploitation and development of future rock deposits.

Fig. 1 indicates the change that has taken place in rock quality in Florida as the higher grade deposits have gradually been mined out.

FIG. 1 PRODUCTION OF FLORIDA/N. CAROLINA ROCK BY BPL GRADE^(1,2)
 (Expressed in Thousands of Tons)

	<60 BPL	60-66 BPL	66-70 BPL	70-72 BPL	72-74 BPL	>74 BPL	Total For Year
1959	81.0	547.0	3567.0	2128.0	2082.0	3355.0	11760.0
1965	28.0	1858.0	6312.0	2593.0	2123.0	6279.0	19193.0
1970	38.0	1735.0	12442.0	3155.0	8377.0	4544.0	30291.0
1975	34.4	5091.2	18920.0	3852.8	3956.0	2545.6	34400.0
1979	91.0	5733.0	28392.0	5778.5	3412.5	2093.0	45500.0

Typical analyses of various grades of Florida rock are tabulated in Fig. 2 in conventional format whilst Fig. 3 expresses these in the form of ratios. It is, in fact, in the latter form that guidelines towards acceptable rock quality can most effectively be discussed.

FIG. 2^(3,4)

TYPICAL ANALYSES OF FLORIDA ROCK BY GRADE (% by weight)

COMPONENT % W/W	60 BPL	62 BPL	64 BPL	66 BPL	68 BPL	70 BPL	72 BPL	75 BPL	77 BPL
P ₂ O ₅	27.10	28.40	29.38	30.27	31.19	32.11	33.02	34.39	35.31
CaO	42.60	42.70	45.08	45.65	46.10	46.80	48.10	49.70	50.10
SO ₃	2.10	1.40	1.02	1.10	1.05	0.95	0.95	0.82	0.78
Al ₂ O ₃	1.02	1.17	1.42	1.40	1.40	1.30	1.15	1.00	1.02
Fe ₂ O ₃	1.43	1.63	1.61	1.10	1.30	1.30	1.25	1.10	1.03
MgO	1.70	0.48	0.58	0.57	0.51	0.45	0.38	0.28	0.23
Na ₂ O	0.77	0.35	0.25	0.55	0.53	0.52	0.50	0.45	0.40
K ₂ O	0.12	0.11	0.16	0.12	0.12	0.11	0.10	0.09	0.08
F	3.20	3.70	3.54	3.50	3.60	3.65	3.70	3.82	3.87
Cl	0.014	0.007	0.011	0.009	0.009	0.008	0.007	0.006	0.005
SiO ₂	11.80	13.00	10.85	9.80	9.50	8.60	6.10	3.35	3.05
CO ₂	3.10	2.90	4.38	3.85	3.70	3.50	3.40	3.13	2.98
Organic C	0.98	1.03	0.80	0.75	0.75	0.70	0.65	0.60	0.60

FIG. 3 ANALYSES OF FLORIDA ROCK BY GRADE: EXPRESSED IN WEIGHT RATIOS

GRADE	% P_2O_5	CaO - (CaO \mp SO ₃)	Al ₂ O ₃	Fe ₂ O ₃	R ₂ O ₃	MgO	F	F	Organic C x 1000	CO ₂
		$\frac{P_2O_5}{P_2O_5}$	$\frac{P_2O_5}{P_2O_5}$	$\frac{P_2O_5}{P_2O_5}$	$\frac{P_2O_5}{P_2O_5}$	$\frac{P_2O_5}{P_2O_5}$	$\frac{P_2O_5}{P_2O_5}$	$\frac{SiO_2}{P_2O_5}$	$\frac{P_2O_5}{P_2O_5}$	$\frac{P_2O_5}{P_2O_5}$
60 BPL	27.10	1.518	0.038	0.053	0.091	0.063	0.118	0.271	36.2	0.114
62 BPL	28.40	1.469	0.041	0.057	0.098	0.017	0.130	0.285	36.3	0.102
64 BPL	29.38	1.510	0.048	0.055	0.103	0.020	0.120	0.326	27.2	0.149
66 BPL	30.27	1.483	0.046	0.036	0.082	0.019	0.116	0.357	24.8	0.127
68 BPL	31.19	1.454	0.045	0.042	0.087	0.016	0.115	0.379	24.0	0.119
70 BPL	32.11	1.437	0.040	0.040	0.080	0.014	0.114	0.424	21.8	0.109
72 BPL	33.02	1.437	0.035	0.038	0.073	0.012	0.112	0.607	19.7	0.103
75 BPL	34.39	1.428	0.029	0.032	0.061	0.008	0.111	1.140	17.4	0.091
77 BPL	35.31	1.403	0.029	0.029	0.058	0.007	0.110	1.269	17.0	0.084

The BPL content has no significance in itself and serves only as a convenient label in discussing various grades of rock. A nominal 68 BPL grade may, for instance, vary from 67.0 to 68.5 BPL. A study of ten different nominal 68 BPL rocks from different mines in Florida revealed the following range of components:

FIG. 4 RANGE OF COMPONENTS IN 68 BPL FLORIDA ROCK (% by weight)

P_2O_5	30.7	-	31.3
CaO	43.9	-	47.4
SO_3	0.8	-	1.2
Al_2O_3	0.34	-	1.37
Fe_2O_3	0.70	-	2.14
MgO	0.0	-	0.6
Na_2O	0.32	-	0.89
K_2O	0.08	-	0.24
F	3.6	-	4.3
Cl	0.003	-	0.014
SiO_2	7.0	-	11.4
CO_2	1.8	-	4.1
Organic C	0.1	-	0.6

It is quite possible to have two 68 BPL rocks from the same deposit which exhibit quite different processing characteristics. One cause of this would be a difference in the content of acid soluble impurities due, for example, to the presence of free dolomite ($CaMg(CO_3)_2$) in the apatite crystal lattice.

Over the years, but particularly since about 1965, the trend of declining rock grade has caused the major Florida producers to consider firstly whether or not acid clarification circuits were necessary in order that DAP as 18-46-0 could be achieved and later what changes and improvements to the clarification systems were necessary to protect their marketing position. It was generally considered that little more could be economically achieved with respect to beneficiation, although some developments in this area have also occurred recently.

In 1965 the majority of Florida producers employed very little in the way of clarification, usually limiting this to settling of the 30% P_2O_5 acid ex-filtration. At least one company at that time used no clarification whatsoever. 68 BPL rock was generally used at that time with a R_2O_3/P_2O_5 ratio of 0.087. No major difficulties were experienced by the producers in achieving 18-46-0 except in cases of plant upset when, for example, the solids level in the ex-filter acid rose above about 2% due to holes in the filter cloth or operation with very thin cakes. Post-precipitation of the 54% P_2O_5 acid and indeed the chemical impurities in the acid itself were not at that time significant obstacles to the achievement of grade analysis.

As rock grade gradually declined, the relative importance of the acid soluble impurities increased such that it became more and more difficult to achieve DAP grade. Combination effects due to solids in the filter acid together with higher levels of Fe_2O_3 and Al_2O_3 tended to make DAP grade difficult and sometimes impossible to achieve.

The experience in Florida, therefore, has been to retain the established beneficiation methods as rock grade declined and to modify acid clarification techniques in order to bring back the acid quality to a level suitable for production of 18-46-0. This trend is likely to continue although different clarification methods may be needed in order to process higher MgO rocks.

DEVELOPING A NEW DEPOSIT

Turning now to the broader question of the exploitation of a new deposit, it is clear that the overall concept is the conversion of insoluble phosphorus in the rock to a soluble form which will then be returned to the ground as fertiliser resulting in increased crop growth.

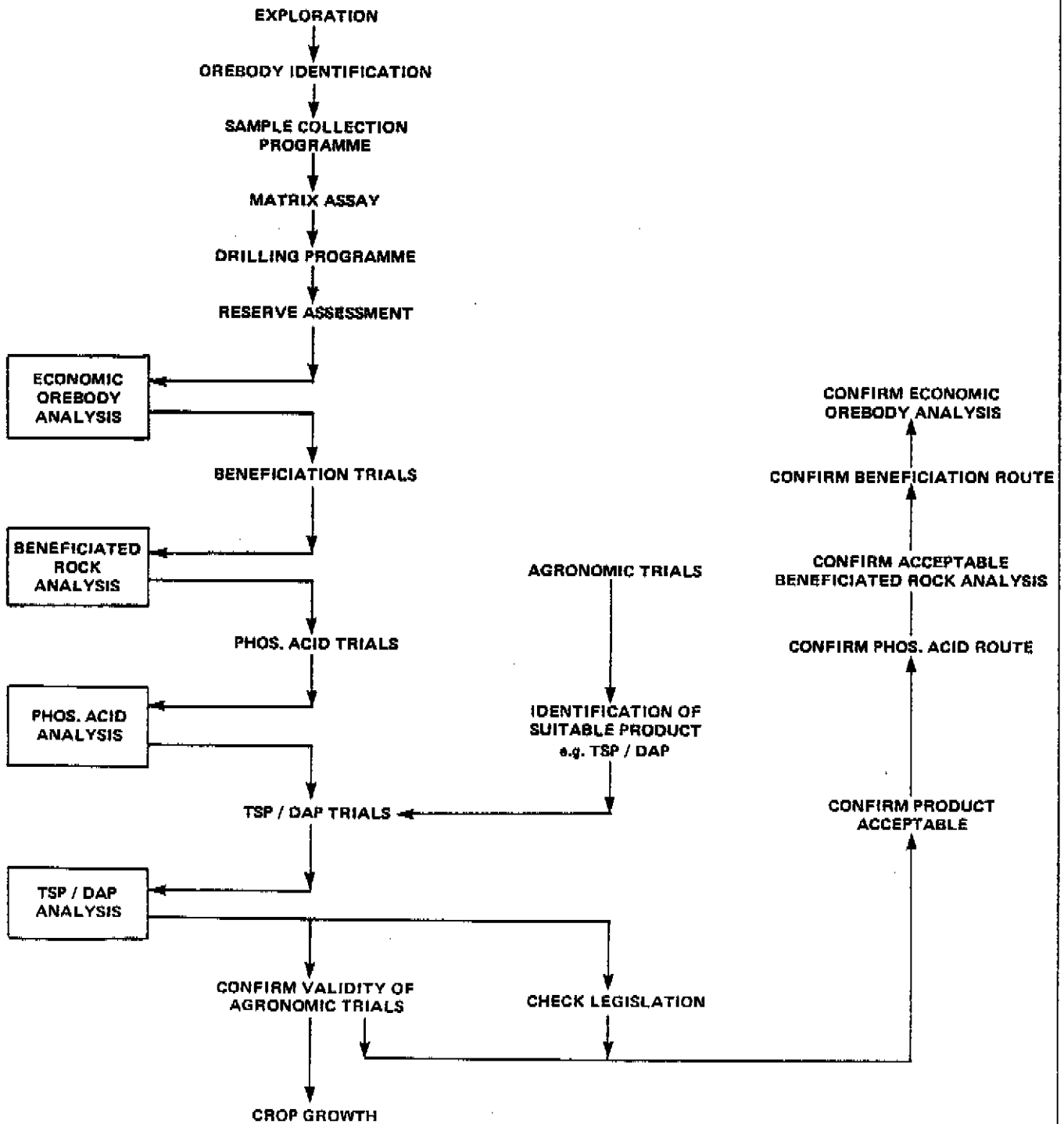
There are many stages in this apparently simple chain of events. Fig. 5 summarizes these in a simplified form. If it was possible to optimise these stages, the result would be an economic balance between the cost of producing and distributing the fertiliser and the resulting increase in crop growth. In practice, an overall optimisation is not possible because no one company or government has control over all links of the chain. Thus a compromise is reached based on a number of key anchor points with optimisation around these being attempted. Referring to Fig. 5, the key anchor points are as follows:

- Economic Orebody Analysis
- Beneficiated Rock Analysis
- Phosphoric Acid Analysis
- TSP/DAP Analysis

As far as possible, those concerned with planning a fertiliser development of this kind should aim to understand the relationships between these various anchor points and try to integrate the activities in such a way that key decisions are taken at a time when maximum vital information on all relevant aspects is available. For example, it is highly desirable that agronomic data is available at about the same time that beneficiation trials are undertaken so that the phosphate processing route can be developed along appropriate lines.

Fig. 5

PLANNING ROUTE – OREBODY TO FERTILISERS



ECONOMIC OREBODY ANALYSIS

Economic orebody analysis is determined by two principle considerations:

- a. Difficulty and cost of mining
- b. Tonnage of various qualities available to be mined

The term "economic" in this context, although apparently related only to a mining operation, cannot in fact be divorced from the downstream processing and distribution of the rock. For example, the cost of beneficiating the rock to a form acceptable to the phosphoric acid plant operator is clearly an integral part of the economics of the mining operation. Similarly the location of the rock deposit with respect to the envisaged fertiliser market is an important consideration. This sometimes leads to relatively small, low grade deposits being considered as "economic" in countries striving towards self-sufficiency by means of import substitution.

Evaluation of the above considerations related to economic orebody analysis follows the general stages of activity listed below:

1. A drilling program to establish the geological strata, depth, extent, and P_2O_5 content of the phosphate seams.
2. Selection of basic mining method ie. open pit, underground, or a combination of both.
3. Evaluation of overburden/ore ratios in various parts of the deposit.
4. Selection of suitable areas for pit waste disposal.
5. Economic analysis of above data to establish cost of extraction together with useful life of the deposit thus determining cut-off limits for the mining operation.

BENEFICIATED ROCK ANALYSIS

In the development of a mining project, the establishment of a beneficiation route may take several years to achieve. The form of development often involves a series of laboratory bench trials followed by the construction of pilot plant and/or semi-industrial scale beneficiation plant. While this work is to a large extent controlled by mining engineers, advice and guidance from chemical engineers who may be involved in the downstream utilisation and processing of the beneficiated rock is necessary.

Initially the beneficiation trials can be directed towards the achievement of a broadly acceptable analysis based on other commercially known phosphates. Figs. 2 and 3 tabulate such data for Florida rock. Similar data on other phosphate rocks is summarized in Figs. 6 and 7.

It is likely that after a series of bench scale trials have been undertaken, there may be two or three beneficiated rock analyses which appear to be theoretically within or close to the target ratios specified. At this stage, a number of chemical trials could usefully be performed in order to establish a preliminary opinion as to the actual suitability of the rock for phosphoric acid production. Gradually by means of a series of overlapping trials of this nature, the beneficiation route can be firmly established.

It must be stressed that the chemical trials mentioned above provide a vital input to the evaluation, and that estimation of rock performance in a phosphoric acid plant from theoretical considerations alone can lead to dangerously inaccurate conclusions. Impurities are sometimes not totally soluble in the process and, furthermore, insoluble complexes can be formed either at the weak acid or strong acid stage. Such effects are difficult to predict from theory.

FIG. 6^(5,6,7) CHEMICAL ANALYSIS OF PHOSPHATE ROCKS (% by weight)

<u>Component</u> <u>% W/W</u>	<u>Khouribga</u>	<u>Youssoufia</u>	<u>Florida</u>	<u>Taiba</u>	<u>Togo</u>	<u>Jordan</u>	<u>Nauru</u>	<u>Phalaborwa</u>	<u>Tapira</u>	<u>Araxa</u>
P ₂ O ₅	33.4	32.21	31.6	37.5	36.80	33.9	38.5	36.75	39.1	34.9
CaO	50.6	51.70	46.5	51.2	50.5	52.2	52.4	52.11	53.3	46.2
SO ₃	1.62	1.28	0.76	0.08	0.17	1.3	0.03	0.17	0.03	2.21
Al ₂ O ₃	0.43	0.36	1.26	1.10	1.00	0.20	0.215	0.15	0.48	0.46
Fe ₂ O ₃	0.20	0.25	1.44	1.10	1.14	0.17	0.13	0.27	0.73	2.86
MgO	0.33	0.43	0.38	0.02	0.06	0.23	0.25	1.06	0.14	0.06
Na ₂ O	0.70	0.76	0.64	0.20	0.23	0.54	0.24	0.04	0.12	0.23
K ₂ O	0.09	0.07	0.10	0.03	0.05	0.02	0.04	0.05	0.01	0.02
SrO	0.10	0.10	0.10	0.08	0.02	0.25	0.01	0.31	0.39	1.11
F	3.97	4.10	3.65	3.91	3.84	3.99	2.66	2.20	1.31	2.10
Cl	0.028	0.03	0.02	0.05	0.12	0.03	0.002	0.02	0.007	0.004
SiO ₂	1.92	3.18	9.50	2.49	3.62	3.15	0.24	2.61	1.03	0.25
CO ₂	4.51	5.60	3.67	1.50	1.28	4.2	2.57	3.50	0.55	2.10
Organic C	0.26	1.00	0.18	0.54	0.14	0.29	1.13	0.03	0.07	0.04

FIG. 7

ANALYSES OF SOME COMMERCIALY AVAILABLE PHOSPHATES: EXPRESSED IN WEIGHT RATIOS

SOURCE	%P ₂ O ₅	CaO-(CaO±SO ₃)	Al ₂ O ₃	Fe ₂ O ₃	R ₂ O ₃	MgO	F	F	Organic C x 1000	CO ₂
		P ₂ O ₅	P ₂ O ₅	P ₂ O ₅	P ₂ O ₅	P ₂ O ₅	P ₂ O ₅	P ₂ O ₅	SiO ₂	P ₂ O ₅
Sedimentary										
Khouribga	33.4	1.48	0.013	0.006	0.019	0.010	0.119	2.1	7.8	0.135
Youssoufia	32.2	1.58	0.011	0.008	0.019	0.013	0.127	1.3	31.0	0.174
Florida	31.6	1.45	0.040	0.045	0.085	0.012	0.115	0.4	5.7	0.116
N. Carolina	33.0	1.55	0.015	0.027	0.042	0.018	0.115	1.5	1.8	0.072
Western Sahara	35.2	1.44	0.013	0.005	0.018	0.003	0.106	0.7	3.0	0.060
Taiba	37.5	1.36	0.029	0.029	0.058	0.0005	0.104	1.6	14.4	0.040
Togo	36.8	1.37	0.027	0.031	0.058	0.002	0.104	1.1	3.8	0.035
Gafsa	29.9	1.55	0.014	0.011	0.025	0.018	0.120	1.1	29.0	0.222
Jordan	33.9	1.51	0.006	0.005	0.011	0.007	0.118	1.3	8.6	0.124
Djebel Onk	29.6	1.62	0.012	0.010	0.022	0.053	0.127	2.1	14.0	0.254
Nauru	38.5	1.36	0.006	0.003	0.009	0.007	0.069	11.1 - 38.6	29.0	0.067
Christmas Is.	36.1	1.42	0.046	0.023	0.069	0.003	0.060	2.2 - 39.3	8.0	0.125
Igneous										
Phalaborwa	36.8	1.41	0.004	0.007	0.011	0.029	0.060	0.8	0.8	0.095
Kola	39.8	1.36	0.012	0.011	0.023	0.001	0.084	4.3	7.5	0.004
Jacupiranga	35.8	1.47	0.010	0.007	0.017	0.022	0.044	1.1	2.7	0.136
Tapira	39.1	1.36	0.012	0.019	0.031	0.004	0.034	1.3	1.8	0.014
Araxa	34.9	1.28	0.013	0.082	0.095	0.002	0.060	8.4	1.1	0.060
Catalao	38.0	1.30	0.024	0.100	0.124	0.003	0.074	2.9	1.3	0.001

Igneous and sedimentary rocks differ in the types of impurities present. In the case of sedimentary rocks the impurities are normally common to all sources, the only differences being in the relative amounts of each. Igneous rocks tend to be totally different from each other and from sedimentary rocks too, often having one major unusual impurity.

For example: Kola (USSR) has high SrO

Tapira (Brasil) has high TiO_2

Araxa (Brasil) has high BaO

Phalaborwa (South Africa) has high CuO and MgO

Often apatite is present in igneous rocks in a relatively pure state with minimum substitution and depending on the extent of beneficiation, extremely pure acids can be produced directly. The concentrates often contain significant quantities of rare earths.

Igneous rocks normally have a lower specific surface area and, thus, a relatively low reactivity. Often these igneous rocks produce needle crystals with a corresponding increase in the specific filter area requirement compared with normal sedimentary phosphates.

PHOSPHORIC ACID ANALYSIS

Mention has been made above of the value of preliminary chemical trials in the establishment of the beneficiation route. Once the route and the mining techniques have been firmly established, a continuous phosphoric acid pilot plant trial can be undertaken on a representative sample of the beneficiated phosphate. This type of trial simulates actual full scale operation and thus provides quantitative data on operating conditions and product quality on which the full scale design can be based. Furthermore, the acid produced can be used for TSP/DAP trials so that the complete processing picture can be evaluated.

The phosphoric acid pilot plant trials may be based on one or more types of process (dihydrate, hemihydrate, hemi-dihydrate, etc). Often the selection of the type of process is made by the potential phosphoric acid producer for reasons unassociated with product acid quality. For example, non-availability of steam has led some producers to select high strength hemi-dihydrate processes. However, the route does affect to some extent the phosphoric acid analysis and consequently the downstream DAP/TSP analysis and this can sometimes have far-reaching implications.

Acid produced by the dihydrate route and acids produced by the weak acid (30% P_2O_5) routes using single-stage hemi-dihydrate processes and dihemihydrate processes normally produce very similar acid qualities. In fact, where impurities are only partially soluble in the process finer grind, higher reaction temperatures and longer residence times required by some of these processes may produce acids with higher levels of impurities.

Acid leaving the gypsum filter contains other impurities but evaporation and ageing reduce some of these to lower levels. Defluorination can take place in 30% acid by addition of Na^+ and active silica. During evaporation partial defluorination takes place though this depends greatly on the final P_2O_5 strength and the components present in the 30% acid. Further precipitation of complexes, some containing phosphate, occurs in the storage tanks during cooling and ageing. Clarification removes most of these precipitated impurities leaving a purer acid. However, this post-precipitation effect is extremely slow and equilibrium is often not reached even after two weeks storage. Furthermore, settling effects are difficult to predict because fine solids are often pseudo-chelated with soluble organic/carbon particles.

The single-stage hemihydrate process produces a 45-50% P_2O_5 acid with the following characteristics when compared with 50% acid ex-evaporator from a weak acid process:

- . Low SO_4
- . Low CaO
- . Low Al_2O_3
- . Low Post-precipitation

Acid direct from the filter of a strong acid process is essentially in equilibrium and is not highly super-saturated, thus virtually no post-precipitation takes place. Solids content of the acid is controlled by the size of the "cloudy port", the quality of cloths used on the filter and their state of repair.

The quality of acid produced by the single-stage hemi-hydrate process (HH) is compared with the normal dihydrate acid (DH) after evaporation and ageing (Fig. 8). In all three cases cited the Al_2O_3 level of HH acid is 0.2% or below, while SO_4 is less than 2.0%.

FIG. 8

COMPARISON OF ACIDS PRODUCED BY
DIHYDRATE, HEMIHYDRATE & HEMI-DIHYDRATE PROCESSES

		P ₂ O ₅	SO ₄	Al ₂ O ₃	Fe ₂ O ₃	Solids	MgO
Morocco 73/75 BPL	DH	50.2	4.3	0.5	0.4	4.3	0.5
	HH	50.1	1.9	< 0.1	0.3	< 1.0	0.4
	HDH	50.0	2.0	0.1	0.4	< 1.0	0.4
Florida 75 BPL	DH	50.5	4.5	1.3	1.5	4.5	0.3
	HH	50.0	1.8	0.2	1.4	1.0	0.3
	HDH	50.0	2.0	0.4	1.45	1.0	0.3
Togo 80 BPL	DH	50.0	4.5	0.9	1.5	4.8	0.2
	HH	50.0	2.0	0.1	1.6	< 1.0	0.1
	HDH	50.0	2.0	0.2	1.6	< 1.0	0.1

Values are presented in % weight/weight

A modification of the Hemihydrate process is available which has an additional recrystallisation stage. This process, the Hemi-Dihydrate (HDH) process, recovers the phosphate co-crystallised in the calcium sulphate lattice giving an improved recovery, but the level of impurities in the acid is marginally higher (Fig. 8).

TSP/DAP ANALYSIS

There are two main implications arising from the analysis of the final fertiliser.

a. Extent of Crop Growth.

Agronomic trials are needed to determine the optimum rate of application and the type of fertiliser needed for each crop and each soil. Although the study of agronomics is outside the scope of this paper, it can broadly be assumed that the solubility of a phosphate fertiliser is not necessarily a good indication of its effectiveness as it is the products formed by reaction between the fertiliser and the soil components which ensure nutrition of the crop. Nevertheless, as a general rule, crops with a high requirement for phosphate early in their life respond best to water soluble forms of P_2O_5 whereas crops with a long growing season can respond well to citrate soluble phosphate depending however upon the existing reserve of phosphorus in the soil and soil acidity levels.

In many cases the chemical form in which the P_2O_5 is applied (eg. MAP, DAP, SSP, or TSP) is not in itself important. Several references substantiate such a conclusion (8,9,10). Of course, in making this comment, account has to be taken of the fact that some of the various forms also contain Nitrogen which may or may not be needed for the soil and crop in question. On the other hand, different crop responses to TSP and DAP might be expected due to differences in their cations and also because of the very different pH values of saturated solutions leaving the granules (11). It can however be concluded that there is no fundamental reason, other than commercial, for an arbitrary upper limit to be imposed on fertiliser analysis and that the vital emphasis should be on the degree of solubility, the form of the insoluble compounds present and the nature of the phosphate reactions in the soil.

b. Legislated Analysis.

In practice, nearly all countries legislate on fertiliser quality and analysis. Minimum nutrient content together with permitted deviations from the declared analysis are normally specified but methods of analysis can vary considerably. On TSP for example, the product is sold in USA on the basis of available P_2O_5 as measured by the AOAC method whereas in the EEC there are minimum limits on both citrate soluble P_2O_5 (neutral ammonium citrate method) and water soluble P_2O_5 . The method of analytical measurement of citrate soluble P_2O_5 is different in the two cases, as is the permitted deviation. In Brasil, citrate solubility is analysed by a method involving citric acid, which again gives different results to the AOAC and EEC methods.

In situations where a rock mining and beneficiation facility already exists, the legislated method of analysis for the fertiliser can influence the choice of phosphoric acid production route.

In order that the effect of impurities can be better understood and quantified, it is necessary to consider the probable compounds formed upon ammoniation to DAP. Several published papers (12, 13, 14) provide data on this subject and these enable a base point to be established from which a series of calculations can be made to estimate the effect of a variation in wet process acid impurities on DAP grade. A summary calculation is shown in FIG. 9.

Fig. 10 provides data measured during 1980 on three DAP Plants in Florida. The calculation method described above was applied to these cases as a means of comparison and a fairly satisfactory correlation was obtained as summarised in Fig. 11. The calculated DAP analyses (average 18.9 - 46.6) makes an interesting comparison with the results of a survey undertaken in 1965 of five major producers in the Florida area which showed average DAP analyses at that time of 18.7 - 47.6.

In the special case of high MgO rocks, recent data published by IMC and TVA (15, 16) has also been subjected to this calculation method where again a close correlation with measured results was obtained.

FIG. 9

CALCULATION OF DAP ANALYSIS FROM 40% P₂O₅ ACID ANALYSIS

<u>Components in 40% P₂O₅ Acid</u>		<u>Species After Ammoniation</u>		<u>N</u>	<u>P₂O₅</u>
<u>Component</u>	<u>KG/100 KG (Acid)</u>	<u>Component</u>	<u>KG/100 KG (Acid)</u>	<u>KG/100 KG (Acid)</u>	<u>KG/100 KG (Acid)</u>
Fe ₂ O ₃	1.45	FePO ₄	2.74	-	1.29
F	1.83	(NH ₄) ₃ AlF ₆	3.13	0.67	-
Al ₂ O ₃	1.4	AlPO ₄	1.39	-	0.81
MgO	0.55	MgNH ₄ PO ₄ ·H ₂ O	2.09	0.19	0.97
CaO	0.65	CaSO ₄	1.58	-	-
SO ₄	4.6	(NH ₄) ₂ SO ₄	4.8	1.02	-
P ₂ O ₅	43.4	(NH ₄) ₂ HPO ₄	75.05	15.92	40.33
Inerts			1.9	-	-
H ₂ O			1.9	-	-
			94.58	17.80	43.4

N Content of DAP = $\frac{17.8}{94.58} \times 100 = 18.8\%$

P₂O₅ Content of DAP = $\frac{43.4}{94.58} \times 100 = 45.9\%$

WS P₂O₅ Content of DAP = $\frac{40.33}{94.58} \times 100 = 42.6\%$

FIG. 10

MEASURED PHOSPHORIC ACID AND DAP ANALYSES - FLORIDA ROCK (% by weight)

COMPONENT	<u>PLANT A</u>		<u>PLANT B</u>		<u>PLANT C</u>	
	<u>Phosphoric Acid</u>	<u>DAP</u>	<u>Phosphoric Acid</u>	<u>DAP</u>	<u>Phosphoric Acid</u>	<u>DAP</u>
P ₂ O ₅ - Total	38.2	46.7	40.4	46.9	43.4	46.53
P ₂ O ₅ - C.I.	-	0.16	-	0.51	-	0.35
P ₂ O ₅ - W.S.	-	41.7	-	42.9	-	42.08
CaO	0.35	-	0.40	-	0.65	0.79
SO ₃	1.85	3.02	2.71	3.84	3.83	4.33
Al ₂ O ₃	1.32	1.66	1.11	1.27	1.40	1.42
Fe ₂ O ₃	1.85	2.31	0.81	1.01	1.45	1.50
MgO	0.51	0.64	0.52	0.61	0.55	0.57
Na ₂ O	0.095	-	0.13	-	0.20	0.24
K ₂ O	0.10	-	0.11	-	0.15	0.15
F	1.88	-	1.47	-	1.83	1.91
SiO ₂	0.21	-	0.17	-	0.36	0.38
N	-	18.21	-	19.01	-	18.20

FIG. 11 COMPARISON BETWEEN MEASURED AND CALCULATED DAP ANALYSES
- FLORIDA ROCK

	<u>PLANT A</u>	<u>PLANT B</u>	<u>PLANT C</u>
Measured Analysis	18.21 - 46.54	19.01 - 46.39	18.20 - 46.18
Calculated Analysis	18.66 - 47.00	19.20 - 46.98	18.80 - 45.90

Other specific case histories have been examined with a view towards evaluating the effect of rock analysis and process route on the fertiliser grade. FIG. 12 summarises some pilot plant work undertaken on Western Sahara rock where two different grades were processed into phosphoric acid. The resulting MAP, DAP, and TSP analyses are tabulated, indicating in the case of DAP a fall in analysis from 20.1 - 49.1 to 19.3 - 48.7 as the rock grade fell from 80 BPL to 75 BPL.

(17)
FIG. 12 CASE HISTORY - WESTERN SAHARA ROCK

	<u>ROCK</u>		<u>ACID FROM 75 BPL ROCK</u>		<u>ACID FROM 80 BPL ROCK</u>	
	<u>75 BPL</u>	<u>80 BPL</u>				
P ₂ O ₅	35.2	36.6	31.0	50.0	31.6	50.0
SO ₃	0.48	0.44	1.65	2.39	1.78	2.24
Al ₂ O ₃	0.44	0.35	0.31	0.50	0.10	0.20
Fe ₂ O ₃	0.16	0.14	0.15	0.25	0.33	0.52
MgO	0.11	0.06	0.10	0.16	0.10	0.16
F	3.73	3.93	2.96	0.93	1.79	0.55
SiO ₂	5.48	4.52	1.19	0.02	0.85	0.02

	<u>Fertiliser From 75 BPL Rock</u>				<u>Fertiliser From 80 BPL Rock*</u>			
	<u>NH₄-N</u>	<u>Total P₂O₅</u>	<u>W.S. P₂O₅</u>	<u>C.S. P₂O₅</u>	<u>NH₄-N</u>	<u>Total P₂O₅</u>	<u>W.S. P₂O₅</u>	<u>C.S. P₂O₅</u>
MAP	12.2	55.2	53.7	55.2	12.9	60.4	50.2	60.0
DAP	19.3	48.7	47.8	48.6	20.1	49.1	48.3	49.0
TSP	-	51.0	48.5	50.5	-	-	-	-

* Calculated results

In a pilot plant evaluation of Langebaan rock, the effect of two different routes (dihydrate and hemihydrate) on phosphoric acid analysis and TSP grade was studied. This work summarised in FIG. 13 indicates a marginally higher TSP analysis based on the hemihydrate acid as a result of lower Al_2O_3 and solids level in the acid derived from the hemihydrate route.

(17)

FIG. 13 CASE HISTORY - LANGEBAAN ROCK

	<u>ROCK</u>	<u>DIHYDRATE ACID</u>	<u>HEMIHYDRATE ACID</u>
P_2O_5	30.5	50.0	50.0
SO_3	0.57	2.5	1.5
Al_2O_3	0.95	1.77	1.06
Fe_2O_3	1.21	2.43	2.15
MgO	0.48	0.84	0.7
F	2.79	1.14	0.57
SiO_2	12.0	0.19	0.11
Solids	--	3.6	2.74

TSP ANALYSES

	Total P_2O_5	W.S. P_2O_5	C.S. P_2O_5	Free Acid % P_2O_5
Dihydrate Acid	45.1	36.6	42.6	8 - 10
Hemihydrate Acid	45.6	37.9	43.7	5 - 6

The above analyses indicate a slightly better TSP product from hemihydrate based acid even with a lower excess free acid which would be expected to lower the citrate solubility. Calculations of the P_2O_5 combined in phosphates of Al_2O_3 , Fe_2O_3 and MgO support the above analyses within the limits of experimental error giving a marginally lower citrate solubility but underestimating the water soluble P_2O_5 by several percent. This is no doubt due to the masking effect of insoluble $Ca(H_2PO_4)_2$.

A similar trend was reported (18) on the Windmill fertilisers plant in Holland where phosphoric acid is produced by both dihydrate and hemihydrate routes using Togo rock. MAP based on hemihydrate acid analysed at 11.5 - 58.0 compared with 10.5 - 53.0 for the unclarified dihydrate acid.

CONCLUSION

As lower grade rock deposits are opened up in the future, plant designers and operators will be faced with many of the problems which have been experienced in Florida in recent years. These include the need to develop more sophisticated beneficiation and acid clarification techniques. Greater difficulty in achieving legislated fertiliser analyses together with possible physical problems in granulation can also be expected. The situation facing such operators can be eased by judicious advance planning and route optimisation. Calculation techniques derived from actual experience, as described in this paper, have a role to play in the planning and development of new phosphate projects.

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DISCUSSION : (Rapporteur R. Schoemaker, UKF, Netherlands)

Q - Mr. R. van HARDEVELD, D.S.M., Netherlands

Your paper suggests that elaborate research programs are necessary not only on rock beneficiation, acid preparation and further acid processing but also the agricultural effect of the products has to be taken into account to obtain the economic optimum. Can you give your views on how these elaborate and costly research programs could be organized?

A - This is a difficult problem because, as I have said, there are many different parties involved in the decision making, often including also government agencies. There are different restrictions, budgets and so on to consider in each case.
I think that all that can be said is that at the outset of a project strong attempts should be made to explain to the decision makers the whole extent of the problem together with the costs involved and the repercussions of wrong decisions so that, hopefully, the program can be directed along the most appropriate lines.

Q - Mr. M. SMANI, Cerphos, Morocco

In the development of a new project, could you indicate:
The time required for the total evaluation program?
The approximate cost of the research on phosphate, phosphoric acid and the related fertilisers TSP and DAP?

A - It could be envisaged that the period required between discovery and exploitation of a phosphate deposit would be at least five years, probably more. This would include the time for thoroughly evaluating the characteristics of the deposit by means of an extensive drilling programme, an evaluation of the most suitable mining methods and a programme for establishing the beneficiation route. Regarding beneficiation, it will be necessary to undertake bench trials, then to establish a pilot plant and after that probably a semi-industrial scale beneficiation unit of several thousand tonnes/annum capacity. Whilst this is proceeding, it is recommended that preliminary phosphoric acid bench scale trials possibly involving more than one type of process are undertaken in parallel.
As far as cost is concerned, this will obviously be considerable if the semi-industrial scale unit is taken into account but the benefits will be justified by the avoidance of many problems at the full commercial scale. For one definitive phosphoric acid pilot plant trial and including also the TSP and DAP trials, the cost would be around £ 50,000. This should be undertaken on a representative beneficiated rock sample, probably obtained from the semi-industrial scale unit, at an appropriate time.

Q - Mr. T.W. DEVEREUX, Esso Chemical, Canada

Your data, (fig.3), show that $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ generally increases as BPL decreases. However, the ratio $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ peaks at 66/68 BPL.

- Do you consider this peak significant?
- Why does it occur?
- How might it affect the production of acid and DAP?

A - I could not say definitively why it occurs except that it appears that, in the case of the very low BPL grades now being exploited (and by this I mean around 60 BPL), there is a considerable increase in the magnesium and a relative fall in the Al_2O_3 to Fe_2O_3 ratio.

I do not think that the peak you have mentioned at 66/68 BPL is significant in itself because these grades are being satisfactorily processed at present. However what I can say is that we recently studied a phosphate with a much higher Al_2O_3 to Fe_2O_3 ratio than is found in Florida and we experienced tremendous problems of filtration, post-precipitation etc..., far greater for example than when the ratio is reversed. So personally, I believe that Al_2O_3 is likely to be much more of a problem than Fe_2O_3 .

Q - Mr. J.J. MILCKHUYSE, UKF, Netherlands

I think that in the western world we go through a lot of costs to arrive at a required rate such as 18-46-0. This is mainly for competitive reasons as far as I could see because the plant would not know if you feed it a 46% or 40% P_2O_5 -formula at a required rate of application. However, I do not agree with your philosophy if we look at developing countries. If they can produce with much less costs lower grades from their own phosphate rocks for their own markets, there is no reason whatsoever to spend a lot of money on beneficiation. Please give your opinion about this.

A - I agree, however the philosophy is provided to meet a need. The United States has pioneered the production and use of DAP and much of this material has found its way out the export market. Now when tenders are called for DAP from overseas they invariably refer to 18-46-0 as a requirement. The problem is that the legislation demanded in the U.S. has clouded everyone else's judgement.

I think that for the developing countries there is a lot to be said for avoiding DAP and making say MAP or even single superphosphate where the same problems of legislation do not occur.

Q - Mr. T.R. BOULOS, National Research Centre, Egypt

In view of the generalized conflicting remarks of the role of the different gangue minerals, do you think it is easy to formulate the best production pattern of phosphatic fertilisers in view of the chemical characteristics of the phosphate concentrate?

- A - This is a complicated question which would take a long time to answer fully and I am not really the best person to answer such questions of mineralogy. It can be said however that there is certainly no substitute for a properly directed pilot plant programme and for any new deposit you will need to go through the steps I have mentioned. The calculation methods and other techniques I have described are not intended to replace pilot planting in any way but they will help in establishing an optimised basis for an experimental programme.