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

THE INTERNATIONAL SUPERPHOSPHATE MANUFACTURERS' ASSOCIATION

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LE/610 (a) (4)

AAREUS TECHNICAL MEETINGS September 19-22 1955

THE EVOLUTION OF FLUORINE DURING THE MANUFACTURE
OF SUPERPHOSPHATES.
(ETS KUMMER) By H. DELOMENIE.

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Some years ago we undertook a series of laboratory tests to determine experimentally the amount of sulphuric acid needed for the manufacture of superphosphates from different types of natural phosphate rock. During these experiments, as a check on the total amount of sulphuric acid consumed, we made a separate test on each of the components of the mineral to find out what happened when acidulation by sulphuric acid began. These components were: calcium carbonate, calcium phosphate, calcium fluoride, compounds with a silicon base, iron oxide, aluminium oxide and the oxides of alkaline bases (clays, feldspars, etc.)

We noticed at that time that the reaction of fluorine compounds varied within fairly wide limits, not only with the types of natural phosphates, but also with the conditions under which acidulation took place. And as these differences in the behaviour of fluorine compounds when subjected to acidulation by sulphuric acid has a direct influence on the amount of acid consumed, the study of it will certainly be of interest to manufacturers of superphosphates.

The results which are presented in this paper were obtained from laboratory tests where the superphosphate was made by the old-fashioned method of dens; in our opinion they cannot be applied directly to the conveyor-belt process of manufacturing superphosphates where the release of gases and vapours occurs under totally different conditions.

Types of Phosphates used for Tests.

We made our tests on the following rocks:

- a) Morocco phosphates
 - phosphate 79/30 %
 - " 75 %
 - " 70 %
- b) Gafsa phosphate 63/65 %
- c) M'Dilla phosphate 65 %
- d) Land Pebble phosphate
- e) Kola phosphate

In Tables I and 2 we have grouped the chemical analyses and the analyses of particle-size for these various natural phosphates. (See separate sheets for tables)

Methods used for determining the quantity of fluorine

Two methods were used:

- 1) The old, Berzelius-Rose method, where the fluorine is distilled with sulphuric acid to give SiF₄. The gas is collected in a soda solution, the silicon is eliminated by ammonium carbonate in the presence of a small quantity of zinc oxide in a solution of ammonia.

LE/610 (d)(4)

The liquid, now containing sodium fluoride and sodium carbonate, is treated at boiling point with calcium chloride. The precipitate, a mixture of calcium carbonate and calcium fluoride, is collected, washed and dried. This precipitate is taken up in dilute acetic acid to remove the calcium carbonate. Finally, the precipitate of calcium fluoride is collected, dried, calcined and weighed.

Even today this method is still one of the best we know. But it has the disadvantages of being complicated, requiring very skilled handling and of being very long.

2) Lead chlorofluoride method.

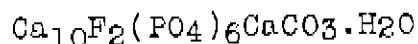
(Nouyrigat - Congress of Industrial Chemistry, Brussels 1954)
As in the other method, the fluorine is distilled in the form of silicon fluoride. Then it is precipitated in the form of lead chlorofluoride in the presence of a known quantity of chloride ions. The excess of chloride is titrated by potentiometer and the fluorine is computed from the quantity of chlorine precipitated in the form of lead chlorofluoride.

Fluorine content of natural phosphates and types of fluorine compounds.

It is agreed that fluorine occurs in natural phosphates in the form of calcium fluophosphate or apatite, to which the formula $Ca_5F(PO_4)_3$ is generally attributed, where for each molecule of $Ca_3(PO_4)_2$ there is one third of a molecule of CaF_2 .

In Kola phosphate all the fluorine is in the form of simple apatite.

In the North African phosphates, some authorities consider the fluorine to be held in a complex combination: staffelite, which is said to be a fluoro-phospho-calcium carbonate:



But even in this complex, there would still be one third of a molecule of CaF_2 to one molecule of $Ca_3(PO_4)_2$, as in fluoro-apatite.

Now, if we look at the analyses of the various natural phosphates, we can see that most of them have a higher calcium fluoride content than that which is theoretically contained in apatite.

The following table shows the ratio between the molecules of calcium fluoride and those of tricalcium phosphate found in the phosphates which were examined.

TABLE 3

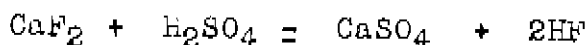
Type of phosphate	7 molecules of CaF_2 to 1 molecule of $Ca_3(PO_4)_2$
Theoretic apatite $Ca_5F(PO_4)_3$	0.333
Morocco phosphate 79/80	0.402
" " 75	0.437
" " 70	0.446
Gafsa phosphate 63-65	0.432
M'Dilla phosphate 65	0.441
Land Pebble phosphate	0.420
Kola phosphate	0.298

LE/610 (d) (4)

As the foregoing table shows, all the natural phosphates examined, with the exception of Kola phosphate, contained an excess of calcium fluoride as compared with tricalcium phosphate. In the commonest African phosphates, 75-77% of the fluorine corresponds to the P₂O₅ assumed to be in the form of apatite, and 23-25% of the fluorine may be assumed to be in some other form. If we take the particular example of Morocco phosphate, where three different forms were examined (36.13%, 34.10% and 32.10% of P₂O₅), we notice that the proportion of calcium fluoride is lower when the tricalcium phosphate content of the mineral is higher, and this invalidates the hypothesis that all the excess calcium fluoride is present in the form of a solid solution in the apatite alone, but shows on the contrary that calcium fluoride not in combination with calcium phosphate in the form of apatite is also found disseminated among the inert components, especially calcium carbonate.

Reaction of Fluorine Compounds when sulphuric acid acidulation of natural phosphates is performed in the manufacture of super-phosphates.

During acidulation of the natural phosphates by sulphuric acid, a certain proportion of the acid reacts at first with the carbonated rock (gangue), if it is present; a larger proportion reacts with the various forms of calcium phosphate and calcium fluoride. In addition to phosphoric acid, calcium monophosphate and calcium sulphate, which occur in superphosphates, hydrofluoric acid is also formed:



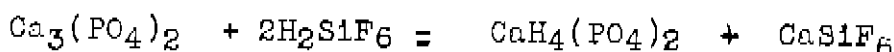
A part of the hydrofluoric acid which has been formed reacts with the silica and silicates contained in the phosphate rock, to give silicon fluoride:



A certain amount of silicon fluoride and even of hydrofluoric acid is released. The remaining silicon fluoride is decomposed by the action of the water and water vapour to give fluosilicic acid:



The hydrofluoric and fluosilicic acids also react with the calcium phosphate and contribute to the solubilization of the P₂O₅.



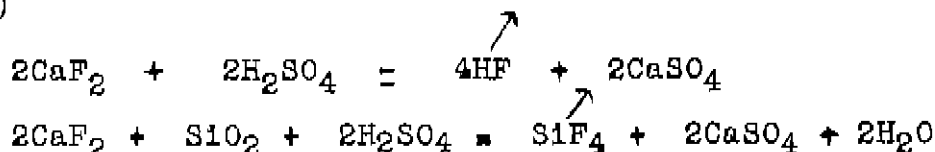
This phenomenon is further complicated by the fact that under the influence of the temperature reached in the den and in the presence of water-soluble calcium salts and water, the calcium fluosilicate is partly decomposed into CaF₂, SiO₂ and HF by the following reaction:



From this long series of reactions, it is clear that the acidulation of calcium fluoride finally produces three categories of fluorine derivatives:

- 1 - the volatile fluorinated compounds HF and SiF₄ which are removed with the carbon dioxide and other gases:

LE/610 (d)(4)



Note that the formation of either 4HF or SiF₄ involves an equal consumption of sulphuric acid, which is then lost and not available for the solubilization of the P₂O₅.

- 2 The soluble fluorine compounds formed by fluosilicic acid and its salts (calcium fluosilicate, which may occur with aluminium, iron or magnesium fluosilicates, all very soluble in water, and other less soluble alkaline fluosilicates):



In order to calculate the sulphuric acid consumed in this reaction, we assume that the fluosilicic acid occurs solely in the form of metallic fluosilicates and not in the form of free fluosilicic acid. In reality a part of it must be in the form of free acid, causing an error in the determination of free phosphoric acid. But at the time of the determination of the free phosphoric acid in the superphosphate, all the free acid, of whatever kind, has already been expressed in terms of free P₂O₅. If we allowed for the existence of solubilized fluorine in the form of free fluosilicic acid, then the same consumption of sulphuric acid would be counted twice. Note that in these conditions the acidulation of calcium fluoride, which gives solubilized fluorine uses only two-thirds the amount of sulphuric acid as when the acidulation of calcium fluoride gives the volatile fluorine compounds (HF or SiF₄).

- 3 Finally, part of the fluorine is found in the superphosphate in the form of insoluble calcium fluoride. This insoluble calcium fluoride is not principally formed by the unreacted calcium fluoride of the original fluorine or apatite; it is chiefly the result of the series of more or less complex reactions which we have just described. But from the point of view of accounting for the consumption of sulphuric acid, it is exactly as if some of the calcium fluoride has resisted acidulation.

Thus it is plain that as the formation of one or other of the fluorine compounds predominates during the acidulation of the natural phosphates, consumption of sulphuric acid will vary depending upon the acidulation of the calcium fluoride.

Maximum consumption will occur if all the fluoride is released in the form of hydrofluoric acid or silicon fluoride, whereas it will be nil if all the fluorine remains in the superphosphate in the form of calcium fluoride.

Conditions under which the tests were carried out.

For these experiments, we created working conditions reminiscent of the laboratory of the Comptoir des Phosphates. Here is a brief description:

The phosphate and sulphuric acid at 35° are hand-mixed with a spatula in a cylindrical vessel (height 35 cm., diameter 20 cm.) previously heated to 60°.

After hand-mixing for one minute, the lid is put on and the whole is placed in the drying-oven at a temperature of 98-100° for four hours. The vessel, which is now acting as a den, is kept

LE/610 (d)(4)

under a pressure of 15mm. When the vessel has been in the oven for 4 hours at 98-100°, it is cooled and weighed. Then the superphosphate is broken up and screened, even if it is agglomerated. Then it is placed in a closed container and left for precisely 30 days in a drying oven maintained at 25°. At the end of this time it is analysed.

Each test was carried out on 2Kg of phosphate, weighed dry, but brought up for the purpose of these experiments to a uniform humidity of 1.5%, which required the use of 1800-1900 grams (according to the case,) of sulphuric acid at 53-54Bé. These proportions allowed us to weigh to the nearest gram on the Roberval balance and were quite suitable for the determinations of the precision we required.

The total fluorine content of the superphosphate could be used to calculate the exact percentage of fluorine released in the form of silicon fluoride or hydrofluoric acid (by working out the ratio of fluorine to a fixed element easy to determine, P₂O₅, for instance, or to the weight of superphosphate obtained.)

By determining the insoluble fluorine we can calculate by difference the content of the water-soluble fluorine in the superphosphate. For this calculation we adopted the official French method for the preparation of an aqueous solution for the determination of water-soluble P₂O₅.

We are aware that this method of determining soluble fluorine may be criticized on account of the instability of the fluosilic ion in the presence of the soluble salts of calcium, but we took the precaution of performing this extraction at a temperature of less than 20°, as is always done with an acid medium, and we think that the determination of fluosilic ions by this method is hardly more open to criticism than the determination of water-soluble P₂O₅ in superphosphate, especially when these are rich in salts of iron and calcium.

For ease of expression during this paper, we shall use the term acidulated fluorine to indicate the fluorine released in the form of silicon fluoride or hydrofluoric acid and the solubilized fluorine in the form of fluosilicic acid. The insoluble fluorine in the superphosphate is considered as non-acidulated fluorine, whatever its origin may be, because after all it has not caused the consumption of any sulphuric acid.

RESULTS OBTAINED.

The whole of the results we have obtained show that the acidulation of the calcium fluoride in phosphates varies considerably with:

- 1) type of phosphate
- 2) concentration, temperature and quantity of sulphuric acid used
- 3) size of particles of the rock

1. - Influence of the type of phosphate

In Table 4 we have grouped some of the results obtained by the acidulation of several natural phosphates with 68.25% sulphuric acid at 35°. For the Kola phosphate, however, we used 63.50% sulphuric acid at 50°, as acidulation was unsatisfactory with a 68% sulphuric acid.

In all cases the quantity of sulphuric acid used was enough

LE/610 (d)(4)

to ensure that after curing for a month solubilization of P_2O_5 (water + citrate soluble) would equal 95-98%.

For the M'Dilla and Gafsa phosphates, we observed, all other conditions being the same, that acidulation of the calcium fluoride was much more vigorous than with Morocco, Land Pebble and Kola phosphates. The Kola phosphate however, should be set aside, in view of the special conditions which are needed for a satisfactory acidulation. The most important differences mainly affect the water soluble fluorine.

TABLE 4

ACIDULATION OF CALCIUM FLUORIDE.

Type of phosphate	Total SiO_2	SiO_2 as quartz	% of total P_2O_5 sol. w + c after 30 days curing.	% of total F released	% of F made water soluble	% of total F released and solubilized.
Morocco phos. 75 fairly fine.	2.32	0.90	97.7	17	15.9	32.9
Morocco phos. very coarse.	2.80	1.50	97.56	24.2	14.65	38.85
M'Dilla phos. 65 coarse	4.10	0.80	95.7	18.05	40.15	58.2
Gafsa phos 65 fairly coarse	5.40	0.65	95.3	22.85	39.50	62.35
Land Pebble phos. fine	6.40	4.20	96.18	12.60	13.7	25.30
Kola phos. fine	3.03	0.4	95.2	12.65	9.35	22

As the release and solubilization of the fluorine are due to the silicon, it is tempting to attribute this difference in acidulation of calcium fluoride to the different content of silicon and silicates of the various phosphates.

We therefore determined for the various phosphates, not only the total silicon, but by X ray diffraction also the silicon in the form of quartz. The results obtained are shown in Table 4.

Various authors agree that the silicates in natural phosphates are not, or very little, acidulated during the manufacture of superphosphates, and that only silicon in the free form (quartz) is involved in the formation of silicon fluoride and its derivative fluosilicic acid. But a study of the above table seems to show plainly that the silicate silicon is substantially involved in the building-up of fluorinated silicon compounds.

LE/610 (d) (4)

In an attempt to demonstrate the influence of the free silicon on the formation of silico-fluorine compounds, we made two tests after mixing with Morocco phosphate 70: (a) 5% of its weight of very finely ground Fontainebleau sand (particle-size less than 75,) and (b) 5% of Kieselguhr.

Here are the results we obtained, set out in Table 5.

TABLE 5

	% of total F released	% of total F made water soluble	% of total F released and made water soluble.
Morocco phos. 70 untreated (coarse)	24.2	14.65	38.85
Morocco phos. 70 plus 5% Fontainebleau sand	22	16.30	38.3
Morocco phos. 70 plus 5% Kieselguhr	26	14.2	40

The foregoing results show that the addition of considerable quantities of either quartz or Kieselguhr to the phosphate has practically no effect on the release and solubilization of the fluorine. These results agree with those obtained by Whynes (Whynes - Release and absorption of fluorine during manufacture of superphosphate - ISMA Technical Convention, Cambridge, 1953.) who observed no appreciable increase in the release of fluorine gases from the addition of sand or precipitated silicon to the mineral.

It must therefore be allowed that the silicate content of the natural phosphates and above all, the type of silicates they contain have a great influence on the formation of silicon fluoride. The silicon of silicon fluoride and its derivative, fluosilicic acid, seems to be mainly derived from certain natural silicates in the rock which are easily acidulated, and the acidulation of these silicates by sulphuric acid is helped by the hydrofluoric acid resulting from the acidulation of the calcium fluoride.

2. - Influence of concentration, temperature and quantity of sulphuric acid used.

(a) The concentration of the sulphuric acid strongly affects the release of the fluorine, even when it varies within limits as narrow as 65-70%. Thus, with Morocco phosphate 75 (fairly fine) we obtained the following results using the same quantity of sulphuric acid for the acidulation at concentrations of 68.25% and 66%.

TABLE 6

	% of total F released.	% of F made water soluble	% of total F released & made water soluble
Sulphuric acid at 68.2%	17	15.9	32.9
Sulphuric acid at 66%	11	12	23

LE/610 (d)(4)

(b) The fluorinated gases are released mainly in the very first moments of acidulation. Use of heated sulphuric acid produces an increase in the proportion of volatile fluorine. On the other hand, if the mixture is cooled at the time of mixing, the release of fluorinated compounds is greatly reduced. Thus with the coarsely ground Morocco phosphate 70, we carried out a test where the temperature was not allowed to rise above 55° during the first 10 minutes of acidulation, all other conditions being the same, and compared it with normal acidulation.

TABLE 7

Test conditions	% of total F released	% of total F solubilized	% of total F released and solubilized.
Normal	24	14.65	38.85
Mixture maintained at 55° for first 10 mins. of reaction.	10.4	14.4	24.8

(c) Finally, the quantity of sulphuric acid used, even when it varies within the amounts commonly used for acidulation of phosphates, has a certain influence on the proportion of fluorine compounds released and solubilized. In the following table (Table 8) we have grouped the different results obtained by varying the proportions of sulphuric acid in the acidulation of M'Dilla and Gafsa phosphates, all other conditions remaining unchanged.

TABLE 8

	H ₂ SO ₄ 100% used for 100 kg dry phosphate	% of total F released	% of F solubilized	% of F released and solubilized
M'Dilla phos. 65 coarse.	66.7 kgs	21.4	45.5	66.9
	63.2	18.05	40.15	58.20
	58.9	18	26.7	44.70
Gafsa phos. 63-65 fairly coarse	65.17	26.4	41.4	67.8
	62.65	22.85	39.5	62.35
	60.90	19.25	39.25	58.50

3. - Influence of the particle-size of the mineral.

Our laboratory tests confirmed that the fineness of the phosphate rock had a great influence on the different proportions of volatile and soluble fluorine.

In the following table (Table 9) we have grouped two series of comparative tests which were carried out with Morocco phosphate 70 and M'Dilla 65 with very different particle-sizes.

LE/610 (d)(4)

TABLE 9

Note: Particle-sizes of the rocks are shown in Table 2.

	H ₂ SO ₄ 100% used for 100 kg dry phosphate	% of total F released	% of F solu- bilized	% of F released and solubilized
<u>Morocco phos.70</u>				
coarse	65.3 kgs	24.2	14.65	38.85
fine	65.3	8.65	17.80	26.45
<u>M'Dilla phos.65</u>				
coarse	63	18.05	40.15	58.20
fine	63	4.37	47.20	51.57

With very finely ground phosphates the proportion of fluorine released is very definitely less and that of soluble fluorine slightly more. In this case, acidulation proceeds rapidly and vigorously, the fluid and slurry stages are much shorter, and the concentration of the sulphuric acid declines rapidly as a result of the speed of the reaction, and these conditions are unfavourable for the release of silicon fluoride.

Influence of the long curing of supers on the evolution of F.

Determinations of fluorine in all the superphosphates we have been discussing were carried out after curing for one month at 25° in a closed atmosphere. We also carried out many determinations of fluorine (total and water soluble) on products which had cured for 15-18 months. The results obtained showed only slight differences in comparison with the others.

We noticed, however, that the superphosphates prepared with a smaller amount of sulphuric acid showed a slight drop in the water soluble fluorine, due no doubt to incomplete reaction of calcium fluosilicate due to the low acidity of the medium.

Influence of acidulation of fluorine compounds on the consumption of sulphuric acid.

The determination of total fluorine and water-insoluble fluorine in superphosphates makes it possible, given the fluorine content of the mineral, to calculate quite simply the percentage of total fluorine released, and the percentage of solubilized fluorine. We can then easily compute the quantity of sulphuric acid consumed in the acidulation of calcium fluoride. Thus, if we call:

- F the fluorine content (%) of the natural phosphate
- a percentage of total fluorine released
- b percentage of total fluorine solubilized
- Q = quantity of sulphuric acid (100%) consumed by acidulation of the calcium fluoride in 100 kgs of dry natural phosphate

we have :

$$Q = \frac{98 \times F \times a}{38 \times 100} + \frac{2 \times 98 \times F \times b}{3 \times 38 \times 100}$$

$$Q = F(0.0257 a + 0.0171 b)$$

LE/610 (d)(4)

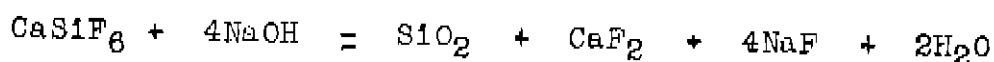
We thus calculated from the proportions of fluorine released and fluorine solubilized (given in Table 4) the percentage of sulphuric acid used for the manufacture of superphosphate which was consumed in each case by acidulation of fluorides.

TABLE 10

Type of phosphate	% of H ₂ SO ₄ used consumed for release of F	% of H ₂ SO ₄ used consumed for solubilized F	% of H ₂ SO ₄ used consumed for acidulation of fluorides.
Morocco phos.75 (fairly fine)	2.71	1.70	3.42
Morocco phos.70 (coarse)	3.67	1.48	5.15
M'Dilla phos.65 (coarse)	2.58	3.87	6.45
Gafsa phos.64 (fairly coarse)	3.18	3.66	6.84
Land Pebble phos.	2.07	1.51	3.58
Kola phos.	1.54	0.76	2.30

As the above figures show, the consumption of sulphuric acid caused by acidulation of fluorides is far from negligible, especially with M'Dilla and Gafsa phosphates.

The results presented in this paper show that there exist in superphosphates variable but sometimes substantial quantities of fluorine in the form of fluorine compounds. But even if we assume that all the fluosilicic acid is in the form of metallic salts, we should in conclusion like to draw attention to an error caused by these fluosilicic compounds in the direct determination of free acidity in superphosphates resulting from partial decomposition, even with cold mixtures, of calcium fluosilicate when the pH of the aqueous solution rises to the end point of the chosen indicator.



CONCLUSIONS.

The release of silicon fluoride or of hydrofluoric acid represents only one of the aspects (the most obvious) of the acidulation of calcium fluoride in the manufacture of superphosphates.

In calculating the sulphuric acid required for the manufacture of superphosphates, we must not forget the proportion of acid which is consumed by the transformation of calcium fluoride into the metallic fluosilicates which are found in superphosphates.

In this paper we have shown the factors which affect the degree of acidulation of the calcium fluoride in natural

LE/610 (d)(4)

phosphate rocks. The results we have been discussing are results obtained in the laboratory under pre-determined conditions. The amounts of fluorine which may be found to be released and solubilized in an industrial process may vary greatly according to the working conditions adopted for the manufacture of superphosphates.

These results have been, we repeat, extracted from earlier work on the experimental determination of the quantity of sulphuric acid required for the manufacture of superphosphates by the den process for each of the types of natural phosphates commonly used in France. We should have liked to be able to show a parallel series of results for the acidulation of calcium fluoride in the conveyor-belt manufacture of superphosphate; but we have not had time for such a study. Nevertheless, the fragmentary results we have obtained seem to show that in the conveyor-belt process a higher proportion of fluorine is released in the form of calcium fluoride or even of hydrofluoric acid, while a smaller percentage of fluorine is solubilized.

TABLE 1ANALYSES OF NATURAL PHOSPHATE ROCKS USED

(The analyses are given for rock oven-dried at 105-110° - all in percentages)

ORIGIN	P ₂ O ₅	F	CO ₂	SiO ₂	SO ₃	CaO	MgO	Al ₂ O ₃	F ₂ O ₃	Na ₂ O	K ₂ O	Loss on heat: (organic mat and H ₂ O in compounds)
Morocco phos. 79/80	36.13	3.88	2.91	1.37	1.38	53.35	0.08	0.60	0.36	0.46	0.25	0.74
Morocco Phos. 75	34.12	3.99	4.3	2.32	1.47	51.31	0.79	0.57	0.22	0.4	0.2	-
Morocco phos. 70	32.11	3.83	6.10	2.80	1.47	50.96	0.85	0.49	0.18	0.68	0.23	-
Gafsa phos. 63-65	29.25	3.37	5.7	5.40	2.86	47.01	1.35	0.90	0.44	1.06	0.24	1.80
M'dilla phos. 65	29.78	3.52	5.97	4.10	3.22	49.14	0.83	0.80	0.54	0.80	0.38	2.17
Land Pebble phos.	34.53	3.87	2.54	6.40	0.56	48.34	0.43	1.17	1.05	0.40	0.20	-
Kola phos,	39.30	3.13	trace	3.03	0.01	51.82	0.57	1.17	0.64	1.99	0.17	-

TABLE 2

ANALYSES OF PARTICLE-SIZE OF PHOSPHATE ROCKS USED

TYPE OF PHOSPHATE	% rejects from screening with the following mesh:				
	395 μ	250 μ	180 μ	150 μ	75 μ
Morocco phos. 79-80	0	0.001	0.008	1.38	68.15
Morocco phos.75	0.10	0.60	3.44	7.82	47.41
Morocco phos.70 (coarse)	0.62	4	17.55	31.25	87.06
(fine)	0	0.03	-	1.80	50.70
Gafsa phos. 63-65 (fairly coarse)	0.80	3.78	12.16	20.56	67.58
(very fine)	0	0	0	0	9.3
M'Dilla 65 (coarse)	0.37	2.75	13.12	31.07	90.02
(fine)	0	0	0.02	0.40	23.6
Land Pebble	0.03	0.12	0.79	2.97	31.73
Kola phos.	0.09	0.27	2.18	5.80	41.80