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**THE USE OF DIFFERENT
TYPES OF PHOSPHATE
ROCK IN SINGLE AND
TRIPLE SUPERPHOSPHATE
PRODUCTION**

by

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THE USE OF DIFFERENT TYPES OF PHOSPHATE ROCK IN SINGLE AND TRIPLE SUPER-PHOSPHATE PRODUCTION

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Introduction.

In introducing the paper Mr. T. P. Dee said he thought it was fairest to indicate where the responsibility lay. Mr. Sharples had provided a script on the technical considerations involved, both general and in relation to different phosphate rocks. Mr. Nunn had been responsible for the more recent work in the laboratory. He, himself, had aimed to produce a coherent paper by writing an introductory section based on published articles and a little work of their own, followed by sections based on reports by Mr. Nunn and two of their earlier colleagues, and Mr. Sharples' script. The draft had been read through by his co-authors and some modifications were agreed on. Of their earlier colleagues, Mr. Knight was mentioned in the paper and Mr. R. N. Woodward, now in New Zealand but still a member of the Society, was responsible for the first experiments.

Until recently, ideas on differences between phosphate rocks had lacked correlation. It was known that rocks from some deposits were a little slower or perhaps a little faster to react with sulphuric acid than that from Morocco, but there was no real basis for a quantitative comparison, nor was it known what were the main factors (assuming the same degree of fineness) which decided the reactivity of a given rock. The position had recently, however, been considerably clarified by the work of Mr. W. L. Hill and his colleagues in the Fertiliser Section of the Agricultural Research Service of the United States. Mr. Hill's interest was in the use of phosphate rock as a fertiliser, but it was found that the correlations which he and his colleagues had established applied also to the behaviour of the rocks towards mineral acids.

The American workers had found the best correlation to exist between the reactivity of the rock and its solubility (at a given degree of fineness) in 2% citric acid. This was in line with a statement given on page 60 of a booklet published by the O.E.E.C. in 1953 ("Sulphuric acid and the manufacture of phosphatic fertilisers") to the effect that in France importance in regard to the agronomic value of a phosphate rock is attached to its solubility in citric acid. The highest values were obtained with South Tunisian and Curaçao phosphates; Algerian and Morocco phosphates followed closely; Florida phosphates were less soluble,

and crystallized apatite phosphates, such as Kola, gave much lower values.

The information set out in the Paper showed that in regard to the investigation of a new phosphate rock there now existed

1. A useful tool, namely extraction with 2% citric acid, to determine its reactivity.
2. Criteria, namely CO₂ content and determination of certain physical properties, which gave further evidence as to reactivity and would probably explain the behaviour of the rock.
3. The possibility that even a very unreactive rock could be reacted successfully with sulphuric acid to make phosphoric acid.

It was pointed out in a paper by two of the authors in 1954¹ that the factors which determine the speed of interaction between phosphate rock and sulphuric acid to make superphosphate, and the composition of the product, are : (1) the nature of the rock, (2) the degree of fineness to which it is ground, (3) the concentration of the sulphuric acid, (4) the proportions in which acid and rock are mixed, which may be stated in lb. of H₂SO₄ per 100 lb. of phosphate rock, and (5) the temperature of reaction.

Variations in the nature of phosphate rock.

Hill et al² determined the surface areas of a number of phosphate rocks by measurement of adsorption from gaseous nitrogen at the temperature of liquid nitrogen. The following figures were obtained for 100.-150 mesh (U.S.S.) fractions :

Source of rock	Sq. metres per gm.
Tunis, Gafsa	19.4
Morocco	14.5
Florida land pebble	10.3
Florida land pebble concentrate	8.6
Curaçao	3.6
Tennessee brown	6.8
S. Carolina	6.5
Idaho	3.0
Montana	1.6
Virginia apatite	0.6

These values are due almost entirely to internal surfaces, the area of the outer surfaces of the particles being negligible by comparison. In agreement with this, with five American rocks there was little increase in surface area in grinding from average particle

sizes of 100 mesh to 200 mesh and on to 325 mesh (U.S.S.). With a Morocco rock and a Florida pebble rock however, surface area was found to increase considerably with finer grinding, suggesting blocked voids within the particles.

The above surface areas compare with 1,700 sq. m/gm. for coconut charcoal, 400 - 900 for silica gel, 15 - 100 for clays, 12-40 for diatomaceous earth. Grain sizes, calculated from the surface areas, are about 0.05 microns for the N. African rocks, 0.10 for Florida pebble, and 0.15 for the other American phosphates except the apatite, for which the value is about 0.33.

Caro and Hill³ have reported the correlation of growth data of lucerne on three acid soils with certain laboratory measurements made on the ground phosphate rocks used as fertilisers. The rocks and some analytical data are listed in Table 1. The best correlation was with the solubility of sized portions of the rocks in 2% citric acid ; such figures varied, for 100 to 150 mesh fractions,

TABLE 1.

Chemical composition (%) of 100 - 150 mesh fractions of phosphate rocks

Source	P ₂ O ₅	CaO	F	CO ₂		Bound CO ₂ / P ₂ O ₅
				In * Calcite	Bound	
Tunis, Gafsa	29.9	44.3	3.6	0.3	5.5	0.184
Morocco	32.1	51.6	4.2	0.6	4.9	0.153
S. Carolina land rock	27.1	43.3	3.7	0.2	4.6	0.170
Curaçao	37.9	50.0	0.7	0.6	3.3	0.087
Florida land pebble	30.9	46.6	3.5	0.0	3.7	0.120
Florida land pebble (flotation concen- trate)	33.2	44.7	3.5	0.0	2.0	0.060
				Total		Total CO ₂ /P ₂ O ₅
Idaho, Conda	33.0	47.1	3.4	1.8		0.055
Tennessee brown rock	35.0	48.6	3.7	1.3		0.037
Montana, Garrison	36.4	50.5	3.9	1.3		0.036
Virginia apatite	40.3	51.8	2.9	0.1		0.002

* CO₂ found as free calcite by method of Silverman, Fuyat, Weiser⁴

tested at 24°C., from 37 to 5% of the total P_2O_5 present. The next best correlation was with the phosphate-bound CO_2 content of the rock. Phosphate rocks with high CO_2 contents generally have a very small grain size, with a correspondingly high surface area and low particle density. The apatite constituent in phosphate rock appears to be hydroxyl-apatite, in which the hydroxyl is replaced partly or wholly by fluorine and the phosphate group by carbonate. Fluorination lowers reactivity, whereas carbonation enhances it, and the influence of the latter often outweighs that of the former.

Solubility of the phosphate rock in neutral ammonium citrate solution was not quite so good a criterion of reactivity as its solubility in citric acid. Particle density was a fairly good criterion of reactivity, this being measured by displacement of glycerine and reflecting the degree of compactness, or lack of pore space, of the material.

Caro and Hill³, referring to a publication not yet available⁵, state that the constituent grains of phosphate rock are not agglomerated in a uniform manner.

Taking the average grain size of North African rocks as 0.05 microns compared with 76 microns for a rock particle passing a 200 mesh sieve, and relating this to 2 mms. for an average granule of fertiliser, we can picture the rock particle as analogous to a lump of caked fertiliser roughly 10 ft. each way and containing about three thousand million granules, stuck together in the usual haphazard manner, and with irregular voids between them, making a porous mass. Another analogy with the caked fertiliser is that we are uncertain of the nature of the cementing medium, if any. Taking account of the hardness of some phosphate rocks, a porous block of concrete might be a better analogy.

The above description may well apply to a sedimentary rock. Where the rock is an igneous one, formed by slow cooling from a molten mass, the picture is likely to be quite different. Here the solid might be formed as a non-porous mass, with impurities segregated between the grains of crystalline apatite, like a metal.

Hill et al² give values for "average apparent particle density," determined by displacement of Dekalin, using phosphate rocks ground to pass 150 mesh and lie on 100 mesh screens. These values are quoted in Table 2.

Some idea of the porosity of a particle of Gafsa rock may be gained by taking the apparent particle density as given in the table, and assuming the specific gravity of apatite to be 3.2. If we suppose the basic crystal lattice to be the same in each case, and the effect of the impurities to be negligible, the volume of the pores into

which Dekalin failed to penetrate was $(1 - 2.76/3.2) 100 = 14\%$ of the total volume.

Incidentally, the unit cell dimension of apatite is about 15 Ångstrom units, so that there are about 500^3 unit cells in a grain of North African phosphate rock. It has already been noted that there are about $1,500^3$ of such grains in a rock particle which just passes a 200 mesh sieve, and these figures illustrate the tremendous range of sizes which come into consideration.

TABLE 2.

Average apparent particle densities, by displacement of Dekalin. 100 - 150 mesh fractions of phosphate rocks.

Source of rock	Gm/cc
Tunis, Gafsa	2.76
Morocco	2.89
S. Carolina (land rock)	2.75
Curaçao	2.96
Florida (land pebble 1)	2.90
Florida (land pebble 2)	2.93
Idaho, Conda	2.93
Tennessee (brown)	2.90
Montana, Garrison	3.10
Virginia (apatite)	3.19

Determinations of total P_2O_5 contents, and of percentages of P_2O_5 soluble in 2% citric acid solution, under standard conditions of agitation and temperature, have been made in our laboratories on samples of a number of different types of phosphate rock, with the following results. The entire sample was in each case ground to the degree of fineness shown.

As regards Gafsa, Morocco and Florida rocks, the correlation between the values of the citric-soluble P_2O_5 fractions given in Table 3 and those for surface areas given earlier, and CO_2/P_2O_5

TABLE 3.

Citric acid solubilities at 25°C.

Source of rock	Fineness of grinding		% P ₂ O ₅ in sample.		Cit. sol. as % of total P ₂ O ₅ .
	% thro 100+	% thro 300+	Total	Cit. sol.	
Gafsa	78.0	27.6	29.04	6.96	24.0
Morocco	88.6	40.3	33.26	6.64	20.0
Florida	92.3	28.3	34.73	6.09	17.5
Senegal*	87.0	29.1	37.50	6.15	16.4
Nauru	83.1	34.4	38.10	6.14	16.1
Sukulu**	92.8	28.1	40.12	3.31	8.3
Kola‡	83.8	38.7	38.70	2.66	6.9
Palabora	84.7	40.7	34.95	0.69	2.0

+ B.S. Mesh

* Senegal calcareous rock

** Sample kindly supplied by the Director of the Chemical Research Laboratory, Teddington

‡ Sample kindly supplied by Mr. P. M. R. Versteegh, of Albatros Superfosfaatfabrieken N.V.

ratios given in Table 1, is remarkably good. When all the rocks are arranged in order according to the decreasing value of their citric-soluble P₂O₅ fractions, as in Table 3, they are also roughly in the order of decreasing activity with mineral acids, as will be seen from the later sections of the paper. In particular, the behaviour of Palabora rock towards nitric acid suggests that this rock is almost completely non-porous.

Marshall et al⁶ reacted phosphoric acid at various concentrations with a number of phosphate rocks. In one series of experiments, the rock samples were ground to pass an 80 mesh U.S.S. sieve and were reacted for 20 minutes, with vigorous agitation, with 10% excess of acid of different concentrations. The residual solid was immediately filtered off and washed. Some of the results are given in Table 4, together with the analyses of the

TABLE 4.

Reactivities towards phosphoric acid of various phosphate rocks.

Type of phosphate	Analyses (%) on air-dry basis							Conversion to available P ₂ O ₅ after 20 mins.	
	P ₂ O ₅	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	F	CO ₂	Acid of 41% P ₂ O ₅	Acid of 46% P ₂ O ₅
Fluorapatite*	37.7	49.0	—	—	—	3.05	1.41	29	39
Montana	36.3	50.3	0.6	0.6	4.1	4.01	0.93	35	60
Idaho	33.0	46.1	1.1	0.9	6.8	3.30	1.76	50	65
Tennessee brown	34.4	48.5	1.2	2.5	5.9	3.79	1.96	45	65
Florida pebble No. 2	35.9	48.7	1.1	0.7	7.4	3.90	1.47	50	80
Tennessee blue	31.8	45.1	1.3	3.4	9.1	3.77	2.59	55	82
Florida pebble No. 3	31.8	48.0	1.0	1.6	7.1	3.93	3.61	65	—
Curaçao	37.9	50.0	0.4	0.6	0.5	0.70	3.88	82	82

* From Quebec.

samples used. It is remarkable how closely the percentage conversion to available P_2O_5 in 20 minutes correlates with increasing CO_2 content, in spite of other differences in analysis. In other experiments with Florida, Tennessee brown and Idaho rocks, using acid of 46% P_2O_5 , percentage conversion to water-soluble P_2O_5 was only about 4% below the conversion to available P_2O_5 .

In a Technical Bulletin of the U.S. Department of Agriculture, Jacob et al⁷ gave comprehensive analyses of a number of phosphate rocks found in the U.S.A. and elsewhere, including rocks from Morocco, Gafsa and Nauru, and other details. They remark that rock containing more than 5 to 6% of the sesqui-oxides (Fe_2O_3 and Al_2O_3) is considered unsuitable for superphosphate production, mainly because of the poor mechanical condition of the product. Silica however has no other harmful effect than as a diluent.

Contents of iron and aluminium.

Lehrecke⁸ stated that iron present in superphosphate is one of the chief causes for part of the P_2O_5 being insoluble in water but soluble in ammonium citrate solutions. A superphosphate made from Swedish apatite (7 to 8.5% Fe) had initially 9.2% w.sol., 15.0% cit. sol. and 16.5% total P_2O_5 . Kept for a month at 70° C., the citrate-soluble P_2O_5 fell from 91 to 81% of the total P_2O_5 . Analysis of precipitates from the liquid phase showed that much of the iron was present initially as $H_3FeP_2O_8 \cdot 2.5H_2O$, but on keeping was converted to the crystalline $FePO_4 \cdot 2H_2O$, which is almost insoluble in citrate solution (in which however amorphous $FePO_4$ is readily soluble).

Marshall and Hill⁹ experimented with an Ocean Island phosphate rock to which measured proportions of phosphates of iron and alumina were added and the whole thoroughly mixed in a ball mill before acidulation. Day-old superphosphates were of good physical condition where the R_2O_3 content of the raw phosphate was equivalent to 5% Fe_2O_3 (i.e. $Fe_2O_3 + 1.56 Al_2O_3 = 5.0$), but their condition fell to "fair" with the equivalent of 7.5% Fe_2O_3 . Where the aim is available P_2O_5 the upper limit of R_2O_3 content might again be between 5 and 7½% equivalent Fe_2O_3 , but for water-soluble P_2O_5 , judging from the graphs of the paper, the upper limit is somewhere between 2½% and 5%. These writers suggest that reversion during curing, caused by iron, is due to the formation of a partially citrate-soluble calcium iron phosphate.

Marshall et al⁶, investigating the reaction of phosphoric acid with American phosphate rocks, found an effect of the forms in which iron and aluminium were present, since they remark: "The

aluminium in Florida land pebble seems to be more reactive towards phosphoric acid than that in the Tennessee and Idaho phosphates. As indicated by its conversion into the water-soluble condition, the iron in Florida land pebble and Idaho phosphates is readily acted upon by phosphoric acid of 46% P₂O₅, whereas the iron in Tennessee brown rock is attacked to a much smaller extent."

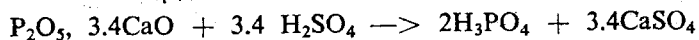
Effect of particle size.

Marshall et al⁶ found, in the case of Montana phosphate rock, reacted with phosphoric acid of different concentrations for a period of 20 mins., and immediately filtered and washed, that decrease in particle size had a definite effect on the extent of conversion in that time. For instance, with acid of 40% P₂O₅, values were :

Sieving fraction (mesh)	100-150	150-200	<200
Conversion (%) of insol. into available P ₂ O ₅	34.5	35.4	42.2

In our own laboratory investigation with Morocco rock (reported later) we have not found any such effect with phosphoric acid, while T.V.A. Chemical Engineering Report No. 51⁰ states on p. 39, that, with Florida and Tennessee rocks (the former varying in fineness from 50 to 85% through 200 mesh) and acid of 53% P₂O₅, conversions were substantially independent of particle size.

The small effect, or even lack of effect, of the particle size of the rock on the rate of attack by phosphoric acid is in marked contrast to the behaviour towards sulphuric acid, where the speed of the first stage of the reaction :



is greatly dependent on particle size.

Whereas, with phosphoric acid, the acid presumably enters the pores of the particle with relative freedom, and the reaction takes place mainly at the large internal surface ; with the sulphuric acid the pores near the surface doubtless become choked quickly with calcium sulphate, and reaction must take place by diffusion of the acid, through a coating of calcium sulphate, to the outside of the particle.

The chemical reaction with phosphoric acid is slow ; with nitric acid however, which has similar access to the inner surface of the rock particle, reaction with Morocco rock is so rapid that conversion to available P₂O₅ is almost complete in about five minutes.

Acid : rock ratio.

. Shoeld et al¹¹ give a nomogram, produced on the basis of laboratory experiments and works experience, from which can be found the weight of sulphuric acid, per unit weight of a given rock, required to give a certain degree of conversion to available P_2O_5 under given conditions. In order to use the chart it is only necessary to determine the P_2O_5 and CO_2 contents of the rock. The study was based on six Florida pebble rocks with P_2O_5 contents from 31 to 34% and CO_2 contents from 1.5 to 4%. The authors were concerned with the attainment of minimum raw material costs, and point out that the CO_2 content of the rock causes consumption of sulphuric acid without increase in available P_2O_5 content. They found that the proportion of fluorine driven off depended on the degree of conversion of the P_2O_5 , as well as the concentration of sulphuric acid and temperature (see also Whynes and Dee).¹²

The quantity of sulphuric acid (lb. 100% H_2SO_4) required per 100 lbs. of phosphate rock for complete conversion of the P_2O_5 present to monocalcium phosphate can be calculated from the results of a complete analysis as follows: Multiply the percentages of each of the basic components by the appropriate factor, these being:

CaO	1.75	MnO	1.38
MgO	2.43	Al_2O_3	2.88
Na_2O	1.58	Fe_2O_3	1.84
K_2O	1.04		

From the sum of the quantities so obtained is to be deducted the sum of the H_2SO_4 equivalents of the acidic components of the rock which remain unaffected. Not more than 30% of the fluorine content of the rock is driven off during superphosphate production. There is however some formation of compounds like $CaSiF_6$ and $Ca(HPO_3F)_2$, and the result of calculations made by Marshall and Hill¹³ suggests a factor for fluorine of 1.10. The factors for P_2O_5 and SO_3 contained in the rock are, respectively, 0.69 and 1.22. Such calculations seem to lead to too high an acid requirement in the case of Morocco rock, and it seems better to allow a factor of 1.80 for the fluorine present in the rock, this being 70% of the factor which would be used if no fluorine was driven off.

Such calculations as the above are useful when a new type of phosphate rock is to be used, but the matter is of course complicated by incomplete reaction and by the presence of free phosphoric acid in the product. It is desirable to determine the best ratio of sulphuric acid to rock by experiments such as are described in the next section of the paper.

Investigation of Single Superphosphate Production

In the earlier paper by two of the present authors¹, a detailed investigation of the production of superphosphate from Morocco (Kourigha) rock was reported, and the following is a summary:

One difficulty in imitating, in the laboratory, conditions obtained on a large scale, is to get the same reaction temperature. On a large scale, the surfaces of the mixer and den are far smaller per unit weight of reactant than they are when the reaction is carried out on a laboratory scale, and in consequence losses of heat are much smaller and the reaction temperature tends to be much higher. The method we adopted was to carry out in each case a preliminary experiment in a Dewar flask. Suitable quantities of the reactants were mixed in this flask, and the temperature attained was noted. The temperature in the mixing vessel for the later experiment was generally fixed at this adiabatic temperature.

The operating conditions in continuous superphosphate plants are determined by the physical conditions of the product that are necessary (a) at the entrance of the den and (b) at the den exit. The slurry entering the den must be fluid enough to run across it, but it must not be so fluid that it would for instance run between the slats of a Broadfield den. At the exit the superphosphate must have set to an extent sufficient for the cutter and conveyor to deal with it. In order to obtain a comparative measurement of the fluidity of the slurry during mixing, the laboratory reaction vessel was mounted on a turn-table. A stirrer was arranged to be operated by a motor mounted above the vessel, and independently of the turn-table. The force exerted by the motor, through the slurry, on the turn-table, was measured by observing the extension of a spring.

When the desired fluidity had been obtained, the reaction vessel was unclamped from the turn-table, covered with a clock-glass, and placed in a cupboard, maintained at 15°C. below the reaction temperature, for 45 minutes, thus imitating roughly the period of retention in a Broadfield den.

To imitate as nearly as possible the conditions below the surface of a large storage pile, the superphosphate, after removal from the reaction vessel, was placed in a bottle, which was provided with a rubber bung and a Bunsen valve, and this was kept for three weeks at a temperature 35° below that of the reaction vessel.

For many of the experiments, it was sufficient to analyse the products by the ordinary methods of chemical analysis used in the fertiliser industry. Such methods, however, are not suitable when, for research purposes, the extent of interaction is to be

measured during its early stages. It is well known that the interaction that takes place in the superphosphate after it has left the den is a slow one, so that, even after say three weeks, there are sometimes considerable proportions of free acid and of unchanged phosphate rock still present. When analysis is preceded by extraction of the superphosphate with water, interaction between the free acid and previously unchanged rock is comparatively rapid after the superphosphate is dispersed in the water. Thus the result of the analysis, although useful for comparative or practical purposes, does not indicate the precise composition of the superphosphate.

The discrepancy between the results obtained by analysis after extraction with water and the true composition of the superphosphate is much greater during the early stages of the reaction, so that aqueous extraction is quite unsuitable for determining the extent of interaction. For this purpose, it is necessary to bring the reaction to a stop before analysis is carried out. A technique with this object was developed by Mr. R. F. Knight, working in the Research Department of Fisons Limited.

The organic solvent, dioxan, has the property of combining with sulphuric and phosphoric acids to form 'loose' compounds, the speed of interaction of which with phosphate rock is very low. When working with triple superphosphate it was found that dispersion of a sample in dioxan caused further interaction to be so slow that separation of the dioxan solution of the phosphoric acid from the solid matter could be carried out without interaction proceeding simultaneously to any appreciable extent. In the presence of sulphuric acid, however, dioxan alone was unsuitable, since, with certain proportions of sulphuric acid, water and dioxan, the liquid separated into two layers. With a mixture of equal volumes of acetone and dioxan this separation into two layers did not occur, and the rate of interaction between acid and rock was again lowered to such an extent that their separation could be carried out.

After separation of the free acids in this way, the solution was analysed by normal methods for the proportions of sulphuric and phosphoric acids. The solid residue from the extraction was treated with a saturated solution of sodium oxalate at boiling point to extract the monocalcium phosphate as sodium dihydrogen phosphate, the proportion of which could then be determined. The phosphate (unchanged phosphate rock) remaining in the solid residue was determined.

Series 1. In this series of experiments the fineness of grinding of the phosphate rock was fixed; characteristics of the particle size distribution are seen in Table 5. Four concentrations of sul-

phuric acid were used, these being 70, 60, 55 and 45% H_2SO_4 ; each of these concentrations was used in acid/rock ratios of 60, 55, 50 and 45 gms. 100% H_2SO_4 per 100 gms. phosphate rock. In these experiments the organic-solvent technique was not used. The temperatures used varied from 104° with the most concentrated acid to 78°C. with the least concentrated. The fluid period varied from $\frac{1}{2}$ min. with the lowest acid/rock ratio and more concentrated acids to over 15 mins. at the other extreme, mixing being stopped when the standard final fluidity* was reached.

* The standard final fluidity was that reached in three minutes when acid of concentration 70% H_2SO_4 , at 35°C., was used with Morocco rock ground to give 70% through a 100 mesh B.S. sieve, in the ratio of 60 gms. 100% H_2SO_4 per 100 gms. of rock.

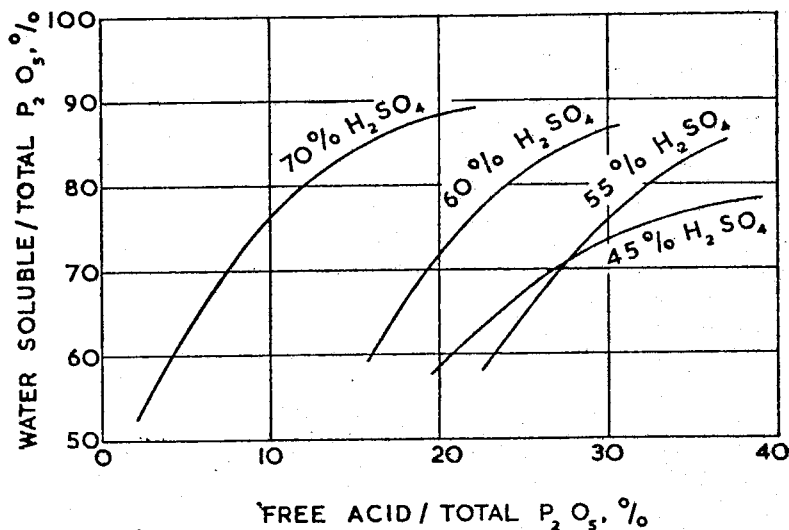


FIG. 1. RELATION BETWEEN FREE ACIDITY OF PRODUCT & CONVERSION.

The results after 3 weeks maturing are illustrated by Fig. 1, showing the relation between the free acidity of the product and its water-soluble P_2O_5 fraction. The available (AOAC)¹⁴ P_2O_5 fraction was about 8% higher than the w.sol. P_2O_5 fraction at all acid/rock ratios except with the 45% H_2SO_4 , where the difference increased to about 13%. The products made with 45% H_2SO_4 also differed from the others in losing 10% more weight when heated to constant weight at 100°C than when heated at 50°C., which was taken as evidence that, in these products, much of the calcium sulphate was in the form of gypsum.

Series 2. In this series the main object was to study the speed of the interaction between phosphate rock and sulphuric acid, but the chemical composition of the products was also determined.

The acid/rock ratio was fixed at 60 gms. of 100% H_2SO_4 per 100 gms. of rock throughout the series, and there were two sub-series, one with acid of concentration 70% H_2SO_4 and the other with acid of concentration 76% H_2SO_4 . In each sub-series the fineness of grinding of the rock varied to give from 21 to 93% passing a 100-mesh sieve (see Table 5).

In order to determine the speed and course of the reaction, 11 or 12 samples of the reacting mass were taken in each experiment at times ranging from five minutes up to three weeks after mixing. Each sample was immediately dispersed in a weighed amount of acetone-dioxan, and analysed as previously indicated.

For purposes of comparison, samples were taken from the exits of mixer and den of a Broadfield superphosphate plant. Portions of these samples were at once dispersed in acetone-dioxan. The remainder was stored under the same conditions as for the laboratory products, and portions were taken for analysis at various intervals of time.

TABLE 5

Characteristics of Morocco rock.

Sample	Cumulative percentage passing B.S. mesh No.			Mean particle size μ .	Total P_2O_5 %
	170	100	60		
Series 1	44	68	92	109	33.2
Series 2					
1	5	21	70	215	33.6
2	27	51	91	150	33.2
3	47	70	93	100	33.8
4	56	93	100	75	34.0

The results were set out in a series of graphs, in which the logarithm of time (in minutes plus one) was plotted against percentages of the total P_2O_5 present as free acid, monocalcium phosphate, water-soluble phosphate and insoluble P_2O_5 . The percentage of the initial H_2SO_4 still present was also plotted. Fig. 2 herewith is typical of all, including that for the plant samples.

It is seen that the general course of the reaction is as follows. While free sulphuric acid is present a little monocalcium phosphate is formed but the principal reaction is the formation of free phosphoric acid. With the disappearance of sulphuric acid (which, with rock of the usual fineness of grinding* and acid of concentration 70% H_2SO_4 , takes place in 30 to 40 minutes) formation of free acid P_2O_5 ceases. The free acid now forms 40 to 50%

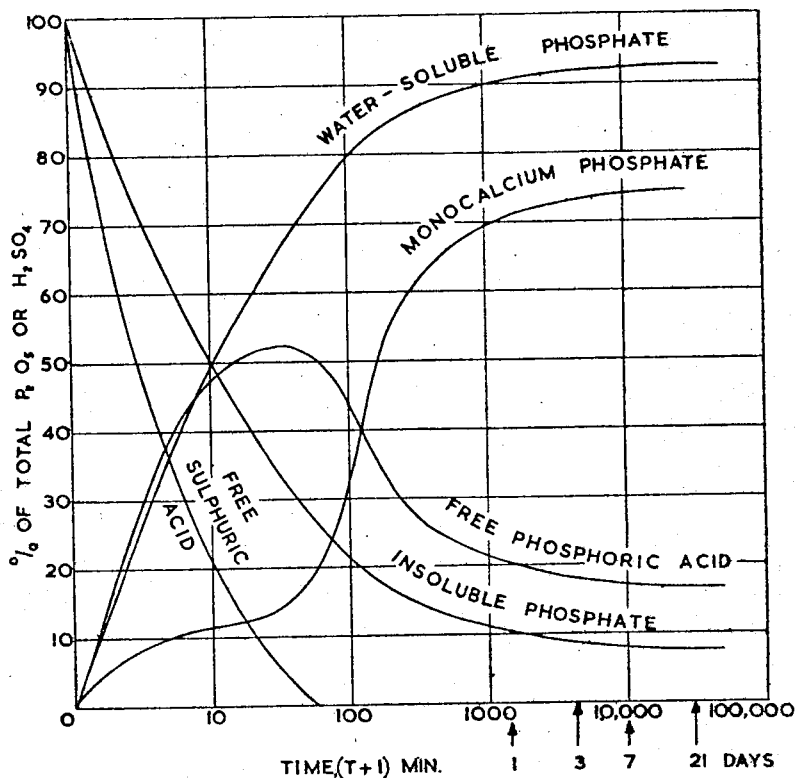


FIG. 2. INTERACTION OF 76% SULPHURIC ACID WITH MOROCCO PHOSPHATE.
70% THROUGH 100 B.S. SIEVE.

of the total P_2O_5 , and further interaction is between this and previously unchanged rock, mainly to form monocalcium phosphate. It is seen that this reaction gradually loses speed, and that, with rock of the usual fineness of grinding*, an almost stationary state has been reached in three weeks, with substantial proportions of free acid and insoluble phosphate still present. The figures shown for water-soluble P_2O_5 represent, in each case, the sum of the free acid P_2O_5 and the monocalcium phosphate.

Visual observation showed that the superphosphate was wet in appearance and sticky as long as appreciable proportions of sulphuric acid were present. In fact, it appeared that the ideal time of retention in the plant, i.e. the time at which the product should reach the cutter, practically coincided with the disappearance of sulphuric acid.

* About 75% through 100 mesh B.S.

Mixing conditions for these experiments varied from 75°C. and 5 mins. with the coarsest rock to 110° and $\frac{1}{2}$ min. with the finest rock. One conclusion from the experiments was that the first stage of the reaction (i.e. to the disappearance of sulphuric acid) was quicker with acid of 70% H_2SO_4 , than with that of 76% H_2SO_4 . Finer grinding, while having its most marked effect on the first stage of the reaction, increased the speed in both stages, so that time in the den and time of curing could both be reduced.

Chemical analyses of the products at 3 weeks showed little variation with either fineness of grinding or concentration of acid.

Taking into account other experimental values, some obtained on the plant, it was considered that the values below represented roughly the results to be expected in a continuous plant using Morocco rock ground so that about 70% passed a 100 mesh B.S. sieve, and acid of concentration 70% H_2SO_4 .

TABLE 6

Acid/rock ratio, lb. of 100% H_2SO_4 per 100 lb. of rock.	Water-soluble/total P_2O_5 , %, in 3-week- old superphosphate.	Quantities, tons, required for one ton of water- soluble P_2O_5 .	
		Rock	H_2SO_4 , 100%
50.0	72.0	4.18	2.09
52.5	76.2	3.95	2.08
55.0	81.0	3.72	2.05
57.5	86.3	3.49	2.01
60.0	91.0	3.31	1.99
62.5	93.5	3.22	2.01
65.0	94.7	3.18	2.07

With an acid/rock ratio higher than 60, the free acidity of the product begins to be excessive, and this value was considered to be the optimum.

Fineness of grinding. At a later date, two batches of Morocco rock were ground, one for 76% to pass 200 mesh B.S., the other for 100% to pass 200 mesh and 55% to pass 380 mesh. Experiments were carried out as before, with acid of 70% H_2SO_4 used in a ratio of 60 gms. 100% H_2SO_4 per 100 gms. rock. The times for disappearance of sulphuric acid were around $1\frac{1}{2}$ minutes, and with the finer rock a w.sol. P_2O_5 fraction of the total P_2O_5 over 90% was attained within 2 hours. The w.sol. P_2O_5 fractions and free acidities at 3 weeks had approximately the same values as with the coarser rock used previously.

With Morocco rock of such small particle size, a rapid mixer would be needed (perhaps of the T.V.A. cone type)¹⁹ delivering on to a short conveyor belt, the total time of retention before

the disintegrator being only in the order of a few mins. If the material was then fed to some sort of storage conveyor it might be taken from the other end in about 2 hours directly to a plant for making granular mixtures. The operating cost in making superphosphate would then depend largely on the cost of grinding.

The range of mean particle size in all experiments varied from about 35 to 215 microns, whereas the time for completion of the first stage of the reaction (i.e. the disappearance of sulphuric acid) varied from about 1½ mins. to 4,000 mins. (2.8 days). The overall difference here is greater than would obtain if the time of reaction varied with the 4th power of the mean particle size. Taking points from a plot of the results, a straight line is obtained by plotting log logs:

$$\log \log t = 6.5 \log \log d - 1.85$$

where t = time in mins. and d = mean particle size in microns. From this equation one can, for instance, calculate to what mean particle size Morocco rock needs to be ground for a continuous plant where the total time of retention in mixer and den is t minutes. There would appear to be no advantage in grinding more finely unless it is intended to reduce the time of retention in the plant, and the-storage time.

Investigation of Triple Superphosphate Production

We are not here concerned with the Dorcco process, as operated in our Immingham factory, since this was described in detail by Porter and Frisken.¹⁵ Instead we are concerned mainly with the production of triple superphosphate in the "den" equipment which is conventional for single superphosphate.

Our investigation of this process started before that on single superphosphate and originally we had not the same experimental facilities. For the most part we have used Morocco rock. The first experiments were with Morocco rock ground to pass a 52 mesh B.S. screen, and with pure phosphoric acid, of concentrations varying from 25 to 48% P_2O_5 . The rock was added to the acid, in the proportion of 2.6 parts P_2O_5 in acid to one part in rock. The time at which setting occurred fell sharply with increasing acid concentration down to about 2 mins. at 41%, then falling more slowly with further increase in concentration.

In stating the chemical results of such experiments one has to be careful to differentiate between the water-soluble P_2O_5 fraction (w.sol./total P_2O_5) in the product and the conversion to mono-calcium phosphate, which may be stated as (w.sol. P_2O_5 - free acid P_2O_5) divided by total P_2O_5 , all referred to the analysis of the product. Thus, in the above experiments, the following were corresponding values:—

W.sol. P_2O_5 fraction (%)	96.0	93.9	92.0
Conversion (%)	83.7	79.5	63.2

At a later stage, use was made of the technique devised by R. F. Knight (see section on single superphosphate) to determine proportions of P_2O_5 present as monocalcium phosphate and free acid at different stages in the reaction, using both pure and "wet process" acids. Some of the results obtained are shown in Tables 7, 8 and 9.

An acid/rock P_2O_5 ratio of 2.6 was used in all these experiments. Tables 7 and 8 refer to samples stored for 21 days before analysis. Table 9 shows the extent of reaction, with coarsely-ground Morocco rock and "wet process" acid of 44.1% P_2O_5 , from 5 mins. to 24 hrs.

TABLE 7

Results with Coarsely-ground Morocco Rock

Concn. (%) of P_2O_5 in acid.	Total P_2O_5 (%) in product.	Division of P_2O_5 in product (%)		
		Acid	M.C.P.*	Insol.
Using pure acid				
19.8	22.3	30.5	54.3	15.2
29.9	31.0	17.0	74.5	8.5
44.1	41.4	8.4	87.4	4.2
49.4	44.1	5.6	91.6	2.8
Using "wet process" acid				
29.9	30.9	20.8	68.8	10.4
44.1	40.8	8.5	87.3	4.2
49.4	44.1	5.4	91.9	2.7

*Monocalcium phosphate

TABLE 8

Results with Acid of 29.9% P_2O_5

Type of rock.	Fineness of Grinding (through 100 mesh B.S.).	Division of P_2O_5 in product (%)		
		Acid	M.C.P.	Insol.
Using pure acid				
Morocco. Coarsely ground	32%	17.0	74.5	8.5
Morocco. Finely ground	90%	19.4	70.9	9.7
Gafsa. Coarsely ground	54%	11.6	78.8	9.6
Using "wet process" acid				
Morocco. Coarsely ground	32%	20.8	68.8	10.4
Morocco. Finely ground	90%	18.2	(72.7)	(9.1)
Gafsa. Coarsely ground	54%	16.4	(74.7)	(8.9)

Some doubt as to accuracy of bracketed figures

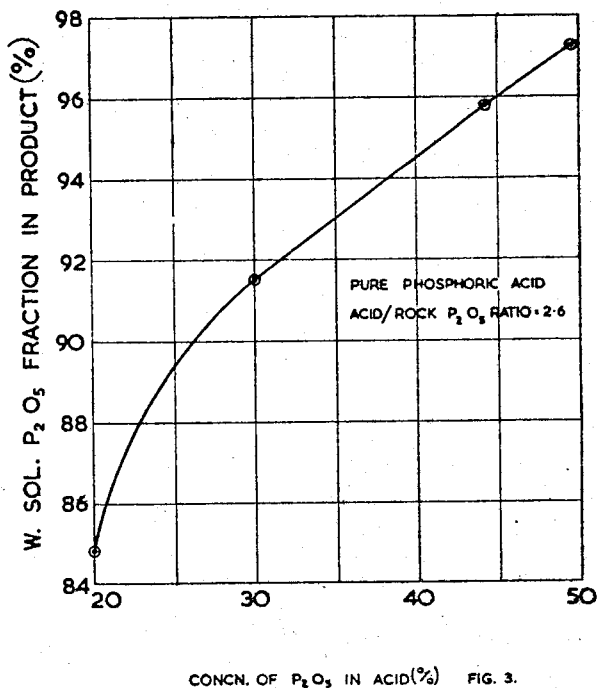
TABLE 9

Speed of Reaction

(Figures are percentages of total P_2O_5 in product)

Time	Zero	5 mins.	15 mins.	1 hr.	2 hrs.	5 hrs.	24 hrs.
Free acid	72.2	45.2	39.0	31.0	27.0	21.6	12.4
Monocalcium phosphate	0.0	38.0	46.6	58.0	63.3	70.7	83.6
Insoluble	27.8	16.8	14.4	11.0	9.7	7.7	4.0

Fig. 3 illustrates graphically the values for pure acid given in Table 7.



CONCN. OF P₂O₅ IN ACID(%) FIG. 3.

From some of the results obtained in these experiments, and from earlier experiments in which aqueous extraction was carried out at 24 hrs., it seemed clear that fineness of grinding had but little effect on the rate of reaction. In the earlier experiments, a Morocco rock of which only 3% passed 200 and 32% passed 100 mesh B.S. gave a w.sol. P₂O₅ fraction of 89.3% at 20 hrs. and 94.8% at three weeks, while a batch ground for all to pass 200 mesh gave figures of 94.2 and 95.2% respectively. These experiments were with acid of 45% P₂O₅, and an acid/rock P₂O₅ ratio of 2.6. The major effect of the different degrees of grinding was on the length of the fluid period, which varied from 12 hrs. with the coarsest rock to 24 secs. with the finest.

In a series of experiments with varying proportions of sulphuric acid in the phosphoric acid, acid of 36.5% P₂O₅ was used. The products were partly dried and stored at 60°C. for three weeks before analysis. The presence of 3% or 4% of H₂SO₄ appeared to be detrimental, causing appreciable decreases in the w.sol. P₂O₅ fraction with a constant acid/rock P₂O₅ ratio (calculated with allowance for the H₂SO₄ content).

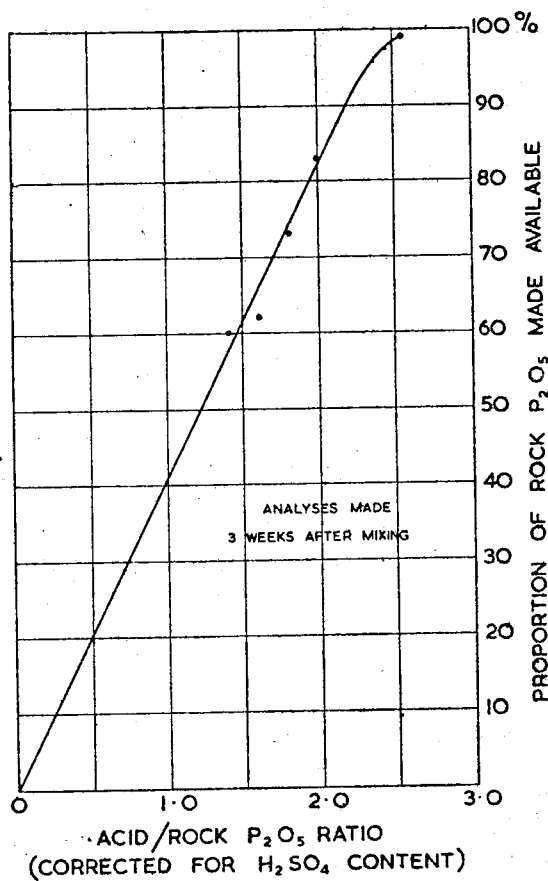
Another series of experiments was carried out under conditions such as to imitate as nearly as possible the procedure in the Dorco process, but using different temperatures of mixing. Acid of 38% P_2O_5 was used, at an acid/rock P_2O_5 ratio (H_2SO_4 content allowed for) of 2.55. As regards both w.sol. P_2O_5 fractions and residual free acidities, results at 31 and 38°C. were undoubtedly better than those at 85 - 95°C, and on the whole were better than those at 5°C. Since the adiabatic temperature reached in the reaction is 30 - 40°C, and this would be attained on the large scale without heating or cooling, we have kept within this range in all our later experiments.

The most recent work on the den process was carried out in 1951, when three series of experiments were made. In the first series an acid/rock P_2O_5 ratio (corrected for H_2SO_4) of 1.8 was used, with "wet process" acid of concentrations from 30 to 45% P_2O_5 . In each case, the approximate adiabatic temperature was found by mixing in a Dewar flask. Larger quantities were then mixed in the pot of the Fluidity Apparatus, where stirring was continued until the standard final fluidity for single superphosphate was reached or up to a maximum of 15 minutes. The product was then maintained at a temperature intermediate between the adiabatic temperature and that of the atmosphere for three weeks in a bottle open to the atmosphere only through a Bunsen valve.

With the rock used (Morocco, ground for 68% to pass 100 mesh B.S.) it needed acid of 40 - 45% P_2O_5 , both to give a fluid period short enough for a Broadfield mixer and to give a product of good physical condition. The average w.sol. and available (AOAC) P_2O_5 fractions were respectively 81.5 and 89.5%. Variation of w.sol. P_2O_5 fraction with acid concentration was not very consistent in these experiments, but free acidity rose from 6 to 18% of the total P_2O_5 with falling acid concentration.

The next series of experiments was carried out similarly, but with acid of 45% P_2O_5 and a rock of much coarser grinding (26% passing 100 mesh). The corrected acid/rock P_2O_5 ratio was varied from 2.55 to 1.4. The products were all in good physical condition but, where the ratio was above 1.8, the fluid period was longer than the normal retention period in a Broadfield mixer. That is to say, with acid of 45% P_2O_5 , a rather more finely ground rock would be needed in practice.

The triple superphosphate was analysed at one and three weeks. It was found that, between these times, free acidity fell considerably and available P_2O_5 rose slightly. At three weeks, the free acidity was low in all experiments, varying from 2.0 to 2.7% by weight of the sample. The figures at three weeks are illustrated by the accompanying graphs Nos. 4 and 5. They are in good agreement with the results of some experiments made earlier with acid of 45% P_2O_5 and acid/rock P_2O_5 ratios from 2.4 to 2.8.



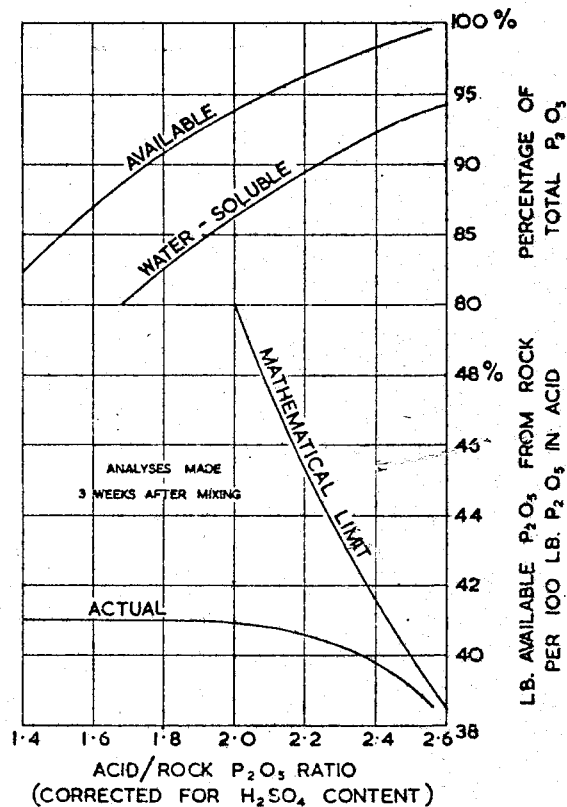
PROBABLE RESULTS OF PRODUCING T.S.P. IN SUPERPHOSPHATE DEN, USING ACID OF 45% P₂O₅ & COARSE MOROCCO ROCK. FIG. 4

From Fig. 5 it is seen that, for acid/rock P₂O₅ ratios up to about 2.0, 41 gms. (mols) available P₂O₅ are produced for 100 gms. (mols) P₂O₅ in the initial acid. Since $100/41=2.44$ one can write, ignoring the free acid and citrate-soluble P₂O₅ in the product :—



Taking both halves of Fig. 5 into account, it is suggested that the most practical combination of (1) efficiency of acid utilisation with (2) high proportions of water-soluble and available P₂O₅, would be attained by using an acid/rock P₂O₅ ratio (corrected for H₂SO₄) of 2.3 with Morocco rock.

In the third series of experiments, with the finer Morocco rock,



PROBABLE RESULTS OF PRODUCING T.S.P. IN SUPERPHOSPHATE DEN, USING ACID OF 45% P_2O_5 & COARSE MOROCCO ROCK. FIG. 5.

mixtures of 44.5 lb. 100% H_2SO_4 and 22.3 lb. 100% acid P_2O_5 were used per 100 lb. rock. The sulphuric acid was introduced at a concentration of 91-92%, while the concentration of the phosphoric acid was varied. With acid of 32% P_2O_5 , the product was in good physical condition and the w.sol. P_2O_5 fraction at three weeks was over 90%, but so long a mixing period (> ten mins.) would be needed to make the slurry stiff enough for a Broadfield den that a Broadfield mixer would not be suitable. It was noted that all the products from the mixed acids set very hard during storage.

Some early experiments were made with Kola rock and "wet process" phosphoric acid. Acid of 45% P_2O_5 was used at an acid/rock P_2O_5 ratio of 2.2, this being roughly equivalent to a ratio of 2.6 with Morocco rock. The fluid period was very long (1½ hrs.) and the final product of a plastic nature. After three weeks, the w.sol.

P_2O_5 fraction was 89%, while the free acid was 16% of the total P_2O_5 .

We have been given data from a factory in Europe making triple superphosphate, and believed to be using acid of 53% P_2O_5 and Morocco rock ground to give 95% passing a 100 mesh sieve. These are given in Table 10, while Table 11 gives derived values, those in the last column being based on certain assumptions.

TABLE 10

Factory Superphosphates. % Analyses			
Total P_2O_5	W.sol. P_2O_5	Free acid P_2O_5	H_2O
45.2	40.2	4.3	6.7
46.6	43.2	5.0	5.9
48.2	45.2	7.1	6.5
48.4	45.15	9.8	6.5

TABLE 11

Factory Superphosphates. Derived Data		
Percentages of total P_2O_5 contents		Acid/rock P_2O_5 ratios
W.sol.	Free acid	
89.0	9.5	2.20
92.8	10.7	2.47
93.8	14.7	2.68
93.3	20.3	2.87

The first three samples give values for (w.sol. P_2O_5) versus (acid/rock P_2O_5 ratio) very close to those shown in Fig. 5 in spite of the difference in acid concentration and the great difference in coarseness of grind.

Hill and Hendricks¹⁶ gave analyses of some commercial samples of triple superphosphate, of ages ranging from 2 months to 6 years, and some of their figures are quoted below. It is of interest to note that, when using the American rocks, with their rather high iron and aluminium contents, one can get a high percentage of available P_2O_5 with a low acid/rock ratio, the evidence of the latter being the low contents of w.sol. and free acid P_2O_5 in the superphosphates. A striking example of this is shown by Sample 4 in Table 12.

Copson, Newton and Lindsay^{17, 18, 19} gave a number of papers describing the development of the T.V.A. batch process for producing triple superphosphate from finely-ground rock and furnace acid of 50 to 60% P_2O_5 . They used a number of Tennessee phosphate rocks of widely-varying analysis.

In T.V.A. Chemical Engineering Report No. 5¹⁰ it is stated

TABLE 12

Phosphate rock	Florida pebble 9 mths.	Florida pebble 2½ yrs.	Tenn. brown 9 mths.	Tenn. brown 6 yrs.	Idaho 2 mths.
Age of sample					
% P ₂ O ₅ in sample :					
Total	46.2	49.3	48.4	43.9	47.3
Water-soluble*	38.3	41.6	42.2	29.9	41.3
Citrate-insoluble	0.49	0.07	0.48	0.70	2.37
Free acid	1.44	3.56	0.52	0.78	1.95
% Al ₂ O ₃	1.40	1.27	0.98	2.62	1.73
% Fe ₂ O ₃	2.04	1.62	1.25	3.48	0.83
% of total P ₂ O ₅					
Available	98.9	99.9	99.0	98.4	95.0
Water-soluble*	83.0	84.4	87.2	68.0	87.3
Free	3.1	7.2	1.1	1.8	4.1

* Determined by the American method of washing on a filter paper.

(p. 99) that the product of the later continuous process shows a considerably higher conversion than that of the batch process because of better mixing and the possibility of using acid of slightly lower concentration and a slightly higher acid/rock ratio.

Technical Considerations

Receipt and storage of rock. In the case of rocks shipped with a high proportion of material passing 100 mesh (these include Kola, Gafsa and Morocco rocks), a covered belt conveyor seems the only practical method of transfer from ship to store. With other methods at present practised, there is, on windy days, considerable loss of fine material, which causes damage to surrounding vegetation. Pneumatic methods have been tried, but it is understood that power and maintenance costs are high.

Weighing and sampling are necessary, and the latter presents some difficulties where a high proportion of lumps is present, as with Nauru and some Florida pebble rocks.

With the finer rocks it is necessary that the store be enclosed to prevent loss of rock and pollution of the atmosphere when discharging from conveyor to heap. For retrieving the rock, drag scrapers are suitable for the free-flowing materials, but Nauru needs mechanical shovels or bulldozers.

Grinding. Ring-roll mills are in general use. In the older type, material which has passed through the mill is "classified" in an air separator, which returns oversize particles to the mill.

In the pneumatic type, a current of air sweeps through the mill and removes the material when it has been ground to the required size. Cost of operation of the latter tends to be higher, but they are capable of more exact control, are smaller, and lead to less dust nuisance. To give material of 80% through 100 mesh B.S., pneumatic mills are desirable, and for finer grinding they are considered essential.

The high moisture content of such rocks as Nauru makes it necessary to provide some heat for the air feed to the pneumatic mills to prevent condensation in the system and consequent choking with wet powder.

The pneumatic mills are kept under suction to avoid dust loss, with the consequence that fresh air is drawn in, and a corresponding proportion of the circulating air has to be blown off, and passes to the atmosphere through bag filters. With North African rocks, a woollen fabric has been used for the bags and gave satisfactory service. With Ocean Island, Nauru and Florida phosphates, this fabric lasted only about three weeks. A Terylene staple fibre cloth (16 ozs./sq. yd.) appears to be as efficient a filtering medium as the wool, and shows no sign of deterioration after twelve months.

In grinding Morocco rock in an air-swept mill to the following degrees of fineness:

	% thro' 100 mesh B.S.	% thro' 200 mesh B.S.
Medium	77.5	46
Fine	98.5	85

it was found that mill capacity was 15 to 16 tph for medium fineness against 8 to 9 tph for the fine material. For the medium fineness 17 to 18 units of electricity were needed per ton against 30 to 32 units for the fine material. There is no appreciable difference in maintenance costs incurred in grinding rock to the two degrees of fineness shown above.

Perry²⁰ gives the following data for a Raymond five-roller mill with integral air separation:

TABLE 13

Capacity and horse power when grinding to give 90-95% through 60 mesh*.

Source of rock	Tons/hr.	Horse power
Florida (pebble)	6.5	17
Morocco	8	12
Nauru	7	13
Gafsa	8	12

* 50-55% through 200 mesh, U.S.A. specification.

When the Florida pebble was ground for 90-95% to pass 200 mesh, the capacity fell to 3.5 tons/hr., the horse power rose to 24, and the cost per ton was 43% higher than in the above case.

Control of acid and rock feeds. Of the methods in use for the control of acid feed we consider the most satisfactory is the rotating cup feeder driven by a D.C. motor, speed variation being obtained by a rheostat control graduated in terms of volume delivered per minute. Gravimetric feed of the rock by means of a belt weigher is desirable. Accurate control of both feeds is important in order to use the raw materials to the best advantage and to ensure a product of constant analysis.

Mixing of acid and rock. The requirements here depend on the den in use. For a Broadfield or Moritz continuous den, the entering slurry must be sufficiently viscous not to run through narrow openings. With Morocco rock ground to the usual degree of fineness, and using acid of about 70% H_2SO_4 at the usual acid/rock ratio, this means a retention time in the mixer of about 3 minutes, for which the Broadfield and Moritz mixers are suitable. With these mixers, most of the gases released in the course of superphosphate production are liberated at this stage, and ample provision must be made for carrying them away.

The Maxwell den will take a much more fluid slurry, and the mixer used has a retention time of only about 24 seconds. It is a shallow trough with a central rotating shaft to which are fitted paddles forming an interrupted scroll. The clearance between blades and trough is very small and very little cleaning is needed.

Dens. A description of superphosphate dens was given by Mr. Walter Packard²¹. We have experience of the Broadfield, Moritz-Standaert and Maxwell continuous types. The standard Broadfield den has moving sides, and this is a desirable feature where a variety of phosphate rocks is to be used. With North African rocks it was found to be advantageous to have fixed sides. For the greater part of their length these are parallel, but near the inlet end they incline slightly towards one another so that the cake of superphosphate, carried forward by the moving floor, is gradually released from the walls. For Nauru rock, however, this type of den seems less suitable.

The Moritz den has been used successfully with many types of rock. It has more moving parts than other dens, and its maintenance cost is high. With Florida rock in particular, corrosion of the internal metal surfaces, such as the cone, bulkhead, sealing plates and fixing bolts, is severe.

The Maxwell den has been used successfully for a variety of rocks. This den needs no bulkhead, and there are no clearances between fixed and moving parts through which slurry can

penetrate and cause friction or binding. With the Maxwell mixer, much of the gas evolution occurs in the den and this results in a porous superphosphate which is readily broken up by the cutter. Unfortunately, indraught of air at this part of the den is often inadequate, with the consequence that steam rises in clouds and causes corrosion of neighbouring steelwork unless special provisions are made to deal with it.

Economics

In 1948, calculations were made of the cost to the producer of single superphosphate, except for depreciation of plant, overheads and the sales costs. This cost, based on Morocco rock, was found to be made up as follows:

Phosphate rock (f.o.b.)	24.5%
Freight on rock	14.2%
Handling and storage	2.1%
Grinding	2.0%
Acid requirement	25.2%
Cost of manufacture, bags, transport and labour	32.0%
					100.0%

With rocks of lower P_2O_5 contents, freightage and handling costs rise per unit of P_2O_5 , while in many cases acid requirement also rises, so that the advantage lies heavily with the rock of high P_2O_5 content. In general then a rock of high P_2O_5 content is favoured unless some such factor as low reactivity counts against it.

Choice of rock. In choosing a rock one has to take account not only of its P_2O_5 content and chemical analysis in general, its reactivity and cost at source, but of freight charges and continuity of supply (including the political stability of the country of origin). In regard to a particular factory, the capacity of the grinding equipment, the size of the rock store, the size of ship which can be berthed and the rate at which it can be unloaded, may all be important factors.

Morocco Rock

Since the Second World War, the largest proportion of phosphate rock used in our organisation has been that from the Kourigha mines, referred to here as Morocco rock. It is with this rock therefore that we have had most experience, both in the research laboratory and the factory.

Generally it has a P_2O_5 content close to 33.3%, with approximately 4% each of CO_2 and fluorine, about 0.5% of Al_2O_3 , plus Fe_2O_3 , and 0.9% SiO_2 . It is a comparatively easy rock to acidulate, being reactive, while its low content of Al_2O_3 and Fe_2O_3 allows high w.sol. P_2O_5 fractions to be attained and does not cause appreciable reversion during storage. The laboratory investigation on the single

superphosphate reactions was carried out entirely, and that on triple superphosphate mainly, with this rock.

As received, the rock has about 20% passing 100 mesh B.S., and, though moderately hard, it is readily ground. There are no special difficulties in its use in any of the continuous dens described, and a typical analysis of the single superphosphate produced is:

Total P ₂ O ₅	19.7%
W.sol. P ₂ O ₅	18.4%
Loss at 100°C.	8.5%

On acidulation, 20-30% of the fluorine in the rock is evolved as SiF₄, making the production of fluosilicates a reasonable proposition in connection with moderately large plants.

In making phosphoric acid from this rock we have not experienced undue foaming, and the gypsum produced has allowed rapid filtration. The only troubles have been scaling and corrosion in the evaporators.

This phosphate is very suitable to be used as secondary rock in triple superphosphate production. Made in the Broadfield den with acid of 50% P₂O₅, a typical analysis of the product is:

Total P ₂ O ₅	46.0%
W.sol. P ₂ O ₅	44.0%
Loss at 100°C.	8.0%

Gafsa Rock

This is a very soft rock, with a rather low P₂O₅ content (approx. 29%), high contents of silica and carbonate, and appreciable Fe₂O₃ and Al₂O₃ contents. We have used it only for single superphosphate production, for which a fineness of 80% through 100 mesh is usual, with 61 lb. of 100% H₂SO₄ per 100 lb. of rock. Compared with the P₂O₅ content of the rock, the above acid/rock ratio is high, but the w.sol. P₂O₅ fraction is only in the order 89 to 90%. The amount of fluorine evolved is almost as great as from Morocco rock.

Safi Rock

A laboratory investigation was made with a sample of this rock containing 32.4% P₂O₅ and 4.2% fluorine. Using acid of 70% H₂SO₄ it was found that, with the rock ground for 80% to pass 100 mesh B.S., and using 60 gms. 100% H₂SO₄ per 100 gms. rock, the sulphuric acid disappeared in 25 minutes. In order to get a product of good physical condition, the above acid/rock ratio appeared to be a maximum. After 3 weeks storage, the superphosphate had a w.sol. P₂O₅ fraction of about 92%.

This rock again has only been used in the factory for single superphosphate production. As received it contains 1.5 to 2% water, which may be compensated by increasing the acid concen-

tration to 71% H_2SO_4 . With 65 lb. 100% H_2SO_4 per 100 lb. rock, the analysis of a superphosphate was:

Total P_2O_5	19.0%
W.sol. P_2O_5	17.9%
Loss at 100°C.	9.4%

The amount of fluorine evolved is about the same as from Morocco rock.

The general run of this rock has about 30.5% P_2O_5 . With the above acid/rock ratio, the consumption of sulphuric acid per ton of w.sol. P_2O_5 made is considerably higher than with Morocco rock.

Nauru Rock

As received, this rock has a size range from 4 ins., with 35% lying on a $\frac{1}{2}$ " screen, down to 3% passing 100 mesh B.S. Considerable quantities of shell fragments and other relics of war are liable to be present. At one of our factories, up to 56 lb. of "tramp iron" are removed weekly by two magnets, which have a joint rating of 6.3 amps at 180 volts. A Sturtevant Cone Crusher reduces the oversize material to a maximum size of $\frac{1}{2}$ ".

The need for heating the air feed to the mills, because of the high moisture content of this rock, has already been mentioned. The abrasive nature of the rock greatly increases maintenance costs. The average rate of output from a Bradley-Poitte mill (nominal 12 tph) was 10 $\frac{1}{2}$ tph when grinding to a fineness of 70% through 100 mesh B.S.

The rock has about 37.7% P_2O_5 content with 3.7% H_2O , or 39.1% P_2O_5 on the dry basis. It is low in fluorine content and very low in CO_2 content, compared to North African rocks.

In a laboratory investigation, it was found that, with acid of 70% H_2SO_4 , an acid/rock ratio of 57 gms. 100% H_2SO_4 per 100 gms. of rock was sufficient for superphosphate production. The first stage of the reaction (disappearance of sulphuric acid), when Nauru rock ground for 70% to pass 100 mesh was used, was more rapid than with Morocco rock.

In the factory, the conditions found most suitable have been acid of 73% H_2SO_4 used in the ratio of 56 lb. 100% H_2SO_4 per 100 lb. of rock. The average analysis of the superphosphate has been:

Total P_2O_5	23.0%
W.sol. P_2O_5	20.9%
Loss at 100°C.	7.0%

With the Moritz mixer, the outgoing slurry was more fluid than with Morocco rock. Where the slurry touched a cool surface, however, it hardened quickly. In a Broadfield den, it tended to form a bridge between the sides, so that, if these were fixed, the block of superphosphate did not move with the floor. These difficulties

were overcome by increasing the speed of the floor and lessening the depth of the block.

The Moritz den proved more suitable for making superphosphate with this rock, but it was necessary to see that the sealing plates at the base of the bulkhead were accurately fitted, otherwise dangerous leakage of hot slurry occurred. Corrosion was more serious than with North African phosphates.

The Maxwell den was operated for a trial period on Nauru phosphate; no difficulties were encountered, and a good superphosphate was produced.

Thanks to its low moisture content, the superphosphate gave rise to but little steam at the cutter and on conveyor belts, thus tending to reduce maintenance work.

Fluorine emission from this rock during superphosphate production is small; the fluorine is presumably all present in the rock as fluorapatite (whereas a good proportion of that in North African rocks is there as unbound calcium fluoride). The silica content of the rock is very low, and there is some evidence of emission of fluorine in the form of HF.

Short runs have been made with this rock in the phosphoric acid plant. At first rock ground for 75% to pass 100 mesh was used. Excessive foaming occurred and caused mechanical difficulties, while the crystal size of the gypsum fell and losses of P_2O_5 in the filter cake increased. Foaming was reduced to manageable proportions by contacting the rock with dilute phosphoric acid before introducing the sulphuric acid, and losses of P_2O_5 in the filter cake were brought back to normal by grinding the rock for 90% to pass 100 mesh B.S.

When the phosphoric acid from Nauru rock was used, with Morocco rock, to make triple superphosphate, frothing again caused trouble until it was reduced by means of a mechanical device.

Ocean Island Rock

We have carried out only a brief laboratory investigation with a sample of this rock which contained 39.4% P_2O_5 and 2.75% fluorine. Ground to give 70% passing 100 mesh, used with acid of 70% H_2SO_4 , and with analysis of the product at seven days, it gave the following results:

Gms. H_2SO_4 /100 gms. rock	...	56	60	64
Total P_2O_5 (%)	...	22.5	22.8	22.0
W.sol. P_2O_5 (%)	...	20.1	20.8	20.8
W.sol. P_2O_5 fraction (%)	...	89	91	94
Available P_2O_5 fraction (%)	...	93	98	99
Free acid P_2O_5 fraction (%)	...	16	20	25
Loss at 100°C. (%)	...	9.8	10.6	11.5

As with Nauru rock, the proportion of fluorine liberated was small (about 9% of that in the rock in the present case).

Florida Rock

A laboratory investigation with rock of 34.6% P_2O_5 and using acid of 70% H_2SO_4 showed that an acid/rock ratio of 60 gms. 100% H_2SO_4 per 100 gms. rock was suitable. Using rock ground for 70% to pass 100 mesh, it required 50 to 60 minutes for disappearance of sulphuric acid, as compared with about 30 mins. in the case of Morocco rock. The conversion to w.sol. P_2O_5 at three weeks was also lower, by about 1½%. Nevertheless, the w.sol. P_2O_5 content in the superphosphate was 18.8%, due of course to the higher P_2O_5 content of the rock. Also the proportion of w.sol. P_2O_5 produced to H_2SO_4 used was a little higher, due mainly to the lower carbonate content of the rock.

In the factory, supplies were received from Virginia and the Coronet mines with the following contents of P_2O_5 and R_2O_3 :

				<i>Virginia</i>	<i>Coronet</i>
P_2O_5	35.3%	35.3%
Fe_2O_3	1.4%	0.7%
Al_2O_3	0.9%	0.6%

Owing to shortage of storage space the batches of rock had to be mixed. No preliminary crushing of these rocks was required. In order to get sufficiently rapid reaction for superphosphate production, it was found necessary to grind for 90% to pass 100 mesh B.S. (75% through 200 mesh), and even then 14 to 17 days were needed to reach the maximum w.sol. P_2O_5 content, as against 3 to 4 days with Morocco rock of similar fineness.

Single superphosphate was made in a Broadfield den with moving sides, using an acid/rock ratio of 60 lb. 100% H_2SO_4 per 100 lb. rock. In contrast to North African rocks, the bulk of the fluorine liberated from this rock is liberated in the den, so that special attention should be given to the ventilation both of the den and the space round the cutter.

Production of phosphoric acid from Florida rock has presented no difficulties. There has been slightly more scaling in the pipes and perhaps some increased corrosion as compared with Morocco rock.

Attempts to make triple superphosphate from this rock in the Dorr plant met with some difficulty due to its rather unreactive nature, and were discontinued, since Morocco rock was available. Production in the Broadfield den, using acid of 50% P_2O_5 , has been more successful.

Senegal Calcareous Rock

We understand there are two kinds of deposit of phosphate rock in French West Africa. There are large quantities of a type of rock containing high proportions of alumina, and smaller amounts of a more normal type. The work here recorded was on a sample of the latter type, and was limited to the research laboratory.

The sample had a high P_2O_5 content (37.5%) with appreciable proportions of Fe_2O_3 and Al_2O_3 (1.8 and 0.7%). It was less reactive than Morocco rock, requiring to be ground for 90% to pass 100 mesh in order that the sulphuric acid should disappear in less than 45 minutes. With acid of 70% H_2SO_4 , a ratio of 60 gms. 100% H_2SO_4 per 100 gms. rock was the maximum to give a product of satisfactory physical condition. This had a water-soluble P_2O_5 fraction of 85% at three weeks, with a free acid P_2O_5 fraction a little over 20%, again showing slower reaction than with Morocco rock.

Kola Rock

This rock has a P_2O_5 content of 38 to 39% and is practically free from carbonate, though its fluorine content is about 3.2%.

In our laboratory investigation of triple superphosphate production, recorded earlier, we found Kola rock very unreactive.

It is already finely divided when received, about 89% passing 100 mesh. It needs therefore no grinding but special care to prevent loss and nuisance when transferring from ship to store.

In making single superphosphate from this rock there is said to be an advantage in adding up to 9 lb. chalk per 100 lb. rock. The release of CO_2 gives a more porous structure, and this facilitates release of steam and fluorine-containing gas, and makes cutting out easier. An acid/rock ratio about 68 lb. 100% H_2SO_4 per 100 lb. rock is then suitable.

Kola rock is used in Europe for phosphoric acid production, particularly in mixtures with Florida rock. Its use enables the capacity of the plant to be increased with the same mill capacity, and cuts down frothing.

A small consignment of this rock, received recently, had from 1 to 2% moisture content, having become wet during transit. With this moisture content, it could be handled by grab crane without loss, but was readily compressed to a paste and tended to cling to conveyor belts and "hang up" in hoppers. Passage through a mill reduced its moisture content to 0.5%, and after this it gave no further trouble. Used to make single superphosphate, the behaviour of the rock confirmed its unreactive nature. A w.sol. P_2O_5 fraction in the matured product of 85% was attained, but at the expense of a free acidity of 30% of the total P_2O_5 .

Palabora and Sukulu Rocks.

The Palabora deposit is in the N.E. Transvaal, in South Africa. The sample of rock received had 35.0% P_2O_5 and was low in Fe_2O_3 and Al_2O_3 (0.7 and 0.3%) and was also low in CO_2 (1.5%).

This rock has proved in the laboratory to be very unreactive. In two experiments, both with rock ground to pass completely a 100 mesh B.S. sieve (57% through 200 mesh), and an acid/rock ratio of 60 gms. 100% H_2SO_4 per 100 gms. rock, results were:

1. When acid of 70% H_2SO_4 was used, 17% of this was still left after 60 minutes.
2. When acid of 60% H_2SO_4 was used, it disappeared in 20 to 25 minutes.

Even under the latter conditions, which gave a superphosphate of satisfactory physical condition, analysis at 3 weeks gave the following results:

Total P_2O_5	19.8%
W.sol. P_2O_5	15.0%
W.sol. P_2O_5 fraction	75.5%
Free acid P_2O_5 fraction	25%

The use of acid at 50% H_2SO_4 , an initial acid temperature of $120^\circ C.$, the addition of chalk, and an acid/rock ratio of 65, have all been tried without increasing the w.sol. P_2O_5 fraction above 80% after 3 weeks storage, the available P_2O_5 fraction being practically the same.

In an extreme test, the fine rock was treated with nitric acid at 60% HNO_3 in a ratio equivalent to 92 gms. H_2SO_4 /100 gms. rock. With Morocco rock, the w.sol. P_2O_5 fraction would have been practically 100% in 10 minutes, but here it was only 66% after 5 hours.

At this point in our investigation, we almost gave up attempts to obtain from this rock by acidulation a product with a high w.sol. P_2O_5 fraction. We were encouraged to have another try by the following considerations:

- (a) The low reactivity towards nitric acid might be due to lack of porosity, which would have less effect on the reactivity towards sulphuric acid.
- (b) In fact, as regards the first stage of the superphosphate reaction (formation of phosphoric acid) the reaction with acid of 60% H_2SO_4 had been fairly rapid.
- (c) We remembered some work by the Chemical Research Laboratory, Teddington,²² on rock from the Sukulu deposit, in Uganda, which might be of a similar nature to the Palabora rock.

Accordingly, we have recently carried out an experiment in which we heated a mixture of the finely-ground Palabora rock with acid of 50% H_2SO_4 , in the ratio 90 gm. 100% H_2SO_4 per 100 gm. rock, for 5 hours at $80^\circ C$. Agitation could only be carried out for the first 45 minutes, as the slurry then became too stiff. Dilution, filtration, washing, and analysis of solution and solid showed that 90% of the P_2O_5 had become water-soluble. It may therefore be practicable to make phosphoric acid from Palabora rock.

There are at least three other known phosphate rock deposits of appreciable size on the eastern side of Africa south of the Sahara Desert, and our impression is that these are all of an igneous nature. These five deposits are likely to be of great importance in the agricultural development of this part of the African continent.

It seems that these igneous phosphate rocks are not well suited for the type of process which we are accustomed to use with the sedimentary phosphate rocks, but that it should be possible to devise techniques by which they can be converted to satisfactory fertilisers.

Acknowledgements.

We wish to acknowledge our indebtedness to several colleagues (past and present) who have taken part in the experimental work here recorded, and our gratitude to the directors of Fisons Limited for permission to present this paper.

APPENDIX

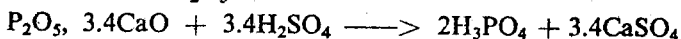
CALCULATION OF ACID/ROCK RATIO IN T.S.P. PRODUCTION. ALLOWANCE FOR H₂SO₄ CONTENT.

The H₂SO₄ content of phosphoric acid is liable to cause confusion in calculations. First we have to decide how it is itself to be arrived at. Determination of SO₄ content is not very helpful, since sulphates of calcium, sodium etc. are also present. It was decided to take the value given by electrometric titration, although this may be affected by the presence of H₂SiF₆ etc.

Having decided on a value, we can then proceed as follows :

100 gms. of phosphoric acid of analysis P'% P₂O₅, C'% CaO and S'% H₂SO₄ are to be reacted with phosphate rock of analysis P''% P₂O₅, C''% CaO, the "corrected" ratio (P₂O₅ in acid)/(P₂O₅ in rock) to be R.

Assume that the first reaction of the rock is with the H₂SO₄ to form more acid P₂O₅ :



Hence, each gm. of H₂SO₄ reacts with 0.427 gms. rock P₂O₅ to give acid P₂O₅.

To get a corrected acid/rock P₂O₅ ratio of R, we need *secondary* rock with a P₂O₅ content, per 100 gms., of

$$\frac{P' + 0.427S'}{R}$$

Thus, for 100 gms. of phosphoric acid, we need a *total* quantity of phosphate rock containing

$$\frac{P' + 0.427S'}{R} + 0.427S' \quad \text{gms. P}_2\text{O}_5$$

The figure thus arrived at is of course to be multiplied by 100 and divided by P'' to find the weight of rock required. In order to arrive at a formula by which we can calculate R from the analysis of the product and starting materials, we proceed :

The product will contain

$$\frac{P' + 0.427S'}{R} + 0.427S' + P' \quad \text{gms. P}_2\text{O}_5 \dots (1)$$

The weight of CaO in the total rock used is

$$\frac{C''}{P''} \left\{ \frac{P' + 0.427S'}{R} + 0.427S' \right\}$$

The product will thus contain

$$\frac{C''}{P''} \left\{ \frac{P' + 0.427S'}{R} + 0.427S' \right\} + C' \text{ gms. CaO} \dots (2)$$

The ratio P_2O_5/CaO in the product (Q) is then :

$$\frac{(1) P''}{(2) C''} \left\{ \frac{P' + 0.427S' + 0.427S'R + P'R}{P' + 0.427S' + 0.427S'R + C'RP''/C''} \right\} = Q$$

Writing $QC''/P'' = Z$, we find that

$$R = \frac{P' + 0.427S' - ZP' - 0.427S'Z}{QC' + 0.427S'Z - 0.427S' - P'}$$

$$R = \frac{(P' + 0.427S')(1 - Z)}{QC' - P' + 0.427S'(Z - 1)} = \frac{(Z - 1)(P' + 0.427S')}{P' - QC' - 0.427S'(Z - 1)}$$

whence R can be evaluated from the analytical values of the acid, rock and product.

Example. Taking an example where R has already been calculated by another method :

Values given in report of 4.3.52 are :

Acid* : 39.15% P_2O_5 , 2.4% H_2SO_4 (by electrometric titration),
0.30% CaO.

Rock : 33.8% P_2O_5 , 51.9% CaO.

TSP : 50.05% P_2O_5 , 24.67% CaO, $Q = 2.03$.

Hence $Z = 2.03 \times 51.9/33.8 = 3.12$, and $Z - 1 = 2.12$,

and $0.427S' = 1.0$,

$$\text{and } R = \frac{2.12(39.15 + 1.0)}{39.15 - (2.03 \times 0.30) - (1.0 \times 2.12)} = 2.34$$

which was the value arrived at in the original report.

Rock required, for experiments of 4.3.54 :

$$\frac{P' + 0.427S'}{R} + 0.427S' \text{ gms. } P_2O_5$$

$$P' = 41.6$$

$$S' = 1.9, 0.427S' = 0.8$$

$$\text{For } R = 2.1,$$

$$\frac{41.6 + 0.8}{2.1} + 0.8 = 21.0 \text{ gms. } P_2O_5$$

* This acid was cloudy. The values were obtained by filtering and analysing both the sediment and the filtrate.

Wt. of rock required for 2,000 gms. acid

$$21.0 \times 20 \times 100/33.7 = 1,247 \text{ gms.}$$

For $R = 2.5$,

$$\frac{41.6 + 0.8}{2.5} + 0.8 = 17.8 \text{ gms. P}_2\text{O}_5$$

Wt. of rock required for 2,000 gms. acid

$$17.8 \times 20 \times 100/33.7 = 1,056 \text{ gms.}$$

Another example. A sample of TSP obtained from Immingham in connection with the above work was analysed for P_2O_5 and CaO .

Assume analysis of acid as before :

39.15% P_2O_5 , 2.4% H_2SO_4 , 0.3% CaO , and

Rock : 33.3% P_2O_5 , 51.7% CaO .

TSP : 49.0% P_2O_5 , 22.85% CaO , $Q = 2.145$.

$Z = 2.145 \times 51.7/33.3 = 3.33$, $Z - 1 = 2.33$.

$0.427S' = 1.0$

$$R = \frac{2.33 (39.15 + 1.0)}{39.15 - 0.65 - 2.33} = \frac{2.33 \times 40.15}{36.15} = 2.59$$

Summary

The paper starts with an introductory section in which it is shown that the reactivities of phosphate rocks from different sources towards mineral acids can be correlated with two physical properties of the rocks, both related to their porosities. The reactivities are also correlated with the carbon dioxide contents of the rocks, and with the extent to which their P_2O_5 contents dissolve in 2% citric acid solution under carefully standardised conditions. The importance of the iron and aluminium contents of the phosphate rocks is also mentioned.

Laboratory investigations of the production of both single and triple superphosphate are described in some detail. In both cases relations are arrived at for Morocco (Kourigha) rock between the ratio of acid to rock used and the conversion to water-soluble P_2O_5 attained. It is shown that fine grindings greatly facilitate speedy reaction in single superphosphate production, but not in that of triple superphosphate.

The next section deals with certain practical considerations, namely: receipt and storage of rock, grinding, control of acid and rock feeds, mixing of acid and rock, superphosphate dens. This section finishes with a note on economics and choice of rock.

Finally, information on the behaviour of various phosphate rocks both in the laboratory and in the factory is brought together. The rocks considered in this section are those from Morocco (Kourigha), Gafsa, Safi, Nauru, Ocean Island, Florida, Senegal (calcareous type) and Kola.

Finally, some laboratory work is recorded on a sample of phosphate rock from the Palabora deposit in South Africa. Whereas most of the other rocks dealt with are undoubtedly of sedimentary origin, this one is an igneous rock. The evidence was that the rock was unsuitable for the production of superphosphate in the ordinary type of plant, but could be used to make phosphoric acid by reaction with sulphuric acid. It is thought that substantially the same is true of a number of other phosphate rock deposits on the eastern side of Africa south of the Sahara Desert.

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