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MANUFACTURE AND GRANULATION OF ENRICHED SUPERPHOSPHATES

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in relation to rate of sulphuric acid substitution and total moisture content.

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I Introduction

Between single superphosphate with a content of 17 to 20% available P_2O_5 and the so-called triple or concentrated superphosphates with 44 to 50% P_2O_5 there is room for a whole range of intermediate products known as enriched superphosphates. The decision to manufacture these enriched superphosphates may be justified either by the economics of the process or by their use in the formulation of compound fertilisers.

There are 2 possible methods of manufacture:

- 1) to mix single and concentrated superphosphate in appropriate proportions
- 2) to react the phosphate rock with a mixture of sulphuric and phosphoric acid.

Has the second method any advantage other than avoiding the necessity for mixing two solids which is always a laborious and costly process? The answer is "Yes" if the sulphuric acid which is available is concentrated enough, e.g.: 93% H_2SO_4 . Before an acid of this strength can be used for the manufacture of single superphosphate, water must be added to bring it down to about 68-72%. On the other hand, the wet-process acid used for triple manufacture which contains about 28-32% P_2O_5 when it leaves the vacuum filters must be concentrated to a strength of 50-55% P_2O_5 .

To make enriched superphosphate by mixing two solids, we should first have to add water and later evaporate it. It is much more sensible to use the excess water in the phosphoric acid to dilute the sulphuric acid. Reacting the rock with a mixture of acids would thus reduce the required concentration of the phosphoric acid and possibly even cut out the concentration stage altogether. This would substantially reduce fuel and power consumption and cut maintenance.

It is, of course, essential that we should be able to carry out the reaction of the rock with the mixed acids in the plant which is normally used for the manufacture of single or triple superphosphate.

This is what we propose to investigate.

This is not a new problem. A U.S. Patent of 1926 (1) deals with it. Some laboratory trials are summarized by Bridger (2). Fox & Hill (3) have published a theoretical and experimental study of the question. Much fuller laboratory and pilot-plant trials have been reported by Yates, Nielsson, Fox & Magness (4).

In their most recent paper to ISMA, Messrs. Dee, Nunn and Sharples (5) mention a series of experiments carried out by them. There must certainly be other work we do not know about.

The sole purpose of the present paper is to round off the results already obtained. We have tried in particular to present data of practical use to any manufacturer who may decide to make enriched superphosphate.

II Calculating the amount of raw materials

It is a simple matter to determine how much phosphoric acid must be substituted for a given quantity of sulphuric acid in reacting with the phosphate rock. Since the phosphoric acid will be converted into monocalcium phosphate, a di-acid salt, only one hydrogen atom will be available in the reaction. Hence, one unit of H_2SO_4 (98) must be replaced by two units of H_3PO_4 (2×98), that is twice the weight, i.e. 142 of P_2O_5 , or in other words the weight of P_2O_5 must be 1.45 times the weight of H_2SO_4 . To put it another way, for a given weight of phosphate we must always supply the same number of H^+ ions as determined by methyl orange, but they may be supplied either by the sulphuric or phosphoric acid.

In practice, this rule is only a rough guide, because as the proportion of phosphoric acid increases, the reaction of the impurities, principally calcium fluoride, is less violent and a slight reduction may be made in the ratio active H^+ ions: rock.

For example, given 100 units of 75% Morocco phosphate, the added acid expressed as H_2SO_4 equivalent may be reduced from 61.5 to about 60 as between single and triple super.

In practice, these considerations are not sufficiently precise. The manufacturer wants to be sure that when the reaction is complete he will have a superphosphate with a definite content of available P_2O_5 . What should be the ratio of sulphuric to phosphoric acid, and at what concentration? These are the vital questions.

We can attempt to answer them by working out the complete raw materials balance sheet, taking, for example, the factor of the replacement of sulphuric by phosphoric acid as the unknown. This would involve long and tedious calculations and we should have to make rash assumptions as to the influence of the impurities, the amount of water evaporated, etc. Moreover, how could we determine the optimum water content of the acids?

There is another method which is simpler and more reliable: it consists of considering an enriched superphosphate any desired concentration as a mixture of single and triple, their proportions being determined by simply applying the mixtures rule. Since the data relating to the upper and lower limits of superphosphate are well established, it is easy to work out the quantities required to obtain the desired product.

Let us assume that we wish to obtain from Morocco rock with a 33.5% P_2O_5 content a product with a final content of 30.0% available P_2O_5 .

We know from experience that we get:

- a) 1,000 kgs single super with an available P_2O_5 content of 18.6% after curing from the following raw materials (losses excluded):

rock	576 kgs
sulph. acid (70%)	506 kgs (= 354 kgs H_2SO_4)

- b) 1,000 kgs triple super with an available P_2O_5 content of 45.0% after curing from the following raw materials (losses excluded):

rock	382 kgs
phos. acid (52%)	639 kgs (= 332 kgs H_3PO_4)

Now, from the equation:

$$30 = 18.6x + 45(1 - x)$$

we get:

$$x = \frac{45 - 30}{45 - 18.6} = 0.568$$

$$1 - x = 0.432$$

Thus, to obtain 1,000 kgs enriched super with 30% available P_2O_5 after curing, we should have to consume:

rock	$576 \times 0.568 + 382 \times 0.432 = 492$ kgs
Sulph. acid 70%	$506 \times 0.568 = 288$ " (202 H_2SO_4)
Phos. acid 52% P_2O_5	$639 \times 0.432 = 276$ " (144 P_2O_5)

You can, of course, use acids of different strengths; but the mixture must provide, for 492 kgs rock, 202 kgs H_2SO_4 and 144 kgs P_2O_5 , and their total weight must be $288 + 276 = 564$ kgs.

We can avoid calculations altogether by the use of a graph. Figure 1 was obtained by using the content of available P_2O_5 after curing as the ordinate and as the abscissa the consumption of rock, H_2SO_4 , and P_2O_5 from the acid, as well as the total weight of acid for 100 kgs of enriched superphosphate. The straight lines connecting the appropriate points for single and triple super give a direct reading of the amounts needed to make an enriched super of any given strength by intersection with the corresponding ordinate.

We thought it would be useful to include the straight line which shows the total amount of water introduced with the acids, making due allowance for the impurities of the wet-process phosphoric acid, which are also shown. From the lines showing water introduced by the acid and total weight of acid we may easily obtain the curve representing the water content of the acid, which is a hyperbolic arc.

In order to find the corresponding total water content of the superphosphate product, we need rather more detail as to raw material consumption in the manufacture of single and triple super, and we have provided this in tables I and II.

It will be observed that the calculated water content is appreciably higher than that obtained by analysis: stove-drying for 4 hours at 100° is not sufficient to drive off all the water of crystallization, and the free phosphoric acid also contains water. All enriched supers included in fig. 1 will have an analysed water content of about 10%, like the single and triple super from which they are derived as a mixture, but in fact their actual water content will vary between 11.5 and 13.6%.

We are unable to assume that this is the water content which gives optimum operating conditions, and we may very well wish to manufacture a product with a different actual water content. In this case, it is more convenient to use fig. 2, where the ordinate is the available P_2O_5 content of a supposedly completely dehydrated superphosphate and the abscissa the quantities which will make 100 kgs of dehydrated product.

Fig 2 was constructed using the same basic data as Fig 1 viz:-

	<u>Single</u> <u>as</u> <u>obtained</u>	<u>Super</u> <u>de-</u> <u>hydrated</u>	<u>Triple</u> <u>as</u> <u>obtained</u>	<u>Super</u> <u>de-</u> <u>hydrated</u>
Content of available P ₂ O ₅ %	18.6	21.0	45.0	52.1
Total H ₂ O content of super%	11.5	0	13.6	0
Rock (as % of super)	57.6	65.1	38.2	44.02
H ₂ SO ₄	35.4	40.0	0	0
P ₂ O ₅ from phos.acid	0	0	33.2	38.4
Total weight of acid	50.6	44.2	63.9	58.3
H ₃ PO ₄	0	0	45.9	53.2
Impurities of phos.acid	0	0	4.5	5.2
H ₂ O of acid mixture	15.2	4.2	13.5	-0.1

Example : to manufacture a super with content of 30% available P₂O₅ after curing with a total water content of 15%, or 12% by analysis.

The corresponding dehydrated product would contain $\frac{30}{0.85} = 35.3\%$ of available P₂O₅. According to fig. 2, we should require:-

	<u>per 1000 kgs.</u> <u>dehydr.super</u>	x	<u>per 1000 kgs. product</u> <u>as obtained</u>
Rock	555	0.85	472
H ₂ SO ₄	217	"	184
P ₂ O ₅ (from phos.acid)	177	"	151
total weight acid	507	"	431+150 = 581
(impurities	(24	"	(20
(H ₃ PO ₄	(244	"	(208
(H ₂ SO ₄	(217	"	(184
(H ₂ O	(22	"	19+150 = (169
H ₂ O in acid			29.1%

It would be useful to be able to read off a single diagram the amount of available P₂O₅ as a function of both the water content of the product obtained and the substitution factor for sulphuric acid, expressed as the equation:

$$x = \frac{\text{acidity of H}_3\text{PO}_4}{\text{acidity of H}_3\text{PO}_4 + \text{H}_2\text{SO}_4} = 1 - \frac{\text{H}_2\text{SO}_4}{\text{H}_2\text{SO}_4 \text{ equal to total acidity}}$$

(acidity referred to is as indicated by methyl orange)

or

$$x = \frac{\text{weight of H}_3\text{PO}_4}{\text{wt of H}_3\text{PO}_4 + (\text{H}_2\text{SO}_4 \times 2)} = \frac{0.69 \text{ P}_2\text{O}_5}{0.69 \text{ P}_2\text{O}_5 + \text{H}_2\text{SO}_4}$$

Figure 3. corresponds to this equation. The curve giving the % water content has been deducted from the H₂SO₄ and H₃PO₄ curves in fig.2. The others may easily be deducted from these. They are all hyperbolicates.

Thus, for the substitution rate x, we must use for 100 units of Morocco rock:

$$\begin{aligned} \text{H}_2\text{SO}_4 &: 61.5 (1-x) \\ \text{P}_2\text{O}_5 \text{ from phos.acid} &: 87x, \text{ or H}_3\text{PO}_4 : 120x \end{aligned}$$

These figures are adequate if the product is to be dried to a pre-determined total water content (especially when granulated). It will

then be satisfactory if the acids supply water at least equal to the amount required for a good reaction. Fig. 3 will be found particularly useful in such cases.

Note

The impurities of wet-process phosphoric acid consist of acids (sulphuric and fluosilicic) and bases (CaO, Al₂O₃, Fe₂O₃, MgO, Na₂O, etc.) According to whether the anions or the cations are in excess, the acidity as measured by methyl orange may be more or less than that corresponding to the P₂O₅ content. This difference is negligible except when there is trouble with the phosphoric acid process. Normally, the acidity indicated by methyl orange is practically the same as the P₂O₅ content, as we have assumed in fig. 2.

III Laboratory trials

Laboratory trials in the manufacture of enriched superphosphate were carried out following a definite working procedure worked out from a systematic study of the conditions of manufacture of superphosphate from different rocks.

Equipment

The mixing was done in a stainless steel bowl - diameter 225mm, height 250 mm - fitted with a central agitator consisting of two paddles 23mm wide, inclined at an angle of 45° and moving in a circle of 190mm diameter. Speed of the agitator can be adjusted over a wide range.

Procedure

The bowl is wrapped in a heat-resistant jacket. The correct amount of acid for 1000 g of rock (1200 g for single super) is placed in the bowl and its temperature noted.

The agitator is started up, and the 1000g of rock added quickly, in less than 15 seconds. The speed of the agitator is set to give the best possible mix, which in practice is between 100 and 150 rpm.

Timing starts from the time the first rock is added. At 30 sec. dead the agitator is stopped and removed from the bowl, but if coarsely ground rock is used, mixing is continued for as long as necessary to give a thick enough mix to prevent the rock from settling.

After 15 minutes the jacket is removed and the bowl is plunged into a boiling-water bath (100°). At 60 minutes, heating of the bath is stopped and it is allowed to cool naturally. At 1 hour 45 min. the superphosphate is removed from the bowl, crumbled and passed through a square-mesh sieve (2.7mm aperture), unless the product is too plastic and sticky, in which case a larger sieve (3.8mm aperture) is used. An average sample of about 1200g is stored in a glass flask at room temperature.

While the test run is proceeding, the following points are noted:-

- temperature of the reaction mass in relation to the passage of time
- moment when the product sets (when a rod, which may be the thermometer, thrust into the product leaves an imprint). We call this the set, and it marks the end of the period when the mixture flows freely.
- moment when the product hardens (when an 8mm rod weighing 60g (actually, the thermometer) can be stood upright in the product without going in)
- moment when the product could be removed from the reactor. This is the shortest time from the beginning of the mixing until the product is dry, hard and friable enough to be turned out into the den.

- free acidity of the product, expressed as % free P₂O₅, at the end of 10 min, 30 min, 1 hr, 2 hrs, 6 hrs, the analysis being made immediately the sample is taken.
- complete analysis of the product after 24 hrs, 7 days, 1 month.

The definitions given above for set, hardening and suitability for removal from the reactor may appear vague and subjective. Nevertheless, experience has shown that the information obtained in this way by an experienced operator gives a sufficiently exact picture of the physical phenomena observed during the manufacture of superphosphate. In a study of this kind it is very important that laboratory and plant personnel should speak the same language. Some authors have used a more elaborate method involving measuring and recording the energy transmitted by the agitator to the vessel in which the mixing is done. Unfortunately, this method, though it gives good results in the early stages, tends to prolong the mixing beyond normal industrial practice and this destroys the alveolar structure of the superphosphate. This spoils the subsequent reactions.

It may also be objected that our working method involves keeping the sample of superphosphate after it is removed from the reactor at a temperature quite different from what it would be in the middle of a heap at the works; tests have shown that temperature after removal had only a negligible influence on the subsequent development of the product, while the temperature in the initial period was of prime importance.

After each run, the superphosphate made was submitted to two additional tests at the end of 2, 6 and 24 hours. These tests which tell us something about the physical quality of the product are described below:-

a) Test for "sticking power"

This shows the more or less plastic and moist nature of the product by measuring its ability to stick to a surface against which it is lightly kneaded. Procedure is as follows:- 100 g of superphosphate are placed in a porcelain dish (diameter 200mm, depth 45mm) and spread evenly over the whole surface. 10 porcelain balls of 40mm diameter are then added each weighing 80 g. The dish is placed on a special device which agitates it by a combined lifting and rotating movement. Each full lift of 100mm is completed in 1 second while the dish turns one quarter turn about its centre. After 1½ min of this treatment, the balls are removed and the porcelain dish is turned upside down over a stainless steel vessel of slightly larger diameter and the whole is subjected to the same agitation for 1 minute. After this, the superphosphate collected in the stainless container is weighed. The "sticking power" is expressed as the percentage of the product left sticking to the porcelain dish and balls.

b) Test for "caking"

100 g of the superphosphate being studied are passed through a 2.7mm mesh and put into a stainless steel cylinder 50mm diam, height 100 mm, with a removable stopper closing the bottom. A plug of equal interior diameter is then inserted in the top, weighing 1.8kg₂ and loaded with a 10g weight. The pressure applied is 0.60 kg/cm². This load is kept on for 6 days, when the caked product is turned out of the mould. Hardness is measured by vertically inserting a needle 3mm in diameter fitted at its lower end with a cone 15mm high and 1.5 mm at its smallest diameter. This needle has at the top end a container to which are added progressively, by means of a vibrating distributor, 50 g per second of steel balls. When the needle has penetrated the sample to a depth of 25mm, the total weight of moving parts plus balls is recorded. Thus, caking tendency may be expressed in terms of the total weight employed. The less it is, the less difficulty will there be in excavating the product.

A series of trials was carried out under the above conditions with Morocco rock and another with Florida rock.

1. Trials with 75% Morocco rock

Analysis and particle size of the rock used are given in Table 3. For purposes of comparison, we have assembled in Table 4 the results obtained in the manufacture of single and triple super. Even when the rock is ground to pass an 80-micron mesh at only 58%, the Morocco rock reacts rapidly with 68% sulphuric acid; it is possible to effect removal only 8 minutes after mixing has begun (trial no.1). The rate of attack, defined as $\frac{\text{available P2O5}}{\text{total P2O5}}$ exceeds 97% after 1 week. The initial reaction of the same rock (admittedly ground more finely) with 50.4% phosphoric acid (and 1.9% SO3), that is 23% water, is much more rapid (trial no.4). Four minutes in the den is enough. But the secondary reaction proceeds more slowly. In this case the rate of attack (A) is defined as follows:

$$A = \frac{\text{available P2O5 from rock}}{\text{total P2O5 from rock}} = 1 - \frac{\text{insol. P2O5}}{\text{rock P2O5}} = 1 - \frac{K \text{ insol. P2O5}}{\text{total P2O5}}$$

$$\text{where } K = \frac{\text{acid P2O5} + \text{rock P2O5}}{\text{rock P2O5}} = 1 + \frac{\text{acid P2O5}}{\text{rock P2O5}}$$

In the trial in question, $K = 1 + 2.62 = 3.62$

The reaction rate had not reached 93% ten days after manufacture.

For information, we mention trial no.3 carried out with unground phosphate. The reaction begins very slowly, but manufacture can be carried out batchwise.

Table 5 summarizes the results of a series of trials on the manufacture of enriched superphosphate. In all these trials the rate of substitution of sulphuric by phosphoric acid, as previously defined equals 32.8% or approximately one third.

The mixture of sulphuric acid and phosphoric acid was used hot (72 and 80°) in nearly all the trials for the following reason: when mixtures of 93% sulphuric acid with 29-37% phosphoric acid are prepared, the mixture heats up by about 60°. On the actual plant it would be difficult to cool such a mixture without causing precipitation and incrustation. We shall see, moreover, in the next paragraph, that it is better not to mix the acids in advance.

A study of Table 5 shows that with an acid at 80°C the best results are obtained where the water content of the acid is about 31% (trial no.7). The mixture can be dedenning after about 10 minutes. The reaction rate is about 92% after 24 hours and 93.5% after one week. If the water content is reduced to 29%, the results are still excellent, but the product is very hard and care must be taken to remove it from the den without delay (trial no.6). With 27% of water in the acid, the reaction is observed to take place more slowly; the mixture must be kept in the den for 20 minutes. The product then sets very hard, but the secondary reaction is quite satisfactory (trial no.5). It looks very dry and stickiness is nil after 6 hours.

A water content of 35% in the acid appears to be the limit to an upward direction. Deddenning can be effected after 15 minutes and the superphosphate obtained is rather moist (trials nos.8 and 9). However, sticking power is less than that of ordinary super.

A few trials (nos.10 to 13) were, however, carried out with a higher water content (40.5 to 41.7%). It would have been useful to have been able to mix with the 93 or 98.5% sulphuric the 30% phosphoric straight from the filters. We had hopes, by keeping the temperature down, of getting some of the water to crystallize out as gypsum. But

this did not happen, even when we started with acid at 18°C. The resulting product is too moist.

To conclude, with a substitution rate of 33%, we can recommend that the acid mixture should contain between 27 and 35% water, preferably 29 to 33%. This is more than that shown in fig.1, which is 24.7%. We think there are two reasons for this:

- 1) contrary to what one might expect, the manufacture of enriched superphosphate does not proceed in a manner intermediate between triple and single super manufacture.
- 2) in the control trials 1 and 4, we used acid at 20°C instead of 80°, while 20 - 40° is normal plant practice. Now, it is well known that the hotter the acid used in superphosphate manufacture, single or triple, the more dilute it must be. Let us take an extreme case: plant experience has shown that excellent quality superphosphate can be produced with 93% H₂SO₄ which has not been previously diluted, provided that the necessary amount of water to bring the strength to 66% is simultaneously sprayed into the reactor. If there is less water, the reaction soon stops and the product remains a slurry; but where the sulphuric acid has been previously diluted and cooled to about 40°, the concentration may rise to 72% without any ill effect. In the first case, the heat given off by the dilution of the acid causes extra evaporation of water and the final residual moisture of the product is the same in both cases. The moisture content of the final product is certainly an essential factor in a good reaction. It will be seen that in trials 6, 7 and 8 the moisture analysed between 10 and 12%, which is normal for both single and triple super.

2. Trials with Florida phosphate

Some trials were carried out with various particle sizes of Florida rock, and these are summarized in Table 6. The analysis of rock XI is given in Table 3. For comparison, we also give the results of the manufacture of single and triple super with another Florida rock, No. VIII. Let us summarize the results obtained by varying the substitution rate.

a) Single super (0% substitution)

Florida rock in the same particle size is much less reactive than Morocco at the same temperature and sulphuric acid strength (trial no.14). The retention time in the den must be extended to 40 minutes. By increasing the acid strength and temperature and reducing the amount by 2.5%, retention time may be halved (trial no.15). The product had good sticking power.

With rock no. VIII ground to 75% through 80-micron mesh, results are better, though not as good as with Moroccan rock (trial no.16).

b) 21-23% substitution (trials 17 & 18)

For the enriched super trials, rock XI was ground to pass 70% through 80-micron mesh. In spite of this, the reaction proceeds very slowly. With acid containing 29% water at 92°C, den retention time was 45 minutes. Secondary reaction was satisfactory.

c) 33% substitution (trial no.19)

The reaction is even slower. For 25.5% water in the acid, den retention time was 1½ hrs and the resulting product was tacky. Secondary reaction was normal; reaction rate 95% after 1 month.

d) 100% substitution (triple super)

Results are substantially better, but very much poorer than those obtained with Morocco rock, since a den retention time of $\frac{1}{2}$ hour is necessary with 50.4% phosphoric acid at 50°, using rock XI (trial 20).

With Florida rock VIII and 51.4% phosphoric at 20° (trial no.21) reaction speed is much faster, as is shown by the evolution of free P₂O₅ and setting time (10 mins.) A further trial showed that when the acid temperature was 50°, setting time was reduced to 3 minutes.

To sum up, the trials in the manufacture of enriched superphosphate from Florida rock XI showed a very slow physical evolution, with the slurry phase unduly extended. Chemical evolution, on the other hand, was quite satisfactory. There are known to be very marked differences in the behaviour of different Florida rocks of the same commercial grade.

A comparison with sample VIII shows that this is a very unreactive rock and there is no doubt that other samples would give much better results.

Of course, before proceeding to plant-scale operations, it would be necessary to find the optimum acid water content for a given substitution rate.

IV Manufacture on plant

We have just seen that the manufacture of enriched superphosphates shows more or less distinct differences from single super. Thus, if we wish to use the same plant for both, there are certain special arrangements to be made.

A) Adding the acids.

When we mix 93-98% sulphuric acid with wet-process phosphoric with 30-40% P₂O₅ content, we get heat given off and the fluosilicic acid in the phosphoric acid is given off as SiF₄ + 2HF. The extent to which this happens depends on the temperature reached, and this in turn depends on the ratio between the acids. Because of the formation of HF, the acid mixture is extremely corrosive. There is also simultaneous precipitation of CaSO₄. Therefore it is better not to mix the acid beforehand. They will be sprayed into the reactor from two separate pipes, after the amounts have been measured or the flow controlled, according to whether the plant is batch-type or continuous.

B) Mixing

With a high substitution rate, the set may occur very quickly; the reactor becomes blocked if it is run under the conditions for ordinary super. Retention time in the reactor must be reduced. A simple way of doing this in a continuous horizontal reactor is to bring in the acids at the back end while the rock enters at the normal place. Thickening may also be delayed by using a coarser rock, lowering the acid temperature, reducing the water content or the acid-rock ratio, but all these methods have the drawback of affecting the behaviour of the mixture in the den.

C) Den

Sometimes the fluid and slurry stages are very long. This does not matter in a batch process, except that it cuts production capacity. Some dens will not take a very fluid mixture because it leaks through the joints. Usually a little attention to the joints will settle this matter. There may be still a difficulty when the plant is started up after a long pause; as the equipment is cold, the mixture may be very fluid. In this case, the acid input should be reduced to give a stiff slurry at the beginning.

Of course, the acid feed and the den speed should be adjusted to give the required retention time in a continuous den. Care must be taken to avoid exceeding the retention time, as the enriched superphosphate may be very hard and the work of the cutters will become difficult if not impossible. For the same reason, when production is stopped, it is advisable to empty the den. Obviously, it is better to use a continuous den without joints or cutters. We think the best equipment at present available is the rotary drum. Its flexibility of adaption to different processes and its very modest maintenance costs make it the ideal instrument for the production of all superphosphates, single, enriched and triple.

V Production Costs.

Now we know that it is possible to manufacture enriched superphosphate directly, let us work out an example of the cost compared with that of a mixture of single and triple super. We will take the figures quoted above for a product with 30% available P2O5 and 15% moisture. We calculate the acid mixture needed for 1,000 g of super:-

H3PO4	208 (P2O5 : 151)
H2SO4	184
Impurities	20
H2O	169 (% H2O : 29.1)
	<hr/>
	581

Thus, we will mix 196 kgs of 93% H2SO4 with 385 kgs of phosphoric acid containing 39.2% P2O5. To make triple super, this acid would have had to be about 50% P2O5. Starting from 30% acid, we should have to evaporate per kg P2O5, 0.78 kg water for the enriched and 1.33 kg for triple. Thus, the direct manufacture of enriched super gives an economy of over 40% of the cost of concentrating the phosphoric acid. Taking a conservative estimate of 3fr/kg evaporated water from the phosphoric acid, we find the saving per ton of enriched super equals:

$$3 \times 0.55 \times 151 = 250 \text{ francs}$$

which is considerable.

VI Chemical Sampling

As for single superphosphate, it is necessary to determine for an average sample the total available, water-soluble and free P2O5 content. As the secondary reaction is not complete at the time of the analysis, the results of the analysis must be interpreted so as to confirm that the ratio total acid used to rock is correct. For this, we have to extend the rules established for the acidulation of single superphosphate and apply them to enriched and concentrated superphosphate. The appendix supplies a study of this matter, showing principally that the

formula for the calculation of the ion ratio $\frac{H^+}{PO_4^-}$ in the product

remains unchanged, but that the value to be applied to this constant declines from 2.08 to 2.025 in inverse proportion to the substitution rate.

The concept of maximum acidity is more useful : its value must lie between 1 and 2% of free P2O5 whatever the concentration of the superphosphate, and it can be determined in a few minutes by a simple and rapid analytical method, which makes it possible to make a frequent check on the acidulation during manufacture. When the acidulation is correct, the total P2O5 content of the product will show if the correct proportion of sulphuric to phosphoric acid has in fact been used.

VII Simultaneous Drying and Granulation

Nowadays it is normal practice to produce granulated triple super by the following continuous process:-

Dilute phosphoric acid (28-30% P2O5) is added to the rock. The fluid slurry is mixed with a large amount of dried recycled fines which provides a basis for the agglomeration of the fine particles. The moist mixture is dried by hot gases in a rotary drum. On leaving the drier, the product is screened on a double-deck screen, the granules of the required size being removed to the store while the fines and oversize, the latter after grinding, are recycled for mixing with the slurry. This process gives a good quality granular product; the granules are round and very hard.

It should be noted that the attack of the phosphate occurs mainly during drying: if there were no evaporation, the reaction would be curtailed. For instance, with ground Morocco rock in a slurry containing 40% water at a temperature held at 60°, the actual attack rate remains steady at 45%, even after a very long time.

At 100°, without evaporation, the attack rates do not exceed 56% after 4 hours and 62% after 24 hours. But if we dry at the same temperature, the attack rate varies as shown below in accordance with the water content:-

H2O	33	23	17	11	4	2
Attack rate	57	62	64	88	96.5	88

If drying is continued too long, reversion occurs.

Trials have shown that it is also possible to get much the same results by using unground Morocco rock so long as a part of the dried product is redissolved in the acid or in the slurry and the mixture is agitated for a sufficiently long time before drying, as laid down in a French patent. (6)

We thought it might be possible to apply the same process to the manufacture of enriched superphosphates. We first did a laboratory study to make certain that there were no untoward chemical reactions. Three trials were carried out in identical conditions with unground Morocco rock (sample no. VA) treated in turn with dilute sulphuric acid (50% H2SO4), a mixture of sulphuric acid and phosphoric acid (substitution rate 50%, water content 45%), and phosphoric acid with 30% P2O5 (53% water). In each case, the course of the reactions after drying was the same for final moisture contents lying between 8 and 18%. Here are the attack rates after 24 hours:-

Substitution rate	0	50	100
Actual attack rate	91%	85%	80%

After 1 month, the attack rate had reached 95% in all three cases. The speed of the initial reaction is thus greater when the substitution rate is lower and, from the chemical point of view, manufacture of enriched superphosphates with simultaneous drying presents even more advantages than for triple super.

Now that we were sure of this, it remained to study the question of granulation. For this, we proceeded to carry out pilot-plant and plant-scale trials, using ground Morocco rock.

- a) For single super, the trials showed that it was necessary to use a very dilute sulphuric acid (only 40% H2SO4).

By limiting retention time in the reactor, it is in fact possible to obtain a fluid enough slurry by using a more concentrated acid and this can be mixed with the recycled dry product; unfortunately, the granules formed in this manner do not harden but crumble away in the drier. The final product is a powder superphosphate.

Diluting the acid to 40% H₂SO₄, however, gives relatively hard granules. It is true that such a process is only of theoretical interest: for each ton of granulated product, 510 kg water must be evaporated, and this is out of the question, unless there is available a dilute by-product sulphuric acid which would in any case have to be concentrated. For the purposes of comparison, we would mention that where granulation is carried out by water spraying and drying the product as it leaves the den, the weight of water to be evaporated is less than 150 kg/ton of product.

These are the analyses after 3 days of two of the products made in these trials:-

H ₂ O	Total P ₂ O ₅	Available	Water sol.	Free	Attack
11.75	18.9	18.25	17.6	2.6	96.55
13.7	18.7	18.15	17.0	2.35	97.05

- b) A trial for the simultaneous manufacture and granulation of enriched superphosphate was carried out in the same conditions, with a substitution rate of 50%. The acids used contained respectively 93% H₂SO₄ and 30% P₂O₅, which made the water content 45%. The resulting slurry, which was close to the optimum consistency, was easily made into dry granules of even size and very hard.

Here are the analyses of two stages of this trial, carried out on samples after 3 days:-

	H ₂ O	total P ₂ O ₅	available	water-sol.	free	P ₂ O ₅ avail total	attack
slurry	26.75	28.5	27.75	27.0	4.4	97.4	94.0
dry gran product	6.3	36.85	35.75	34.9	4.4	97.0	93.1

A simple calculation shows that in the above case the amount of water to be evaporated is in the neighbourhood of 345 kg per ton of finished product. For comparison, where triple super is made from phosphoric acid with 30% P₂O₅, 605 kg water per ton must be evaporated.

Thus, the process of manufacture with simultaneous drying and granulation can perfectly well be applied to enriched superphosphates. The process is particularly attractive if the phosphoric acid contains enough water to cut out the need for adding any, which means that it already has quite a high P₂O₅ content.

VIII Conclusion

We can say as a result of the study described above that although the manufacture of enriched superphosphates by the den process differs in some ways from that of single super, it does not present any insuperable difficulties. When a few alterations in the operating procedure have been effected, the normal equipment can be used.

Where the P₂O₅ content is relatively high the product may also be granulated without difficulty.

In spite of its potentialities, there has not as far as we know been any significant industrial development of the production of enriched superphosphates.

Doubtless there are practical difficulties in adding new grades of superphosphate to those already stocked, but it seems that insufficient attention has been paid to the substantial economy that can be effected by cutting down the concentration of the phosphoric acid which would be enough to justify some extra capital cost.

This advantage will be enhanced as the old chamber sulphuric acid plants are replaced by contact plants producing more concentrated acid.

Thus, we may look forward in the not too distant future to seeing some industrial development of enriched superphosphates. We hope that this paper may be of some practical help to anyone wishing to undertake this.

IX REFERENCES

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- (5) DEE T.P., NUNN R.J. and SHARPLES h, The International Superphosphate Manufacturers' Association, Technical Meeting 1957.
- (6) Société de SAINT GOBAIN, French Patent No. 1.140.368 dated 2.9.55.

TABLE I

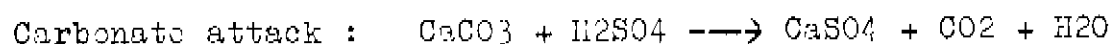
SINGLE SUPERPHOSPHATE - CHEMICAL BALANCE SHEET

Morocco rock - analysis:-	P2O5 % = 33.5	Ca ₃ (PO ₄) ₂ % : 73.2
	CO ₂ = 4.0	CaCO ₃ : 9.1
	F = 3.9	CaF ₂ : 8.0
	H ₂ O = 0.9	

Using for each 100 units of rock, 61.5 of H₂SO₄ in the form of 70% acid, at a temperature of 30°C, we got a superphosphate with the following analysis after the secondary reaction:

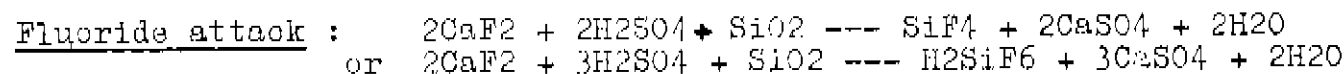
H ₂ O	Total P ₂ O ₅	Available P ₂ O ₅	W/sol.P ₂ O ₅	Free P ₂ O ₅	Attack
10.0	19.3	18.6	18.3	2.7	96.4

To calculate the required amount of water, allowance must be made for the attack of the carbonate and fluoride



For 100 of rock, 4 units of CO₂ are given off, forming

$$4 \times \frac{18}{44} = 1.6 \text{ H}_2\text{O}$$



Assume that 15% of the fluorine is given off as gas and 20% solubilised.

For 100 of rock, we get $0.15 \times 3.9 \times \frac{104}{76} = 0.8 \text{ SiF}_4$,

forming $(0.15 + \frac{2}{3} \times 0.20) \times 3.9 \times \frac{18}{38} = 0.5 \text{ H}_2\text{O}$

Total raw material requirements, taking into account the water, are thus as follows, per 1000 units of superphosphate produced:

<u>INPUT</u>	:	:	<u>P2O5</u>	:	<u>H2O</u>	
Phosphate	:	576	:	193	:	5
70% sulphuric	:	506	:		:	
{ H2SO4	:		:		:	
{ H2O	:		:		:	152
H2O formed by	:		:		:	
reactions	:		:		:	12

Total	:	1082	:	193	:	169
 <u>OUTPUT</u>						
Superphosphate	:	1000	:	193	:	115
produced	:		:		:	
Gas given off	:	82	:		:	
{ CO2	:		:		:	
{ SiF4	:		:		:	
{ H2O	:		:		:	54

Total	:	1082	:	193	:	169

Note

Notice the difference between the calculated (11.5%) and the analysed (10.0%) water content. Stove drying for 4 hours at 100° does not remove all the water.

TABLE 2

TRIPLE SUPERPHOSPHATE - CHEMICAL BALANCE SHEET

Morocco rock - analysis same as Table I.
 Wet-process phosphoric acid : H3PO4 : 71.8 (% P2O5 = 52.0)
 Impurities 7
 H2O 21.2
 100

The acidity of this acid, as determined by methyl orange, is presumed to correspond exactly to its H2PO4 content because its SO3 content corresponds to the metallic cations.

Using for 100 units of rock the amount of acid at 30°C which contains 87 units of P2O5 equal in acidity to $\frac{98}{142} \times 87 = 60.0$ H2SO4, we get after curing a superphosphate which gives the analysis below:

H2O	Total P2O5	Avail. P2O5	W/Sol. P2O5	Free P2O5	Avail. P2O5 Total P2O5	Attack
10.0	46.0	45.0	44.0	4.0	97.8	92.2

The carbonate reaction produces 1.6 H2O and gives off 4.0 CO2. The calcium fluoride reaction is negligible.

Thus, total raw material requirements and water calculation are as follows per 1000 units of superphosphate produced:

(TABLE 2.) (continued).

INPUT		P2O5	H2O
Phosphate rock	: 382 :	: 128 :	: 3 :
Phosphoric acid	: 639 :	: 332 :	: :
{ H3PO4	: :	: :	: :
{ impurities	: :	: :	: :
{ H2O	: :	: :	: 135 :
H2O formed by reactions	: :	: :	: 6 :
Total : 1021 :		: 460 :	: 144 :
OUTPUT			
Superphosphate produced	: 1000 :	: 460 :	: 136 :
Gas given off	: 21 :	: :	: :
{ CO2	: :	: :	: :
{ H2O	: :	: :	: 8 :
Total : 1021 :		: 460 :	: 144 :

Here again there is a marked difference between the calculated water content (13.6%) and that obtained in the analysis after 4 hours' drying at 100°C (10.0).

TABLE 3.

ANALYSIS OF THE PHOSPHATE ROCK USED IN THE TRIALS

Rock Sample No.	Morocco V	Florida VIII	Pebble XI
H2O	: 1 :	: 1.0 :	: 1.5 :
Total loss in fire	: 2.7 :	: 3.7 :	: 3.5 :
P2O5	: 33.2 :	: 33.9 :	: 33.7 :
CO2	: 4.1 :	: 2.83 :	: 3.0 :
F2	: 3.7 :	: 3.7 :	: 4.0 :
SO3	: 1.7 :	: 0.96 :	: 0.88 :
SiO2	: 1.75 :	: 3.03 :	: 3.3 :
Fe2O3+Al2O3	: 0.85 :	: 2.16 :	: 2.5 :
MgO	: 0.40 :	: :	: 0.6 :
CaO	: 51.0 :	: 50.0 :	: 48.8 :
Ca3(PO4)2	: 72.5 :	: 74.1 :	: 73.6 :
CaCO3	: 9.3 :	: 6.44 :	: 6.8 :
CaF2	: 7.6 :	: 7.6 :	: 8.2 :
Particle size - % passing mesh size:-	: Raw :	: Ground :	: Ground :
	: A :	: B :	: C :
0.30mm	: 74 :	: 96.0 :	: 99 :
0.2 mm	: 42 :	: 89.0 :	: 98 :
0.16mm	: 20 :	: 73.0 :	: 89.5 :
0.11mm	: 6 :	: 58.0 :	: 71 :
0.08mm	: 3 :	: 42.0 :	: 56 :
0.05mm	: 1 :	: :	: :
			: A :
			: B :
			: 10 :
			: 99 :
			: 85 :
			: 70 :
			: 63 :

MOROCCO ROCK Type VC : P205-33.2%

% H2SO4 substitution by H3PO4 : 32.8.

H2SO4 : 41.0
For 100 units of rock : H3PO4 : 40.0 (P205
Impurities: 4.1 29.0
Total acidity : H2SO4 equivalent : 61.0

Trial No.	5	6	7	8	9
<u>ACID</u>					
Total weight% rock:	116.5	120.0	122.8	127.0	132.2
H2O % of aci	27.0	29.1	30.7	33.0	35.7
Temperature °C	72	80	80	80	80
<u>CHEMICAL REACTION</u>					
P205 free after					
10 minutes	13.65	11.45	12.4	12.75	11.55
30 "	9.70	9.8	8.7	10.05	10.85
1 hour	8.45	8.4	8.25	9.1	10.4
2 hours	6.95	6.7	6.8	7.75	7.8
6 "	5.45	4.75	5.1	5.65	5.65
24 "	4.45	3.85	4.4	4.25	5.2
8 days	3.7	3.6	3.35	3.8	4.6
30 "	3.5	2.8	3.4	3.5	3.4

ANALYSIS

Time in days	1	8	30	1	8	30	1	8	30	1	8	30	1	8	30
H2O %	8.25	7.8	7.6	10.1	10.3	9.75	10.8	10.65	9.7	11.75	10.6	10.55	13.6	13.35	12.85
P205 total	30.7	30.33	31.02	29.51	30.06	30.15	29.85	29.9	29.93	30.15	29.88	29.96	28.79	28.79	28.96
" available	29.7	30.06	30.06	28.88	29.30	29.60	28.56	28.84	28.93	28.7	28.88	29.24	27.59	27.41	28.24
" water sol.	28.95	28.88	29.24	28.24	28.96	28.75	28.19	28.14	28.42	28.24	28.33	28.55	27.06	27.06	27.42
" free	4.45	3.70	3.50	3.85	3.60	2.8	4.4	3.35	3.4	4.25	3.8	3.5	5.2	4.6	3.4
P2o5avail/total %	96.7	99.1	96.9	97.8	97.4	98.1	95.7	97.0	97.0	95.2	96.6	98.0	95.85	95.20	97.5
Attack rate %	93.8	98.3	94.2	96.0	95.3	96.45	91.9	93.35	93.8	91.0	93.7	95.5	92.1	91.1	95.3
Ion ratio(H)(PO4)	2.055	2.065	2.024	2.06	2.05	2.03	2.04	2.03	2.03	2.03	2.04	2.04	2.08	2.06	2.04

PHYSICAL CONDITIONS

Maximum temp. °C.	106	103	103	105	102
reached after:mins:	10	5	3	3	1
Duration until:-					
Set	2 min.	1 min.	1 min.	1.25 min	1 min
Hardening	3.5 "	2 "	2 "	1.75 "	2 "
Dedanning poss.:	20 "	10 "	10 "	15 "	15 "
Condition after					
1 hour 45 min	Very hard	Very hard	Hard	Fairly hard	Fairly moist
Time in hours	2 : 6 : 24	2 : 6 : 24	2 : 6 : 24	2 : 6 : 24	2 : 6 : 24
Sticking power %	2	3	5	6.5	20
Subsequent caking	4.7 : 3.55 : 2.55	3.55 : 2.75 : 2.9	3.4 : 2.6 : 2.5	3.8 : 2.5 : 2.4	3.4 : 2.65 : 2.65

TABLE 4.

MANUFACTURE OF SINGLE AND TRIPLE SUPER FROM MOROCCO ROCK

Type of Super	Single	3	Triple	4
Trial No.	1	3		4
Phosphate No.	VB	VA		VC
% through screen				
No. 200.	58	3 (unground)		75
Total weight Acid				
as % of rock	90.4	154		172.5
H ₂ SO ₄ as % of rock	61.5	0		0
P ₂ O ₅ " " " "	0	83.2		87
Acidity H ₂ SO ₄ equiv:	61.5	57.5		60.0
H ₂ O % of acid	32	18		23.2
Temperature °C	20	22		18
<u>Chemical reaction</u>				
Free P ₂ O ₅ after				
10 minutes	12.35	29.4		12.5
30 "	8.63	18.05		9.7
1 hour	8.13	11.55		7.85
2 hours	6.84	9.68		8.0
6 "	5.42	9.04		6.3
24 "	4.05	8.92		5.1
7 days	3.15	5.7		4.75
30 "	2.5	3.3		3.55

Analysis

Time (days)	1	7	30	1	7	30	1	7	30
H ₂ O %	11.2	10.8	10.3	8.9	8.15	6.45	11.3	9.7	8.5
P ₂ O ₅ total %	19.11	19.0	19.1	47.47	47.25	47.98	45.85	45.45	45.65
available %	18.05	18.45	18.65	43.37	44.9	46.7	44.25	44.55	45.2
water.sol. %	17.7	18.05	18.5	42.7	43.9	45.08	43.15	43.5	43.45
free %	4.05	3.15	2.5	8.9	5.7	3.3	5.1	4.75	3.55
P ₂ O ₅ avail/total %	94.2	97.1	97.7	91.4	95.0	97.6	96.5	98.0	99.0
Attack rate %	"	"	"	70.1	82.7	91.6	87.4	92.8	96.5
Ion ratio(H)(PO ₄)	2.08	2.08	2.08	2.0	2.0	1.98	2.02	2.04	2.02

Physical conditions:

Temp. max °C	104	106	83
reached after : min:	5	60	60
duration until:-			
set	1 min.	20 min.	45 sec.
hardening	3 "	45 "	1 min.
dedenning)			
possible)	8 "	60 "	4 "
Condition after			
1 hour 45 minutes	fairly hard	fairly hard	very hard
Time in hours	2 : 6 : 24	2 : 6 : 8days	2 : 6 : 24
Sticking power)			
% sticking	20 : 10 : 7	10 : 13.5 : 0.5	8 : 3 : 1
Subsequent caking	3.3 : 3.0 : 2.6	7.1 : 7.0 : 3.2	5.35 : 5.5

TABLE 6 (part 2)

MANUFACTURE OF SINGLE, ENRICHED & TRIPLE SUPER FROM FLORIDA ROCK

Trial No.	:	17	:	18	:	19
Rock No.	:	XI B	:	XI B	:	XI B
%through screen 200:		70	:	70	:	70
<u>ACID</u>	:		:		:	
Total weight as %	:		:		:	
of rock	:	118.7	:	107.2	:	116.5
H2SO4 as % of rock	:	47.5	:	47.5	:	41.0
P2O5 " " " "	:	20.75	:	18.0	:	29.0
% replacement H2SO4:		23.2	:	20.9	:	32.8
H2O % of acid	:	32.3	:	29.1	:	25.5
Temperature °C	:	100	:	92	:	78
Modity H2SO4 equiv:		61.8	:	60	:	61
<u>CHEMICAL REACTION</u>	:		:		:	
Free P2O5 after	:		:		:	
10 minutes	:	20.0	:	16.65	:	21.3
30 "	:	16.0	:	13.25	:	19.5
1 hour	:	15.05	:	12.2	:	16.0
2 hours	:	12.35	:	10.65	:	11.95
6 hours	:	10.0	:	9.0	:	11.05
24 "	:	7.1	:	5.7	:	8.45
8 days	:	4.45	:	3.9	:	4.35
30 "	:	3.30	:	2.85	:	3.7
<u>ANALYSIS</u>						
Time (days)	:	1 : 8 : 30	:	1 : 8 : 30	:	1 : 8 : 30
H2O	%:	13.25:12.25:11.8	:	11.5 : 10.2 : 9.3	:	10.25: 9.2 : 8.5
P2O5 total	:	26.88:27.02:26.97	:	26.78:26.97:27.15	:	31.1 : 30.7 : 31.75
" available	:	25.09:26.2	:	26.42:24.77:25.77	:	26.19:28.32:29.6
" Water sol.	:	24.05:25.3	:	24.86:23.59:24.32	:	24.36:27.6 : 28.2
" free	:	7.1 : 4.45: 3.3	:	5.7 : 3.9 : 2.85	:	8.45: 4.35: 3.7
P2O5avail/total %	:	93.4 : 96.9:97.95	:	92.5 : 95.5 : 96.45	:	91.05:96.4 : 97.4
Attack rate	:	89.2 : 95.0:96.7	:	88.5 : 93.8 : 94.55	:	82.4 : 93.3 : 95.3
Ion ratio (H)(PO4)	:	2.09: 2.07: 2.02	:	2.02: 2.0 : 1.96	:	2.07: 2.02: 2.02
<u>PHYSICAL CONDITIONS:</u>	:		:		:	
Maximum temp. °C	:	106	:	111	:	100
Reached after mins.	:	15	:	5	:	30
Duration until	:		:		:	
Set	:	9 min.	:	4 min	:	22 min
Hardening	:	18 "	:	6.5 "	:	29 "
Debenning poss.	:	60 "	:	45 "	:	90 "
Time in hours	:	2 : 6 : 24	:	2 : 6 : 24	:	2 : 6 : 24
Sticking power as	:		:		:	
% sticking	:	100 : 33.5 : 17.5	:	58 : 39 : 12.5	:	47.5 : 27.5 : 11.0
Subsequent oaking	:	4.5 : 3.1 : 2.45	:	6.4 : 2.7 : 2.1	:	10 : 7.1 : 5.0

TABLE 6 (Part 3).

MANUFACTURE OF SINGLE, ENRICHED & TRIPLE SUPER FROM FLORIDA ROCK.

Trial No.	:	20	:	21
Rock No.	:	XI B	:	VIII
% through screen 200	:	56	:	75
<u>ACID</u>	:		:	
Total weight % rock	:	170.6	:	169.2
H ₂ SO ₄ as % of rock	:	0	:	0
P ₂ O ₅ " " " "	:	86	:	87
% replacement H ₂ SO ₄	:	100	:	100
H ₂ O % of acid	:	20.4	:	19
Temperature °C	:	50	:	20
Acidity H ₂ SO ₄ equiv	:	59.3	:	60
<u>CHEMICAL REACTION</u>	:		:	
Free P ₂ O ₅ after	:		:	
10 minutes	:	17.4	:	14.85
30 " "	:	13.8	:	11.65
1 hour	:	14.15	:	10.8
2 hours	:	13.25	:	9.45
6 " "	:	11.85	:	8.75
24 " "	:	8.5	:	5.8
8 days	:	6.6	:	4.35
30 " "	:	4.2	:	3.85
<u>ANALYSIS</u>	:		:	
Time (days)	:	1 : 8 : 30	:	1 : 8 : 30
H ₂ O %	:	11.55:10.9 : 11.4	:	10.3 : 9.6 : 8.95
P ₂ O ₅ total	:	45.95:45.5 : 45.1	:	47.15:46.85:46.5
" available	:	42.5 : 43.15:44.15	:	44.4 : 44.8 : 45.5
" water soluble	:	40.8 : 41.65:42.1	:	43.3 : 43.15:43.15
" free	:	8.5 : 6.6 : 4.2	:	5.8 : 4.35: 3.85
P ₂ O ₅ avail/total %	:	92.55:94.9 : 97.9	:	94.2 : 95.6 : 97.85
Attack rate	:	73.4 : 81.7 : 92.6	:	79.4 : 84.4 : 92.3
Ion ratio (H)(P ₀₄)	:	1.99: 2.00: 2.00	:	1.98: 1.97: 1.99
<u>PHYSICAL CONDITIONS</u>	:		:	
Maximum temp °C	:	93	:	84
reached after : min	:	60	:	60
Duration until	:		:	
Set	:	2 min.	:	1.5 min
Hardening	:	3 " "	:	2.5 " "
Deddening poss.	:	30 " "	:	10 " "
Time in hours	:	2 : 6 : 24	:	2 : 6 : 24
Sticking power as	:		:	
% sticking	:	98 : 14	:	1.5 :
Subsequent caking	:	4.05 : 4.3 : 3.55	:	3.4 : 4.55: 3.85

APPENDIX

Chemical tests and adjustments in the proportion of acid to rock in the manufacture of single, enriched or concentrated superphosphate.

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1) INTRODUCTION

It is known that when a superphosphate comes off the manufacturing plant it is very far from having reached a stable composition. The reactions of the solubilisation of the P₂O₅ continue for days and sometimes weeks, although slowing up all the time. In spite of this, the complete analysis of the product is usually made the day following manufacture. The results obtained represent a transitional phase and in order to be able to draw practical conclusions from them we have to interpret them and as far as possible predict the future reaction of the superphosphate.

One essential piece of information which the analysis must supply is whether the acid/rock ratio is correct or whether it requires adjustment, and if so, how much. In this connection, the criticism is justified that the time interval between manufacture and the availability of the results of the analysis is excessive and there is a risk that quantities of superphosphate will be produced which are either too acid or under-reacted. Thus, a more rapid check method would be desirable.

The manufacturer has two main requirements:

- to be able to interpret the results of the daily analysis
- to find a rapid method for checking the acid/rock ratio

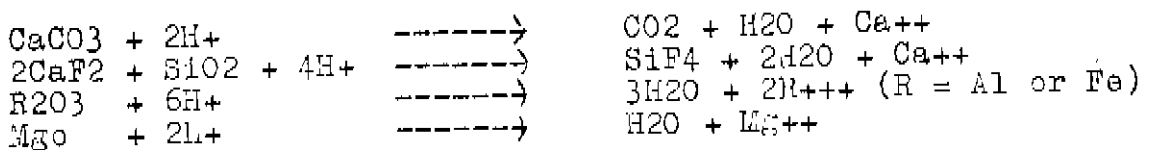
This is the object of the present study.

2) NO. OF H+ IONS PRESENT IN THE SUPERPHOSPHATE

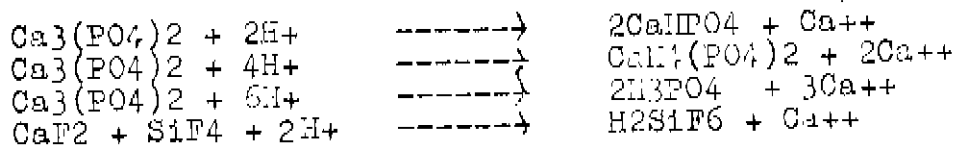
The manufacture of single, triple or enriched superphosphate consists of reacting phosphate rock with either sulphuric or phosphoric acid, or with a mixture of the two. In each case, the rock is exposed to the action of H⁺ ions and this is the basis of all the reactions.

Let us see what happens to these H⁺ ions; some are neutralized

and thus put out of the reaction by attacking the impurities:-



Others, and they are much more numerous, are present in the product in the form of more or less acid calcium phosphates, phosphoric acid and fluosilicic acid.



In all the above reactions, the H⁺ ions are preserved, although their acidity may be significantly reduced.

Let us make use of the results of the analysis to calculate the remaining quantity of hydrogen ions by means of the following equation:-

$$R = \frac{\text{Number of H}^+ \text{ ions}}{\text{total no. of PO}_4 \text{ ions}} = \text{ion ratio } \frac{(\text{H})}{(\text{PO}_4)}$$

We shall use the following symbols:

- i = P₂O₅ in the superphosphate as Ca₃P₂O₈
- d = " " " " " CaHPO₄
- m = " " " " " CaH₄(PO₄)₂
- lI = " " " " " H₃PO₄
- t = % total P₂O₅ = i+d+m+lI
- a = % water & citrate sol. (available)P₂O₅ = d+m+lI
- s = % water soluble P₂O₅ = m+lI
- l2 = acidity by methyl orange of H₂SiF₆ (& possibly H₂SO₄) conventionally expressed as % P₂O₅ at the rate of 1P₂O₅ for 2H (or 1PO₄ for 1H).
- l = lI + l2 = total acidity by methyl orange, conventionally expressed as % P₂O₅ at the rate of 1P₂O₅ for 2H

Thus, the quantity of superphosphate which contains one gram ion of total PO₄ will contain the fractions $\frac{d}{t}$, $\frac{m}{t}$, $\frac{lI}{t}$ of a gram ion of PO₄ in the form of CaHPO₄, CaH₄(PO₄)₂ and H₃PO₄ and the fraction $\frac{l2}{t}$ of a gram ion of H in the form of acids other than H₃PO₄. Consequently:

$$R = \frac{(\text{H})}{(\text{PO}_4)} = \frac{d + 2m + 3lI + l2}{t} = \frac{(d + m + lI) + (m + lI) + (lI + l2)}{t}$$

Expressed in another way :-

$$R = \frac{(\text{H})}{(\text{PO}_4)} = \frac{\text{available P}_2\text{O}_5 + \text{water-soluble P}_2\text{O}_5 + \text{free P}_2\text{O}_5}{\text{total P}_2\text{O}_5}$$

This is the very simple value, obtained from the results of the current analysis, of the ion ratio $\frac{(\text{H})}{(\text{PO}_4)}$ of a superphosphate (where 'free P₂O₅'

means, as usual, total acidity to methyl orange of the aqueous solution of superphosphate.

3) CURING OF SUPERPHOSPHATES

Usually the attack of the impurities of the rock finishes fairly rapidly, well before the reactions of the solubilisation of P₂O₅ are finished. When this is the case, the ion ratio $\frac{(\text{H})}{(\text{PO}_4)}$ has a constant

value in respect of the secondary reaction:

$$R = \frac{(\text{H})}{(\text{PO}_4)} = \frac{a + s + l}{t} = \text{constant}$$

This constant will equal 2 if the acid added for the reaction of the rock exactly corresponds to that part of the impurities which will be

attacked and to the formation of monocalcium phosphate, where $\frac{(H)}{(PO_4)} = 2$

In practice, in order to improve the solubilisation of the P2O5, a slight excess of acidity is allowed. We would express this:

$$R \frac{(H)}{(PO_4)} = \frac{a + s + 1}{t} = 2 + E$$

E being a constant which is usually positive but may be zero or negative if not enough acid is applied.

This relationship may also be expressed:

$$a + s + 1 - 2t = Et = l_0$$

l_0 is a constant related to a given value of total P2O5. It is the acidity which would remain in the superphosphate if the attack continued to the stage of complete solubilisation of the P2O5 as monocalcium phosphate and phosphoric acid ($a = s = t$) or which would be incomplete if the value of l_0 were negative.

This is why we shall call l_0 maximum acidity or excess acidity. When we introduce insoluble P2O5 and dicalcium P2O5, the fore-going relationship can be expressed:

$$t - i + t - i - d + 1 - 2t = Et$$

or again:

$$1 - 2i = Et + d = l_0 + d = l'_0$$

For a given value of t and d , which in practice hardly vary at all, l'_0 is a constant which also represents a maximum acidity, in this case corresponding to the total solubilisation of the P2O5 and the formation of the quantity d of P2O5 in the form of dicalcium phosphate.

The reaction rule deduced above, $1 - 2i = l'_0$, which we will call the simplified reaction rule, may be derived immediately from the chemical reaction:



according to which we require 2 units of free P2O5 to solubilise one unit of insoluble tricalcium P2O5.

Notice that any continuation of the attack of the impurities in the rock, with consequent neutralization of H ions, would involve a reduction of the quantities E, l_0 and l'_0 . But the formulae given above still have a practical value, even so, because it will quickly be learned from experience what this reduction implies for the secondary reaction, or curing.

4) ACIDULATION STANDARDS

It is clear that the amount of excess acidity introduced into the reaction is one of the important factors affecting the final content of solubilised P2O5 obtained after the curing of the superphosphate. The importance to be attributed to this excess may be conditioned by economic considerations, such as the relative price of rock and acid, but there are overriding technical considerations (physical condition of the product). Other things being equal, if we consider superphosphates of different concentration obtained from the same rock by the use of acids with varying phosphoric acid content, it is logical to assume that the maximum acidity l_0 (excess acidity) should be proportionate, not to the total P2O5 content t , but to t_p , the P2O5 derived from the rock alone, omitting the P2O5 derived from the phosphoric acid.

In other words, we should say:-

$$l_0 = k t_p$$

k being a constant, hence:-

$$a + s + l - 2t = k tp$$

$$R = \frac{(H)}{(PO_4)} = \frac{a + s + l}{t} = 2 + \frac{k tp}{t}$$

$$l - 2t = k tp + d$$

We shall be fairly close to the standards adopted by most manufacturers if we take $k = 0.08$.

For example, for a single superphosphate, we get the following standard acidulation ($tp = t = \text{approx. } 19\%$)

$$\frac{(H)}{(PO_4)} = \frac{\text{avail. P2O5} + \text{w.sol. P2O5} + \text{free P2O5}}{\text{total P2O5}} = 2.08$$

or again:

$$\begin{aligned} \text{maximum free P2O5\%} &= \text{available P2O5\%} + \text{w.sol. P2O5\%} + \text{free P2O5} \\ &- 2 \text{ total P2O5\%} = 1.5 \end{aligned}$$

If we assume that the amount of dicalcium P2O5 is about 0.3 (as it is with Morocco rock) the simplified reaction rule becomes:

$$\text{free P2O5\%} - 2 \text{ insoluble P2O5\%} = l_0 + d = 1.5 + 0.3 = 1.8$$

In the case of triple superphosphate containing 46% total P2O5, about 13% being derived from the rock, the standard acidulation becomes:

$$\frac{(H)}{(PO_4)} = \frac{a + s + l}{t} = 2 + 0.08 \times \frac{13}{46} = 2.025$$

where maximum free P2O5 $l_0 = a + s + l - 2t = 1$

Then, assuming $d = 1$, the simplified reaction rule becomes

$$l - 2t = 1 + 1 = 2$$

With an enriched superphosphate, the values will be intermediate, depending upon the ratio H_3PO_4/H_2SO_4 .

The concept of maximum acidity l_0 is particularly useful. In fact, since we are dealing with excess acidity, the deviations from the accepted standard of l_0 have a value which is not relative but absolute. Under these conditions, there is very little difference between the figure of 1.5 accepted for single super and 1 accepted for triple, so that it is possible to deduce a rule that for any superphosphate the maximum acidity l_0 must lie between 1 and 1.5.

The same will apply to the maximum acidity l_0 when the simplified reaction rule is applied: it should be maintained at about 2.

5) QUICK CHECK OF MAXIMUM ACIDITY

It would be possible to determine directly from freshly manufactured superphosphate the maximum acidity l_0 if some device could be employed to complete the secondary reaction of the tricalcium phosphate. This can be done by boiling the product with a known sufficient quantity of dilute sulphuric acid. The resultant acidity is measured by methyl orange and subtracting the added acidity will give the maximum acidity. Following is the method of working:

The sample of superphosphate from which the acidity is determined should pass a no. 14 screen (mesh opening 1.4mm). Weigh 5 g. Place the sample in a small glass mortar. Mix to a paste with 10 ml. distilled water. Decant, pouring the clear liquid into a 300ml. conical flask (Erlenmeyer). Grind the product and pour it all into the conical flask with the help of a squirt. Add a carefully measured 10 ml. of a 2N solution of sulphuric acid (98 g/l sulphuric acid). The volume should be about 100 ml. Boil for 15 mins. The volume of the solution is reduced to 50 ml. which is sufficiently dilute to avoid attacking the fluorine compounds.

Cool and pour into a 125 ml. measuring cylinder. Filter on a dry filter and draw off 50 ml. of the solution in a pipette. Titrate the remaining acidity with a standard caustic solution (N/1 = 40 g/l NaOH) in the presence of a few drops of methyl orange. Stop adding the caustic at the first drop which changes the colour to yellow.

$$\text{Maximum acidity in \% P2O5} = (N^{\text{ml.}} - 8) \times 3.5$$

Note. In the case of concentrated superphosphate (triple) twice the amount of 2N sulphuric acid must be used, i.e. 20 ml. The final formula then becomes: Maximum free P2O5% = (N - 16) x 3.5

If the value of lo found by this method is negative, then the same amount of phosphoric acid is needed to bring the value $\frac{(H)}{(PO_4)}$ up to 2. Normally the figure found will be between 1 and 2.

6) CALCULATING THE ACID/ROCK RATIO

One can undertake to determine the quantity of H+ ions needed to attack a given amount of phosphate rock, working from the analysis of the rock, and particularly its content of tricalcium phosphate, calcium carbonate, calcium fluoride and metal oxides. This calculation must take into account that the quantity of H+ ions needed to solubilise the tri-calcium phosphate should be in excess of the stoichiometric amount for the formation of monocalcium phosphate, this excess arising from the accepted standard acidulation. Let us try to find the value representing this excess.

Representing by the use of brackets the no. of ions or molecules, we have seen that superphosphate contains:

$$\frac{\text{residual (H)}}{\text{total (PO}_4\text{)}} = 2 + k \frac{\text{(PO}_4\text{) from rock}}{\text{total (PO}_4\text{)}}$$

hence:

$$\begin{aligned} \text{residual(H)} &= 2 \text{ total (PO}_4\text{) + k (PO}_4\text{) from rock,} \\ &= 2 \text{ (PO}_4\text{) from acid + (2+k) (PO}_4\text{) from rock.} \end{aligned}$$

Consequently:

$$\text{residual (H) - 2(PO}_4\text{) from acid} = (2 + k) \text{ (PO}_4\text{) from rock}$$

and since:

$$\text{total (H) from acid} = (n) \text{ neutralised by impurities + residual (H)}$$

we must have:

$$\text{total (H) from acid} - 2(\text{PO}_4\text{) from acid} = \text{neutralised (H) + (2 + k)(PO}_4\text{) from rock.}$$

The first item in this equation may also be written:

$$(H) \text{ from H}_2\text{SO}_4 + 1/3 (H) \text{ from H}_3\text{PO}_4 \text{ or } 2 \text{ (H}_2\text{SO}_4\text{) + (H}_3\text{PO}_4\text{)}$$

The phosphoric acid counts as only one for the purposes of acidity when calculating the H+ ions to react with the rock; the reason for this is obviously because in the course of the reaction the phosphoric acid is converted to monocalcium phosphate, a diacid salt which requires 2H for each PO4.

In other words, where there is a mixture of sulphuric acid and phosphoric acid, only the acidity measured by methyl orange plays an active part in the phosphate rock attack.

The advantage of the foregoing calculation is to link the consumption of active H+ ions to the accepted standard of acidulation: for 1 (PO4) from rock, we require (2 + k) active H+ ions, or a relative excess of k/2 on the stoichiometric quantity required to form CaH4(PO4)2.

Numerical application

Assume a Morocco phosphate with the following analysis:

Ca ₃ P ₂ O ₈	72
CaF ₂	8.4
CaCO ₃	8.5
SiO ₂	2
MgO	0.6
Al ₂ O ₃	0.5
Fe ₂ O ₃	0.3

Let us take $k = 0.08$ and allow for only 40% of the calcium fluoride being converted into SiF₄ (given off as gas or remaining in the super as H₂SiF₆) and for half of the metal oxides being neutralised. For 100 units of rock, the amount of acid H⁺ ions measured by methyl orange corresponding to the different reactions can be computed as follows:

Attack of:

Ca ₃ (PO ₄) ₂	$\frac{72}{310}$	x	2	x	2.08	=	0.966
CaCO ₃	$\frac{8.5}{100}$	x	2			=	0.17
CaF ₂	$\frac{8.4}{78}$	x	1	x	0.4	=	0.086
MgO	$\frac{0.6}{40.3}$	x	2	x	0.5	=	0.015
Al ₂ O ₃	$\frac{0.5}{102}$	x	6	x	0.5	=	0.015
Fe ₂ O ₃	$\frac{0.3}{160}$	x	5	x	0.5	=	0.005

1.257 H⁺ ions or
g H% of rock

For Single super this figure amounts to:

$$1.257 \times 49 = 61.6 \text{ H}_2\text{SO}_4 \text{ per 100 units of rock}$$

For triple super manufactured with pure phosphoric acid free from free sulphuric acid, the figure would be:

$$1.257 \times 98 = 123 \text{ H}_3\text{PO}_4 \text{ per 100 units of rock}$$

or:-

$$1.257 \times 71 = 89.2 \text{ P}_2\text{O}_5 \text{ from acid per 100 units of rock.}$$

In practice, in the case of triple, the attack of the impurities is not complete and the H⁺ ion requirement may be slightly reduced. Moreover, industrial wet-process phosphoric acid often contains sulphuric acid in excess of the cations present and this must be allowed for in the calculations.

The average consumption would be 86-87 P₂O₅ from acid per 100 units rock.

Note that since $\text{H}_3\text{PO}_4 = \text{H}_2\text{SO}_4 = 98$, in terms of acid attack of rock, we must substitute 2 units of H₃PO₄ for one of H₂SO₄.

7) CORRECTIONS TO BE MADE TO THE ACID/ROCK RATIO IN THE LIGHT OF THE RESULTS OF THE SUPERPHOSPHATE ANALYSIS OR THE QUICK CHECK

The problem is as follows: let us suppose that the analysis of the superphosphate (or the quick check) shows that the relation $R = \frac{(H)}{(P_2O_4)}$ or the maximum acidity varies by too much or too little from the amount ΔR or ΔQ of the value corresponding to the accepted acidulation standard. (that is the correction ΔQ to be applied to the acid input Q used (which we will suppose to have a constant content of active H⁺ ions)?)

According to the formulae established above, we shall have for a Morocco type rocks:

$$\Delta Q = \frac{72}{310} \times 2\Delta k = 0.465 \Delta k$$

$$\frac{\Delta Q}{Q} = \frac{0.465 \Delta k}{1.257} = 0.37 \Delta k$$

now:

$$R = 2 + k \frac{t_p}{t} \quad \Delta R = \frac{t_p}{t} \Delta k \quad \Delta k = \frac{t}{t_p} \Delta R$$

$$l_0 = k t_p \quad l_0 = t \Delta k \quad \Delta k = \frac{\Delta l_0}{t_p}$$

consequently:

$$\frac{\Delta Q}{Q} = 0.37 \frac{t}{t_p} \Delta R = \frac{0.37}{t_p} \Delta l_0$$

a) In the case of single super $t = t_p = 19$

$$\frac{\Delta Q}{Q} = 0.37 \Delta R = \frac{0.37 \Delta l_0}{19} = 0.02 \Delta l_0$$

The percentage correction (relative error) to be applied to the sulphuric acid input thus equals 37 times the absolute deviation in relation to the standard maximum acidity l_0 .

b) In the case of triple super $t = 46\% \quad t_p = 13\%$

$$\frac{\Delta Q}{Q} = 0.37 \times \frac{46}{13} \Delta R = 1.3 \Delta R = \frac{0.37 \Delta l_0}{13} = 0.028 \Delta l_0$$

The percentage correction (relative error) to be applied to the acid input equals 130 times the absolute deviation in relation to the standard $R = \frac{(H)}{(PO_4)}$ or 2.8 times the absolute deviation in relation to the standard maximum acidity l_0 .

8) RAPID EXPERIMENTAL DETERMINATION OF THE ACID/ROCK RATIO

We have seen above what must be done when a calculation is attempted from the complete analysis of the rock of the number of active H+ ions needed to react with it.

In practice, this calculation is academic, because it is impossible to predict the degree of attack on the impurities, particularly the calcium fluoride and the metal oxides.

The following experimental method is much easier and safer: it consists of reacting in the laboratory, simulating the normal conditions of manufacture of superphosphate, the rock plus an arbitrary quantity of acid, in the region of the standard acid consumption, for instance, 61 H₂SO₄ per 100 units of rock. After several hours of hot curing, the product is analysed, or perhaps only a quick check of maximum acidity is made. On the basis of the results obtained, a calculation is made of the correction to be made to the acid/rock ratio by applying the arguments put forward in the preceding section (7).

This method does not even require that the rock should previously be analysed and can simply be reduced to the measurement of the maximum acidity; this gives the required result very quickly.

9) CONCLUSION

The important points to be noted from the foregoing are:

a) the expression of the ion ratio $\frac{(H)}{(PO_4)}$ in the superphosphate

$$R = \frac{(H)}{(PO_4)} = \frac{\text{avail. P2O5} + \text{w.sol. P2O5} + \text{free P2O5}}{\text{total P2O5}}$$

This ratio comes into many problems in connection with superphosphate particularly ammoniation. It is an important property of the product because it remains constant once the reaction of the impurities is complete.

b) the meaning of the maximum acidity or maximum free P2O5 l_0 : this is the acidity expressed as % P2O5 which would be present in the superphosphate after complete solubilisation of the P2O5 in the form of monocalcium phosphate and free phosphoric acid.

$$l_0 = \text{maximum free P2O5} = \frac{\text{avail. P2O5} + \text{w.sol. P2O5} + \text{free P2O5}}{\text{total P2O5}} - 2$$

Once the reaction of the impurities is complete, this maximum acidity remains constant and should fall between 1 and 2. It may be approximately determined by a quick check method (see section (5)).

c) the simplified reaction rule:

$$\text{free P2O5} - 2 \text{ insoluble P2O5} = l'_0$$

where l'_0 is a maximum acidity slightly higher than l_0 and which in a well managed superphosphate should be about 2.

d) the correction to be made to the acid/rock ratio in the reaction based upon the deviation found in the product for the value of the ratio $\frac{(H)}{(PO_4)}$ or the maximum acidity l_0 as against the value accepted as standard. (See section (7)).

DIAGRAMME II
SUPERPHOSPHATES ENRICHIS SUPPOSES TOTALEMENT DESHYDRATES
QUANTITES A METTRE EN OEUVRE POUR 100 PARTIES DE PRODUIT

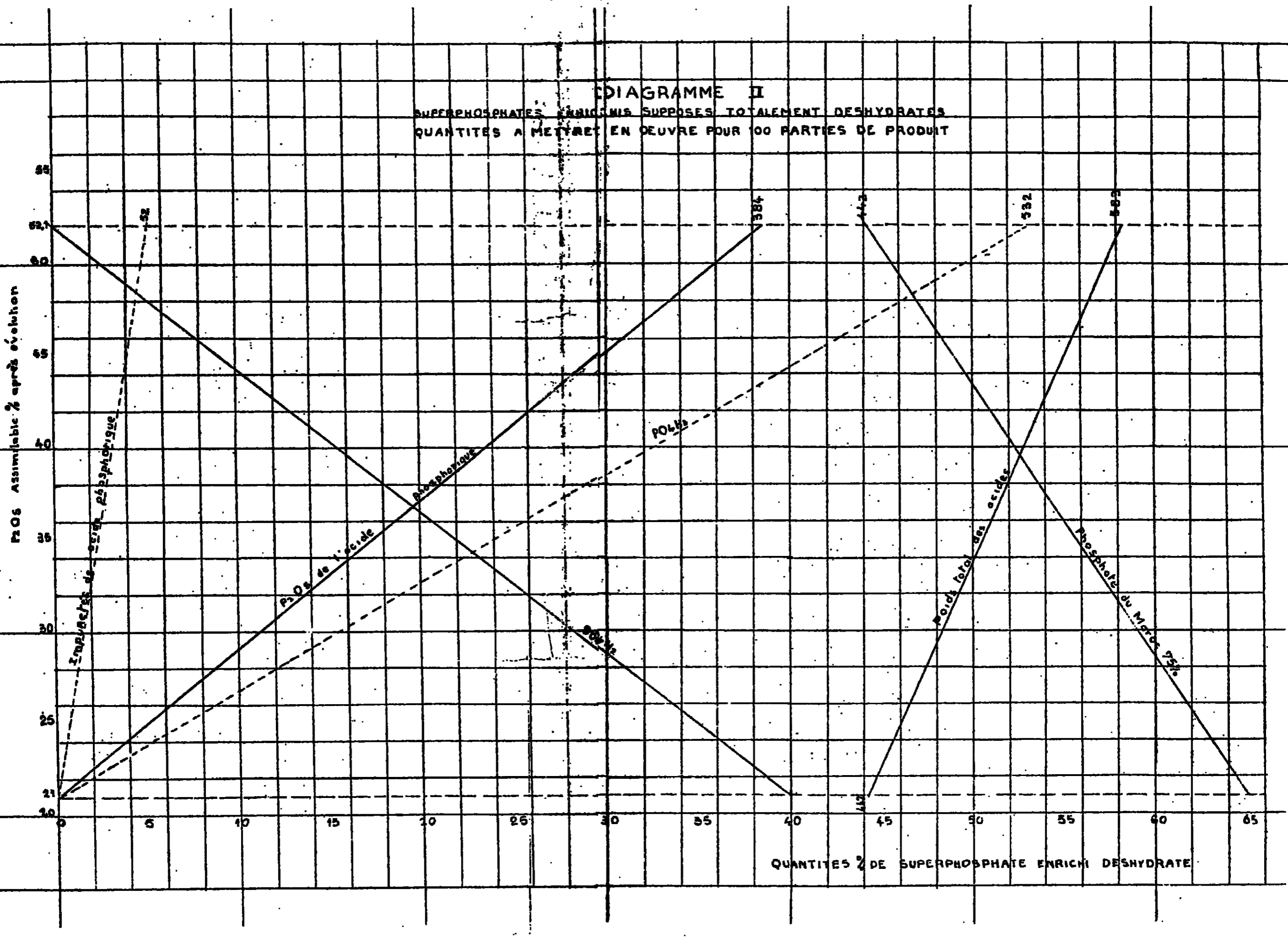
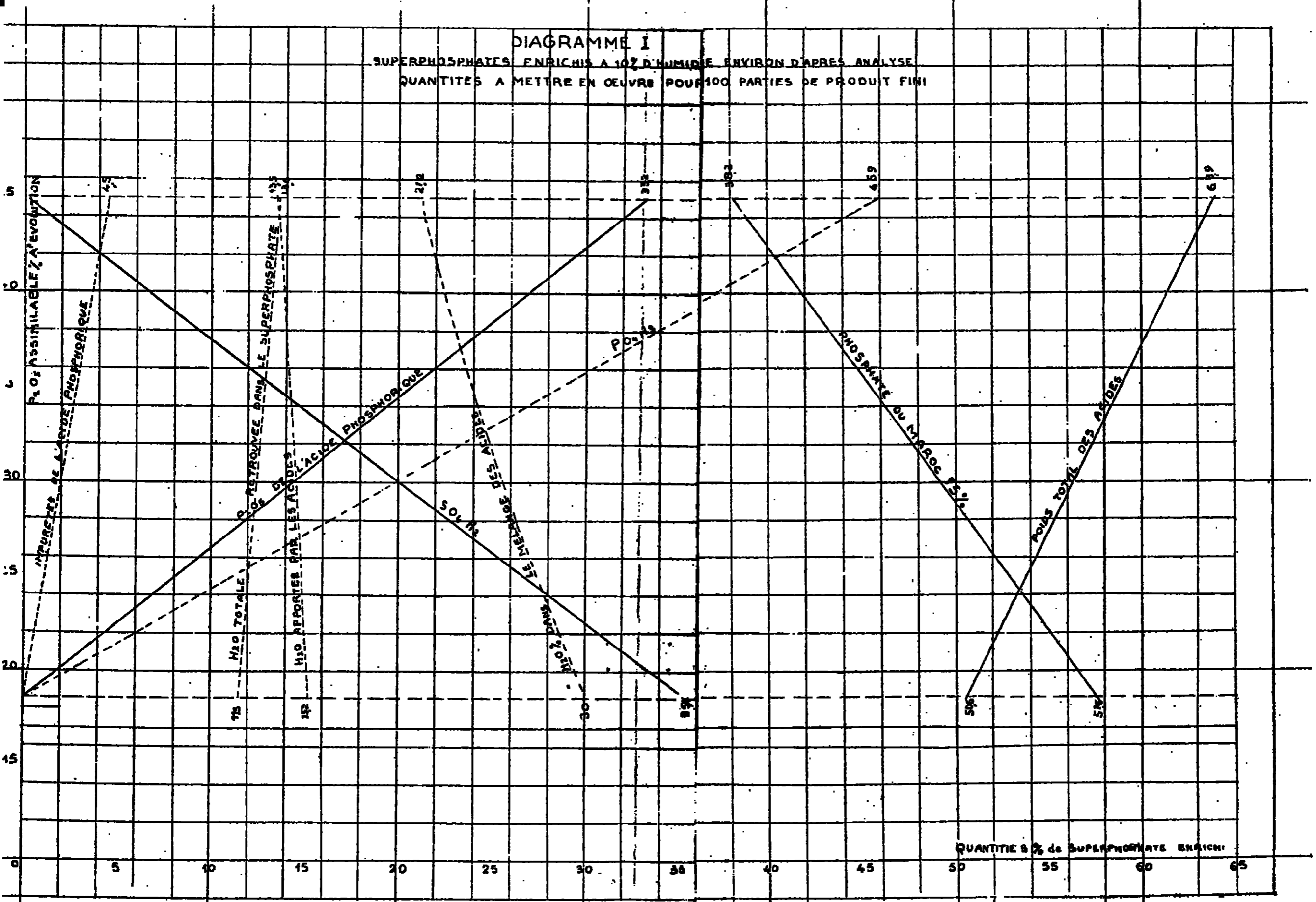


DIAGRAMME I
 SUPERPHOSPHATES ENRICHIS A 10% D'HUMIDITE ENVIRON D'APRES ANALYSE
 QUANTITES A METTRE EN OEUVRE POUR 100 PARTIES DE PRODUIT FINI



ET DE LA TENSUR EN EAUX SALES DU SUPERPHOSPHATE ENCIEN

