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Cie de Saint-Gobain.

MANUFACTURE OF PHOSPHORIC ACID BY THE WET METHOD

Influence of the origin and characteristics of the phosphate used.

(M. BIGOT)

I - GENERAL.

The manufacture of phosphoric acid by the procedure known as the Wet Method requires two principal operations only:

Treatment of the natural phosphate of lime with sulphuric acid
(Attack)

Separation of the solid formed, or not solubilised, from the liquid phase (Filtration).

Under this apparent simplicity, phosphoric manufacture is, in fact, quite complex; it assumes the achievement of perfectly definite equilibria both in order to obtain the maximum possible solubilisation as well as the formation of a "slurry" of which the constituents both solid and liquid shall be suitable to promote good filtration.

Among the causes of the difficulties encountered, the complexity of the constitution of the natural phosphates of lime is the most important.

These minerals contain, besides tricalcium phosphate, combined to a greater or lesser extent in the form of fluorapatite, the following: Fluorides, often accompanied though in lesser amount by other halogen compounds (chlorides and iodides in particular) capable of substituting fluorine in most of its combinations; Carbonates, Sulphates, Silicates (Silica being also found in the form of quartz) cationic compounds: chalk, magnesia, soda, potash, manganese, iron, alumina, chromium, vanadium etc..., most of the metals may be detected though sometimes present only in small amount; substantial amounts of organic matter are also encountered, evidence of the origin of the deposits, as well as various products which have served in the treatment of the phosphate at the mine.

All these elements participate to a certain extent in the reactions, passing into solution, precipitating by interaction, are found entrained in the gaseous phase or consist simply in modifications of the physico-chemical structure.

It may be assumed that these phenomena can influence to a considerable extent the processes of phosphoric manufacture and that they contribute to a large extent in the conditions obtained and the yields both of attack and of filtration.

For natural phosphates have a very variable physical structure and chemical composition, sometimes even within the same deposit or group of deposits, according to their origin.

When it becomes necessary to utilise a new type of phosphate in an existing installation or in a new one to be built, the following questions then arise:

Is this phosphate capable of being used as such in phosphoric manufacture?

To what treatment must it be submitted in order to render it useable or to improve the results?

What modifications must be made in the treatment conditions?

What will be the optimum quantitative and qualitative yields attainable with this phosphate in a given installation?

Or on the other hand:

What characteristics must one give the new manufacturer so that he can obtain the yields imposed when starting with this unknown phosphate?

What are the characteristics of the acid obtained when starting from this phosphate and under these operating conditions, and how suitable will it prove for the purpose intended?

We have sought to put to the test such methods as will permit a reply to these questions with a maximum of precision and reproducibility using samples of 50 to 100 kgs.

II - METHODS OF INVESTIGATION.

The investigation of a sample of phosphate may be divided into two sections: the one purely preparative, which we designate under the term "Conditioning the phosphate", and the second dealing with the utilisation directly of the phosphate for phosphoric manufacture, entitled "Phosphoric Investigation Tests".

A - CONDITIONING THE PHOSPHATE

The first part of these determinations concerns the physico-chemical characterisation of the phosphate as such, and as eventually treated if different treatments appear necessary, prior to a decisive test, according to the characteristics revealed, or after the preliminary trials. It comprises the following items:

- Identification of the Sample. Origin - geographical and geological.
Dates of exploitation and reception.
Quantity - Richness - Classification.
- Subsequent Treatment. Grinding: often indispensable or at least helpful. The degree of grinding necessary is determined by the shortened preparatory tests, to which we shall again refer.

Sometimes however tests of long duration are made on the same phosphate ground to different degrees of fineness in order to determine with the maximum precision the advantage or otherwise of thorough grinding on this type of phosphate.

Calcination: With certain qualities of phosphate this operation may be indispensable or simply advantageous. The conditions of calcination - temperature, duration, the proportion of organic matter that can be left on the fertiliser, are some of the factors to be determined. More often only tests continued for long duration permit the necessity for calcination and its operative conditions to be assessed with sufficient precision.

Other Treatments. Lixiviation with water or with the aid of organic solvents, the separation of certain elements by mechanical treatment or flotation, the reintroduction of various materials.... etc.....

Up to the present none of these treatments has proved necessary or capable of providing a paying improvement in phosphoric manufacture starting from natural phosphates of lime, the sole object of this paper.

- Physical Characteristics.

External Appearance: Homogeneity, Colour, Nature of the rock.....

Fineness: As such.- Percentage passing the following mesh size (m/m).
 Over 50, 50-25, 25-10, 10-5, 5-2, 2-1, 1.0 - 0.5, 0.5 - 0.1, under 0.1 m/m.

After grinding - percentage (cumulative passing the following sieves).....
 40 mesh (0.45 m/m), 60 mesh (0.3) - 80 (0.2), 100 (0.16) - 150 (0.11), 200 (0.08), 300 (0.05).

Density (apparent). Without settlement - dropped from hopper - constant conditions.
 With settlement. 200 taps of height 5-10 m/m.

Chemical Composition. Current determinations: P₂O₅, CO₂, F, SO₃, CaO, MgO, Fe₂O₃, Al₂O₃, H₂O, Loss of heating. These results are calculated on the dry material. In addition the uncombined oxygen in the form of calcium fluoride may be subtracted (F₂ + CaO ---> CaF₂ + O) and the proportion undetermined obtained. Complementary Determinations: Na₂O, K₂O, MnO, TiO₂, Cr₂O₃, V₂O₃,.....

B. Phosphoric Investigation Tests.

- Preliminary Test "S3" A, on a batch basis, made on a reduced quantity of phosphate (500 grams). Carried out fractionally, with sulphuric acid for two hours in a beaker also containing dilute phosphoric acid. The attack is carried out for only 4 hours total before filtration under vacuum on a Buchner. The rate of passing the acid and the proportion passing through the cake is reported as the percentage of the total acid (rate of draining); but the essential determination furnished by this test is the degree of attack.

Sensibly lower than rates of attack attained under industrial conditions, the values obtained in Test "S3" are not perfectly

comparable and show the advantage of accentuating the spread of differences for a given variable. This test is employed in particular to ascertain the necessity or the advantage of grinding the phosphate and the degree of same.

It may be noted further, that this batch test permits precise experimental determination of the quantity of solid formed per unit of P₂O₅ of phosphate under test, a figure employed subsequently under continuous conditions for the establishment of the rate of attack from the P₂O₅ insolubles found in the calcium sulphate cake.

- Continuous Test "S3" C. This test constitutes the essential tool of this investigation. It tends to reproduce with the closest approximation to industrial manufacturing conditions which have been investigated and is employed in the factories of the Société Saint-Gobain.

The separation of the solid and liquid phases is carried out following the same conditions of reproducibility by reference to the conditions of manufacture, a greater latitude can perhaps always be permitted in actual conditions as these do not present any consequence in the ultimate operations.

Separation is carried out on the semi-continuous off-take from the hot slurry by filtration under vacuo, the pressure being purposely limited to 200 m/m Hg to accentuate the variation of speed of filtration. The filter cloths used are those of the factory, the temperature of the slurry is 70°C; the washing is made with the theoretical quantity of water (based on sulphuric acid 78%) but without methodical washing phases, which limits the yield of wash liquor by reference to the manufacturing conditions, but enables a more precise comparison between the phosphates: uniformity of results and spread more marked.

The normal duration of the test is 30 hours, but it is sometimes prolonged when it is desired to follow the evolution very slowly. The consumption of phosphate is of the order of 15 Kgs per test, the sulphuric acid in proportion and strictly measured. The phosphoric acid re-cycled is that produced during the test, after several hours processing with an acid prepared in advance.

During the course of each test about twenty instantaneous checks are made on the rate of attack, the concentration and content of H₂SO₄ in the liquid phase, and about a dozen tests of the characteristics of filtration speed, balance of drainage and washing analyses: P₂O₅, H₂SO₄, F₂, on the acid produced.

From the mean of the results can be deduced with precision, among others the following data:

Attack of the phosphate by the sulphuric acid.

Degree of attack - Ratio of P₂O₅ % solubilised to total P₂O₅ of the phosphate treated.

H₂SO₄ used - Expressed as % of phosphate treated and % of P₂O₅ solubilised.

The global yield as P₂O₅ can also be reported.

Crystallinity - Mean length of crystals in microns.
Ratio of mean length / width.

Separation of liquid and solid phases.

Speed of filtration - expressed in cubic metres of acid filtered per hour per square metre filter surface

m³ / hr / m². Take here only the strong acid before bringing all the water into use. It can also be expressed as P₂O₅ filtered per hour per square metre...

Drainage Factor Proportion of the acid filtered as % of total acid submitted to filtration to the moment of breaking the vacuum.

Washing Factor Ratio as % of P₂O₅ extracted from the solid phase to P₂O₅ of the phosphate. The rate of washing has not been related as P₂O₅ solubilised so as to obtain directly the yield of attack + washings from the two data of the test.

Quantity of Acid produced.

Composition (brief)

AB° (Degrees Baumé at 15°C)

P₂O₅ % (Total)

H₂SO₄% (SO₄ in solution after 24 hours expressed as H₂SO₄)

Imp. (Index of impurity. Value obtained from the equation AB° - (P₂O₅ + H₂SO₄), and giving at constant or slightly variable Baumé and H₂SO₄ content an interesting indication of the amount of impurity contained in the acid formed.

Distribution of the Fluorine

Fluorine % of origin found in the calcium sulphate cake - acid formed - evolved (by difference)

III - APPLICATION TO THE INVESTIGATION OF PHOSPHATES.

A - Phosphates Investigated.

A large number of samples of phosphates, representing most of the important deposits presently exploited have been submitted to a systematic study, sometimes very thoroughly.

The source of these phosphates is as follows:

<u>Europe North:</u>	<u>Kola</u> 85%	} Apatite Crystalline Age of Formation: Primary (Precambrian) Very hard rock of volcanic origin.
<u>Africa North.</u>	<u>Morocco</u> (70-75-80%)	} Amorphous Apatite Age of Formation: Tertiary (Eocene) Relatively soft rock of animal origin.
	<u>Gafsa</u> 65%	ditto.
	<u>M'Dillah</u> 65%	ditto.
	<u>Kossier</u> 65%	ditto.
<u>Africa West.</u>	<u>Thies</u> 80%	ditto.
	<u>Togo</u> 80%	ditto.

<u>America N.W. U.S.A.</u>	Idaho 65-75%)	Apatite amorphous (or submicrocrystalline)
	Montana ")	Age of Formation: Tertiary (Eocene)
	Utah ")	Rock somewhat hard, of organic origin.
	Wyoming ")	
<u>America S.E. U.S.A.</u>	Pebble 68%-75%)	Apatite microcrystalline
	Florida)	Age of Formation: Tertiary (Pliocene)
	Tennessee)	Hard rock of animal origin
<u>America S. (Peru)</u>	Guano 40%) Phosphates of lime and alkaline) Recent Formation: animal origin.

- The distribution of the samples studied is as follows:

3	:	Phosphate Kola
9	:	Groups of North African phosphates
2	:	West African source
6	:	North-west United States (classed Idaho)
10	:	South-east United States (" pebble)
1	:	South American source.

It is not possible, within the scope of this paper, to furnish the results obtained on all the samples; also we have selected some samples from among the most characteristic of a group and presented those of most industrial interest according to their constitution, site, richness of deposits etc.....

Phosphate Kola II	-	85%
" Morocco II		75%
" " V		75%
" Gafsa II		65%
" Togo I		80%
" Idaho III		73%
" " IV		70%
" " VI		68%
" pebble IV		68%
" " V		72%
" " VII		75%
" " IX		75%

B - Physical and Chemical Characteristics.

1. External appearance (phosphate as delivered by the mine)

<u>Kola II</u> 85%	Crystalline powder, somewhat fine, homogeneous, of clear grey colour on dry sample.
<u>Morocco II</u> 75%	Coarse powder, fairly homogeneous, clear sable colour, in which is found a notable proportion of mineralised animal remains (teeth, fangs, shells ...)
<u>Morocco V</u> 75%	Ditto - appearance slightly variable from one sample to another.
<u>Gafsa II</u> 65%	Non-homogeneous powder of dark brown colour
<u>Togo I</u> 80%	Amorphous powder, fairly fine of yellow-orange, in which is also found a notable proportion of animal remains.

<u>Idaho III</u> 73%	Rock granules, greenish grey of puddingstone type, crumbling more or less easily into powder and very hard nodules of 1 to 2 m/m.
<u>Idaho IV</u> 70%	Heterogeneous sample composed of lumps and powder. The rock is less granular than that of Idaho III and harder. The colour is of black mould in the damp state - dark green dry.
<u>Idaho VI</u> 68%	Hard rocks often of puddingstone type, greenish-grey in colour, presenting a strong similarity with sample Idaho III.
<u>Pebble IV</u> 68%	Gravel somewhat coarse and heterogeneous, the grains are many coloured : white, yellow, red, black....., the whole after crushing has a clear sable colour similar to that of Morocco.
<u>Pebble V</u> 72%	Received ground : powder of clear sable colour.
<u>Pebble VII</u> 75%	Coarse powder, heterogeneous containing large pieces of dark colour. The whole is of clear sable colour usual with pebble phosphate.
<u>Pebble IX</u> 75%	Appearance very similar to the previous sample, somewhat coarser.

2. Fineness - on the original samples.

(Expressed as % grains falling between the two dimensions)

Dimensions m/m	Over 50	50-25	25-10	10-5	5-2	2-1	1-.5	.5-.1	under .1
Kola II 85%	-	-	-	-	-	-	1	35	64
Morocco II 75%	-	-	-	-	3	4	8	79	6
Morocco V 75%	-	-	-	-	4	3	4	82	7
Gafsa II 65%	-	-	-	-	2	2	4	52	40
Togo I 80%	-	-	-	-	1	2	3	52	42
Idaho III 73%	20	18	25	7.5	6	9	8	6.5	-
" IV 70%	5	13	18.5	8	17	7	7.5	16	8
" VI 68%	70	15	7	3	4	2	-	-	-
Pebble IV 68%	-	-	3	3	15	46	31	2	-
" V 72%	-	-	-	-	-	-	-	35	65
" VII 75%	-	-	1	8	14	18	11	46	2
" IX 75%	-	-	1.5	3	14.5	13	12	51	2

- Kola phosphate in the form of "Concentrated Apatite" is supplied at a fineness already equal to that lately used for the manufacture of superphosphates.

The African phosphates have been crushed with the object of eliminating the large lumps. The presence of fines (under 0.1 mm) is more or less high according to the friability of the rock; only slightly so for the Morocco, but appreciably higher with the Gafsa and Togo, which appear to have been submitted to a more powerful mechanical action.

Pebble phosphates have also been crushed but owing to their hardness has produced a fineness sensibly inferior to those of Africa.

These phosphates can eventually be supplied after thorough grinding as shewn by Pebble VII, the fineness of which is very close to Kola

Idaho phosphates are usually supplied as rock; the dissemination of deposits, their relative feebleness explains the frequent absence of thorough treatment on the site of extraction.

3. Grinding - minimum necessary before being used in the phosphoric manufacture.

Basis : the attainment of a degree of attack of the order of 98% (\pm 0.2%) under typical conditions.

Phosphates	Grinding necessary.	Grinding achieved	Fines min.%	
			100 mesh, 0.16mm	200 mesh, 0.08mm
Kola II 85%	Sufficiently fine	None	90	55
Morocco II 75%	Used raw	None	20	-
" V 75%	"	Raymond mill trial	20	-
Gafsa II 65%	"	None	60	10
Togo I 80%	"	None	70	20
Idaho III 73%	Crushing + limited grinding	Raymond mill	75	45
" IV 70%	"	Mortar crushed	65	25
" VI 68%	"	Limited grinding	70	35
Pebble IV 68%	Limited	Mortar ground	75	45
" V 72%	Thorough	Hammer Mill	85	60
" VII 75%	Very thorough	Raymond mill	90	70
" IX 75%	"	"	95	75

The African phosphates though relatively coarse can be used as such in phosphoric manufacture. All the same it is interesting in certain conditions to submit them to grinding to a greater or lesser extent. Hence we have included results on Morocco 75% ground.

Kola phosphate is equally useable as such, but the fineness is already high and near the indispensable minimum. In fact, Kola is the most difficult to attack, more so than Idaho and even some of the Pebbles.

Idaho phosphate is very coarse and obviously needs crushing, but this is shewn to be insufficient and limited grinding is always necessary.

Pebble phosphate always need grinding, sometimes very thoroughly. The intensity of grinding must often be high as the content of P₂O₅ is higher. Certain phosphates termed "Concentrates" titrating 80 to 90% tricalcium phosphate need to be taken to a fineness superior to 90% on 200 mesh sieve. This rule seems otherwise sufficiently general and applies to a certain extent to Idaho and African phosphates, among which Gafsa can be used coarser than is shewn here.

Note. The operation of a mill is costly and must be avoided as far as possible. Whenever it is proved indispensable, it is not desirable to limit it to a minimum fineness. This is why the finenesses (see later) of phosphates used in the continuous test ("S₃"C) often deviate from the minimum values determined in the preliminary tests ("S₃" A and even "S₃" C)

1. Characteristics of attack.

<u>Phosphate</u>	<u>Degree of attack</u>		<u>Requirement of sulphuric acid</u>		<u>Ratio of Solid/P₂O₅ ("S3" A)</u>	<u>Crystallinity Length Ratio L/w</u>	
		%	%	%		μ	
Kola II	85%	98.0	90.0	235.0	3.25	50-150	5
Morocco II	75%	97.9	84.6	257.2	3.82	50-200	2
" V	75%	98.25	85.6	259.2	3.80	100-200	2
Gafsa II	65%	99.1	80.0	274.7	4.25	100-300	10
Togo I	80%	98.3	86.6	238.5	3.60	30-200	1.25
Idaho III	73%	98.6	78.7	241.8	3.90	50-200	2.5
" IV	70%	98.75	75.0	238.5	4.00	50-200	8
" VI	68%	98.65	73.5	251.2	4.12	100-200	2.5
Pebble IV	68%	98.1	78.8	255.2	3.95	50	1.5
" V	72%	98.05	82.5	254.5	3.90	75	2.5
" VII	75%	98.3	82.4	245.7	3.75	75	1.75
" IX	75%	97.7	82.0	247.5	3.70	50-100	1.5

2. Characteristics of Filtration

<u>Phosphate</u>		<u>Speed</u>	<u>Degree of Drainage</u>	<u>Degree of Washing</u>
		m ³ /hr/m ²	%	%
Kola II	85%	1.800	39.0	98.2
Morocco II	75%	2.000	61.0	97.9
" V	75%	1.900	70.0	98.1
Gafsa II	65%	2.000	40.0	97.9
Togo I	80%	2.350	54.0	98.25
Idaho III	73%	1.720	62.0	98.7
" IV	70%	1.280	41.0	95.3
" VI	68%	1.950	66.0	98.65
Pebble IV	68%	1.880	73.0	98.6
" V	72%	2.300	58.5	98.1
" VII	75%	2.400	68.0	97.5
" IX	75%	2.000	75.0	97.5

3. Characteristics of the acid made.

<u>Phosphate</u>		<u>Composition of the acid</u>				<u>Distribution of Fluorine</u>		
		ABO	P ₂ O ₅	H ₂ SO ₄	Imp.	Cake	Acid	Evolved
			%	%	%	%	%	%
Kola II	85%	36.80	30.65	1.50	4.65	19.0	71.0	10.0
Morocco II	75%	37.0	32.0	1.65	3.35	51.0	43.5	5.5
" V	75%	37.0	31.9	1.65	3.45	45	45.5	9.5
Gafsa II	65%	37.0	30.2	1.60	5.2	53.5	43.0	3.5
Togo I	80%	37.25	31.35	1.65	4.25	43.0	52.5	4.5
Idaho III	73%	37.0	30.5	1.70	4.8	33.5	54.5	12.0
" IV	70%	36.9	30.55	1.40	4.95	44.0	46.5	9.5
" VI	68%	37.15	30.3	1.65	5.2	35.3	48.8	15.9
Pebble IV	68%	37.0	29.2	1.45	6.35	-	-	-
" V	72%	36.9	30.85	1.45	4.60	-	-	-
" VII	75%	37.1	30.7	1.60	4.80	45.0	49.5	5.5
" IX	75%	37.0	30.8	1.60	4.60	36.0	53.5	10.5

Kola Apatite furnishes the best results from the point of view of sulphuric acid required per unit of P₂O₅ solubilised and proportion of solid formed.

The degree of washing is good despite the formation of long crystals and the poor drainage of the cake.

The degree of attack, speed of filtration, content of impurities in the acid are moderate or slightly unfavourable.

Attention is drawn to the low proportion of fluorine retained in the calcium sulphate cake in comparison with the low content of phosphate; the quantity of fluorine found in the acid or volatilis remains as the same order of absolute value as for the other phosphates.

Morocco 75% furnishes the best results from the point of view of content of impurities in the acid. Its suitability for attack is excellent since the phosphate can be treated raw, giving a convenient rate; on the otherhand thorough grinding did not improve the results, which remained inferior to those of phosphates which were less easily attacked at the start.

The proportion of solid formed, crystallinity, speed of filtration, drainage and washing are moderate to good. The consumption of sulphuric acid is unfavourable.

Gafsa 65% furnishes the best degree of attack and is obtained on the raw. Speed of filtration and degree of washing are moderate.

The results: proportion of solid formed, crystallinity, drainage, content of impurities in the acid are among the most unfavourable, and the consumption of sulphuric acid per unit of P_2O_5 is by far the highest.

Togo 80% is among the best of the whole of the results.

The degree of attack is excellent, placing it in second position for the phosphates treated as received. It also appears in second position on the following data: consumption of sulphuric acid and proportion of solid formed per unit of P_2O_5 , quality of crystals, speed of filtration and content of impurities in the acid made.

The drainage and washing are moderate to good.

Idaho phosphates furnish variable results depending on the samples. For the three samples investigated only the attack is of the same order and is always excellent on ground samples.

The consumption of sulphuric acid places it among the best of two samples and moderate on the third.

The proportion of solid formed varies from moderate to bad.

The crystallisation and filtration characteristics are good on phosphates III and VI, very bad on sample IV.

The content of impurities of the acid is bad to moderate, but here it is the Idaho VI which is so unfavourable.

The distribution of fluorine too is very variable among the samples.

Pebble phosphates are equally inclined to show differences, but less marked than the preceding and limited mainly to the degree of attack and to a certain extent to the filtration characteristics. The degree of attack is poor to moderate despite thorough grinding and the rate of washing is fairly poor on two samples.

The consumption of sulphuric acid, proportion of solid formed, crystallisation and filtration speed are moderate to good. All the same the content of impurity of the acid is less favourable, especially for Pebble 68%.

NOTE. The degree of attack is obtained from the ratio of P_2O_5 (insoluble) to P_2O_5 (total) of phosphate treated. It may be

observed that the P_2O_5 insoluble is not due solely to unattacked material but also to the P_2O_5 occluded or formed according to the retrograde reaction: $CaSO_4 + H_3PO_4 \rightleftharpoons CaHPO_4 + H_2SO_4$ tending towards the right under certain conditions of concentration which arise in the course of the washing. We have retained this method of expression, used industrially, but it must be appreciated that the real degree of attack on the phosphate is superior to the values here indicated by nearly 1%.

IV. UTILISATION OF THE RESULTS.

A. Theoretical.

- Correlation of the characteristics of the phosphates with results.
- Correlation of the various data from these tests.

The very numerous results obtained in the course of our investigations on phosphates have been arranged in tables or graphs showing each of the physical or chemical characteristics of the phosphates as a function of each of the data from the tests under investigation. It is thus possible to show the relationship between certain characteristics or groups of characteristics of the phosphates and certain of the results of the tests, and from which it is possible to draw some general conclusions.

Exceptions, indeed contradictions both apparent or real, also appear, necessitating firstly verification of the results and, if confirmed, research on that element or ratio of elements, responsible for the discrepancy. The accumulation of results which must, of necessity, occur will ensure through the use of statistical methods, the establishment of relationships or laws, more and more numerous and precise, which in addition to their practical applications will contribute to the understanding of the complex phenomena of phosphoric manufacture.

We give here as examples, certain of these conclusions, stressing that they are drawn from the whole of our tests and not merely from among the results given in this paper equally entitled to rank. Certain of these conclusions confirm or emphasise data already known, others tend to invalidate established opinions or simply supply new ideas.

The physical structure of the mineral plays a preponderant role in the proneness to attack of the phosphate, and to a less extent on the formation of crystals of calcium sulphate and, in consequence, on the main characteristics of filtration, drainage and washing. This structure depends on the nature of the rock, its geological age, its degree of mineralisation etc. It is less variable within the same family of phosphates than from one group to another. This, in conjunction with the analogous composition as a whole, produces a very neat classification of families of phosphates, which with few exceptions subsist right through differences of treatment and the content of essential elements in any sample.

Grinding helps, to a certain extent, to reduce the variations due to differences of structure. It leads to a varying re-distribution of grain size depending on the nature of the phosphate. Its efficacy on the improvement of results also varies according to the phosphate: the more difficult of initial attack being the most favourably affected but often this cannot be foreseen logically. The proportion of P_2O_5 attacked but retained in the filter cake and treated as insoluble varies according to the phosphate.

Contrary to generally held opinions and partly verified in the case of attack termed "solid phase" (manufacture of superphosphates ...), the content of carbonate does not influence

to any notable extent the susceptibility of the phosphate to attack. Opinion is thus invalidated not merely as between phosphates of different groups, but within the same group. In the same way the content of organic matter or silica have no influence on attackability. On the other hand it does depend on the content of P_2O_5 - attack becomes more difficult the higher the P_2O_5 content; this observation holds true for pebble phosphate. It is the same with Fluorine in relation to P_2O_5 .

The consumption of sulphuric acid depends on the respective proportions of phosphate and carbonate. In making the calculation for the proportion of sulphuric acid to be employed at the start, it is preferable not to include the fluoride, the attack of which varies with the phosphate and especially in relation with the content of P_2O_5 as against total fluorine.

We have the simplified formula following (taking the constituents of the treated sample)

$$H_2SO_4 \text{ \% phosphate} = \left[(P_2O_5 \times 2.03) + (CO_2 \times 2.22) \right] \times 1.10$$

For greater precision this last coefficient can be varied from 1.08 to 1.13 according to the phosphate group.

The filtration speed is relatively little influenced by the dimensions and form of the crystals of calcium sulphate to which one sometimes is inclined to attach importance. The causes of variation in speed of filtration are to be sought above all in the formation of "semi-colloidal" matter arising from impurities in the phosphate: fluorine compounds (calcium fluoride, sodium fluosilicate...) and organic matter principally. These materials overload the liquid phase, choke up the calcium sulphate cake and the filter cloths. The formation of troublesome fluorine compounds is influenced by the proportion of silica and its form - quartzose or combined, - by alumina soda, potash ... etc.

The influence of organic matter can be sufficiently troublesome to justify or impose preliminary calcination of the phosphate. The degree of washing is influenced by the same elements and in the same sense as the filtration speed; but no systematic relationship between filtration speed and degree of washing is found, due to opposing factors: crystallisation, drainage etc... A too rapid flow of wash-water across the face of the cake is itself undesirable.

The formation of short crystals is favoured by the presence of cationic compounds: metallic oxides (Aluminium principally), and the formation of long crystals by the presence of anionic compounds (SiO_2). But the predominance of one or the other of these elements does not depend simply on their content in the phosphate but also on their attackability, on the proportion of fluorine and of other elements liable to complex with them and it is difficult a priori to foresee the type of crystallisation furnished by a given phosphate from its physico-chemical structure.

There exists a definite relationship between the fineness of crystals and the drainage of the filter cake: short crystals systematically furnish a high rate of drainage and vice versa.

The relationship between drainage and washing is difficult to establish in view of the preceding description of the factors influencing washing. All things otherwise equal, it would seem that an optimum value for degree of draining should be between 60 and 70%.

The content of impurities of the acid made varies mainly as a function of the content of metallic oxides (Fe_2O_3 , Al_2O_3 ...) of the phosphate. (This data is very important for the ultimate utilisation of the acid, especially for the manufacture of sodium salts).

B. Practical.Extrapolation to the industrial scale.

At the commencement of this paper we indicated some of the questions which face the manufacturer before utilising a new type of phosphate in an existing or envisaged installation. It will be seen that the determinations carried out on the phosphate itself and then in its applications in phosphoric manufacture permit us to reply to most of the questions arising at various stages of industrial exploitation :

Reception and storage of the phosphate.

Treatment to which it is to be submitted ; crushing, grinding, calcination etc.

Design of the factory : determination of volumes of attack, filtration surfaces, methodical stages of washing, the removal and utilisation of residues, etc....

Conditions for achieving the above.

Production capacity for a selected phosphate and given factory.

Yields and consumption of materials.

Quality of the production.....etc....

Note that the trials permit a reply to some specific problems of the manufacture, for example consistency of the reaction slurries formation of foam or scum, emulsion formation, sedimentation etc... which condition the starting up (agitators, pumps...) and finally permits a substantial quantity of phosphoric acid, representative of each sample of phosphate to be made available for utilisation trials in the various manufactures envisaged: superphosphates, concentrated in solid or liquid form, complex fertilisers, sodium derivatives .. etc..

What is the exact method of extrapolation of these tests and what is the practical value of the results obtained ?

We have endeavoured from the start of these trials to reproduce with the maximum of precision the conditions for industrial exploitation. But we have all the time admitted some deviations, indicated in the description of the tests and concerning especially the characteristics of filtration. On the other hand the degree of extrapolation might be considered, wrongly for other reasons, as too high to furnish precise data.

These inconveniences are avoided by the method of extrapolation adopted, which consists in utilising the data from these tests, not directly, but by reference to industrial results furnished by the same sample. The results of our tests being already very near to industrial results, the precision by this method gives a full guarantee.

At the start the industrial manufacture from Morocco phosphate 75% has served as the basis of our trials: we now possess the industrial experience of the use of phosphates from the principal deposits under exploitation :

Morocco - Gafsa - Idaho - Kola - Pebble

This experience has enabled us already to verify the efficacy of our methods of investigation, then to put them to the test with some modifications in detail and complementary refinements, last

and above all, to provide new bases of comparison and establish a close network of reference points leaving little place for the unforeseen.

IN CONCLUSION, we provide methods of investigation which possess the immediate advantage of enabling us to recognise in advance, the influence on phosphoric manufacture of the origin and characteristics of a given phosphate, and which we hope will contribute moreover to a better understanding of the complex phenomena of this manufacture.

SUMMARY

Natural phosphates of lime have very complex structures and compositions depending on their origins. These differences in the constitution of phosphates are liable to change considerably the characteristics of phosphoric manufacture which is itself the basis of very complex reactions and which must be carried out with regularity and precision. Using a new type of phosphate in an existing or proposed installation gives rise to a great number of problems amongst which are:

- Possibilities of using phosphate as such, or the necessity of unavoidable treatments or of favourable economic balance.
- Determination of best working conditions.
- Capacity of production in a given workshop or the addition of a new installation with a view to having a certain production capacity.
- The consumption of materials and the production figures; characteristics of the acid made ... etc.

It is of the greatest interest to know in advance data enabling the answers to these various problems to be found. Experiments on an industrial scale usually cannot be undertaken at the outset: the phosphate deposits are often considerably distant and this constitutes an obstacle to providing essential tonnages for merely experimental purposes, and, moreover, the unwillingness of industrial concerns prevents when necessary a systematic study of a great number of alternatives. It was for this reason that we decided to employ working methods based on large quantities of raw materials - 50 to 100 Kgs. of phosphate - but which are used by direct application to industrial manufacture.

These methods give the necessary information for the various operations from the receipt and stocking of the phosphate to the different characteristics of the acid produced and even up to the various uses of this acid,

1. Conditioning the phosphate: comprising

Identification of the sample	:	geographical and geological origin
Treatment	:	grinding, calcination, etc.
Physical characteristics	:	external appearance
		fineness : in natural state and then ground
		apparent density: in natural state with and without settlement
Chemical characteristics	:	composition (Normal and complementary determinations)

2. Tests for phosphoric acid:

Degree of attack of phosphate	
Consumption of H ₂ SO ₄	(% of phosphate - % of P ₂ O ₅ attacked)
Solid formed	(% P ₂ O ₅ of phosphate)
Crystallinity	(Length in microns - Ratio of length/width)
Speed of acid filtration	(m ³ of acid filtered per hour per m ² of filter surface)

Drainage rate (acid filtered as % of total)
Washing rate (P_2O_5 extracted from the solid phase to
% of P_2O_5 of phosphate)
Composition of acid (Baumé (density) P_2O_5 , H_2SO_4 , index of
impurity)
Distribution of other elements (fluorine, etc.)

Some thirty phosphate samples, coming from most of the world's deposits were studied; examples of results obtained have been given for twelve of them.

The comparison of preliminary experiments with industrial results enabled us to perfect methods of study, to make them more accurate and, above all, perfectly adapted to the aim of the research.

We now possess industrial experience in the treatment of a very varied number of phosphate rocks, amongst which the most commonly used are:

Morocco, Gafsa, Pebble, Idaho, Kola

This experiment has enabled us to verify the effect of our methods and to foresee the optimum conditions for using phosphates of these groups or of any other origin according to tests made on a representative sample of this phosphate.

Apart from immediate advantages which can be taken from these studies at an industrial level, the collation of a very large number of results based on materials with very different physical structures and chemical compositions has enabled us to reveal factors influencing the different stages of phosphoric manufacture and thus to understand better the phenomena noticed which can be utilized to improve manufacture.

We have collated in this paper several conclusions to which this work has brought us; some of them confirm or specify data which is already known, while others invalidate accepted opinions or introduce new ideas and perspectives. Important developments may be expected from the remainder of these experiments.

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Fineness: On phosphates submitted to the tests in this paper.

(Expressed as % cumulative of grains passing various sieves)

Sieve No. (N.F.)		40	60	80	100	150	200	300
Mesh aperture m/m		0.45	0.3	0.2	0.16	0.11	0.08	0.05
Kola II	85%	-	99	96	92	69	56	43
Morocco II	75%	86	74	42	20	6	3	1
" V	75%	-	99	96	89	73	56	42
Gafsa II	63%	93	86	73	61	40	11	4
Togo I	80%	95.5	92	88	71	42	21	4
Idaho III	73%	-	98	93	86	63	54	35
" IV	70%	-	95	87	68	41	25	17
" VI	68%	-	98	92	82	57	41.5	32.5
Pebble IV	68%	-	-	86	74	57	45	37
" V	72%	-	96	90	85	68	57	42.5
" VII	75%	-	99	96	90	76	63	43
" IX	75%	-	-	99	98	91	75	65

Apparent Density.

Phosphate.		Phosphate as such.		Phosphate ground	
		Without	With	Without	With
		Settlement		Settlement	
Kola II	85%	1.560	2.220	-	-
Morocco II	75%	1.230	1.455	-	-
" V	75%	1.225	1.445	0.920	1.475
Gafsa II	63%	1.460	1.720	-	-
Togo I	80%	1.282	1.533	(0.952)	1.666
Idaho III	73%	1.520	1.910	1.090	1.750
" IV	70%	1.390	1.800	1.270	1.900
" VI	68%	(1.540)	(1.660)	1.320	1.890
Pebble IV	68%	1.440	1.620	1.330	1.790
" V	72%	-	-	1.140	1.690
" VII	75%	-	-	1.030	1.650
" IX	75%	1.530	1.740	0.980	1.560

The phosphates of Africa, Morocco, Togo, then Gafsa are the least dense, followed by Pebble, then Idaho; and lastly Kola, these latter are very dense.

The density without settlement is highest on the coarse phosphates, but the ground phosphates have a coefficient of settlement much superior (the more so because they are finer) and they tend to attain apparent densities which are finally higher.

6. Composition - Percentage on the dry.

a. Analyses made systematically.

Phosphate	P ₂ O ₅	F ₂	CO ₂	SO ₃	SiO ₂	R ₂ O ₃	CaO	Loss	N%	
						Fe-Al				
Kola II	85%	39.15	3.15	0.05	0.035	1.35	0.76-1.24	51.85	0.10	3.65
Morocco II	75%	33.9	3.7	4.15	1.7	1.75	0.53-0.32	51.45	1.6	2.45
" V	75%	33.9	3.9	4.0	1.4	1.6	0.45-0.33	51.50	1.5	3.05
Gafsa II	65%	30.0	3.5	5.9	3.0	2.7	0.90-0.35	48.6	2.8	3.7
Togo I	80%	37.1	4.0	1.8	0.23	2.6	0.65-1.42	50.55	0.9	2.45
Idaho III	73%	33.35	3.55	1.7	2.1	8.85	1.70	47.4	1.2	1.30
" IV	70%	32.15	3.25	1.8	1.35	7.40	2.22	45.1	3.85	4.25
" VI	68%	29.75	3.30	3.02	2.1	14.10	0.65-0.97	43.7	1.25	2.15
Pebble IV	68%	31.7	3.65	2.95	0.75	10.1	2.4	46.25	1.85	1.9
" V	72%	33.3	3.7	2.95	0.8	6.5	2.05	48.5	1.8	1.9
" VII	75%	34.2	3.75	3.25	0.65	4.35	0.45-1.35	49.45	2.05	2.05
" IX	75%	34.2	3.9	3.0	0.8	4.75	1.02-0.63	49.2	1.85	2.20

b. Elements in addition - Order of quantity according to the groups of phosphates.

	MgO	Na ₂ O	K ₂ O	SrO	MnO	TiO ₂	Cr ₂ O ₃	V ₂ O ₃	UO ₃
Kola 85%	0.20	0.45	0.20	2.10	0.05	0.10	-	-	-
Morocco 75%	0.45	1.0	0.25	-	0.002	0.025	0.045	0.030	0.01
Gafsa 65%	0.60	1.25	0.45	-	0.003	0.050	0.040	0.020	-
Idaho 72%	0.50	0.40	0.15	-	0.010	-	-	0.050	-
Pebble 75%	0.55	0.45	0.35	-	0.020	0.200	0.010	0.015	-

Note that one encounters in these phosphates minimal quantities of Nickel, Copper, Zinc, Silver, Lead, Antimony, Molybdenum ...etc... Kola Phosphate is the only one which gives a ratio Fluorine/P₂O₅ inferior to that of apatite, which is very rich in P₂O₅. The contents carbonate, sulphate, organic matter are remarkably low. Its content of metallic oxides is medium to high. It presents the peculiarity of a high content of strontium.

The various samples investigated have a fairly constant composition.

- The North African phosphates show important differences of composition from one deposit to another; on the other hand the qualities furnished by the same deposits (Morocco, Gafsa, Kouif..) are very constant.

These phosphates are distinguished by a higher content of carbonate;

Morocco 75%, which contains the least in the group is however more highly charged with carbonate than the phosphates of the other groups. Morocco 75% presents the interesting instance of a low content of metallic oxides : particularly Iron and Alumina.

Gafsa and the other phosphates of the group, poorer in P₂O₅ (and Fluorine) than the Morocco, have a higher content of carbonate, then sulphate, silica, metallic oxides and organic matter.

Togo phosphate is distinguished from the phosphates of North Africa by its high content of P₂O₅ (it holds second position after Kola), low in carbonate, sulphate, organic matter ; on the other hand its content of metallic oxides is distinctly higher than those of North Africa.

Idaho phosphate has a very variable composition according to the veins being exploited and for the same designation (a moderate or low content of P₂O₅, Fluorine, Sulphate, metallic oxides,) is generally low in carbonate, very variable in silica or organic matter in which it may attain quite high values.

Pebble phosphates generally exhibit a constant composition. The enrichment of 68 to 75% results by progressive elimination of silica and to a lesser extent of metallic oxides. Pebble 75% has a moderate content of the whole of the elements.

c. Trials on tests of phosphoric manufacture.

In order not to overload this paper, we omit the results of various preliminary tests "S3" A made on each of the phosphates and give only one of the results of the continuous tests, the most representative sample of phosphate studied. Throughout, we have added to the data of attack of the continuous test the values of the ratio: Total dry solid formed / P₂O₅ of the given phosphate obtained during the preliminary tests.

The results are as follows: