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THEORETICAL BASES FOR CONTROLLING AND REGULATING SUPERPHOSPHATE PRODUCTION.

by Cie. de SAINT-GOBAIN.

General Remarks.

However simple the production of Superphosphate may be, it requires, nevertheless, a strict and accurate control if the customer is to be completely satisfied with the product delivered to him.

It is important

- to select a suitable proportion for the weights of the phosphate and the acid used in the process;
- and to be able to modify this proportion quantitatively at will in order to counteract the variations in composition of the raw materials, as well as the findings in regard to the quality of the superphosphate produced.

These conditions present two problems of a different nature:-

- (1) the problem of handling liquids and phosphate;
- (2) the problem of chemical control and the interpretation of the results obtained.

THE PROBLEM OF HANDLING LIQUIDS AND GROUND PHOSPHATE.

The use of fixed proportions of acid and ground phosphate does not present any special difficulties in the case of batch mixing. The phosphate is weighed and the acid is weighed or measured. The degree of regulation depends, in the main, upon the skill or ability of the workman in charge of the mixing.

In the case of a continuous process, however, the problem is much more difficult, at least, as far as the phosphate is concerned. It is then a question of controlling the flow of the powdery material with accuracy.

Whilst in theory, the weigher is suitable, it is found in practice, that its precision, which is usually within about 2%, is not sufficient in the present case, but with a sensitive apparatus and by means of certain simple modifications, it is possible to obtain an accuracy within 0.5% which we consider adequate.

The solution usually adopted is, however, different; it consists of feeding the phosphate volumetrically which is fairly simple; in view of the considerable variations in density to which phosphate is subject, this method, in our opinion, does not possess the accuracy desired.

By means of a bucket wheel the problem of acids can be solved volumetrically with sufficient accuracy. It is important, however, that the phosphate and acid feeds should interact so as to avoid that, in the case of a mechanical defect of one of the feeds, the other continues to feed the mixer.

CHEMICAL PROBLEMS.

The chemical problems to be solved are as follows:-

- (1) analytical study of superphosphate on leaving the den;
- (2) interpretation of results in order to determine quantitatively the extent to which the regulation of phosphate and liquids should be modified.

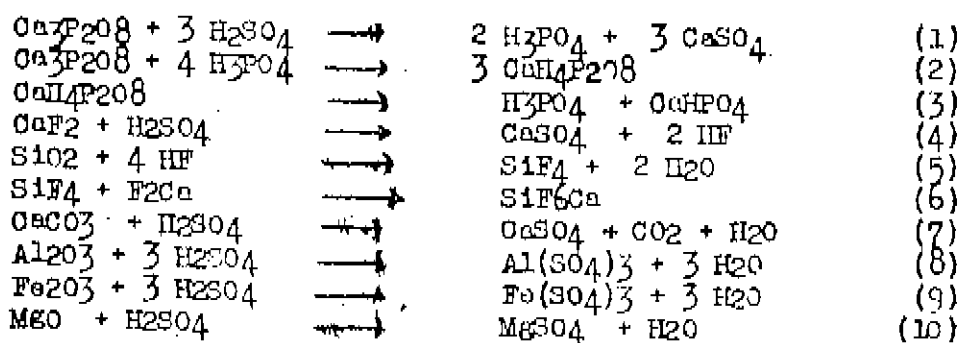
The problem is somewhat complicated by the fact that the product to be analysed is in a state of reaction and in order to deduce from its analysis data for regulation one has to commence by envisaging the end of reaction and bear in mind the fact that the free acid content, which is rather high when the slurry leaves the den, will gradually diminish thereby increasing the available P<sub>2</sub>O<sub>5</sub>.

Generally speaking, the manufacturer applies certain rules and formulas which between them take into account the variations in composition and which enable him to foresee approximately the composition of the products at the end of reaction. Often little is known of the origin of these rules. Their significance and extent of application even less.

We thought that it would serve a useful purpose to recall the theoretical bases. As will be seen, such a study does not represent pure speculation without any practical interest and it is possible to find a basis for a method of a very rapid control of superphosphate production.

DISTRIBUTION OF SULPHURIC ACID DURING THE BREAKING DOWN OF PHOSPHATE.

Natural phosphates represent complex mixtures which vary in composition according to their origin. Apart from tricalcium phosphate, they include numerous impurities: fluorine and calcium carbonate, silica, various oxides, etc. In order to transform the mineral into superphosphate, the former is treated with sulphuric acid. The main reactions which take place may be formulated as follows:-



It is possible to distinguish two portions in the quantity of sulphuric acid introduced.

The first portion serves (directly or indirectly) to convert the tricalcium phosphate to the soluble state. This we propose to call the effective sulphuric acid.

The second portion is consumed during the more or less incomplete breaking down of the various impurities to varying states of completeness; this represents an unavoidable expenditure without useful results as far as the object in view is concerned; this we propose to call wasted sulphuric acid.

In order to be able to compare various phosphates or different methods of production with each other, from the point of view of expenditure of sulphuric acid required for the production of superphosphate, it would be useful to be able to assess separately the two portions defined above; it is possible to calculate them on the basis of the analytical results of superphosphate.

CALCULATION OF THE QUANTITY OF EFFECTIVE SULPHURIC ACID.

We propose to express this quantity by the number of molecules of effective  $H_2SO_4$  per molecule of total  $P_2O_5$  (or per molecule of  $Ca_3P_2O_8$  used). When calculating this quantity, it will be seen that, according to the equations shown above, all the  $H^+$  ions originating from the effective sulphuric acid are retained in the superphosphate (although their acidity is considerably diminished by the fact that the  $H^+$  ions coming from the  $H_2SO_4$  and contained in monocalcium and dicalcium phosphates are not acid to methylorange) whilst the  $H^+$  ions of the wasted sulphuric acid are either released or neutralised.

We propose to utilise the following symbols to denote the quantities of  $P_2O_5$  which are to be found in various forms in 100 parts of superphosphate:

- t = total  $P_2O_5$
- a = available  $P_2O_5$  (water soluble and citrate soluble)
- s = water soluble  $P_2O_5$
- i = insoluble  $P_2O_5$
- p = actual free  $P_2O_5$  (as distinct from the total acidity which originates also from the free sulphuric acid)
- d =  $P_2O_5$  content of dicalcium phosphate
- m =  $P_2O_5$  content of monocalcium phosphate

the quantities t, a, s being directly known through the running analysis of superphosphate.

A quantitative unit of  $P_2O_5$  (the molecule, for example) is distributed in the superphosphate according to the following fractions:-

Fraction  $\frac{1}{t} = \frac{t - a}{t}$  is in the form of  $Ca_3P_2O_8$

Fraction  $\frac{d}{t} = \frac{a - s}{t}$  is in the form of  $CaHPO_4$

Fraction  $\frac{m}{t} = \frac{s - p}{t}$  is in the form of  $CaH_2P_2O_8$

Fraction  $\frac{p}{t}$  is in the form of  $H_3PO_4$

In view of the fact that it is necessary to have

- one molecule of  $H_2SO_4$  per molecule of  $P_2O_5$  in the form of dicalcium
- two molecules of  $H_2SO_4$  per molecule of  $P_2O_5$  in the form of monocalcium
- three molecules of  $H_2SO_4$  per molecule of  $P_2O_5$  in the form of phosphoric acid

the quantity, in molecules, of effective sulphuric acid, n, for one molecule of total  $P_2O_5$  should be

$$n = \frac{d + 2m + 3p}{t} = \frac{a - s + 2(s - p) + 3p}{t} = \frac{a + s + p}{t} \quad (11)$$

Usually i, the total acidity with methylorange expressed in per cent of  $P_2O_5$  is tritrated and not p. This acidity represents phosphoric acid as well as free sulphuric acid which finally remains in the superphosphate. The latter acid must, at least provisionally, be regarded as effective acid because it is capable of reacting with phosphatic compounds. The number of n' molecules of free  $H_2SO_4$  per molecule of total  $P_2O_5$  equals:-

$$n' = \frac{i - p}{t} \quad (12)$$

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since free  $H_2SO_4$  and free  $P_2O_5$  correspond to the same number (2) of  $H^+$  ions acid in methylorange per molecule. The total quantity of effective sulphuric acid per molecule of total  $P_2O_5$  is therefore:

$$N = n + n' = \frac{a + s + 1}{t} \quad (13)$$

It should be noted that in weight per 100 parts of superphosphate, the quantity of effective sulphuric acid equals:

$$98 \frac{t}{142} N = 0.69 (a + s + 1)$$

98 and 142 respectively, being the molecular weights of  $H_2SO_4$  and  $P_2O_5$ .

EVOLUTION OF SUPERPHOSPHATE.

It is known that superphosphate when leaving the den is far from having attained a stable composition. The reactions in the superphosphate are incomplete and continue for weeks and even months in the product which is in the process of cooling but they proceed more and more slowly. If the breaking down of the impurities continues, this is reflected by a decrease in the quantity of effective sulphuric acid thereby increasing the quantity of wasted acid. But it has been determined by experiments that the breaking down of the impurities practically reaches its final stage when the slurry leaves the den. In these circumstances the quantity of effective sulphuric acid in relation to a fixed quantity of  $P_2O_5$  becomes constant and the modification of the composition takes place according to the following law:-

$$\frac{a + s + 1}{t} = N_0 \quad (14)$$

Let us recall the chemical interpretation of the constant  $N_0$ . It is the number of molecules of effective  $H_2SO_4$  contained in the quantity of superphosphate which comprises one molecule of  $P_2O_5$  (142 g); theoretically, in order to convert all the  $P_2O_5$  into monocalcium phosphate, a constant  $N_0 = 2$  is required.

If the breaking down could be carried on until the conversion of  $P_2O_5$  to the state of monocalcium phosphate has been completed ( $N_0$  more than or equal to 2) there would remain in the superphosphate a definite acidity  $l_{lim}$  which could be calculated by means of equation (14) where  $a$  and  $s$  would equal  $t$ , the equation becoming:-

$$\frac{2t + l_{lim}}{t} = N_0$$

from which formula the value of this extreme acidity (expressed in terms of  $P_2O_5$  per cent of super) which element is variable in time is obtained

$$l_{lim} = (N_0 - 2) t = a + s + 1 - 2t \quad (15)$$

This extreme acidity represents to a certain extent the quantity of free sulphuric acid which must remain in the superphosphate in order to ensure the stability of  $P_2O_5$  in the form of monocalcium.

SPECIAL CASE.

Superphosphate always contains dicalcium phosphate, but in small quantities the variations of which may, generally, be ignored with those of  $m$  and  $p$ . Let us assume that  $\frac{d}{t}$  (which is equal to  $\frac{a - s}{t}$ ) is constant.

By replacing  $s$  by  $a + d$  the rule of evolution (14) then becomes:

$$\frac{2a + 1 - d}{t} = N_0$$

hence:  $\frac{2a + 1}{t} = N_0 + \frac{d}{t} = N'_0$  (which is a constant) (16)

We propose to show this relationship in another form by bringing out the rate of attack  $A = 100 \frac{a}{t}$ . Equation (16) then becomes:

$$A + \frac{50 \frac{a}{t}}{t} = 50 N'_0 - K_0 \quad (17)$$

On the other hand, but always in the special case where  $d$   $P_2O_5$  remain in the state of dicalcium per 100 parts of superphosphate, let us examine what  $l$  becomes when the breaking down of tricalcium phosphate is completed.

The symbols used are as follows:-

$l_{lim}$  : maximum acidity remaining in the super  
 $i = t - a$  ; the insoluble in super  
 $l_{lim} = 0$  by hypothesis

By replacing  $a$  by  $t - i$  in equation (16) one obtains:

$$2t - 2i + 1 = N'_0 t \quad (18)$$

$$\text{or } 1 - 2i = (N'_0 - 2)t + \text{constant} = l_{lim} - 2i_{lim} = L_{lim}$$

In this form

$$L_{lim} = 1 - 2i \quad (19)$$

and find what is evident from reaction (2), namely, that two units of free  $P_2O_5$  are necessary to convert one unit of  $P_2O_5$  in the form of tricalcium to the form of monocalcium.

#### APPLICATION TO THE MANUFACTURING PROCESS.

It is evident that the comparatively increased solubilisation of  $P_2O_5$  which is final at the end of the evolution depends upon the comparatively large quantity of effective sulphuric acid. The rule to be adopted in this respect depends upon economic considerations, particularly upon the cost price of phosphate and acid, a fact which has been demonstrated by M. Cambau at Landskrona.

It is customary to admit the following axiom: the quantity of effective  $H_2SO_4$  must exceed by 6% the stoichiometric quantity necessary in order to obtain  $CaH_4P_2O_8$ .

Let  $N_0$  equal 2.12.

In order to determine the value of  $N'_0$  and  $K_0$  it is necessary to formulate a hypothesis in regard to the average quantity of  $P_2O_5$  present in the dicalcium phosphate stage. We will assume that it represents 2% of the total  $P_2O_5$ .

$$\frac{d}{t} = 0.02. \quad \text{hence}$$

$$N'_0 = 2.14$$

$$K_0 = 107$$

The corresponding values of maximum acidities are as follows:-

$$l_{lim} = 0.12 t$$

$$L_{lim} = 0.14 t$$

As to the content of total  $P_2O_5$  approaching 15 to 16% the following may be taken:

$$l_{lim} = 2$$

$$L_{lim} = 2.5$$

By means of these postulates the production may be regulated on the basis of one of the following rules deduced from formulas (14), (15), (17) and (19):

$$\frac{a + s + 1}{t} = 2.12 \quad (20)$$

$$a + s + 1 - 2t = 2 \quad (21)$$

$$A + \frac{50}{t} = 107 \quad (22)$$

$$1 - 2t = 2.5 \quad (23)$$

Rule (20) is universal and applies to all superphosphates irrespective of their grade. It holds good also for triple superphosphate.

Only the value of the constant is subject to modifications according to the qualities looked for in the product.

The other rules which at times are more readily applicable, are valid in the circumstances defined above.

#### MODIFICATION OF QUANTITY OF SULPHURIC ACID.

If in the course of manufacture it is found, by application of one of the rules in the foregoing, that for a given rate of attack superphosphate contains excessive or insufficient quantities of D l unites of free acid calculated as P<sub>2</sub>O<sub>5</sub> for 100 parts of super to what extent should the quantity of sulphuric acid be modified?

It can readily be assumed that the free acid represents sulphuric acid because whether it is the one or the other, the attack remains unchanged as shown by the theoretical reaction:



D l units of free P<sub>2</sub>O<sub>5</sub> equal therefore

$$\frac{98}{142} \text{ D l} = 0.69 \text{ D l units of H}_2\text{SO}_4$$

It is customary to relate the quantity of H<sub>2</sub>SO<sub>4</sub> to 100 parts of ground phosphate; if, in these circumstances, T be the content of P<sub>2</sub>O<sub>5</sub> % of the phosphate utilised, for 100 parts of phosphate, the total quantity Q of H<sub>2</sub>SO<sub>4</sub> should be modified by the quantity

$$DQ = 0.69 \text{ D l} \frac{T}{t}$$

The ratio  $\frac{T}{t}$  is usually in the neighbourhood of 1.75, hence:

$$DQ = 1.2 \text{ D l}$$

In relative value for 100, the modification of the quantity of sulphuric acid equals  $\frac{100 DQ}{Q}$ . Since Q is usually of the order of 60 to 65 kgs of H<sub>2</sub>SO<sub>4</sub> the following is obtained for 100 kgs of phosphate:

$$\text{relative modification of acid in \%} = 2 \text{ D l}$$

Another equally simple formula for regulation but necessitating an analysis of the P<sub>2</sub>O<sub>5</sub> contained in the super in different forms, can be reduced to the formula (20)

$$\frac{a + s + 1}{t} = N_0 = 2.12$$

If the manufacture is not regulated, the following is obtained

$$\frac{a + s + 1}{t} = N \neq 2.12$$

Hence  $D N = N = 2.12$  expressed in number of  $H_2SO_4$  molecules for 142 P2O5.

Expressed in weight per 100 parts of phosphate, the modification to be effected in regard to the acid is:

$$DQ = 0.69 \text{ T.D.N.}$$

Expressed in % the relative correction of the strength of the acid is

$$100 \frac{D Q}{Q} = 0.69 \times \frac{100 \text{ T.D.N.}}{Q}$$

In practice the expression  $100 \frac{T}{Q}$  remains in the neighbourhood of 48.

Hence the following is obtained: relative modification in % =  $100 \frac{DN}{3}$ .

#### METHOD OF RAPID CONTROL OF MANUFACTURE.

A complete analysis of superphosphate has the drawback of taking a long time. It requires more than half a day. In the case of a continuous process the manufacturer runs the risk of producing an appreciable quantity of an unsuitable product before knowing the value of the superphosphate obtained.

It is, therefore, very useful to have at one's disposal a method of rapid control which permits of knowing in less than half an hour the value of one of the constants defined in the foregoing.

It has been noted that  $l_{lim} = a + s + 1 - 2 t$  represents the value of free acid if the breaking down of tricalcium phosphate has been complete.

It is possible to complete it by introducing a known excessive quantity of sulphuric acid. In accordance with that principle we have evolved the following method:-

Dilute 5 grammes of superphosphate in a beaker with 50 cc of water. Pour the mixture into a test tube add 10 cc of sulphuric acid 2N. Bring to the boil for a quarter of an hour, make up to 125 cc by adding water and filter. On 25 cc of filtrate titrate the acidity by means of sodium N in presence of methylorange, viz. n cc. The following is obtained:-

$$l_{lim} = (n - 8) \times 3.55$$

In the above working conditions, impurities are practically not broken down. It is necessary to find for  $l_{lim}$  a value approximating + 2.

Thus a method of control in the works is at one's disposal which can be repeated every hour.

#### CONCLUSION.

In order to obtain a superphosphate of good quality and under most economic conditions it is not sufficient to possess a modern and perfect apparatus. In addition, it must be possible to regulate production with accuracy and with a perfect knowledge of the cause. With this aim in view, we hope the foregoing considerations may be of assistance to those who strive continually to improve the quality of the product.