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## DETERMINATION OF ACID REQUIREMENT IN SUPERPHOSPHATE MANUFACTURE

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### Abstract

A simple analytical procedure has been developed for determining the acid requirement of phosphate rocks. Results agree with those calculated from the complete analysis of the rock and are also in harmony with plant practice. The method can be used for production control.

A sample of rock is dissolved in mixed hydrochloric and nitric acids, a known quantity of sulphuric acid added and the volatile acids removed by evaporating to apparent dryness on the water bath. The residue is treated with water and titrated with sodium hydroxide solution to pH 4.8. The excess of sulphuric acid over sodium hydroxide measures the acid requirement of the rock. A correction has to be made for the fluorine which remains in the superphosphate but is removed in the course of the analysis.

A similar procedure is used to determine the degree of acidulation of samples of superphosphate.

One of the fundamental figures required by the superphosphate manufacturer is the quantity of acid needed per unit weight of rock. This information is often obtained by adjusting the feed on the plant until the product is satisfactory, but the method has obvious disadvantages.

While it has been claimed, with justice, that acid requirements are dependent on reactivity of rock, mixing, curing time, required conversion, etc., it is still true that under good plant conditions, a close correlation exists between acid requirement and the chemical composition of the rock.

Shoeld and coworkers (5) prepared alignment charts by means of which the acid requirement of a rock is related to its  $P_2O_5$  and  $CO_2$  content and found that this provided a very satisfactory basis of control. A limitation of this method is that any large variations in the  $R_2O_3$  content of the rock are liable to cause serious errors. The method is not applicable to calcined rock.

Other formulae (1,3) based on the CaO or P<sub>2</sub>O<sub>5</sub> content of the rock, or both, are likewise applicable only under certain conditions. Marshall and Hill (4) examined the subject fundamentally and developed a formula for the ideal acid requirement of a rock based on its complete analysis. The present work consists chiefly in the substitution of a convenient analytical procedure for the complete analysis required by Marshall and Hill.

### Basic formulae

$$A_u = 49.0 \times 2 \quad (\text{CaO} + \text{MgO} + \text{MnO} + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{SO}_3)$$

$$A_c = A_u - a \times b \times F$$

where

$A_c$  = Acid requirement (corrected) = No. kg. 100% H<sub>2</sub>SO<sub>4</sub> required, ideally to convert 100 kg rock to superphosphate.

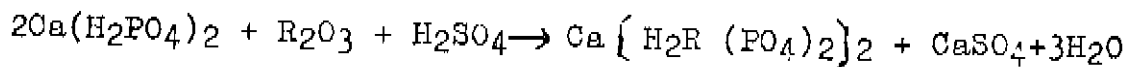
$A_u$  = " " (uncorrected) = no. kg. H<sub>2</sub>SO<sub>4</sub> which would be required were all the fluorine expelled during acidulation.

CaO, MgO etc. = no moles CaO, MgO etc., per 100 kg. rock

a = fraction of fluorine not expelled during acidulation

b = effective equivalent of fluorine remaining in superphosphate.

These formulae have been developed from the following considerations. All components of the rock are expressed as oxides or acids. The mono or di basic metals are acid consumers according to their normal equivalents. Sulphuric acid is a dibasic acid donor. Ideally all the phosphoric acid, apart from that combining with the R<sub>2</sub>O<sub>3</sub>, forms monobasic salts; thus H<sub>3</sub>PO<sub>4</sub> is a donor of 1 equivalent of acid. According to Marshall and Hill (4) R<sub>2</sub>O<sub>3</sub> forms, in cured superphosphate, compounds of the form Ca[H<sub>2</sub>R (PO<sub>4</sub>)<sub>2</sub>]<sub>2</sub> x H<sub>2</sub>O. (The evidence is stronger in the case of iron than of aluminium.) If the acidulation is regarded as a reaction converting all the P<sub>2</sub>O<sub>5</sub> to monocalcium phosphate, followed by a secondary reaction with R<sub>2</sub>O<sub>3</sub>, we have



In effect, then, R<sub>2</sub>O<sub>3</sub> becomes a consumer of 2 equivalents of acid. Any fluorine escaping either as HF or SiF<sub>4</sub> does not enter the acid balance. The fluorine remaining in the superphosphate may be present as fluoride; silicofluoride and perhaps in other forms and will have an effective equivalent of less than one. Silica, whether precipitating or escaping as SiF<sub>4</sub> does not require or donate acid; however some metal silicates may remain undecomposed, but this causes no error if the % Al<sub>2</sub>O<sub>3</sub> etc. refer to the quantities soluble in acid rather than the total present.

### Basis of proposed method.

The basic idea is to add a known quantity of sulphuric acid, in excess of the theoretical, to a sample of the rock, evaporate off any volatile acid and back-titrate with alkali to the neutralisation of the first hydrogen of the phosphoric acid.

The excess of acid over alkali used will give directly the acid requirement ( $A_u$ ) of the rock. It is found that under the conditions of the analysis sulphuric acid does not effect a complete attack on the rock so that a volatile acid must be used to attack the rock, after which the sulphuric acid is added and the volatile acids evaporated off. Nitric acid is required to oxidise organic matter and any

ferrous iron but since this acid is considerably less volatile than hydrochloric an excess of the latter must be added. Fluorine is completely removed as  $\text{SiF}_4$  or  $\text{HF}$ , so that a correction for the fluorine remaining in the superphosphate must be made.  $\text{R}_2\text{O}_3$  precipitates in a form very similar to the tribasic phosphate, which has the same acid consuming value as the double compound which Marshall and Hill found to be present in cured superphosphate. The monosodium phosphate formed in the titration is equivalent to the monocalcium in superphosphate. Since the calcium sulphate has been found to retain some acid it must be completely dissolved prior to the titration. (Note: while the  $\text{HF}$  liberated may attack the glassware to some extent, no appreciable error is to be expected provided that Pyrex glass, which is low in sodium, is used).

Procedure.

Weigh 5 g (w) of rock, add 20 ml  $\text{H}_2\text{O}$ , 30 ml  $\text{HCl}$ , 2 ml  $\text{HNO}_3$  and boil for 5 minutes. Cool, transfer to a 250 ml volumetric flask and dilute to mark. Pipette a 10 ml aliquot into a dish and evaporate to dryness on water bath. Add several ml water and after solids are well moistened add 10 ml 0.5 N  $\text{H}_2\text{SO}_4$ . Evaporate to dryness and leave on water bath for a further 30 minutes. Stir with water, allow to settle and decant the liquid into a 500 ml beaker. Crush the crystals with the aid of a small rubber bung held in a glass tube, slurry with water and decant. Again crush any large crystals remaining, transfer to the beaker, dilute to 300 ml and stir till all the sulphate dissolve. Add 1 ml mixed indicator and titrate with 0.1 N  $\text{NaOH}$ ,  $\text{CO}_2$  free, (a ml). The colour changes from red to blue and the end point is a grey colour free from any red. Let stand for 10 minutes and if necessary add further  $\text{NaOH}$  to restore the colour.

$$A_u = 12.26 \times \frac{50 - a}{w}$$

Mixed indicator: 23 mg Methyl red + 67 mg Brom Cresol Green  
 + 10 mg Cresol Purple + 50 ml Ethanol.  
 Dilute to 100 ml.

Testing the method.

The correct pH for the end point was determined by a titration using a pH meter. The steepest slope was obtained at  $\text{pH} = 4.8$  which corresponds to the grey of the mixed indicator.

Negligible quantities of Cl and F remain after the evaporation. This was tested by combining the solids obtained after evaporating several samples, distilling from  $\text{HClO}_4$  and analysing the distillate.

The formation of neutral ferric phosphate is quantitative under the above conditions. Suitable quantities of ferric ammonium sulphate, p.a., were added to dilute solutions of monosodium phosphate and titrated with sodium hydroxide until the pH returned to 4.8. The titration figure, after allowing for the  $\text{NH}_3$  and  $\text{SO}_3$ , corresponded to an acid consumption of two equivalents per mole  $\text{R}_2\text{O}_3$ . Similar results were obtained when ferric ammonium sulphate was added to solutions of phosphate rock which had already been brought to the correct pH.

The effect of  $\text{Al}_2\text{O}_3$  was tested by dissolving pure aluminium in known quantity of acid and adding aliquots to phosphate solutions as the case of  $\text{Fe}_2\text{O}_3$ . The acid requirement of the  $\text{Al}_2\text{O}_3$  was found to be about 10% lower than theoretical, indicating the formation of somewhat basic phosphates. For the quantities of aluminium normally found in phosphate rocks this difference is not important.

The method was further checked by comparing the experimental value of the  $A_u$  for several rocks with the value calculated from its complete analysis. (The analyses were made on an "acid soluble" rather than "total" basis). In most cases differences of less than 1% were obtained and with the two rocks on which much of the work was conducted the agreement was very close. The method is capable of high precision. A set of 4 parallel determinations often give results differing by no more than 0.2%. The reason is that no separation are involved and random errors are practically confined to those of the volumetric manipulations.

Correction for fluorine.

In order to obtain  $A_c$  from  $A_u$ , a deduction for fluorine must be made. From the analysis of several superphosphate samples Marshall and Hill (4) found that a factor of 0.6 had to be applied to the fluorine remaining in the superphosphate.

H. Delomenie (2) analysed various samples of superphosphate for water soluble and insoluble fluorine. If it can be assumed that the former consist only of silicofluorides and the latter of fluorides, the factors calculated from his results range from 0.67 to 0.93.

Commercial samples of superphosphate were analysed by the authors and gave factors of 0.8 to 0.9 for fluorine on the basis of water soluble and insoluble fluorine.

A factor of 0.80 has been accepted tentatively for the fluorine remaining in the superphosphate. For a plant in which 30% of the fluorine is evolved during acidulation, the overall correction becomes:

$$A_u - A_c = \frac{49}{19} \times 0.80 \times \frac{70}{100} = 1.44 \times \% F \text{ in rock}$$

Degree of acidulation of superphosphate

A method is sometimes required which will determine the degree of acidulation of a sample of superphosphate and which is independent of the degree of curing of the sample.

The same procedure as described above may be employed. It is preferable, however, to use an 8 g sample of super and to acidulate with 10 ml of a weaker (0.1 N)  $H_2SO_4$  solution. the formulae then become:

$$\text{Acid deficiency of super } (A_u) = 12.3 \times \frac{10-a}{w}$$

$$\text{Correction for fluorine} = 2.07 \times \% F \text{ in superphosphate.}$$

Acid Balance in superphosphate.

Samples of superphosphate were tested by the conventional methods for free acid and water insoluble  $P_2O_5$  and also by the above method. The results were as follows:

Sample No.	1	2	3	4
Free acid (24 hrs curing) $P_2O_5\%$	3.5	4.8	5.1	5.1
Water insoluble $P_2O_5\%$	1.9	0.7	1.1	1.2
$A_c$	+0.3	-2.5	-2.0	-1.6
$A_c$ , expressed as kg $P_2O_5/100$ kg rock	+0.4	-3.6	-2.9	-2.3
2 x Water insol. $P_2O_5$ - Free Acid $P_2O_5$	+0.3	-3.4	-2.9	-2.7

The correlation between the two approaches is good, although the formula used in the last line is admittedly only an approximate one.

Acid requirement figures for the rock used on the plant of Fertilisers and Chemicals Ltd., Haifa agreed with production data within the limits of accuracy of plant measurement (about 2%).

Other applications of the method.

The method has been found particularly useful as an aid to the valuation of various samples obtained in the course of experiments on the beneficiation of phosphate rock. The ratio  $R = A/\% P_2O_5$  was used in the calculations rather than A itself, since the former determines the quantity of acid required to produce 1 ton of  $P_2O_5$  in the form of superphosphate. From the quantities of,  $\% P_2O_5$  and R, a sound appraisal of the value of the rock could be made. It seems possible that these values could be used with advantage generally in the valuation of commercial rocks.

For similar reasons the method may prove useful to the phosphate mining industry.

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