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# THE INTERNATIONAL SUPERPHOSPHATE MANUFACTURERS' ASSOCIATION

AGRICULTURAL COMMITTEE  
1. AVENUE FRANKLIN D. ROOSEVELT  
PARIS (8<sup>e</sup>)  
TEL. BALZAC 57-25

CENTRAL OFFICE  
32 OLD QUEEN STREET  
LONDON, S.W. 1.  
TEL. WHITEHALL 7262

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### SUPERPHOSPHATE PRODUCTION. THE INFLUENCE OF VARIOUS FACTORS ON THE SPEED OF REACTION AND THE COMPOSITION OF THE PRODUCT

By R.J. Nunn, B.Sc., A.R.I.C., and T.P. Dee, B.Sc., F.R.I.C.  
M.I. Chem. E., of Fisons Research Department.

The factors which determine the speed of reaction between phosphate rock and sulphuric acid to make superphosphate, and the composition of the product are as follows:

- 1) The nature of the phosphate rock.
- 2) The degree of fineness to which it is ground.
- 3) The concentration of the sulphuric acid.
- 4) The proportions in which acid and rock are mixed, which may be stated in lb H<sub>2</sub>SO<sub>4</sub> per 100 lb of phosphate rock.
- 5) The temperature of reaction.

The phosphate rock used throughout this investigation was that obtained from the Kourigha deposit in Morocco, usually referred to in this country simply as Moroccan phosphate. This material we find to have a very constant chemical analysis. The fineness of grinding of the rock, the concentration of the acid, and the acid/rock ratio, have been varied over considerable ranges.

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

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

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

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

For many of the experiments, it was sufficient to analyse the products by the ordinary methods of chemical analysis used in the fertilizer industry. Such methods however are not suitable when, for research purposes, the extent of reaction is to be measured during its early stages. It is well known that the reaction which takes place in the superphosphate after it has left the den is a slow one, so that even after say 3 weeks there are considerable proportions of free acid and of unreacted phosphate rock still present. When analysis is preceded by extraction of the superphosphate with water, reaction between the acid and previously unreacted rock is comparatively rapid after the superphosphate is dispersed in the water. Thus the result of the analysis, while useful for comparative or practical purposes, does not indicate the precise composition of the superphosphate.

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

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

Having separated off the free acids in this way, the solution could be analysed by normal methods for the proportions of the two acids. The solid residue from the extraction was treated with a saturated solution of sodium oxalate at boiling point to extract the monocalcium phosphate as sodium dihydrogen phosphate, the proportion of which could then be determined. The solid was further extracted with neutral ammonium citrate solution, in order to remove dicalcium phosphate. The phosphate remaining in the solid residue was determined.

### Series 1.

In this series of experiments, the fineness of grinding of the phosphate rock was fixed, and may be defined by saying that 68% of the material passed through a 100 mesh B.S. sieve; a more detailed sieve analysis is given later. Four concentrations of sulphuric acid were used, namely 70, 60, 55 and 45%  $H_2SO_4$ ; each of these concentrations was used in acid/rock ratios of 60, 55, 50 and 45 gms  $H_2SO_4$  per 100 gms of phosphate rock. In these experiments the organic solvent technique was not used, and the table of results given here shows only the analysis of the product after 21 days storage and its physical condition at that time. Mixing was carried out at a temperature which is shown in the table, and was generally continued until a fluidity was reached which was equal to that obtained with this rock in 3 minutes when used with acid of 70%  $H_2SO_4$  in an acid/rock ratio of 60 gms  $H_2SO_4$  per 100 gms of phosphate rock. The times required are also shown in the table; in three cases the fluidity had not fallen to the desired value in 15 minutes, but mixing was stopped at that time.

Figs. 1 and 2 illustrate the results. From the former it is seen that, with any one of the ratios (gms  $H_2SO_4$  per 100 gms rock) used in the experiments, 70%  $H_2SO_4$  gives the best results of the concentrations tried. Fig. 2 shows that, if one wishes to have a w.sol./total  $P_2O_5$  value over about 85%, one must be prepared to put up with a high proportion of free acid in the product; also that, for a given w.sol./total  $P_2O_5$  percentage, the free acidity of the product rises sharply as the concentration of sulphuric acid used is lowered from 70%  $H_2SO_4$ .

In the table of results, attention may be drawn to the values for the moisture contents of the products. Losses at 100°C include some water of crystallisation, whereas those at 50°C are believed to represent fairly accurately the free water contents. The difference between the two values increases slowly between concentrations of 70% and 55%  $H_2SO_4$ , then sharply as the concentration falls to 45%  $H_2SO_4$ . At this concentration it is probable that a high proportion of the calcium sulphate in the superphosphate is present as gypsum, which accounts for the good physical condition of material made with acid of this concentration and acid/rock ratios of 45 and 50. At the higher concentrations, calcium sulphate will be formed mainly as anhydrite and hemihydrate.

At the time of acute acid shortage, it was thought that some saving might be achieved by using low acid/rock ratios, making superphosphate containing a high proportion of dicalcium phosphate, and selling the product on the basis of the proportion of  $P_2O_5$  soluble in ammonium citrate solution. The experimental results however showed only a rather small difference between citrate-soluble and water-soluble  $P_2O_5$ , which did not increase as the acid/rock ratio fell.

Taking into account other experimental values, some obtained on the plant, we consider the following table represents roughly the results to be expected in a continuous plant using Moroccan rock ground for about 70% to pass a 100 mesh B.S. sieve, and acid of 70% H<sub>2</sub>SO<sub>4</sub>:

<u>Acid/rock ratio.</u> Lb. H <sub>2</sub> SO <sub>4</sub> per 100 lb. rock.	W.sol./total P <sub>2</sub> O <sub>5</sub> (%) in 3-week superphos.	<u>Quantities (tons) for one ton w.sol. P<sub>2</sub>O<sub>5</sub>.</u>	
		Rock	H <sub>2</sub> SO <sub>4</sub> (100%)
50.0	72.0	4.18	2.09
52.5	76.2	3.95	2.08
55.0	81.0	3.72	2.05
57.5	86.3	3.49	2.01
60.0	91.0	3.31	1.99
62.5	93.5	3.22	2.01
65.0	94.7	3.18	2.07

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

### Series 2.

In this series, the main object was to study the speed of the reaction between phosphate rock and sulphuric acid, but the chemical composition of the products was also determined. The acid/rock ratio was fixed at 60 gms H<sub>2</sub>SO<sub>4</sub> per 100 gms of rock throughout the series, and there were two sub-series, one with acid of 70% and the other with acid of 76% H<sub>2</sub>SO<sub>4</sub>. In each sub-series, the fineness of grinding of the rock varied to give from 21 to 93% passing a 100-mesh sieve.

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

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

The results are conveniently represented by plots of the logarithm of time (in minutes plus one) against percentages of the initial P<sub>2</sub>O<sub>5</sub> present as free acid, monocalcium phosphate, water-soluble phosphate and insoluble P<sub>2</sub>O<sub>5</sub>. The percentage of the initial H<sub>2</sub>SO<sub>4</sub> present is also plotted (Figs 3 to 11).

It is seen that the general course of the reaction is as follows. While free sulphuric acid is present, a little monocalcium phosphate is formed but the principal reaction is the formation of free phosphoric acid. With the disappearance of sulphuric acid (which, with rock of the usual fineness of grinding and acid of 70%  $H_2SO_4$ , takes place in 30 to 40 minutes) formation of free acid  $P_2O_5$  ceases. This free acid now forms 40 to 50% of the total  $P_2O_5$ , and further reaction is between this and previously unreacted rock, mainly to form monocalcium phosphate. It is seen that this reaction gradually loses speed, and that, with rock of the usual fineness of grinding, an almost stationary state has been arrived at in three weeks, with substantial proportions of free acid and insoluble phosphate still present. The figures shown for water-soluble  $P_2O_5$  represent, in each case, the sum of the acid  $P_2O_5$  and the monocalcium phosphate. The gradual slowing down of the reaction between phosphoric acid and phosphate rock is largely due to the coating of the residues of the original rock particles with calcium sulphate.

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

In Fig. 12, the time for disappearance of sulphuric acid is plotted against the fineness of grinding of the rock. (In drawing the curves, the point obtained with acid of 76%  $H_2SO_4$  and rock ground for 51% to pass 100 mesh has been ignored). It is suggested that this graph gives the minimum fineness of grinding of Moroccan rock for a plant of which the time of retention is known. For instance, with a Broadfield plant which retained the material 3 minutes in the mixer and 30 minutes in the den, and with acid of 70%  $H_2SO_4$ , it should suffice to grind so that about 73% passed a 100 mesh B.S. sieve (always assuming that the sieving graph is similar in slope to those of the samples of rock used in these experiments).

Other conclusions from this series of experiments are 1) that reaction is more rapid with acid of 70 than with acid of 76%  $H_2SO_4$ , and 2) that 'curing' time can be reduced with finer grinding.

The table gives both the experimental conditions, and the chemical analyses of the products (by the usual methods) after 3 weeks storage. The analysis is seen to vary but little with the fineness of grinding of the rock and concentration of acid, with the important exception that both w.sol. and available  $P_2O_5$  percentages were exceptionally high with the finest rock.

### Raw materials.

The acid was initially of 76%  $H_2SO_4$ , produced in a chamber plant. Except where used at this concentration, it was diluted with water and used at the adiabatic temperature of dilution.

The Moroccan rock used was of the following chemical and sieve analyses:

Sample	Cumulative percentage through B.S. mesh No.			Mean particle size (microns)	Total $P_{2O_5}$ (%)
	170	100	60		
Series 1	44	68	92	109	33.2
Series 2					
1	5	21	70	215	33.6
2	27	51	91	150	33.2
3	47	70	93	100	33.8
4	56	93	100	75	34.0

For ease of comparison with other sieve analyses, the key figures chosen are the cumulative percentage through a 100-mesh B.S. sieve, together with the cumulative percentages through 60 and 170 mesh, to indicate the 'slope' of the curve. The mean particle size is also given. Values were determined with nine consecutive freshly-checked sieves, and were plotted as shown in Fig. 13, smooth curves drawn, and the data required taken from these.

### Experimental details.

The reaction vessel (Fig. 14) consisted of a stainless steel beaker of one litre capacity placed concentrically in another of  $2\frac{1}{2}$  litres capacity. The space under and around the inner beaker was packed with asbestos wool, in which was embedded a 400 watt heating element, the top of the annular space being sealed with a cement made with litharge and glycerine. The heater was only needed when the time of mixing exceeded five minutes, and was then controlled by a Sunvic Energy Regulator.

The stirrer was of Monel, with three blades, and was driven by a constant-speed electric induction motor, geared to give 70 revs/min.

For each experiment, the required amount of sulphuric acid was placed in the mixer, the stirrer was started, and 400 gms phosphate rock were added. As the fluidity of the slurry decreased, more of the power of the stirrer was transferred to the turntable to which the reaction vessel was fastened. This stretched the coil spring, and a pointer attached to the turntable moved over a scale. The point was found on the scale which was reached in three minutes when acid of 70%  $H_2SO_4$ , at  $35^\circ C.$ , was used with rock ground to give 70% through a 100 mesh B.S. sieve, in the ratio 60 gms  $H_2SO_4$  per 100 gms rock. Other mixtures were stirred until the indicator came to this same point on the scale.



Method of separating various P<sub>2</sub>O<sub>5</sub> fractions from a sample of superphosphate.

Dioxan and acetone are dried by standing over anhydrous calcium chloride. A mixture of equal volumes of the two solvents is prepared. For each determination, 25 mls of the mixture is placed in a weighing bottle, the ground glass stopper of which has been greased to minimise evaporation. The bottle, with its contents, is weighed. A sample of the superphosphate of about 5 gms weight is taken, and immediately immersed in the solvent. The bottle is then well shaken to extract the free acid, and again weighed.

The mixture is filtered, using a Whatman No. 12 filter paper, and the residue is washed with 25 ml acetone-dioxan mixture, and then with 75 ml. acetone. The filtrate is diluted with 100 ml distilled water, neutralised with approximately normal caustic soda to B.D.H. 4.5 indicator, and evaporated nearly to dryness to remove the organic solvent. 25 ml concentrated nitric acid is then added, and the solution boiled for ten minutes, diluted with 80 ml distilled water, and again boiled. The solution is filtered through a paper pulp pad into a 250 ml graduated flask. Aliquots of this solution are analysed for phosphate and sulphate, giving measures of the free acids in the sample.

The residue is transferred, together with the filter paper and weighing bottle, to a 600 ml beaker, and boiled for five minutes with 200 ml of a saturated solution of sodium oxalate. The solution is then filtered through a Whatman No. 12 paper into a 100ml graduated flask, the residue being washed with hot water. An aliquot of this solution is analysed for phosphate, the result indicating the monocalcium phosphate content of the sample.

The residue is transferred, together with filter paper, to a conical flask containing 100 ml neutral ammonium citrate solution (A.O.A.C.) at 65°C. Digestion at this temperature is continued for one hour, the flask being shaken at intervals of five minutes. The solution is then filtered through a Whatman No. 5 paper on a Buchner funnel, the residue being washed with water at 65°C until the volume of filtrate measures 350 ml.

After ignition of the filter paper, the residue is dissolved in 25 ml concentrated nitric acid, boiled for ten minutes, diluted with 80 ml distilled water, and boiled again. The solution is filtered through a paper pad into a 250 ml. graduated flask. An aliquot of this solution is analysed for phosphate, giving the citrate-insoluble P<sub>2</sub>O<sub>5</sub> content of the sample.

Analytical methods.

(1) Samples Extracted with Organic Solvent.

(a) Phosphate.

This was determined by a single precipitation as ammonium phosphomolybdate, followed by a single precipitation of magnesium ammonium phosphate, and ignition to magnesium pyrophosphate, the details being as follows.

Slight excess of concentrated ammonium hydroxide was added to an aliquot of the solution, and the precipitate just dissolved in concentrated nitric acid. The solution was diluted to 100 ml., heated almost to boiling, and 70 ml ammonium molybdate solution (A.O.A.C.) added. The solution was allowed to stand for one hour at 65°C, tested for complete precipitation, and filtered through a Whatman No. 7 paper, the residue being washed with 1% nitric acid. The precipitate was dissolved in a few drops of concentrated ammonium hydroxide and hot water. The solution was neutralised with concentrated hydrochloric acid to bromothymol blue indicator, and 30 ml magnesia mixture added dropwise from a burette, while the solution was continuously stirred. The solution was allowed to stand for four hours, tested for complete precipitation, and then filtered through a Whatman No. 40 paper. The precipitate was washed with 2% ammonium hydroxide, and ignited at 1000°C. It was then weighed.

#### (b) Sulphate.

An aliquot from the free acid solution was evaporated almost to dryness three times with 25 ml concentrated hydrochloric acid, to expel nitric acid. The solution was neutralised with concentrated ammonium hydroxide to methyl orange indicator, acidified with a few drops of concentrated hydrochloric acid, diluted to 200 ml., heated almost to boiling point, and 10 ml of 5% barium chloride solution added dropwise from a burette. The solution was allowed to stand for one hour, tested for complete precipitation, and filtered through a Whatman No. 42 paper. The precipitate was washed with hot water, ignited at 600°C, and weighed.

#### (2) Other Samples.

##### (a) Total Phosphate.

5 gms of the sample was boiled with 25 ml concentrated nitric acid for ten minutes, diluted with 80 ml. distilled water, and again boiled. The solution was filtered through a pulp pad into a 250 ml. graduated flask. A 25 ml. aliquot of this solution was analysed as in (1).

##### (b) Water-soluble Phosphate.

10 gms of sample was shaken with 400 ml distilled water in a Stohman flask for thirty minutes. The solution was made up to 500 ml., and filtered through a Whatman No. 2 paper. A 25 ml. aliquot of the solution was boiled with 10 ml. concentrated nitric acid to convert all phosphate to the ortho form. The estimation was then carried out as in (1).

##### (c) Citrate-insoluble Phosphate.

1 gm of sample was placed on a Whatman No. 42 paper, and washed with 250 ml distilled water. The residue and filter paper were transferred to a 250 ml conical flask, containing 100 ml. neutral ammonium citrate solution (A.O.A.C.) at 65°C. This temperature was maintained for one hour, the flask being shaken at five minute intervals; then the extract was filtered through a Whatman No. 5 paper on a Buchner funnel. The residue was washed with water at 65°C until the volume of filtrate was 350 ml. The filter paper was ignited, and the residue dissolved in 15 ml concentrated nitric acid; the solution was boiled for ten minutes, diluted with 80 ml distilled water, boiled again, and filtered through a pulp pad into a 400 ml beaker. The solution was analysed for phosphate as in (1).

(d) Free Acid.

This was determined on a 50 ml. aliquot of the water-soluble phosphate solution, which was titrated against decinormal sodium hydroxide to B.D.H. 4.5 indicator.

(e) Moisture content.

A 5 gm sample was placed on a Petri dish, and heated in an oven for four hours at 100°C. The loss in weight was determined.

(f) Free Water.

A 5 gm sample was placed on a Petri dish and heated to constant weight in a vacuum oven at 50°C. The loss in weight of the sample was determined.

The thanks of the authors are due to the Directors of Fisons Ltd. for permission to give this paper and to make known the results obtained in the experiments, and to colleagues who have assisted in the work.

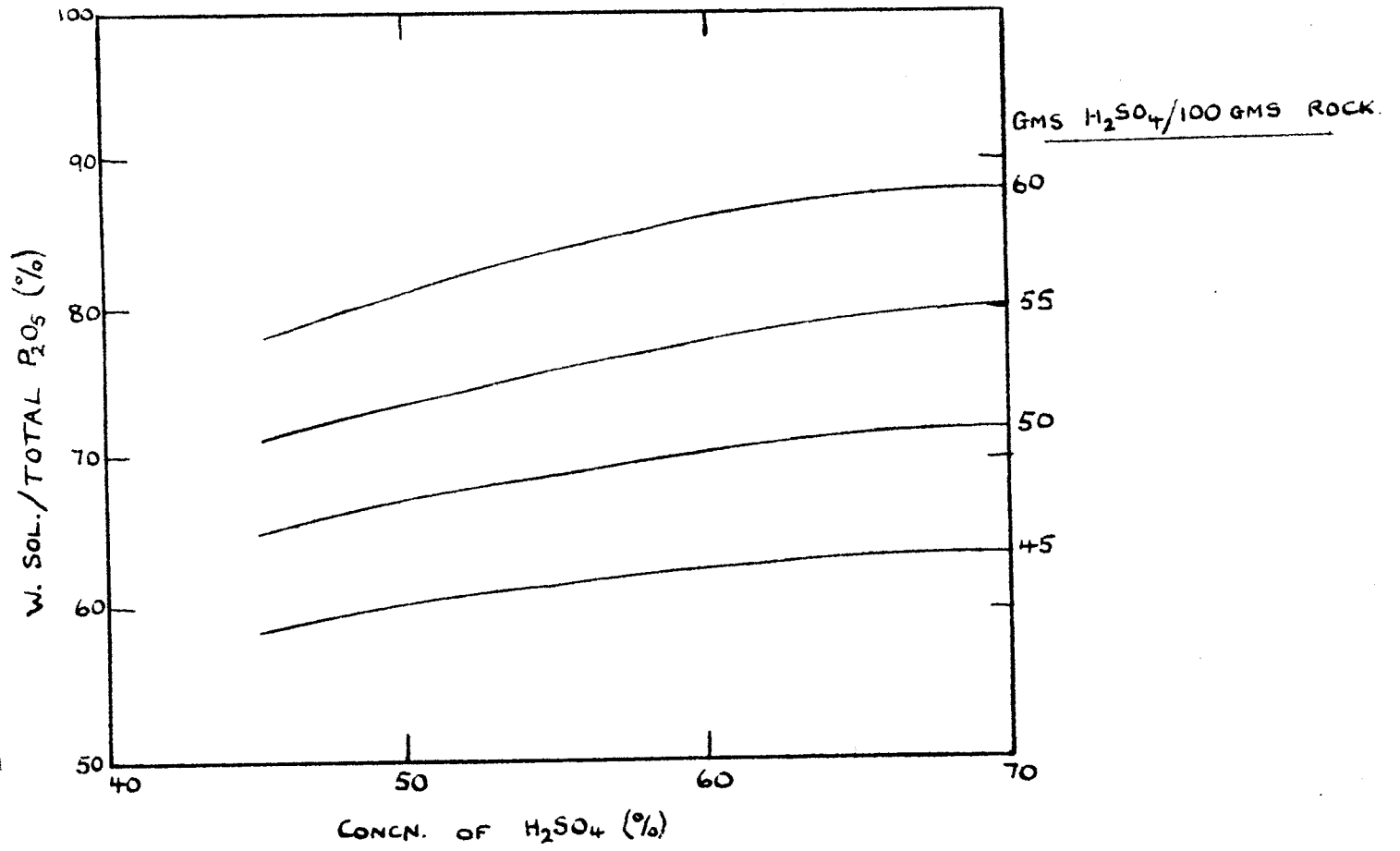


FIG. 1.

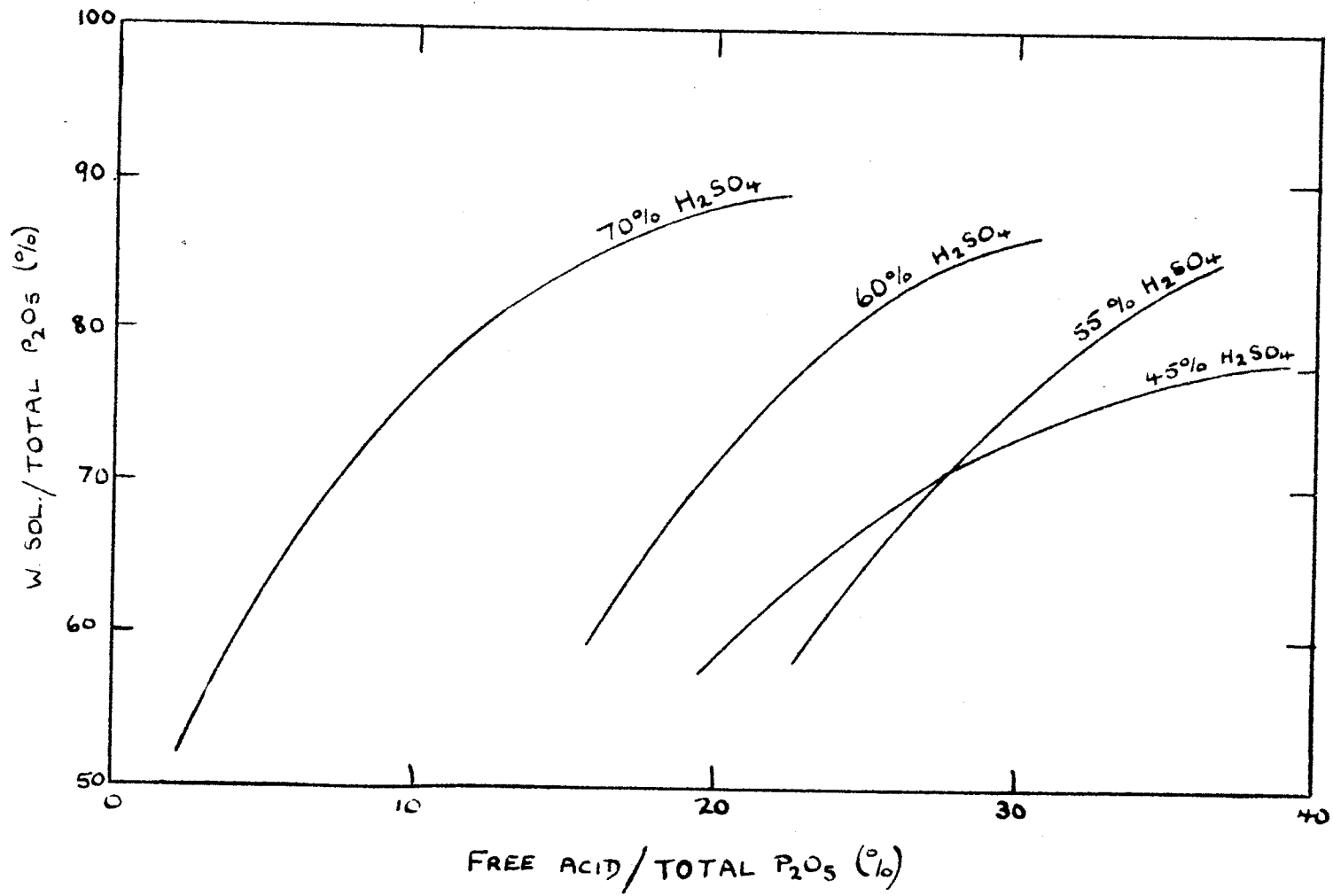


FIG 2

REACTION OF 70% SULPHURIC ACID WITH MOROCCO PHOSPHATE (22% THROUGH 100 B.S.S)

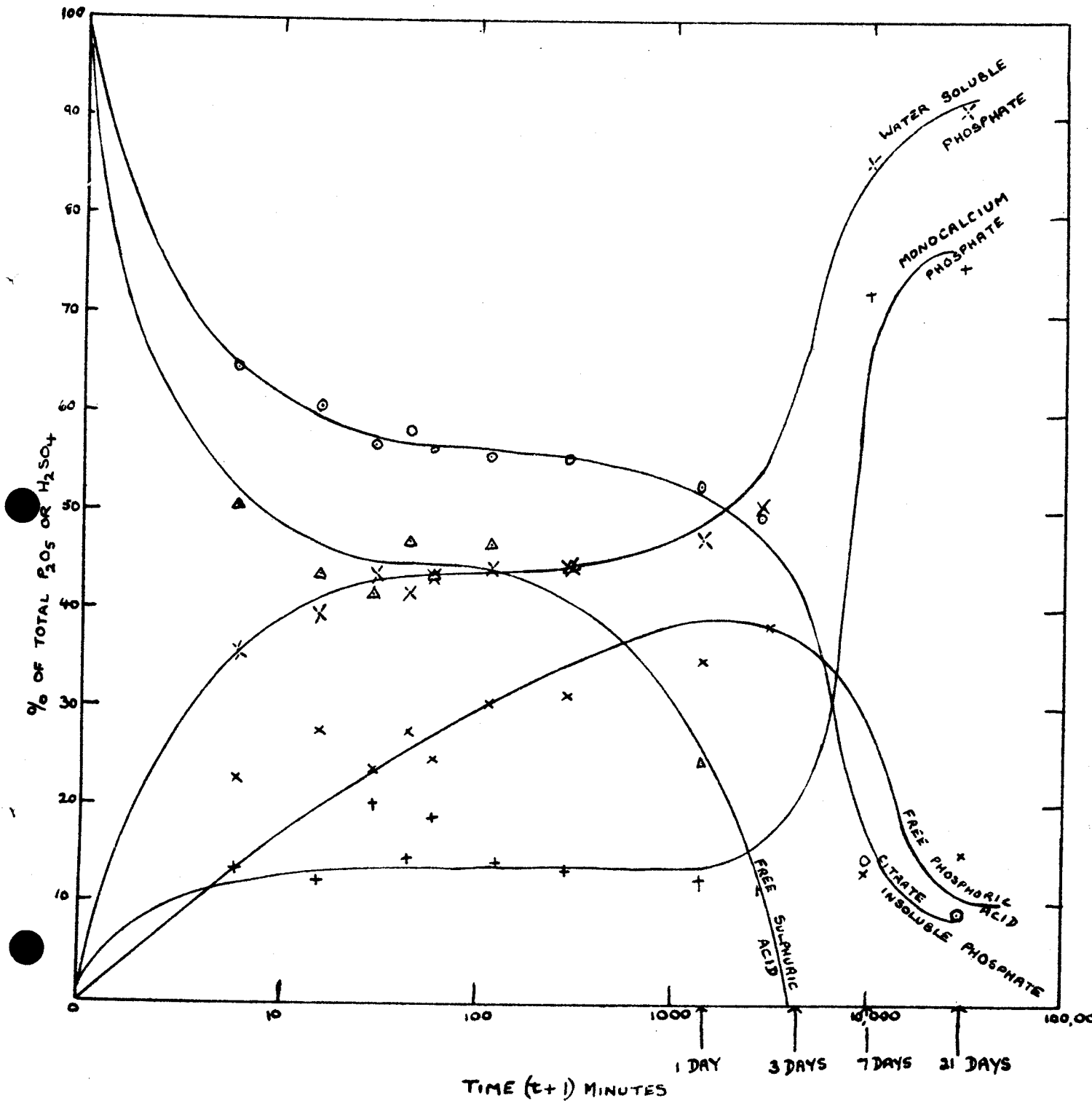


FIG. 3.

REACTION OF 70% SULPHURIC ACID WITH MOROCCO PHOSPHATE (51% THROUGH 100 B S S.)

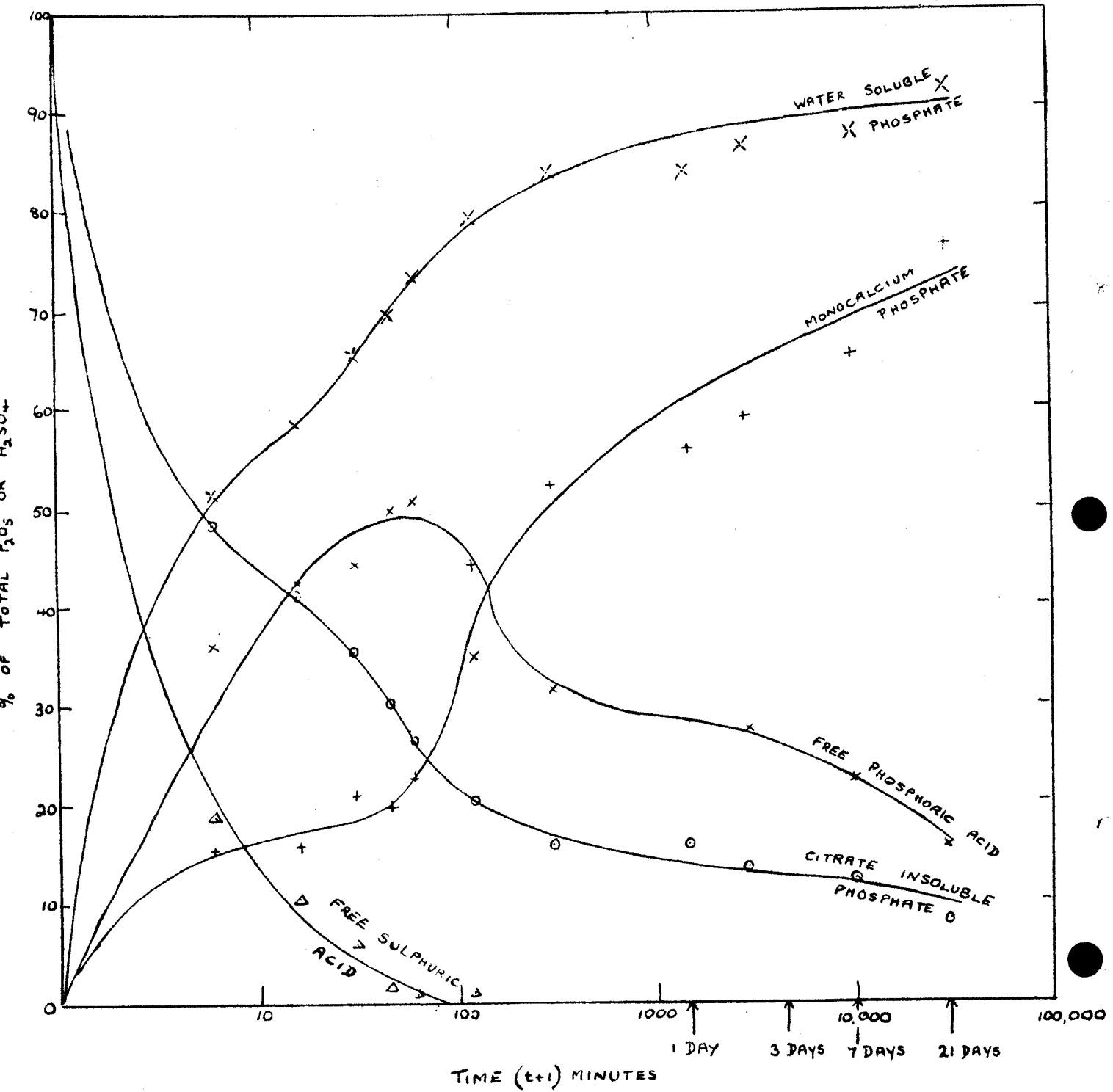


FIG. 4.

REACTION OF 70% SULPHURIC ACID WITH MOROCCO PHOSPHATE (70% THROUGH 100 BSS)

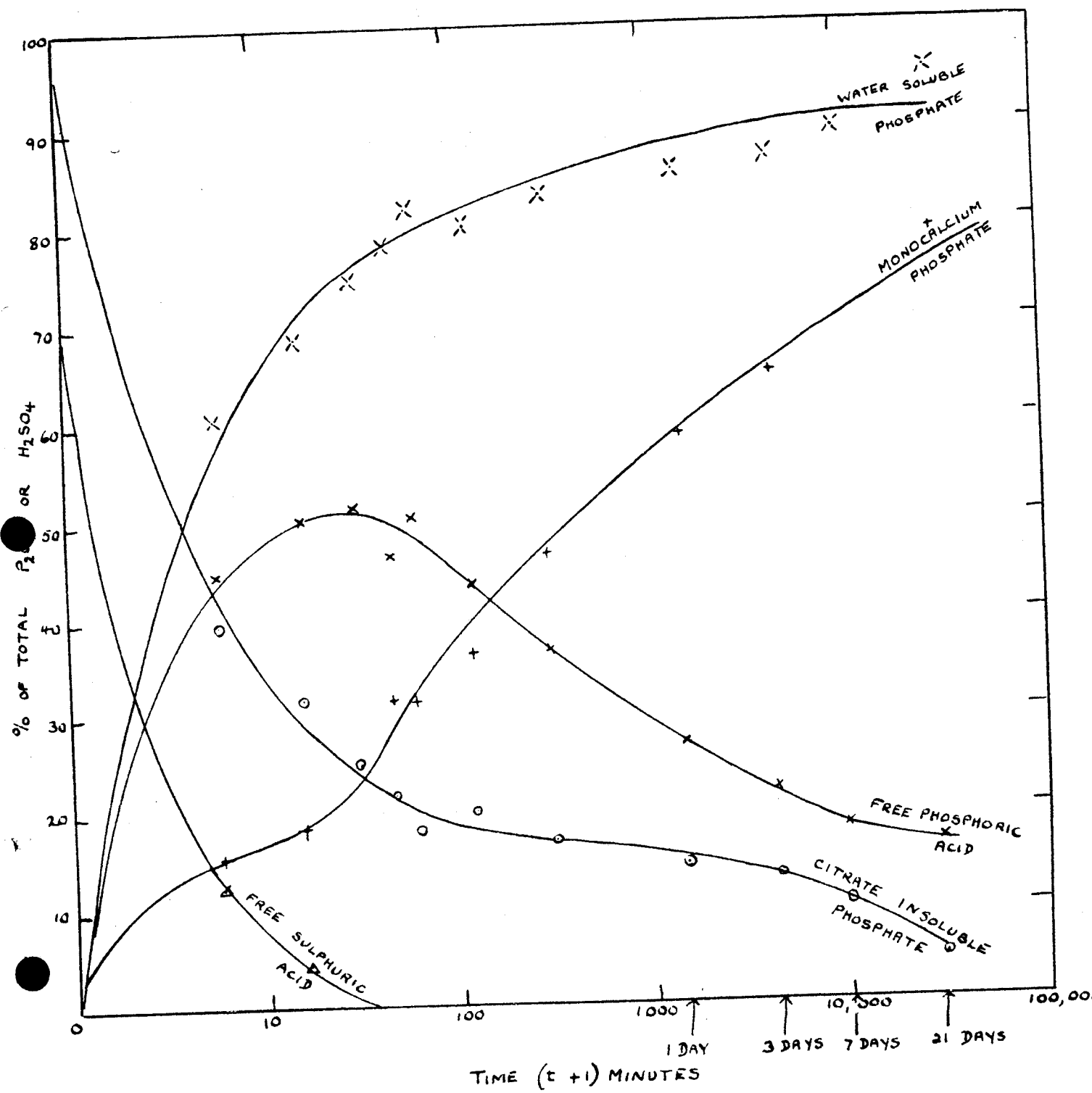


FIG. 5.



REACTION OF 70% SULPHURIC ACID WITH MOROCCO PHOSPHATE (93% THROUGH 100 B.S.S.)

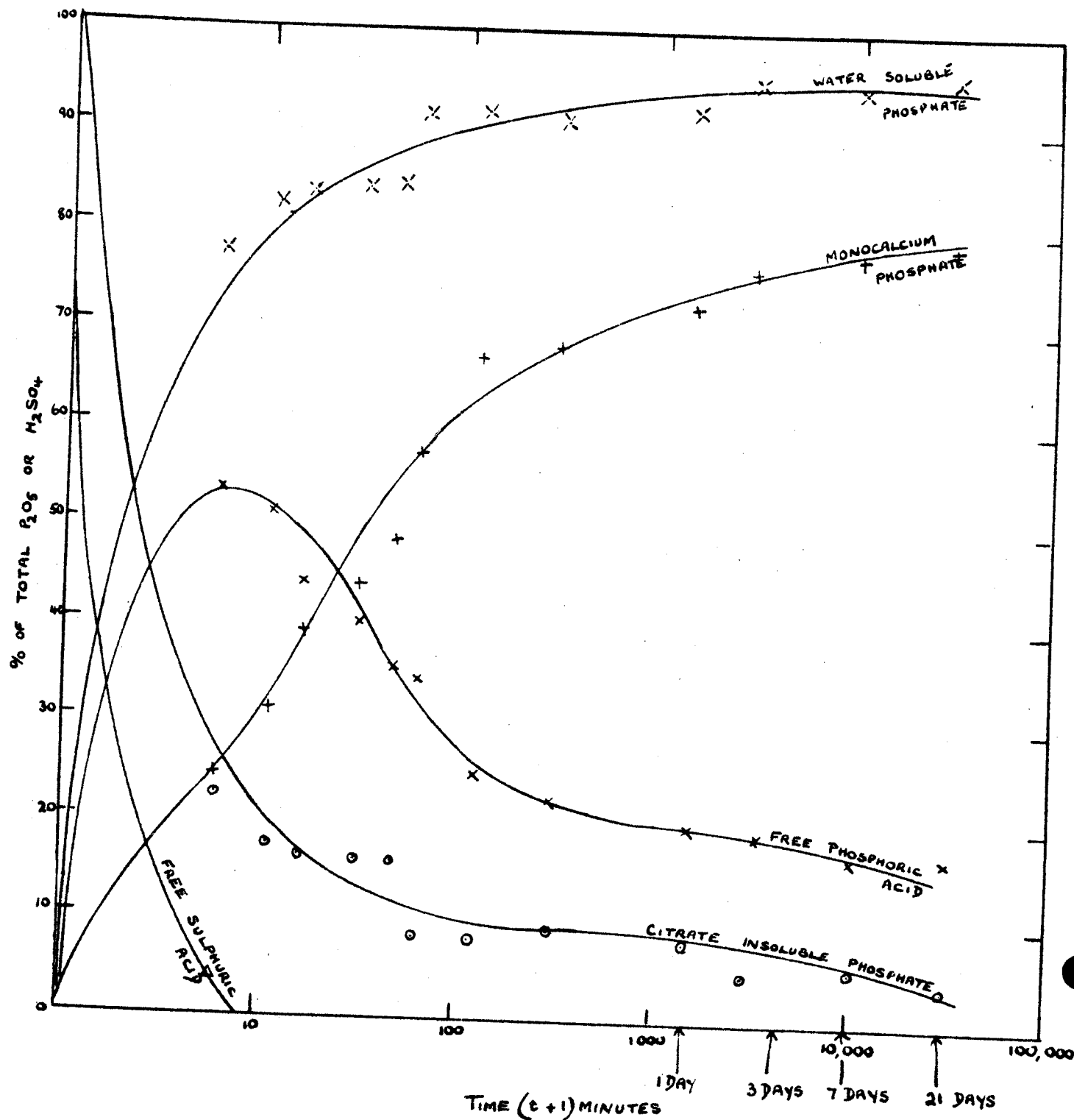


FIG. 6.

REACTION OF 76% SULPHURIC ACID WITH MOROCCO PHOSPHATE (22% THROUGH 100 B.S.S.)

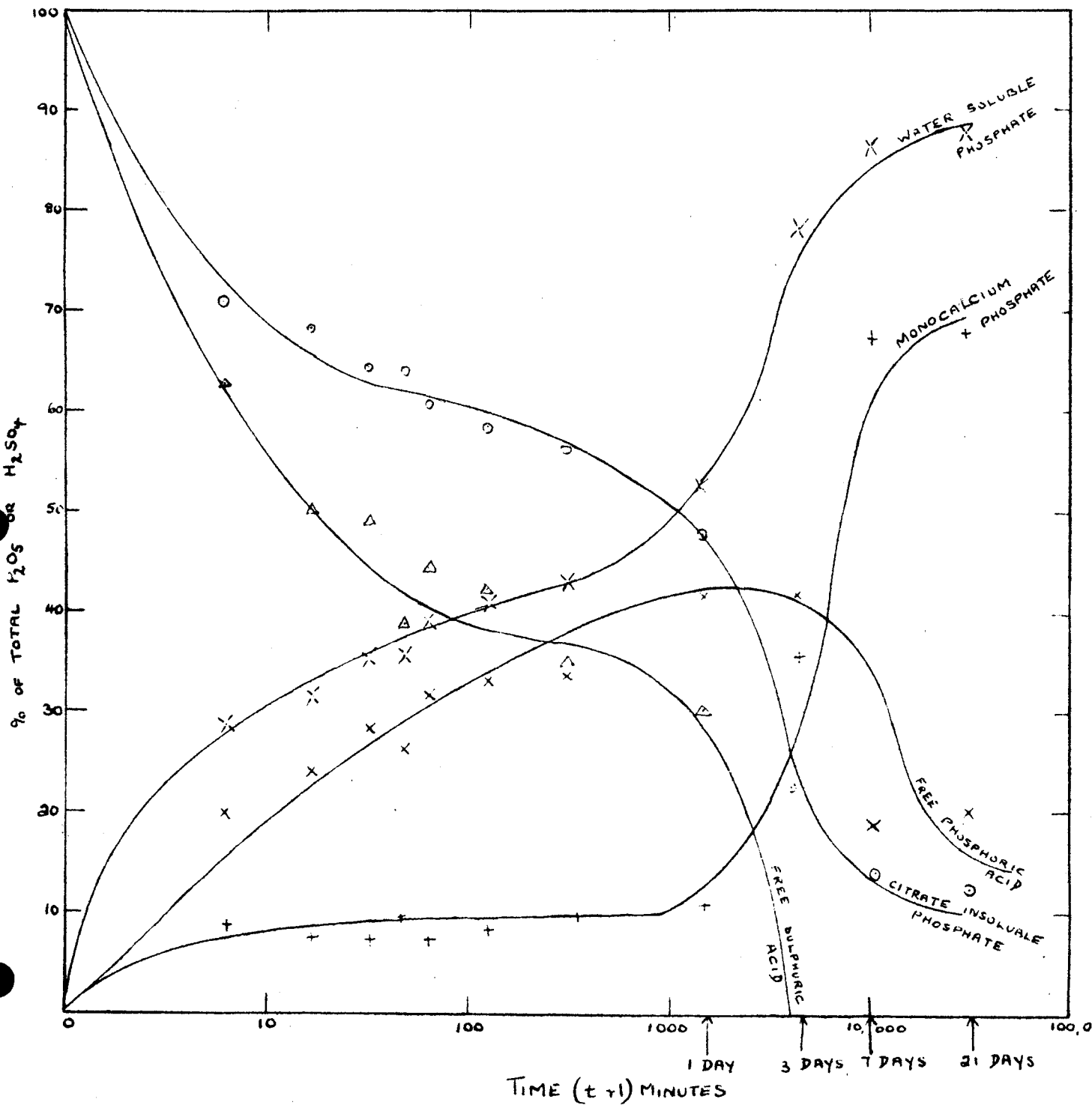


FIG. 7.

REACTION OF 76% SULPHURIC ACID WITH MOROCCO PHOSPHATE (51% THROUGH 100 BSS)

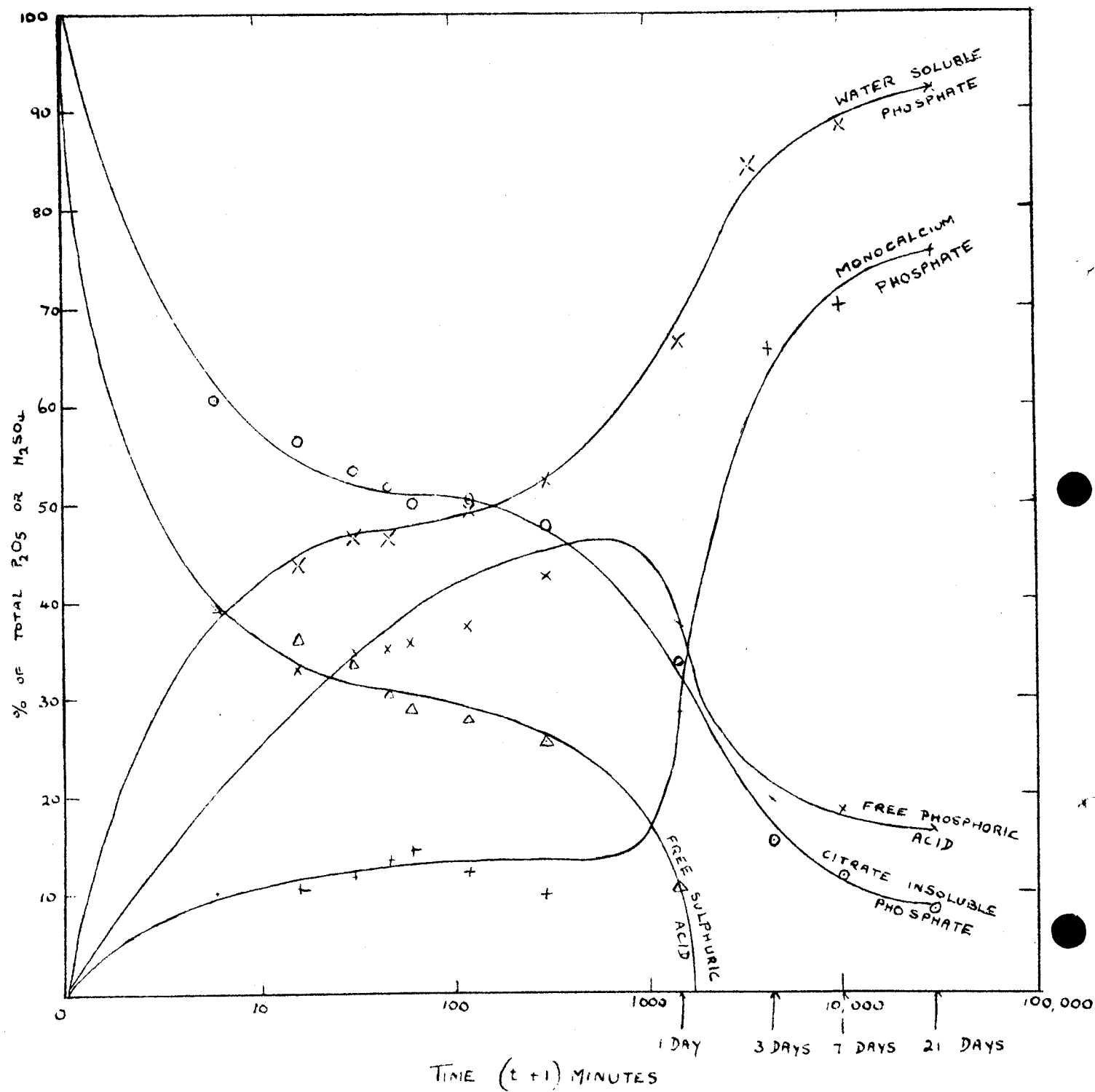


FIG. 8.

REACTION OF 76% SULPHURIC ACID WITH MOROCCO PHOSPHATE (70% THROUGH 100 D.S.S.)

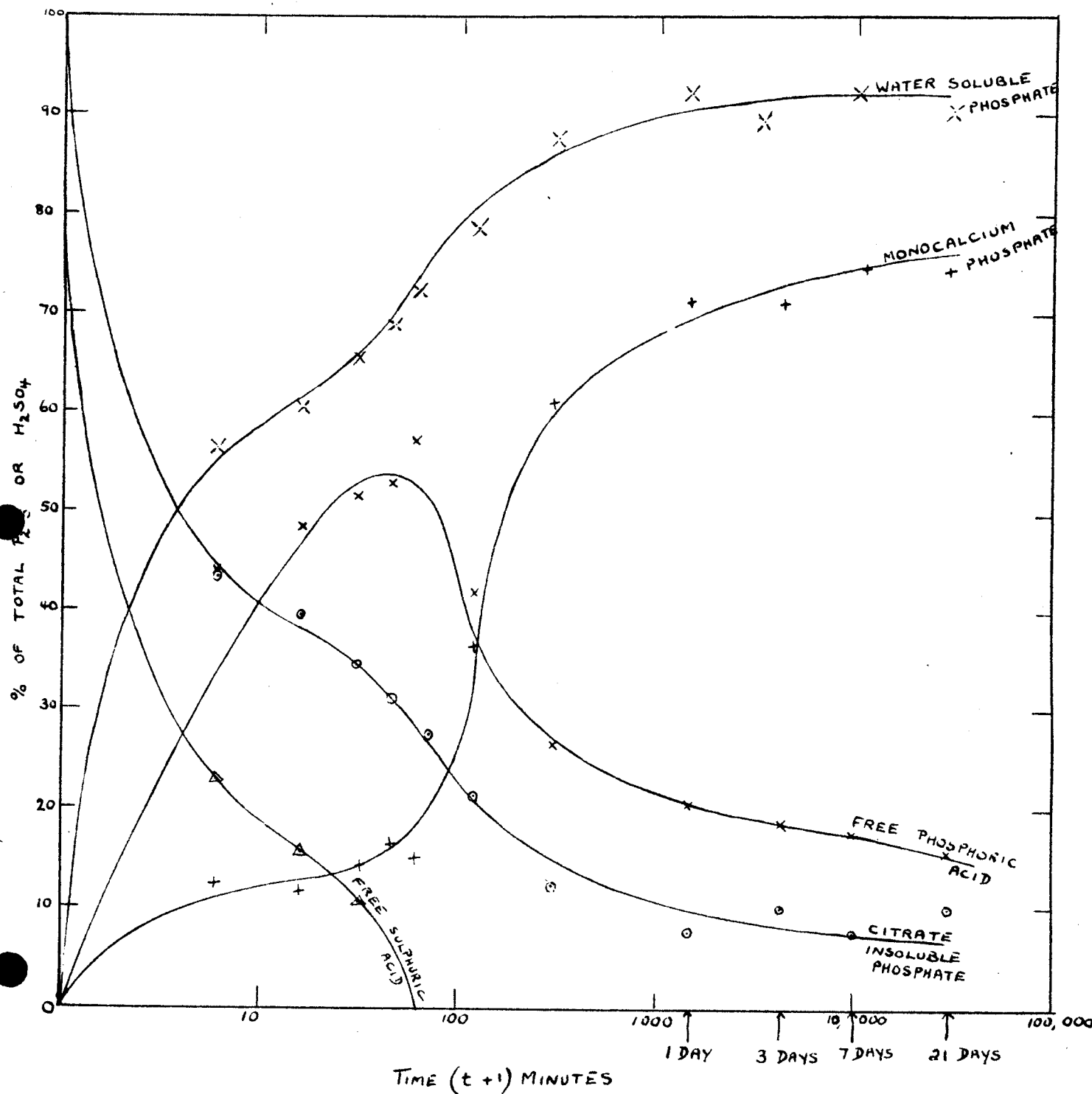


FIG. 9.

REACTION OF 76% SULPHURIC ACID WITH MOROCCO PHOSPHATE (93% THROUGH 100 B.S.S.)

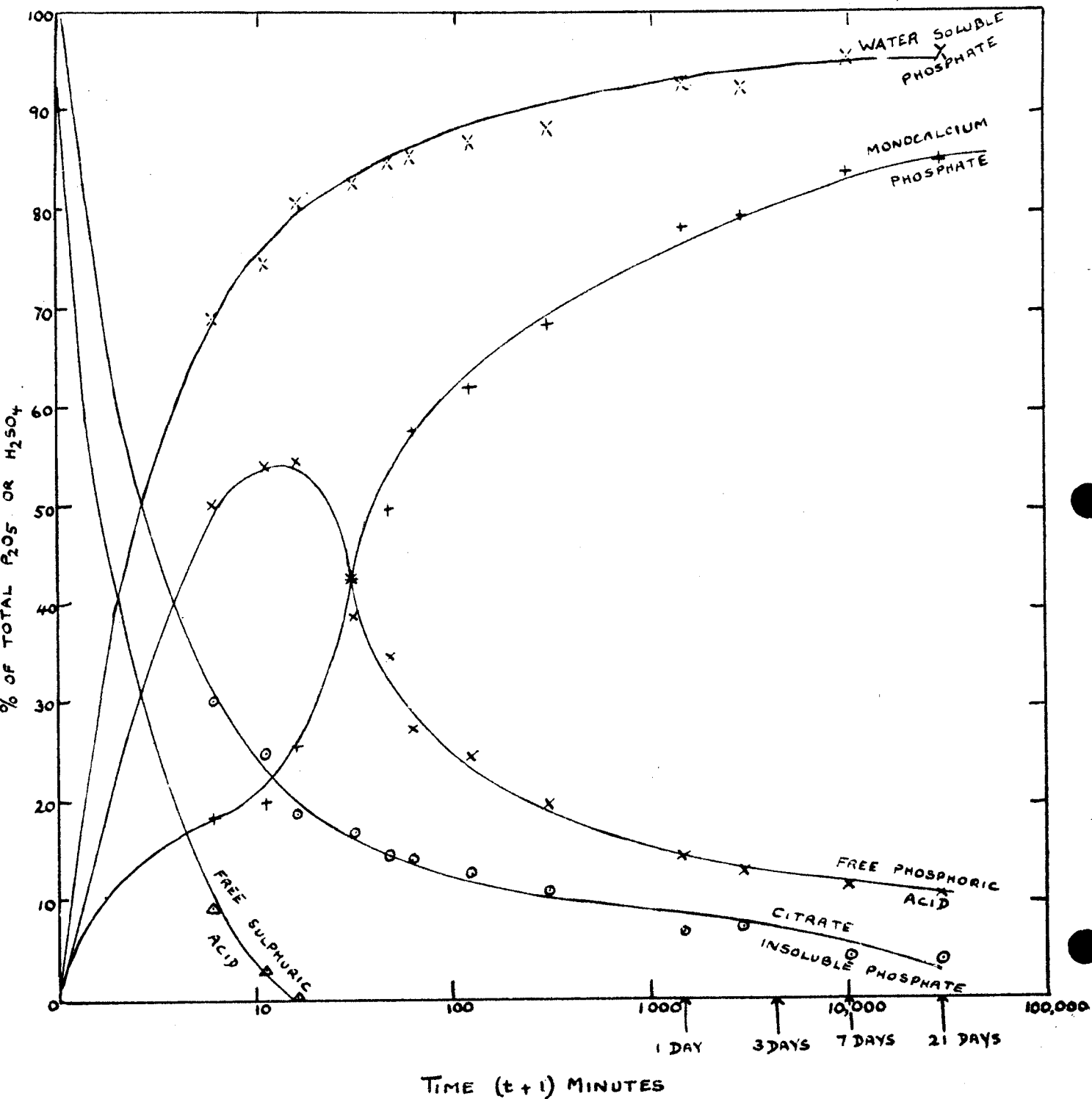


FIG. 10.

SAMPLES TAKEN FROM CONTINUOUS BROADFIELD PLANT.

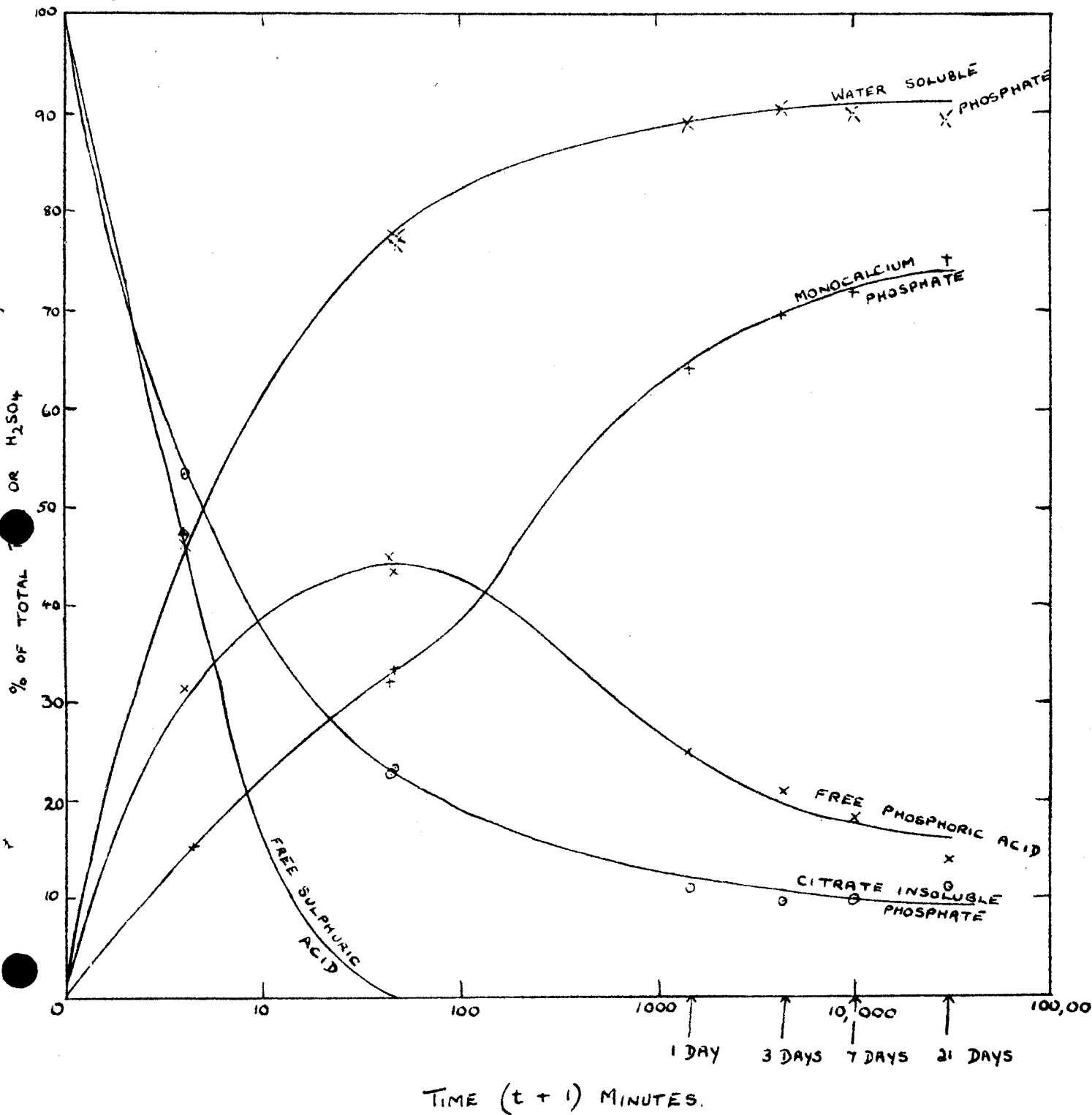


FIG 11.

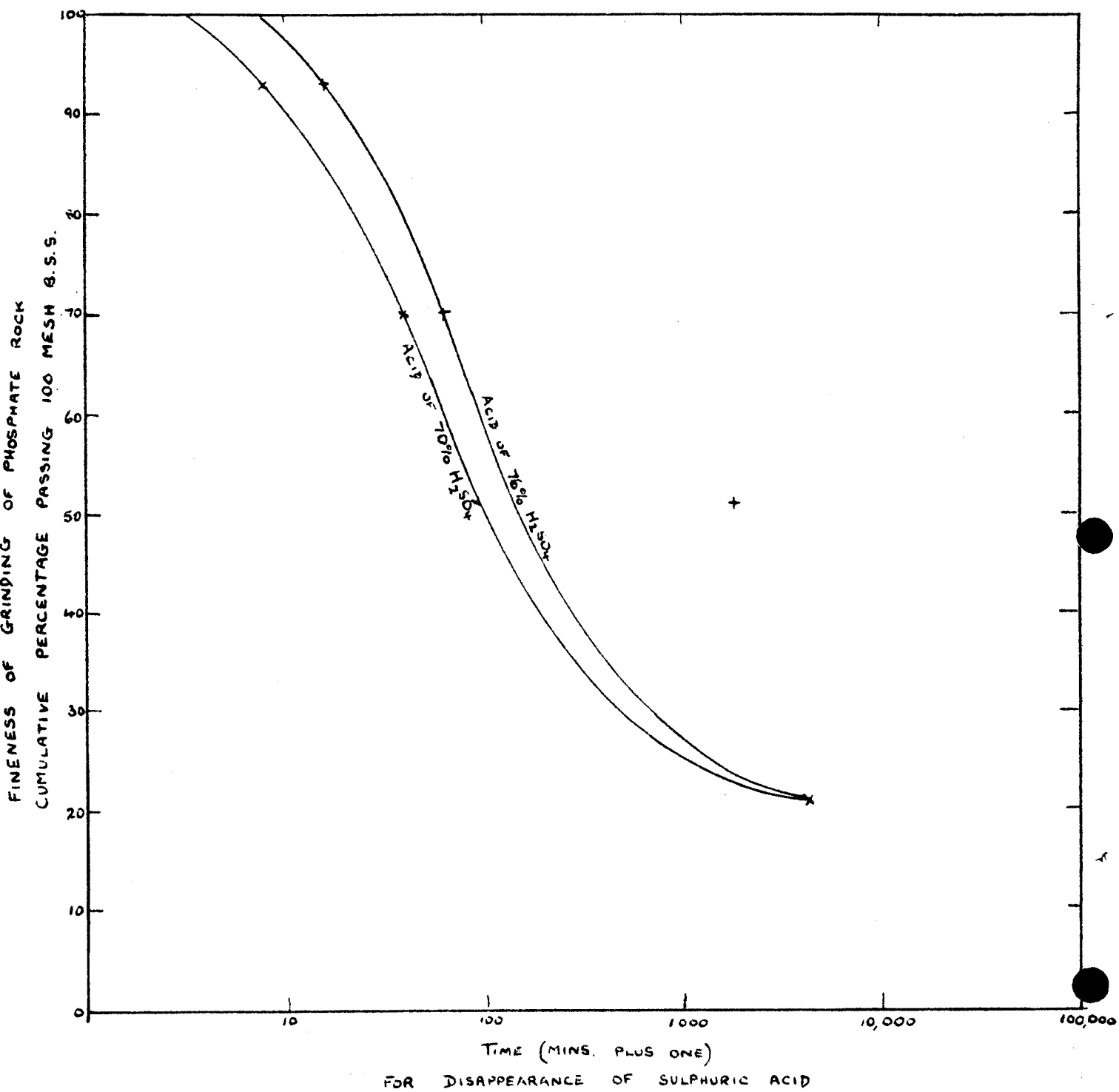


FIG. 12

SIEVE ANALYSIS OF SAMPLES OF MOROCCO PHOSPHATE ROCK.

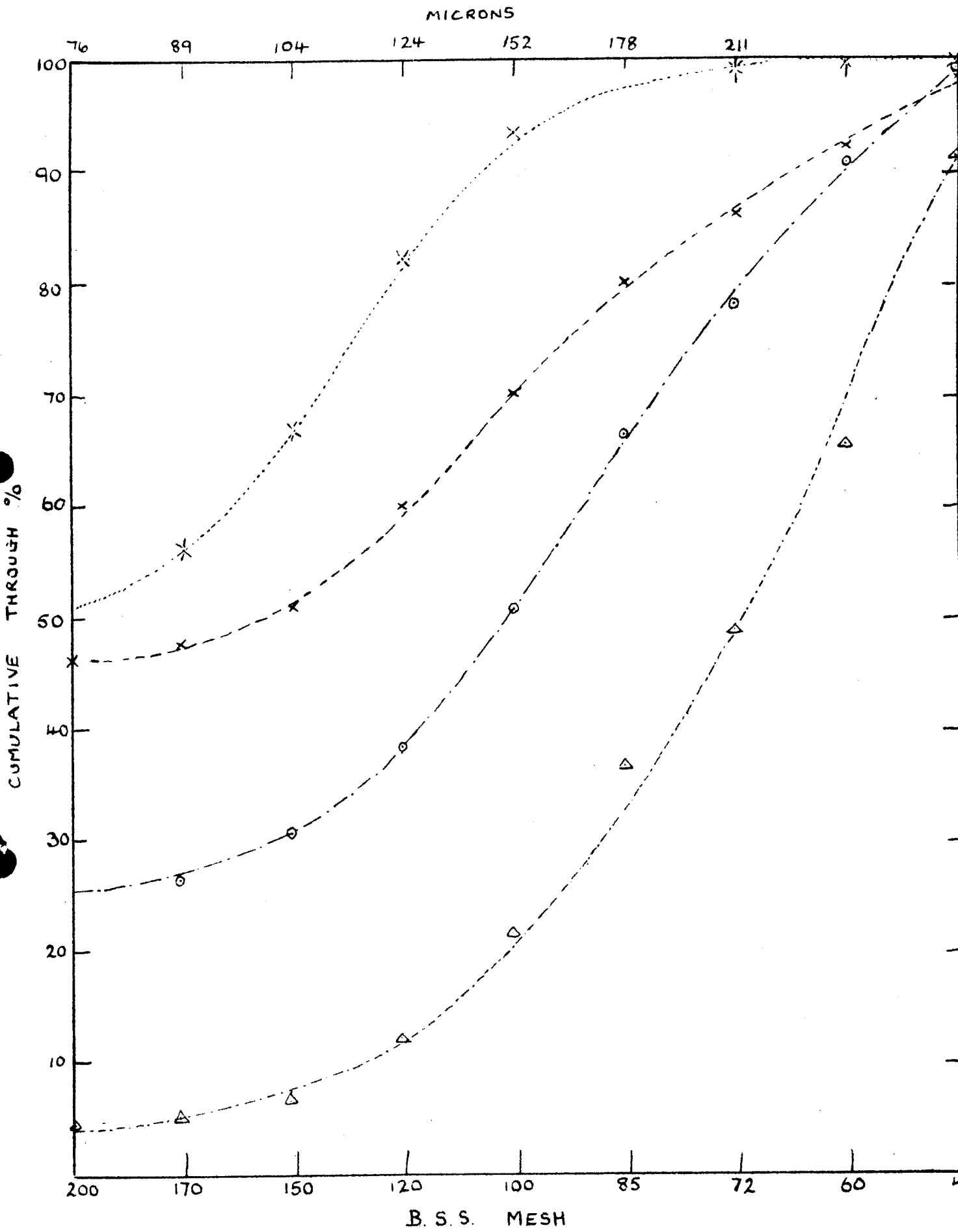
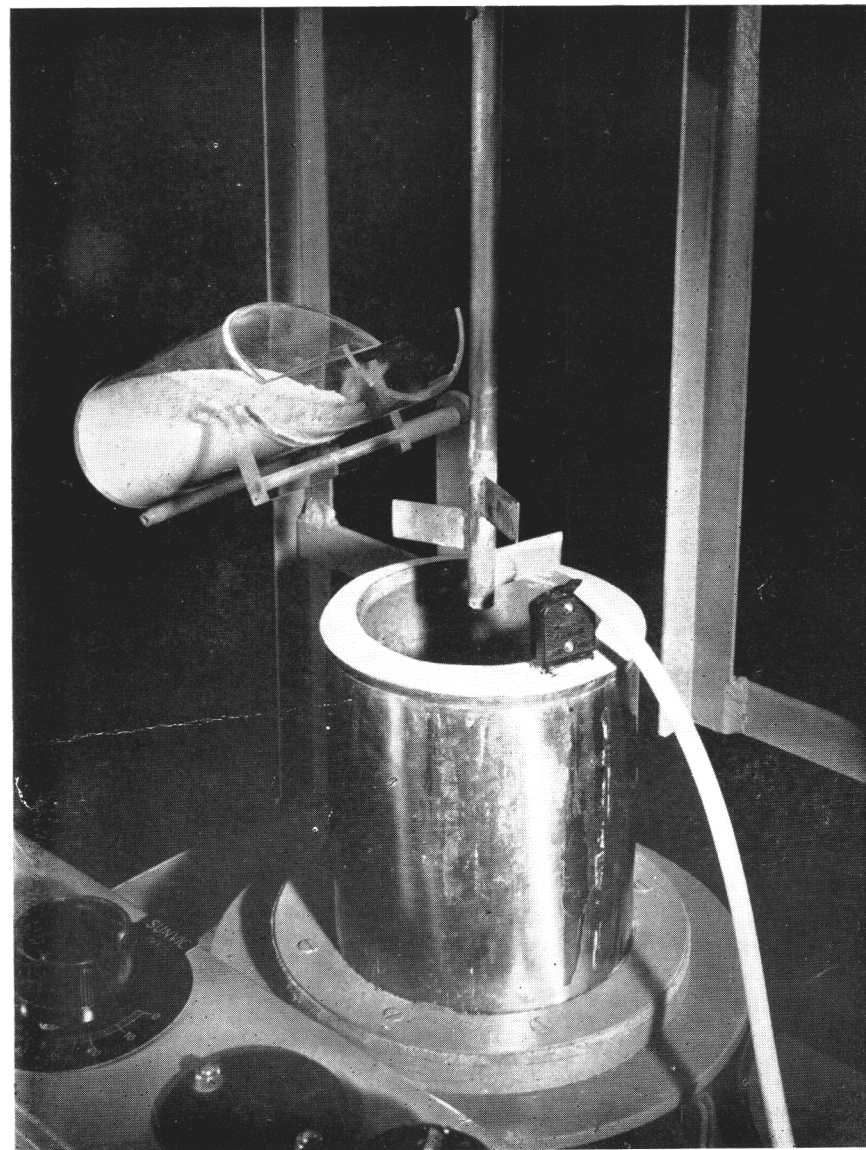


FIG. 13.





*Fig. 14a.* Reaction vessel, turntable and scale.



*Fig. 14b.* Reaction vessel and stirrer.