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THE EFFECT OF OPERATING VARIABLES ON THE CHANGE OF PHYSICAL CONDITION OF A PHOSPHATE ROCK - SULFURIC ACID MIX

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INTRODUCTION

The common phosphatic fertilizers are made by the chemical reaction in an intimate mixture of an acid with ground phosphate rock. The principal phosphatic constituent of phosphate rock is called calcium fluorphosphate, identical in crystal structure with fluorapatite, $Ca_{10}F_2(PO_4)_6$.

When the acid which is used is sulfuric acid, the fertilizer is called ordinary superphosphate. Ordinary superphosphate is a mixture of hydrated monocalcium phosphate and anhydrous calcium phosphate. When phosphoric acid is used, the fertilizer is called double (sometimes triple) superphosphate and is predominately either hydrated or anhydrous monocalcium phosphate.[1]

It is quite apparent that the double superphosphate is a much more concentrated fertilizer because phosphate is obtained from the acid as well as from the rock. This investigation, however, is not directly concerned with the chemical properties of the superphosphate, but with the physical condition of the final product.

The physical changes which occur when phosphoric acid is used make a material of almost ideal properties - that is - the material very rapidly becomes hard and dry and porous. In this condition it can easily be handled in the plant and by the farmer. For reasons of economy, it is desirable to have the fertilizer attain this mechanical condition in a short time. Therefore, it was considered imperative to observe the changes which occur with this acid as a comparison with the changes which occur when sulfuric

acid is used.

The reaction between Tennessee brown phosphate rock and concentrated phosphoric acid proceeds as follows: There is first a fluid stage, then a plastic stage, and finally a dry stage. The time between stages is short and the demarkation is very sharp. The total time required for the material to become dry is in the order of about one minute.

The reaction between phosphate rock and sulfuric acid proceeds very differently from the reaction with phosphoric acid. The mixture of phosphate rock and sulfuric acid very rapidly becomes a plastic mass and it remains in that state for a considerable length of time, very gradually hardening to a solid dry mass. With sulfuric acid, the time for the material to become dry is in the order of about three hours, depending upon many conditions such as temperature, humidity, etc.

In both cases a chemical reaction takes place almost at once, as evidenced by a considerable increase in temperature. The change in physical state is, of course, dependent upon the chemical reaction. When the monocalcium phosphate and calcium sulfate are formed they take up water of hydration and in this way the material becomes dry and easily handled. The reaction with phosphoric acid takes place at a lower temperature than the reaction with sulfuric acid and this fact seems to make a tremendous difference in the time necessary to obtain a dry, hard product. Both the monocalcium phosphate and the calcium sulfate take up water of hydration at the temperature at which the double superphosphate is produced, but in the case of the ordinary superphosphate, only the monocalcium phosphate takes up

any appreciable amount of water of hydration and, therefore, it takes considerably longer for the ordinary superphosphate to dry.

Variables such as temperature of the mixture, concentration of the acid, previous dispersion of some of the rock in the acid, etc.,do not have any appreciable affect on the final chemical properties of the superphosphate, but they do have a considerable effect on the physical condition of the material.

Copson, Newton, and Lindsay[2] have made quite an intensive study of the change in physical state of a phosphoric acid - phosphate rock mixture. This present work is modeled after the work on phosphoric acid, with this modification - the change in state of a sulfuric acid - phosphate rock mixture was studied.

Although three million tons of superphosphate were manufactured in the United States in 1935, the manufacturers are still largely governed by empiricisms - the old "rule of the thumb", therefore an attempt was made to make a study of the problem so that the superphosphate may be manufactured on a more logical basis.

"In the course of the investigation" (by Copson, Newton, and Lindsay on the reaction rate with phosphoric acid)[2] "it was found that finely divided phosphate rock formed a very stable suspension or dispersion in concentrated phosphoric acid when the amount of rock thus dispersed was less than one-fifth that required to react with the acid. It was found that the fluid stage was very much shortened by adding a small portion of the rock first, allowing it to become dispersed, and then adding the remainder of the rock to this slurry."

This investigation has been carried out with the specific purpose of finding what effect certain variables have on the change

in physical state so that the time of production may be shortened materially. The variables investigated were: quantity and concentration of acid, temperature of the mixture, dispersion, and phosphoric acid - sulfuric acid mixtures.

It is now generally conceded[3] that the phosphate rock must be ground rather fine (smaller than 100 mesh) in order to obtain the best results. The use of such finely ground phosphate rock has proven economical in that appreciably less sulfuric acid is required, the reactions between the acid and mineral take place more rapidly and a higher grade product in a better mechanical condition is obtained. Therefore the effect of particle size was not studied.

HISTORICAL BACKGROUND

The chemical nature of superphosphate made from sulfuric acid and phosphate rock is more or less standard, but the methods of manufacture vary widely. A study of some of the more common methods of manufacture reveals that the superphosphate is obtained in a very crude manner. There have been some developments in the past few years, but there is a tremendous field for research along this line.

In the early days of superphosphate manufacture, the freshly prepared material was dumped upon open piles almost immediately after mixing, a practice which so cooled the mass that the chemical reactions were checked and the moisture content of the product was objectionally high.

Practically all the larger and more progressive manufacturers of superphosphate have abandoned the open dump method for the closed chamber or den system. As fast as the charges of phosphate rock and acid are mixed they are dropped into a concrete den which is filled to within a short distance of the top. Here the chemical reactions taking place raise the temperature of the mass well above 100 degrees centigrade.

The present method of manufacture of superphosphate requires a period of 6 to 24 hours in the den before the material is in a proper mechanical condition to be handled. It is for the purpose of shortening this time that the work here reported was done.

Even if the den method as practiced at the present time is used to produce the superphosphate, a considerable decrease in time that the material has to remain in the den will make for an increase

in the capacity of the plant.

There is a possibility of even greater advance in the art. The present trend is towards continuous operations wherever possible. It might just barely be possible that if the time of drying were shortened tremendously, that the superphosphate could be manufactured in a spray tower similar to the process suggested by Dr. H. A. Curtis[4] for the making of double superphosphate. The following is quoted from this source.

"It might be possible to mix the acid and the dust, properly proportioned, in a spray nozzle set at the top of a tall tower. The fluid mixture leaving the nozzle would assume the form of droplets, and by proper control of spray conditions, these droplets might be made directly in sizes suitable for fertilizer, thus avoiding subsequent grinding of the superphosphate.

It is necessary that the fluid droplets formed by the spray should "set-up" sufficiently in falling through the tower to be relatively dry and non-cohesive by the time that they reach the foot of the tower. The fineness of the rock dust, the temperature of the acid, and the strength of the acid all affect the rate of "setting" of the mixture, and all of these may easily be controlled. And, in order to facilitate the completion of the reaction, the droplets may be allowed to fall through an upward-moving current of warm air."[4]

It is quite likely, however, that such a system would be quite out of the question with sulfuric acid because the time would have to be shortened so radically that it would be almost impossible. It is much more likely that a continuous process of another type would be

much more feasible. There are several such processes in operation at the present time. This other type of continuous process makes use of a travelling den of some sort or another in which the product is carried for a considerable length of time.

The Maxwell method[5] (England) uses phosphate rock which is ground to 85% through 90 mesh and sulfuric acid which is from 54 to 56 degrees Baumé. The mixed material goes to a tire-shaped den which revolves at a speed of 1/4 rph. In the den a slowly revolving cutter of stainless steel shaves off the superphosphate.

In the United States there is a patent[6] which embodies the same principle; a rotary drier is used and the moisture is reduced to 10%.

MATERIALS USED

The phosphate rock which was used in all the runs was a Tennessee brown phosphate rock with the following screen analysis:

mesh	65	80	100	150	200
cumulative % thru	99.3	98.8	97.3	90.5	79.8

A chemical analysis of the rock follows:

P_2O_5	32.3 %
CaO	45.6
Fe_2O_3	2.80
Al_2O_3	2.14

The sulfuric acid was a commercially pure grade; concentrations were determined from specific gravity readings.

The phosphoric acid was from the Tennessee Valley Authority pilot plant for the production of phosphoric acid at Muscle Shoals.

DESCRIPTION OF THE METHOD AND APPARATUS USED

Much time and labor was spent on the construction of a rather elaborate apparatus so that quantitative measurements may be made of the time required for the superphosphate to lose its plasticity. The apparatus was almost identical to that used by Copson, Newton, and Lindsay in their studies of the initial reaction rate between phosphate rock and phosphoric acid.[2] It was discovered after the apparatus was in operation that the change in physical state of the superphosphate differed so radically from the change in state of the double superphosphate that the apparatus was unfeasible and hence abandoned.

It was decided to rely upon a visual examination of the superphosphate to determine the time required for the material to lose its plastic properties. The superphosphate was examined as to its color, hardness, plasticity, porosity, etc. In most cases (as far as possible) simultaneous runs were made so that the products could be compared with each other.

It was considered desirable to use less than the theoretical quantity of acid in order to avoid the presence of free acid produced. Ninty-six per cent of the theoretical amount of acid required to react with the phosphate rock was used except when otherwise indicated. One-hundred grams of phosphate rock was added to the required amount of acid in beakers.

The mixture was stirred with a glass rod for several minutes until the acid was thoroughly mixed with the rock. The mass was stirred occasionally during the run to aid in the examination of the

material.

The apparatus which was used to study the effect of temperature was very simple as was most of the apparatus. An iron plate about 1/4 of an inch thick, 6 inches wide, and 30 inches long was set up on tripods and heated red-hot at one end. The superphosphate was mixed in casseroles and then placed at regular intervals along the length of the plate. Thermometers were placed into the mixtures to determine the actual temperature. The run was considered ended when the product was dry enough to be handled without sticking together.

A constant temperature was used when the concentration, dispersion, etc. were varied. A steam bath was used in several runs but this was changed to a sand bath in order to lessen the humidity. The steam bath gave an indication of the optimum concentration of acid, etc. but the time for drying was somewhat longer than it should have been with better conditions because of the high humidity.

The sand was contained in an open iron box about 10 inches square and 6 inches deep. The top of the box was divided into 9 parts by iron rods brazed on to the top of the box so that the beakers would be separated. A gas flame was used at the bottem and the temperature of the sand bath was rather constant.

CALCULATIONS TO DETERMINE THE QUANTITY OF ACID TO BE USED

The following are the reactions which are assumed to represent the reaction between phosphate rock and sulfuric acid.[3] No water of crystalization is shown.

$$\overset{310}{Ca_3(PO_4)_2} + 2\ \overset{196}{H_2SO_4} = \overset{234}{CaH_4(PO_4)_2} + 2\ \overset{272}{CaSO_4} \qquad (1)$$

$$\overset{78}{CaF_2} + \overset{98}{H_2SO_4} = 2\ \overset{40}{HF} + \overset{136}{CaSO_4} \qquad (2)$$

$$\overset{160}{Fe_2O_3} + 3\ \overset{294}{H_2SO_4} = \overset{400}{Fe_2(SO_4)_3} + 3\ \overset{54}{H_2O} \qquad (3)$$

$$\overset{102}{Al_2O_3} + 3\ \overset{294}{H_2SO_4} = \overset{342}{Al_2(SO_4)_3} + 3\ \overset{54}{H_2O} \qquad (4)$$

$$\overset{100}{CaCO_3} + \overset{98}{H_2SO_4} = \overset{136}{CaSO_4} + \overset{44}{CO_2} + \overset{18}{H_2O} \qquad (5)$$

The analysis of the rock is: P_2O_5, 32.3%; CaO, 45.6%; Fe_2O_3, 2.80%; Al_2O_3, 2.14%.

Sulfuric acid required to react with 100 grams of phosphate rock.

Basis: 100 grams of phosphate rock.

P_2O_5 = 32.3/142 = .2275 mols of $Ca_3(PO_4)_2$

CaO = 45.6/56 = .814 mols of Ca

.2275 × 3 = .6825 mols Ca in $Ca_3(PO_4)_2$

.814 − .6825 = .1315 mols Ca in CaF_2 + $CaCO_3$

2.80/160 = .0175 mols of Al_2O_3

.2275 × 2 = .4550

.1315 = .1315

.0175 × 3 = .0525

.021 × 3 = .063

.7020 mols of acid required

.7020 × 98 = 68.75 grams of 100% acid required/100g rock.

The concentration of the carboy acid was 56.4 degrees Be.,(71.3%)[7] found from specific gravity readings. The concentration of 56.4 degree Be sulfuric acid expressed in grams per liter is 1160.

68.75/1160 = cc/1000

cc = 68750/1160 = 59.2 cc (71.3%) acid/100g rock

59.2 × .96 = 56.8 cc acid/100g rock (96% of the theoretical amount of acid required to react with the rock).

Quantity of acid required for 100 grams of rock when less than theoretical proportions are used.

Theoretical amount of acid	cc of 71.3% acid
100%	59.2
95	56.2
90	53.2
85	50.3

Quantity of phosphoric acid required/100g phosphate rock is 122.5g. for conversion of the rock to monocalcium phosphate. (The concentration of the phosphoric acid used is 79.2%).

EXPERIMENTAL RESULTS

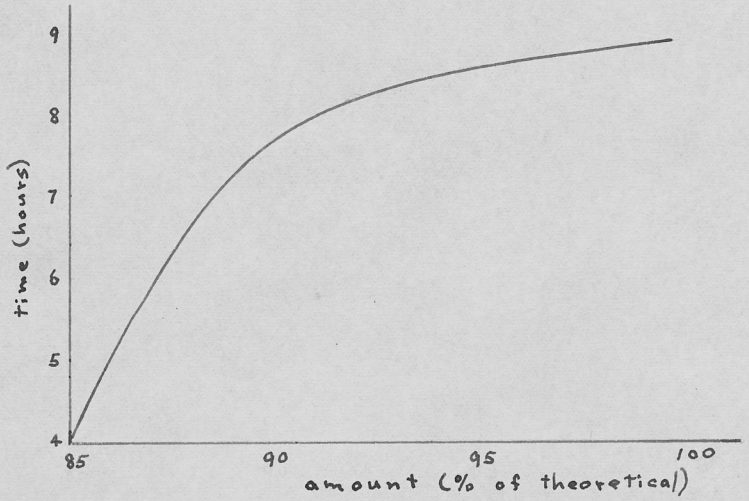
Table I

Effect of varying amount of sulfuric acid on drying time of superphosphate dried over water bath at 206 degrees F.

Quantity of acid used	Time required for drying
85%	4 hours
90	7:30
95	7:25
98	8:40

It should be noted that there are rather apparent discrepancies. Since the examination was visual and therefore not very exact, the time of drying is correct to within certain limits - say about plus or minus 5%.

The time of drying is directly proportional to the amount of acid. The observations seem to indicate that a curve of the following general characteristics is obtained:



The theoretical amount of acid seems to make a considerable difference in time in the range from 90 - 95%.

It is not considered advisable to use too small an amount of acid or much of the product will be unreacted phosphate rock. When almost 100% of the theoretical amount of acid is used, the time of drying is prolonged exceedingly - amounts which will give free acid in the product will remain plastic indefinitely.

Table II

Variation of temperature on time of drying.

Temperature	Time of drying
388 degrees F.	2:15 hours
300	2:15
235	2:30
170	3:30 (not quite dry)
145	4:30 " " "
112	4:50 " " "
86	plastic after 2 days

No attempt was made to get any absolute values - as soon as the desired optimum condition was found, that set of runs was stopped, although the samples under less desirable conditions were not yet dry.

The time of drying seems to vary inversely as the temperature, but the difference is not as marked at the higher temperatures as at the lower temperatures.

The condition of the product which was dried at the higher temperatures differs considerably from the product dried at the more moderate and the lower temperatures. The mixture at 388 degrees F.

lost its plastic properties in 2¼ hours, but the mechanical condition of the product was not very good - it had a slight tendency towards gumminess, and was otherwise a very hard black solid which was not nearly as soluble as the other superphosphate produced. When the material was dissolved, however, it gave the characteristic gray cloudy solution of superphosphate.

The mixture at 300 degrees also became dry in about 2¼ hours, while at 235 degrees it took 2½ hours to dry, but the product was in much better mechanical condition, being easily disintegrated and fairly soluble in water. Below 235 degrees the time for drying was lengthened considerably.

At room temperature (about 86 degrees), the mixture was still a very plastic mass after 2 days.

Phosphoric acid gives a hard dry product in about one minute.

Table III

Variation of concentration of acid on condition of superphosphate.

concentration of acid	time	condition
60%		2nd best
70	1:40	dry (best)
80		3rd best

The effect of concentration is somewhat akin to the effect of temperature. The higher concentrations give a product which is in a rather poor mechanical condition - being black and inclined towards gumminess. The time of drying is longer at both extremes of concentration, the optimum range is from 68 - 71% acid.

Table IV A

Effect of previous dispersion of phosphate rock in acid on drying time.

Temperature of sand bath 230 degrees F. Rock dispersed in the acid for $2\frac{1}{2}$ hours before the final addition.

number	% dispersion	time to dry
1	10	1:45
2	20	1:45
3	30	1:45
4	40	1:45

Table IV A shows that in the range from 10 to 40% dispersion, the time of drying is not changed appreciably - all the samples becoming hard at about the same time, approximately one and three quarter hours. The set of runs is repeated in Table IV B covering a wider range of the amount of previous dispersion, and also incorporating several runs with varying times of previous dispersion.

Table IV B

Effect of time and amount of dispersion on drying over sand bath at 220 degrees F.

number	amount of previous dispersion (%)	time of dispersion	condition (in order of dryness) after 16'	35'	1 hr.	2hrs.
1	20	20 hrs.of previous dispersion	3	3	3	
2	40		4	4	4	
3	60		6	6	6	
4	80		5	7	7	all
5	0	0	7	5	5	dry
6	40	1:30	1	1	1	
7	40	0:15	2	2	2	

The results of this set are not as conclusive as might be desired. The products did not differ very much in their mechanical condition, but an attempt was made to arrange the runs in order of dryness. As stated before - the examination was visual and therefore could not be very exact.

The time which the dispersed rock is allowed to remain before the final addition is made does not seem to affect the time of drying. The amount of previous dispersion also does not seem to affect appreciably the time of drying. A previous dispersion in the range of 20 to 40% seems to be slightly better than other dispersions. The time of drying is about one hour regardless of the time the dispersion is allowed to "set" before the final addition, while the time under the same conditions, but with no previous dispersion is about two hours.

Table V

Effect of mixing phosphoric acid with sulfuric acid on the condition of superphosphate.

number	% H_2SO_4	time	condition
1	75	4 hours	plastic mass
2	50	3:10	plastic mass
3	25	1 min.	dry
4	0	1 min,	dry
5	40	3:15	dry
6	30	2½ min.	dry

The time for solidification with mixtures of phosphoric acid and sulfuric acid took a long time unless at least 70% of the mixture was phosphoric acid. With amounts of sulfuric acid less than 30% of the amount required to react with the rock, the time of drying takes about one minute, that is approximately the same time as with phosphoric acid alone. The product obtained with such a high percentage of phosphoric acid would be an impure double superphosphate.

With percentages of sulfuric acid greater than 30%, the time of drying increases tremendously and the material takes on the characteristics of a sulfuric acid - phosphate rock mix.

CONCLUSIONS

With the best conditions investigated, the time of drying is about one hour. It is undesirable to make any quantitative statements unless humidity and temperature readings, etc. are incorporated in the report because the physical condition of the superphosphate differs considerably with changes in weather conditions, especially humidity. Some samples which had just been dried and were non-cohesive became rather moist and sticky when the humidity of the air was great. Several runs had to be discontinued because of excessively high humidity; the time of drying became very prolonged during a rain.

It was also necessary to discard several sets of runs because the runs in the set were not made simultaneously. Little information could be obtained unless the runs were started at the same time so that the products could be compared.

A. The amount of acid. - The amount of acid which is considered best is 96% of the theoretical amount necessary to react with the rock. If the amount used is 85% or less, the time of drying is shortened very much, but this fact is over-ruled in that much of the rock would remain unreacted upon and the phosphate in this rock is unavailable to plant life.

If almost 100% of the theoretical amount of acid necessary to react with the rock is used, there is the possibility that there may be some free acid present due to improper mixing. In such a case the time of drying is very long - sometimes a matter of weeks or more.

Therefore it is concluded that within the range of operating

conditions used, about 96% of the theoretical amount of acid which is required to react with the rock is best.

B. Temperature of the sulfuric acid - phosphate rock mixture. The optimum temperature is found to be about 235 degrees F. Temperatures above 235 degrees give a slightly gummy product in a little shorter time than at 235 degrees, and temperatures below this give a product in a satisfactory mechanical condition but it takes a longer time to dry.

C. Concentration of acid. The best concentration is about 68 - 71% sulfuric acid. Concentrations higher or lower than 68 - 71% take a longer time to dry.

D. Dispersion. A previous dispersion of about 40% for several minutes before the final addition of rock gives highly satisfactory results - shortening the time of drying by about one-half.

E. Phosphoric acid - sulfuric acid mixtures. It was desired to find out if a small quantity of phosphoric acid could be added to the sulfuric acid and thus shorten the time of drying considerably, but it was found that at least 70% of the acid must be phosphoric acid before the time of drying is shortened appreciably.

RECOMMENDATIONS FOR FUTURE WORK

It is very advisable when making visual observations, to make a set of runs, all starting at the same time. In this way all the runs are very nearly under the same conditions of temperature and humidity, and there is the decided advantage of being able to make comparisons of various runs in the same set.

It is strongly recommended, however, that a more exact and absolute means be used to measure the amount of moisture in a given sample. It is suggested that after the sample has been subjected to certain conditions of concentration of acid at a certain temperature for a length of time - that the amount of moisture be determined by weighing the sample and then drying over concentrated sulfuric acid or anhydrous calcium chloride for several hours and then reweighing to determine how much water was lost.

It should be pointed out here that the results obtained in this present work are not very exact. It is quite possible that if a more (or a less) concentrated acid were used in determining the optimum temperature that the results may be somewhat different than the results actually obtained with the specific concentration which was used. Much more work is indicated - such as finding the inter-relation of concentration, temperature, etc.

It was noticed that the sulfuric acid - phosphate rock mixtures have a tendency to "freeze-up" for a short time when first mixed. The material would clot and form lumps which would soon disappear and then the whole mass becomes plastic. It is barely possible that this may cause trouble in a mixer and investigations should be made

along this line before any mixer is planned.

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APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statements made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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