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UNIVERSITY OF LOUISVILLE

ACCELERATED CURING OF SUPERPHOSPHATE FERTILIZER
//

A Thesis

Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

Gus W. Loop, Jr.
///

March 1948

ACCELERATED CURING OF SUPERPHOSPHATE FERTILIZER

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Approved by the Examining Committee.

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March 1948

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ABSTRACT

Simultaneous drying of curing superphosphate is shown to be of definite value in increasing the available P_2O_5 content. Raw superphosphate heated at $80^\circ C.$, and analyzed after 1 hour, 4 hours, 24 hours, and 48 hours of curing contained 16.92%, 19.67%, 20.66%, and 20.78% of available P_2O_5 respectively. For the same periods of time samples cured at room temperature contained 15.28%, 17.1%, 17.7%, and 18.82% of available P_2O_5 . There was a larger amount of P_2O_5 available after 4 hours heating than after 48 hours at room temperature. This increase represented a 12:1 time-ratio in favor of the heated sample. The increase in available P_2O_5 was apparently accomplished by drying since little further reaction of acid and rock occurred, as indicated by an essentially constant citrate insoluble content of about 2%.

For commercial purposes, it is indicated that drying should be discontinued, or the drying temperature decreased, when the product has a moisture content of approximately 3-4%. This procedure will prevent excessive evaporation of the liquid phase and allow the continued action of the acid on the remaining rock, with a resultant reduction in the insoluble fraction of the rock.

Commercial superphosphate is a mixture of monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, dicalcium phosphate, CaHPO_4 , and calcium sulfate, together with associated impurities such as iron and magnesium phosphates, silica, and calcium fluoride. At present the sole use of the superphosphate is as a fertilizer to provide available phosphorus for plants. In 1945, 15 million tons of superphosphate were sold in the United States.

The phosphate rock, from which the superphosphate is produced, normally consists of fluor-apatite $(\text{Ca}_5(\text{PO}_4)_3\text{F})$, the principal constituent, calcium carbonate, iron oxide, silica, aluminum silicate, calcium fluoride, calcium silicofluoride, and alumina. This list does not include some of the compounds present in very small amounts, but it clearly indicates the complex nature of the rock.

The normal manufacture of superphosphate fertilizer consists of grinding the phosphate rock to a fine powder, mixing this ground rock with sulfuric acid, and allowing the product to cure for 80 to 90 days. This curing time is necessary to allow the action of phosphoric acid on the rock to approach completion, and to permit the product to dry. During the past one hundred years refinements such as control of temperature and concentration of acid, control of temperature and fineness of rock, proper ratio of acid to rock, and improved grinding methods have been introduced in order to increase the quality of the fertilizer. Generally speaking, however, there has been little success in overcoming the handicap of a long curing period. The reduction of this curing time by artificial drying of raw superphosphate is the problem under consideration in this thesis.

INTRODUCTION

HISTORICAL

In the early days of the industry the phosphate and acid were mixed on a brick floor like mortar, or the acid was thrown into a brick lined pit, the finely ground phosphate being thrown into the acid and the mass agitated manually. (1) (2)

As the industry grew the mixing pit was discarded in favor of the den, a brick lined, square or rectangular chamber with a top inlet through which the semi-liquid mass was dropped from a small mixer. The dens usually held from 30 to 50 tons of superphosphate. Since large volumes of steam and gases were produced during mixing, it was necessary to conduct them through wooden troughs to a chimney. After three or four hours the dens were opened and emptied by hand.

By 1910 the mechanized den had been invented. These were square or rectangular chambers with a moving end, fed forward by a screw in such a manner that the charge of superphosphate was gradually pushed out. The dens were equipped with revolving or descending knives to cut out the raw material. Mixing plants used in connection with these dens were capable of dealing with quantities up to two tons.

By 1930 overhead railways or portable narrow gauge railway tracks were provided for conveying the finished product to the storage site; mechanical excavators were adopted for breaking down the superphosphate from the storage heap; machine disintegrators took the place of the pick, shovel, and the inclined screen. Such a plant also included conveyors for moving the ground rock, mechanical weighing and feeding of ground phosphate and acid to the mixer. The superphosphate excavated from the den by a revolving knife, was picked up by an automatic elevator and discharged to a conveyor belt which delivered it to a predetermined spot for curing.

In the past ten years the most important change in the manufacturing process has been the development of the mechanical dens to produce superphosphate continuously. These units are the so-called Broadfield, Moritz-Standaert, and Maxwell. Since this thesis deals with superphosphate manufactured in a Broadfield unit, only this one will be discussed.

Instead of mixing raw materials intermittently for a short time in large batches, the acid is continuously added to the phosphate rock and kneaded for about 5 minutes. The acid flows to the mixing chamber from a small tank through a special regulating valve, while the ground phosphate is measured in uniformly regular quantities from a hopper which is always kept full. The mixing and agitating trough, located above the den conveyor, consists of two compartments, the short mixer in front and then the longer stirring and kneading compartment. In the first section the acid and phosphate are intimately stirred together, and the mass flows into the stirring compartment in which it remains for about four or five minutes under the intensive action of the stirring paddles.

While still in a semi-liquid state the mass falls into the den conveyor, a moving endless wooden floor, with two similar side walls, which, with the fixed cover, form a closed compartment. The conveyor, an endless chain made of wood slats, moves very slowly so that the superphosphate remains on it for about three quarters of an hour before reaching the excavator. This is shown in Figure I.

One of the best features of this plant is that it gives a thorough mixing of phosphate and acid which results in a very good product, the water soluble content of which continues to rise satisfactorily while it

Figure I. Flow Sheet of Regular Superphosphate Process

lies in the curing heap.

The Oberphos process was the first invented in a direct attempt to overcome the long curing period and was patented in 1931. It is quite distinct from any other method of making superphosphate in that a steam jacketed autoclave replaces the usual den. The autoclave is in the form of a horizontal cylinder that is rotated during manufacture and is kept under vacuum. There is no mixer, as in the other methods of manufacture. Compressed air is used to force predetermined charge of sulfuric acid and ground phosphate rock from separate containers into the autoclave through a valve. The charge of about eight tons is introduced in about ninety seconds; then the autoclave is closed. The heat of reaction and heat from the steam jacket together help to dry the superphosphate and to intensify the chemical action of the mixture. After about an hour the autoclave is emptied through a suitable opening, the product having a hard gritty and granular character containing about 11% moisture. The superphosphate made by this means is so gritty that it can be ground very soon after manufacture to any degree of fineness desired without any fear of pasting.

The second process for producing a quick-curing superphosphate is known as granulation. Granulated superphosphate is prepared by a process based on the discovery that an increase in curing rate as well as improvement in physical condition is obtained by adding a small amount of water to den superphosphate and agitating it at atmospheric pressure and temperature to nodulize it, and, directly after, without intermediate storage-curing, removing the excess water from the superphosphate by drying with heat while agitating it at atmospheric pressure. The material is required

to stay in storage for only two or three weeks. The process requires the use of den superphosphate with a moisture content of 11%-15%. This material is produced by adding either ground rock or water to the den product in a rotary kiln. The rotary motion causes the superphosphate to ball-up into small round pellets. The product from this machine is passed into a rotary drier where the temperature is closely controlled at approximately 180° F. and the moisture of the fertilizer is reduced to about 2%.

The following literature citations indicate that heat applied to raw superphosphate has proved successful in decreasing the curing time and producing a material which has improved mechanical properties.

Larison (3) reports the following process being used in the manufacture of superphosphate by the Anaconda Copper Co. at their mine in Anaconda, Montana. "The superphosphate after curing is still far too wet to be ground and used as a fertilizer material, and must have its moisture content reduced to 3 or 4% by artificial drying. This operation is carried out in driers of special construction."

Collins (4) says, "Special machines with rotary movement also are constructed for drying superphosphate in a continuous manner. The removal of water modifies the relationship between the four forms of phosphorus in the superphosphate, viz. between the tricalcium, dicalcium, and monocalcium phosphates and the free phosphoric acid. In the case of well-made superphosphate, the amount of free phosphoric acid is reduced by drying, since the removal of water permits the free phosphoric acid to react with dicalcium phosphate with the formation of monocalcium phosphate. By careful drying, the percentage of water-soluble phosphate is raised, and

the mechanical condition improved."

According to Grey (5) one of the largest European manufacturers about 1931 installed a drying plant and marketed a product with 2 to 4% moisture. This result was obtained without reversion of the water soluble phosphate to dicalcium phosphate by strict control of the drying temperature.

T H E O R E T I C A L

Phosphorus occurs in four forms in the fertilizer, viz., tri-, di-, and mono-calcium phosphates and phosphoric acid, the last three being available to plants. The industry identifies these forms of phosphorus in the following manner:

- (1) All forms of phosphorus are represented in terms of phosphoric anhydride, P_2O_5 , or the equivalent tricalcium phosphate, referred to as Bone Phosphate of Lime or "B.P.L."
- (2) Water soluble phosphate, (phosphoric acid and monocalcium phosphate) as the name implies, is readily soluble in water.
- (3) Citrate soluble phosphate (di-calcium phosphate) is soluble in neutral ammonium citrate solution but not in water.
- (4) Available phosphate includes water and citrate soluble material.
- (5) Total phosphate includes the available and insoluble phosphate material, such as unreacted flueroapatite.

If apatite is mixed with a sufficient quantity of sulfuric acid the following reactions will take place in the order listed:

- (1) $(Ca_3(PO_4)_2)_3 CaF_2 + 3H_2SO_4 = 6 CaHPO_4 + 3 CaSO_4 + CaF_2$
- (2) $6 CaHPO_4 + 3H_2SO_4 + 3 CaSO_4 + 3 Ca(H_2PO_4)_2$
- (3) $3 Ca(H_2PO_4)_2 + 3H_2SO_4 = 3 CaSO_4 + 6H_3PO_4$

The overall reaction is

However, this series of reactions can take place only if sufficient time

is allowed. If the reaction is halted before completion, a mixture of CaHPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, and H_3PO_4 would result in the product. In any case the extent of the reaction at equilibrium under atmospheric pressure depends upon the quantity of free water in the system, and upon the temperature. Since the solubilities of calcium sulfate and calcium fluoride are so small in the presence of solid monocalcium phosphate that the calcium sulfate and fluoride content of the solution phase can be disregarded, the system with its acid content for this range of composition can be treated as though it were the three component system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$. Figure II is a phase diagram for this system at 25°C ., where solvent water is not represented on the coordinates but may be determined at any point on the diagram by subtracting the sum of percent CaO and percent P_2O_5 from 100 percent.

The chemical reaction between apatite and phosphoric acid involves two distinct processes. Solution of the apatite is the primary process which, will proceed toward completion with a sufficient amount of liquid phase present. Precipitation of one or more of the products is a secondary process although it may occur simultaneously with the primary process.

Apart from such factors as fineness of the rock and the reactivity of its phosphate constituents, the rate and extent of the primary process is influenced by the temperature, composition, and quantity of liquid phase. In the presence of a relatively large quantity of solution, as is obtained with high acidulations, this process may go to virtual completion within a few days, but in this case the physical characteristics of the product normally are poor because of the presence of large amounts of liquid. Drying concentrates the liquid phase in free phosphoric acid and thereby

FIGURE II. FIELDS OF STABILITY OF CALCIUM PHOSPHATES AT 25° C.

increases the hygroscopicity of the material. However, the resulting improvement of the mechanical condition is more or less temporary. At low acidulations, on the other hand, the liquid phase tends to disappear as a result of the continuous decrease in the amounts of both free water and phosphoric acid, the first largely by hydration of salts or by volatilization, and second by reaction with raw phosphate. In the event of an unchecked loss of water from the curing superphosphate, the amount of liquid phase soon becomes too small to support the primary process at a significant rate, so that the final product contains an excessive amount of raw phosphate, although its mechanical condition may be excellent.

In superphosphates of lower acidulations, dicalcium phosphate instead of monocalcium phosphate separates from the liquid phase. This occurs when the free acid-water ratio of the mixture becomes equal to or less than the critical value for the reference system. As free-acid is consumed, without loss of water and with the accompanying separation of monocalcium phosphate, the composition of the liquid phase eventually becomes favorable to the separation of dicalcium phosphate. At this stage a continuance of the primary process to complete conversion necessitates the decomposition of some monocalcium phosphate formed in the first stage of curing. This decomposition is required in order to supply the free acid in the liquid phase at the critical point where dicalcium phosphate formation becomes possible, and is markedly increased with an increase in temperature. Therefore an increase in the temperature of curing superphosphate should favor this conversion. (7)

If water is allowed to escape from a system formulated in an open vessel to yield a final product containing mono-calcium phosphate, and

dicalcium phosphate, there may result a product of monocalcium phosphate, apatite, and a very small amount of liquid phase. This type of product results from the removal of water from the reaction at such a rate that the composition of liquid phase (i.e., its free acid-water ratio) never falls below the critical value for the precipitation of dicalcium phosphate. Therefore, monocalcium phosphate continues to separate from the liquid until the amount of the latter becomes too small to support further reaction at an appreciable rate.

As an example of what happens in superphosphate when the free-acid water ratio is controlled, consider an active material containing 10% CaO, 20% P₂O₅, and 70% H₂O. If this material is dried the composition will change along a diagonal line so that the ratio of CaO to P₂O₅ will always remain 1:2. When the composition of the material reaches line AB it passes in to a region favorable to the precipitation of both monocalcium phosphate and dicalcium phosphate.

In the manufacture of superphosphate the object is to convert as much as possible of the calcium phosphate in the phosphate rock to water and citrate-soluble phosphates. Impurities in the rock introduce a requirement of additional sulfuric acid. Solution of apatite by sulfuric acid produces calcium sulfate, phosphoric acid, and calcium fluoride. Calcium and magnesium carbonates form sulfates. Iron and aluminum whether present as oxides or silicates form phosphates.

The analysis of a typical superphosphate is given by Dr. C. Krugel, director of the Hamburg Experimental Station of the International Superphosphate Manufacturers' Association in July, 1939.

TABLE I. FULL ANALYSIS OF SUPERPHOSPHATE 18% P_2O_5

Constituent		percent by weight.
Moisture		9.72
Water of crystallisation		3.72
Free Phosphoric Acid ¹	H_3PO_4	4.14
Monocalcium Phosphate ¹	$Ca(H_2PO_4)_2$	24.72
Dicalcium Phosphate ²	$CaHPO_4$	0.42
Tricalcium Phosphate ³	$Ca_3(PO_4)_2$	0.44
Phosphate of Iron	$FePO_4$	0.26
Phosphate of Aluminum	$AlPO_4$	0.79
Calcium Sulfate	$CaSO_4$	50.54
Silicic Acid	SiO_2	0.44
Calcium Fluoride	CaF_2	2.66
Alkalies		0.70
Organic matter and rare elements		0.97

¹Water soluble ²Citrate soluble ³Insoluble

Krugel presents another analysis of superphosphate in a form which separates the phosphoric acid, lime, and sulphur trioxide: this analysis has the advantage of showing the conversion from the various forms of calcium phosphate to phosphoric acid and also the percentage of calcium which remains in combination after the phosphate rock is dissolved.

TABLE II. ANALYSIS OF 18% SUPERPHOSPHATE

(Hamburg Experiment Station)

Constituent	Analysis %	Equivalent %		
		P ₂ O ₅	CaO	SO ₃
Moisture	12%			
Monocalcium phosphate corresponding to Ca(H ₂ PO ₄) ₂ H ₂ O	12.3	12.00	4.73	
Phosphoric acid corres. to (H ₃ PO ₄)..	8.3	5.00		
		<u>18.00</u>		
		water soluble		
Dicalcium phosphate	1.0	0.4	0.33	
		citrate soluble		
Rock Phosphate not broken down	1.0	0.35	0.45	
		insoluble		
Gypsum (CaSO ₄ .2H ₂ O)	50.0		16.28	23.25
Magnesium sulfate (MgSO ₄)	0.4			0.26
Aluminum sulfate (Al ₂ (SO ₄) ₃).. ..				1.75
Sulfate of iron (Fe ₂ (SO ₄) ₃)	1.2			0.72
Silicic acid (SiO ₂)	0.7			
Calcium fluoride (CaF ₂)	1.2		0.86	
Undetermined (alkalies, traces of iodine etc.)	0.4			
	<u>100.0%</u>			
water-soluble		18.00		
citrate-soluble		0.4		
insoluble		0.35		
		<u>18.75%</u>		
		Total P ₂ O ₅		
			<u>22.65</u>	<u>25.98</u>

If the foregoing analysis of superphosphate does not make clear

just what happens in the process of manufacture, the following table by Schucht will explain the changes that occur when sulfuric acid is mixed with ground rock. This table is termed "The Breaking Down of Phosphate." The chemical analysis of the ground phosphate rock is given at the head of the table. It is assumed that the material has lost hygroscopic moisture in the grinding process because of the heat engendered by the friction in the mill, plus the drying effect of air-separation. Therefore, of 100 kilograms of this material originally put into the mixing process, only 96 kilograms will be present for solution. Each constituent in the extreme left-hand column of the lower table is accordingly reduced in proportion to the amount listed in the first table. The content is given in percentage by weight in the top table because there 100 kilograms is represented, but the weight only is given in the lower table of the four kilograms remaining undissolved.

In the second column of the table the theoretical quantity of 100% H_2SO_4 required to convert the various constituents of the phosphate rock is given; thus the tribasic phosphate of lime requires in theory 46.13 kilograms; the iron and alumina 1.82 kilograms, and 4.14 kilograms respectively; the calcium fluoride 6.4 kilograms; and so on. In the next column Schucht gives the quantity of water (again theoretical) to be added to the acid to bring the acid down to the mixing strength, 54° Baume, or 68.13% H_2SO_4 . At the foot of each column is listed the theoretical total of acid and water respectively, but he shows beneath each such total, the quantity actually used i.e., the quantity which experience has demonstrated to be essential rather than the quantity calculated from theory. Thus experience teaches that 11.16 kilograms of acid and 2.76 kilograms of water have to be

TABLE III. THE BREAKING DOWN OF PHOSPHATE

Composition of Ground Florida Hard-Rock Phosphate

0.65%	Hygroscopic H ₂ O	0.91%	SiO ₂
2.84%	Chemically Combined H ₂ O	4.09%	CaCO ₃
76.00%	Ca ₃ (PO ₄) ₂	0.50%	MgCO ₃
1.95%	FePO ₄	0.01%	CaI ₂
4.14%	Al ₂ (SiO ₃) ₃	0.63%	Undetermined
7.96%	CaF ₂		

Details of the Process of Breaking Down Phosphate

Of 100 kg. Phosphate
96 kg. were dissolved
containing:

	H ₂ SO ₄	H ₂ O	Gases	Initial Slurry	Final Product
3.35 kg. H ₂ O	—	1.80 kg.	1.55 kg. H ₂ O	8.07 kg. H ₂ O	5.29% H ₂ O
72.97 kg. Ca ₃ (PO ₄) ₂	46.13 kg.	21.19 kg.	—	59.31 kg. Ca(H ₂ PO ₄) ₂ ·H ₂ O	5.29% Ca(H ₂ PO ₄) ₂ ·H ₂ O
1.87 kg. Fe ₃ (PO ₄) ₂	1.82 kg.	1.00 kg.	—	80.98 kg. CaSO ₄ ·2H ₂ O	11.75% H ₃ PO ₄
3.97 kg. Al ₂ (SiO ₃) ₃	4.14 kg.	3.80 kg.	—	2.48 kg. Fe ₂ (SO ₄) ₃	59.40% CaSO ₄ ·2H ₂ O
7.64 kg. CaF ₂	6.40 kg.	2.35 kg.	2.61 kg. HF	1.21 kg. H ₃ PO ₄	0.34% MgSO ₄
0.87 kg. SiO ₂	—	—	1.98 kg. SiO ₂	4.82 kg. Al ₂ (SO ₄) ₃	2.41% Al ₂ (SO ₄) ₃
3.93 kg. CaCO ₃	3.85 kg.	0.71 kg.	1.73 kg. CO ₂	0.55 kg. SiO ₂ (K ₂ SiO ₃)	1.24% Fe ₂ (SO ₄) ₃
0.48 kg. MgCO ₃	0.56 kg.	0.61 kg.	0.25 kg. CO ₂	2.55 kg. CaF ₂	1.27% CaF ₂
0.31 kg. CaSO ₄	—	—	—	11.27 kg. CaSO ₄ ·H ₂ O	0.70% SiO ₂ Total
0.01 kg. CaI ₂	—	—	trace	0.87 kg. SiO ₂	2.00% Phosphate
0.60 kg. undetermined	0.04 kg.	0.01 kg.	—	6.76 kg. CaSO ₄	0.31% Undetermined
4.00 kg. undissolved	—	—	—	0.69 kg. MgSO ₄	100.00%
100.00 kg. theoretical	62.94 kg.	31.47 kg.	8.12 kg.	0.31 kg. CaSO ₄	
actual	74.10 kg.	34.23 kg.		0.02 kg. CaSO ₄ ·2H ₂ O	
required excess	11.16 kg.	2.76 kg.		0.06 kg. undetermined	
				4.00 kg. Phosphate undissolved	
				11.16 kg. H ₂ SO ₄	
				4.56 kg. H ₂ O	
				200.21 kg.	

added to the theoretical quantity, so that 108.33 kilograms of 54° Baume acid are necessary to dissolve 96 kilograms of hard-rock phosphate. During the mixing process and until solidification takes place such gases as carbon-dioxide, hydrogen fluoride, and water vapor are evolved. A total of 8.12 kilograms of gases, 6.57 kilograms of dry gas, plus 1.55 kilograms of water, escape from the mass. The weight of the slurry is thereby reduced from 208.33 kilograms to 200.21 kilograms.

The initial slurry, which is in a semi-liquid condition immediately prior to solidification, shows the partially converted elements of the phosphate rock and acid, still in terms of actual weight, and the column headed "Final Product" gives the percentage composition of the superphosphate. This final analysis should be compared with the percentage composition of the ground phosphate.

EXPERIMENTAL

Since the curing time of superphosphate is governed by the reaction rate of sulfuric acid on the phosphate rock, it was decided to investigate the effect of heat on the reaction. It is known that heat applied to reacting materials will usually cause an increase in the reaction rate. Shreve (8) reports the temperature at which monocalcium phosphate reverts to dicalcium phosphate to be 200°C . On this basis it was decided to heat samples of raw superphosphate at 180°C . for varying lengths of time and to compare the amount of available P_2O_5 in these samples to that in samples cured at room temperature. Two other room temperature samples were prepared in order to determine the maximum temperature reached during the reaction and how long this increased temperature would persist. To accomplish this the following experimental work was conducted.

Four samples of superphosphate, each containing 27 grams of $50^{\circ}\text{Be}^{\circ}\text{H}_2\text{SO}_4$ and 30 grams of washed brown phosphate rock containing approximately 35.8% P_2O_5 and ground to a fineness of 85% through 200 mesh were prepared. Each sample was mixed with a thermometer and the maximum temperature was found to be approximately 72°C . The room temperature was 22°C .

Two of the samples were placed in an oven at a temperature of 180°C . and two were left at room temperature. The temperature of one of the room-temperature mixtures was recorded every half hour for the first five hours. These data are reported in Table IV. One heated sample was used to obtain a weight versus time of heating relationship as presented in Table V. A weighing of this mixture was made every 30 minutes for the first hours of curing. Samples to be analysed for available P_2O_5 were taken from the second mixture at room temperature and from one mixture in the oven at the intervals specified in Table VI.

TABLE IV. TIME-TEMPERATURE RELATIONSHIP OF MIXTURE

CURING AT ROOM TEMPERATURE

Samples A & B 30 grams rock, 27 grams acid

Time (Hours after initial mixing)	Air Temp °C	Sample A Temp °C	Sample B Temp °C
0	21.5	71.0	71.2
1/2	22.0	64.0	64.5
1	22.0	28.0	28.0
1 1/2	22.0	24.0	24.0
2	22.0	24.0	23.5
2 1/2	22.0	23.7	23.0
3	22.0	23.4	22.7
3 1/2	22.0	23.0	22.5
4	22.0	23.0	22.5
4 1/2	22.0	23.0	22.3
5	21.8	23.0	22.2

TABLE V. MOISTURE LOST DUE TO HEATING AT 180°C.

Weight of Samples A & B (30:0 grams rock, 27 grams acid) 57.0 grams.

Time (Days of Curing)	Weight Loss Sample A	Weight Loss Sample B
0.25	13.51 gm	- - - gm
1.0	14.16	13.74
2.0	14.36	14.04
3.0	14.36	14.24
4.0	14.36	14.04
7.0	13.66	14.14
8.0	13.86	14.14
9.0	13.86	14.04
10.0	13.85	14.04
11.0	13.86	14.14
Final Weight Loss	24.32%	24.81%
Average Weight Loss	24.6%	

TABLE VI. SUMMARY OF LABORATORY PREPARED SUPERPHOSPHATE

(Samples prepared as stated)

Sample Number	Treatment	T	% P_2O_5 W	CI	CS	A
1.	5 hr. curing at room temperature	18.17	13.18	2.48	2.42	16.22
2.	4 da. curing at room temperature	18.8	15.0	1.8	2.00	17.0
3.	9.2 da. curing at room temperature	19.5	--	--	--	--
4.	16 da. curing at room temperature	20.8	17.1	0.98	2.72	19.82
5.	23 da. curing at room temperature	20.7	16.82	0.69	3.2	20.02
6.	5 hr. curing at 180° C.	23.2	7.0	6.71	9.49	16.49
7.	1 da. at 180° C. & 10 da. at rm. temp.	22.4	6.36	6.3	9.74	16.10
8.	2 da. at 180° C. & 2 da. at rm. temp.	21.4	6.5	6.0	8.9	15.4
9.	2 da. at 180° C. & 14 da. at rm. temp.	23.4	13.75	4.52	5.13	18.88
10.	7 da. at 180° C. & 4 da. at rm. temp.	23.2	--	--	--	--

Note: T - Total
W - Water Soluble
CI - Citrate Insoluble
CS - Citrate Soluble
A - Available

The data in Table IV show that in small samples the heat created by mixing the acid and rock is dissipated within five hours, and no further heat effect is produced. The maximum temperature rise of 50° C. was reached during mixing.

Table V shows that the maximum weight loss from the mixture at 180° C. occurs within the first five hours.

The data in Table VI show that in the small samples at room temperature the P_2O_5 becomes nearly completely available in 16-23 days. This is attributed to the fineness of the original rock which produced an increased surface area and resultant increased reaction rate. The fact that the sample was thoroughly mixed during each sampling and given every opportunity to dry is also considered to have affected the drying rate.

Heating the mixture at 180° C. serves only to decrease the available P_2O_5 by decreasing both citrate and water solubilities. A comparison of samples Nos. 8 and 9 show that water soluble P_2O_5 has increased from 6.5 to 15.75% by merely remaining at room temperature for 12 days both having been originally heated for two days. Likewise, the water solubility of sample No. 4 was more than 3% higher than that of sample No. 9, both having been cured for 16 days, but the first two for sample No. 9 were at 180° C, indicating that the two-day heating applied to No. 9 retarded the development of water solubility.

The total P_2O_5 content of samples 1,2,3,4, and 5 show a gradual increase, while those of samples 6,7,8,9, and 10 remain essentially constant. As the samples at room temperature gradually dry, the percent relative total P_2O_5 increases to the point where no further moisture is lost. As was seen by Table V, the samples at 180°C lost the major portion of their moisture during the first five hours of heating. Therefore the percent of "total" P_2O_5 in the last five samples remains nearly constant.

Heating at 180°C. during the curing produces within 5 hours a superphosphate with approximately 16% available P_2O_5 . The heating, however,

drives off moisture needed for the hydration of the calcium monophosphate and causes it to be converted to the citrate soluble dicalcium phosphate. Heating also dries the liquid phase of the mixture at such a rate that a large per cent of the rock is not given time to react with the acid. This accounts for the high citrate insoluble content. By allowing the heated samples to remain at room temperature after being heated the monocalcium phosphate and dehydrated acid are given a chance to absorb water from the air. The acid then continues its reaction with the remaining rock, causing a reduction in insoluble matter, and the citrate soluble phosphate is reduced to water soluble phosphate. Heating at a lower temperature or in an autoclave is indicated by these results.

In view of these conclusions the following experimental work was conducted. One hundred thirty-five grams of phosphate rock, ground to 85% minus 200 mesh and containing 36.2% P_2O_5 , was mixed with 120.15 grams of 54°Be' H_2SO_4 , and the resulting mass allowed to cure for one hour at room temperature, 25° C. This large sample was then divided into five small samples, four weighing 55 grams and one weighing 24.7 grams. Two of the 55-gram samples were placed in an oven at 80° C., and the other two were left at room temperature. Samples for P_2O_5 and moisture determinations were taken from both the heated and room temperature samples after 1 hr., 4 hrs., 24 hrs., and 48 hrs., of curing. Percent moisture was determined by drying a 2-gram sample at 98-100°C. for five hours. This value is reported in Table VII.

The 24.7-gram sample was placed in a bomb and kept under a pressure of 100 pounds per square inch for one-half hour. The bomb, a cylinder approximately ten inches long and three inches in diameter, and equipped with

a pressure guage, was placed in an oven and heated for one-half hour at 100 psi. The sample was then removed and analyzed for available P_2O_5 .

Before considering the data in Table VII, it should be remembered that the material at room temperature was cured under the most desirable condition, that is, small sample size and repeated mixing when samples were taken. This superphosphate will, therefore, cure much more quickly than that prepared commercially. Hence, any improvement noted by comparing the results of heating to those at room temperature may be greatly increased when applied to material cured commercially.

An examination of the final available P_2O_5 obtained under both conditions shows that the heated sample has the greater amount. It will be noted that at the end of 48 hours at room temperature the available P_2O_5 has not reached the value obtained after 4 hours when heated. This is a curing time ratio of 12:1.

The citrate insoluble content of the room temperature sample shows a continued decrease, while that of the heated material remains essentially constant after four hours of heating. Therefore, it may be said that there is no further action of acid on rock after this time. This lack of action is caused by drying the liquid phase.

The percent of water soluble material increases constantly in the case of the room temperature curing, but shows a decrease after four hours of heating. This decrease was expected since continued mild heating causes the conversion of monocalcium to dicalcium phosphate.

A comparison of the sample cured under pressure with both other samples shows that excellent results were achieved by this method. After $1/2$ hour the available P_2O_5 content of this sample is equivalent to that

obtained after 48 hours at room temperature.

The data in Table VIII are calculated values based on the same total P_2O_5 - 22.9%. This was the value obtained after 48 hours heating when the sample is nearly dry. This comparison is valuable in that it puts all the figures on the same basis. It will be noted that the same trends prevail on this basis as on the "as analyzed" basis. The available P_2O_5 contents are higher in the heated samples than in those of room temperature, and the available P_2O_5 in the sample cured under pressure is higher than either of the others except those cured for 48 hrs. at room temperature.

These data show definitely that the available P_2O_5 increases as moisture decreases and are in complete agreement with the theory of curing presented earlier in this thesis. The sudden increase in water solubility of the heated material over that cured at room temperature is due to the high free acid water ratio discussed in the theoretical section. As water is evaporated the acid becomes more concentrated and its action on the remaining rock is increased. The only way for the liquid phase (of the material cured at room temperature) to become concentrated is through normal evaporation of the water present. This drying is slower than the evaporation of water from heated material, and therefore the action of acid on the rock is slower. This is borne out by comparing the citrate insoluble contents of both samples which have been cured for the same length of time.

TABLE VII. COMPARISON OF SUPERPHOSPHATE CURED AT ROOM TEMPERATURE
TO THAT CURED AT 80° C.

A. Cured at Room Temperature 25° C.

B. Heated at 80° C.

C. Cured under 100 lbs. per square inch pressure

Sample	Length of Curing	% Moisture	T	W	% P ₂ O ₅ CI	CS	A
A	1 hr.	12.8%	19.95	11.77	4.67	3.51	15.28
	4	12.4	20.2	14.0	3.1	3.1	17.1
	24	10.1	*20.2	15.29	2.5	2.41	17.7
	48	9.81	*20.25	16.42	1.43	2.40	18.82
B	1 hr.	8.15	20.64	14.0	3.72	2.92	16.92
	4	3.4	21.8	15.35	2.13	4.32	19.67
	24	1.04	*22.8	14.4	2.14	6.26	20.66
	48	0.92	*22.9	14.45	2.12	6.33	20.78
C	0.5 hr.		*22.3	15.18	2.64	5.48	20.66

TABLE VIII. CALCULATED VALUES OF ABOVE DATA BASED ON A TOTAL P₂O₅
CONTENT OF 22.9%

(Samples as above)

A	1 hr.	22.9	13.5	5.4	4.0	17.5
	4	22.9	15.9	3.5	3.5	19.4
	24	22.9	17.34	1.83	3.73	21.07
	48	22.9	18.55	1.62	2.73	21.28
B	1 hr.	22.9	15.5	4.12	3.28	18.78
	4	22.9	16.1	2.2	4.6	20.7
	24	22.9	14.5	2.15	6.25	20.75
	48	22.9	14.45	2.12	6.33	20.78
C	0.5 hr.	22.9	15.55	2.71	4.64	21.19

Notes:

T - Total

W - Water Soluble

CI - Citrate Soluble

CS - Citrate Insoluble

A - Available

* - These figures based on weight loss

All analyses were conducted according to instructions presented in the 1946 edition of "Official Analyses of Association of Official Agricultural Chemists." The gravimetric procedure was used. This method consists of first dissolving a sample of phosphatic material in a solution of HCl and HNO₃. After adjusting the acidity and temperature of the solution, the phosphate is precipitated as ammonium-phospho-molybdate. This yellow precipitate is then dissolved in ammonia. From the diluted solution magnesium phosphate is precipitated and subsequently fired to magnesium pyrophosphate in an electric muffle furnace, then weighed, and converted to per cent P₂O₅ by calculation.

The water soluble phosphate is removed by washing a one gram sample with 250 ml. of water then treating the solution as above. The residue from this washing is digested at 65° C for one hour in a solution of neutral ammonium citrate. The remaining unreacted phosphate and mulched filter paper is filtered, and then redissolved in a mixture of HCl and HNO₃ and the process continued as above.

S U M M A R Y

Heating superphosphate at 180° C. destroys its value as a fertilizer by drying the liquid phase, thus allowing the formation of a minimum amount of monocalcium phosphate. The high citrate insoluble content of this material shows that the action of acid on the rock is far from complete. An available P_2O_5 content of only 15-16% was obtained by this high temperature heating.

Superphosphate cured at 80° C. showed much better results. Curing time was greatly reduced, the available P_2O_5 content was high, and the mechanical condition of the fertilizer was good. After 4 hours of curing, the available P_2O_5 of the heated sample was 19.67%. This was 2.5% P_2O_5 higher than that obtained by curing a similar sample for the same length of time at room temperature, 25° C. Even after 48 hours of curing, the available P_2O_5 content of the room-temperature sample is nearly 1% P_2O_5 less than what the heated sample contained after 4 hours of curing. The heated sample reached an ultimate available P_2O_5 content 12 times more quickly than the room temperature sample.

The material at room temperature was cured under the most desirable conditions, that is, a small sample size and repeated mixing when samples were taken. This superphosphate will, therefore, cure much more quickly than that prepared commercially. Hence, any improvement noted by comparing the results of heating to the results at room temperature may be greatly increased when applied to material cured commercially.

A comparison of the sample cured under pressure with both other samples shows that good results were achieved by this method. After 1/2 hour, the available P_2O_5 content of this sample was greater than that obtained after 48 hours at room temperature and approximately equal to that

obtained after 24 hours of heating.

It is therefore concluded that mild heating of curing super-phosphate is of definite value in speeding up the curing. However, the overall conversion of phosphate rock to a soluble form must be increased in order that this form of curing may be commercially attractive.

L I T E R A T U R E C I T E D

1. Packard, Walter, Trans. of Inst. of Chem. Eng. 15; 981
London, (1927)
2. Morfit, C., "Practical Treatise on Pure Fertilizers", Vol. 1,
p. 315, London, Trubner and Co. (1873)
3. Larison, E.L., Ind. and Eng. Chem., 21:1172 (1929)
4. Collins, S.H., "Commerical Fertilizers and Parasiticoides",
pp. 153-158, D. Van Nostrand Co., New York, (1920)
5. Grey, A.N., "Phosphates and Superphosphates", p.126,
Interscience Publishers, London (1942)
6. Marshall, H.L., Hill, W.L., Ind. Eng. Chem., 33:1131 (1940)
7. Marshall, H.L., Hill, W.L., Ind. Eng. Chem., 33:1224 (1941)
8. Shreve, R.N., "Chemical Process Industries", p. 336, New York,
McGraw-Hill Book Co. (1945)

A P P E N D I X

BIBLIOGRAPHY

- (1) Curtis, H.A., Copson, R.L., Brown, E.H., Pole, G.R., Ind. Eng. Chem., 29:766-70 (1937)
- (2) Elmore, K.L., Farr, T.D., Ind. Eng. Chem., 32:580-7 (1940)
- (3) Fishburne, G.R., American Fertilizer, 62(9):21-5 (1939)
- (4) Fox, E.J., Hill, W.L., Jacob, K.D., Reynolds, D.S., Ind. Eng. Chem. 38:329-33 (1946)
- (5) Guernsey, E.W., Yee, J.Y., Ind. Eng. Chem., 16:228-238 (1924)
- (6) Hardesty, J.O., Ross, Wm., Chem. and Ind., 58:885 (1939)
- (7) Hendricks, S.B., Hill, W.L., Ind. Eng. Chem., 30:304-8 (1928)
- (8) Hendricks, S.B., Ind. Eng. Chem. 28:440-7 (1936)
- (9) Jacob, K.D., Hill, W.L., Ross, W.H., Rader, L.F., Ind. Eng. Chem., 22:1385-90
- (10) Jacob, K.D., Ind. Eng. Chem. 25:1312-22 (1933)
- (11) Keenen, F.G., Ind. Eng. Chem., 22:1378 (1930)
- (12) Keenen, F.G., Ind. Eng. Chem., 24:44-9 (1932)
- (13) Keenen, F.G., Morgan, W.A., Ind. Eng. Chem., 29:197-201 (1937)
- (14) Kobe, K.A., Hamm, Wm.S., Leipper, A., Ind. Eng. Chem., 32:981-4 (1940)
- (15) Mackall, J.H., Shoeld, M., Chem. Met. 47:102-5 (1940)
- (16) MacIntire, W.H., Hardin, L.J., Oldham, F.D., Ind. Eng. Chem., 28:48 (1936)
- (17) MacIntire, W.H., Hardin, L.J., Oldham, F.D., Hammond, J.W., Ind. Eng. Chem., 29:758-766 (1937)
- (18) MacIntire, W.H., Hardin, L.F., Ind. Eng. Chem., 32:88-94 (1940)

- (19) MacIntire, W.H., Hardin, L.J., Ind. Eng. Chem., 32:574-9 (1940)
- (20) Marshall, H.L., Hill, W.L., Ind. Eng. Chem., 32:1224-1232 (1930)
- (21) Marshall, H.L., Hill, W.L., Jacob, K.D., Ind. Eng. Chem., 23:1120-4 (1931)
- (22) Marshall, H.L., Rader, L.F., Reynolds, D.S., Jacob, K.D., Ind. Eng. Chem., 23:87-91 (1935)
- (23) Marshall, H.L., Reynolds, D.S., Jacob, K.D., Rader, L.F., Ind. Eng. Chem., 27:205-9 (1935)
- (24) Marshall, H.L., Reynolds, D.S., Jacob, K.D., Rader, L.F., Ind. Eng. Chem. 28:678-82 (1936)
- (25) Marshall, H.L., Reynolds, D.S., Jacob, K.D., Tremearne, T.H., Ind. Eng. Chem., 29:1294-8 (1937)
- (26) Marshall, S.B., Hill, W.L., Ind. Eng. Chem., 34:722-9 (1942)
- (27) McBride, R.S., Chem. Met., 47:102-5 (1940)
- (28) McBride, R.S., Chem. Eng. 54:92-5 (1947)
- (29) Waggaman, Wm. H., Wagner, C.R., Ind. Eng. Chem., 10:443 (1918)
- (30) Waggaman, W.H., Menninger, C.G., Whitney, W.T., Ind. Eng. Chem.
- (31) Weber, W.C., Chem. Met., 40:72-5 (1933)

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V I T A

VITA

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