ROTARY KILN APPLIED TO CALCINATION OF PHOSPHATES

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The rotary kiln applied to
calcination of phosphates

THE ROTARY KILN

APPLIED TO

CALCINATION OF PHOSPHATES

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THE ROTARY KILN

Applied To

CALCINATION OF PHOSPHATES

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CHEMISTRY OF HIGH TEMPERATURES.

The field of Chemistry, relating particularly to chemical changes and chemical re-actions taking place between different compounds at high temperatures, is one that has been given but little systematic study by chemists and engineers, until within the last few years. Very little is known, considering the extent and importance of this branch of chemistry, as to just what changes do occur at these high temperatures.

Portland Cement clinker is produced at temperatures ranging from 2200 to 2600 degrees Fahrenheit. Portland Cement was invented by Joseph Aspdin in 1824. Last year this country produced over eighty million barrels of Portland Cement, and yet, the exact changes which take place during

the clinkering process are not fully understood. Another recent application of the chemistry of high temperatures to the commercial field is in the manufacture of Cyanamid, which is a product produced from calcium carbide, in which the calcium carbide is treated to about 6000 degrees Fahrenheit, in electric furnaces, and air under pressure passed over the material; during this process the nitrogen is absorbed from the air and stored up in the material, and is available for plant food when this material is distributed and incorporated in the soil.

Of Nature's three great forces, heat, pressure, and moisture, heat is probably the most important, and it has remained for the chemical engineer to produce in a comparatively short space of time, with the aid of high temperatures, what it required Nature a great many thousand years to accomplish. For example:

In nature, decayed vegetation first becomes a soft "muck" deposit in a swamp; heat, pressure and moisture act for centuries and peat is

produced; later, the lower grades of coal, such as lignite; then, semi-bituminous; then bituminous, and then anthracite, graphite, and finally diamond, which is the purest form of carbon, and yet chemists have been able to manufacture diamond by means of very high temperatures in a very short time, while Nature required millions of years.

THE ROTARY KILN.

The use of the rotary type of furnace has increased wonderfully since its adaptation to the manufacture of Portland Cement in the 70's, before which time all cement was manufactured in the vertical or stationary kiln. Today practically 99% of the Portland Cement produced is manufactured in the rotary kiln. The rotatable furnace is not the most economical type so far as fuel consumption is concerned, as the vertical or stationary kiln consumes but forty-five to fifty pounds of coal per barrel of cement, while the rotary kiln requires one hundred to one hundred fifty pounds. However, the rotary kiln is

much more economical in point of labor, and produces an absolutely uniform product, which is not possible with the stationary type.

The rotary kiln had been adapted commercially to the manufacture of lime, which has heretofore been burned in a stationary vertical kiln. It has been successfully used for nodulizing low-grade iron ores, for "sintering" iron ores, has been successfully adapted for treating iron ores high in sulphur by removing the sulphur and thereby rendering the iron ore available for commercial purposes, and during the year 1912 it was successfully applied to the Calcination of Phosphates for fertilizer purposes.

FERTILIZER.

Leibig was probably the first to advance the theory of soil restoration. In the United States, however, James Mapes first introduced phosphates in 1849.

The fertilizer industry is one of vital importance to this and all other countries. In

1898, Sir William Crookes calculated that the bread-eaters of America and Europe numbered at that time 516,000,000 and were increasing annually at the rate of 6,000,000. In that year there were 167,000,000 acres devoted to the production of cereals, and only 100,000,000 acres more available for such crops. The average yield per acre of wheat was 12.6 bushels, and the annual per capita consumption was 4.6 bushels. From this data it was calculated that the wheat fields of the world in 1941 must cover 292,000,000 acres, in order to feed a population of 819,000,000 bread-eaters.

Only by fertilization could the production per acre of the wheat fields be increased to meet the needs of the increasing population. This has been accomplished, and for years Europe had been producing from 50% to 125% more food products per acre than the United States. It is very true that crop rotation and careful attention to tillage, etc., produce many beneficial results, but the most important factor in increased production is in proper fertilization.

Last year this country consumed over 6,500,000 tons of fertilizer. Different crops and different food products require different characters of fertilizer. What is known as a "complete" fertilizer, consists of different proportions of the three principal plant foods, phosphoric acid, nitrogen and potash. A popular formula for a "complete" fertilizer, and oneused extensively, on cotton crops, is a "2-8-2" mixture, which means 2% nitrogen, 8% phosphoric acid and 2% potash. In nature none of these materials occur in a pure or concentrated form, but are more or less contaminated with other natural minerals, so that in assembling the mixtures, the actual weight of the product containing these percentages may amount to, say, 1400 pounds, and the balance of the ton, or 600 pounds, is supplied by an artificial "filler" which at present may be sand, ashes, coal or any other cheap material.

At the present time, the source of nitrogen for fertilizer is ammonium nitrate imported from Chili, fish-meal, slaughter house refuse, hair, leather, ammonium sulphate, which is a by-product in the manufacture of coke, and Cyanamid, the new

electric-process product by which nitrogen is extracted from the air.

Substantially all of our potash is imported from Germany. At present, however, many attempts are being made to treat feldspathic rocks and "kelp" and "brines" in order to produce potash for our use, and thus reduce the existing high cost.

SOURCES OF PHOSPHORIC ACID.

Our source of supply of phosphoric acid exists in the phosphate rock deposits in Florida, Tennessee, South Carolina, Arkansas, Idaho, and Nevada, and in a few islands in the West Indies where small amounts of guano is secured. Very little development has been done in Arkansas and the Western States, and Florida leads in the production at present.

The various deposits of phosphates in the United States are phosphates of lime, or tricalcium phosphate, a typical analysis being:

(Tennessee Brown Rock)

B.P.L. (Bone Phosphate of Lime)	72.0%
Fe_2O_3 and AL_2O_3 (Iron & Alumina)	4.0%
SIO_2 (Silica)	6.0%
MgO (Magnesia)	0.25%
Loss	5.0%

Note:- The above 72% B.P.L. is equal to 32.9% P_2O_5 (Phosphoric acid).

There are extensive deposits of phosphates on several of the West India Islands, notably the islands of Redonda and Connetable, from which several thousand tons annually are exported to the United States and Europe. These phosphates, however, are not phosphates of lime, but phosphates of iron and alumina. An analysis of a Redonda phosphate is:

Water	24.20%
P_2O_5 (Phosphoric acid)	38.52%
Fe_2O_3 & AL_2O_3 (Iron & Alumina)	35.33%
Insoluble	1.95%

These phosphates are not treated by the usual acid process, but are heated to a tempera-

ture of about 1000 degrees Fahrenheit, when the water of combination is driven off and the phosphoric acid is rendered temporarily "citrate-soluble." The change is not permanent and considerable difficulty is experienced in marketing the product, due to the dissimilarity of analyses of samples, these differences being caused by "reversion" of the "available" or "citrate-soluble" phosphoric acid to a <u>less</u> soluble form.

The so-called guanos from the West Indies contain substantial portions of their phosphoric acid in an available form, and often contain some nitrogen. After drying, they are generally applied direct to the soil with very beneficial results.

Following is an analysis of a guano from the Isle of Mono:

Available Phosphoric acid	8.00
Insoluble Phosphoric acid	17.30
Total P_2O_5	25.30
Nitrogen	1.21
Sulphate of Lime (Gypsum)	38.88

In Canada are a few deposits of Apatite which is a crystallized mineral phosphate, and contains as much as 85% Bone Phosphate of Lime.

In some parts of Europe there are found phosphatic iron ores, and in the Bessemer process in use extensively in Germany, so-called Thomas Powder, or Basic Slag is produced, in which the lime content may be possibly 50%, and 18% to 20% P_2O_5 or Phosphoric acid. This phosphoric acid occurring in Basic Slag is known as "citrate-soluble" instead of"water-soluble". In other words, it is soluble in a solution of ammonium citrate, or in a stronger citric acid solution as designated by the Wagner method of analysis.

SOLUBILITY AND AVAILABILITY.

The phosphoric acid in raw phosphate rock exists as tri-calcium phosphate and is insoluble in water, and not "available" for plant food. The rock is therefore treated with substantially equal weights of sulphuric acid, whereby the phosphoric acid is changed to mono-calcium-phosphate, is soluble in water and a neutral solution of ammonium citrate, this resulting product

being known as Acid Phosphate, or Superphosphate. Upon standing, water-soluble phosphoric acid (mono-calcium-phosphate) gradually "reverts" or "retrogrades" to less soluble forms, and is called "di-calcium-phosphate".

Originally all acid phosphate was sold upon a unit basis of "water-soluble" phosphoric acid. Due, however, to the variations in analyses of the producers and the consumers, the "citrate-soluble" test has come into almost universal use. Estensive tests, both here and in Europe, have proven that "citrate-soluble" phosphoric acid is just as "available" for plant food as "water-soluble"; in fact, upon application to the soil, "water-soluble" phosphoric acid "reverts" almost instantly, and in the case of a clay soil which is high in iron and alumina, phosphates of iron and alumina are formed which are not easily assimilable by the plants.

It is true, however, that the phosphoric acid must be in the "citrate-soluble" form in order to be assimilated by the plants, and for

the reason that the neutral solution of ammonium citrate is the nearest approach to the actual soil moistures, the chemist has been able to produce, it has been adopted by the Society of Agricultural Chemists.

Acid Phosphate is now sold on a basis of "unit available", which is the sum of the "water-soluble" and "citrate-soluble". A majority of the State Laboratories use only the "citrate-soluble" test.

In Europe the Wagner method of analysis was devised to test Basic Slag, which contains 15% to 25% phosphoric acid, and 40% to 50% lime. It yields only about 50% of its phosphoric acid to a neutral solution of ammonium citrate, but 90% or more to a strong citric acid solution used in the Wagner test.

PROCESSES.

There are, in Kentucky, Florida, Tennessee and Arkansas, and some other widely separated locations in this country, enormous deposits of phos-

phatic limestone or "low-grade" phosphate rock, containing possibly 15% to 25% P_2O_5, whereas, the minimum grade commecially permissable for treatment by the sulphuric acid process must contain 31%, equivalent to 68% of Bone Phosphate of Lime.

If some method could be devised, whereby the phosphoric acid occurring in these low-grade materials could be rendered "available" for plant food, then, this renders valuable great areas of, at the present time, practically valueless minerals, since the lime occurring in these deposits is essential to a majority of the soils and phosphoric acid is the most important plant food used in the country, and forms practically 50% of all fertilizer. In the present process, in order to render all of the phosphoric acid available, an excess of sulphuric acid is generally added. When applied to the soil, this acid, of course, has detrimental affects, and a great many users are opposed to applying it to the soil, but at present it is the only source of commercially "available" phosphoric acid.

A large number of attempts have been made during the past century, looking towards evolving a process for the treatment of phosphates, by which the phosphoric acid would be rendered "available" for plant food without the use of sulphuric acid. The work was first taken up in Europe, and in this country, the problem has received considerable attention, but to our knowledge the work has never progressed past the theoretical or laboratory stage.

Among the more recent investigators, Spencer B.Newberry, George R.Fishburne and Harvey N.Barrett spent about four years making various tests in their laboratory on the work, and in February last year, the writer, together with W.P.Putnam of Detroit, joined in working out this process from the laboratory stage to a commercial application.

PRIOR ART.

Following is a list of the principal British and American Patents pertaining to the Art.

Patentee	Date	Claims
(British)		
Ville	1863	Disintegrates or alters chemical constitution by calcining with addition of salts - forms compounds of highly beneficial effects for "agricultural purposes."
Leibig	1865	Roasts or smelts phosphates of iron and alumina, producing "water-soluble" alkali-metal sulphates.
Williams	1876	Treats phosphates of iron, alumina and lime with salts of soda and coal in the furnace. Mix - 3 parts soda to 1 part phosphoric acid with carbon.

Patentee (British)	Date	Claims
Bazin	1887	Treats in nodule form to temperatures of 2300 to 2700 degrees Fahrenheit for several hours in regenerative furnace. Claims chemical changes.
Wiborgh	1896	Pulverizes phosphates, mixes with carbonate of sodium, potassium or caustic soda or potash; heats to red heat or yellow heat in order to get a tetra-calcium-sodium (or potassium) phosphate. Mix - 20% to 30% soda.
Hasslacher	1889	Mixes phosphates of lime with alkaline sulphate and coal - heats to red heat - product contains all of original materials. Mix - 2 parts alkali, 1 part phosphate.

Patentee	Date	Claims
(British)		
Wolkey	1906	Mixes 10 parts phosphate, 1 part sawdust and 2.5 parts coal; bright red heat; claims calcium oxide and mono-calcium-meta-phosphate.
(Norway)		
Palmaer	1907	By electrolysis produces "citrate-soluble" phosphoric acid in "di-calcic" form. Must have very cheap electric power and high grade rock, preferably apatite.
(American)		
Dunne	1885	Mixes 100 parts phosphate rock, 6-14 parts potassium sulphate, 59-94 parts sodium sulphate. Furnaces to "high temperature." Produces "water-soluble" alkali metal sulphate.

Patentee	Date	Claims
(American)		
Day	1895	Phosphates of lime calcined with carbonate of lime, with or without silica and potassium sulphate to temperature below partial fusion.
Wallers	1898	Mixes 100 parts phosphate, 80 parts chalk, 30 parts silica. Furnaced in Seimens type oven to not less than 2192 degrees Fahrenheit, or to a thin fluid molten mass.
Meriwether	1908	Fuses phosphate rock with carbonate or fluoride of lime and magnesia at 2610 degrees Fahrenheit. Claims chemical reaction at this temperature. States addition of silica will lower fusing temperature, but all phosphoric acid will be driven off.

Patentee	Date	Claims
(American)		
Lowman	1908	Mixes 1000 pounds phosphate rock, 250 pounds salt, 200 pounds dolomite, 50 pounds fluorspar; furnaced to 800 degrees Fahrenheit for 12 hours. Claims phosphoric acid released or converted into "available" phosphoric acid.
Connor	1908	Crushes rock to 16-mesh. Mixes 1525 pounds rock, 275 pounds alkali, 200 pounds lime, stationary furnace, 1500 to 2000 degrees Fahrenheit.
Peacock	1909	Adds silica and lime, volatilizes phosphoric acid and has Portland Cement as by-product.
Levi	1909	Heats mixture of phosphate rock, silica and anhydrous salt of sodium in electric furnace to fluid; claims P_2O_5 is separated.

Patentee (American)	Date	Claims
Galt	1910	Adds lime-mud to phosphate rock, mixes 120 parts phosphate rock, 150 part lime, 40 parts soda ash.
Downs	1911	Mixes 100 parts phosphate rock, 25 parts silica, briquetted and furnaced to maximum temperature of 2012 degrees Fahrenheit for six hours. Claims citrate-soluble product after grinding.
Dunham	1912	Grinds rock to 80-100 mesh. Mixes 100 parts rock, 15 parts sulphuric acid, 30 parts water, furnaced 1 hour to fairly high heat.
Washburne	1912	Heats in electric furnace to fluid condition, mixture of phosphate rock, silica and carbon with evolution of phosphoric acid.

HISTORY OF PRESENT DEVELOPMENT.

In the Spring of 1908, Fishburne suggested to Newberry the idea of using silica as a flux with phosphate rock, and possibly subjecting this mixture to a treatment similar to the process of cement manufacture. Some of the earliest attempts to supplant the sulphuric acid process were made along this line, but it has been necessary for the cement industry to be completely revolutionized and modernized and commercialized during its growth, really starting in the 70's and growing from a quarter million barrels production in the States in 1890 to 81,000,000 barrels in 1912, before success could be hoped for by such an application. Hence, any efforts by the first investigators to apply these methods must have been, at best, but crude makeshifts and even though the same general conditions might have satisfied both materials, still in the light of our recent work, the phosphates present certain conditions peculiar to themselves, while still subject to the same general treatment as cement materials.

Newberry's first work was possibly an effort to produce a product similar to Basic Slag in which the phosphoric acid is soluble in a citric acid solution, according to the Wagner method of analysis, and containing a large lime content. Sulphuric acid, lime, and phosphates of soda or potash, were used as "re-agents", the work being carried on in a small Fletcher furnace, with varying degrees of success.

Later, lime and sodium carbonate were successfully used; carbon and gypsum were added to the list. Next, sodium and potassium were found to yield better results. Sodium carbonate alone, it was found, was equally successful. It was discovered it was not necessary to add lime at all, unless the phosphate rock treated contained more than 8% of silica. Tests were made showing 80% conversion of the phosphoric acid present to citrate-solubility *without* the presence of *any* re-agent, by *longer exposure* and *greater temperatures* than in the previous experiments. Bazin, however, im 1887, was granted the first broad claim

of Calcination of Phosphates with no "re-agent".

During the tests the preparations were as follows:

The phosphate rock was ground fine, (about 95% passing a 200-mesh seive) thoroughly mixed with predetermined proportions of the re-agent to be used; water added to insure a thorough mixture, and then dried and broken into pieces and placed in a small Fletcher furnace, a vertical cylinder open at the top, and a gas flame inserted at the side near the base, the flames passing up through the material. The material produced was a soft porous clinker easily crushed between the fingers.

Various temperatures and exposures were tried, it being found, however, that one hour at from 2200 to 2400 degrees Fahrenheit was sufficient to produce good results.

Due to the low fluxing temperature of silica, especially in the presence of an alkali, it was found necessary to use a furnace constructed of magnesite, and later, the rotary kilns were

lined throughout the "hot" or clinkering zones with magnesite brick.

Next, a small rotary kiln, 8 inches inside diameter by 10 feet long was built, and lined for thirty inches with magnesite brick:. Many tests were made before good results were finally secured in this kiln.

In 1911, about 60 tons of materials in the proportions of 100 parts of rock to 30 parts of sodium carbonate were fed to one of the cement kilns (7ft X 125ft) at Bay Bridge, Ohio; the silica lining fused quickly with the material, the product coming out in hard brittle, fused, black balls. Upon analysis, it was found that the silica had "diluted" the phosphoric acid to a large extent but a conversion to 15% citrate-soluble phosphoric acid was secured.

This material was ground and furnished to three State Agricultural Experimental Stations (Ohio, Indiana and New Jersey) where field and pot tests have been made in comparison with equal amounts of acid phosphate on an available unit

basis. These tests, together with many pot tests by other investigators using material produced during 1912, among them being the United States Bureau of Soils, have proven that "citrate-soluble" phosphoric acid in Calcined Phosphate is just as "available" as that in Acid Phosphate.

The following statement by Dr.Harvey W. Wiley is fairly indicative of the general opinion expressed by those who have investigated this material:

> "I have had your product as manufactured by the Newberry process tested, and find that it contains the full quantity of citrate-soluble phosphoric acid claimed. I also believe that for most crops, especially the legumes, this form of phosphate fertilizer is superior in character to the ordinary acid phosphate as manufactured by the sulphuric acid process. Citrate-soluble phosphoric acid is given the same commercial value as water-soluble phosphoric acid."

CALCINED PROCESS AND PRODUCT.

As a result of the experiments so far, it has been found that the conditions necessary for perfect results are greater in number and confined within narrower limits than in the manufacture of Portland Cement. In making Cyanamid there are twenty variables. There have been determined in this process, so far, fourteen, as follows:

1. Character of Fuel.
2. Temperature.
3. Fineness of Feed.
4. Moisture in Feed.
5. Character and amount of Re-agent.
6. Time of Exposure.
7. Percentage of Silica in Feed.
8. Pitch of kiln.
9. Length of Kiln.
10. Diameter of Kiln.
11. Speed of Kiln.
12. Velocity of Gases.
13. Draft.
14. Volume of Gases.

No favor able results whatever were secured with silica as a re-agent. It was found that if the rock treated contained over 8% or 10% of silica, the material easily fused and very low conversion resulted; in fact, the actual fusing or "balling" or heating to a "molten fluid" even in the absence of silica, apparently defeated the action necessary to produce citrate-soluble phosphoric acid.

From a study of the Prior Art and in the light of these recent experiments, it will be noted that practically all of the previous investigators claimed a product *chemically* different from the raw phosphate rock used as raw material with the possible exception of one or two; and assuming that they secured the results claimed, in *none* of the processes was the "re-agent" substantially *all volatilized*, but remained in the finished product possibly in some combined form, and "diluting" the phosphoric acid contained in the original rock. For example:

Wallers adds 80 parts chalk and 30 parts silica to 100 parts phosphate. Assume CO_2 driven

off from the chalk, then the total weight of the mix is:-

$$100 + 48 + 30 = 178,$$

and if the original phosphate contained, say 32% P_2O_5, then the resulting product will contain:-

$$32 \div 1.78 = 18\%\ P_2O_5.$$

In this process, if the raw materials are proportioned as 2000 pounds rock to 350 pounds sodium sulphate, the sodium sulphate is substantially *all volatilized* during the furnacing, and the loss by weight about equals the weight of the sodium sulphate added. It is quite possible that during the lower temperatures, say from 1000 degrees Fahrenheit to 2000 degrees Fahrenheit, certain chemical re-actions occur, and possibly some of the sodium combines with the phosphate to form calcium-sodium-phosphate. From the following facts established by the tests so far, however, it would appear that due to the high temperature there is a pronounced *re-arrangement* of the moleclues, thereby producing a *physical* or *mechanical* rather than a *chemical* change, and rendering the

tri-calcium-phosphate in the raw rock *citrate-soluble*.

Reasons for this theory are:

1. By *longer* exposure and *higher* temperature with *no* re-agent nearly as high a percentage of *citrate-solubility* may be produced as when a re-agent is used.
2. Practically the same results may be obtained with either sodium sulphate, sodium carbonate, nitre cake, or carbon; and the substance added is substantially *all volatilized* during calcination. In order to determine the effect, if any, of the impurities existing in the phosphate rock, such as iron, silica and alumina, etc, upon the action, a test was made in which 500 parts of *pure* bone-ash was mixed with 75 parts of pure soda ash (Na_2Co_3); an analysis of the product gave:

Total P_2O_5	38.88
Citrate Soluble P_2O_5	35.29
Insoluble P_2O_5	3.59

Note:- In the preceding test, Tennessee Brown Rock was used, and the raw mixture contained 19.74% Sodium Sulphate, (NA_2SO_4). The sodium oxide remaining in the clinker is but a fractional part of the amount necessary to combine chemically with the phosphate.

4. The specific gravity of the clinker is practically the same as that of the raw phosphate rock, as follows:

Specific Gravity Raw Rock	2.8%
Specific Gravity "Clinker" (28.25% Citrate Soluble P_2O_5)	2.91%

Several materials may be cited which possess <u>identical chemical</u> analyses but <u>entirely different physical</u> properties. For example: Red and Yellow Phosphorus have the same chemical analyses but almost opposite physical properties:

	Phosphorus	
	Yellow	Red
Formula	P_4	P_4
Molecular Wgt	124.	124.
Specific Gravity	1.83	2.296
Melting Point	44.2°	350.0°
Solubility	Insoluble in water. Soluble in carbon bi-sulphide.	Insoluble in carbon bi-sulphide.
Remarks	Red phosphorus is formed when yellow phosphorus is exposed to light or heated without access of air.	
	Must be kept under water and in dark place.	
	Poisonous.	Not poisonous.

Note:- The cause of the great difference of the properties is not known.

CURVES.

The three plates of curves represent three successive stages in the evolution of the experimental work and the attempt to effect a really practical commercial adaptation of the process. Practically no difficulty was experienced in putting the 20-foot kiln into operation and producing good "clinker" i.e. one containing, at least, 95% conversion to citrate-solubility.

The attempt was first made to operate the 40-foot kiln with data secured from the 10-foot kiln; but not until the 20-foot kiln had been in operation some time were the conditions discovered which were vital to the successful operation of the larger kiln.

Plate No.1 shows the Temperatures, percents of re-agent, and Insoluble P_2O_5 for the 10-foot kiln. The temperatures were taken with a Le Chetelier Pyrometer, the couple being inserted through holes drilled through the shell and lining. The Re-agent and P_2O_5 curves were plotted from analyses of samples taken at regular distances throughout the length of the kiln. It will be noted how closely

the variations in the two curves correspond; as the re-agent is volatilized, the insoluble phosphoric acid decreases, until in the finished clinker substantially all the phosphoric acid is soluble and the re-agent has been driven off.

Plate No.2 shows similar curves for the 20-foot kiln, the data being secured in the same manner. It was necessary to reproduce practically the <u>same</u> conditions for this kiln that obtained in the smaller kiln, before perfect results were secured. A slightly better and more uniform clinker was produced from this kiln.

Plate No.3 represents the conditions obtaining in the 40-foot kiln when producing good material. It will be noticed that the temperature curve for this kiln is nearly a mean of the temperature curves of the other two kilns.

Due to the silica present in the ash of the pulverized coal, it was found necessary to use oil as fuel in the 40-foot kiln, because of the

fluxing action of the silica and phosphoric acid. In a permanent commercial installation, due to the high price of oil, however, it will be necessary to use either a very low ash coal, or producer gas.

COST OF PRODUCTION.

Because of the close similarity of the important steps of this process to the manufacture of Portland Cement, and using data secured in the development of this process, the cost of the production of Calcined Phosphate has been quite accurately determined. Following are the chief differences between the two processes:

1st. Phosphate rock can be ground and pulverized at about 80% to 85% of the cost of reducing ordinary finely crystalline limestone.

2nd. The temperature to which the phosphate rock is treated in the kilns will not vary more than 100 to 200 degrees from that obtaining in Portland Cement kilns. The loss by volatilization in the cement process is about 40% of the weight of the materials treated. The loss in the Calcination Process is from 12% to 18%. So far as we have been

able to determine, there are no endothermic nor exothermic actions during the process of calcination.

3rd. The "grindability" of the clinker is about 20% to 30% of that of Portland Cement clinker, i.e., a cement grinding machine producing, say, one ton of cement clinker per hour, will produce three to four tons of Calcined Phosphate per hour.

4th. Assuming that ordinary limestone and clay or shale are used, with coal at $2.00 per ton, and labor at $1.75, a modern 1500 barrel mill should produce cement, including a "reasonable overhead" expense at $0.65 per barrel or $3.25 per ton. Deducting from this the quarrying cost of, say, $0.50, would make the process cost $2.75 per ton, which is a conservative

figure, if used to represent the production cost of Calcined Phosphate. Adding to this, Phosphate Rock purchased in the open market at $5.00 per ton containing 32.5% phosphoric acid, and 350 pounds of sodium sulphate at $10.00 per ton, the total cost would be about, as follows:

	Per Ton
Process (including "overhead")	$2.75
One Ton Phosphate Rock	5.00
350 pounds Sodium Sulphate	1.75
Total	$9.50

$9.50 represents the total cost of one ton of Calcined Phosphate containing 31% "available" phosphoric acid, out of a total of 32.5%, and the cost per "unit-available" would be

$$\$9.50 \div 31 = \$0.307.$$

In a commercial plant the average insoluble phosphoric acid should not exceed 1%.

From the foregoing statements, it is evident that the "furnacing" or "calcining" is the one operation of the process whose cost may be doubtful.

In order that the comparison between the two processes may be more closely drawn, the following calculations have been made, in which certain data was assumed, and data derived from the past work used, to present a more logical reason for the basis of the statement that the fuel requirements are substantially equal to those in the burning of the Portland Cement clinker.

Data Observed:

Mix:

2000 lbs Tennessee Brown Rock.

350 lbs Sodium Sulphate (NA_2SO_4).

45% Moisture.

Temperatures:

Air 62 degrees F.

Stack Gases 1200 degrees F.

Clinkering 2600 degrees F.

Discharged Clinker 1800 degrees F.

Analysis of Oil:

C	87.1%
H	11.7%
O	1.2%

Analysis of Stack Gases:

CO_2	10.3%
O_2	1.5%
CO	0.0

Note:- By careful measurements, it was determined that the weight of the finished product or clinker was substantially equal to the weight of the phosphate rock fed to the kiln; practically all of the "re-agent" or sodium sulphate having been volatilized during the calcination process. It is sufficiently accurate to assume then, that: 2000 lbs of dry phosphate rock plus 350 lbs of sodium sulphate, will produce 2000 lbs of "clinker" or Calcined Phosphate.

Heat Requirements:	B.T.U.s
1. Heating the wet mix to 212 degrees requires	147,487
2. Converting the water into steam and heating to 1200 degrees F. (Temperature of escaping gases).	2,772,481
3. Sodium Sulphate decomposed	206,850
4. Heating dry mix to 1700 degrees (Temperature of Volatilization of SO_3)	804,287
5. Heating Material (Less re-agent) from 1700° to 2600° (Maximum temperature).	414,000
6. Loss through discharged clinker	834,240
Total	5,179,345
7. Add 20% for radiation, conduction and other losses	1,035,868
8. Carried out by escaping gases, discharged at 1200 degrees F.	2,541,332
Grand Total	8,556,545

The heating value of oil is 19,787 B.T.U's per pound.

Then,-

8,556,545 ÷ 19,787 = 430 lbs of oil, required per ton of clinker.

If coal is used with calorific value of 13,500 B.T.U's per pound, the fuel consumption would be 634 pounds per ton of clinker. The fuel consumption of Portland Cement is 125 pounds per barrel or 625 pounds per ton of clinker.

The temperature of the stack gases were 1200 degrees F. By utilizing this heat in dryers, under boilers, or in some other practical manner, and reducing this temperature to, say 500 degrees F., a saving of 1,405,386 B.T.U's per ton of calcined clinker may be effected, equal to 104 pounds of coal per ton, which is nearly one-half the power necessary to operate an entire plant of 100 tons daily production.

Further economies may be easily made by utilizing the radiating heat from the discharged clinker by preheating the air required for combustion.

COMPARISON OF ACID AND CALCINED PHOSPHATES.

Following are the chief points of difference between Acid Phosphate and Calcined Phosphate:

	Acid Phosphate	Calcined Phosphate
1.	Phosphoric acid (P_2O_5) contained is water-soluble and citrate-soluble.	Phosphoric acid (P_2O_5) contained is citrate-soluble (1% to 2% water-soluble).
2.	Assuming rock treated in both processes to contain, say 32% P_2O_5 in an insoluble form, then:	
	One ton contains 16% to 17% "available" Phosphoric acid.	One ton contains 31% to 32% "available" phosphoric acid, hence saving 50% in freight and the production of concentrated fertilizer.
3.	Affected by moisture.	Not affected by moisture.
4.	Upon application to soils high in iron, alumina and magnesia, phosphates of iron, etc, are formed which are not easily available for plant food.	No re-action whatever with these substances.
5.	Continued use turns soils "acid" or "sour" and lime is required to "sweeten" them.	Being neutral, it can never turn land "sour".
6.	The acid destroys the bag fibers.	Can be shipped in paper or cloth bags without injury to either.

	Acid Phosphate	Calcined Phosphate
7.	Disagreeable odor.	Odorless.
8.	Sand, shale, ashes, coal and other food-valueless materials are used as "fillers" in making up "complete" fertilizer with acid phosphate. Limestone cannot be used as "filler".	Limestone can be used as a "filler" and practically all soils require liming.
9.	Cannot be used with Cyanamid in proportions less than 1000 pounds acid Phosphate to 75 pounds Cyanamid without destroying to a large extent, the availability of both materials through chemical re-actions.	Can be used in any desired proportions with Cyanamid without chemical re-actions.
10.	Mechanical condition is coarse, granular and easily becomes "gummy" upon handling.	Is in the form of fine dry powder and can be intimately mixed with other materials.
11.	The phosphoric acid "reverts" upon long standing to more insoluble forms.	Does not "revert" with age.
12.	In order to meet the minmum percentage of phosphoric acid permissable in "complete" fertilizers, it is necessary to use "high-grade" rock, containing 31% or more P_2O_5.	So-called"low-grade" rock may be used, since the phosphoric acid in the original rock is not "diluted" i.e. a rock containing only 16% P_2O_5 may be successfully treated by this process.
13.		Assuming the same cost of raw rock in both processes, Calcined Phosphate can be produced at 60% to 70% of the cost by the acid process, per unit available.

	Acid Phosphate	Calcined Phosphate
14.	Percentage of iron and alumina in rock must not exceed 3-1/2%.	Presence of iron and alumina in any amount does not affect this process.

While Calcined Phosphate meets all the present requirements of the National and State fertilizer tests, it is recognized that extensive field trials and applications must be made before it will finally be accepted by the average consumer as a product of equal unit-availability with Acid Phosphate. The process, however, is one that a large number of scientists and chemists have been striving to commercialize, since it should not only lessen to some extent, the cost of fertilizer, but it is inevitable that the present acid process must ultimately be supplanted by some method, which at least, "dilutes" no further the food value of the raw material which nature has already reduced to 30 per cent.

Chattanooga, Tenn.,
May 1, 1913.