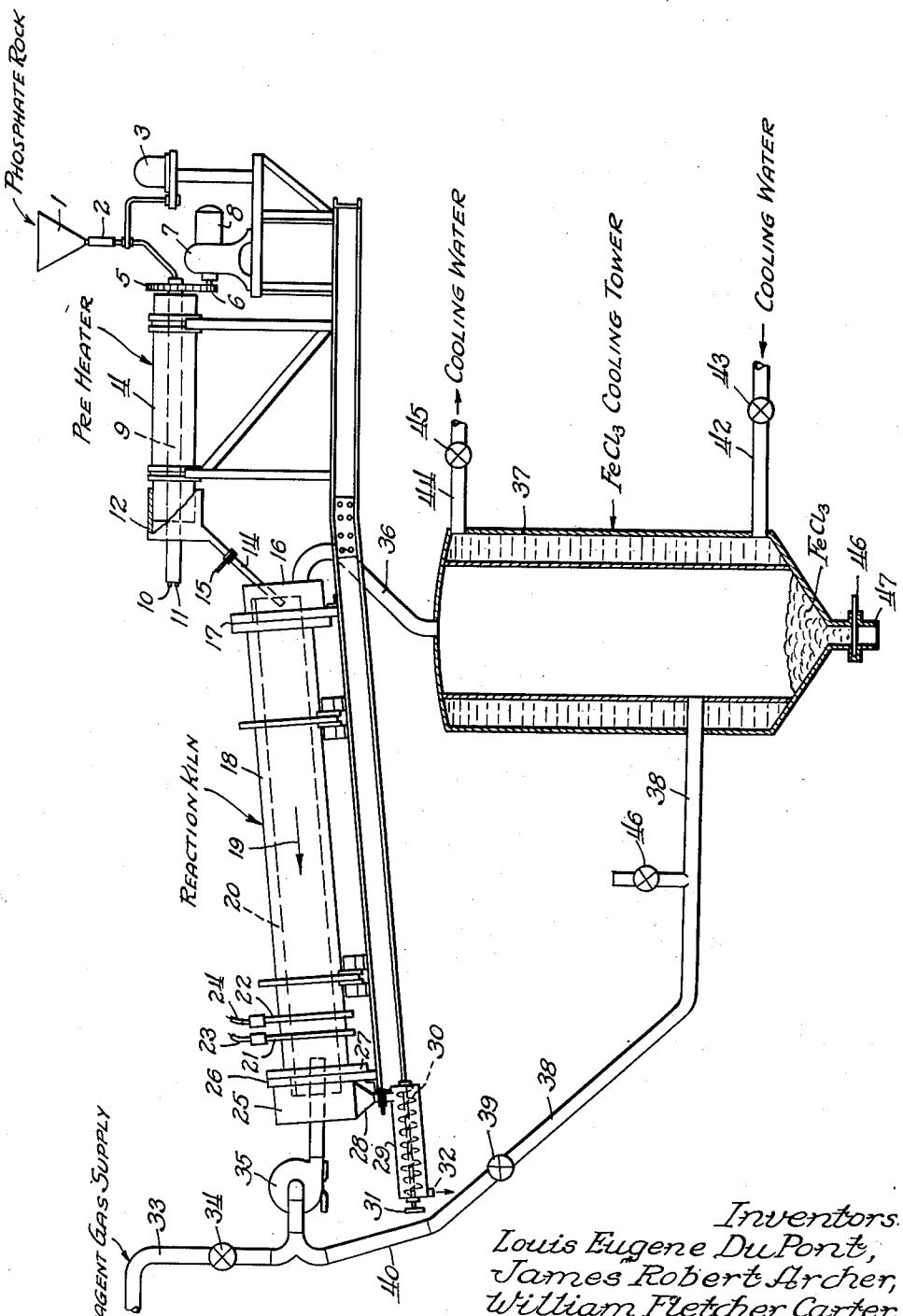


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METHOD OF PURIFYING PHOSPHATE ROCK  
CONTAINING IRON IMPURITIES  
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## UNITED STATES PATENT OFFICE

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METHOD OF PURIFYING PHOSPHATE ROCK  
CONTAINING IRON IMPURITIES

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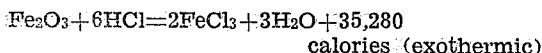
4 Claims. (Cl. 23—108)

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The present invention relates to improvements in the art of treating phosphate-bearing minerals, such as phosphate rock and sand, so as to eliminate iron which, if allowed to remain in the mineral, would impair its usefulness for various purposes. The present application is a continuation in part of our pending application Serial No. 484,108, now abandoned, which was filed on April 22, 1943, and which is assigned to the assignee of the present invention.

A further object of the invention is to effect an increase in the content of the useful or available ingredients or chemicals in the mineral. For example, phosphate rock obtained from various deposits in Tennessee is comparatively low in B. P. L. (bone phosphate of lime or the normal phosphate of lime  $\text{Ca}_3(\text{PO}_4)_2$ ), and it is very desirable that the B. P. L. of such rock should be raised in order that the finished product may be of greater economic value than similar rock having a relatively lower B. P. L. content.

Our improved process makes use of the principle involved in the following reaction:



This reaction takes place at a temperature of 300° C. or more. So far as we are aware, though reactions such as the above apply to pure materials in the laboratory, they have never been successfully applied to the commercial purification of phosphate minerals because certain requirements have, heretofore, never been recognized.

In the experiments and tests which we have made in an effort to apply the aforesaid reaction to the commercial purification of phosphate minerals, we have discovered that the following principles or considerations are important or essential:

(1) The reaction gas which will give up sufficient chlorine to satisfy the requirements of the iron should be in excess. In order to satisfy this requirement, it is desirable for commercial reasons to recover the unreacted reaction gas for re-use in the system.

(2) In order to prevent undesirable or harmful side reactions with the ferric chloride in the reaction zone, or elsewhere in the system, oxidizing conditions must be avoided so far as possible. This consideration makes it desirable to operate the process as a closed system from which air is substantially excluded.

(3) In order to insure a satisfactory reaction, the temperature should be over about 315°, as the

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ferric chloride which results from the reaction is a vapor at these temperatures and may be conveniently conducted away from the reaction zone. However, in the case of phosphate rock, the use of a temperature over about 400° C. is undesirable because higher temperatures alter the physical structure of the rock to the point that the treated rock may not be used in the production of superphosphate or other similar valuable phosphate compounds.

(4) In order to obtain efficient operation and a high yield coupled with a reasonably complete elimination of the unwanted impurities, it is necessary to have the mineral reduced to a relatively small particle size, and also there should be a very intimate contact between the reagent gas and the mineral particles within the reaction zone.

(5) Preferably, to prevent undesirable reactions between the ferric chloride which is formed by the reaction and the treated or untreated mineral, the gaseous ferric chloride should be conducted promptly away from the treated or untreated mineral and, of course, out of the reaction zone.

(6) All parts of the equipment with which any corrosive gases or other materials may contact must be constructed of refractory materials which will not be affected by such corrosive gases or materials. Furthermore, the equipment must be sealed effectively against the escape of corrosive vapors and against the entrance of air, which as above pointed out, would adversely affect the operation of the process.

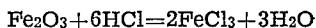
Various types of equipment may be used for carrying out the process, but of all the types of equipment which we have used, we obtained the best results with an inclined rotary kiln provided with suitable means for feeding the comminuted mineral downwardly through the kiln and for conducting the reaction gas upwardly through the comminuted mineral. Also, it is advisable to equip the apparatus with some form of internal heating device, for example a suitable electrically heated refractory rotary core element which, on the exterior thereof, may also be equipped with a worm or other suitable arrangement for effecting a downward propulsion of the mineral.

In using such equipment, it is advisable to heat the comminuted mineral before it is fed into the kiln, so as to reduce to a minimum the amount of internal heating which may be required. Also, in order to effect proper contact between the reaction gas and the comminuted mineral, it is advisable to keep the kiln fairly full for the lower

part of its length, the exit at the lower end being suitably controlled in accordance with the various conditions so as to maintain the required level of material within the kiln. Any suitable arrangement of sealed discharge may be employed in order to withdraw the treated material without permitting any substantial amount of air to enter the system, and in this connection, it is advantageous to keep the pressure at the discharge end of the kiln at about the same as that of the atmosphere, so that there will be no substantial pressure differential and consequent escape of gas or ingress of air in the event that the sealing arrangement is not perfect.

The principles and considerations which have been previously stated as being important or critical to the progress of the reaction will now be more fully described.

Insofar as we know, hydrogen chloride gas is the only reaction gas which may be successfully employed with phosphate minerals. This is due to the fact that the reaction gas must supply large amounts of chlorine for the reaction and the temperature of the reaction must be below about 400° C. to prevent injury to the structure of the phosphate material. Where hydrogen chloride gas is used as the reagent and the iron appears in the mineral as ferric oxide, the reaction is as follows:



(at over about 300° C.)

As before stated, it is desirable that the reagent be in excess both to increase the rate and effectiveness of the reaction and to avoid oxidizing condition. We have discovered that it is critical to the operation of the process of the present invention that the concentration of the hydrogen chloride gas in the reaction zone be maintained at a value of at least about 70 percent by volume. If the concentration of the hydrogen chloride gas falls below 70 percent by volume, or if the volume of other gases including air are in excess of 30 percent by volume, the removal of iron becomes an extremely slow and expensive procedure.

Ferric chloride is vaporized at about 300° C., so that the temperature in the reaction zone must be kept over this value if the ferric chloride is to remain a vapor. We have discovered, however, that the practical lower temperature limit for iron removal in the process of the present invention is about 350° C. We have also discovered the upper temperature limit for the process of the present invention to be about 400° C. and the preferred operating temperatures to be in the range between 350° C. and 380° C. While higher temperatures, above 400° C., remove iron, they tend to calcine the rock, e. g. carbonate materials present in the rock, and to alter the physical structure of the rock so that after treatment the rock is unsuitable for further processing, as for example, conversion into superphosphate, for use in soil fertilizers, etc.

We have also discovered that the rock being treated should be comminuted to a degree such that it passes a 35 mesh screen, and is retained on a 65 mesh screen to insure efficient utilization of the hydrogen chloride gas (the screen sizes referred to in the description and claims are Tyler Standard Screen sizes). Larger sized particles do not expose sufficient area to the reagent gas or allow the required penetration of the reagent gas into the particle, and extremely small particles pack so closely together that the reagent can-

not penetrate the mass of material being treated.

The period of time that the phosphate mineral remains in contact with the reagent gas is, as would be expected, also important. The results of a series of tests on the process of the present invention, in which the rate of material fed to the reaction kiln was varied, show that the time required for a reasonably complete removal of iron from the rock without effecting undesirable changes in the rock structure is from about 20 to 30 minutes. This time was determined for the preferred conditions of 350° to 380° C. temperatures, 35-65 mesh, particle size, and a reagent composition of over about 70 percent hydrogen chloride by volume.

In the drawing accompanying this application, we have illustrated in somewhat diagrammatic form an apparatus which was successfully used in carrying out the principles of this invention. In the apparatus, it will be observed that the phosphate rock which has previously been crushed to about between 35 and 65 mesh is introduced into the hopper 1. To the bottom of the hopper 1, there is flexibly connected a pipe or conduit 2 which is vibrated by a conventional type of vibrator motor 3, so that the crushed rock will feed uniformly down through the conduit 2 and into the center of the right-hand end of a rotary pre-heater 4. The rotary heater 4 is equipped with a large end gear 5 which meshes with a small pinion 6 on a shaft which is driven at slow speed through a reducer 7 by a motor 8.

The kiln or heater 4 is supplied with heat by a stationary electric heating element 9 extending into the center of the kiln 4 and supplied with current through terminals 10 and 11. The exit end of the heater or kiln 4 which may, if desired, be inclined slightly down towards said exit end, is equipped with a hood 12 into which the delivery end of the kiln 4 extends for a distance as shown.

The heated rock which passes out of the end of the barrel of the kiln 4 flows into the end of an inclined pipe 14 equipped with a suitable gate 15 for regulating the flow, and the lower end of said pipe 14 extends into a stationary housing 16 having a flange 17 in which rotates the upper end of the reaction kiln, so that a reasonably gas-tight seal is effected between the stationary housing 16 and said reaction kiln 18. As shown, said reaction kiln is quite inclined so as to effect the delivery of the material from right to left in the direction of the arrow 19.

The reaction kiln is heated by a cylindrical electrical resistance heating element 20 which extends throughout the length of the barrel of the reaction kiln and rotates therewith. The current for supplying said electrical resistance element 20 is collected by a pair of rings 21 and 22 contacting with stationary brush elements respectively connected to conductors 23 and 24.

At the delivery end of the reaction kiln 18, there is arranged a stationary housing 25 having a flange 26 which cooperates with a flange 27 on the lower end of the reaction kiln to provide a reasonably gas-tight joint as the reaction kiln rotates relative to said housing 25.

At the lower end of the delivery housing 25, there is arranged a spout or cone 28 which delivers into one end of a housing 29 within which housing rotates a suitable screw conveyor or worm 30 driven in the proper direction by a pulley or gear 31 so as to deliver the finished, treated ore out through the exit duct 32.

The reaction gas (hydrogen chloride) is introduced through the duct 33 and controlling valve

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34 into the suction of a pump 35 which delivers into the exit housing 25 of the reaction kiln. Any gas which is produced in, or flows through, the reaction kiln is discharged through a gas exhaust pipe 36 from which it flows into a cooling tower 37 in which any  $\text{FeCl}_3$  produced in the reaction kiln is collected. Surplus reagent flows out of the cooling tower 37 through a duct 38 controlled by a valve 39 and leading into a pipe 40 which connects with the lower end of the pipe 33 leading into the inlet of the pump 35 previously described, so that said surplus gas is in effect recirculated through the kiln.

Condensation of the  $\text{FeCl}_3$  which enters the cooling tower 37 is facilitated by the use of a cooling jacket 41 filled with water or other coolant which is disposed about the tower 37. Said cooling water is supplied by a pipe 42 connected to a suitable supply of water. The flow of cooling water is controlled by a valve 43 so that the gas from the reaction kiln is cooled to below about 300° C. in order to insure the complete condensation of the ferric chloride. The water is conducted to a suitable drain system by means of the pipe 44 which includes a valve 45. When necessary a relief valve or vent 46 may be employed to prevent undue pressure from accumulating in the system due to formation of unused gases. The condensed ferric chloride is conducted from the cooling tower 37 by means of a valve 46 and a pipeline 47.

Phosphate rock was treated in the equipment just described under the conditions which we have found critical for commercial and practical operation. The material feed analyzed 68.0% B. P. L., 5.10%  $\text{Fe}_2\text{O}_3$ , and 4.20%  $\text{CaCO}_3$ , the feed was comminuted so that 95% was in the critical size range of 35 to 65 mesh (Tyler Standard Screen). The comminuted rock was preheated to 350° C., approximately the reaction temperature and the rate of feed into the reaction kiln was such that the comminuted rock remained in the reaction zone for about from 20 to 30 minutes where the temperature was maintained in the range between 350° and 380° C. The reagent, hydrogen chloride gas, was kept over about 70% by volume and the products of the reaction were rapidly removed and condensed.

The product after treatment as above analyzed 71.80 B. P. L. and 2.50%  $\text{Fe}_2\text{O}_3$ , and 3.04%  $\text{CaCO}_3$ . The B. P. L. of the final product was raised 3.8% and the iron was reduced by about 51%. When this product was treated with sulfuric acid in the conventional manner a good textured superphosphate resulted.

The scope of the invention should be determined by reference to the appended claims.

We claim:

1. The method of purifying phosphate rock containing iron impurities, which comprises: exposing the rock in comminuted form to gaseous hydrogen chloride containing at least about 70 percent of hydrogen chloride by volume at a temperature between about 350° and 400° C., whereby the iron is separated from the rock in the form of ferric chloride vapor, withdrawing the

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ferric chloride vapor and the excess hydrogen chloride from the reaction zone, and separating the ferric chloride from the hydrogen chloride.

2. The method of purifying phosphate rock containing iron impurities, which comprises: exposing the rock in comminuted form to gaseous hydrogen chloride containing at least about 70 percent hydrogen chloride by volume at a temperature between about 350° and 400° C., whereby iron is separated from the rock in the form of ferric chloride vapor, withdrawing the ferric chloride vapor and the excess hydrogen chloride from the reaction zone, and separating the ferric chloride from the hydrogen chloride, the comminuted rock under treatment having a substantial part of its particles between about 35 and 65 mesh.

3. The method of purifying phosphate rock containing iron impurities, which comprises: exposing the rock in comminuted form to an excess of gaseous hydrogen containing at least about 70 percent hydrogen chloride by volume at a temperature between about 350° and 380° C., whereby iron is separated from the rock in the form of ferric chloride vapor, withdrawing the ferric chloride vapor and the unreacted hydrogen chloride from the reaction zone and separating the ferric chloride from the hydrogen chloride, the comminuted rock under treatment having a substantial proportion of its particles between 35 and 65 mesh.

4. The method of purifying phosphate rock containing iron impurities, which comprises: exposing the rock in comminuted form to an excess of gaseous hydrogen containing at least about 70 percent hydrogen chloride by volume at a temperature between about 350° and 380° C. for a period from about 20 to 30 minutes, whereby iron is separated from the rock in the form of ferric chloride vapor, withdrawing the ferric chloride vapor and the unreacted hydrogen chloride from the reaction zone, separating the ferric chloride from the hydrogen chloride, and recycling the unreacted chloride through the reaction zone, the comminuted rock under treatment having a substantial proportion of its particles between 35 and 65 mesh.

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## REFERENCES CITED

The following references are of record in the file of this patent:

55

## UNITED STATES PATENTS

Number	Name	Date
991,096	Schroder	May 2, 1911
1,129,407	Lay	Feb. 23, 1915
1,147,832	Kugelgen	July 27, 1915
1,406,595	Wescott	Feb. 14, 1922
1,845,342	Saklatwalla	Feb. 16, 1932
1,979,280	Mitchell	Nov. 6, 1934
2,070,161	Flinn	Jan. 21, 1935
2,290,843	Kinney	July 21, 1942

60  
65