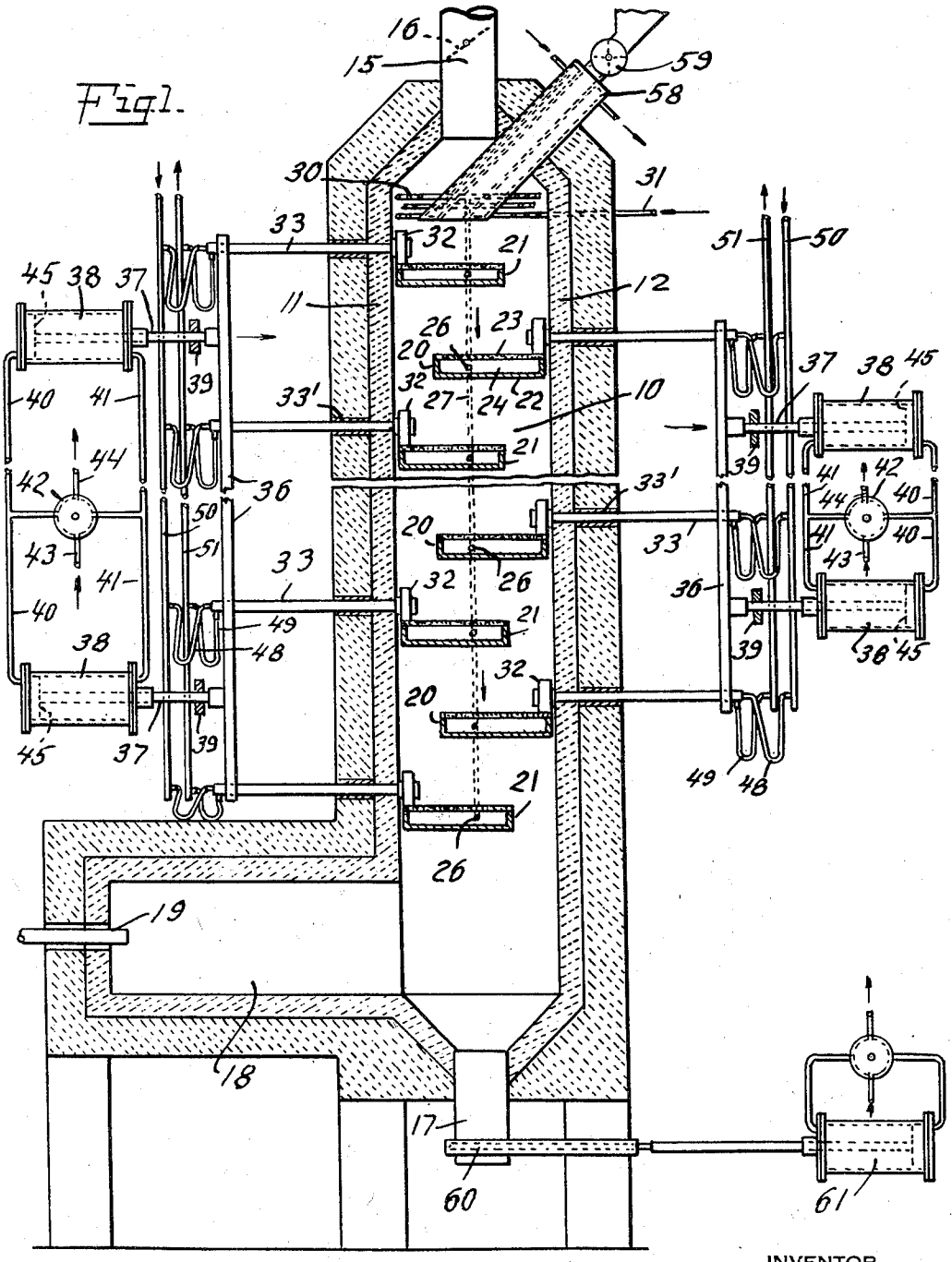
Nov. 21, 1950 E. J. MAUST 2,531,068

DEFLUORINATING PHOSPHATIC MATERIAL

Filed June 25, 1946 3 Sheets-Sheet 1

Fig. 1.



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Fig. 2.

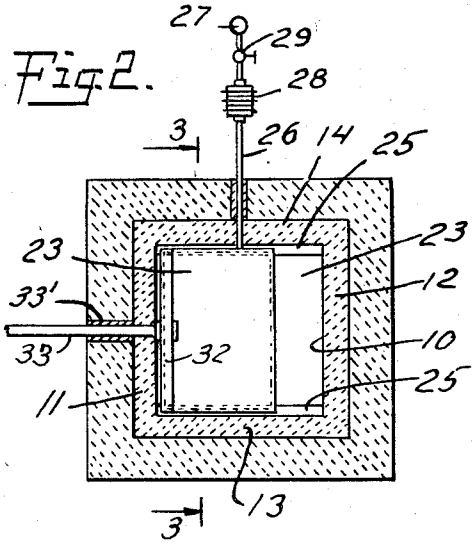


Fig. 3.

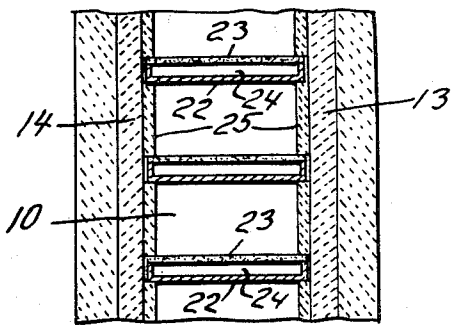


Fig. 4.

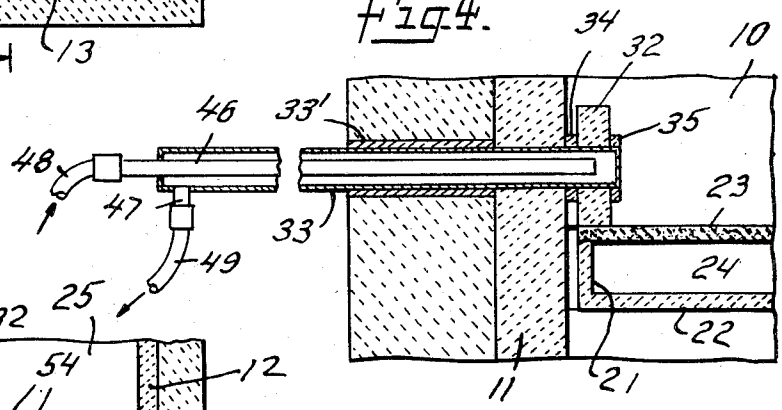


Fig. 6.

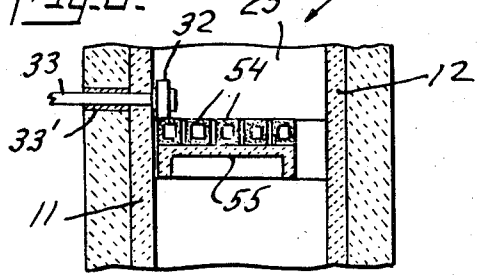


Fig. 5.

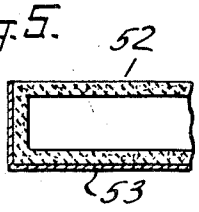
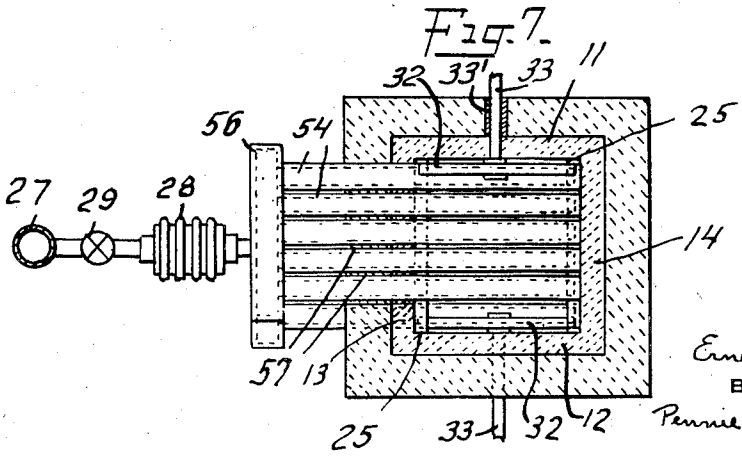


Fig. 7.



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Fig. 8.

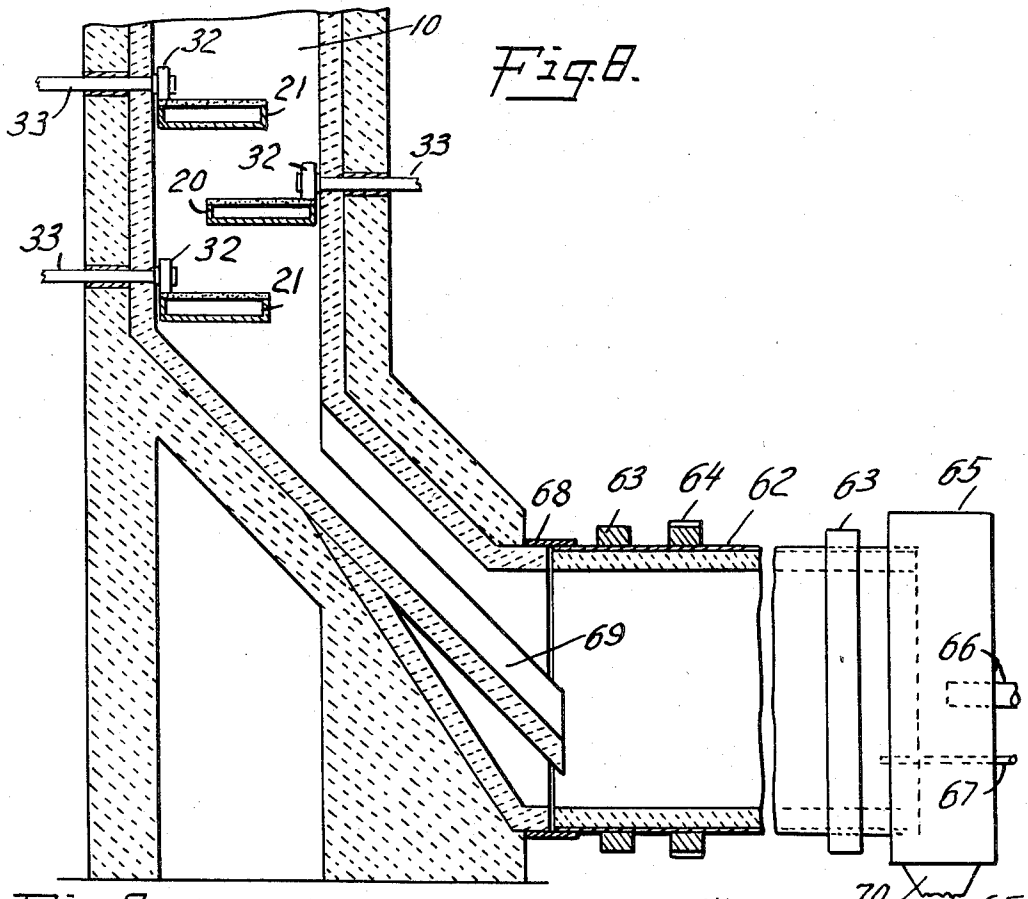
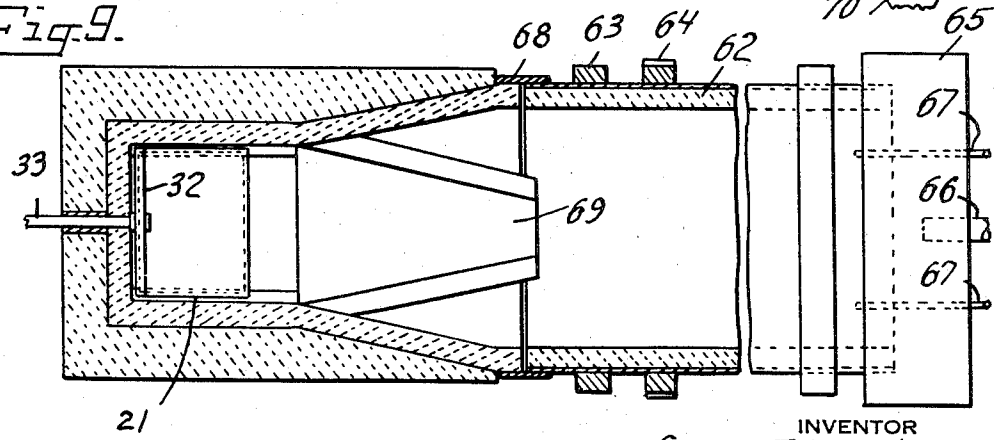


Fig. 9.



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Patented Nov. 21, 1950 2,531,068

UNITED STATES PATENT OFFICE

2,531,068

DEFLUORINATING PHOSPHATIC MATERIAL

Ernest J. Maust, Lakeland, Fla., assignor to Coronet Phosphate Company, New York, N. Y., a corporation of New York

Application June 25, 1946, Serial No. 679,173

7 Claims. (Cl. 71—44)

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This invention relates to the treatment of phosphatic materials with gases, and has for its object the provision of an improved method of treating a material at an elevated temperature with a gas. The invention is more especially concerned with the defluorination of phosphate rock or other fluorine-containing phosphatic material by calcination in the presence of water vapor, and in this connection aims to provide certain improvements in defluorinating phosphatic materials by treatment with gas, and more particularly water vapor, at elevated temperature.

In its broad aspect, the method of the invention involves supporting a plurality of layers of the material to be treated by a gas in vertically spaced positions within a vertical heating chamber, progressively moving the material downwardly through the chamber from one material-supporting position to the next lower position, and passing a finely disseminated gas upwardly through the entire mass of each layer of the material while so supported. Fresh material is introduced to the uppermost material-supporting position and a substantially equivalent amount of treated material is discharged from the lower end of the heating chamber in correlation with the passage of material from one position to the next lower position, so that the operation as a whole is conducted in a substantially continuous manner. The temperature of the material being treated is preferably controlled within a predetermined temperature range by regulating the amount and temperature of the gas passing through the supported layers of material. The application of the invention to various methods of defluorinating phosphate rock is hereinafter more particularly described.

The foregoing and other novel features of the invention will be best understood from the following descripiton taken in conjunction with the accompanying drawings, in which,

Fig. 1 is a sectional elevation of a multiple porous hearth furnace particularly adapted for practicing the invention,

Fig. 2 is a transverse section immediately above one of the porous hearths,

Fig. 3 is a detail sectional elevation on the section line 3—3 of Fig. 2,

Fig. 4 is an enlarged sectional detail of the cooling arrangement for the pushing device,

Fig. 5 is a sectional detail of a modified construction of porous hearth,

Figs. 6 and 7 are vertical and transverse sectional views, respectively, of another modified construction of porous hearth, and

Figs. 8 and 9 are vertical and transverse sectional views of the combination of the multi-hearth vertical furnace with a rotary kiln.

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The furnace illustrated in the drawings comprises a vertically elongated brick-work structure of inner heat-resistant brick surrounded by ordinary brick. The structure encloses a vertical heating chamber 10 of generally rectangular or square section, and for convenience the opposite vertical walls 11 and 12 of the heat-resistant brick will be called the end walls and the other opposite vertical walls 13 and 14 will be called the side walls. A gas outlet 15 having a damper 16 communicates with the upper end of the heating chamber, and a material-discharge chute 17 communicates with the lower end of the chamber. A laterally disposed combustion or firing chamber 18, of the commonly called "Dutch Oven" type, communicates with the lower end of the heating chamber, and is provided with fuel burners 19 adapted to burn oil, gas, powdered coal or other suitable fuel. The heating chamber may be heated in any other appropriate manner, as for example electrically or by the hot combustion gases from a rotary kiln as hereinafter more particularly described.

The heating chamber 10 is provided with a plurality of vertically spaced superposed porous hearths. As illustrated in the drawings, there are two sets of these hearths 20 and 21 alternating with one another. The porous hearths 20 of one set extend from approximate the end wall 12 to a short distance from the opposite end wall 11. The porous hearths 21 of the other set alternate with the hearths 20 and extend from approximate the end wall 11 to a short distance from the opposite end wall 12. While Fig. 1 of the drawings shows a furnace with four porous hearths 21 and three alternately positioned porous hearths 20, any desired number of hearths may be provided within the heating chamber.

As shown in Figs. 1, 2 and 3, the porous hearths are made up of an impervious tray or sagger plate 22 covered by a pervious tile or plate 23, thus providing a hollow interior 24. The hearths are supported in their spaced relation by heat-resisting tile 25 set closely against the side walls 13 and 14 (Figs. 2 and 3). The trays 22 may advantageously be made of a gas impermeable or impervious ceramic such for example as dense silicon carbide or fire brick, while the plates 23 may be made of coarsely bonded alunite or alundum, or other heat-resistant gas permeable ceramic. The top plate 23 is fastened to its cooperating tray by a suitable high temperature cement.

Gas is admitted to the hollow interior of each hearth by a ceramic tube 26 extending through the side wall 13 of the furnace structure. The tubes 26 may be made of dense silicon carbide, quartz or the like, and are connected to a common header 27 through a metal bellows 28 for taking up contraction and expansion. A valve 29 is associated with each gas inlet tube to regulate and control the amount of gas supplied to each porous hearth. Where it is advantageous or desirable to preheat or superheat the gas, as is frequently the case with water vapor, the header 27 may be connected to the delivery end of a heating coil 30 suitably mounted in the upper part of the heating chamber 10. The coil 30 may be made of nickel or other suitable heat-resistant material. Gas is supplied to the other or feed end of the coil 30 by a supply pipe 31. The header 27 and exposed portions of the tube 26 may be appropriately insulated to conserve the heat of the hot gas flowing therethrough. The amount and temperature of the gas supplied to each porous hearth can be adjusted and controlled through the valves 29, the amount of preheating in the coil 30, and the heat conservation or dissipation characteristics of the header 27 and pipes 26.

Each porous hearth is provided with a pusher 32 for pushing the material supported or resting on the hearth towards the end of the hearth spaced a substantial distance from the adjacent end wall. The hearths 20 are separated from the end wall 12 (and the hearths 21 are similarly separated from the end wall 11) by just sufficient distance to permit material to drop off this end of the hearth, and hence not build up behind the pusher, as the pusher returns to its initial or "in" position. The other ends of the hearths are separated from their respective adjacent end walls by a considerably greater distance, sufficient to permit material to drop from hearth to hearth and to provide an unrestricted zig-zag path for the flow of hot heating gases and spent treating gas upwardly through the heating chamber. The pushers of the hearths 20 and the pushers of the hearths 21 are actuated alternately by separate and independent mechanism positioned respectively on opposite ends of the furnace, and since the two mechanisms are identical they are indicated on the drawings by the same reference numerals.

Each pusher is attached to the inner end of a pipe 33, as for example between a washer 34 and cap 35 screw-threaded or otherwise secured to the pipe. Near their other outer ends the pipes 33 are secured to a vertical operating bar 36. The bar is operatively secured to the piston rods 37 of two vertically spaced fluid pressure actuated cylinders 38. The piston rods pass through stationary guide plates 39. A suitable fluid under pressure, such as compressed air, can be admitted to either end of each cylinder 38 through supply pipes 40 and 41, respectively. A rotary valve 42 controls the admission of fluid from a supply pipe 43 to either the pipes 40 or the pipes 41, and the exhaust of fluid through a pipe 44. When the valve 42 is in position to admit fluid to the pipes 40, the piston 45 of the cylinders 38 are actuated and, through the piston rods 37, operating bar 36 and pipes 33, move the pushers 32 of one set of hearths to push material off those hearths onto the other set of hearths. Thereupon, the valve 42 is moved to admit fluid to the pipes 41, and the pistons 45 are actuated in the reverse direction and return the pushers to their initial

or "in" positions adjacent the end wall 11 (or 12 as the case may be).

The pushers 32 are rectangular slabs made of silicon carbide, fire brick or other suitable heat-resistant ceramic or refractory. The pipes 33 are made of heat-resistant metal such for example as nickel or inconel metal (an alloy of about 83% nickel, 13% chromium and 6% iron), and are additionally protected by artificial cooling as shown in Fig. 4. Thus, with the pipe 33 closed at each end, a cooling medium, such as water, is introduced at the inner end of each pipe 33 through an inclosed pipe 46 of smaller diameter, and the heated or spent cooling medium is discharged through an outlet 47 at the opposite end of the pipe 33. The pipes 46 and outlets 47 are connected by flexible hose or the like 48 and 49 to vertical supply and exhaust headers 50 and 51, respectively. The pipes 33 have a fairly tight sliding contact with the heat-refractory end wall 11 (or 12 as the case may be) through which they pass, while their sliding contact with the outer brick end wall structure may be loose with the space between the pipe and end wall filled or packed with a silicone or other suitable heat-resistant lubricant 33'. This lubricant seeps into the contact between the pipe and heat-refractory wall to provide effective lubrication, and also provides a suitably gas-tight connection between the moving pipes and the stationary furnace structure.

When the porous hearth is constructed of an impervious tray 22 and a pervious cover 23 cemented thereto, materials for these parts should have as nearly as possible the same coefficients of expansion to avoid rupturing the cemented joint. In the modified hearth construction of Fig. 5, this difficulty is overcome by a monolithic box-like structure 52 made of pervious ceramic or refractory material, with a hollow interior. An impervious shell or coating 53 is applied to the bottom and sides of the structure 52, whereby gas supplied to the hollow interior can pass only through the uncoated and pervious top. In the modified construction of Figs. 6 and 7, the hearth is made up of tubes 54 of pervious ceramic or refractory material, of rectangular section and closed at their inner ends. The tubes 54 are supported on an inverted sagger plate or tray 55 of impervious refractory or the like. The tubes 54 extend through the side wall of the furnace structure and are connected at their outer open ends to a common gas manifold 56 supplied with gas from the header 27 as hereinbefore described. The tubes 54 are cemented together (57) where they pass through the side wall of the furnace structure and the assembly of tubes is tied into the furnace wall in a substantially gas-tight manner.

In practicing the method of the invention in the furnace shown in the drawings, material to be treated is fed to the uppermost porous hearth 21 through the feed chute 58. Since the chute extends into the heating chamber 10, it is preferably water jacketed. Uniform weighed or measured amounts of material are periodically fed to the uppermost hearth through a star wheel feed 59 which seals the chute against the passage therethrough of any gas from the heating chamber. Assuming the operative elements of the furnace to be in the positions indicated in Fig. 1, with layers of material undergoing gas treatment on all the hearths 21 and the hearths 20 unloaded or empty, the valve 42 moves to admit actuating fluid to the pipes 40 of the cylinders

38 (left end mechanism of Fig. 1), and the operatively-related pushers 32 push the load of material on the hearths 21 onto the hearths 20 immediately below. The same valve 42 then moves to admit actuating fluid to the pipes 41 of the same cylinders 38, and the pushers 32 are returned across the hearths 21 to their initial or "in" positions. Thereupon, the valve 42 and cylinders 38, of the right end mechanism of Fig. 1, similarly actuate the pushers 32 of the hearths 20, pushing the load of material on those hearths to the then-empty hearths 21 below, and simultaneously a predetermined amount of fresh material is dropped through the chute 58 onto the uppermost empty hearth 21. From the lowermost hearth 21, the material drops into the discharge chute 17, from whence a predetermined amount of material is periodically withdrawn by means of a slide valve 60 controlled and actuated by a fluid pressure cylinder 61. The slide valve prevents entrance of cold air into the lower end of the heating chamber. Preferably, the slide valve 60 is actuated simultaneously with the star wheel feed 59 to permit the withdrawal from the chute 17 of an amount of treated material equivalent to that fed to the uppermost hearth 21. The cycle of operation is thus for the mechanism on one end to reciprocate in unison all of the pushers of one set of hearths whereby the loads on those hearths are pushed off and drop onto the then-empty hearths below and the pushers are returned to their initial or "in" positions, and then the mechanism on the other end similarly reciprocates the pushers of the other set of hearths. The cycle can be made as slow or as rapid as desired, depending upon the time required to complete the reaction between the gas and the material being treated.

While supported on each of the porous hearths, gas in a finely disseminated state passes upwardly through the layer of material on the hearth. Moreover, as the material drops from hearth to hearth it passes through an upward stream of the gas issuing from the pervious tops of the empty or unloaded hearths. Thus, intimate, positive and continuous contact of the gas with all parts of the material undergoing treatment is assured. The valves 42, star wheel 59 and slide valve 60 may be automatically synchronized to operate in the sequence hereinbefore described, i. e. (1) valve 42 of left end mechanism and (2) valve 42 of right end mechanism simultaneously with star wheel 59 and slide valve 60. The furnace is preferably operated under a slight pressure so that hot gas tends to push out at any openings in the wall of the heating chamber. Such slight pressure is obtained by throttling the gas discharged through the outlet 15 by suitable adjustment of the damper 16.

The method of the invention is admirably adapted for the defluorination of phosphate rock by calcination in the presence of water vapor by the method described in my aforementioned patent applications, or by the methods described in the copending patent applications of Clinton A. Hollingsworth and myself Ser. Nos. 665,344 filed April 26, 1946, issued as Patent No. 2,479,389 August 16, 1949, 665,345 filed April 26, 1946, now abandoned, and 665,346, filed April 26, 1946, issued as Patent 2,478,200 August 9, 1949. The method of the invention may also be applied with advantage in defluorinating phosphate rock by replacing the fluorine of the fluorapatite by chlorine as described in the patent application of Clinton A. Hollingsworth Ser. No. 665,347, filed

April 26, 1946. In the defluorinating methods with water vapor, temperatures of from about 2600° F. up to 3000° F. are required, while in the defluorinating method with a chlorine-containing gas, temperatures of from about 2000° F. up to 2400° F. are required. One of the advantages of the invention is that these required operating temperatures can be accurately maintained and controlled, even with flame temperatures in the combustion chamber 18 of 3200 to 3400° F. Thus, by regulating the amount and temperature of the gas supplied to the porous hearths and passing through the layers of material on those hearths, the treating or reaction temperature can be held at 2600° F., or even lower, although the heating gases entering the heating chamber from the combustion chamber may be considerably hotter. In this way the length of the effective hot zone can be greatly extended, and can be much longer than obtainable in a rotary kiln.

In the defluorinating of phosphatic material by any of the methods hereinbefore mentioned, superior results are generally attained by forming the finely divided material into nodules, pellets, briquets or the like. For example, suitable nodules, generally round in shape and varying in diameter from $\frac{1}{8}$ to 1 inch, may be made by moistening the finely divided material with water and tumbling at room temperature in a rotating cylinder, barrel or the like. Such nodules or other agglomerated shapes of the finely divided phosphatic or other material may be fed to the furnace and treated on the porous hearths as hereinbefore described.

The invention is admirably adapted for the decarbonizing by water vapor of nodules of finely divided material mixed with carbonaceous material for the production of porous nodules by the method described in the copending patent application of Clinton A. Hollingsworth and myself Serial No. 665,348, filed April 26, 1946. In accordance with that method, nodules made up of a mixture of the finely divided material and from 5 to 50% by weight of carbonaceous material are subjected to the action of water vapor at a temperature between about 2000° F. and about 2400° F. to eliminate substantially all of the carbon of the carbonaceous material with evolution of the resulting gaseous products, and thereby imparting a highly effective porosity to the nodules. Where the invention is applied to the practice of that method, or to the treatment of any material with a gas at a relatively low elevated temperature (e. g. 1800 to 2500° F.), the vertical heating chamber may advantageously be heated by the exhaust gases of a rotary kiln, as illustrated in Figs. 8 and 9 of the accompanying drawings.

In the apparatus of Figs. 8 and 9, the main features of the furnace structure are the same as hereinbefore described and are indicated by the same reference numerals. The furnace, however, has no directly-communicating combustion or firing chamber, but is heated by the hot gaseous products discharging from the upper or material-feed end of a slightly-inclined rotary kiln 62. The rotary kiln has a heat-refractory lining and may be of the conventional construction commonly used in the cement industry and has the usual circumferential trunnion rails 63, driving gear 64 and fire box 65 with fuel burners 66 at its lower or firing end. Water vapor (steam) or other suitable treating gas, is introduced into the firing end of the kiln through appropriately positioned pipes 67. The lower end of the heating

chamber 10 of the furnace is structurally tied and communicates directly with the upper end of the rotary kiln, and a gasket or the like 68 provides a substantially gas-tight connection between the rotary kiln and the adjacent stationary furnace structure. Material pushed off the lowermost porous hearth 21 of the furnace slides down a chute 69, of heat-refractory material, and constitutes the feed of the rotary kiln. Treated material is discharged from the lower end of the kiln through a discharge device 70.

In defluorinating phosphate rock in accordance with the method described in the aforementioned application Ser. No. 665,348, in the combined apparatus illustrated in Figs. 8 and 9, nodules of mixed phosphatic and carbonaceous materials are fed to the uppermost porous hearth, and from there are progressively moved from hearth to hearth and subjected to the action of water vapor at a temperature of about 2000–2400° F. The water vapor is introduced through the porous hearths, and may be appropriately preheated or superheated, as hereinbefore described, and its temperature thereby suitably regulated to maintain the nodulized material at the required treatment temperature. The water vapor reacts with the hot carbon of the carbonaceous material with the evolution of hydrogen and carbon monoxide ($C+H_2O \rightarrow H_2+CO$), in much the same way that water gas is formed. The furnace is so operated that by the time the nodules reach the lowermost porous hearth substantially all of the carbon has been eliminated, and the nodules have consequently acquired a high degree of porosity, which will depend upon the amount of carbonaceous material initially mixed with the finely divided material. Air in controlled amount is preferably admitted to the heating chamber 10, through the porous hearths or in other appropriate manner, for combustion with the evolved hydrogen and carbon monoxide, thereby extending the zone at which effective reaction takes place between the hot carbon and water vapor, and economically utilizing the heat value of the carbon.

The decarbonized and hence porous nodules discharged from the lowermost hearth 21 and fed to the rotary kiln are therein subjected at a temperature of from about 2600° F. to 3000° F. to the action of water vapor (supplied through the pipes 67) for the elimination of fluorine according to any of the methods hereinbefore referred to. The hot gases discharged from the upper end of the kiln (which include the fluorine compounds resulting from the defluorination of the phosphate rock) pass upwardly through the heating chamber 10 and impart the requisite elevated temperature to the nodules undergoing decarbonization therein. The fluorine compounds may, if desired be recovered from the gases exhausting from the top of the heating chamber. The rotary kiln is preferably operated under a pressure slightly in excess of atmospheric pressure in order to assure positive penetration of water vapor throughout the mass of the nodulized charge while passing through the kiln, and hence substantially complete defluorination, as more particularly described in my application Ser. No. 530,156 filed April 8, 1944, issued as Patent 2,446,978 August 10, 1948. The vertical furnace is likewise operated under a slight pressure for reasons hereinbefore mentioned. The defluorinated product discharged from the rotary kiln is in the form of individual clinkered nodules, and after grinding is ready for marketing and use as a mineral supplement in animal feeds or as a fertilizer.

The two-stage defluorinating method of the aforementioned Hollingsworth application Ser. No. 665,347, may be advantageously carried out in accordance with the present invention in the combined apparatus of Figs. 8 and 9. Thus, porous nodules of finely divided phosphatic material are fed, to the uppermost hearth of the vertical furnace and in progressively moving through the heating chamber 10 are subjected at a temperature of from about 2000 to about 2400° F. to a chloridizing gas (such as hydrochloric acid gas, chlorine gas and water vapor etc.) introduced through the porous hearths. The fluorine content of the phosphatic material is thereby substantially replaced by chlorine, and is evolved principally, if not solely, as hydrofluoric acid gas. The resulting chlorinated, but defluorinated, nodules are discharged from the lowermost porous hearth into the rotary kiln and therein subjected at a temperature of from about 2600° F. to 3000° F. to the action of water vapor (supplied through the pipes 67), for the elimination of chlorine. The evolved chlorine-containing gases pass with the hot gases discharged from the upper end of the kiln upwardly through the heating chamber 10, and thus supplement, and correspondingly decrease the required amount of, the chloridizing gas supplied through the porous hearths. Fluorine as well as chlorine compounds in the gases discharged from the top of the heating chamber may be appropriately recovered.

While the aforementioned two-stage treatment methods for defluorinating phosphatic material are preferably carried out in the combined apparatus of Figs. 8 and 9, they may be satisfactorily practiced in the furnace of Fig. 1 by maintaining the required temperature gradient in the heating chamber 10. Thus, in the aforementioned two-stage decarbonizing and defluorinating treatment, decarbonization may be carried out in the upper half or so of the heating chamber 10 and defluorination carried out in the lower half or so of the chamber, with water vapor supplied to all of the porous hearths. To this end, the decarbonizing zone is maintained at a temperature gradient of from about 1900 to 2500° F., and the defluorinating zone is maintained at a temperature gradient of from about 2500° F. up to the required maximum temperature which may be as high as 3000° F. Similarly, in the aforementioned two-stage defluorinating and dechlorinating treatment, the defluorinating zone in the upper part of the heating chamber 10 is maintained at a temperature gradient of from about 1800 to 2500° F. with a chloridizing gas supplied to the porous hearths of that zone, and the dechlorinating zone in the lower part of the chamber is maintained at a temperature gradient of from about 2500° F. up to the required maximum temperature, with water vapor supplied to the porous hearths of that zone. By suitably regulating and controlling the amount and temperature of the gas supplied to the porous hearths, the contemplated temperature gradients are readily established and maintained, and the treatment of the material with gas is carried out as a substantially continuous process or operation.

I claim:

1. In the method of defluorinating phosphatic material in which the finely divided material is subjected to the action of water vapor at ele-

vated temperature, the improvement which comprises supporting a plurality of layers of the finely divided material on porous hearths in vertically spaced positions within a vertical heating chamber, maintaining a temperature of between 1800° F. and 2500° F. in the heating chamber, progressively moving the material downwardly through said chamber from one hearth to the next lower hearth, passing finely disseminated water vapor upwardly through the porous hearths and the entire mass of each layer of the material while supported as aforesaid, introducing fresh material onto the uppermost hearth, discharging treated material from the lowermost hearth into the higher end of an inclined rotary kiln, heating said kiln by the combustion of fuel at its lower end, passing the hot combustion gases from the kiln upwardly through said vertical heating chamber, and maintaining an atmosphere of water vapor and a temperature exceeding 2500° F. within said rotary kiln.

2. In the method of defluorinating phosphatic material in which the material is subjected to the action of a gas at elevated temperature, the improvement which comprises supporting a plurality of layers of the phosphatic material on porous hearths in vertically spaced positions within a vertical heating chamber, progressively moving material downwardly through said chamber by transferring the material on each of said hearths to the next lower porous hearth respectively of a plurality of such hearths in vertically spaced positions between and alternating with said first mentioned porous hearths and then transferring the material on each of said next lower of the alternating porous hearths to the next lower porous hearth respectively of said first mentioned porous hearths, introducing fresh material onto the uppermost porous hearth, discharging treated material from the lowermost porous hearth, continuously passing finely disseminated gas upwardly through each of said porous hearths and through the entire mass of material while supported thereon as aforesaid, the material transferred from each porous hearth to the next porous hearth as aforesaid passing through an upwardly moving stream of gas issuing from said next lower porous hearth at a time that it supports no material, and maintaining a temperature above 2500° F. in the heating chamber.

3. The improvement in the method of defluorinating phosphatic material as set forth in claim 2 in which a temperature between 1900° F. and 2500° F. is maintained in an upper portion of the heating chamber and a temperature above 2500° F. is maintained in a lower portion of the heating chamber.

4. In the method of defluorinating phosphatic material in which the material is subjected to the action of water vapor at elevated temperature, the improvement which comprises supporting a plurality of layers of the phosphatic material on porous hearths in vertically spaced positions within a heating chamber, progressively moving material downwardly through said chamber by transferring the material from each porous hearth to the next lower porous hearth, introducing fresh material onto the uppermost porous hearth, discharging treated material from the lowermost porous hearth, continuously passing finely disseminated water vapor upwardly through each of said porous hearths and through the entire mass of material supported thereon, the material transferred from each porous hearth to the next lower porous hearth passing through an upwardly moving stream of water vapor issuing from the porous hearths therebelow, and maintaining a temperature above 2500° F. in the heating chamber.

5. The improvement in the method of defluorinating phosphatic material as set forth in claim 4 in which a temperature between 1900° F. and 2500° F. is maintained in an upper portion of the heating chamber and a temperature above 2500° F. is maintained in a lower portion of the heating chamber.

6. In the method of defluorinating phosphatic material in which the material is subjected to the action of water vapor at elevated temperature, the improvement which comprises supporting a plurality of layers of nodules of mixed phosphatic and carbonaceous material on porous hearths in vertically-spaced positions within a vertical heating chamber, maintaining a temperature of from 1800° F. to 2500° F. in the heating chamber, progressively moving the nodules downwardly through the chamber from one hearth to the next lower hearth, passing finely disseminated water vapor upwardly through the porous hearths and the entire mass of each layer of nodules while supported as aforesaid, introducing fresh nodules onto the uppermost hearth, discharging treated nodules from the lowermost hearth into one end of a calcining kiln, heating the kiln to a temperature above 2500° F. by the combustion of fuel at its other end, maintaining an atmosphere of water vapor within the kiln, and passing the hot products of combustion and water vapor from the kiln upwardly through the heating chamber and into contact with the nodules passing downwardly therethrough, whereby the water vapor will react with the carbonaceous material of the hot nodules with the evolution of gas to leave the nodules with a porous structure better adapted for their subsequent treatment in the kiln.

7. In the method of defluorinating phosphatic material in which the material is subjected to the action of water vapor at elevated temperature, the improvement which comprises supporting a plurality of layers of nodules of mixed phosphatic and carbonaceous material on porous hearths in vertically-spaced positions within a vertical heating chamber, maintaining a temperature of from 1800° F. to 2500° F. in the heating chamber, progressively moving the nodules downwardly through the chamber from one porous hearth to the next lower porous hearth, introducing fresh nodules to the uppermost porous hearth, discharging treated nodules from the lowermost porous hearth into one end of a calcining kiln, heating the kiln to a temperature above 2500° F. by the combustion of fuel at its other end, maintaining an atmosphere of water vapor within the kiln and passing the hot products of combustion and water vapor from the kiln upwardly through the heating chamber and into contact with the nodules passing downwardly therethrough, introducing additional water vapor into the heating chamber through the porous hearths, the water vapor in the heating chamber reacting with the carbonaceous material of the hot nodules with the evolution of hydrogen and carbon monoxide to leave the nodules with a porous structure better adapted for their subsequent treatment in the kiln, and introducing air into the heating chamber for combustion with hydro-

gen and carbon monoxide evolved from the nodules.

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