Nov. 5, 1940. E. LÜSCHER 2,220,575

PRODUCTION OF PHOSPHATIC FERTILIZERS

Filed Aug. 14, 1937 3 Sheets-Sheet 1

Fig. 1

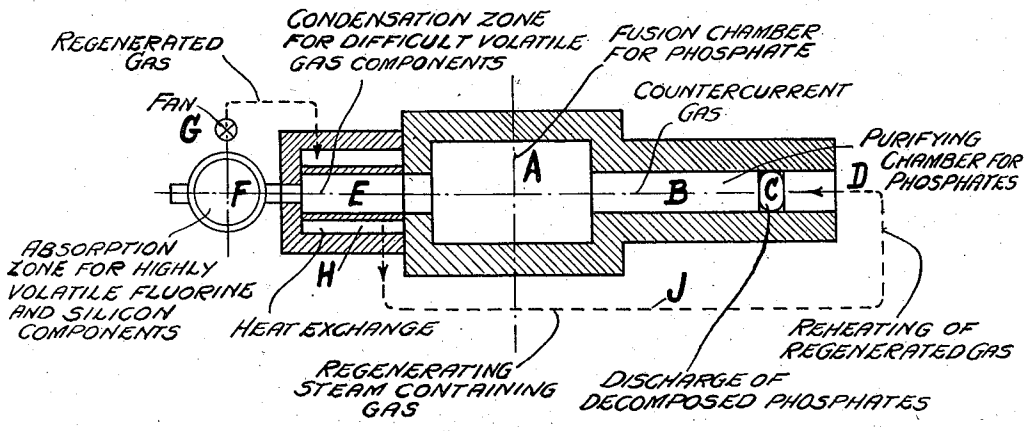
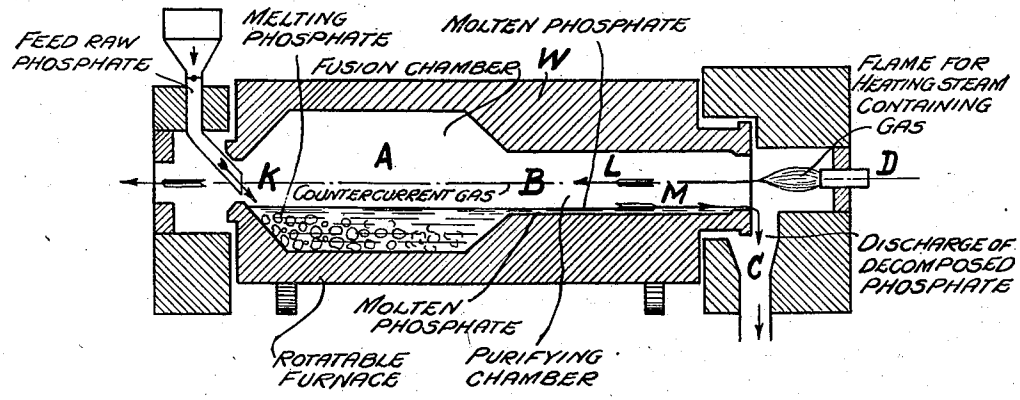


Fig. 2



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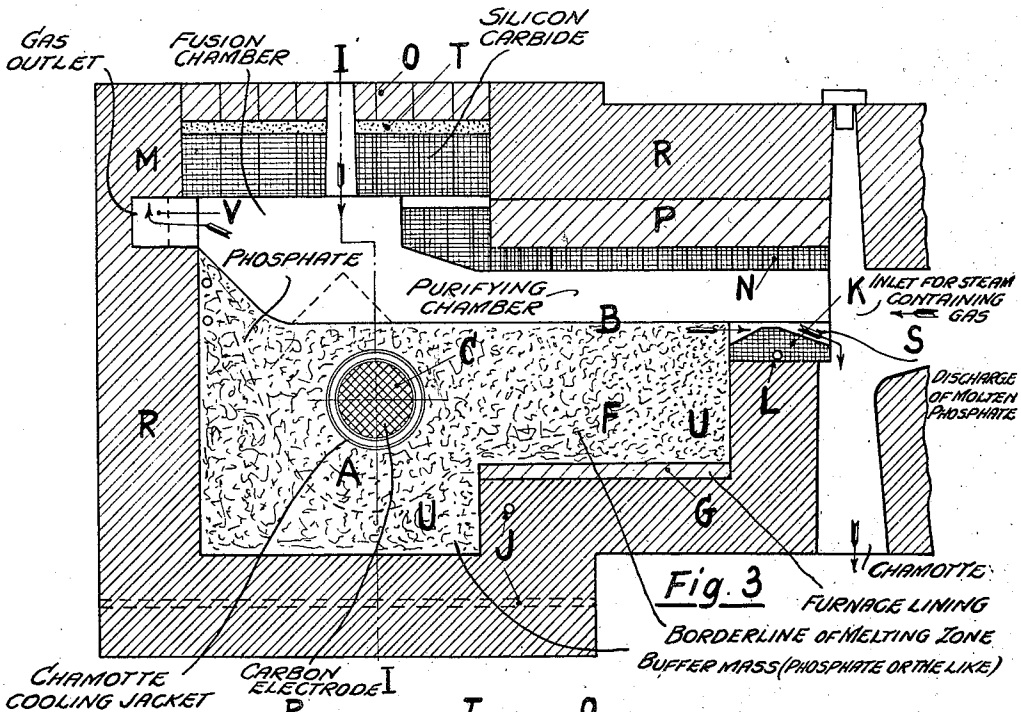


Fig. 3

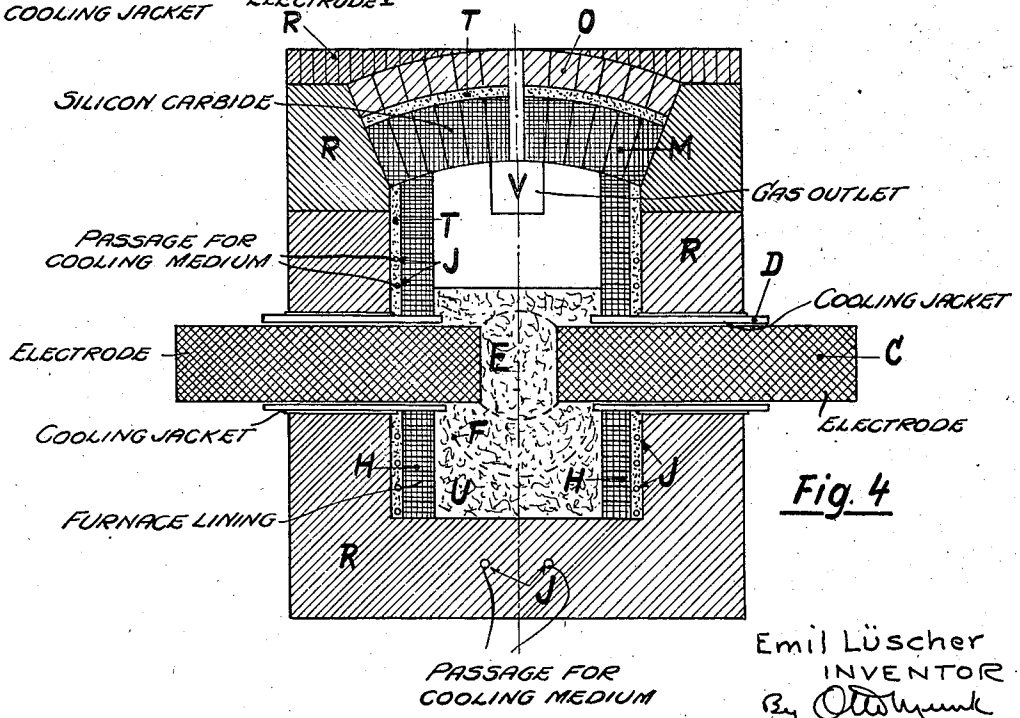


Fig. 4

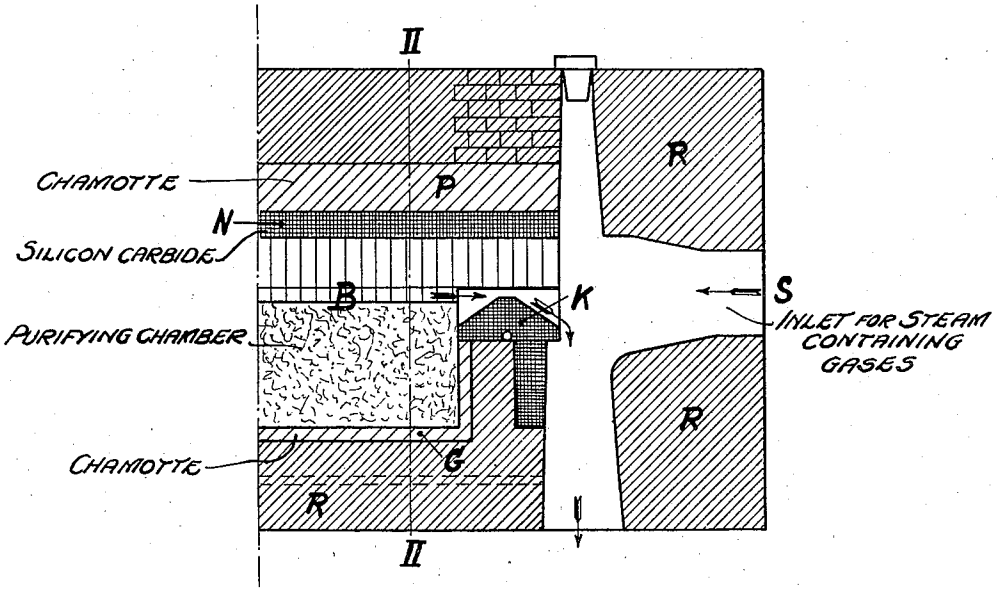
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PRODUCTION OF PHOSPHATIC FERTILIZERS

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Fig. 5



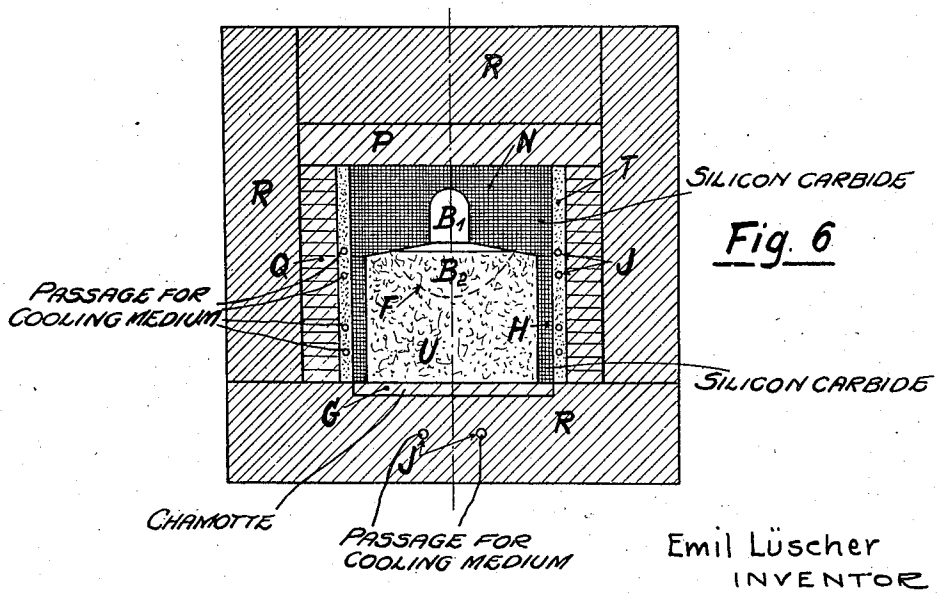


Fig. 6

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Patented Nov. 5, 1940

2,220,575

UNITED STATES PATENT OFFICE

2,220,575

PRODUCTION OF PHOSPHATIC FERTILIZERS

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Application August 14, 1937, Serial No. 159,074
In Switzerland September 2, 1936

6 Claims. (Cl. 71—44)

Many attempts have already been made to convert raw phosphates or more or less difficulty soluble artificial phosphates, such as Thomas slags, alone or with the assistance of added materials, such as quartz, lime, alkali-containing rock and the like, into fertilizers by fusion more particularly in the presence of gases containing steam, so that the phosphoric acid is contained in a form which is easily assimilated by the plants.

Until now none of these attempts have culminated in any really practical result. Only those processes have been successful which had as their object the decomposition of the raw phosphates by means of large quantities of alkali compounds at sintering temperature (for example in accordance with the so-called "Rhenania" process).

The reasons for the failure of known processes of this kind are of very varying nature. The processes proposed in part operate too uneconomically and in part lead to insufficiently decomposed final products, or else the operation of these processes on a large scale leads to difficulties of a technical kind which it has not hitherto been possible to overcome satisfactorily.

The present invention relates to the production of phosphates by fusion, that is to a phosphate decomposition process in which the whole of the reaction mass is converted into a molten condition. Experiments have shown that in these fusion processes it is above all important that the fluorine contained in the natural raw phosphates should be expelled to the last possible degree for example so that only about 0.01 to 0.03% remains, particularly when operating with small quantities or in the entire absence of alkalies.

According to this invention it has been found that a practically complete removal of fluorine can be effected in economically favourable and technically simple conditions, if to the furnace chamber, hereinafter called the "fusion chamber," in which the actual fusion of the material takes place and in which the main quantity of fluorine is already expelled during the fusion process, a chamber is connected which is hereinafter called the "melt chamber," in which the highly heated fused material is brought into intimate contact and mutual reaction with steam or a gaseous medium containing steam. It is advisable progressively to raise the temperature of the fused material up to the point of its discharge from the furnace and at the same time to allow the fresh steam or the fresh steam-containing gas to flow thereover in countercurrent and thus to expel the last residues of fluorine from the very mobile liquid reaction mass continuously, i. e. during its passage through the melt chamber. The intimate contact between the gaseous and fluid phases and the rapid change of surface of the melt which favourably influence the process may be promoted by the provision of cascade-producing or other elements and/or by rotating the furnace.

Generally the melting point of the raw phosphates or of the reaction mixture rises considerably to the degree that the fluorides and other compounds if present, such as alkalies, are volatilized. Consequently the fused material during its passage through the above-mentioned melt chamber must be heated considerably and progressively above the temperature of the initial fusing operation. In consequence on the one hand the last residues of the fluorine are expelled under the most favourable reaction conditions and on the other hand the normally relatively large actual melt furnace can be continuously operated with a minimum of wear.

The furnace may be heated in the most varied ways, for example by burning coal dust, oil or gas with oxygen or gases rich in oxygen, and by passing the hot combustion gases through the furnace chamber. The furnace may also be heated electrically, for example by electric resistance heating or according to the principle of electric high tension arcs, as well as electrical radiation and induction heating. Further the various methods of heating, for example by gas and electrically, can be combined.

In the case of fuels which contain large quantities of hydrogen the steam formed during combustion is generally sufficient for rapidly expelling the fluorine. In the case of coal dust firing or of exclusive electrical heating, however, the necessary steam must be introduced, previously heated for example to high temperatures by a high tension arc. The hot steam or the hot gases containing steam are preferably introduced at the point where the highly heated melt leaves the, for example channel-shaped, melt chamber at the highest temperature.

Electrical heating, in which the reaction product itself is used as electric resistance mass, has proved to be particularly advantageous. The melt chamber connected with the fusion chamber can in this case be heated in the aforementioned manner by an additional heat supply, preferably by the introduction of hot steam-containing gases, for example by an oil gas flame. Certain undesirable reaction products, which may be formed in small quantities by reduction pro-

cesses at the electrodes, for example calcium phosphide, are decomposed or oxidised in the melt chamber by the steam and the excess oxygen generally present.

The selection of electrodes to be used plays an important part when the material to be fused is heated directly by electric resistance. If carbon or graphite electrodes are used, then as far as possible it must be avoided that these take part in the reaction and reduce the phosphates to phosphorus. In the case of graphite electrodes completely, for example laterally, immersed in the mass this can to a great extent be avoided by sufficient cooling. When the electrodes are introduced vertically they must also be efficiently protected against the attack of the reaction gases.

The correct choice of the materials to be used for the construction of the furnace is also important. On the one hand the aggressive action of the fused reaction products must be taken into account and on the other hand the corrosive influence of the reaction gases, in particular the fluorine compounds. None of the known highly refractory ceramic masses for example can withstand the high-melting basic phosphorites in continuous operation. The known products, such as Chamotte, Dinas brick or Pythagoras mass are corroded in a short time.

According to this invention it has been found that these difficulties regarding materials can be overcome in a simple manner by introducing between the actual furnace lining and the molten material a buffer mass composed of material similar to, or the same as, the reaction product. By means of suitable cooling devices, such as tubes introduced at suitable positions in the furnace walls and traversed by a gaseous or liquid cooling medium, such as water or air, and/or by suitably dimensioning the furnace walls such a temperature gradient can be produced in the buffer mass from the interior of the furnace to the furnace lining that the buffer mass where it comes into contact with the highly heated molten material is at about the temperature of fusion, whilst the parts thereof abutting the actual furnace walls at the most attain the sintering temperature of the buffer mass. It is possible thereby to so dam in and thermally buffer the highly heated melt by means of the same material as the reaction product or a mass of similar composition by virtue of a temperature gradient as aforesaid, that the adjacent pressure-bearing elements of the furnace are no longer endangered. This applies both to the actual fusion chamber and also to the melt chamber. It is essential in this connection that the materials constituting the furnace lining should not give rise with the buffer substance to any, or any substantial, depression of the melting point, if the latter should at any time happen to sinter or soften too considerably in the contact zone. These requirements are for example fulfilled by silico-carnotite or basic silico-carnotite containing a high percentage of lime, such as the fusion products having approximately the following compositions:

$P_2O_5.5CaO.SiO_2$ to $P_2O_5.9$–$10CaO.3SiO_2$

corresponding to contents of about 16 to 30% of P_2O_5, 58 to 64% of CaO and 12 to 21% of SiO_2, or a phosphate mixture which yields with the fused material a similarly very high melting compound. Highly refractory materials, such as bricks of silicon carbide, sintered corundum and chromite and also in part magnesite bricks have proved very satisfactory for the production of the pressure-bearing parts of the furnace which are subjected to high temperatures and of the furnace lining, particularly when the aforementioned buffer masses are used. Silicon carbide and corundum bricks have proved to be particularly suitable as furnace materials for the parts coming into contact with the fluorine-containing gases.

When fusing raw phosphate mixtures, which enable a relatively low reaction temperature to be used, or in the presence of relatively large quantities of steam-containing gases, such as occur for example when employing only oil-firing and whereby a high concentration cannot be obtained owing to the volatile reaction products, such as fluorine and alkali compounds, the known mullite and sillimanite bricks or similarly composed highly refractory aluminium silicate masses may for example also be used.

The hot, steam-containing gases after their entry into the furnace first pass through the aforementioned melt chamber and then through the actual fusion chamber, where, as already mentioned, they take up the main quantity of the fluorine. Thence the reaction gases rich in fluorine pass into the separating or absorption plants, for example first into a somewhat cooler zone of the furnace constructed as a separator, in which, in addition to some flue dust, relatively difficultly volatile compounds, such as alkalies, fluorine compounds of alkalies, of aluminium and of iron can be condensed. The easily volatile compounds, such as HF and SiF_4, then pass into the actual absorption plant, in which they can be absorbed by solid or liquid, for example alkaline-reacting, substances or by water alone, depending on the purposes for which they are required. It is particularly advantageous to wash the gases with water or aqueous solutions or suspensions at boiling temperatures, so that the steam contained in the waste gases can be again directly used for the (cyclic) fusion process, whereby moreover the absorption of the volatile constituents contained in the waste gases, particularly the fluorides, is promoted. The possibility of using the acid waste gases for the decomposition of raw phosphates and other raw materials is valuable. In this way it is for example possible to obtain phosphoric acid and acid phosphates in a simple manner. This is of particular interest if the material to be fused contains considerable quantities of chlorides or sulphates of alkalies, alkaline earths or magnesium.

The maximum possible utilisation of the heat employed in the fusion process is of great importance for the economy of so cheap a product as the calcined phosphates. Use should therefore be made as far as possible of the heat in the waste gases and the molten mass for heating up the fresh reaction products and the fresh gases. This may be effected in known manner by means of suitable heat exchangers and, if necessary, by means of at least partial circulation of the waste gases.

After passing through the melt chamber in which above all the fluorine is expelled as quantitatively as possible, the highly heated, mobile mass can be caused to flow for example over a draining spout into a receiver or a water sump. The fused mass is cooled rapidly or slowly depending on its properties. It may also be atomised, for example immediately during draining.

The composition of the material to be fused

may vary within the widest limits depending on particular requirements. Thus for example in the case of electric resistance heating of the material to be fused, the addition of special materials rich in alkali and containing lime, which for example give rise to the formation of tetraphosphate types and of compounds still richer in alkali and lime, results in a considerable reduction in the specific resistance of the molten mass as compared with the more easily fusible, but less electrically conductive, meta-silicates. Phosphate mixtures of high melting point and rich in silica, which for example give rise to the formation of the known silico-carnotite type of compounds, as well as raw phosphates without any additions, can however also be easily fused in this manner. The ratio of P_2O_5 to CaO and SiO_2 can be varied within very wide limits. Additions of alumina, iron, magnesium and borax have also proved to be particularly suitable, especially in the presence of large quantities of lime.

Three embodiments of a furnace adapted for carrying out the process of this invention are illustrated by way of example in the accompanying diagrammatic drawings, wherein

Figure 1 is a sectional plan view of a stationary chamber furnace with gas heating. A is the fusion chamber, into which the raw phosphate mixture is introduced from above or from the side. The molten material passes through the channel-shaped melt chamber B to the outlet C. Highly heated steam-containing gases are introduced at D, for example by means of a water gas-oxygen blast flame. The hot gases first traverse the melt chamber B and thereby come into intimate contact with the relatively thin layers of fused material flowing therethrough towards the outlet C, whereby the fused material is heated to a high temperature and the last residues of flourine are expelled therefrom. The gases then pass into the fusion chamber A where they cause the reaction material to melt and thereafter into a separator E, in which the difficultly volatile compounds are condensed, and finally into an absorber F. This consists of a wash tower, in which the hot gases are washed, for example at boiling temperature, by means of an aqueous solution. A part of the steam-containing gases evolved can be sucked out by the fan G, and after passing through the heat exchanger H may be led back through a by-pass J to the melt zone B.

Figure 2 is a sectional elevation of another embodiment of a furnace according to this invention, in which a particularly efficient action of the hot steam-containing gases on the melt is ensured by employing a rotary furnace W. A is the fusion chamber, into which the phosphorite initial mixture is introduced at K, and B is the melt chamber. C is the discharge opening for the molten end product. The arrow L indicates the direction of flow of the hot steam-containing gases and the arrow M indicates the opposed direction of travel of the fused material.

Figures 3 to 6 illustrate an embodiment of a fusion furnace having a melt chamber directly connected with the fusion chamber, in which the fused material serves as electric resistance and a thermally graduated buffer mass is inserted between the actual lining of the furnace and the fused mass.

Figure 3 shows the furnace in longitudinal section with the fusion chamber A and the melt chamber B constructed in the form of a channel,

Figure 4 is a section through the fusion chamber A along the line I—I of Figure 3.

Figure 5 is a further longitudinal section through the melt chamber or channel B and

Figure 6 is a section through the latter along the line II—II of Figure 5.

C are graphite electrodes provided with water cooling D and E is the molten reaction mass which serves as electric resistance. The broken line F is the bounding line between the molten reaction mass around the electrodes and in the melt channel and the likewise molten to sintered liquid buffer mass U, which latter however is cooled to such a degree by an outwardly decreasing temperature gradient that the buffer mass is already hardened in the zone of contact with the actual furnace lining G and H. The necessary temperature gradient is attained by correctly regulated cooling, for example by means of the cooling tubes J traversed by air or water, which tubes are introduced at determined points in the furnace. K is a draining spout mounted at the end of the melt channel. The temperature of K must be very exactly regulated by the cooling tube L, in order to ensure regular draining over of the fused material. The opening S serves for the introduction of the hot steam-containing gases which leave the furnace by the flue V.

No.	Phosphate	Initial mixtures per 1000 parts of phosphate				Analysis of the end products				
		River sand	Acetylene sludge	Soda	Potash	Melting point about	P_2O_5 total	Soluble in—		F
								Citric acid	Ammonium citrate	
		Parts	*Parts*	*Parts*	*Parts*	*°C.*	*Percent*	*Percent*	*Percent*	*Percent*
1	Pebble					1650	38.3	85.0		0.04
2	do	250	125	75		1420	24.5	95.6	68.3	0.02
3	Morocco	320	100	75	25	1610	23.0	100.0	79.3	0.02
4	Pebble	250	100	50	100 $10FeO_3$	1400	23.5	99.6	61.0	0.03
5	do	438	137	40		1480	22.5	95.0		0.05
6	do	100				1450	31.8	99.5	45.6	0.03

The acetylene sludge contained 61.4% of CaO, the potash 40% of K_2O.

The ammonium citrate solubility was determined by Petermann's method.

The following is a complete analysis of a fertilizer produced from pebble phosphate, which was

fused with small quantities of calcareous sand and river sand:

	Per cent
Total P_2O_5	32.24
Total soluble in citric acid	93.5
Total citrate, soluble	50.4
Total F	0.03
Total CaO	48.97
Total MgO	0.17
Total SiO_2	13.62
Total Al_2O_3	1.19
Total Fe_2O_3	1.00
and	
Total Na_2O	1.10

The following materials may be used for the construction of the furnace: Silicon carbide and corundum bricks for the side walls H, the crown M of the fusion chamber, the ceiling N of the melt channel and the draining spout K. Highly refractory chamotte with satisfactory heat insulation properties for the hearth G of the melt channel, the crowns O, the ceiling P and the side walls Q. The buffer mass U consists of the same or similar material as the material to be fused, for example of silico-carnotite. The entire furnace is finally enclosed in a wide surround R of ordinary insulating bricks or masonry. Hollow spaces T, which may, if necessary, be filled, for example with powdered alumina or a highly refractory furnace cement or the like, are provided at suitable places between the various insulating layers.

The process and apparatus hereinbefore described may with advantage be employed after suitable adjustment to any fusion-phosphate process.

Example

The following two products were used as initial materials:

	P_2O_5	CaO	F
	Percent	*Percent*	*Percent*
Pebble phosphate	34.27	49.25	3.70
Morocco phosphate	33.35	51.24	Approx. 3

The raw phosphates were fused with various additions in a furnace provided with fusion chamber and melt zone in the presence of steam. The following products were obtained:

What I claim is:

1. The herein described continuous process for producing available phosphatic fertilizers, which process comprises feeding raw phosphate to a fusion zone of relatively large cross-section, heating and melting the phosphate in said fusion zone to form therein a sump of liquid phosphate passing a continuous substantially horizontal stream of completely molten phosphate from said fusion zone in a relatively thin layer through a purifying zone of considerably reduced cross-section immediately adjoining said fusion zone, introducing into the purifying zone near the discharge point of the molten phosphate a steam-containing gas of a temperature higher than the melting temperature of the phosphate, and passing said gas in countercurrent to and in immediate contact with the phosphate through said purifying and fusion zones, whereby the temperature of the completely molten phosphate flux advancing through said purifying zone rises continuously and the phosphate is freed from practically all its fluorine contents by reaction thereof with the steam.

2. A process, as claimed in claim 1, in which the exhausted gas discharged from the fusion zone is freed from its fluorine components and other volatile reaction products, whereupon at least part of the regenerated steam-containing gas is reheated and recirculated into said purifying zone near the discharge point of the molten phosphate.

3. A process, as claimed in claim 1, in which the exhausted gas discharged from the fusion zone is treated in an absorption zone with a liquid adapted to react at about its boiling temperature with the components of the gas formed by reaction with the fluorine in the phosphate without reducing the steam content of the gas, whereupon at least part of the regenerated steam-containing gas is reheated and recirculated into the purifying zone near the discharge point of the molten phosphate.

4. A process, as claimed in claim 1, in which the exhausted gas discharged from the fusion zone is treated in an absorption zone with an aqueous non-acidic phosphate containing liquid to fix the hydrofluoric acids and the other acid components of the gas, whereupon the renegerated steam-containing gas is reheated and recirculated into said purifying zone near the discharge point of the molten phosphate.

5. A process, as claimed in claim 1, in which the exhausted gas discharged from the fusion zone is first led through a condensation zone at a temperature causing separation of the difficultly volatile components from the gas, and the gas is then treated in an absorption zone at a temperature above the condensation temperature of the steam with a substance reacting with the highly volatile fluorine and silicon components of the gas, whereupon at least part of the regenerated steam-containing gas is reheated and recirculated into said purifying zone near the discharge point of the molten phosphate.

6. A process, as claimed in claim 1, in which the heating of the phosphate in said fusion zone is effected by means of electric resistance heating, the phosphate itself being used as the resistance.

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