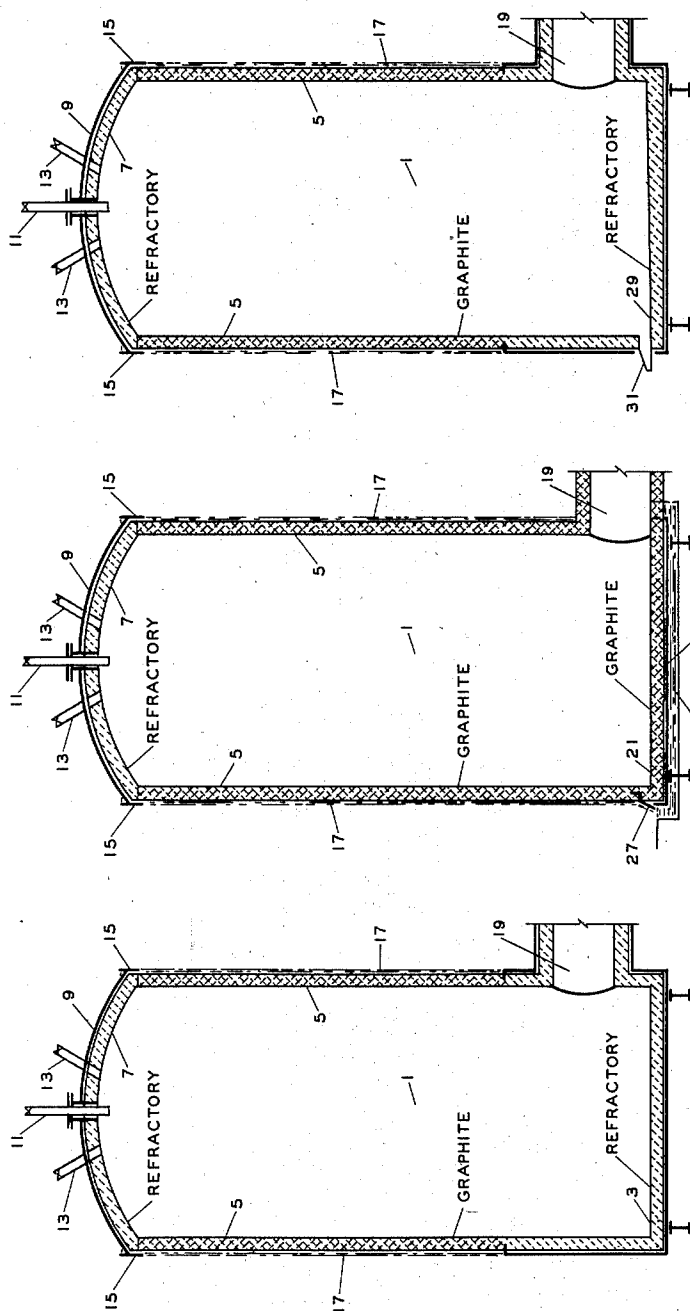


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PHOSPHORUS COMBUSTION FURNACE

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## PHOSPHORUS COMBUSTION FURNACE

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The invention herein described may be manufactured and used by or for the Government for governmental purposes without the payment to me of any royalty thereon.

This invention relates to the art of furnace construction, particularly adapted to the recovery of valuable oxidation products, such as the production of phosphorus pentoxide and the recovery of phosphoric acid in the combustion of elemental phosphorus.

The principal object of this invention is to provide a furnace with a combustion chamber in which the combustion products may be cooled rapidly without dilution. Another object of this invention is to provide a furnace in which material containing an appreciable portion of slag-forming impurities may be oxidized and such impurities may be deposited from the oxidation products and readily removed from the furnace. A further object of this invention is to provide a furnace which may be economically constructed and maintained and in which valuable material may be recovered by the combustion of substances having a high calorific value. Other objects of this invention include the provision for an improved method for the operation of the furnace described herein in the production of phosphoric acid.

The usual method of producing phosphoric acid from phosphorus or phosphorus-bearing gases is to burn the phosphorus with air in a combustion chamber, thus oxidizing the phosphorus to  $P_2O_5$ , and then hydrate the  $P_2O_5$  to orthophosphoric acid.

The common method for hydrating the  $P_2O_5$  is to pass the combustion gases into direct contact with a spray of water without prior cooling of the gases. The acid is then collected from the gases by an electrostatic precipitator or other suitable mist-collecting device.

This method of cooling and hydration has several disadvantages:

1. The large volume of steam evaporated into the gases in cooling by the direct introduction of liquid water results in a substantial increase in total gas volume and decrease in acid concentration. This has the effect of requiring a larger precipitator and causing a greater stack loss for a given final acid concentration in the stack gases wasted to the atmosphere.

2. The excessive partial pressure of water vapor in the gases encourages the formation of weak or dilute acid. In order to obtain acid of commercially desirable strength, it is necessary to operate the hydrator and precipitator at a relatively high

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temperature, which results in high rates of corrosion in the hydrator, precipitator, exhaust fan, conduits and stack.

3. Combustion of phosphorus or smelting-furnace gases in a combustion chamber of ordinary firebrick or refractory construction results in extremely high temperatures attended by rapid deterioration of brickwork. If an attempt is made to overcome this difficulty by spraying liquid water or steam into the combustion space, large amounts of strong acid are formed whose corrosive effect on the refractory walls more than offsets the reduction in temperature. Where excess air is used for cooling the combustion chamber, the gases are diluted with added bad effect on precipitator efficiency and capacity.

The above disadvantages may be avoided by cooling the combustion products before they enter the hydrator, and it has been proposed that at least a portion of this cooling be obtained by transfer of heat from the combustion products to cooling water flowing through tubes embedded in the walls of the combustion chamber. Operations involving such a proposal are unsatisfactory since the combustion chamber walls cannot be cooled uniformly by this method. The heat generated in the combustion chamber is so intense that means for conducting the heat away uniformly and keeping the wall area at a fairly uniform temperature at all points must be provided; otherwise, hot spots develop on the wall surface with consequent injury to the refractory and damage to the cooling tubes by unequal thermal expansion.

One well-known method for the cooling of hot surfaces is to maintain a film of water flowing over the surface. However, the use of walls cooled with a water film in apparatus of this type is attended with major technical problems which have not been solved satisfactorily heretofore.

In the first place, the heat generated in the combustion chamber is so intense that ordinary refractory material does not conduct heat from the combustion gases to the cooling water at a high enough rate. As a result, the gases are not cooled to the desired degree and the walls deteriorate because of the high temperatures. Moreover, those particular construction materials which have the characteristic of high heat transfer rate also have other characteristics which make them unsuitable. Graphite, for example, has a sufficiently high heat transfer coefficient but it oxidizes appreciably at temperatures as low as 840° F. Since the temperature of

the combustion gases even with adequate cooling ranges from 1200° to 2000° F., the latter characteristic would appear to preclude the use of graphite. Also, graphite has a relatively porous structure and would be expected to leak gases out or cooling water in. For these reasons, no one, as far as we know, has ever seriously considered the possibility of building a phosphorus combustion chamber of graphite or similar materials. It has been generally considered that the direct-spray and cooling-tube methods were the only ones which could be used.

The apparatus of the present invention is directed to a furnace construction wherein the combustion products are cooled rapidly by indirect means for the subsequent removal of valuable products and comprises the combination of a refractory hearth, a graphite wall, means for cooling the exterior of said graphite wall and maintaining the inner surface thereof below a temperature at which it will oxidize when in contact with the oxidizing atmosphere within said chamber, and a refractory enclosure opposite said hearth.

In the accompanying drawings which form a part of the specification and wherein reference symbols refer to like parts wherever they occur,

Fig. 1 is a diagrammatic, vertical, sectional view of one form of apparatus for the embodiment of the present invention showing furnace construction wherein the combustion chamber is provided with a graphite wall between the refractory hearth and roof.

Fig. 2 is a diagrammatic, vertical, sectional view of another embodiment of the present invention particularly adapted to operations involving the combustion of elemental phosphorus which does not contain a substantial amount of slag-forming impurities, wherein the hearth is constructed of graphite and cooled by a body of cooling liquid.

Fig. 3 is a diagrammatic, vertical, sectional view of still another embodiment of the present invention particularly adapted to the oxidation of elemental phosphorus carrying an appreciable amount of slag-forming impurities, wherein the hearth is constructed of suitable refractory other than graphite and from which the slag deposited thereon may be removed as required.

In Fig. 1, the combustion chamber 1 consists of a refractory hearth 3, a vertical, cylindrical wall 5 constructed of graphite shapes and containing no joints perpendicular to the line of heat flow from the interior to the exterior thereof, and refractory dome 7, the exterior of which is protected by an outer steel shell 9. Elemental phosphorus or phosphate reduction furnace gas containing elemental phosphorus is admitted through phosphorus burner 11, through dome 7, into combustion chamber 1, together with controlled amounts of air admitted through valved air inlets 13, and through dome shell 9. The products of combustion of the elemental phosphorus carrying phosphorus pentoxide are partially cooled in combustion chamber 1 by heat transfer through graphite wall 5, which is externally cooled by the distribution of water (from water supply not shown) at the top of the wall through distributor 15 to provide a flowing water film 17 over the surface of said wall 5. The combustion products so partially cooled are drawn from combustion chamber 1 through outlet 19.

In Fig. 2, hearth 21, as well as wall 5, is also constructed of graphite shapes with no joints

perpendicular to the line of heat flow through the hearth. This graphite hearth 21 rests in a metal housing 23, the rim of which does not extend upwardly more than the thickness of the hearth 21. This metal housing 23 in turn is substantially surrounded by a body of cooling water 25, the depth of which is less than the height of the housing rim. A flashing ring 27 is provided at the bottom of graphite wall 5 to deflect the falling film of water and prevent it from entering the metal housing 23.

In Fig. 3, refractory hearth 29 constructed of suitable refractory other than graphite serves to collect deposits of slag-forming materials which may be present in some supplies of crude elemental phosphorus. Ordinarily, the amount of such material may not be excessive, but as such a deposit accumulates on hearth 29 it may be withdrawn therefrom through tap 31.

It may be seen that certain problems encountered with combustion of high-calorific material and the recovery of valuable products can be solved by the furnace construction described herein. The combustion chamber has vertical, cylindrical walls of graphite shapes containing no joints perpendicular to the line of heat flow and may have a hearth of like construction. The walls are unjacketed and are cooled by a film of water flowing over the outside surface. When a graphite hearth is employed, it is rested on a steel housing, the rim of which does not extend upwardly more than the thickness of the hearth; this housing is in turn supported in a body of cooling water, the depth of which is less than the height of the housing rim. A flashing ring is also provided at the bottom of the wall to deflect the falling film of water and prevent it from entering the steel housing. A refractory dome which forms the upper enclosure for the chamber is protected by an outer steel shell. A phosphorus burner head is mounted at the top of the dome and the combustion gases leave the chamber through an outlet near the hearth and are thereafter further processed.

As an alternate construction, for use when the phosphorus being burned has a relatively high ash content, the lower walls and hearth may be made of a steel shell lined with firebrick or other refractory material. The upper wall section is bare, unjacketed graphite as in the first design. The purpose of the refractory lined lower section is to provide a zone which can be subjected occasionally to an increased temperature by concentration of combustion in the hearth zone, in order to melt accumulated ash and tap it out.

The use of graphite is the most distinctive feature of the design. Because of its unique property of high thermal conductivity and the particular construction used, the graphite conducts away to the water film the greater part of the heat of combustion and is itself at the same time relatively cool even on the inside surface. Being always cool, the graphite walls are not damaged by oxidation or thermal expansion.

The chamber is made in the form of a vertical cylinder to ensure coverage by the cooling water and to permit effective uniform dissipation of heat. The ratio of height to diameter may be varied to control the temperature of the gases leaving the chamber in the temperature range in which heat transfer by radiation is effective. The most effective ratio is from 2:1 to 3:1 which allows maintenance of the exit gas temperature at 1200° to 1800° F.; this makes possible the use

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of a shell- and tube-type cooler for cooling the gases down to a point just above the "dew point" of phosphorus pentoxide (about 500° F. when burning condensed elemental phosphorus). The walls are kept bare and unjacketed, since any jacketing material would reduce the heat transfer rate and cause the inner surface to heat up to a point where the graphite would be oxidized.

The dome-shaped top is covered with steel to avoid putting a head of water on vertical or substantially vertical joints between the dome blocks. Because of the relatively large air space between the steel and the blocks necessary to permit differential thermal expansion, graphite dome blocks would not be cooled sufficiently even in this relatively cool part of the chamber. The refractory in the dome, and also in the hearth when a refractory hearth is used, is subject to much less severe service than in the ordinary combustion chamber. The large, relatively cool inner surface of the graphite wall in "view" of the dome and hearth removes heat from the refractory by true radiation at such a rapid rate that these portions of the chamber operate normally at a temperature well below red heat, which is very favorable to long life. The refractory hearth is subjected to a higher temperature by deliberate concentration of combustion in that zone only at infrequent intervals to permit fusion and removal of accumulated ash.

The design of the graphite hearth presented a difficult problem. It is necessary to cool the hearth and also to provide some safeguard against the possibility of acid leaking out through the joints in the graphite hearth blocks. This was solved by placing the combustion chamber in a metal pan which sits in a pool of water. It was found that the interposition of metal between the graphite and cooling water is allowable here, although it is not allowable on the walls or dome, because the weight of the furnace bottom gives a close enough contact between the graphite and metal to give sufficient heat transfer to keep the hearth cool. It is important that the metal rim of the pan not extend up the wall above the top of the hearth; otherwise a hot spot will develop on the wall because of the decrease in heat transfer. Because of differential thermal expansion, the metal cannot be made to fit the wall closely enough to give sufficient heat transfer.

The graphite-refractory combination has been found to be the only feasible hearth design for use with high-ash phosphorus. If all-graphite construction is used, the occasional concentration of heat in the hearth section for the purpose of melting out ash deposits would cause oxidation and failure of the graphite. On the other hand, an all-refractory design cannot be used because of the low heat transfer coefficient of the refractory, as discussed above. The reason that refractory can be used in the hearth section is that the graphite wall above it cools the gas to a temperature low enough to prevent appreciable damage to the refractory. The hearth is also cooled, as explained above, by radiation of heat from the hearth to the graphite wall.

The refractory hearth is used only with high-ash phosphorus; the graphite hearth is preferable for low-ash phosphorus both because it is cheaper to build and maintain and also because it allows cooling the gas to a lower temperature. The relatively small amount of ash which collects on the graphite hearth can be removed by

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adding water to the combustion chamber to flush the ash into the hydrator.

It should be emphasized that use of graphite, which has never been regarded hitherto as a suitable material, is made possible only by a certain combination of design features. The chamber must be vertical and cylindrical, in the first place, so that a relatively thick, uniform layer of water can be flowed down the outer surface. Otherwise, the heat will not be removed fast enough and the graphite will oxidize. In addition, cement joints perpendicular to the line of heat flow must not be used, i. e., the wall must be only one block thick. This gives an uninterrupted path of graphite for the heat to follow and makes possible keeping the inner surface at a low enough temperature to protect the graphite. Finally, certain features are necessary in the design of the graphite hearth, as discussed above. By using this combination, a very unpromising construction material has been used with excellent results.

The porosity of the graphite presents no problems, which is an unexpected development. The inner wall is cooled to such a degree in a combustion chamber of the above design that solid metaphosphoric acid condenses on the wall and fills the pores. This prevents appreciable leakage between the inner and outer walls, but it might be expected that a layer of acid would form on the wall surface which would cut down the heat transfer by a significant amount. It has been found, however, that this does not occur at the particular wall temperature used.

The design as shown is intended for use with a countercurrent hydrator, i. e., one in which the cooled combustion gases enter at the bottom and the water spray comes from the top. If a co-current hydrator (one in which both gases and water enter at the top) is to be used, the design of the combustion chamber is substantially the same except that the combustion gases leave the chamber from the top and phosphorus is introduced through two or more horizontal atomizing burners mounted in the walls near the hearth.

It will be seen therefore that this invention actually may be constructed by the use of various modifications and changes without departing from its spirit and scope.

I claim:

1. In a phosphorus combustion furnace comprising a combustion chamber having an outlet for hot combustion gases adjacent to an end thereof, a burner adapted to burn phosphorus disposed in said chamber adjacent to an end thereof farthest from said outlet, and means for introducing air in quantity sufficient to maintain an oxidizing atmosphere within said chamber disposed adjacent to said burner, that improvement which comprises, in combination, a container for a pool of water; supporting members disposed in said container; a flat metal pan disposed in said container adapted to be supported by said supporting members in intimate contact with said pool of water in said container; a circular hearth floor formed of a single thickness of graphite blocks disposed in said metal pan; a vertical cylindrical wall formed from a single thickness of graphite blocks disposed upon the periphery of said hearth floor; a substantially dome-shaped top disposed upon said cylindrical wall to cooperate with said wall and said hearth floor to enclose a vertical combustion chamber having a ratio of height to diameter of from 2:1 to 3:1; a burner adapted to burn phosphorus

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centrally disposed in said combustion chamber adjacent to said top; an outlet for hot combustion gases disposed adjacent to said hearth floor; and means for continuously flowing a film of water of substantial thickness downward over the exterior surface of said wall disposed adjacent to the exterior of said chamber.

2. In a phosphorus combustion furnace comprising a combustion chamber having an outlet for hot combustion gases adjacent to an end thereof, a burner adapted to burn phosphorus disposed in said chamber adjacent to an end thereof farthest from said outlet, and means for introducing air in quantity sufficient to maintain an oxidizing atmosphere within said chamber disposed adjacent to said burner, that improvement which comprises, in combination, a metal shell disposed to surround a vertical, cylindrical hearth section; a lining of refractory material other than carbon disposed in said metal shell to surround a lower, minor portion of the combustion chamber; a vertical cylindrical wall formed from a single thickness of graphite blocks disposed upon the periphery of said hearth section; a substantially dome-shaped top disposed upon said cylindrical wall to cooperate with said wall and said lining to enclose a vertical combustion chamber having a ratio of height to diameter of from 2:1 to 3:1 and having a major upper portion bounded by said cylindrical wall; a burner adapted to burn phosphorus disposed in the combustion chamber adjacent to said top; an outlet for hot combustion gases disposed in said hearth section;

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and means for continuously flowing a film of water of substantial thickness over the exterior surface of said wall disposed adjacent to said top.

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