Jan. 20, 1925. 1,523,417

H. A. GRINE

PROCESS AND APPARATUS FOR PRODUCING METAL OXIDES

Filed May 16, 1922 3 Sheets-Sheet 1

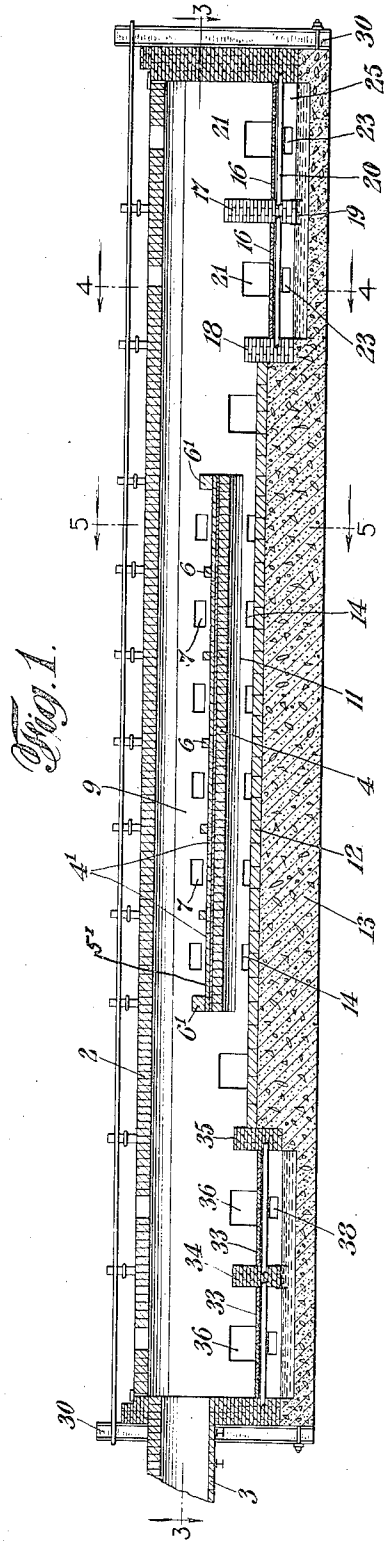


Fig. 1.

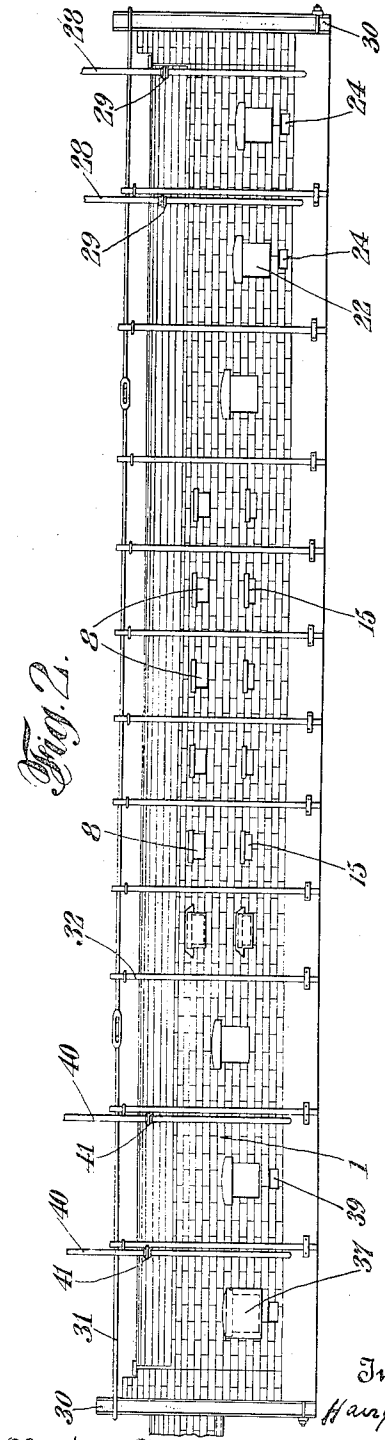


Fig. 2.

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Filed May 16, 1922 3 Sheets-Sheet 2

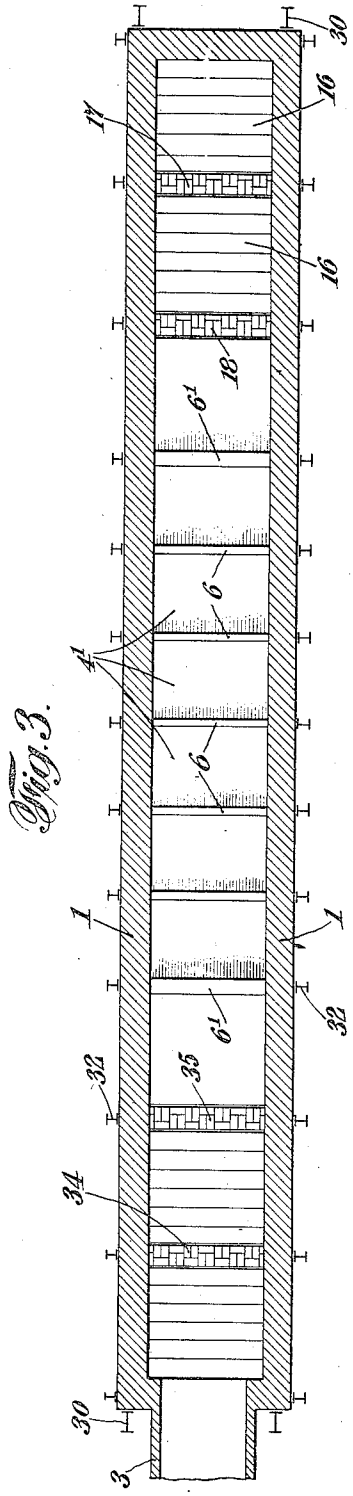


Fig. 3.

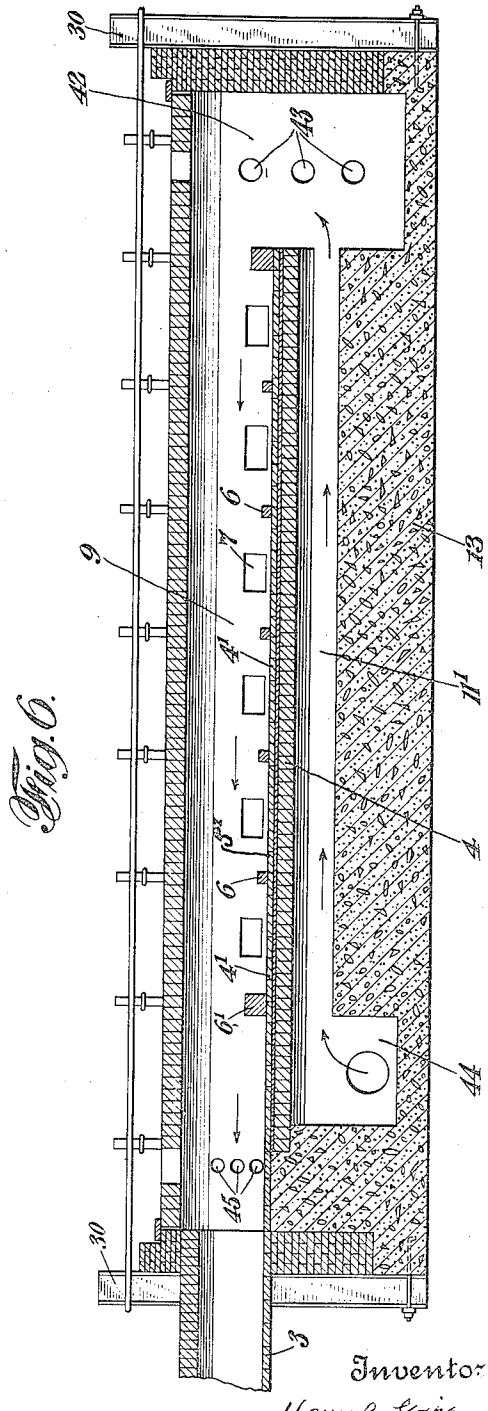


Fig. 6.

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PROCESS AND APPARATUS FOR PRODUCING METAL OXIDES

Filed May 16, 1922 3 Sheets-Sheet 3

Fig. 4.

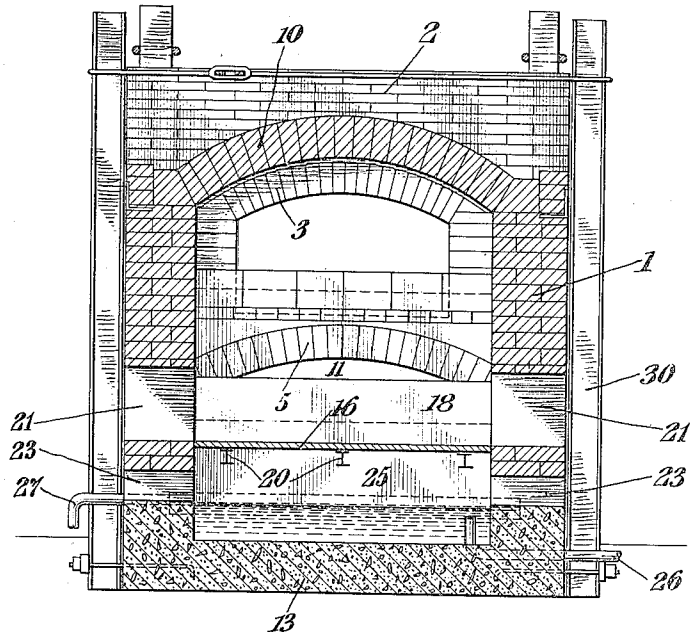
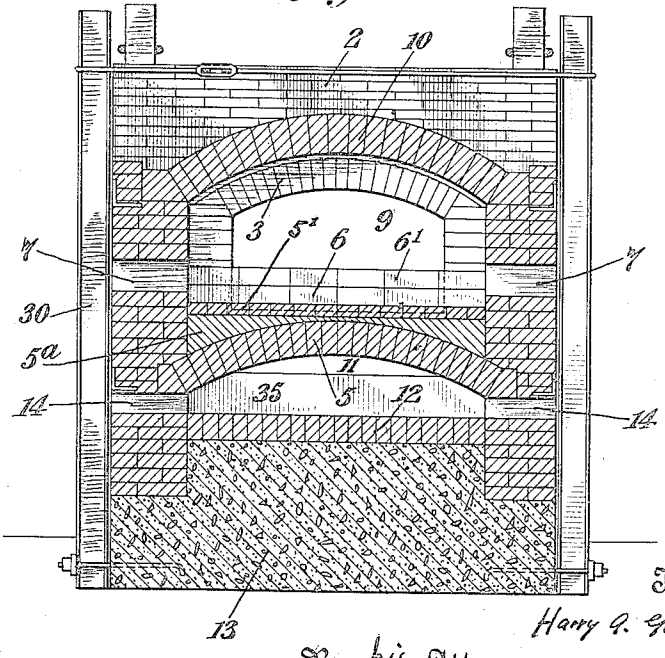


Fig. 5.



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Patented Jan. 20, 1925. 1,523,417

UNITED STATES PATENT OFFICE.

HARRY A. GRINE, OF LANGELOTH, PENNSYLVANIA.

PROCESS AND APPARATUS FOR PRODUCING METAL OXIDES.

Application filed May 16, 1922. Serial No. 561,288.

To all whom it may concern:

Be it known that I, HARRY A. GRINE, a citizen of the United States, and resident of Langeloth, in the county of Washington and State of Pennsylvania, have invented certain new and useful Improvements in Processes and Apparatus for Producing Metal Oxides, of which the following is a specification.

The invention relates to an improved process and apparatus for the production of metallic oxides, and particularly to an improved process for manufacturing zinc oxide, suitable for use as pigment and for other commercial uses, and improvements in apparatus which may be utilized in carrying out such process.

The invention may be considered, in some aspects of the same, as an improvement upon that disclosed in my application Serial No. 524,084, manufacture of zinc oxide, filed December 22, 1921. In the said application a process is described in which metallic oxides, and particularly zinc oxide suitable for commercial uses, are produced by subjecting metallic zinc, on an open hearth, to volatilization and oxidation in an oxidizing atmosphere, the zinc oxide vapors thus produced being removed to a collecting system.

In the form of the invention which is specifically described in the said co-pending application, zinc dross or zinc scrap or other metallic zinc is volatilized on a solid hearth by heat produced by the combustion of fuel on a grate underneath the solid hearth. Air is forced through the grate and the resulting hot gases and air passed above the solid hearth. By this method the metal on the solid hearth is volatilized, partly by the direct application of heat through the hearth and partly by the heat of the gases above the hearth; the metallic vapors thus produced are oxidized by the air which passes above the solid hearth from the lower grate or hearth. Also, in the construction specifically described in my said co-opending application, the residue on the solid hearth after distillation of the metallic zinc is transferred to the lower grate hearth. This residue contains zinc oxide. A reducing fuel is added to it on the lower or perforated grate hearth and the zinc oxide subjected to reduction and reoxidation, the resulting zinc oxide vapors mingling above the upper hearth with the zinc oxide vapors there produced.

I have found that where a pin hole grate or other heating hearth is situated directly below the solid hearth on which the metal is distilled, the supporting structure of the solid hearth is subjected to excessive heat action from the fire on the grate hearth beneath the same, which in time will cause it to deteriorate. Also, various impurities, such as lead oxide and sulfate, and iron oxide, etc., are often contained in zinc dross and similar materials. These substances act energetically on common refractories, and I have found that, in operation, such impurities in the charge will cause considerable deterioration of the surface material of the solid hearth, if special measures are not taken to prevent the same.

In accordance with my present invention, the pin hole grate or other heat producing means is placed in such a position that flames therefrom cannot impinge directly on the lower side of the solid hearth. In the preferred construction hot gas and air are caused to pass over the metal on the solid hearth and hot gas and air, or hot gas alone, caused to pass through a passage or space extending underneath the solid hearth. With this arrangement also, preferably, the solid hearth is formed or surfaced with a material which will not be acted on harmfully to any marked extent, at the temperature used, by the residual impurities in the metal on the solid hearth.

Broadly speaking, it may be said that my improved process, in one aspect of the same, comprises the utilization of materials in the hearth construction which will not be acted on harmfully by impurities in the metal at certain temperatures, and conducting the distillation of the metal in such a manner that the temperature of the hearth and the metal thereon will lie within the desired range of temperature. Preferably, the hearth will be formed of materials which will unite with residual impurities in the charge, to form compounds which will not

flow readily at the temperatures provided by my process, so that the hearth will not be destroyed. Other aspects of the improved process will be pointed out hereinafter.

The invention consists in the novel processes and process steps and in the novel construction, arrangement and combination of parts hereinafter described according to the preferred embodiments thereof. The invention will be more particularly pointed out in the appended claims.

In order that the invention may be more clearly understood, attention is hereby directed to the accompanying drawings illustrating certain forms of apparatus embodying the invention and by which the improved process may be practiced. In the drawings, Fig. 1 represents a vertical longitudinal section taken through one form of furnace embodying the invention. Fig. 2 is a front elevation of the same construction. Fig. 3 is a horizontal section take on line 3—3 of Fig. 1. Figs. 4 and 5 are transverse vertical sections taken on line 4—4 and 5—5 respectively of Fig. 1; and Fig. 6 is a vertical longitudinal section taken through a modified form of construction.

Referring first to Figs. 1 to 5 of the drawings, a furnace is illustrated having enclosing walls 1, a top 2 and an exit passage 3 at one end thereof. These parts may be formed of usual refractory materials. The exit 3 may suitably be formed of an arched construction as is indicated in Figs. 4 and 5. It may lead to a collecting system for the zinc oxide vapors, this collecting system comprising a large combustion chamber from which a large cooling pipe line leads to a filtering bag house. Such construction is well known and accordingly is not illustrated.

The solid or open hearth, represented as a whole by reference character 4, may be supported by the arch 5 which extends across the furnace from side to side as is shown in Figs. 4 and 5. The hearth is provided with an upper surface 5′ which is preferably formed of chrome brick or other basic material, a filling material 5ª, preferably of basic ground material, being used to fill in the space between arch 5 and the surface material 5′ as will be more fully described hereinafter.

The hearth so formed extends entirely across the furnace from side to side and preferably extends lengthwise of the furnace for a considerable distance at the intermediate portion of the furnace. It is preferably divided into a plurality of individual hearths 4′ separated from each other by low walls 6 extending across the furnace. Similar low walls 6′ are positioned at the two ends of the hearths.

Zinc dross or other material to be treated may be charged on the individual hearths 4′ through openings 7 in the opposite side walls of the furnace, these openings being provided with doors 8.

The construction described provides an open space or passage 9 extending above the solid hearth and below the arch 10 which supports the top portion 2 of the furnace. A passage or space 11 is also provided beneath the solid hearth, passages 9 and 11 both being open at both ends. The roof of passage 11 is formed by the arch 5 of the solid hearth while the floor or bottom of this passage is formed by the surface of tiles or bricks 12 laid on the solid base 13 which may be formed of any suitable material. Openings 14 extend through the side walls of the furnace into passage 11 at suitable spaced intervals to provide access to the passage for cleaning, etc., openings 14 being provided with doors 15.

In the construction shown one or more perforated grates 16 are provided in the furnace at the end of the same opposite to exit opening 3, that is, to the right of the solid hearth referring to Fig. 1. Preferably a plurality of such grates are used, the grates preferably being of a pin hole or Wetherill type. One grate is shown as extending between the end wall of the furnace and a low division wall 17 while the other grate is shown as extending between division wall 17 and a low wall 18.

Wall 17 may be supported by a channel bar 19 or the like so as to provide a space beneath the same, while wall 18 is mounted on the base 13. The perforated grates 16 may be supported by eye-beams 20 or the like secured at their ends in walls 18 and 17 and the end wall of the furnace.

Fuel, or fuel and residue from the solid hearth, containing zinc oxide, may be charged on grates 16 through openings 21 in the opposite side walls of the furnace, these openings preferably being provided with doors 22. Access to the space beneath the grates may be had through opening 23 in the side walls, these openings preferably being provided with doors 24.

The space or chamber underneath the pin hole grates is indicated by reference numeral 25. A water seal is preferably maintained in this chamber, the water level being as indicated slightly above the bottom of division wall 17. The water may be led into the space by pipe 26 suitably positioned and the water level maintained at the desired point by suitably positioning the outlet pipe 27 as is indicated in Fig. 4. The water will assist in cooling the Wetherill grates and will also serve to saturate the air with moisture so as to assist in preventing hard clinkering on the grates.

Air is introduced into the space beneath

the Wetherill grates through pipes indicated at 28 in Fig. 2, the air supply being controlled by suitable valves indicated at 29.

The furnace may be reinforced in any suitable manner as by means of vertical members 30 connected together by horizontal tie-rods 31, vertical members 32 being also shown as extending along the opposite sides of the furnace and suitably secured thereto and to each other at their lower and upper ends.

Preferably a heat producing chamber is additionally provided at the opposite end of the furnace, that is, between the solid hearth and the exit opening. In the construction illustrated this comprises a plurality of pin hole or Wetherill grates 33 which extend across the furnace from side to side and extend longitudinally between the end wall of the furnace and the low division wall 34 and between the latter and the low wall 35. The construction is in all respects similar to that of the heat producing chamber at the opposite end of the furnace already described, material being charged on the grates through openings 36 provided with doors 37 and access to the space beneath the grates being had by openings 38 provided with doors 39. Air may be introduced beneath the grates through pipes 40 provided with valves indicated at 41 and a water seal may be provided in the manner already described.

In operation the furnace may be started by igniting wood on the Wetherill hearths 16 or on the hearths 16 and 33 on which beds of live fire are obtained, after which coke or other reducing fuel may be charged on these hearths, and the fire blasted until the entire furnace has been brought to a temperature of between 1200° F. and 1800° F. A charge of zinc dross or scrap zinc or other material to be treated is then put upon each of the solid hearths 4^1, the hearths being charged serially with intervals between so that they are in various stages of working, some just charged, some at their maximum evolution of oxide and some almost worked off and ready for recharging so that a uniform evolution of oxide is maintained. If desired sufficient fine coke or anthracite coal to prevent execessive oxidation on the metal surface may be placed on the metal, this not, however, being essential.

The charges on the solid hearths will be heated by the hot gases and air passing from the space above grates 16 through passage 9 above the hearths and through passage 11 beneath the hearths. By this means the solid hearths are maintained at a desired temperture without the excessive direct flame action which may be caused when pin hole grates are located directly beneath the solid hearths. In a short time volatilization of the metal on the solid hearths begins and the vapors ignite over the charge, the oxidation of the metallic zinc vapors adding heat to the system. The charge on each upper hearth may be rabbled from time to time with a hand rabble which may be inserted through one of the openings 7 to facilitate the volatilization and combustion of the zinc.

The hot gases from the pin hole grate hearths 33 located between the solid hearths and the exit opening 3 serve to increase the heat of the gases passing out of the furnace through outlet 3 so that these gases will have a desired temperature when they reach the combustion chamber (not shown), situated beyond the furnace and constituting part of the collecting system as stated. It is desirable to maintain a temperature of about 1600° F. in this combustion chamber.

When the evolution of the zinc vapors from the charge on each of the solid hearths has practically ceased the remaining residue consisting of a crust comprising zinc oxide and any foreign materials which are contained in the zinc dross or scrap are raked out through openings 7 and may be charged through openings 21 and 36 on to the Wetherill grate hearths 16 and 33. A new charge of zinc dross or the like is now charged on the solid hearth just cleaned and the operation on the solid hearths repeated while the residue from the previous charge is being worked off on the Wetherill grate hearths. The reduction of the zinc oxide contained in the residue, in admixture with coke or anthracite reducing fuel, is completed on the pin hole grates 16 and 33, the zinc vapors being subsequently oxidized as they rise sufficiently above the charge. The gases passing upwardly above grate hearths 16 will contain zinc oxide and air, part of these gaseous products passing above the solid hearths as stated and mingling in passage 9 with the vapors which rise above the charges on the solid hearths, the metallic zinc vapors from the solid hearths being oxidized to a very substantial extent in contact with the hot gases and air from the pin hole grate hearths 16. The gases passing upwardly from the pin hole grates 33, between the solid hearths and the exit opening 3, similarly contain zinc oxide vapors and air which mingle with the vapors which have risen from the solid hearths, the gases which have passed over the solid hearths and the gases which have passed under the solid hearths, these gases all being thoroughly mingled and the heat of the same increased as previously stated.

Also as stated the gases are now carried off through the flue 3 into a large combustion chamber (not shown) where any incompletely oxidized zinc or material is oxidized. From the combustion chamber the gases carrying the zinc oxide may be drawn by fan suction through a large cooling pipe line and discharged into a filtering bag

house in the same manner as when operating on ores. In the pipe line the gases are sufficiently cooled to be discharged into the bag house filter where the zinc oxide, for use as pigment or otherwise, is filtered from the gas and collected in the same manner as is now practiced with zinc oxide made from ores.

A modified arrangement is shown in Fig. 6 in which the pin hole grate hearths 16 and 33 are eliminated. In place of the Wetherill grate hearths 16 a combustion or heat producing chamber 42 is shown in Fig. 6 in which air is introduced by pipe connections indicated diagrammatically at 43. Gas may be burned in the chamber 42 and the hot resulting gas and air caused to pass through the passage 9 extending above the solid hearth 4 in the same manner as has been described.

A passageway 11^1 is also shown as extending underneath the solid hearth through which hot gas may pass in one direction or the other to aid in applying the necessary heat to the solid hearth. In the construction shown in Fig. 6 hot gas, produced in a gas producer, is intended to be utilized, this gas entering a chamber or extension of passage 11^1 adjacent the end of the solid hearth which is directed towards the exit opening 3. This chamber or extension is indicated at 44 in Fig. 6. Hot gas entering the same passes through passageway 11^1, underneath the solid hearth, in the direction indicated by the arrows, this hot gas entering chamber 42 where it meets the air admitted through pipes 43 and is ignited. The hot gases and air will then flow over the solid hearth as indicated by the arrows to aid in volatilizing the zinc and to oxidize the zinc vapors. The mingled gases will pass out through flue 3 as before. Additional heat may be given to the gases at a point between the solid hearth and the exit opening 3 in any desired manner so as to bring the temperature of the gases up to that required for the combustion chamber beyond the furnace. I have indicated a number of pipe connections 45 as entering the furnace between the solid hearth and the exit flue 3 through which pipes additional air may be introduced to cause a more complete combustion of the gas from the gas producer to raise the temperature to the desired point. Pipe connections 45 will, of course, be provided with suitable valves so that the rate at which air is introduced at this point may be suitably regulated.

In operation with either of the forms of construction illustrated the temperature of the combustion chamber beyond the furnace may suitably be maintained at a temperature of about 1600° F. to 1650° F. This temperature may be controlled by operation of the valves 41 on the air pipes 40 for the pin hole grates between the solid hearth and the exit opening in the form of construction first described and by operation of the valves on the air pipes 45 in the form of construction last described. The temperature to be maintained on the solid hearth may be regulated by operation of the valves controlling the air supply for the heating chamber at the end of the construction opposite to the exit opening or by otherwise regulating the rate of heat production in the said heat producing chamber.

The impurities which remain after the zinc dross has been distilled act energetically upon common refractories as stated, at elevated temperatures. I minimize this action as stated by constructing the solid hearth of basic materials and by properly regulating the temperature maintained. The supporting arch 5 for the solid hearth may be formed by hydraulic pressed fire brick or the like. I fill the space above this arch with a basic ground material such as crushed chrome or magnesite, preferably to level up to a point about one inch above the crown of the arch. Over this is laid a level smooth hearth as indicated at 5′ which may be say from two to four inches thick. This hearth surface is formed of basic material such as chrome brick or plates, the joints between the same being filled with chrome or other basic cement.

The residual impurities in the zinc dross such as iron oxide, lead oxide and sulphate, tend to form slags with the basic hearth lining at and above the temperature at which the zinc volatilizes. No material damage will, however, be effected if such slag or compound is not permitted to become very fluid. A feature of my improved process accordingly consists in maintaining the temperature on the solid hearth above the point at which zinc volatilizes but below the temperature at which the slags formed from the basic hearth material and the residual impurities of the zinc become markedly fluid. As has been stated, the temperature used may range between 1200° F. and 1800° F.

In the preferred construction the furnace is sufficiently narrow so that all parts of the solid hearths may easily be reached from one side or the other for cleaning purposes. After the zinc volatilization and the oxidation process has been completed, the residual material may be removed through openings 7 by means of cutter bars which may be introduced through these openings 7 on either side of the furnace. This residual material may as stated, be recharged on the perforated grate hearths 16 and 33 for further treatment.

It should be understood that while I have described certain forms and features of the invention with particularity, the invention is not limited to the exact details which

have been described, but that various modifications may be employed as will be clear to those skilled in the art after reading this specification, the scope of the invention being indicated by the accompanying claims.

What I claim is:—

1. In a furnace of the character described, the combination of an open hearth adapted to contain molten metal, a chamber out of vertical alignment with said hearth, means for producing hot oxidizing gas in said chamber, means providing a passage extending under said hearth and connecting with said chamber, means providing a passage extending from said chamber immediately above said hearth, and means for conducting from the furnace gases which have passed above said hearth through said last named passage.

2. In a furnace of the character described, the combination of an open hearth adapted to contain molten metal, a perforated grate out of vertical alignment therewith, and adapted to receive fuel, means for introducing air under said grate, means providing passages for conducting hot gases and air from above said grate both over and under said open hearth to heat the latter, the space above said grate communicating directly with both of said passages, and means for conducting gases and air from the furnace.

3. In a furnace of the character described, the combination of a solid hearth having a surface of basic refractory material adapted to contain molten metal, a chamber at one side of said hearth, means for producing hot oxidizing gas in said chamber, means providing a passage extending under said hearth and connecting with said chamber, means providing a passage extending from said chamber immediately above said hearth, and means for conducting gases and air from the furnace.

4. In a furnace of the character described, the combination of an enclosing structure having an exit opening in one end, an open hearth adapted to contain molten metal, means providing a passage for hot gas extending under said hearth, means providing a passage extending immediately above said hearth, and a chamber at the side of said hearth opposite to the exit opening communicating directly with both of said passages, and means for producing hot oxidizing gas in said chamber, said upper passage being adapted to carry hot gas and air over the metal on the hearth, and communicating with said exit opening.

5. In a furnace of the character described, the combination of an enclosing structure having an exit opening at one end, an open hearth adapted to contain molten metal, with gas passages above and below the same, a heat-producing chamber at the side of said hearth opposite to the exit opening, communicating with said passages, and an additional heat producing chamber between said hearth and exit opening, said upper passage opening into said last named chamber.

6. In a furnace of the character described, the combination of an enclosing structure having an exit opening at one end, an open hearth adapted to contain molten metal, with gas passages above and below the same, a perforated grate at the side of said hearth opposite to the exit opening, the space above said grate communicating with said passages, and means for introducing air beneath said grate, said upper passage being adapted to carry hot gas and air from the space above said grate over the metal on the hearth, and communicating with said exit opening.

7. In a furnace of the character described, the combination of an enclosing structure having an exit opening at one end, an open hearth adapted to contain molten metal, with gas passages above and below the same, a perforated grate at the side of said hearth opposite to the exit opening, a perforated grate between said hearth and said exit opening, the spaces above said grates communicating with both of said passages, and means for introducing air beneath said grates.

8. In a furnace of the character described, the combination of an enclosing structure having an exit opening at one end, an open hearth adapted to contain molten metal, with a gas passage above the same, heat producing chambers at the side of said hearth opposite to the exit opening and between the hearth and the exit opening, respectively, communicating with said passage, and means introducing air into said first named chamber.

9. In a furnace of the character described, the combination of an enclosing structure having an exit opening at one end, a series of open hearths extending for a portion of the length of the furnace, each hearth extending across the width of the furnace with low division walls between the same, with a gas passage extending above all of said hearths, leading to said exit openings, a heat-producing chamber beyond the end of said hearths distant from the exit opening, and means for introducing air into said gas passage.

10. A process of producing a metallic oxide which comprises, subjecting a readily oxidizable volatilizable metal, containing impurities having higher volatilization points than the metal, to distillation and oxidation on an open hearth, having a surface of a material which is not harmfully attacked by such impurities at temperatures used, and maintaining the temperature of the metal and hearth at a point above that

at which the metal volatilizes but below that at which the residual impurities in the metal will act harmfully upon the hearth material.

11. A process of producing a metallic oxide which comprises, providing an open hearth with a surface of a material which will form a comparatively high melting point slag with impurities in the metal to be treated, subjecting a readily oxidizable volatilizable metal to distillation and oxidation on such hearth, the metal containing impurities which will remain in the residue when the metal is volatilized, and maintaining the temperature of the metal and hearth at a point above that at which the metal volatilizes, but below the point at which slags formed by the residual impurities and the hearth surface material become markedly fluid.

12. The process of producing zinc oxide which comprises, placing a charge comprising metallic zinc on a solid hearth having open spaces above and below the same, conducting hot gases beneath and above the hearth, from a source or sources located away from the space beneath the hearth, to volatilize the zinc, the gases passing above the hearth containing air to oxidize the zinc vapors, and causing the removal of the zinc oxide vapors thus produced to a collecting system.

13. The process of producing zinc oxide which comprises, placing a charge comprising metallic zinc on a solid hearth having open spaces above and below the same, conducting hot gases beneath and above the hearth, from a source or sources located away from the space beneath the hearth, to volatilize the zinc, the gases passing above the hearth containing air to oxidize the zinc vapors, increasing the heat of the zinc oxide thus produced to a point desirable in the combustion chamber of a collecting system, and causing the removal of the vapors to such combustion chamber.

In testimony whereof I have signed my name to this specification, at Langeloth, Pa., on this 12th day of May, 1922.

HARRY A. GRINE.