

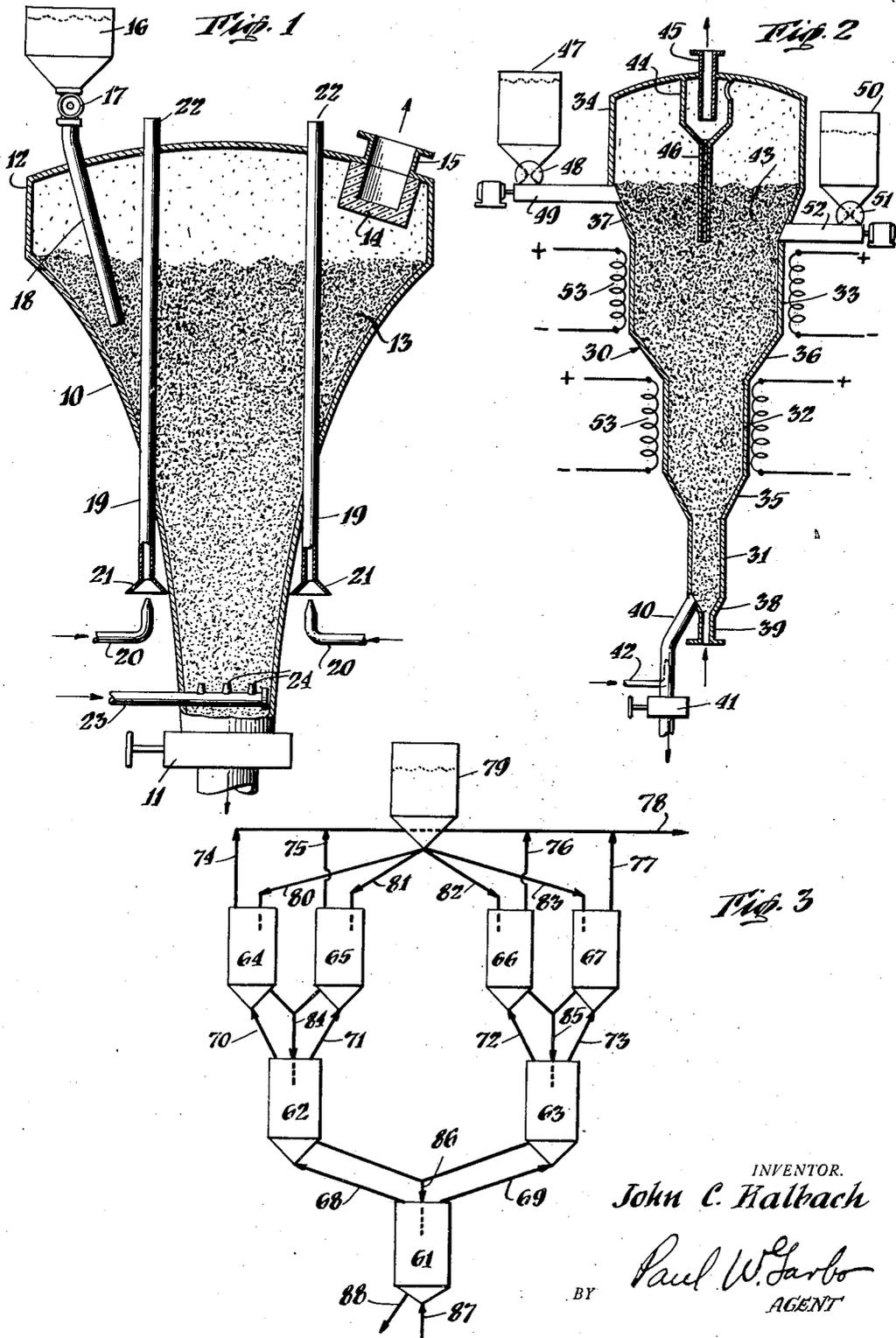
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FLUIDIZING PROCESS FOR PRODUCING ZINC

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FLUIDIZING PROCESS FOR PRODUCING ZINC

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10 Claims. (Cl. 75—26)

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This invention relates to a process for the recovery of zinc by the reduction of zinc compounds and, more particularly, to a process wherein the zinc compound undergoing reduction is maintained in a fluidized condition.

In the course of the long history of zinc metallurgy, there have been numerous proposals to treat finely divided zinc compounds with reducing agents in a continuous and rapid manner. A few patents of recent issue have even disclosed proposals for reducing compounds of metals in the right hand side of group II of the periodic system, which includes zinc, under fluidizing conditions. In spite of continued efforts to bring to light new methods for producing zinc, current commercial operations have remained basically unchanged from a technical viewpoint for two or three decades.

In the last few years the fluidizing technique has gained tremendous prestige because of its applications in the petroleum refining field and it is only natural that technical men have been quick to propose the application of this technique to problems in other fields. However, experience has shown that all problems are not amenable to the simple adoption of the fluidizing technique as practiced in the petroleum industry. The recent patents proposing the production of metals by processes involving fluidization fall within this category. Strangely enough, these proposals are from a practical viewpoint substantially inoperable because the disclosed processes fail to provide satisfactory fluidization during the reduction of the metal compound.

A principal object of this invention is to provide a simple but effective method for carrying out the reduction of zinc compounds under fluidizing conditions.

Another primary object is to maintain a substantially uniform condition of fluidization through all parts of the mass undergoing reduction as well as at all times over an extended period of operation.

A further object is to provide a fluidizing process for reducing zinc compounds which is characterized by the fact that the gaseous effluent from the reducing zone is relatively rich in zinc vapor; accordingly, the separation of the zinc vapor from the gaseous effluent by condensation is materially facilitated.

These and other objects of my invention will be apparent from the description which follows.

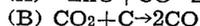
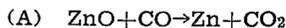
For the purposes of this invention, the term, zinc compound, embraces the oxide, hydroxide, silicate and carbonate of zinc since these zinc

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compounds are readily reduced to metallic zinc. Generally, however, the oxide form of zinc is charged to the reducing zone. The most prevalent type of mineral or ore contains zinc as a sulfide which is roasted to the oxide form prior to reduction for the recovery of metallic zinc. Typical of sulfide type ores is sphalerite, the sulfide of zinc. A lower grade ore or mineral is marmatite, a double sulfide of zinc and iron, which when found substantially free of richer zinc minerals is considered too lean in zinc for economic working by conventional processes of reduction. After roasting, these ores contain not only the oxides of zinc and iron but other natural occurring contaminants. The process of the present invention is well suited for the reduction of zinc compounds having such impurities associated therewith. It is understood that the minerals or ores which are to be treated for the recovery of zinc are usually concentrated by jigging, flotation, etc., but these ore concentrates in general still have an appreciable content of impurities.

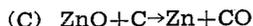
I have discovered that the maintenance of satisfactory fluidization in all parts of a mass of a comminuted zinc compound which is undergoing reduction is only possible when the operation is conducted with a bed of increasing horizontal cross-section, the smallest cross-section being at the bottom thereof. This seemingly simple specification, namely, that the reduction be conducted with a deep, upwardly flared bed, has a profound influence on operability of the entire fluidizing process. The important role of a tall, flared fluidizing zone or chamber for the reduction of zinc compounds is readily appreciated from a consideration of the principal phenomena taking place during the reduction.

Thus, for instance, if zinc oxide is reduced with gaseous carbon monoxide in the presence of solid carbon, the chemical reactions which take place may be represented by the following equations:



It is clear from these equations that (1) the reactions generate substantial volumes of gases and (2) carbon monoxide is continuously being consumed and reformed in cyclic fashion. In connection with the latter point, it is well to observe that in spite of the cyclic consumption and regeneration of carbon monoxide, the volume of carbon monoxide passing through the reducing zone increases steadily and exponentially during said passage, if the vessel is so shaped as to maintain a constant gas velocity throughout. There

is some evidence to believe that the reduction takes place by direct reaction between the solids as follows:



If this reaction mechanism accounts for part or all of the reduction, the same exponential increase in the volume of carbon monoxide and zinc vapor occurs; it will be noted that Equation C corresponds to the sum of Equations A and B.

Prior suggestions of fluidizing processes for the reduction of oxides of volatilizable metals have overlooked these impediments to good fluidization which depends on suspending the comminuted solids in an upwardly flowing gaseous stream having such a velocity that slippage or "hindered settling" of the solid particles is permitted. Examination of the foregoing equations further reveals that carbon monoxide is generated volume for volume of zinc vapor.

Because the process of my invention is carried out in a tall reducing vessel of upwardly increasing cross-section, I have found it possible to use such small quantities of gas as the fluidizing medium that the zinc vapor in the gases leaving the vessel approaches closely the concentration it would have according to theory, i. e., 50% by volume concentration based on the pure zinc oxide equivalent content of the material charged to the reducer. However, it is to be remembered that roasted or calcined ores and other forms of zinc compound frequently contain reducible compounds of iron and other metals which naturally decrease that concentration of zinc vapor in the gases leaving the reducing zone which is theoretically obtainable with the reduction of the pure zinc compound. In any event, through the use of a long flared reducer and the injection thereto of relatively minute quantity of gas to support fluidization, the gaseous effluent contains not less than 40% by volume, and preferably not less than 45% by volume, of zinc vapor, based on only the reaction gases deriving from the pure zinc oxide equivalent content of the material entering the reducing zone and the injected fluidizing gas.

By referring the concentration of zinc vapor in the gaseous effluent to the pure zinc oxide equivalent content of the material charged to the reducing zone, a common basis is provided for evaluating the effectiveness of the process of the invention with all sorts of materials that are suitable for reduction. To begin with, there are the pure zinc compounds, hereinbefore referred to:

Name	Formula	ZnO Equivalent
zinc oxide.....	ZnO.....	ZnO
zinc hydroxide.....	Zn(OH) ₂	ZnO·H ₂ O
zinc carbonate.....	ZnCO ₃	ZnO·CO ₂
zinc silicate.....	ZnSiO ₃	ZnO·SiO ₂

The above table shows that the hydroxide, carbonate and silicate of zinc have one equivalent content of zinc oxide. The hydroxide and carbonate of zinc will during reduction release water vapor and carbon dioxide, respectively, and will thus naturally decrease the concentration of zinc vapor in the gases leaving the reducer. Because the water vapor and carbon dioxide react with the solid reducing agent to produce a larger volume of gas (hydrogen and carbon monoxide) which further dilutes the zinc vapor, it is generally advisable to calcine the hydroxide and carbonate of zinc to eliminate the water and carbon dioxide, respectively, as a pretreatment step prior to reduction. Since the silica (SiO₂) of zinc sili-

cate is not volatilized like the water and carbon dioxide of the hydroxide and carbonate, there is no reason for first calcining zinc silicate other than to drive off physically associated moisture. Furthermore, as already mentioned, the zinc compounds are generally found in nature associated with impurities. When these impurities, for instance, the oxides of iron and lead, are reduced under the conditions selected for the reduction of the zinc compound, the gases leaving the reducing vessel will contain carbon monoxide resulting from the reduction of the impurities as well as the carbon monoxide resulting from the reduction of the zinc compound. Accordingly, reducible impurities associated with the zinc compound fed to the reducer cause a diminution of that concentration of zinc vapor in the effluent gases which is theoretically obtainable with the reduction of the pure zinc compound.

To achieve the purposes of my invention, it is advisable to operate with a fluidized mass of at least 5 foot depth, preferably 15 to 50 foot depth. The rate of increase of gas volume, and hence horizontal cross-section of vessel, with depth of bed depends upon the reactivity of the zinc compound and solid reducing agent used, the gas velocity maintained, the temperature of operation and the recovery of zinc metal is regarded as satisfactory (since the entire fluidized bed is of residue composition). This rate of increase may be conveniently expressed as the "gas doubling height," that is to say, that height of vessel within which the volume of gas passing therethrough is doubled. In practice, this height may vary from 1 to 20 feet but preferably falls in the range of 3 to 12 feet. It will be appreciated that the vessel height and the gas doubling height must in each case be correlated so that the gases leaving the reducer contain the zinc vapor in the high concentrations stipulated hereinabove. Another useful guide in properly correlating the vessel height and the gas doubling height is to provide a vessel of such height that the gaseous effluent is at least 8 times, and preferably at least 12 times, the volume of the fluidizing medium charged at the bottom of the vessel.

The comminuted zinc compound, notably impure zinc oxide obtained by roasting a sulfide type of zinc ore, is generally supplied to the reducing zone in the form of particles all of which pass through a 60-mesh screen and 20% to 40% of which pass through a 325-mesh screen. The carbon or solid reducing agent, such as coal, charcoal or coke, is usually supplied to the reducer in the form of particles somewhat coarser than the zinc compound particles because of the lower specific density of carbon and consequent tendency of these carbon particles to become fluidized at a gas velocity which will fluidize the finer but denser particles of zinc compound. The average gas velocity through the reducing zone will usually be in the range of about 0.2 to 2.0 feet per second, preferably about 0.4 to 1.5 feet per second. However, all of the foregoing factors may have values larger or smaller than the indicated advantageous ranges, as will be obvious to those skilled in the art.

Satisfactory temperatures for reducing zinc compounds by the process of this invention fall in the range of 1600° to 2300° F., preferably in the range of 1800° to 2000° F.

To facilitate understanding of the invention, reference is now had to the drawings accompanying this specification and forming a part thereof, of which:

Figure 1 is a schematic sectional elevation of one form of reducing vessel in which the invention may be carried out;

Figure 2 is a similar view of another form of reactor suitable for the operation of the invention; and

Figure 3 is a diagrammatic representation of a plurality of vessels arranged in a manner to permit the conduct of the process of this invention.

Referring to Figure 1, a deep, flared vessel 10 is provided at its base with a slide valve 11 which serves to control the discharge of reacted solids from the vessel. The upper end of vessel 10 is in the form of a cylindrical section 12 wherein the reaction gases emerging from the fluidized mass 13 tend to become disengaged from the bulk of entrained particles and pass through filter element 14 which eliminates residual particles from the gases leaving vessel 10 by way of outlet 15. A feed hopper 16 with a rotary bucket-type valve 17 serves to introduce a comminuted mixture of zinc compound and carbon to the reducing zone by way of standpipe 18. A plurality of fire-tubes 19, uniformly distributed around the vessel 10 and passing therethrough to supply heat to the fluidized mass 13 undergoing reduction, are charged with a fluid fuel such as natural gas or fuel oil through injectors 20 which cooperate with Venturi-like openings 21 for the aspiration of air to support combustion within the tubes 19. The combustion or flue gases leave these tubes through the upper ends 22, discharging into the atmosphere or a suitable stack. At the lower end of vessel 10 and above slide valve 11, an inlet pipe 23 provided with nozzles 24 is used for the introduction of a relatively small quantity of a fluidizing gas such as carbon monoxide, carbon dioxide or nitrogen; this small gas stream not only maintains fluidization in the bottom of vessel 10 but also facilitates the removal of reacted solids from the vessel through valve 11.

In Figure 2, the reducing vessel 30 comprises a plurality of cylindrical sections 31, 32, 33 and 34 of increasing diameter connected by frusto-conical sections 35, 36 and 37. The lowermost cylindrical section 31 terminates in a tapered section 38 connecting with inlet pipe 39 for the introduction of a small stream of fluidizing gas. Attached to the tapered section 38 is a draw-off pipe 40 for the withdrawal of reacted solids from vessel 30. Slide valve 41 is used to control this withdrawal and tube 42 above valve 41 is used to introduce a small quantity of gas to ensure the free flow of solids discharging through pipe 40. The uppermost cylindrical section 34 of vessel 30 provides the disengaging space wherein most of the entrained particles tend to settle out from the reaction gases leaving the fluidized mass 43. The gases then proceed through cyclone separator 44 disposed within section 34 to be further separated from suspended particles. Substantially dust-free gases leave the reducing vessel 30 through outlet pipe 45 and solids removed from these gases within separator 44 drop back into the fluidized mass 43 by way of standpipe 46. Finely divided carbon is charged to the reducing vessel 30 from hopper 47 by means of rotary valve 48 and screw conveyor 49. Similarly finely divided zinc compound is fed from hopper 50 by valve 51 and screw conveyor 52. In this instance, the necessary heat for the reduction of the zinc compound is furnished by electrical resistance heaters 53.

Figure 3 shows an arrangement of seven ves-

sels 61, 62, 63, 64, 65, 66 and 67 whereby the reaction gases from vessel 61 pass by lines 68 and 69 to vessels 62 and 63, respectively, and the gases from these vessels flow by way of lines 70, 71, 72 and 73 into vessels 64, 65, 66 and 67 and finally discharge therefrom through lines 74, 75, 76 and 77 into a common outlet line 78. Flowing as a fluidized mass in countercurrent relation to these gases is a mixture of comminuted carbon and zinc compound charged from hopper 79 through lines 80, 81, 82 and 83 into vessels 64, 65, 66 and 67, respectively, the solids moving from these vessels to vessels 62 and 63 through branched lines 84 and 85 and thence to vessel 61 through branched line 86. A relatively small quantity of fluidizing gas enters the reaction system through line 87 and reacted solids are withdrawn through line 88. The lines connecting the several vessels are provided with conventional valves or equivalent control means to establish the described flows of solids and gases. Heat for the endothermic reduction is supplied through heating tubes, electric arcs or like means. It is thus seen that the fluidized mass of zinc compound undergoing reduction may be disposed in a plurality of chambers or reactors to achieve the upwardly increasing cross-section of the mass as taught by this invention. Expressions like "a bed of increasing horizontal cross-section in the upward direction," as used in the appended claims, are intended to include beds which are divided into a plurality of sections as shown in Figure 3.

A specific example of the process of the invention will be given in terms of a reactor of the type shown in Figure 1. The vessel 10 is 2.3 feet in diameter at the point where carbon monoxide is fed through line 23 and is 9.3 feet in diameter at the upper surface of the fluidized mass 13 which is 34 feet in depth. Fifty-six fire-tubes 19 of 4-inch diameter are uniformly spaced around the axis of vessel 10 in a four-ring arrangement. Natural gas is burned with air within tubes 19 to maintain the fluidized mass 13 at a reaction temperature of 1840° F. A mixture of impure zinc oxide (weight analysis of ZnO 78.5%, ZnS 1.5%, ZnSO₄ 2.2%, Fe₂O₃ 10.0%, PbO 2.8% and the remainder comprising the oxides of copper, cadmium, manganese, magnesium, calcium and silicon) and coke in the proportions of 3 lbs. of impure zinc oxide per lb. of coke and in the form of a powder passing through a 60-mesh screen (40% thereof passing through a 325-mesh screen) enters the reducing zone by way of pipe 18 at the rate of 4295 lbs. per hour. Under the selected reaction conditions and with the increase of horizontal cross-section in vessel 10, an average gas velocity of about 0.5 foot per second is established with the introduction of 1600 cubic feet (standard conditions) per hour of carbon monoxide through pipe 23. The reaction gases discharging from pipe 15 contain 42% by volume of zinc vapor (46.7% by volume of zinc vapor, based on only the reaction gases deriving from the pure zinc oxide equivalent content of the material charged to the reactor and the gas supplied by pipe 23) which is recovered by conventional condensation, the recovery amounting to 2000 lbs. of zinc per hour. Spent or reacted solids are discharged from vessel 10 through slide valve 11 at the rate of 1160 lbs. per hour. Through the combination of the foregoing factors, the mass 13 is maintained in a uniformly well fluidized state ensuring the facile flow of heat from tubes 19 to all parts of the reacting

mass 13 and the effluent gases are rich in zinc vapor thus facilitating the separation of zinc from the uncondensable gases, predominantly carbon monoxide.

At times it may be advantageous to use a comparatively low gas velocity, say 0.5 foot per second, through the lower part of the reactor in order to permit the zinc concentration to build up in the gaseous product stream but to have the gas velocity in the upper part of the fluidized bed somewhat higher, say 1 foot per second, in order to obtain maximum capacity per unit of horizontal cross-section. This may be done without departure from the spirit of this invention by modification of the curvature of the whole vessel or by designing a vessel in which about one half of the total gaseous effluent is generated in the flared section and the remainder is generated in a straight cylindrical section superimposed upon the flared section. Such a vessel would have the appearance, for instance, of that of Figure 1 except that the cylindrical section 12 would be taller and the fluidized mass would extend partly therewith. Thus, for instance, a vessel to answer the same purpose and to have the same capacity as the one described in the foregoing example would have a lower flared section increasing from a diameter of 2.3 feet to a diameter of 6.6 feet in a vertical rise of 26 feet and an upper cylindrical section (6.6 feet in diameter) of sufficient height to permit the fluidized mass to extend 14 feet up in the bottom portion thereof. The overall depth of the fluidized bed would therefore be 40 feet, approximately one half of the gaseous products being formed in the flared section and the remainder in the contiguous upper straight section.

Those skilled in the art will visualize many variations of the invention without departing from its spirit or intent. For instance, the fire-tubes 19 of the reactor of Figure 1 may be bowed or set in obliquely to get more heat exchange surface in contact with the fluidized mass. Also, the reducible compounds of other metals such as cadmium, usually occurring in small proportions with the zinc compounds, may be simultaneously reduced and their metal vapors recovered along with the zinc vapor.

As is known, one of the liquid-like properties of a fluidized mass or bed is its fluidstatic pressure corresponding to a liquid's hydrostatic pressure. It will therefore be appreciated that the gases and vapors ascending through a fluidized bed are exposed to a diminishing fluidstatic pressure (the product of the depth and density of the fluidized bed). The varying pressure alters somewhat the exponential increase in the gaseous volume herebefore described as occurring during the reduction of zinc oxide. In most cases that will be encountered in practice, deviations from truly exponential volume increases, attributable to such varying pressures, will be less than about 20%. If desired, the flare of the reducing vessel may be designed to compensate for deviations from a truly exponential increase of the gas volume.

The foregoing disclosure should be interpreted as being illustrative of the invention and not restrictive; only such limitations should be imposed as are indicated in the appended claims.

What I claim is:

1. In the production of zinc by the fluidizing process involving the reduction of a solid inorganic oxygen-containing compound of zinc by a solid carbonaceous reducing agent, both said solids being in comminuted form, wherein a gaseous stream containing the zinc vapor generated by

said reduction is withdrawn from the zone of reduction, the improvement of producing said gaseous stream with a high concentration of zinc vapor, which comprises effecting said reduction while fluidizing the reacting solids disposed as a bed of about 15 to 50 feet in height and of increasing horizontal cross-section in the upward direction, charging a fluidizing medium at the bottom of said bed to support fluidization therein, maintaining the rate of said reduction such that the volume of the gaseous stream flowing up through said bed doubles with an increment of bed height in the range of about 1 to 20 feet, and withdrawing from said bed said gaseous stream when it has attained a volume at least 8 times the volume of said fluidizing medium charged at the bottom of said bed.

2. The process of claim 1 wherein the solid inorganic oxygen-containing compound of zinc is essentially zinc oxide.

3. The process of claim 2 wherein the fluidizing medium is essentially carbon monoxide.

4. The process of claim 1 wherein the withdrawn gaseous stream contains at least about 40% by volume of zinc vapor, based on only said fluidizing medium and the reaction gases deriving from the pure zinc oxide equivalent content of said inorganic oxygen-containing compound of zinc.

5. In the production of zinc by the fluidizing process involving the reduction of a solid inorganic oxygen-containing compound of zinc by a solid carbonaceous reducing agent, both said solids being in comminuted form, wherein a gaseous stream containing the zinc vapor generated by said reduction is withdrawn from the zone of reduction, the improvement of producing said gaseous stream with a high concentration of zinc vapor, which comprises effecting said reduction while fluidizing the reacting solids disposed as a bed of about 15 to 50 feet in height and of increasing horizontal cross-section in the upward direction, charging a fluidizing medium at the bottom of said bed to support fluidization therein, maintaining the rate of said reduction such that the volume of the gaseous stream flowing up through said bed doubles with an increment of bed height in the range of about 1 to 20 feet, and withdrawing from said bed said gaseous stream when it has attained a volume at least 12 times the volume of said fluidizing medium charged at the bottom of said bed.

6. The process of claim 5 wherein the solid inorganic oxygen-containing compound of zinc is essentially zinc oxide.

7. The process of claim 6 wherein the fluidizing medium is essentially carbon monoxide.

8. The process of claim 5 wherein the withdrawn gaseous stream contains at least about 45% by volume of zinc vapor, based on only said fluidizing medium and the reaction gases deriving from the pure zinc oxide equivalent content of said inorganic oxygen-containing compound of zinc.

9. The improved process of treating a comminuted solid material containing zinc oxide for the recovery of zinc, which comprises introducing said comminuted material and comminuted coke as reducing agent into a fluidized bed of said comminuted solids having a height of about 15 to 50 feet and an increasing horizontal cross-section in the upward direction, charging a fluidizing medium at the bottom of said bed to support fluidization therein, effecting reduction of

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zinc oxide in said bed at a rate which doubles the volume of the gaseous stream flowing up through said bed with an increment of bed height in the range of about 3 to 12 feet, and withdrawing from said bed said gaseous stream when it has attained a volume at least 8 times the volume of said fluidizing medium charged at the bottom of said bed, the thus withdrawn gaseous stream containing at least about 40% by volume of zinc vapor, based on only said fluidizing medium and the reaction gases deriving from the pure zinc oxide equivalent content of said comminuted material.

10. The process of claim 9 wherein the reduc-

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tion of zinc oxide is effected at a temperature in the range of 1800° to 2000° F.

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