July 10, 1951 J. C. KALBACH 2,560,175

FLUIDIZING REDUCTION OF ZINC COMPOUNDS WITH STAGEWISE FEEDING OF SOLIDS

Filed May 12, 1948

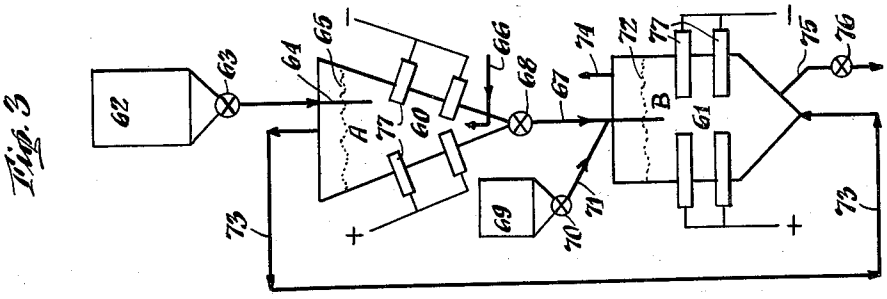

Fig. 3

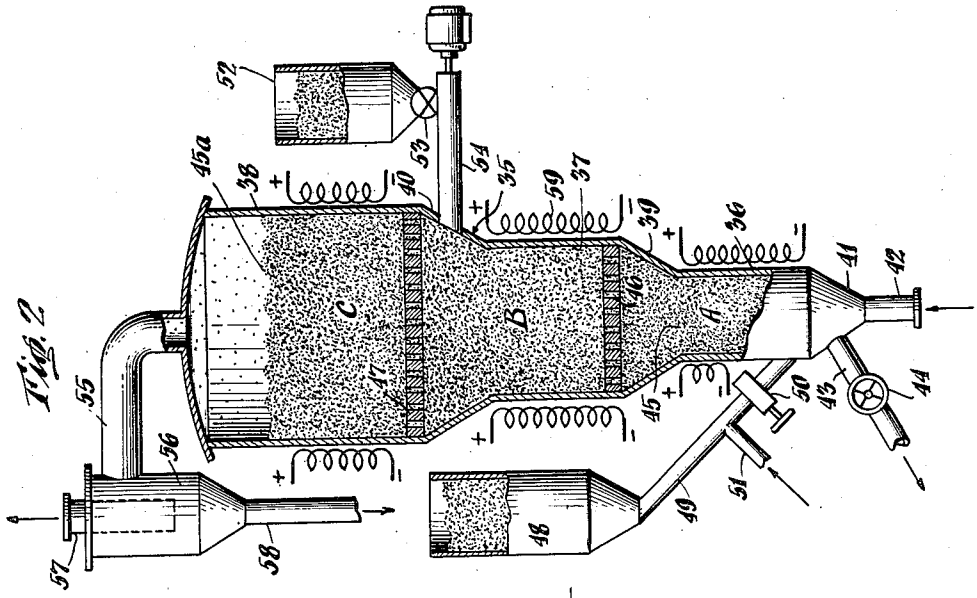

Fig. 2

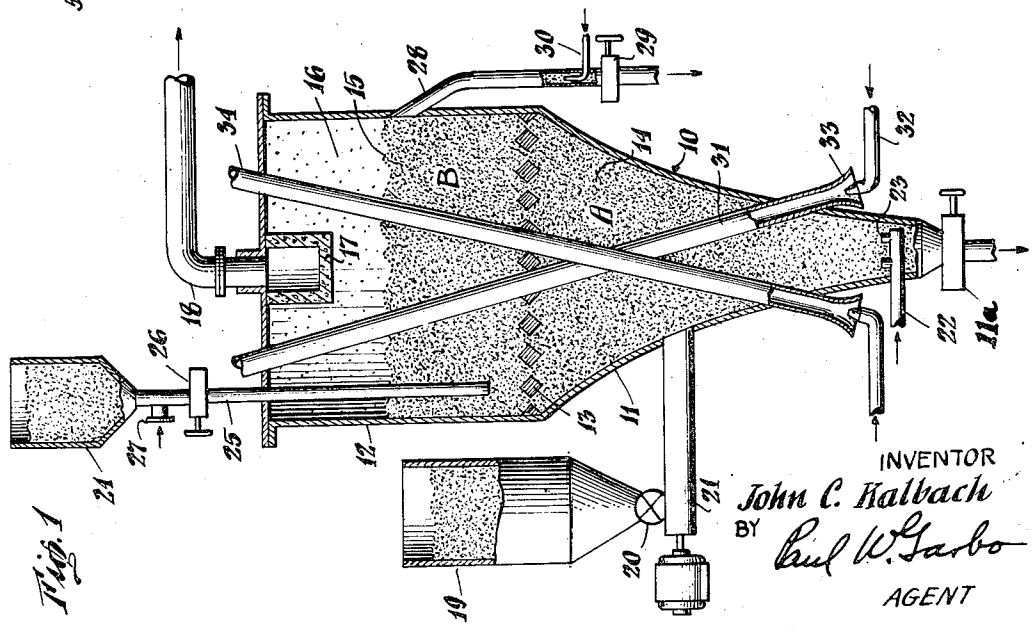

Fig. 1

INVENTOR

John C. Kalbach

BY Paul W. Garbo

AGENT

Patented July 10, 1951 2,560,175

UNITED STATES PATENT OFFICE

2,560,175

FLUIDIZING REDUCTION OF ZINC COMPOUNDS WITH STAGEWISE FEEDING OF SOLIDS

John C. Kalbach, New York, N. Y., assignor to The American Metal Company, Limited, New York, N. Y., a corporation of New York

Application May 12, 1948, Serial No. 26,484

9 Claims. (Cl. 75—26)

1

This application is a continuation-in-part of the copending application Serial No. 759,545, filed July 8, 1947, now U. S. Patent 2,485,604, wherein I have disclosed a process for producing zinc by reducing comminuted zinc compounds, such as the oxide and the silicate of zinc, under fluidizing conditions and in a manner such that the gaseous effluent from the reducing zone is rich in zinc vapor. This application is also a continuation-in-part of the copending application Serial No. 767,548, filed August 8, 1947, which is directed to a stagewise fluidizing process for the reduction of zinc compounds.

The present invention is in the nature of an improvement of the processes of copending applications Serial Nos. 759,545 and 767,548.

A primary object of this invention is to conduct the fluidized reduction of zinc compounds with a minimum inventory of solids in the reaction zone. A corollary object is to use apparatus of decreased size in effecting the reduction of zinc compounds by the fluidizing technique.

Another important object is to ensure good fluidization throughout the reduction of zinc compounds notwithstanding any inherent tendencies of these compounds to agglomerate in the course of reduction.

Still another object is to curtail the proportion of carbon dioxide in the gaseous effluent flowing from the fluidized reducing zone to the condensers employed for the recovery of the zinc contained in the gaseous effluent.

A further object is to conduct the fluidized reduction of zinc compounds under conditions which prolong the life of the reducing apparatus.

Additional objects and advantages of my invention will become evident 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 compounds are readily reduced to metallic zinc. It will be noted that all of the foregoing zinc compounds are solid inorganic oxygen-containing compounds of zinc. Generally, 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 mineral is considered too lean in zinc for economic

2

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. Some of these impurities like iron promote agglomeration of the particles in the fluidized mass as the particles become depleted in zinc in the course of the reduction. Agglomeration is undesirable because it interferes with good fluidization and decreases the reactivity of the solid particles.

Copending application Serial No. 759,545 sets forth in detail the advantages of conducting the fluidized reduction of a comminuted zinc compound in a bed of increasing horizontal cross-section, the smallest cross-section being at the bottom of the bed. The use of a tall, flared fluidizing zone or chamber to hold the bed of increasing horizontal cross-section makes it possible to introduce such small quantities of gas as the fluidizing medium that the gaseous stream leaving the chamber is rich in zinc vapor. Furthermore, an upwardly flared reduction zone permits the maintenance of a substantially uniform gas velocity therethrough in spite of the exponential increase of the volume of gas with the evolution of zinc vapor and carbon oxides in the reduction of the zinc compound. Those skilled in the art will appreciate that the recovery of molten zinc from a gaseous stream rich in zinc vapor is materially facilitated since there is less tendency to form blue powder.

Copending application Serial No. 767,548 points out that the reduction of zinc compounds under fluidizing conditions is advantageously carried out in a series of stages through which the solids and the fluidizing and reaction gases pass concurrently. In accordance with the teachings of the earlier filed application, the preferred embodiment of the process of application Serial No. 767,548 involves a first reducing stage in which the fluidized mass is of increasing horizontal cross-section in the direction of the gaseous flow therethrough.

In the processes of my copending applications, the comminuted zinc compound is charged into the reducing zone along with a comminuted reducing agent selected from the class of carbonaceous solid fuels like coal, coke, lignite and char-

coal. The ratio of the weights of reducing agent and zinc compound fed to the reducing zone is set to provide sufficient carbon for the reduction in accordance with the reaction:

(A) $ZnO+C \rightarrow Zn+CO$

However, since the zinc compound usually contains impurities which foster agglomeration of the particles undergoing reduction, the weight ratio of reducing agent to zinc compound is increased from that value indicated by the reaction to that value which will sustain satisfactory fluidization through dilution of the sticky or agglomerating ore particles with nonagglomerating carbonaceous particles. It is thus seen that the weight ratio is in most cases set at a high value to ensure satisfactory fluidization in spite of the agglomerating propensity of the zinc compound undergoing reduction. Furthermore, the reduction of zinc compounds involves the reversible reaction:

(B) $ZnO+CO=Zn+CO_2$

and it is obviously advantageous to suppress the presence of carbon dioxide in the reaction gases through the producer gas reaction:

(C) $CO_2+C \rightarrow 2\,CO$

For this additional reason, the weight ratio of carbonaceous reducing agent to zinc compound is generally made high to provide excess carbon and thus minimize the presence of carbon dioxide in the gaseous effluent leaving the reducing zone. A high weight ratio means that the inventory of solids in the reducing zone is larger than is stoichiometrically required. A large solids inventory, in turn, means large apparatus and large heat losses. I have now found a way to decrease the solids inventory without encountering any of the difficulties which are avoided by resorting to a higher weight ratio of carbonaceous reducing agent to zinc compound than is dictated by stoichiometry.

In accordance with this invention the fluidized reduction of a zinc compound is carried out in at least two stages arranged for the concurrent flow of solids and fluidizing and reaction gases from the first stage to the last. A distinguishing feature of the process of the invention is the introduction of a finely divided nonagglomerating solid, which may be inert like burnt dolomite or sand or reactive like coke, into the fluidized mass beyond the first stage in a reducing stage where the agglomerating tendency of the zinc compound undergoing reduction becomes appreciable or where a solid carbonaceous reducing agent is needed to complete the reduction of the zinc compound. If both the agglomerating tendency has to be corrected and the need for additional solid reducing agent satisfied in a reducing stage subsequent to the first, a finely divided carbonaceous fuel like coke can be used in a dual capacity. Furthermore, a carbonaceous fuel added to the fluidized mass in a reducing stage subsequent to the first serves to decrease the presence of carbon dioxide in the gaseous effluent flowing to the zinc condensers.

To permit the withdrawal of a gaseous effluent rich in zinc vapor from the last stage of reduction, the first stage is made the smallest in horizontal cross-section so that a relatively small quantity of fluidizing medium, say carbon monoxide, injected thereinto can support fluidization; preferably, the first stage is of increasing horizontal cross-section in the direction of the gaseous flow therethrough. While the subsequent stages of reduction are as large or larger in horizontal cross-section than the uppermost horizontal cross-section of the first stage, in general they necessitate relatively slight upward flaring of the fluidized mass which they hold and often they are substantially uniform in horizontal cross-section. For example, a two-stage reducer may have a first stage wherein the horizontal cross-section increases 16-fold from bottom to top and the second stage has an invariant horizontal cross-section equal to the uppermost section of the first stage. In another illustration, a three-stage reducing operation may involve a first stage with a 14-fold increase in horizontal cross-section in the upward direction, a second stage of relatively slight upward flaring such that the overall increase in horizontal cross-section from the bottom of the first stage to the top of the second stage is about 17-fold, and a third stage of the same horizontal cross-section as the uppermost section of the second stage.

It is advisable to effect reduction and vaporization of at least 60% of the zinc in the compound charged into the first reducing stage and to effect a decreasing percentage of the overall reduction in each succeeding stage. I have found that optimum results are obtained by proportioning and regulating the several stages of the reduction, two or three stages sufficing in most cases, so that the conversion or percentage of reaction effected with the solids entering each reducing stage is approximately constant for all the stages. For instance, if it is desired to recover about 98.5% of the available zinc in a roasted ore of the zinc sulfide type in a three-stage reduction, optimum staging is attained when a conversion of about 75% is effected in each stage, i. e., the first stage reduces about 75% of the zinc content of the charged material, the second stage then reduces about 75% of the residual zinc content (25% of that originally available) and the third stage reduces about 75% of the available zinc in the solids passing from the second to the third stage. Thus, of the available zinc in the roasted ore, 75% is reduced in the first stage, 19% in the second and 4.5% in the third, giving an overall recovery of 98.5% for the three-stage process.

The advantages of stagewise operation are still realized to a somewhat lesser extent when the conversions for the several stages differ among themselves within reasonable limits. From experience I have determined that it is desirable to limit the deviations in conversion in the several stages to 10% of the constant value which, as hereinbefore stated, gives optimum results. Thus, for optimum operation of a two-stage reducer to recover 99% of the zinc content of the charged ore, a conversion of 90% is effected in each of the two stages, while good results are still obtained if, for example, the first-stage conversion is 85% (deviation of 5.6%) and the second-stage conversion is 93.3% (deviation of 3.7%). As is frequently the case with a two-stage operation, when the agglomerating tendency of the ore is so great as to prevent design for minimum reactor size according to the criterion of equal conversions in the stages and at the same time the use of a low ratio of carbon to ore, the best compromise is in the direction of a departure from equal stage conversions as illustrated by the immediately preceding example of a two-stage process.

As used in this specification and the appended

claims, the term, stage, means a division of the reducing operation or the apparatus in which reduction is performed, there being two or more such divisions in series arranged for the concurrent progress or movement of reaction solids and gases therethrough. It will be understood that any stage of reduction may be carried out in a portion of a reducer, a separate reducer or a plurality of vessels interconnected to function effectively as a single reducer. A plurality of vessels will function as a single zone or vessel when they are arranged in parallel and have equal hold-up times.

In accordance with the preferred practice of this invention, the zinc compound is fed to the first reducing stage with only about one-half of the proportion of carbon ultimately required in the last reducing stage. The volume of solids in the first reducing stage is thus made comparatively small since the excess carbon required to drive the reducing reaction to the desired degree of completion and the diluting solids (which may also be carbon) required to minimize agglomeration are not passed through the first reducing stage but are introduced into a subsequent stage. As previously stated, a solid carbonaceous fuel in comminuted form may be charged to the subsequent stage, say the second and/or third stage, to satisfy both requirements.

For the first stage of reduction, I prefer to maintain the fluidized solids as a deep bed of upwardly increasing horizontal cross-section because I am then able to use such small quantities of gas as the fluidizing medium that the zinc vapor in the gases discharged by the process 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 compounds 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 tall, flared reducer and the injection thereinto of a 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 injected fluidizing gas and the reaction gases deriving from the pure zinc oxide equivalent content of the material entering the reducing zone.

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	$Zn(OH)_2$	$ZnO \cdot H_2O$.
zinc carbonate	$ZnCO_3$	$ZnO \cdot CO_2$.
zinc silicate	$ZnSiO_3$	$ZnO \cdot SiO_2$.

The preceding 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 (SiO_2) of zinc silicate 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.

For the preferred embodiment of my stagewise reduction process involving a first stage of increasing horizontal cross-section, it is advisable to operate in the first stage with a fluidized mass of at least 5 foot depth; preferably, the depth is of the order of 10 to 40 feet.

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 which is regarded as satisfactory for each stage (since the fluidized mass of each stage is of residue composition for that stage). This rate of increase may be conveniently expressed as the "gas doubling height," that is to say, that height of bed within which the volume of gas passing therethrough is doubled. In practice, the gas doubling height may vary from about 1 to 20 feet but preferably falls in the range of about 3 to 12 feet.

It will be appreciated that the overall depth of bed in the several stages of a given reduction process and the gas doubling height must in each case be correlated so that the gases discharged by the process contain the zinc vapor in the high concentration stipulated hereinabove.

Another useful guide in properly correlating the overall bed depth for a stagewise operation and the gas doubling height is to provide such a total bed depth that the gaseous effluent from the last stage is at least 8 times, and preferably at least 12 times, the volume of the fluidizing medium charged at the bottom of the first stage.

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 1750° to 1950° F.

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

Figure 1 is a schematic sectional elevation of one form of reducing apparatus in which a two-stage reduction may be carried out;

Figure 2 is a similar view of a three-stage reducer suitable for the process of this invention; and

Figure 3 is a diagrammatic representation of two vessels arranged for a two-stage operation conducted in accordance with the principles of this invention.

Referring to Figure 1, a reducing vessel 10 is provided with a lower flared section 11 and an upper straight section 12 communicating with lower section 11 through the openings in a grill 13. The fluidized mass 14 disposed in the contiguous sections 11 and 12 has an upper pseudo-liquid level 15 defining the region where the reaction gases emerge from the fluidized mass and flow through space 16 wherein the bulk of entrained particles tend to become disengaged from the reaction gases. The filter element 17 serves to eliminate residual particles from the gases leaving the reducer 10 by way of outlet 18. In effect, the grill 13 divides the fluidized mass 14 into a lower portion A wherein the first stage of reduction is carried out and an upper portion B wherein the second stage of the reduction is performed. A feed hopper 19 with a rotary bucket-type valve 20 serves to introduce a comminuted mixture of zinc compound and carbon to the first reducing section or stage 11 by way of screw conveyor 21. At the lower end of section 11 an inlet pipe 22 provided with nozzles 23 is used for the introduction of a relatively small quantity of a fluidizing gas such as carbon monoxide, carbon dioxide or nitrogen.

Because of the restricted openings in grill 13, the fluidized solids in flared section 11 move into the contiguous section 12 with little or no tendency of the solids in section 12 to flow back into section 11. Additional reducing and/or inert solids are fed from hopper 24 through standpipe 25 into the second stage 12 to drive the reducing reaction toward completion and/or to ensure good fluidization in spite of any agglomerating tendency of the reacting solids in this stage. The flow of solids through pipe 25 is regulated by slide valve 26 and is facilitated by injecting an aeration gas, say carbon monoxide or air, into pipe 25 by way of tap 27. The reacted solids are withdrawn from section 12 or the second stage of the reducer through draw-off pipe 28. A slide valve 29 is used to control this withdrawal and tube 30 above valve 29 is used to introduce a small quantity of gas such as carbon monoxide to ensure the free flow of solids discharging through pipe 28.

The reducer 10 has a plurality of fire-tubes 31 set obliquely through the fluidized mass in sections 11 and 12 to supply the heat required for the reduction of the zinc compound. A fluid fuel such as natural gas or fuel oil is charged through injectors 32 which cooperate with Venturi-like openings 33 for the aspiration of air to support combustion within the tubes 31. The combustion or flue gases leave these tubes through the upper ends 34, discharging into the atmosphere or a suitable stack.

The lower end of reducing vessel 10 has a slide valve 11*a* which may be used to withdraw the solids from the vessel to permit cleaning or repairing of the apparatus. Valve 11*a* may also be used during the operation of the reducing vessel for the periodic or continuous withdrawal of such coarse particles which may accidentally enter section 11 or be formed therein by agglomeration that they settle out of the fluidized mass and accumulate at the bottom of vessel 10. By withdrawing these coarse particles which drop to the bottom of the vessel, their accumulation to the point at which fluidization within section 11 would be impaired is thus avoided.

In Figure 2, the reducer 35 comprises a plurality of cylindrical sections 36, 37 and 38 of increasing diameters connected by frusto-conical sections 39 and 40. The lowermost cylindrical section 36 terminates in a tapered section 41 connecting with inlet pipe 42 for the introduction of a small stream of fluidizing gas. Attached to the tapered section 41 is a draw-off pipe 43 having valve 44 for the withdrawal of solids as hereinbefore discussed in connection with valve 11*a* of Figure 1. The fluidized mass 45 having an upper pseudo-liquid level 45*a* is divided by perforated plates 46 and 47 into a lowermost portion A to serve as the first stage of the reduction, a middle portion B for the second stage, and an uppermost portion C for the third stage of the reduction. The perforations in plates 46 and 47 permit the flow of reaction gases and fluidized solids from the first stage to the third stage of reducer 35 and prevent the solids of the fluidized mass from dropping back from one stage to a lower stage. Accordingly, the reaction gases and fluidized solids move concurrently from the first stage to the last stage of the reducer 35. Hopper 48 is used for charging a mixture of finely divided zinc compound and carbon or like reducing agent into the first stage of the reducer 35. Hopper 48 discharges into portion A of the fluidized mass through standpipe 49 and slide valve 50. A connection 51 is used to introduce a small quantity of gas, say carbon monoxide or air, to keep the solids in line 49 in a free-flowing condition. A further addition of powdered solids like sand or coke is made from hopper 52 by way of rotary bucket-type valve 53 and screw conveyor 54 which discharges into the second reducing stage. The reacted solids are conveyed by entrainment in the reaction gases leaving reducer 35 by way of outlet pipe 55. The reaction gases and suspended particles enter cyclone separator 56 wherein the gases and solids are separated, the gases leaving by way of outlet 57 and the solids flowing out of standpipe 58. The reaction gases emerging from outlet 57 pass to suitable condensers or equivalent means for separating the

zinc vapor from the remainder of the gaseous effluent issuing from outlet 57. In this instance, the necessary heat for the reduction of the zinc compound is furnished by electrical resistance heaters 59.

Figure 3 presents an arrangement of reducing equipment comprising a tapered vessel 60 and a cylindrical vessel 61. Vessel 60 holds portion A of the fluidized mass in which the first stage of reduction is effected and vessel 61 holds portion B of the fluidized mass for the second stage of the reduction. A mixture of zinc compound and solid reducing agent in powdered form flows from hopper 62 through rotary-type valve 63 into standpipe 64 discharging below the pseudo-liquid level 65 of portion A of the fluidized mass. A limited quantity of fluidizing gas is introduced into the bottom of tapered vessel 60 by way of line 66. The reaction gases from the first stage of reduction pass through line 73 into vessel 61 wherein the second stage of the reduction is carried out. The final reaction gases including zinc vapor are withdrawn from vessel 61 by way of outlet pipe 74 and conducted to a condenser for the recovery of molten zinc. The partially reacted solids flow from vessel 60 through standpipe 67, controlled by a valve 68, and discharge below the pseudo-liquid level 72 of portion B of the fluidized mass within vessel 61. The reacted solids leave the second stage of the reducing equipment through line 75 and control valve 76. The arrangement of reducing equipment shown in Figure 3 is advantageously used where the zinc compound to be reduced is in the form of a material which has a considerable tendency to agglomerate during reduction. In such a case, the agglomerates will readily pass with the fluidized mass from vessel 60 or the first stage of reduction to vessel 61 or the second stage of the reduction and the residue of the operation can be easily withdrawn through line 75 at the bottom of vessel 61. As shown, the apparatus of Figure 3 is provided with electric arcs 77 which supply heat to the fluidized reaction mass in vessels 60 and 61.

Specific examples of the stagewise reduction process of this invention are given in the following table in terms of a reactor of the type shown in Figure 1. The coke to ore ratios shown in the table for the first stage are based on the ore fed to the first stage and the coke fed to the first stage; the ratios for the second stage are based on the ore fed to the first stage and the total coke fed to both stages.

Table

	Control Run X	Example Run 1	Example Run 2	Control Run Y	Example Run 3
Roasted Ore (weight analysis):					
ZnO, percent	78.3	78.3	78.3	81.0	81.0
ZnS, do	0.1	0.1	0.1	0.3	0.3
$ZnSO_4$, do	2.4	2.4	2.4	3.6	3.6
Fe_2O_3, do	11.3	11.3	11.3	4.1	4.1
PbO, do	1.9	1.9	1.9	1.5	1.5
Other Components, do	6.0	6.0	6.0	9.5	9.5
Reactor Diameters:					
At Line 22, feet	3.0	3.2	3.0	3.1	3.2
At Grill 13, do	9.1	9.7	9.1	9.0	9.7
Height of Fluidized Mass:					
Portion A, do	17.0	6.3	17.0	15.7	9.4
Portion B, do	7.0	9.6	7.0	6.5	6.5
Total, do	24.0	15.9	24.0	22.2	15.9
Volume of Fluidized Mass:					
Portion A, cu. ft.	478	177	478	434	267
Portion B, cu. ft.	397	547	397	355	355
Total, cu. ft.	875	724	875	789	622
Temperature of Mass:					
Portion A, °F.	1,850	1,850	1,790	1,850	1,850
Portion B, °F.	1,850	1,850	1,850	1,850	1,850
Roasted Ore Fed to:					
Portion A, lb./hr.	3,140	3,140	3,140	3,030	3,030
Coke Fed to:					
Portion A, lb./hr.	1,570	785	785	1,515	758
Portion B, lb./hr.	0	785	785	0	757
Coke to Ore Ratio:					
Portion A	1:2	1:4	1:4	1:2	1:4
Portion B	1:2	1:2	1:2	1:2	1:2
Fluidizing Gas (CO) Fed by Line 22, std. cu. ft./hr.	3,980	3,980	3,980	4,200	4,200
Reacted Solids Withdrawn from Portion B, lb./hr.	1,262	1,262	1,262	1,124	1,124
Zinc Vapor in:					
Total Reaction Gases, volume percent	40.0	40.0	40.0	42.0	42.0
Reaction Gases from ZnO alone, do	44.5	44.5	44.5	46.7	46.7
Conversion to Zinc:					
In Portion A, percent	89.8	85.0	89.8	89.8	89.8
In portion B, do	90.2	93.4	90.2	90.2	90.2
Overall, do	99.0	99.0	99.0	99.0	99.0

In each of the tabulated runs:

1. The gases flow up through the reactor at an average velocity of 0.45 foot per second.

2. Zinc vapor is recovered from the gaseous effluent leaving the reactor at the rate of 2000 lbs. per hour.

3. Heat is supplied to the endothermic reaction mass within the reactor by closely spaced fire-tubes passing therethrough.

Control run X provides the basis for evaluating the benefits of this invention in example runs 1 and 2, while control run Y bears the same relation to example run 3. Control runs X and Y are examples of the invention of my copending application Serial No. 767,548, the present invention being an improvement thereover.

Referring to the table, it will be observed that the roasted zinc ore of runs X, 1 and 2 has a fairly high content of Fe_2O_3 and PbO which gives the ore appreciable agglomerating propensity during reduction. Runs 1 and 2 exemplify two ways in which such an ore can be treated in accordance with the principles of this invention.

In run 1, the conversion to zinc in the first reducing stage is limited to 85% because a higher conversion in this stage with only a 1:4 ratio of coke to ore would lead to serious agglomeration which in turn would interfere with proper fluidization. Because of the selected lower conversion and lower ratio of coke to ore, the height of the fluidized mass in the first stage (6.3 ft.)

of run 1 is 63% less than the corresponding height (17.0 ft.) in run X. To effect an overall conversion of 99%, the second stage in run 1 has to operate with a conversion of 93.4% to compensate for the relatively low conversion of 85% in the first stage. This makes the second stage of run 1 somewhat larger than the corresponding stage in run X; the height of the fluidized mass in the second stage (9.6 ft.) of run 1 is thus 37% more than that (7.0 ft.) of run X. In spite of this increase, the total height (15.9 ft.) of fluidized material in both stages of run 1 is 34% less than the total height (24.0 ft.) in run X. Similarly, the volume of fluidized solids in run 1 is considerably smaller than in run X.

In run 2, the benefit of introducing part of the coke into the first stage and part into the second is taken in a different form. The reactor dimensions are held the same as those for run X. This permits the coke deficient mixture fed to the first stage of run 2 to have a longer residence time therein than does the mixture fed to the first stage of run X. To effect 89.8% conversion with a longer residence time, a lower reaction temperature is required. Thus, the first stages of runs 2 and X are maintained at temperatures of 1790° F. and 1850° F., respectively. Because of the lower temperature, the agglomerating tendency is less pronounced and a first-stage conversion of 89.8% can be countenanced in run 2 while it was limited to 85% in run 1. In decreasing the temperature of the first stage from 1850° F. to 1790° F., the allowable stress on the metal parts of the reactor may be increased from about 550 lbs. per sq. in. to about 750. This increase of 36% in design stress is of considerable advantage from the points of view of capital investment and maintenance of the reactor.

The roasted ore used in control run Y and example run 3 has appreciably less Fe_2O_3 and PbO than the ore of runs X, 1 and 2 and therefore shows less tendency to agglomerate during reduction. In decreasing the proportion of coke fed to the first stage pursuant to this invention, the more agglomerating ore made it necessary in run 1 to limit the conversion in the first stage or in run 2 to lower the temperature in the first stage. With the less agglomerating ore, there is no need to lower either the first-stage conversion (89.8%) or the temperature (1850° F.). Comparing run 3 with control run Y, it is seen that the height of the fluidized mass in the first stage of run 3 is 9.4 ft. or 40% less than the corresponding dimension (15.7 ft.) in run Y. The total height of the fluidized mass for run 3 is 15.9 ft. while in run Y it is 22.2 ft.; the total height is thus decreased 28%. Similar decreases will be noted by comparing the volumes of the fluidized masses in the first stage and in the whole reactors of runs 3 and Y.

The reactor diameters in the vicinity of gas feed line 22 are slightly larger in runs 1 and 3 than in control runs X and Y, respectively, because in these runs the depth of the fluidized mass is less and consequently the fluidizing gas is introduced against less fluid-static pressure. Under these circumstances, a given quantity of gas occupies a somewhat larger volume. The upper diameters of the reactors in runs 1 and 3 are also larger than those in runs X and Y, respectively, for the reason that these shorter reactors must accommodate a larger number of fire-tubes (of shorter length) to provide the necessary heat transfer area within the fluidized mass.

In my copending application Serial No. 767,548 there is disclosed a fluidizing vessel for the reduction of zinc compounds in which the fire-tubes are disposed horizontally therethrough. This form of reactor is useful in the present invention, particularly inasmuch as a relatively large area of heat transfer surface can be built into the reactor.

It is contemplated that under certain circumstances it may be advisable to maintain different gas velocities and/or different temperatures in the succeeding stages of the reduction. Thus, it may be advisable to use a comparatively low gas velocity, say 0.5 foot per second, through the first stage in order to permit the zinc concentration to build up in the gaseous product stream but to have the gas velocity in the succeeding stage higher, say 1 foot per second, in order to obtain maximum capacity per unit of horizontal cross-section. Where the feed material containing the zinc compound which is to be reduced is in a poorly reactive form, it will often be beneficial to maintain a higher reducing temperature in the last stage than that in the first stage of the reduction. In the final stages of a reduction, resort to higher temperatures which generally aggravate agglomeration is made feasible by the introduction of diluting, nonagglomerating solids pursuant to this invention. Thus, solids which are added to the fluidized mass primarily to ensure good fluidization enter the mass at that stage or stages of the reduction where agglomeration requires correction and not at the first or early stages of the reduction where the diluting solid particles serve no useful purpose.

While I have referred to the concurrent flow of solids and gases from one stage to a succeeding one, it is clear that the solids and gases do not progress through the stages at the same velocity because of the slippage or "hindered settling" of the solid particles within the fluidized mass of each stage. As a matter of fact, the residence time of the solids in each stage will usually be very much greater than that of the gases therein.

Those skilled in the art will visualize many variations of the invention without departing from its spirit or intent. For instance, 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. Accordingly, 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 is claimed is:

1. In the stagewise reduction of a solid inorganic oxygen-containing compound of zinc by a solid carbonaceous reducing agent, both said solids being in comminuted form, under fluidizing conditions for the recovery of zinc, wherein said reduction is conducted in at least two stages with concurrent movement of the gases and solid particles of the fluidized mass from the first stage successively to the subsequent stages while preventing substantially all back-flow of said solid particles from any stage to preceding stages, the improvement which comprises introducing into a stage subsequent to said first stage a solid nonagglomerating particulate material, and maintaining the presence of said particulate material in said subsequent stage by the continued intro-

duction of said particulate material into said subsequent stage.

2. The process of claim 1 wherein the particulate material is a carbonaceous fuel.

3. The improved process of treating a comminuted solid material containing zinc oxide for the recovery of zinc, which comprises introducing said comminuted material and a comminuted solid carbonaceous reducing agent into a fluidizing and reducing zone adapted to hold a deep fluidized bed of increasing horizontal cross-section in the upward direction, injecting a fluidizing medium into the base of said bed, passing gases and solids from said reducing zone into a subsequent reducing zone to effect further reduction of zinc oxide while preventing substantially all back-flow of said solids from said subsequent reducing zone to the first said reducing zone, introducing into said subsequent reducing zone a solid nonagglomerating particulate material, maintaining the presence of said particulate material in said subsequent reducing zone by the continued introduction of said particulate material into said subsequent reducing zone, withdrawing from said subsequent reducing zone gases and solids, and recovering zinc from the withdrawn gases.

4. The process of claim 3 wherein at least 60% of the zinc content of the solid material introduced into the reducing zone adapted to hold a deep fluidized bed of increasing horizontal cross-section is vaporized by reduction within said reducing zone and the particulate material introduced into the subsequent reducing zone is coke.

5. In the production of zinc by the fluidizing process involving the reduction of a solid inorganic oxygen-containing compound of zinc by reaction with a solid carbonaceous reducing agent, both of said reacting solids being in comminuted form, wherein a gaseous reaction stream containing the zinc vapor generated by said reduction is withdrawn from the zone of reduction, the improvement of producing said gaseous reaction stream with a high concentration of zinc vapor, which comprises effecting said reduction while passing said reacting solids and said gaseous reaction stream successively through a series of fluidized beds thereof while preventing substantially all back-flow of said reacting solids from any bed to any preceding bed of said series, charging a fluidizing medium at the bottom of the first of said beds to support fluidization therein, said first bed being about 10 to 40 feet in height and of increasing horizontal cross-section in the upward direction, introducing into one of said beds subsequent to said first bed a solid nonagglomerating particulate material, maintaining the presence of said particulate material in said subsequent bed by the continued introduction of said particulate material into said subsequent bed, and withdrawing from the last of said beds said gaseous reaction stream after it has attained a volume at least 8 times the volume of said fluidizing medium charged at the bottom of said first bed.

6. The process of claim 5 wherein the solid inorganic oxygen-containing compound of zinc is essentially zinc oxide and both the solid carbonaceous reducing agent and the particulate material are essentially coke.

7. The process of claim 6 wherein the conversion to zinc effected with the reacting solids entering the first bed is approximately equal to the conversion to zinc effected with the reacting solids entering each subsequent bed.

8. In the stagewise reduction of a solid inorganic oxygen-containing compound of zinc by reaction with a solid carbonaceous reducing agent, both of said reacting solids being in comminuted form and being introduced into the first reducing stage, under fluidizing conditions for the recovery of zinc, wherein said reacting solids and the resulting reaction gases concurrently move successively through a series of fluidized reducing stages with substantially no back-flow of said reacting solids from any stage to any preceding stage of said series, the improvement of introducing additional solid carbonaceous reducing agent in comminuted form into a stage subsequent to the first stage of said series.

9. The process of claim 8 wherein the additional solid carbonaceous reducing agent in comminuted form introduced into a stage subsequent to the first stage of said series amounts to about one-half of the proportion of said reducing agent ultimately required in the last stage of said series.

JOHN C. KALBACH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
694,947	Davies	Mar. 11, 1902
2,316,664	Brassert et al.	Apr. 13, 1943
2,342,368	Queneau	Feb. 22, 1944
2,379,408	Arveson	July 3, 1945
2,379,711	Hemminger	July 3, 1945
2,393,704	Ogorzaly	Jan. 29, 1946
2,397,352	Hemminger	Mar. 26, 1946
2,398,443	Munday	Apr. 16, 1946
2,425,098	Kassel	Aug. 5, 1947
2,431,630	Arveson	Nov. 25, 1947
2,475,607	Garbo	July 12, 1949
2,478,912	Garbo	Aug. 16, 1949
2,485,604	Kalbach	Oct. 25, 1949