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METHOD OF PURIFYING AND DESULFURIZING ZINC SULFIDE ORES AND CONCENTRATES

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This invention relates to a method and apparatus for purifying zinc sulphide ores and commercial zinc sulphide concentrates, whereby there is attained a high degree of purification, and subsequently roasting the purified concentrates in a highly economical manner. Briefly, this invention contemplates initial purification of the concentrates by removal therewith of the major portion of such constituents as lead, cadmium, tin, and the like, but with only partial oxidation of the sulphide constituents. The so-purified concentrates, partially depleted of fuel value (i.e., sulphide sulphur), are then in a subsequent and separate operation desulphurized and oxidized by roasting in a fluidized bed. Both the initial purification and the subsequent desulphurization are carried out essentially autogenously. The combination of purification and subsequent final desulphurization as separate steps carried on in substantially separate apparatus but with both being achieved autogenously marks a distinct forward step in zinc metallurgy and in the economy of zinc smelting.

In the art of zinc metallurgy, one of the most challenging problems is the production of high grade low-lead zinc from a zinc sulphide concentrate containing substantial amounts of lead. Zinc concentrates containing less than 0.1% lead are much less commonly available than those concentrates containing 0.1% to 1.0% lead. Even more abundant are zinc concentrates containing more than 1% lead; and in fact, lead contents as high as 3% are not unusual.

In the present state of the art, production of high grade zinc metal or zinc oxide requires either preselection of concentrate feed, wet purification, or rectification of the product metal. Rectification of product metal involves fractional distillation of zinc; e.g., prime western grade. This method, while technically satisfactory, inherently involves added cost of the extra metallurgical step. Wet purification by the well-known electrolytic zinc process is generally more costly than the processes of pyrometallurgy and finds its most extensive use only where the zinc ores contain significant values in by-product metals such as gold and silver. Direct production of high grade zinc metal by pyrometallurgical processes is achieved only when the lead content of the zinc concentrate feed is limited to what can be removed in the roasting and sintering operations. For example, in the well-known electrothermic method for zinc production, it is generally found necessary to limit the lead content of the concentrate feed to 0.5% lead if the lead content of the product metal (or oxide) is to be less than 0.025% lead.

Supply of low-lead concentrate are far less than the demand. Operators of zinc mines and concentrators find a ready market for high-lead zinc concentrates; i.e., those containing more than 0.5% lead, and so are loath to increase the purity of their concentrates, especially when to do so results in lower recovery of zinc, as happens in the present state of the art of beneficiation. High-lead zinc concentrates are used to produce prime western zinc for which there is a large and steady demand. There is also a large and increasing demand for high grade zinc. In view of the ready outlet for high-lead zinc concentrates, there appears little possibility of substantially improving the supply of low-lead zinc concentrates at the mines. The producers of zinc metal must, therefore, develop more efficient and lower cost purification processes.

An object of this invention is to provide a method and apparatus whereby a relatively pure high grade zinc calcine may be made at reasonable cost from a high-lead relatively impure zinc sulphide concentrate.

Another object of this invention is to provide a method and apparatus for beneficiating a high-lead relatively impure zinc sulphide concentrate whereby two products are produced; one a low-lead relatively pure zinc calcine suitable for the production of high grade zinc, the other a lead-enriched calcine suitable for the production of prime western zinc.

Another object of this invention is to provide a method and apparatus whereby the above-described objects may be achieved by essentially autogenous means without necessity of combustion of substantial amounts of added fuel.

A still further object of this invention is to produce as a by-product of this purification and desulphurization process a high-strength sulphur dioxide gas suitable after purification and dilution with air for manufacture of sulphuric acid by the contact process.

Another object of this invention is to provide a method and apparatus for purifying and roasting zinc sulphide concentrates at an over-all cost substantially lower than that achieved by prior art methods.

The term “zinc calcine” as used in this specification is that commonly employed in the art to designate an essentially dead roasted material; i.e., the product obtained by substantially complete oxidation of a zinc sulphide concentrate.

It is known that by subjecting the commercial zinc sulphide concentrates containing relatively large amounts of impurities to an oxidizing roast in any of well-known processes such as roasting in multiple hearth roasters, suspension-type roasters, rotating drum roasters, and the like, appreciable amounts of volatile impurities such as lead, cadmium, and the like, remain in the final roasted product, making the product unsuitable for production of high grade zinc metal or zinc oxide pigments without further purification.

By the method of the invention disclosed herein, low-lead calcine suitable for the production of high grade zinc metal or zinc oxide can be produced from high-lead zinc sulphide concentrates; i.e., zinc concentrates containing more than 0.5% lead. Briefly, the invention consists of obtaining purification and subsequent desulphurization in two distinct steps, whereby in the first step the lead-containing zinc sulphide material is subjected to a high temperature and a high sulphide sulphur environment wherein the major portion of the impurities is eliminated, and then, in the second step, passing the thus-purified material through a fluid bed reactor for substantially complete removal of the sulphur by oxidation.

Under these conditions, the lead-containing constituents readily sublime and are carried off with the exit gases.
from the first step or purification operation, while other minor metals whose sulphides, oxides, or intermediate reaction products are volatile, such as cadmium and tin, are vaporized in substantial amounts and are removed along with the lead.

In the usual method of carrying out the purification step, a portion of the original sulphide content of the concentrate feed is oxidized to provide the necessary heat. The purified partially oxidized intermediate product—which, for nomenclatural convenience will hereinafter be designated as PDC, i.e., "partially desulphurized concentrate"—ordinarily does not contain enough heat value to permit completely autogenous roasting by the methods conventionally employed in the art. That is to say, PDC cannot be dead roasted in a multiple hearth furnace, a suspension roaster, a rotary kiln, or the like, without the use of substantial quantities of auxiliary fuel, such as natural gas. The invention described herein provides a method and apparatus by which the roasting of PDC may be completed entirely autogenously.

In one of the preferred methods of the invention, as the first step in purification and desulphurization or roasting procedure, sulphide zinc concentrates are fed to the top hearth of a conventional type multiple hearth roaster. The concentrates successively pass downwardly through a multiplicity of hearths while being mechanically agitated by means of rabbles and being spread over several hearths and transported toward the bottom discharge opening while hot gases are circulated upwardly over the several hearths.

This method of operating such an assembly, whereby practically complete elimination of impurities such as lead and very high percentage elimination of cadmium and the like is obtained, differs from the conventional roasting of zinc concentrates in multiple hearth roasters as follows:

The top open hearth of the multiple hearth roaster is used mainly for drying of the concentrates. Depending upon the capacity desired, the first, second, or third hearths following immediately below the top hearth are used to gradually heat the material to a temperature permitting ignition of sulphidic materials in the charge whereby when the material drops on to the next following hearth below the sulphidic minerals begin to ignite. This hearth and the several hearths following are used as "reaction" hearths in which sufficient preheated oxygen-lean gases of high sulphur dioxide content are allowed to circulate upwardly over each one of the several reaction hearths partially oxidizing the sulphidic minerals to maintain a temperature and atmosphere in each of several hearths which will permit volatilization of the volatile compounds of metals such as lead, cadmium, and the like. As the products of combustion, due to strict control of air supply, are maintained at or near maximum possible concentration with respect to sulphur dioxide content, a correspondently reducing atmosphere surrounds the material being agitated and transported downwardly over the reaction hearths. Preferred temperature range for volatilization of impurities in the zinc concentrates and for incidental partial oxidation thereof as they pass over the reaction hearths, is between 850° to 950° C. The lowest two or three hearths in the multiple hearth furnace immediately below the lowest reaction hearth are used for the dual purpose of preheating the small amount of air required to temperatures sufficient to oxidize the minerals in the lowest of the reaction hearths and, also, to cool the purified material before its discharge from the roaster. The preheated air may comprise hot gas from another furnace, such as a subsequent desulphurization reactor or other desirable source, and may be so regulated as to be capable of burning sufficient sulphidic minerals in the reaction hearths to maintain the desired temperature. Additional air or heated gas is supplied to each one of the reaction hearths necessary to oxidize an increment of sulphidic minerals to maintain optimum operating conditions.

When purifying commercial zinc concentrates having 30% to 32% sulphur, oxidation of somewhat less than one-half of the sulphur content of the concentrates is usually sufficient to furnish the heat necessary to complete the purification step by partial desulphurization operation as outlined hereinafter during normal operations without the necessity of supplying extraneous heat. Assays of product discharged from the multiple hearth roaster show from 18% to 20% sulphur remaining in the partially desulphurized product. Zinc ores and zinc concentrates containing sulphur partial desulphurization of higher than 30% to 32% can be purified by this method.

This method of operation yields excellent results even with concentrates containing 1% lead or more. For the treatment of very high-lead content zinc sulphide concentrates, however, a further improvement is employed. By thoroughly drying and preheating if necessary the concentrate before it is fed onto the top hearth of the multiple hearth furnace, the furnace can be run with a hot top. By this means that the temperature of the upper hearths of the furnace is kept sufficiently high to prevent chilling and smothering of lead sulphide, lead oxide, and other impurities on and with the incoming ore. Without wishing to confine the invention to a particular theory, it is thought that for very high lead content feeds the furnace gases in the upper part of the roaster may become supersaturated, with respect to constituents volatilized from the charge, if the temperature is allowed to drop too much. Presumably the supersaturation is relieved by condensation from the gas of the excess sublimed constituents. Some of the so formed particulate matter may settle out on the incoming ore where it has the effect of increasing the percentage of impurities in the charge.

Whether the above hypothesis be correct or not, the practical effect and the remedy as described have been discovered.

The volatile impurities in the zinc concentrates that are driven off in the reaction hearths together with very fine particles of zinc concentrates entrained in the gases from the multiple hearth roaster are carried out of the furnace, and are recovered in well-known apparatuses such as cyclones, electrical precipitators, and the like. A typical analysis of the fume and dust collected from the gases discharged from the multiple hearth furnaces which are used for purification and partial desulphurization shows lead assay of 18% to 20%, zinc assay of 38% to 42%. The amount of solid fume material discharged with the furnace gases from such an operation is in the neighborhood of 2.5% of the weight of concentrates fed to the furnace. When a multiple hearth roaster is being used in a conventional manner for dead roasting of commercial zinc concentrates, the amount of dust and fume driven out of the furnace with the furnace gases usually runs from 12% to 15% of the weight of concentrates fed to the furnace with a typical average assay of 4.5% to 5% lead and about 50% zinc. It is evident that in the practice of the present invention, due to low volume of gases being circulated in the furnace and consequent low velocity and lower exist temperature, much less zinc concentrate is driven out of the furnace as dust, and the dust collected in the multiple hearth furnace, or electric precipitators is much higher in lead content, making it more economical to further process the same for separation of lead, cadmium, zinc, etc.

As the second step in the purification and roasting of commercial zinc concentrates in accordance with this method, the partially roasted and purified product from the multiple hearth furnace is passed through another furnace where complete desulphurization is obtained. To obtain autogenous roasting of concentrates, substantial savings in fuel and economical operation, it is preferred to carry on the second step in a fluid bed furnace.
arranged so that a substantial depth of the PDC is maintained upon the furnace hearth and so that the air required to complete the oxidation is so injected as to obtain the agitation of the PDC being oxidized. A mixture of gases such as SO₂ and air or SO₃ and oxygen may also be the vehicle of agitation.

It is well-known in the art of zinc metallurgy that a certain amount of lead is removed from zinc sulphide concentrates under strongly oxidizing conditions in multiple hearth furnaces under carefully controlled conditions. In the pyrometallurgical zinc process, for example, lead content of the product metal is influenced in major degree by the amount of lead eliminated during roasting. With good practice, it is possible to eliminate about 90% of the lead during the usual roasting in the multiple hearth furnace. For example, a concentrate containing 0.5% lead can be made to produce a calcine containing about 0.05% lead. From a concentrate containing 1% lead, a calcine containing 0.1% to 0.15% lead can be produced.

In the subsequent operation of sintering, additional— but less important—amounts of lead are removed, making it possible to produce from the melting furnaces a high grade metal containing as low as 0.025% lead when the feed to the roaster contains as much as 0.5% lead. When an attempt is made to remove lead by roasting; i.e., oxidation, this invention makes it possible to remove lead and similar impurities more effectively by minimizing oxidation and maintaining as high a concentration of sulphides as possible. In this process there is practically no free oxygen in the exit gases from the first stage or purification reactor, quite in contrast to prior art processes in which the exit gases commonly contain 6% to 7% sulphur dioxide and 7 to 10% oxygen. In the process of this invention, the sulphur dioxide content of the exit gases approximates 14% to 16%, depending on the composition of the air or other fluidizing gases entering the reactor.

The process is preferably operated continuously with high-lead zinc concentrate feed entering the purification reactor at a predetermined rate and delead PDC being withdrawn from the reactor at a related rate. Heat is normally supplied by admitting air to the reactor and partially burning the concentrates.

When a multiple hearth roaster is operated according to this method for initial purification and partial desulphurization of commercial zinc concentrates, much larger tonnages can be treated in a given size of furnace than when the same furnace is used for roasting in conventional manner.

In a typical run of the purification step, zinc sulphide concentrates are fed at the rate of 132 tons per day to a Nichols-Herreshoff furnace 20'-6" inside diameter, with twelve super-imposed hearths and having a normal oxidizing or dead roasting capacity of 60 to 70 tons of concentrates per day. The zinc concentrate feed contains 1.05% lead and 31.4% sulphur. As the ore progresses downwardly through the furnace, its temperature is increased so that on seven of the twelve hearths the temperature is above 900° C., and on four of the hearths the temperature is above 950° C. At the same time, a small amount of air is admitted in the lower part of the roaster in order to partially burn the concentrates to secure the necessary heat. The lead content progressively decreases as the ore passes downward through the roaster.

The ore (PDC) discharged from the roaster contains 0.027% lead and 18.1% sulphur.

In another run, the same species of zinc concentrates are fed at the rate of 125 tons per day to the aforementioned multiple hearth furnace; and the discharged product contains 0.012% lead and 17.1% sulphur. Other runs, described more fully hereinafter, give similar results.

During some of these runs, it is found convenient to burn fuel gas on the fourth, tenth, and the twelfth hearths of the furnace in order better to control the temperature distribution. With some concentrates auxiliary fuel may be used as a convenience, but its use is not a necessity. In another run for example, 122 tons per day of concentrate containing 0.53% lead are fed to the multiple hearth furnace; and the discharged material contains 0.020% lead. No fuel gas is burned during this run.

The elimination of cadmium by the method of this invention is also much greater than that of prior art processes. In the run first-mentioned hereinbefore, the cadmium content of the feed material is 0.10% while the cadmium content of the material discharged from the furnace is only 0.027%.

In another run, zinc sulphide concentrate is fed to the aforesaid multiple hearth furnace at the rate of approximately 100 tons per day. The feed assays approximately 57% zinc, 0.55% lead, and 52% sulphur. During operations, temperature of the second hearth from the top is maintained at approximately 800° C., the third hearth at 880° C., fourth to ninth hearths inclusive at 900 to 935° C., tenth hearth at 800° C., eleventh hearth at 765° C., and the twelfth hearth at 525° C. The following results are obtained. For a 24-hour period when 93.9 tons of concentrate fed to the roaster is 98.6 tons, the product assays 0.007% lead and 19.5% sulphur. For a 24-hour period when the amount of concentrate fed to the roaster is 98.6 tons, the product assays 0.09% lead and 19.0% sulphur.

As mentioned in the first described run, when the furnace is fed with a zinc sulphide concentrate assaying 55.0% zinc, 1.05% lead, and 31.4% sulphur at the rate of 132 tons per day, the product assays 0.027% lead and 18.1% sulphur. When the furnace is fed with zinc concentrates assaying 54.0% zinc, 2.08% lead, and 31.5% sulphur at the rate of about 90 tons per day, the product assays 0.054% lead and 16.5% sulphur.

While specific runs have been described, it is not wished to limit this invention to the conditions described in the runs. In other runs, the invention is practiced successfully using different temperatures than the ones recited hereinbefore. It will be readily understood that the concentrate production of various mines will influence to a considerable extent the temperature and atmospheric conditions required, the more refractory ores or concentrates requiring temperature and reduction conditions of the higher order. In some of the runs, temperatures in excess of 950° C. are used on two to five or more of the hearths with good results. By means of preheated gases such as derived from combustion of auxiliary fuel or as derived from the subsequent desulphurizing step to be described, great leeway is provided in exercising control both over temperatures and over sulphur content of the concentrates during passage through the furnace.

It is necessary to remove the sulphur from the PDC in order to prepare a high grade calcine suitable for agglomeration for feeding to reduction furnaces. To this end, an autogenous desulphurizing step is carried out in a gas agitated bed operated under oxidizing conditions. The preferred practice of this invention, therefore, calls for the passing of the purified product (PDC) discharged from the multiple hearth furnace into a builting bed reactor. Through tuyeres in the wall or floor of this reactor, air or other oxidizing gas is introduced in quantities sufficient both to agitate and to oxidize the particles of zinciferous material. By means of this process, it is possible to desulphurize autogenously purified PDC containing as little as 10% sulphide sulphur.

The purified and desulphurized zinc calcine produced by the practice disclosed herein is suitable after agglomeration for making of high purity zinc metal direct from reduction furnaces without the necessity of subsequent redistilling or refining and for manufacture of commercial lead-free zinc oxide pigments.
The invention will be described further with reference to the drawings wherein:

Fig. 1 is a diagrammatic view of one form of apparatus in which the process of the invention is performed; and Fig. 2 is a diagrammatic view of another form of apparatus suitable for carrying out the process of the invention.

Referring to the drawings, particularly to Fig. 1, 10 represents a multiple hearth furnace and 11 a fluidized bed reactor. Zinc sulphide zinc concentrate feed, preferably dry, enters the multiple hearth furnace 10 through seal 12 from suitable conveyors 13 through a bin 14. Part of exit gases from the fluidized bed reactor 11 may enter the multiple hearth furnace directly or, after being directed through duct 16, pass through waste heat boiler 18, through fan 19, through a dust and fume separating device 26, which suitably may be a Cottrell type electrostatic precipitator, and through duct 21 to further processing apparatus such as a contact sulphuric acid plant which is not shown. The shaft 22 of the multiple hearth furnace 10 and the raffle arms 23 attached thereto are rotated at a suitable speed such as 1 R.P.M. by drive unit 24. The rotating raffle causes the concentrate to feed across the hearths and down through the roaster in a manner well-known to those skilled in the art. The ore which has been treated in the multiple hearth furnace leaves through conveyor 25 and star valve 26 which discharges to surge bin 27. From this bin pipe 28 delivers the dealed concentrate to feeder 29 which supplies dealed sulphur-containing ore to fluidized bed reactor 11. Feeder 29 may suitably be a screw conveyor driven by a variable speed drive 30. The material delivered by feeder 29 to reactor 11 is maintained in a fluidized state in the bed 31 by means of gas such as air blown in through tuyeres 32 located preferably in the floor of the reactor 11. Air is supplied to tuyeres 32 from a suitable supply such as a blower 33. An amount of air is supplied which will give a linear upward gas velocity in reactor of between one and three feet per second. Gases leaving reactor 11 pass through duct 34 to enter dust separation device 15, suitably a refractory-lined cyclone. Part of the gas leaving the cyclone 15 through exit duct 35 is diverted to the lower portion of the multiple hearth furnace through duct 16 as described hereinbefore, while the remainder of the gas passes through duct 36 to waste heat boiler 37 whence these gases, Cottrell 39 and on through a further processing apparatus such as a sulphuric acid plant which is not shown.

Overflow of oxidized calcine from the fluidized bed 31 passes through an overflow port 41 and seal 42 through conveyors 43 to a bin 44 thence by way of conveyor 45 to the next processing step. Dust separated in cyclone 15 and in waste heat boiler 37 join through conveyors 46 and 47 the overflow product delivered into bin 44. Dust and fume recovered by Cottrell 39 pass by conveyor 48 to a further processing step. Alternatively, the Cottrell dust from conveyor 48 may be diverted to the bin 44 or may be returned, if desired, to raw concentrate feeding furnace 10 through conveyor 13.

Dust recovered in waste heat boiler 18 passes through conveyor 49 to the next processing step or suitably may be returned to multiple hearth furnace 10 through conveyor 13. Lead furnaces collected by Cottrell 20 passes by conveyor 50 to the next processing step.

In another variation of the invention, referring to Fig. 1, exit gases from the reactor 11 are passed directly into multiple hearth furnace 10. It is also possible to discharge PDC from the bottom hearth of furnace 10 directly into reactor 11.

In some circumstances, it is not necessary to place a dust catcher 15 ahead of waste heat boiler 37. Also, it is not always necessary to pass multiple hearth furnace exit gases through waste heat boiler 18, for example when operating with a cold top furnace. For purposes of illustration, however, there has been shown a more general arrangement of our invention.

The process of this invention, it is convenient to vary the proportion of fluidized reactor exit gases diverted through duct 16 to multiple hearth furnace 31 by varying the proportion of either duct 34 or duct 35. Enough gas is diverted through furnace 10 to develop and maintain temperatures suitable for efficient deleading. Experiments have shown that it is desirable to maintain temperatures in excess of 900°C, on at least two of the hearths of furnace 10 and refer to maintain temperatures in excess of 950°C on at least five hearths. The concentrate feed rate through the system is adjusted so that with an air velocity through reactor 11 of one to three feet per second there will be a suitable stoichiometric excess of oxygen in the exit gases passing through duct 34. In general, it is desirable to maintain an oxygen concentration of 1% to 7% in these exit gases.

In another of the preferred methods, as the first step in purification of sulphidic zinc concentrates, the concentrates are fed continuously through a fluid bed reactor and thereafter through a second fluid bed reactor. Fig. 2 illustrates this arrangement of the invention. In purifying reactor 51 a bed of zinc concentrates is maintained in an agitated condition by injection of air through tuyeres 53 located in the floor of the reactor. Air is supplied from any convenient source such as blower 54. Zinc concentrates, preferably thoroughly dry, are delivered from a stockpile or other facilities, not shown, by conveyor 55 to feed bin 56. A conveyor 57, which suitably may include a conveying device, delivers concentrate to reactor feeder 58 which may suitably be a screw conveyor driven by a variable speed drive 59.

Temperature of the reactor 51 may be controlled by varying the ratio between air input rate and concentrate feed rate. In general, it is found preferable to maintain a fixed air input rate and to vary the concentrate feed rate, for example by means of variable speed drive 59, to control the temperature within the reactor bed 52. It is particularly convenient to control the bed temperature automatically by means of a conventional temperature recorder and controller which, through suitable linkage, adjusts the concentrate feed rate in response to variations indicated by a thermocouple in the boiling bed. A thermocouple may be located 6° to 18° above the bottom of the bed; but because of the remarkable uniformity of temperature in a properly operated fluidized bed, location of thermocouple is not at all critical.

It is the preferred practice to maintain as high a bed temperature as possible without incipient fusion of the particles in the bed. If too high a temperature is reached, the bed may sinter and lose its mobility characteristics. The highest workable temperature depends upon the species of concentrates being treated as some compositions fuse at lower temperatures than others. In general, it has been found possible to operate consistently with bed temperatures of the order of 1000°C. It is also interesting to note that in comparative tests in which the same species of zinc concentrates was treated in a multiple hearth furnace and in the mobile bed reactor, the operating temperature attainable before sintering or agglomeration occurred was significantly higher in the latter reactor.

Gaseous reaction products together with the sulfide impurities and smaller particle size constituents of the concentrate feed leave the top of the reactor 51 and flow through short duct 60 to a dust separating device 61 which may conveniently be a cyclone separator. Alternatively, the cyclone can be replaced within the reactor 51 or in an upward extension thereof. However, with presently available materials of construction, it is usually
more convenient to locate the deduster exteriorly to, but contiguous with, the reactor. Exit gases leave cyclone 61 through a duct 62 and pass successively through a waste heat boiler 63, a fan 64, a fume-separating device 65, which suitably may be a Cottrell electrostatic precipitator, and on through a duct 66 to further processing apparatus, not shown, such as a contact sulfuric acid plant. Dust settled in waste heat boiler 63 is withdrawn through pipe 67 and delivered to bin 68 or alternatively is returned to feed bin 56 by suitable conveying means, not shown. Lesty fume and other impurities volatilized by the reactor are recovered in Cottrell 65, withdrawn by conveyer 69, and are passed to a further processing operation for recovery of the contained metal values.

Dust caught in the cyclone 61 passes through down-spout 70 to bin 71 which may deliver through pipe 72 to a feed bin 73 or the dust may be returned to reactor 51 as described hereinafter. The nature of the cyclone dust depends on the mode of operation of the reactor and the temperature of the gas in the deduster, as will be disclosed hereinafter. In general, the greater the linear gas flow rate upward through the reactor and the smaller the size of the concentrate particles, the more will be the amount of dust carried over with the exit gases. Convective flow and the larger particle sizes tend to lessen the amount of dust in the exit gases. There is a lower limit to the gas flow rate below which the boiling bed tends to lose its mobility characteristics. In general, gas flow rates of 1 to 3 feet per second maintain satisfactory mobility of the bed. Particle size and particle size range vary considerably from one species of concentrate to another. Even fairly large size particles, such as pellets formed by the rolling action of concentrates in storage or in passing through a dryer or tumbling action conveyor, will fluidize satisfactorily if the size range is not too narrow.

If the reactor 51 is allowed to chill before or when it enters the deduster 61, there is a tendency for some of the sublimed and volatile compounds to come down with the dust. If it is desired to blend this dust with the purified concentrates which overflow from the reactor 51, the gases are kept hot until they leave the deduster. On the other hand, if it is desired to produce a lead-enriched product as well as a lead-impoverished material, it is convenient to chill the gases before they enter or while they pass through the deduster. For this latter purpose the deduster may take the form of a waste heat boiler with a variable speed drive for reasons; circumstances it is desirable to recirculate a part of the cyclone dust from the bin 71 back through the reactor 51. For this purpose the dust is passed through pipe 74 to join with the concentrate at feeder 58 through bin 56, or it can enter the reactor 51 through a similar but separate feeder, not shown.

As indicated above, one of the methods of practicing this invention contemplates chilling the exit gases leaving reactor 51, by passing said gases first through a waste heat boiler and thereafter through a cyclone in the reverse order of that shown in Fig. 2. By operating in this manner it is possible to produce a lead-enriched product suitable, after desulphurization, for the production of prime western zinc metal, leaded zinc pigments, and so forth. For this mode of beneficiation, cyclone dust from bin 71 and boiler dust from bin 68 are comingled and desulphurized in a fluidized bed reactor not shown which, in effect, operates in parallel with reactor 75 and is essentially a duplicate of the equipment associated therewith. As concentrate enters through feeder 58, PDC is withdrawn from the reactor 51. This may be done in any convenient manner—e.g., one especially convenient way being to allow the boiling bed 52 to overflow through a conduit 76, star valve 77 and pipe 78 to bin 73 which supplies the delead product to the fluidized bed desulphurizer 75. Contrary to what one might expect, we have found that there is little danger of "short circulating" between feed and overflow. Whether the product is withdrawn from the surface of the bed, from the bottom, or from an intermediate level, or whether the feed is introduced above, at, or beneath the top of the bed, seems to make little difference; the overflow product is not contaminated with feed material.

From bin 73 PDC is withdrawn at regulated rate through conduit 79 by feeding device 80, suitably a multiple screw conveyor driven by variable speed drive 81. Feeder 80 discharges PDC into reactor 75 where it forms the fluidized bed 82. Air for agitation and oxidation of boiling bed 82 is supplied by suitable means such as blowers 83 through tuyeres 84 suitably disposed in the bottom or lower wall of the reactor 75. An amount of air is supplied which will give an upward gas velocity in reactor 75 of the order of 1 to 3 feet per second. Gases leave reactor 75 through short duct 85 and enter dust separation device 86, which suitably may be a refractory-lined cyclone or a cyclone lined with corrosion-resistant steel of the 28% chromium variety. Gases pass from dust separation device 86 through duct 87 to waste heat boiler 88, thence through fan 89 and Cottrell 90 and on through pipe 91 to further processing operation such as a sulfuric acid plant, not shown. Fume collected by Cottrell 92 is conveyed to a subsequent processing step. Dust recovered in waste heat boiler 88 passes by conveyer 92 to the dust discharged from collection device 86 in bin 93.

Overflow from boiling bed 82 of reactor 75 passes through pipe 95, star valve 96 and pipe 97 to bin 93. This overflow product, together with the dust recovered from cyclone 86 and waste heat boiler 88, constitutes the final purified oxidized zinc calcine product of this process.

Further description of this invention is given in the following example. In this example which pertains to the first or purification step, the reactor consists of a steel shell 25'6" high by 4'11" diameter lined with 4½" of insulating brick and 4½" of firebrick up to 7'3" level and with 4½" of firebrick above this point. To conserve heat the external surface of the reactor is lagged with insulation sufficient to raise the steel temperature to 200-250° C. Reactor gases pass through a cyclone, thence through a flue and variable speed fan to a contact sulfuric acid plant gas purification system. Dry zinc concentrates enter the reactor at about the five-foot level and are fed by a 4" diameter screw conveyor which in turn is supplied by a feeder of the constant weight type equipped with a variable speed weight adjustment. A star gate arrangement seals the entry to the screw feeder.

Air is supplied to the reactor through a number of tuyeres inserted through the refractory floor of the reactor or alternatively through "spokes" of various lengths inserted horizontally through the wall of the reactor at floor top level.

Reactor bed overflow ports are provided at various levels, but for the results reported here the overflow ports at 5-foot and 3½-foot elevations are used.

To start a reactor of this type it is usually sufficient to preheat the brickwork by means of a bright cherry red temperature, turn on the air and start the concentrate feed. Some species of concentrate ignite more readily than others. Sometimes it is convenient to light off with a readily burnable high iron concentrate and then switch to the less readily combustible material. On occasion it has also been found helpful to preheat the air before it enters the reactor.

Temperature of the boiling bed is measured with thermocouples inserted through the reactor wall. In a properly operating bed there are no more than minor temperature differences from side to side and from top to bottom of the bed. Temperature is controlled by rate of feed addition. With dry concentrates and unheated air it is entirely practical to maintain a sulphide sulphur...
concentration in the bed of 24% with a 52% sulphur feed and to operate at 1000-1100° C. In Table 1 are presented data typifying the operation of the above-described reactor when purifying zinc sulphide concentrates. In runs 17A through D the gases emerging from the boiling bed are chilled before and during their passage through the cyclone deduster. In runs 19, 20A, and 20B, an attempt is made to conserve the heat in the gases between the time they leave the bed and the time they leave the cyclone. Heat conservation is accomplished by lagging the upper part of the reactor with heat insulation material and by using a refractory-lined cyclone. With bed temperature of 1050°C, the temperature of the gases leaving the cyclone is 950°C.

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<th>Run No.</th>
<th>Bed Depth, feet</th>
<th>Feed Rate, PPM</th>
<th>Airflow Rate, C.F. M. F.T.P</th>
<th>Bed Temperature, °C</th>
<th>Percent of Product Appearing in Bed Overflow</th>
<th>Percent of Product Appearing in Cyclone Header</th>
<th>Percent of Product Appearing in Cyclone Lights</th>
<th>Percent of Lead in Feed, percent</th>
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Concentrate feed enters the highest reactor in the series and passes downward through appropriately disposed overflow conduits to the gas agitated bed below. While theoretically any number of stages may be placed in series as described, practically it is considered that three such stages are the workable limit in the present state of the art, especially if bed temperatures of the order of 1000°C are employed.

In another arrangement it is found desirable to combine in stagewise relationship a boiling bed purification section and a boiling bed desulfurizing section. The operation of the boiling bed desulphurizer is the same as that previously described for the purifier except that an excess of air is employed in the desulphurizer whereas a stoichiometric deficiency of air, with respect to the rate of input of metallic sulphides, is maintained in the purification step. Temperature control in the desulphurizer can be achieved by varying the quantity of excess air or by introducing into the bed a vaporizable coolant such as water or drip liquor from nearby acid plant or by means of water or steam-generating tubes suitably placed. Automatic temperature control can be achieved by regulating the addition of coolant by means well-known in the art.

In desulphurizing in a gas agitated bed we have found it not only possible but entirely practical to operate with only a few percent stoichiometric excess of air and yet obtain calcine running consistently less than 1% total sulphur content. The gas from such a reactor contains approximately 12-14% SO₂. It is convenient to regulate the concentrate feed rate automatically by means of an oxygen analyzer such as the "Bennck Oxygen Analyzer" and controller. This device continuously samples and determines the oxygen content of the gases leaving the gas agitated desulfurizing bed and in turn adjusts the concentrate feed rate to maintain the oxygen content of the exit gases at a predetermined value. Good results are obtained even when the oxygen content is held as low as 1% O₂ in the exit gases.

When superimposing a purifying bed furnace on a desulphurizing bed furnace, it is necessary to adjust the gas flow rates to give a linear flow rate in each of the reactors in series of about 1 to 3 feet per second.

Again using lead as an example, it has been observed that the lead content of the solids which pass out of the purifying reactor with the gases tends to be associated with the smaller particles. This circumstance first stage is recycled through the delead by recycling the cyclone, boiler, and fluxes through the delead reactor or reactors and passing the gases through an electrostatic precipitator (Cottrell) for recovery of lead fume. For an extreme degree of lead concentration a multiple stage Cottrell is used. Material collected in the first stage is recycled through the deleaders while a high lead product is recovered from the second and third stages of the precipitator.

The gas agitated bed desulfurizer and oxidizer is a

Other modes of practicing the invention are described hereinafter.

It has been found that, for a given set of conditions, the higher the sulphide sulphur content of the bed of a first or purifying reactor, the greater is the degree of volatilization of impurities. In the simplified version of the invention described above—and which is entirely adequate for most applications—heat and temperature of the bed are developed by burning a portion of the sulphides in the bed. The amount of sulphide thus required to be burned can be substantially lessened by preheating the incoming air and by preheating the incoming zinc sulphide concentrates. For example, with air preheated to 800°C and concentrate Feed preheated to 500°C, the attainable sulphide sulphur content of the bed rises from about 24%, when operated under the conditions previously described, to about 29%.

Air preheating is conventionally accomplished by recuperative or regenerative means such as shell and tube heat exchanger or a pebble heater. We have found, however, that a much simpler and cheaper way of preheating air consists of burning the fuel, such as natural gas, under pressure right in the air duct (brick-lined) ahead of the tuyeres. The hotter the mixture of air and products of combustion, the less sulphide sulphur needs to be burned in the bed fluidized by these gases.

In certain applications all or a part of the heat required in the purification step is supplied by heat transfer surfaces suitably disposed in or around the boiling bed. Such heat transfer surfaces may consist of refractory or alloy tubes through the interior of which pass hot fluid, for example, flame and products of combustion from gas burner positioned at lower end of tube. Tubing and other heat transfer surfaces may also be heat intercooler by within contained electrical resistance elements. Alternatively, molten salts or molten metal or alloy at suitable temperature may be circulated through the tubes.

Further enhancement of impurity elimination may be attainable by stagewise arrangement of boiling beds. In such an arrangement, exit gases from the lowermost bed pass through tuyeres in a refractory septum separating the lowermost reaction chamber from the one immediately above it and fluidize the solids in the higher reactor.
highly desirable component of this invention if it is to be practiced in its most economical form. Other desulphurization methods suffer major disadvantages by comparison. Sulphide sulphur content of PDC from the purification step ordinarily may vary from a low of 10% to a high of 24 to 26% S. To dead roast this material in a multiple hearth roaster requires the combustion of large amounts of auxiliary fuel such as natural gas. The sulphur dioxide content of gas from such a roaster is of the order of 6 to 7% SO$_2$ by volume. Desulphurization of PDC in a suspension roaster also requires the use of substantial amounts of auxiliary fuel. The exit gas from this roaster would contain about 7 to 9% SO$_2$ by volume.

By carrying out the desulphurization step in a gas agitated bed, it is possible to roast PDC entirely autogenously and to produce an exit gas of the order of 12% SO$_2$ by volume. Compression of the SO$_2$ into so much smaller volume yields important economies in the operation of the subsequent gas purification equipment and catalyst system of the acid plant. For example, at 6% SO$_2$, the volume of gas required to make one ton of H$_2$SO$_4$ is about 128,000 cubic feet (at 95% conversion efficiency in the acid plant); whereas, at 12% SO$_2$, the volume required for one ton of H$_2$SO$_4$ is only 64,000 cubic feet.

Compared with suspension roasting, a gas agitated bed desulphurizer as disclosed in this invention, is relatively non-sensitive with respect to particle size of the PDC to be roasted. With a suspension roaster, on the other hand, it is necessary to comminate the feed to a high degree to insure satisfactory operation even with the use of auxiliary fuel.

When operated as a finish desulphurizer, the fluidized bed reactor is not efficient as a purifier. By the methods disclosed in this invention, it is now possible to accomplish the substantially complete elimination of those impurities which under controlled conditions of temperature and atmosphere will sublime or become volatile, such as compounds of lead, tin, cadmium, and the like. This invention provides means to accomplish both purification and desulphurization in an economical and commercially practicable manner. By doing the purification before the desulphurization we are able to utilize the gas agitated bed method with all its advantages; whereas, if, for example, non-deleaded concentrates were fed to the fluidized bed desulphurizer, only a lead-containing calcine would be produced.

We claim:

1. The process for purifying and desulphurizing zinc sulphide ore containing volatilizable compounds of metallic impurities such as lead, tin and cadmium which comprises passing an oxidizing gas in contact with the ore in a first oxidizing zone at a rate regulated to oxidize at least 10% and not more than 70% of the sulphite content of the ore and to maintain the temperature in at least a substantial portion of said first zone in the range of 850° C. to 1050° C., and thereafter completing the oxidation of the ore by transferring the partially oxidized ore to a second oxidizing zone through which an oxidizing gas is blown to maintain a bed of the ore in a fluidized state and to oxidize autogenously the remaining sulphide content of the ore.

2. The process as defined in claim 1 wherein said first zone comprises a plurality of interconnected, vertically superposed, horizontal sub-zones and said ore and gas are passed therethrough in countercurrent relation.

3. The process as defined in claim 1 wherein, in said first zone, said gas is passed upwardly through a bed of said ore at a velocity to maintain the bed in a fluidized state.

References Cited in the file of this patent

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<table>
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<tr>
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<th>Inventor(s)</th>
<th>Issue Date</th>
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,847,294
August 12, 1958

Carleton C. Long et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 14, line 15, for "sulphite" read -- sulphide --.

Signed and sealed this 21st day of October 1958.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents