United States Patent Office 2,756,136 Patented July 24, 1956

2,756,136

METHOD OF CHLORIDIZING SINTERING OF ZINCIFEROUS MATERIALS WITH ELIMINATION OF LEAD AND SIMILAR CONTAMINANTS

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No Drawing. Application June 14, 1952, Serial No. 293,683

10 Claims. (Cl. 75—5)

The present invention relates to the treatment of zinciferous ores and their concentrates that contain substantial amounts of one or more of the contaminating metals usually found present in varying minor amounts in zinc ores, particularly lead and cadmium, as well as in some cases one or more of the metals gold, silver and germanium, and sometimes also one of the metalloids arsenic and bismuth.

Various procedures have been proposed or practiced for eliminating contamiating metals and metalloids from zinc ores. According to the practice that is being most generally followed at the present time in the pyrometallurgical treatment of zinc sulfide ores, the ore, usually in the form of a flotation concentrate, is first subjected to a desulfurizing or roasting treatment in which the sulfur content is usually brought down to 3% or less. The roasted ore is then mixed with a small amount, say 4 to 12%, of a cabonaceous fuel high in fixed carbon, such as coke, anthracite or the like, and with sufficient sodium chloride or another appropriate chloridizing agent to satisfy the chlorine requirements of the lead, cadmium and any other metal or metalloid impurities that may be present and which may be caused to react with chlorine to form chlorides when the ore charge is appropriately heated and subjected to a conventional blast sintering treatment.

When the proportion of impurities is relatively small and an appropriate temperature is maintained during the blast sintering step, as disclosed for example in my earlier U. S. Pat. No. 1,999,209, it is possible in a single pass through the sintering machine to effect the complete removal of such contaminating metals as lead, cadmium, gold, silver and germanium from an oxidized, i. e., roasted, zinc ore or concentrate.

It often occurs, however, that zinc ores or concentrates carry higher proportions of lead and cadmium, in some instances up to 5% or more of lead and as much as 2% of cadmium. When zinciferous materials containing upward of about 1% of lead are treated, it becomes increasingly difficult to free such materials from lead and cadmium by the methods of pyrometallurgy without resort to expensive retreating operations. When a close examination is made to determine what takes place in the course of a typical chloridizing sintering treatment of zinciferous materials containing relatively high proportions of lead and cadmium, it is found that the relatively large amounts of lead and cadmium chlorides as well as other chemical compounds formed during the sintering treatment tend to condense within the lower part of the charge and especially in the zone adjacent the iron grate bars of the sintering machine. This results in the rapid clogging of the openings of the grate bars of the machine, and is followed by the practical cutting off of the air that should be drawn through the ore bed and the grate bars by the suction fan which aspirates the air required for the burning of the fuel content of the charge. The chloridizing sintering operation is thus brought to an end with the major portion of the metallic impurities, lead, cadmium, gold, silver, germanium, etc. left in the charge.

Under the usual conditions that obtain in the chloridizing sintering process as heretofore practiced, the successful operation is further hindered by the water required for the thorough mixing and distribution throughout the charge of the chloridizing and pelletizing agents. The presence of water in the pellets at the beginning of the sintering operation was also considered to be necessary in order to insure that the pellets would become sufficiently permeable to the blast gases when the water had been driven off in the initial stages of the sintering treatment. The heating and vaporizing of this added water as well as any combined water that may be present absorbs a relatively large percentage of the available calories liberated by the burning of the carbon and any other fuel components of the ore charge. This results in an important lowering of the potential temperature that otherwise would be reached by reason of the combustion of the fuel components of the charge. Under these conditions the temperature in the wind box of the sintering machine may be and usually is near the boiling point of water.

Furthermore, such operating conditions produce an incomplete sintering of the zinc ore charge, with the result that a large percentage of the charge is not converted into a satisfactory sinter and falls out as dust at the discharge end of the machine.

It has also been proposed to subject zinc ores carrying varying proportions of lead and other metal and metalloid impurities to a chloridizing sintering treatment wherein the ore carrying the impurities is disposed on a sintering bed in superposed relation to a layer of relatively low grade ore and then subjected to a down draft blast sintering treatment in which the lead and other impurities are vaporized and driven off from the high grade ore layer and recondensed in the layer of low grade ore. The layer of high grade ore is then scraped off and reduced in the customary manner. However, this process involves handling a relatively large amount of material and does not bring about a direct recovery of the lead and other metal and metalloid impurities separately from the ore, since they are in large part concentrated as their chlorides in the layer of low grade ore along with the zinc and any other values present in the low grade ore. Furthermore, the effectiveness of the blast diminishes as the porosity of the ore bed decreases due to the condensation of the chlorides.

The present invention has for a principal object to provide an improved chloridizing sintering process that is particularly adapted for the treatment of zinc ores that carry relatively high proportions of lead with or without one or more of the various other metals and metalloids that may happen to be present as impurities.

It is a further object of the invention to provide an improved chloridizing sintering process wherein it is made possible during the course of a hot blast chloridizing sintering treatment of zinc ores or concentrates carrying a relatively high proportion of lead and similar impurities to drive off and recover relatively free from zinc substantially all of the lead and similar impurities present in the ore or concentrate supplied to the process.

It is a still further object of the invention to provide an improved blast roasting and chloridizing sintering operation wherein a raw or unroasted sulfide ore or concentrate is treated in a combined roasting and sintering operation to drive off the sulfur as well as such metal impurities as lead and cadmium and produce a zinc oxide sinter that is substantially free of lead and cadmium and of sulfur compounds.

It is still another object of the invention to provide a process of desulfurizing raw or unroasted zinc sulfide ores and concentrates on a conventional sintering machine in which the desulfurizing reactions are greatly

speeded up as compared with the practices heretofore followed without bringing about undesired fusion or partial melting of the ore charge and without creating undesirable conditions as regards overheating of the grates or other metal parts of the sintering machine.

Other objects and advantages of the invention will appear as the description proceeds.

I have found as a result of extensive investigations that it is possible to prevent the condensation of the lead and cadmium chlorides in the portions of the ore bed adjacent the suction side thereof with consequent plugging of the interstices of the charge and the openings of the grate bars, provided the temperature within the ore bed, and especially in the portions thereof adjacent the wind box or suction side is increased sufficiently to insure that the volatile chlorides, such as lead chloride, that are formed and become vaporized during the sintering operation shall remain in vapor form and pass off as such without condensation within the ore bed. My investigations show that this condition will be realized in a down draft chloridizing sintering operation when using an appropriately prepared charge by so controlling the heating of the charge both by the amount of heat units supplied by the burners and the amount of heat units supplied by the fuel content of the charge as to insure that the temperature within the charge on the sintering machine as measured in the lower part of the ore bed adjacent but in spaced relation to the grates is brought to at least 1200° C. and preferably to or even above 1300° C. Stated differently, I have found that if the temperature of the gases and vapors leaving the wind box is increased to 400° C. or over, this will insure that the lead and cadmium chlorides will remain in vapor form and pass off leaving the remaining zinc oxide sinter substantially completely free of contaminating metal and metalloid impurities.

Under the conditions that obtain in a chloridizing sintering operation carried on in the conventional Dwight-Lloyd or Greenewalt type of sintering machine, it is not, however, a simple matter to increase the temperature of the ore charge to insure an adequate temperature throughout the sintering bed. Merely increasing the fuel content of the charge does not solve the problem. For example, if the carbon content is increased to 10% or more, there is a tendency to develop temperatures in the charge of such magnitude as to bring about softening or even melting of iron grate bars. Even when more heat resistant metals are substituted for the conventional iron grate bars, an inacceptable increase in maintenance cost may result.

I have found that it is possible to maintain relatively high temperature conditions in the ore charge without overheating the grate bars and other metal parts of the sintering machine and at the same time bring about striking improvements in the operating results, far beyond what were foreseeable on the basis of the expected influence of the higher temperature conditions alone, by introducing the modifications in the chloridizing sintering practice that are set out more fully below.

More specifically, I have found that improved results are obtained by limiting the amount of fuel incorporated in a roasted ore charge to 4½ to 6% or thereabouts of carbon or an equivalent amount of sulfide sulfur, based on the dry weight of the ore charge, forming the charge into a relatively thin bed of controlled porosity, and then increasing the amount of heat supplied by the ignition burners or an equivalent outside source of heat as distinguished from the combustion that takes place within the charge. When the ore charge is formed into a bed of suitable porosity as more particularly hereinafter described, the optimum thickness of the bed is a function of the draft produced by the fan and is also affected by the mechanical condition of the sintering machine, such as tightness of the enclosure for the traveling grate and the presence or absence of cracks and openings through which air may be drawn into the charge around the burners or directly into the wind box without passing through the ore charge on the grate. These factors also have an important bearing on the extent to which heat may be applied effectively to the ore charge from the burners, and the more efficiently the suction of the fan is applied to draw the products of combustion from the burners through the charge the thicker the bed may be and yet insure a satisfactory continuous progression of the sintering operation without plugging of the interstices of the bed with condensed chlorides and other compounds formed during the sintering.

In the operations hereinafter described and which were carried on with a twelve inch wide Dwight-Lloyd sintering machine which allowed considerable bypassing of inspirated air around the sintering grate and considerably lowered the vacuum that otherwise would have been obtainable, the most satisfactory sintering runs were conducted with the ore charge formed into a bed three inches in thickness. In a full sized sintering machine in a good condition of repair, the thickness of the bed may be from four to six inches when operating under similar suction conditions, and by increasing the suction the thickness of the bed may be increased. However, as contrasted with the present practices in the art of operating with ore charges formed into beds of 12 to 18 inches in thickness, the practice of my invention will usually involve operating with relatively thin beds. Nevertheless, the operating advantages of my invention greatly outweigh the decrease in the capacity of the sintering machine considered on a once through basis.

It is a further and important aspect of my invention that the operating conditions are so maintained as to insure that the products of combustion supplied by the ignition burners are caused to be drawn through the ore bed by appropriately controlling the suction in relation to the porosity of the charge so that not merely is there an impingement of the flame upon the exposed surface of the charge as it passes beneath the burners but also the hot combustion gases and an appropriate excess of air are drawn down into and through the bed. The proportion of fuel supplied by the burners is also very substantially increased as compared with prior practice and the burners are so operated as to create a powerful stream of combustion gases which together with the excess air bathe and permeate the pellets and rapidly bring the main body of the charge to a relatively uniform temperature. In other words, the burners act not only to rapidly ignite the charge but also to bring about a much greater and more direct application of heat to the inner portions of the charge without overheating, since the porosity of the charge insures that the combustion gases and the volatile compounds formed in the sintering operation are continuously withdrawn. The more uniform and higher temperatures created within the body of the charge also serve to promote vaporization of the chlorides of lead and other contaminants as they are formed and to maintain such chlorides in the vapor state. In addition, the combustion gases act to entrain the chlorides and other volatile compounds and carry them along into the wind box from which they are led to appropriate recovery and separating apparatus such as electrostatic separators, preferably of the wet type, wherein the chlorides are precipitated and collected.

I have found, for example, that the increased heat input from a source outside of the ore charge may be advantageously brought about by increasing the burner capacity of the ignition furnace that is ordinarily disposed over the head end of the sintering machine and also using a fuel gas of high thermal value. Preferably a pair of ignition burners are disposed adjacent one another at the head or feed end of the sintering machine. With such a disposition and by supplying appropriate amounts of a high quality fuel such as propane to the burners, it is possible to develop a temperature within the ore bed, close to but

in safely spaced relation to the grate, of the order of 1200° C. and over, or correspondingly a temperature of 400° C. and over in the wind box, provided the ore is suitably pelletized and the voids and interstices between the ore pellets or agglomerants are not allowed to plug up with condensed chlorides.

In order further to promote relatively high temperatures throughout the charge and particularly in the portion thereof close to the grate bars, I remove substantially all moisture from the charge after the ore has been pelletized and preferably while the ore charge is disposed in situ on the bed of the sintering machine. Advantageously, the sintering machine may be modified by introducing a drying section ahead of the sintering hearth with a separate suction fan connected to the drying hearth and discharging directly to the atmosphere. The drying hearth will usually be provided with burners to supply heat to promote the drying action, but ignition of the combustible components of the charge is not initiated in this stage. Instead of providing a drying section in the sintering machine ahead of the ignition burners, the pellets may be dried in a known type of dryer before they are fed to the sintering machine.

In preparing zinc ores or concentrates for the chloridizing sintering treatment, I also find that it is advantageous as a preliminary to the pelletizing step, to add to the otherwise suitably proportioned mixture of zinc ore, carbon and chloridizing agent (preferably sodium chloride) from 2½ to 6% by weight of crude zinc sulfate or ferrous sulfate, based on the dry weight of the charge, together with a suitable proportion of sinter fines or of crushed sinter as returns. An amount of chloridizing agent approximating 100 to 150% of the stoichiometric requirement for converting all of the lead and cadmium into chlorides will be ordinarily used, but this proportion may be increased in special cases. The chloridizing agent and the sulfate addition are preferably dissolved in water before addition to the other ingredients of the charge.

The proportion of returned sinter fines or crushed sinter may be varied considerably and may be omitted entirely in the initial chloridizing sintering step when the process is being practiced by subjecting the ore to more than one pass through the sintering machine. Usually when treating an ore containing around 2–3% of lead, an addition of sinter fines and/or crushed sinter equal to 25% to 50% of the dry weight of the charge is recommended. The proportion should be increased when treating ores containing higher proportions of lead and cadmium since this reduces the tendency of the chlorides of these metals to recondense in the ore bed rather than to be carried away in the blast gases drawn through the charge.

Following the various additions the mixture is pelletized in a drum pelletizer. The pellets are then screened and those larger than one-fourth inch are crushed and returned to the pelletizing drum. The ore charge is then dried to the point where substantially all moisture is eliminated. Preferably the drying is carried on after the pellets have been fed to the sintering machine and while they are disposed in situ on the sintering bed.

EXAMPLE 1

Roasted ore

In one specific instance, using a roasted zinc sulfide ore concentrate assaying 2.65% lead and 1.85% cadmium, and having a fineness of approximately 100% −16 mesh, the concentrate was mixed with anthracite coal, crushed sinter returns, salt, ferrous sulfate and water to form a charge of the following proportions:

Roasted zinc concentrate, −16 mesh	58 lbs.
Crushed sinter returns	42 lbs.
Anthracite coal (89% fixed carbon, 2% sulfur)	5 lbs.
Sodium chloride	4 lbs. 5 ozs.
Ferrous sulfate	6 lbs. 6 ozs.
Water	7 lbs.

The charge was mixed in a pelletizing drum, and the resulting pellets were then dried and screened over a 4-mesh sieve. The pellets were thereafter fed to a laboratory twelve-inch Dwight-Lloyd sintering machine and deposited on a previously prepared hearth layer of one-half inch thickness composed of plus one-fourth inch sinter from a previous run on the same type of concentrate. This sinter had been produced under somewhat different operating conditions and contained 0.29% lead and no cadmium. The thickness of the ore charge was three inches inclusive of the one-half inch hearth layer.

The machine as operated gave a suction through the bed equivalent to a vacuum of fourteen and one-half inches of water, and the traveling grate moved at the rate of one and one-half inches per minute first past two high intensity ignition burners supplied with propane gas and positioned one after the other at the feed end of the machine with their centers disposed 20 inches apart and then along the rest of the length of the machine. A higher vacuum would have been desirable but was not attainable with the condition of the machine as it was. The first pallet was taken off the machine 34 minutes after the beginning of the run and the last pallet was removed 1 hour and 6 minutes after the start of the operation. The sinter produced had a very good appearance and came off the pallets in good cakes. A sinter was formed all the way to the grates, and the grate bars stayed very clean. The sintering was accompanied by very heavy fuming. A temperature of 382° C. was attained in the wind box and the highest stack temperature recorded was 227° C. The temperature of the charge as measured 1" above the level of the grate was 1299° C. Analysis of the sinter showed that only 0.01% lead remained at the conclusion of the run. The cadmium had been completely removed. A small amount of fines, 5½ lbs., from the sintering operation assayed 0.22% lead. The yield of good sinter was 90 lbs.

EXAMPLE 2

Roasted ore

In another series of tests, using a roasted zinc sulfide concentrate assaying 5.50% lead and 0.24% cadmium, and containing about 0.6% of sulfide sulfur and 2.4% of sulfate sulfur, principally as calcium and magnesium sulfates, a first chloridizing sintering run was made with an ore charge made up as follows:

	Pounds
Roasted zinc concentrate, −18 mesh	300
Anthracite coal containing 89% fixed carbon and 2% sulfur, crushed to −10 mesh	15
Ferrous sulfate	18
Sodium chloride	9
Water	30

The ferrous sulfate and sodium chloride were dissolved in water and then mixed with the other ingredients in a pelletizing drum. The pellets were then dried sufficiently to permit of screening and then were screened over a 4-mesh sieve. The pellets passing the 4-mesh sieve were then fed to the sintering machine and disposed on the sintering bed as a layer two and one-half inches thick in superposed relation to a one-half inch layer of relatively coarse chloridized sinter from a previous operation. This bottom layer consisted of sinter granules which remained on a 4-mesh sieve. The moist pellets were then further dried in situ by causing hot air to be drawn through the charge until substantially all moisture was removed. Thereafter the charge was sintered under similar operating conditions as were maintained in the test previously described. The resulting sinter carried only 1.0% lead and no cadmium.

A second run was then made with an ore charge proportioned as follows:

	Pounds
Roasted zinc concentrate of the same composition and fineness as used in the first test under this example above described	150
Sinter returns, i. e., the sinter produced in the first test of this series and crushed to —18 mesh	150
Anthracite coal	18
Ferrous Sulfate	15
Sodium chloride	7
Water	30

After mixing and pelletizing in the same manner as described above, the pellets were screened and the —4 mesh pellets were fed to the sintering machine and thoroughly dried in situ to substantially completely remove all water present therein. They were thereafter subjected to sintering under similar conditions as were maintained in the next previous test. The sinter resulting from this run contained 0.67% lead with no cadmium.

In order to further purify the concentrate with respect to lead, the sinter from the second test of this series was crushed and re-sintered after first mixing and pelletizing with fuel and reagents in the following proportions:

Sinter from second test, crushed to —18 mesh	270 lbs.
Anthracite coal	12 lbs.
Ferrous sulfate	13½ lbs.
Sodium chloride	2 lbs. 6 ozs.
Water	19 lbs.

As before, the pellets were reduced to complete dryness after being fed to the sintering machine and before initiating the blast-sintering operation. The charge was then sintered under the same operating conditions as were maintained in the first two tests of this series. The resulting sinter contained only 0.04% lead. It was also noted that the sulfur, both sulfide and sulfate sulfur, had been completely removed.

In all of the tests carried on under this example and described above, double ignition burners supplied with propane gas were used and the heat input was regulated to produce a temperature of about 1300° C. as measured by thermocouples inserted in the charge about one-half inch above the sintering grate.

Combined desulfurizing and chloridizing sintering

The invention is also applicable in the treatment of raw, unroasted zinc sulfide ores and concentrates, and has the advantage over the prior practice of desulfurizing of raw zinc sulfide ore and concentrates on a sintering machine, sometimes referred to as the Robson process, that it is possible to speed up very materially the desulfurizing operation. Stated differently, it is possible materially to reduce the number of sintering treatments required to bring about elimination of the sulfur.

According to the prior practice of desulfurizing raw zinc sulfide concentrates on a sintering machine, it is customary to conduct the operation so as to remove from 4½ to 5 sulfur units in a single passage through the sintering machine; otherwise, there is danger that the oxidation reaction will generate so much heat as to fuse or partly melt the ore charge and thus hinder further reduction of the sulfur content of the ore. Consequently, under the Robson practice it is usually necessary to pass the ore five or more times through the sintering machine when it is the usual type of zinc sulfide concentrate carrying 30 to 31% sulfur. In the Robson process control of the oxidation is usually brought about by mixing the raw zinc sufide concentrate with sufficient previously desulfurized sinter of the same or a similar ore to reduce the sulfur present to a sufficient amount for the blast roasting operation. It will be appreciated that this involves treating over and over again a relatively large amount of materials and requires a relatively large sintering machine capacity for a given output of roasted concentrate.

The following is a typical example of an operation of my process as applied to the treatment of raw zinc sulfide ore concentrates:

EXAMPLE 3

Raw sulfide ore

The charge was made up of the following proportions using a raw zinc sulfide ore concentrate carrying 2.65% lead, 1.85% cadmium and approximately 31% of sulfur, with the balance principally zinc, with minor amounts of iron and of calcium and magnesium sulfates:

Raw (unroasted) zinc sulfide concentrate	58 lbs.
Sinter returns (roasted and chloridized ore)	42 lbs.
Ferrous sulfate	3 lbs. 2 ozs.
Salt	4 lbs. 5 ozs.
Water	7 lbs.

As in the tests described earlier in this specification, the ferrous sulfate and salt was dissolved in the water before addition to the ore charge. After mixing, pelletizing and screening, the screened pellets were fed to a sintering machine provided with a drying hearth section where they were first subjected to a controlled drying treatment designed to drive off the water and reduce the charge to substantially complete dryness while the pellets were disposed in situ on the traveling bed. The dry charge was then passed to the head of the sintering section proper and there subjected to a blast-roasting treatment under similar conditions as to heat input and other operating factors as were maintained in the operations using a roasted concentrate. Likewise as in the tests previously described, the overall thickness of the ore bed was kept at about three inches with a bottom layer of previously roasted and chloridized sinter of about one-half inch thickness and consisting of sized particles insuring adequate porosity, plus 4-mesh. The product resulting from the sintering run over the sintering machine carried only from 0.01 to 0.02 lead and no cadmium and was substantially free from sulfur. Analysis of the fume recovered in this operation showed a lead content of 33.56% with 22.0% cadmium. The proportion of zinc was not precisely determined but was estimated to be in the neighborhood of 12%.

A sinter from a previous chloridizing sintering run using the same ore or concentrate is preferably used in forming the bottom layer. This has the advantage that it is not necessary to effect any separation of the sinter as between the portion disposed in the bottom layer and that produced in the superimposed portions of the charge. However, it will be understood that the desulfurizing and chloridizing reactions will proceed to the same extent regardless of the nature of the bottom layer provided it is sufficiently coarse and porous to be readily permeable by the blast gases and serves to support the sulfides of the charge in spaced relation to the sintering grates.

It was observed that in all cases, whether the zinciferous material had been previously roasted or was in the form of raw sulfides, the proportion of zinc carried over in the fume was relatively low as compared with the amount carried over in the fume from a conventional chloridizing sintering operation conducted according to the prior art commercial practices.

A further advantage resulting from the practice of my invention in the combined desulfurizing and chloridizing sintering of zinc sulfide ores and concentrates resides in the fact that, in contradistinction to the Robson process and similar practices, the sulfur-containing gases produced in the combined desulfurizing and chloridizing sintering step may contain 8 to 10% sulfur without any re-cycling and are, therefore, sufficiently rich in sulfur to make them suitable for use in the manufacture of sulfuric acid either by the chamber or the contact process. Even when a somewhat higher proportion of sin-

fer returns is used than was the case in Example 3, the concentration of sulfur dioxide in the gases passing along with the fume will be sufficiently high to make it commercially feasible to recover the surfur dioxide for use in the manufacture of sulfuric acid. Usually, however, when it is aimed to utilize the sulfur content of the gases, it is preferred to regulate the proportion of sinter returns in relation to the sulfur content of the unroasted sulfide ore or concentrates so as to insure that the charge shall contain at least 15% of sulfur as the sole fuel component of the charge. It will be understood, of course, that all of the chlorides and other objectionable impurities must be removed from the gases before they are used to make sulfuric acid.

It will be understood that various changes may be made in the details of the procedures outlined above without departing from the invention which is not to be deemed as limited otherwise than is indicated by the language of the appended claims. For example, reference has been made herein to the addition of zinc sulfate or ferrous sulfate to aid in binding the ore particles during the pelletizing step. It is to be understood that other binding agents may be employed which do not give rise to undesired reactions in the subsequent desulfurizing and chloridizing sintering treatment or a subsequent chloridizing sintering treatment alone, as the case may be. As examples of other suitable binding agents mention is made of molasses, flour, waste sulfite liquors, bentonite and other clays.

It will also be understood that the drying of the pelletized ore preliminary to the sintering step may be omitted, in which case the duration of the blasting operation will usually need to be prolonged or else additional fuel will need to be provided in the charge. However, the operation is speeded up and very much improved by subjecting the ore pellets to drying to substantially complete dryness either in situ or in some other suitable manner.

It is to be understood that the term "ore" as used in this specification and in the appended claims is inclusive of the zinc ores in their natural state and also in their beneficiated form customarily referred to as "concentrates."

I claim:

1. In the process of forming a chloridized sinter of zinciferous material containing in excess of 1% of lead to eliminate lead and any other associated metal and metalloid impurities therefrom wherein the zinciferous material is prepared for the sintering treatment by subjecting a mixture of said ore, fuel and a chloridizing agent to a pelletizing treatment with addition of sufficient water and a binder to bind the mixture into self-sustaining pellets; the improvement which consists in increasing the porosity of the charge in a step preliminary to the ignition of the charge by drying the pellets to substantial dryness while disposed in situ on a sintering grate and thereby concomitantly decreasing the fuel requirements of the charge, thereafter applying a blast flame to the upper side of said charge and applying suction at the grate side to draw air and combustion products through said charge while the charge is disposed in a relatively thin layer on the sintering grate, the suction and the amount of fuel being supplied to the blast flame being regulated so as to maintain a temperature of at least 1200° C. as measured approximately one inch from the bottom of the bed as it is disposed on the sintering grate but below the temperature at which fusion of the charge will occur, thereby chloridizing and vaporizing the lead and other associated metal and metalloid impurities, and withdrawing said vaporized chlorides as formed.

2. In the recovery of zinc from zinciferous materials containing, in addition to zinc at least 1% of lead and other associated metal impurities, the improvement which comprises admixing the zinciferous material with a chloridizing agent, from 4 to 6% carbon, and sufficient water and a binder to form the mixture into self-sustaining pellets, forming the charge into pellets, disposing said pellets in a layer having a thickness of 4 to 6 inches on a sintering bed in superposed relation to a highly porous layer of sinter of sufficient porosity to inhibit plugging of the grate apertures and sufficient thickness to prevent overheating of the sintering grate during the blasting step, in a step preliminary to the ignition of the charge drying the pellets to substantially complete dryness while disposed in situ on said bed, directing an oxidizing flame onto the exposed surface of said bed while applying suction to the opposite side thereof, and regulating the oxidizing flame in relation to the thickness and porosity of the bed and to the reduced pressure created at the opposite side of said bed so as to insure a relatively uniform temperature throughout the body of said charge and a temperature in the lower part of said charge taken at approximately one inch from the grate of about 1200–1300° C., said oxidizing flame being further so regulated as to prevent fusion of the charge, thereby driving off lead and other associated metal chlorides substantially as fast as formed, and recovering said chlorides.

3. In the recovery of zinc from its sulfide ores the method of desulfurizing and chloridizing said ore in a single operation with simultaneous elimination of lead and any other associated metal and metalloid impurities, which comprises mixing said ore, previously reduced to finely divided form with finely divided substantially desulfurized zinc oxide sinter and with sufficient chloridizing agent to satisfy the chlorine requirements of the non-zinc metal impurities in a subsequent chloridizing blast-sintering treatment of the charge, regulating the proportion of sulfide ore in said charge so as to provide at least 15% of sulfur as the sole fuel component of the charge, subjecting the mixture to a pelletizing treatment with addition of sufficient water and a binder to bind the mixture into self-sustaining pellets, disposing said pellets in a bed of 4 to 6" thickness on a sintering grate, in a step preliminary to ignition of the charge passing heated gases through said bed until the pellets have been reduced to substantially complete dryness, and thereafter simultaneously chloridizing and blast-sintering the pelletized ore by directing an oxidizing flame on to the exposed surface of said bed while applying suction to the opposite side thereof to maintain a temperature of at least 1200° C. as measured approximately one inch from the bottom of the bed as it is disposed on the sintering grate but below the temperature at which fusion of the charge will occur.

4. In the recovery of zinc from zinciferous materials containing in excess of 1% of lead, the method of eliminating lead and other associated metal and metalloid impurities therefrom which comprises oxidizing the metal values of the ore, crushing the oxidized ore and adding a chloridizing agent and sufficient carbon to bring the fuel content of the charge within the carbon equivalent range of 4 to 6% based on the dry weight of the ore charge, subjecting the mixture to a pelletizing treatment with addition of sufficient water and a binder to bind the mixture into self-sustaining pellets, in a step preliminary to ignition of the charge heating said pellets under drying conditions to drive off substantially all of the free water contained therein, disposing the pellets as a bed on a traveling sintering grate, thereafter simultaneously chloridizing and blast-sintering said bed of pelletized ore by applying a blast flame to the upper side of said bed and applying suction at the grate side to draw air and combustion products through said bed, regulating the suction and the amount of fuel supplied to the blast flame to establish and maintain a temperature of at least 1200° C. as measured approximately one inch from the bottom of the bed as it is disposed on the sintering grate but below the temperature at which fusion of the charge will occur, thereby chloridizing and vaporizing substantially all of the lead and other associated metal and metalloid impurities, and withdrawing said vaporized chlorides as formed.

5. The method according to claim 4 wherein the thick-

ness of the ore charge on the sintering bed is maintained within the range 4 to 6 inches.

6. In the recovery of zinc from its ores containing in excess of 2% lead, the method of eliminating lead and other associated metal and metalloid impurities therefrom which comprises oxidizing the metal values of the ore, crushing the oxidized ore and admixing therewith a substantial proportion of sinter fines relatively low in lead and other metal impurities obtained from a preceding chloridizing sintering treatment, adding a chloridizing agent and sufficient carbon to bring the fuel content of the charge within the carbon equivalent range of 4 to 6% based on the dry weight of the ore charge, subjecting the mixture to a pelletizing treatment with addition of sufficient water and a binding agent to bind the mixture into self-sustaining pellets, in a step preliminary to ignition of the charge heating the pellets while disposed in situ on a traveling sintering grate to drive off substantially all of the water, thereafter simultaneously chloridizing and blast-sintering the pelletized ore by applying a blast flame to the upper side of said bed and applying suction at the grate side to draw air and combustion products through said bed, regulating the suction and the amount of fuel supplied to the blast flame to establish and maintain a temperature of at least 1200° C., as measured approximately one inch from the bottom of the bed as it is disposed on the sintering grate, but below the temperature at which fusion of the charge will occur, thereby chloridizing and vaporizing substantially all of the lead and other associated metal and metalloid impurities, and withdrawing said vaporized chlorides as formed.

7. In the recovery of zinc from its sulfide ores, the method of desulfurizing said ore with simultaneous elimination of lead and any other associated metal and metalloid impurities which comprises mixing said ore previously reduced to finely divided form with finely divided substantially desulfurized zinc oxide sinter and with sufficient chloridizing agent to satisfy the chlorine requirements of the lead and any other associated metal and metalloid impurities in a subsequent chloridizing blast-sintering treatment of the ore, the proportion of desulfurized sinter being sufficient to prevent overheating of the charge during the subsequent blast-sintering treatment, subjecting the mixture to a pelletizing treatment with addition of sufficient water and a binder to bind the mixture into self-sustaining pellets, removing any fines and oversized pellets, disposing the remaining pellets on a traveling sintering grate, in a step preliminary to ignition of the charge heating the pellets under drying conditions in situ as a bed on said grate to drive off substantially all of the moisture present therein, thereafter simultaneously chloridizing and blast-sintering the pelletized ore by applying a blast flame to the upper side of said bed and applying suction at the grate side to draw air and combustion products through said bed, regulating the suction and the amount of fuel supplied to the blast flame to establish and maintain a temperature of at least 1200° C., as measured approximately one inch from the bottom of the bed as it is disposed on the sintering grate, but below the temperature at which fusion of the charge will occur, thereby chloridizing and vaporizing substantially all of the lead and other associated metal and metalloid impurities, and withdrawing said vaporized chlorides as formed.

8. In the recovery of zinc from its ores containing in excess of 1% of lead, the method of eliminating lead and any other associated metals and metalloid impurities therefrom which comprises admixing the ore with a chloridizing agent, carbon and sufficient water and a binder to form the mixture into self-sustaining pellets, forming the mixture into pellets and disposing said pellets in a relatively thin layer on a sintering bed in superposed relation to a previously deposited highly porous layer of sintered ore of sufficient thickness and porosity to inhibit plugging of the grate apertures and prevent overheating of the sintering grates during the blasting step, in a step preliminary to ignition of the charge drying said pellets to substantially complete dryness while disposed in situ on said bed, and thereafter sintering said pellets by applying an oxidizing flame to the upper side of said bed and applying suction at the grate side to draw air and combustion products through said bed, and regulating the suction and the amount of fuel supplied to the blast flame to establish and maintain a temperature of at least 1200° C., as measured approximately one inch from the bottom of the bed as it is disposed on the sintering grate, but below the temperature at which fusion of the charge will occur, thereby chloridizing and vaporizing substantially all of the lead and other associated metal and metalloid impurities, and withdrawing said vaporized chlorides as formed.

9. In the recovery of zinc from zinciferous materials containing, in addition to zinc, in excess of 2% of lead and also cadmium and other metal impurities, the improvement which comprises admixing with the zinciferous material a zinc oxide sinter relatively low in lead and other metal impurities, adding a chloridizing agent in an amount sufficient to satisfy the chlorine requirements of the non-zinc metal impurities in a subsequent chloridizing sintering treatment of the charge, and so regulating the proportions of zinc oxide sinter and of fuel present in the charge as to insure that the temperatures developed within the charge during a blast sintering operation will not cause fusion of the charge, subjecting the mixture to a pelletizing treatment with addition of sufficient water and a binder to bind the mixture into self-sustaining pellets, in a step preliminary to ignition of the charge drying the pellets to substantial dryness while disposed in situ as a bed in a relatively thin layer on a traveling sintering grate, thereafter simultaneously chloridizing and blast-sintering the pelletized ore by applying a blast flame to the upper side of said bed and applying suction at the grate side to draw air and combustion products through said bed, regulating the suction and the amount of fuel supplied to the blast flame to establish and maintain a temperature of at least 1200° C., as measured approximately one inch from the bottom of the bed as it is disposed on the sintering grate, thereby chloridizing and vaporizing the lead and other associated metal and metalloid impurities, and withdrawing said vaporized chlorides as formed.

10. In the recovery of zinc from its sulfide ores, the method of desulfurizing and chloridizing said ore in a single operation with simultaneous elimination of lead and any other associated metal and metalloid impurities, which comprises mixing said ore previously reduced to finely divided form with finely divided substantially desulfurized zinc oxide sinter and with sufficient chloridizing agent to satisfy the chlorine requirements of the lead and any other associated metal and metalloid impurities in a subsequent chloridizing blast-sintering treatment of the ore, regulating the proportion of sulfide ore in said charge so as to provide at least 15% sulfur as the sole fuel component of the charge, subjecting the mixture to a pelletizing treatment with addition of sufficient water and a water dispersible binder to bind the mixture into self-sustaining pellets, disposing the pellets in a relatively thin bed on a sintering grate, in a step preliminary to ignition of the charge drying the pellets to substantial dryness, and thereafter simultaneously chloridizing and blast-sintering the pelletized ore by applying a blast flame to the upper side of said bed and applying suction at the grate side to draw air and combustion products through said bed, regulating the suction and the amount of fuel supplied to the blast flame to establish and maintain a temperature of at least 1200° C., as measured approximately one inch from the bottom of the bed as it is disposed on the sintering grate, but below the temperature at which fusion of the charge will occur, thereby chloridizing and vaporizing the lead and other

associated metal and metalloid impurities, and withdrawing said vaporized chlorides as formed.

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