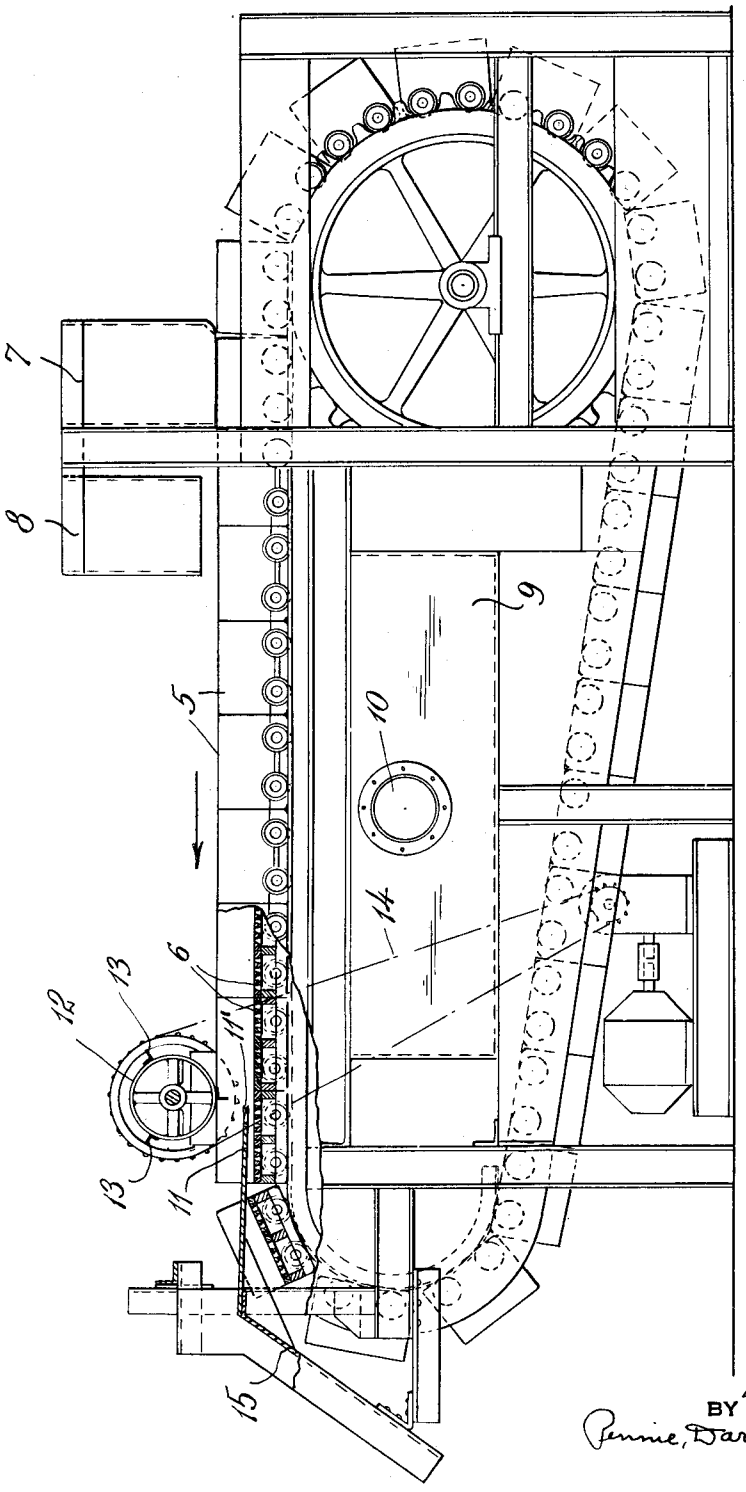
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TREATMENT OF ZINCIFEROUS MATERIALS CONTAINING LEAD AND/OR CADMIUM

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INVENTOR
LLOYD E. TETER
BY
Pennie, Davis, Marvin & Edmonds
ATTORNEYS

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LLOYD E. TETER, OF PALMERTON, PENNSYLVANIA, ASSIGNOR TO THE NEW JERSEY ZINC COMPANY, OF NEW YORK, N. Y., A CORPORATION OF NEW JERSEY

TREATMENT OF ZINCIFEROUS MATERIALS CONTAINING LEAD AND/OR CADMIUM

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This invention relates to the treatment of zinciferous materials containing lead and/or cadmium and perhaps other contaminating metals. The invention aims to provide an improved method of effecting a substantial removal or elimination of lead and/or cadmium and other contaminating metals from such zinciferous materials.

Lead and cadmium are common contaminants of zinc ores and their concentrates. In addition, certain metals such as tin, antimony, bismuth, etc., are commonly present in zinc ores. Appreciable amounts of these contaminating metals find their way into the product of the zinc recovery operation and thereby contaminate the zinc product obtained therefrom. Lead and cadmium are technically the most commonly recognized contaminants of zinc ores and their concentrates, and when present in relatively small amounts economically prevent the production of high grade zinc products, such as zinc metal, zinc oxide, zinc dust, etc., substantially free of lead and cadmium. A relatively large tonnage of zinc concentrates containing up to 5% of lead and substantial percentages of cadmium are available for zinc smelting, but it appears that no entirely satisfactory pyrometallurgical method has heretofore been proposed for effecting a substantial removal or elimination of lead and/or cadmium from such zinc concentrates.

The object of the present invention is to provide a pyrometallurgical treatment for zinciferous materials containing lead, cadmium or other contaminating metal in the course of which a substantial removal of the contaminating metals is effected, thereby making possible the recovery of a purer and more desirable zinc product from the zinciferous material than could otherwise be obtained. Since, in the practice of the invention all of the contaminating metals appear to behave similarly, I will herein more particularly describe the invention with respect to the elimination of lead and cadmium. The invention may be practiced primarily for the elimination of lead without special regard to the elimination of other metals, or it may be practiced for the elimination of any one or more of the contaminating metals. In general, the elimination of substantially all of the lead from the zinciferous material by the practice of the invention will at the same time effect a substantial elimination of such others of the contaminating metals as may be present.

The present invention is based on my discovery that in blast roasting a charge of zinciferous material a substantial segregation or concentration of lead and cadmium takes place in any relatively cool area of the charge. Based on this discovery, my present invention involves subjecting the zinciferous material in the presence of a suitable combustible agent to a blast-roasting treatment in the course of which a substantial amount of lead and/or cadmium segregates in a relatively cool area of the material, and then mechanically separating such area or portion in which lead and/or cadmium has so segregated from the remainder of the material. Since the volatilization of lead and cadmium is very materially promoted by the presence of a chloridizing agent, if such a chloridizing agent be added the concentration or segregation of lead and cadmium in the relatively cool areas of the charge will be materially increased.

The present invention is particularly applicable to the treatment of flotation concentrates. On account of their fine state of subdivision, such concentrates are difficult to handle, more particularly in the smelting operation. In accordance with the present invention, these concentrates are first subjected to an ordinary desulfurizing or roasting treatment, in the course of which the sulfur content is preferably reduced to around 2–3%. The roasted concentrate is then mixed with a small amount of carbonaceous

fuel, such as coke, coal, or the like, and then subjected to a sintering operation by passing a combustion supporting gas through an appropriately supported layer of the material in the course of which operation a substantial amount of lead and/or cadmium is removed from the zinciferous material by volatilization and condenses in part near the cooler layer at the gas-exiting surface. The portion in which the lead and cadmium have segregated is then separated from the remainder of the resulting sintered material in any appropriate way.

Chloridizing agents of any kind added to or brought in contact with the zinciferous material react with the lead and cadmium present therein to form volatile chlorides. These chlorides, and thus the lead and cadmium, are removed in part from the zinciferous material by volatilization, and condense in part near the blast-exiting surface of the charge.

The practice of the present invention in its complete and preferred aspect provides a combination of the following features:—

1. A preliminary roasting operation followed by a roasting treatment with a small amount of carbonaceous material on a sintering machine.

2. Chloridizing sintering, that is, the combination of a sintering blast roast with a chloridizing roast.

3. Fractional volatilization of lead chloride and cadmium chloride.

4. Completion of the removal of the lead and cadmium by (*a*) shaving off the bottom portion of the charge into which lead and cadmium have concentrated and by (*b*) screening out the pulverulent cadmium-bearing material on the top of the sintered charge.

As a result of this treatment the finely divided ore is sintered, thus agglomerating it and rendering it easier to handle than the original roasted concentrate. Furthermore, desulfurization is completed, the remnant of sulfur in the roasted concentrate (2 to 3%) is substantially removed or reduced to less than 0.5% by the blast-roasting treatment. And finally a very effective removal of lead and cadmium is accomplished, thereby permitting the production of purer and more desirable zinc products from the zinciferous material.

Any zinc expelled as oxide from the zinciferous material during the blast-roasting treatment, together with the volatilized lead and cadmium, may be recovered in the form of fume by passing the waste gases from the sintering machine through any appropriate form of fume collector, such, for example, as a bag-house.

The preliminary roasting of the zinc ore may be carried out in any appropriate roasting apparatus. I prefer to conduct this roasting operation so as to leave not more than from 2 to 3% of sulfur in the roasted product. If desired, however, a larger percentage of sulfur may be left in the product of this preliminary roasting operation and may be utilized as the combustible agent or fuel in the subsequent blast-roasting treatment. While I prefer to carry out the blast-roasting treatment in the presence of a suitable chloridizing agent, the advantages of the invention, although in lesser degree, are secured in the absence of the chloridizing agent.

While the invention is of peculiar advantage for the treatment of zinc sulfide ores or concentrates in a fine state of subdivision, such as flotation concentrates, it is equally applicable to the treatment of other finely divided zinciferous material containing lead and/or cadmium.

In carrying out the invention in its preferred form, the zinciferous material containing lead and cadmium, such as a roasted flotation concentrate, is mixed with 4 to 12% of coal and 2 to 5% of sodium chloride or calcium chloride or other chloridizing agent. The mixture is then charged into a sintering machine of the blast roasting type, such, for example, as the well-known Dwight-Lloyd sintering machine. The pallets of the sintering machine are, as is usual, protected by a hearth layer or grate dressing of previously treated charge. This hearth layer is advantageously prepared of sinter or inert material through ½ inch screen and on ¼ inch screen. The charge of the sintering machine is ignited by an oil burner or other appropriate means and then sintered and roasted by an air blast drawn through the charge. In the Dwight-Lloyd sintering machine, this air blast is drawn downwardly through the charge on the pallets. Thus, with the Dwight-Lloyd sintering machine, a very substantial segregation or concentration of lead and cadmium occurs in the bottom inch or half-inch of the charge and hearth layer.

The surface portion in which lead and cadmium have concentrated is then removed from the remainder of the resulting sintered charge. Thus, with the Dwight-Lloyd sintering machine substantial removal of lead and cadmium can be effected by separating the bottom inch or half inch of the sintered charge from the overlaying portion. This separation may be effected in any appropriate manner.

The single figure of the accompanying drawing diagrammatically represents a blast roasting or sintering machine of the Dwight-Lloyd type equipped with a sinter separating means for practicing the present invention. The sintering machine comprises an endless series of traveling pallets 5 provided with perforated grates or hearths 6. A feed hop-

per 7 is provided for charging the zinciferous material into the pallets and an oil burner hood 8 is provided for igniting the charge. Air is drawn downwardly through the charge into a wind-box 9 and to an outlet 10 by a fan (not shown).

The pallets 5 move in the direction of the arrow. A horizontal knife 11 is appropriately supported near the discharge end of the sintering machine. This knife is positioned at such a level as to shave off the bottom inch or half-inch of the charge and the hearth layer. The sintered charge is forced against this knife by the motion of the pallets and is held down against the grate by a roller 12 appropriately mounted above the charge and provided with flanges 13 to force the charge against the knife. The roller is driven by a sprocket wheel and chain 14 at a slightly greater peripheral speed than the speed of the pallets.

It has been found advantageous to equip the knife 11 with saw teeth 11', which may be beveled alternately up and down. It is also advantageous to produce a reciprocal motion of the knife, either back and forth parallel to the motion of the charge, in which case the knife acts as a chisel, or to and fro at right angles to the motion of the charge, in which case the knife acts as a saw.

The portion of the sintered charge above the knife 11 is advanced into a chute 15 and appropriately collected. That portion of the sintered charge beneath the knife 11 moves along with the pallets and is discharged therefrom and appropriately collected, as the pallets turn over in their return to the charging end of the machine. This portion of the charge collected from the pallets is relatively rich in lead and cadmium, and may be appropriately treated for the recovery therefrom of its lead and cadmium content.

A certain amount of lead and cadmium is found at the top surface of the sintered charge, partly in the form of a soft pulverulent sublimate containing cadmium, lead and zinc, and partly in the soft top of the sinter, which has been only partly sintered on account of the rapid cooling to which it has been subjected by the blast of the sintering machine. This lead and cadmium-rich top surface is discharged with the bulk of the sintered material into the chute 15, and, where the sinter is sufficiently hard, may be screened out with the fines from the remaining sinter, thus further decreasing the lead and cadmium content of the latter. This top portion may also advantageously be subjected to a repeated or multiple sintering action.

The following examples illustrate the advantageous results secured by the practice of the invention on zinc concentrates made by differential flotation. The zinc concentrate was first roasted in accordance with customary practice.

In one case, the roasted concentrate was mixed with an appropriate amount of carbonaceous fuel and sintered on a Dwight-Lloyd machine. The distribution of the lead and cadmium in the vertical cross section of the resulting sinter was as follows:

	Pb	Cd
	Per cent	*Per cent*
Top ½-inch section	1.3	0.012
Second ½-inch section	1.3	0.014
Third ½-inch section	1.4	0.007
Fourth ½-inch section	1.7	0.007
Fifth ½-inch section	3.0	0.010
Sixth ½-inch section	7.4	0.13
Seventh ½-inch section	8.4	0.25
Eighth (bottom) ½-inch section	8.8	0.25

In accordance with the principle of the present invention, the cutting knife would be adjusted to separate the bottom inch of the sinter from the overlaying portion. The portion of the sinter above the knife would then contain about 2.7% lead and about 0.05% cadmium, while the portion below the knife would contain about 8.6% lead and about 0.25% cadmium.

In another case, a roasted zinc concentrate was mixed with 2½% of sodium chloride, together with the usual amount of carbonaceous fuel for sintering, and treated in accordance with the principle of the present invention. The roasted concentrate analyzed approximately as follows:

Zn	Pb	Cd	S
65.1	4.3	0.12	2.8

The top and bottom portions (divided by the cutting knife) of the sintered product analyzed as follows:

	Zn	Pb	Cd	Cl	S
Portion of sinter above knife	63.6	1.5	.01	.117	.60
Portion of sinter below knife	60.7	2.9	.05	.944	1.20

In another case, a roasted zinc concentrate, of approximately the same composition as in the preceding case, was mixed with 5% sodium chloride and carbonaceous fuel and treated in accordance with the present invention. The top and bottom portions (divided by the cutting knife) of the sintered product analyzed as follows:

	Zn	Pb	Cd	Cl	S
Portion of sinter above knife	65.6	.41	.003	.25	.46
Portion of sinter below knife	61.9	1.30	.030	1.13	.77

In another case, the roasted zinc concentrate was mixed with 4½% calcium chloride, together with carbonaceous fuel for sintering, and treated in accordance with the present invention. The top and bottom portions

(divided by the cutting knife) of the sintered product analyzed as follows:

	Zn	Pb	Cd	Cl	S
Portion of sinter above knife	63.7	.46	.005	.120	.32
Portion of sinter below knife	62.0	1.00	.010	.560	.57

In still another case, the roasted zinc concentrate was first mixed with 2½% of sodium chloride and carbonaceous fuel and sintered on a Dwight-Lloyd machine without separation of the top and bottom portions of the resulting sinter. This sinter was appropriately crushed and mixed with additional carbonaceous fuel and 2½% of sodium chloride and treated in accordance with the principles of the present invention. The top and bottom portions (divided by the cutting knife) of the resulting resintered product analyzed as follows:

	Zn	Pb	Cd	Cl	S
Portion of sinter above knife	64.0	.26	.002	.058	.14
Portion of sinter below knife	62.2	.72	.004	.698	.52

The distribution of the lead and cadmium in the vertical cross section of the resintered product was as follows:

	Pb	Cd
Top ½ inch section	0.39	0.003
Second ½ inch section	0.27	Not detected
Third ½ inch section	0.24	" "
Fourth ½ inch section	0.34	" "
Fifth ½ inch section	0.21	" "
Sixth ½ inch section	0.25	" "
Seventh ½ inch section	0.34	" "
Eighth (bottom) ½ inch section	1.2	0.004

I claim:

1. The improvement in the treatment of zinciferous material containing lead and/or cadmium which comprises subjecting said material to a sintering operation by passing a combustion supporting gas through an appropriately supported layer of the material and a suitable combustible agent in the course of which operation a substantial amount of lead and/or cadmium segregates near one surface of said layer, and mechanically separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the resulting sintered product.

2. The improvement in the treatment of zinciferous material containing lead and/or cadmium which comprises subjecting said material to a sintering operation by passing a combustion supporting gas through an appropriately supported layer of the material and a suitable combustible agent in the presence of a chloridizing agent in the course of which operation a substantial amount of lead and/or cadmium segregates near one surface of said layer, and mechanically separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the resulting sintered product.

3. The improvement in the treatment of zinciferous material containing lead and/or cadmium which comprises subjecting said material to a sintering operation by passing a combustion supporting gas through an appropriately supported layer of the material and a suitable combustible agent in the course of which operation a substantial amount of lead and/or cadmium segregates near one surface of said layer, mechanically separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the resulting sintered product, and subjecting said remainder of the sintered product to a separative treatment for the removal therefrom of pulverulent material of relatively high lead and/or cadmium content.

4. The improvement in the treatment of zinciferous material containing lead and/or cadmium which comprises subjecting said material to a sintering operation by passing a combustion supporting gas through an appropriately supported layer of the material and a suitable combustible agent in the presence of a chloridizing agent in the course of which operation a substantial amount of lead and/or cadmium segregates near one surface of said layer, mechanically separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the resulting sintered product, and subjecting said remainder of the sintered product to a separative treatment for the removal therefrom of pulverulent material of relatively high lead and/or cadmium content.

5. The improvement in the treatment of zinciferous material containing lead and/or cadmium which comprises subjecting the material in the presence of a suitable combustible agent to a blast-roasting treatment in the course of which a substantial amount of lead and/or cadmium segregates near the blast-exiting surface of the material, and separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the material.

6. The improvement in the treatment of zinciferous material containing lead and/or cadmium which comprises subjecting the material in the presence of a suitable combustible agent and a chloridizing agent to a blast-roasting treatment in the course of which a substantial amount of lead and/or cadmium segregates near the blast-exiting surface of the material, and separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the material.

7. The improvement in the treatment of roasted zinc concentrates containing lead

and/or cadmium which comprises subjecting the roasted concentrate to a sintering operation by blast roasting in the course of which a substantial amount of lead and/or cadmium segregates near the blast-exiting surface of the sintered product, and separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the sintered product.

8. The improvement in the treatment of roasted zinc concentrates containing lead and/or cadmium which comprises subjecting the roasted concentrate to a sintering operation by blast roasting in the presence of a chloridizing agent in the course of which operation a substantial amount of lead and/or cadmium segregates near the blast-exiting surface of the sintered product, and separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the sintered product.

9. The improvement in the treatment of zinciferous material containing lead and/or cadmium which comprises subjecting said material to a sintering operation by passing a combustion supporting gas through an appropriately supported layer of the material and a suitable combustible agent in the course of which operation a substantial amount of lead and/or cadmium segregates near one surface of said layer, mechanically separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the resulting sintered product, and subjecting said remainder of the sintered product to another similar sintering operation.

10. The improvement in the treatment of zinciferous material containing lead and/or cadmium which comprises subjecting said material to a sintering operation by passing combustion supporting gas through an appropriately supported layer of the material and a suitable combustible agent, crushing the resulting sintered material, mixing the crushed sintered material with additional combustible agent, and subjecting said mixture to a sintering operation by passing a combustion supporting gas through an appropriately supported layer of the material in the course of which operation a substantial amount of lead segregates near one surface of said layer, and mechanically separating such surface portion in which lead and/or cadmium has so segregated from the remainder of the resulting sintered product.

In testimony whereof I affix my signature.

LLOYD E. TETER.