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PROCESS FOR PRODUCING LEAD FROM LEAD SULFIDE CONTAINING MATERIALS

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The present invention relates to an improved process for producing lead from materials containing lead sulfide such as ores, concentrates, intermediate products or waste products containing lead sulfide, and is particularly adapted to the production of lead from such materials having a high content of lead sulfide, for example, from concentrates containing 65 to 85% of lead.

Modern flotation processes yield lead ore concentrates which hardly contain any gangue and in which the lead content has been concentrated to 65 to 85%. For example, concentrates are obtained containing 80% lead, 14% sulfur and 6% gangue. The smelting of such concentrates in the generally used shaft furnace processes requires a preliminary sintering with the addition of the supplements required for the shaft furnace. In the shaft furnace the lead concentrate is then reduced by the addition of coke and the agglomerate is reduced to raw lead and slag. The reduction in the shaft furnace only proceeds without disturbances if the lead content of the charge is at most 50%, as, with higher lead contents, the charge bakes together and becomes impermeable to gas before it has completely reacted. It is consequently customary to admix slag, lime and/or silica with the concentrate either before or after the roasting before the charge is introduced into the shaft furnace in order that it be diluted to a lead content of 50%. It is just such diluents which are separated in the flotation or in the shaft furnace, so that the advantages obtained by the concentration during flotation, except for savings in transportation, are substantially reduced as the throughput through the shaft furnace is lowered proportionately to the dilution and the heat required per ton of lead produced is correspondingly increased.

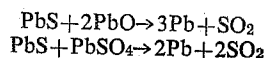
One process for smelting of concentrates without dilution has been proposed, namely, the roasting-reaction process on Newman hearths or Schlippenbach plants. With such a process, about 60% of the lead contained in the ore is converted to raw lead on a hearth furnace. The gray slag obtained in the hearth furnace is sintered and then smelted in a shaft furnace with the addition of coke with a conversion of a further 30% of the lead content of the ore into raw lead. A considerable quantity of dust occurs both in the hearth furnace as well as in the shaft furnace. Such dust approximately contains about 10% of the lead originally contained in the ore and must be recovered by electrostatic gas cleaning apparatus. The high incidence of intermediate products rich in lead renders it necessary to split up the manufacturing process into several streams which entails an increase in labor costs. Also, as the flow of material is divided into several streams, the apparatuses do not operate uniformly and it is difficult to avoid danger to the operators from the large quantities of lead containing dust which occurs. Furthermore, the process entails the use of coke for the smelting of the gray lead containing slag in the shaft furnace.

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The object of the present invention is a process for the efficient recovery of lead from materials rich in lead without the necessity of using coke and without having to add any substantial quantities of foreign materials, particularly reducing material such as coke, and in which the lead is produced at only one point and in which the product of dust is minimized.

In accordance with the invention it has been found that lead could be obtained from fine grained sulfidic lead ores or concentrates by granulating such ores or concentrates, if desired, with the addition of oxidic lead ore, and partially roasting and sintering to produce a mixture of lead sulfide and oxide and possibly lead sulfate which contains a sufficient quantity of chemically bound oxygen that it can be converted to lead and sulfur dioxide in a suitable furnace without further addition of oxygen by the so-called roasting-reaction process.

In the roasting-reaction process, the chemically bound oxygen introduced into the charge during roasting reacts with the chemically bound sulfur retained in the charge to produce metallic lead and sulfur dioxide. The primary reactions involved are represented by the following equations:



In accordance with the present invention it was found that the roasting of the fine grained ore or concentrate to produce a satisfactorily coherent and gas permeable sinter with the desired ratio of chemically bound oxygen to chemically bound sulfur is possible without the necessity of previous granulation of the charge if recycled internal material and/or fly ash is admixed with the fine grained charge to be sintered. The best results are obtained when the ratio of recycled material and/or fly ash to ore or concentrate is more than 1:1 and preferably 1.5 to 2:1. The term fly ash, as employed herein, is intended to mean such fly ash as occurs in the metallurgy of lead.

The sintering roasting can be effected in a known manner on a moving sintering grate. If desired, a small quantity of finely divided lime in the form of limestone, hydrated or unslaked lime can be admixed with the charge to be sintered. The sulfide-sulfur content of the charge to be sintered is adjusted in order to be able to operate with the optimum sintering temperature. With most high percentage lead ores or concentrates a 5-9, preferably about 7%, is suitable. The sintering is effected with oxygen containing gases, such as, air or air in admixture with recycled gas, care being taken that sufficient free oxygen is present therein to produce a sinter in which the molar ratio of bound oxygen to bound sulfur is about 2:1. After the sintered product is discharged from the sintering apparatus, the sinter is crushed and sieved. The quantity of sintered product in the desired grain size required for the sinter roasting is recycled and admixed with the subsequent ore or concentrate to be roasted and sintered. The remaining sintered product is then charged into a furnace and rapidly heated to reaction temperature to produce metallic lead with the liberation of sulfur dioxide.

In accordance with a preferred modification of the process according to the invention the internal reaction of the partially roasted and sintered product is effected at temperatures above 1100° C., preferably at temperatures between 1200 and 1250° C., and heating of the sintered product to reaction temperatures is effected in as short a time as possible. The increase in speed of reaction attained by such high temperatures reduces evaporation losses to a minimum. At the temperatures normally employed for such internal reaction for the production of lead, which are under about 1000° C. and usu-

ally lie between 800 and 1000° C., considerably greater evaporation losses occur.

If the nature of the ore, and especially the composition of its gangue, requires it, it can, in exceptional cases, be necessary to add small quantities of additional materials such as sand, soda, limestone or iron containing materials (pyrites, roasted pyrites, iron ores) in order to assure the production of a good and sufficiently liquid slag. As the gangue content of a good lead ore concentrate does not exceed about 5-8%, the quantity of additional materials which may be required, if at all, is very small and usually only 2-5% of the quantity of the concentrate.

It has been found that the rapid heating to the high temperatures is exceptionally advantageously carried out in a rotary drum flame furnace rotating about a horizontal axis, especially one whose length is no greater than about twice its diameter, and preferably one whose length is about equal to that of its diameter. As the flame path reverses in the furnace, the heat introduced thereby into the furnace is rapidly and directly transferred to the furnace charge during rotation of the furnace and substantially lower evaporation losses occur than when the usual flame and rotary furnaces are employed.

It was also found according to the invention that it is expedient not to carry out the preliminary roasting and sintering so that the exact ratio of lead bound sulfur and lead bound oxygen required for the subsequent inner conversion is achieved thereby, as the exact control of such ratio is difficult to achieve upon a commercial scale operation. The roasting and sintering is, however, carried out so that the molar ratio of lead bound oxygen to lead bound sulfur in the resulting sinter is approximately 2:1 but that such sinter contains either an excess or deficiency in oxygen. By making slight changes in the roasting and sintering conditions, sintered products containing an excess of oxygen and sintered products containing a deficiency in oxygen are alternately produced and by mixing such sintered products the optimum O:S ratio is produced before the charge is introduced into the rotary flame furnace. The oxygen content in the sintered product can be varied by adjusting the velocity of the grate, the quantity of recycled material admixed with the charge, the thickness of the charge as well as the pressure differential above and below the charge. It is furthermore also possible to smelt with an oxidizing flame and compensate for the oxidizing degree of the flame by a corresponding oxygen deficiency in the solid sinter charged into the smelting furnace. In practice it was found that the optimum O:S ratio in the charge when employing an oxidizing flame during the smelting is 1.90 to 1.95 mol O:1 mol S. The simplest procedure is to adjust the O:S ratio, only approximately, by mixing the different sintered products and to adjust such ratio to the desired value during the smelting operation with reference to the oxidizing degree of the flame employed by small appropriate additions of sinter with excess or deficiency in oxygen content or, if desired, with dead roasted or unroasted sulfidic material. This mode of operation is advantageous in that it is simpler to adjust the composition of the charge with reference to the oxidizing degree of the flame employed by suitable additions of solid materials to the charge than to adjust the oxidizing degree of the flame to conform to that required for the charge. The procedure according to the invention furthermore renders it practical to employ an oxidizing flame for the smelting operation so that the highest temperature attainable with the fuel employed can be attained so that rapid heating of the charge with correspondingly lower evaporation losses is promoted.

In the treatment of some ores a small quantity of a slag like lead containing residue can remain after completion of the smelting reaction. The residue preferably is retained in the smelting furnace and retreated with the next charge. After several charges the lead content

thereof is decreased to such an extent that it can be discarded.

The following example will serve to illustrate the process according to the invention:

Example

16.6 parts by weight of a sulfidic lead ore of the composition

	Percent
Pb	80.2
S	14.36
Zn	3.2
CaO	0.5

was mixed with 3.4 parts by weight of an oxidic ore of the following composition

	Percent
Pb	52.0
S	6.7
Zn	5.5
CaO	6.5
CO ₂	17.9

and 2.0 parts by weight of a mixture of fly ashes of varying origin primarily from the sintering apparatus and the rotary flame smelting furnace. The fly ash mixture contained 71.3% Pb and 8.0% S. This mixture was admixed with 20 parts by weight of recycled sintered material of a grain size of 4-12 mm. with the addition of 6-7% of H₂O based upon the whole admixture. The recycled sintered material contained 81.0% Pb of which 40.6% was metallic Pb, 16.4% was in the form of PbS (18.9% PbS), 13.6% was in the form of PbO (14.7% PbO) and 10.4% was in the form of PbSO₄ (15.2% PbSO₄).

The resulting admixture was sintered in the following manner on a sintering apparatus:

A grate covering of finished sintered product from a previous charge of the same composition of the recycled sintered material in the charge about 20 mm. thick was first applied to the moving grate of the sintering apparatus. The grain size of such grate covering was 12-20 mm. An ignition layer 30 mm. thick of the same composition as the charge to be sintered except that the fly ash was omitted was applied over the grate covering. This ignition layer was ignited under the ignition hood of the sintering apparatus while air was drawn downwardly therethrough. Thereafter a 100 mm. layer of the admixture to be sintered was applied over the ignited ignition layer and the entire charge on the grate was sintered while air was passed upwardly through the charge.

The finished sintered product was of the same composition as that indicated above for the recycled sintered material admixed with the charge to be sintered. The weight ratio of oxygen bound to lead to sulfur bound to lead in the sintered product was 1.05:1 which corresponds to a molar ratio of 2.1:1.

One part of this sintered product was admixed with 1.2 parts of a sintered product produced in a similar manner having a deficiency in lead bound oxygen containing 80.5% Pb of which 37.4% was in the form of metallic lead, 9.3% was in the form of PbSO₄ (13.6% PbSO₄), 19.9% was in the form of PbS (23.0% PbS) and 16.6% was in the form of PbO (17.9% PbO). The molar ratio of lead bound oxygen to lead bound sulfur therein therefore was 1.81:1. The resulting mixed sintered product therefore had a molar ratio of lead bound oxygen to lead bound sulfur of 1.93:1. The slight deficiency in oxygen in the mixed sintered product was found in practice to be the optimum for counteracting the oxidizing action of the flame in the rotary smelting furnace.

150 kilograms of this mixed sintered product were introduced into a rotary flame furnace having an internal diameter of 0.7 meter and an internal length of 0.7 meter which had been preheated to 1200° C. The period re-

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quired for the charging of the furnace was 10 minutes. The temperature of the furnace which had been reduced by the introduction of the cold charge and the ensuing reaction was again raised to the original 1200° C. in 140 minutes and then maintained at such temperature for a further 10 minutes. The furnace was then tapped. 110 kg. of raw lead, 4.5 kg. of fly ash containing 70.5% Pb and 29.0 kg. of slag containing 28.8% Pb were produced. The yield obtained upon the basis of the 150 kg. charge is not entirely correct as it is impossible to prevent slag from a previous charge to be admixed with the slag of the new charge or to prevent a certain quantity of the slag from being retained in the furnace.

We claim:

1. A process for the production of metallic lead from materials containing lead sulfide with a content of at least 50% Pb which comprises sintering said lead sulfide containing material without addition of fuel in admixture with at least one material selected from the group consisting of fly ash and recycled sintered material under oxidizing roasting conditions to provide about a sufficient quantity of oxygen bound to lead in the sintered product to react upon heating with the sulfur bound to lead retained in the sintered product, and heating a charge of the sintered product without addition of fuel to reaction temperatures to produce metallic lead and volatile sulfur compounds.

2. A process in accordance with claim 1 in which the admixture of the lead sulfide containing material is alternately sintered under conditions producing an excess of lead bound oxygen in the sintered product and under conditions producing a deficiency of lead bound oxygen in the sintered product, and mixing the sintered products obtained to produce a sintered product containing an optimum lead bound oxygen to lead bound sulfur before such sintered product is heated to reaction temperatures to produce the metallic lead and volatile sulfur compounds.

3. A process in accordance with claim 1 in which the molar ratio of lead bound oxygen to lead bound sulfur is 1.90 to 1.95:1 in the sintered product heated to reaction temperatures and the heating to reaction temperatures is effected with an oxidizing flame.

4. A process in accordance with claim 1 comprising in addition adding small quantities of a material selected from the group consisting of lead bound oxygen and lead bound sulfur containing material while the sintered product is heated to reaction temperatures to adjust the lead bound oxygen to lead bound sulfur in the charge.

5. A process in accordance with claim 1 in which the

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ratio of the material selected from the group consisting of recycled sintered material and fly ash to the lead sulfide containing material is greater than 1:1.

6. A process in accordance with claim 1 in which the ratio of the material selected from the group consisting of recycled sintered material and fly ash to the lead sulfide containing material is 1.5 to 2:1.

7. A process in accordance with claim 1 comprising in addition admixing a small quantity of lime with the admixture to be sintered.

8. A process for the production of metallic lead from materials containing lead sulfide with a content of at least 50% Pb which comprises sintering said lead sulfide containing material without addition of fuel in admixture with at least one material selected from the group consisting of fly ash and recycled sintered material under oxidizing roasting conditions to provide about a sufficient quantity of oxygen bound to lead in the sintered product to react upon heating with the sulfur bound to lead retained in the sintered product, and rapidly heating a charge of the sintered product without addition of fuel to reaction temperatures over 1100° C. to produce metallic lead and volatile sulfur compounds.

9. A process in accordance with claim 8 in which said reaction temperatures are between 1200° C. and 1250° C.

10. A process in accordance with claim 8 in which said heating to reaction temperatures is effected in rotary flame furnaces rotating about a horizontal axis.

11. A process in accordance with claim 10 in which the ratio of the diameter to the length of said flame furnace is at most 1:2.

12. A process in accordance with claim 10 in which the ratio of the diameter to the length of said flame furnace is about 1:1.

13. A process in accordance with claim 8 comprising in addition separating the lead produced from any slag produced and heating such slag in admixture with further quantities of said sintered product to reaction temperatures to produce lead and volatile sulfur compounds.

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