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H. P. MEISSNER ETAL  
PROCESS FOR PRODUCING LEAD

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FIG. 1

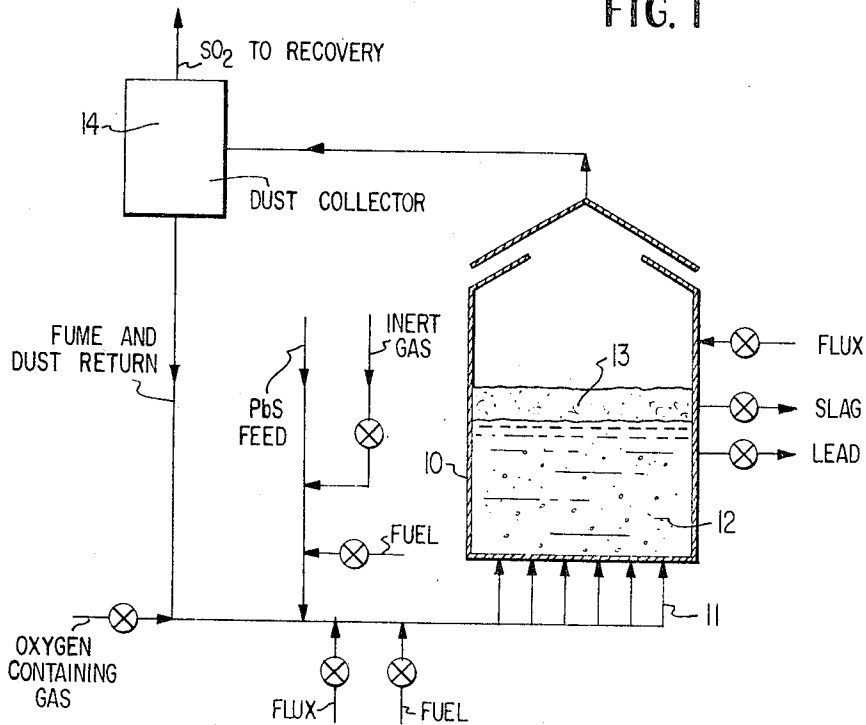
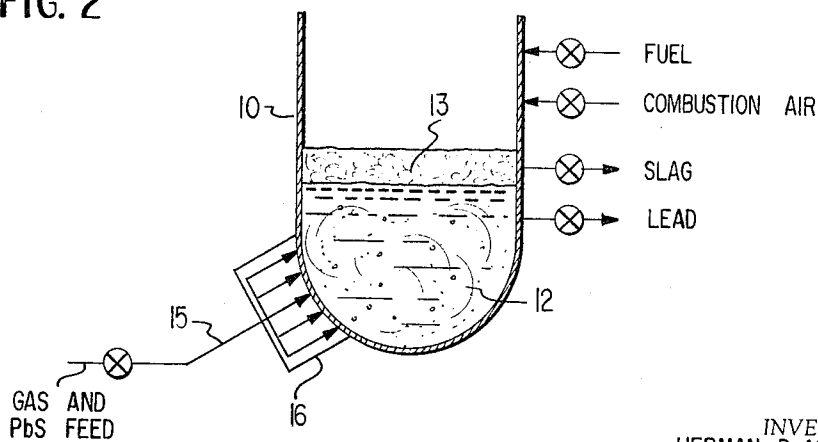


FIG. 2



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## PROCESS FOR PRODUCING LEAD

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14 Claims. (Cl. 75-77)

This invention relates to the production of lead and more particularly to the production of lead from sulfide ores and concentrates.

By far the most important material source of lead is galena ore in which the lead exists primarily in the form of sulfide. Associated with the lead sulfide in galena ore are typically other sulfides, such as zinc blende, silver and iron pyrites. In the recovery of lead from such ores, it is customary, but not essential, to concentrate the lead sulfide through the use of well-known flotation process. The resulting concentrates usually assay out between about 65% and 80% lead.

The now most commonly employed process for the recovery of lead from lead sulfide ores and concentrates comprises two distinct steps. The first step consists of sintering the lead ore on an open grate in the presence of oxygen to convert most of the lead sulfide to lead oxide. The second step, which is carried out in a separate apparatus such as a blast furnace, is the reduction of the lead oxide to lead. The charge in the blast furnace consists of the sintered ore, coke and other materials, such as slags, fluxes and the like which may include iron and calcium silicate. In some instances iron is used as a reducing agent along with the coke. In the blast furnace the reaction products are separated by gravity, the molten lead being discharged from the bottom portion of the furnace.

In this two-step process fuel is required primarily in the second step, and the sintered material must be physically transferred from one apparatus to another. For this reason the process cannot take advantage of the highly exothermic nature of the reaction between lead sulfide and oxygen. Moreover, the gases which are discharged in the two steps of the process are difficult to recover and the SO<sub>2</sub> content of these gases is generally not of a sufficiently high concentration to make its use in acid manufacture economical. Finally, difficulties are also encountered in the two-step process in the recovery of suspended solid matter, dust and fume, from off-gases. Since such solid matter contains unreacted lead sulfide, lead oxide and lead in other forms it is, of course, necessary to be able to recover these materials in the process for economic reasons.

It is therefore a primary object of this invention to provide a process for producing lead from lead sulfide ores and concentrates, the process being carried out as a continuous single stage operation. It is another object of this invention to provide a process of the character described which takes advantage of the exothermic nature of the reaction between lead sulfide and oxygen, yielding molten lead and SO<sub>2</sub>. It is another object to provide such a process which is highly efficient, both with regard to the percentage of lead recovered as well as to the amount of fuel used. It is another object of this invention to provide a lead process which produces SO<sub>2</sub> by-product gas of a concentration which makes it practical to recover. It is another object to provide such a process which permits the economical recovery of solid particles suspended in the effluent gases and their final return to the process.

It is still another object of this invention to provide a process for the production of lead which is flexible in that the rate of supply of raw materials and of associated fuel

(if any) can be varied over wide limits to obtain optimum operational conditions. Other objects of the invention will be apparent hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the apparatus embodying features of construction, combinations of elements, and arrangement of parts which are adapted to effect such steps, all as exemplified in the following detailed disclosure.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings in which:

FIG. 1 is a diagrammatic representation of the apparatus of the invention and a flow diagram of the process steps which are carried out therein; and

FIG. 2 is a modified form of the reaction chamber of the apparatus of FIG. 1.

In brief, the process of this invention for producing lead comprises introducing beneath the surface of a mass or pool of molten lead a material containing lead sulfide and an oxygen-containing gas to bring about reactions yielding metallic lead, slag and gaseous by-products. The exothermic reactions which take place provide at least a substantial portion of the heat required in the process. Of course it is within the scope of this invention to supply additional heat and to recover both the gaseous and the solid phases of the fumes which result from the reactions.

The reaction is carried out at temperatures above about 800° C., and preferably between about 1,000° C. and about 1,150° C. At these temperatures both lead sulfide and lead oxide show a significant solubility in molten lead. By introducing the lead sulfide ore and oxygen source into a sizeable pool of molten lead, it is possible to keep in thermal balance the various reactions which take place. For example, it is known that the reaction between oxygen and molten lead is highly exothermic, while the reaction between lead sulfide and lead oxide is endothermic. Although it is not precisely known what all of the reactions taking place are, or the precise order in which they take place, it has been determined from extensive experimental work that the overall result of the reactions is the formation of additional molten lead, SO<sub>2</sub>, and a slag which contains most of the materials other than lead which were present in the original ore or concentrate. This overall reaction is exothermal. Due to differentials in specific gravities, the slag which forms floats on the molten pool of lead and is withdrawn as needed. Similarly, it is possible to withdraw, either continuously or periodically, molten lead from the pool in amounts essentially equivalent to the amount of lead which is introduced in the form of lead sulfide. Efficiencies up to 95% recovery of lead have been obtained.

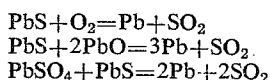
Lead ores or lead ore concentrates may be used in the process. Thus it is possible to introduce crushed galena ore directly into the process, or to use concentrates which are the result of well-known flotation techniques. The particle size of the ore is not critical except that it should be such that it may be entrained in a gas which is used to introduce the lead sulfide into the molten lead. Typically, the ore concentrate will be of a particle size which permits all of it to pass through an 8-mesh sieve. However, operational conditions such as the size of the bubbles created in the molten lead bath, the size of the ports, the temperature of the operation, and the sulfide content in the bath will all contribute to a determination of the optimum particle size of the ore used.

As will be apparent from FIG. 1, it is possible to introduce the lead sulfide feed (whether concentrate or ore) either entrained in the oxygen-containing gas or entrained

in an inert gas which is then premixed with the oxygen-containing gas. Alternatively, it is also possible to introduce the lead sulfide entrained in the inert gas into the molten lead pool separately from the oxygen-containing gas. It will of course be necessary to have the gases which are introduced into the molten pool under some pressure, the minimum being that which is required to overcome the hydrostatic head and the normal pressure drop in the flow through the pipes to the ports where introduction is achieved. It is also possible to supply the gases at velocities up to and even beyond the point where sonic orifice velocities are obtained. The actual choice of gas pressure, and entrance velocity into the bath will depend upon the operational conditions.

The oxygen gas may come from any convenient source, and oxygen concentrations in the gas may range from below the oxygen content of air to substantially 100% oxygen. In most circumstances, air will be the most economical and practical oxygen-containing gas to use. It is also possible to introduce some of the oxygen, although not all of it, in the form of combined oxygen, that is, as lead oxide, lead sulfate or a basic lead sulfate. The amount of lead oxide, and/or lead sulfate used as a source of combined oxygen will depend to a large extent upon the heat balance of the system, for the reactions of both lead oxide and lead sulfate with lead sulfide are endothermic, hence they supply no heat to the system. Rather they absorb heat and thus the thermal balance between exothermic and endothermic reactions is shifted.

A balance between the amount of lead sulfide and the oxygen making up the feed both as a gas and as lead oxide or sulfate should be maintained. The desired balance can best be defined as that which will cause no substantial change in the relative concentrations of lead sulfide and lead oxide in either the molten metal or in the slag phase during the process. Thus, in the reaction vessel the ratio of lead sulfide to oxygen, fed as gas and in combination with lead, should be such that the reaction of lead sulfide to lead should be in balance for the reactions:



etc.

In addition, enough oxygen should be supplied to satisfy any requirements of the slag-forming components in the ore or concentrates.

Some gaseous oxygen may of course pass through the molten lead and slag and break through into the gas phase without having opportunity to react, and if this happens allowance for this quantity of oxygen should be made in determining the lead sulfide to oxygen ratio. The reactions preferably should be essentially in a steady state, and the molten lead pool should not be saturated with respect to lead sulfide, nor should there be a net increase in lead oxide.

It is also desirable to maintain a substantially constant ratio between the molten lead making up the reaction bath and the lead sulfide which is introduced. It is generally preferable to maintain a fairly large quantity of molten lead with respect to the amount of sulfide introduced in order to prevent rapid fluctuation in thermal and chemical balances. Thus, the pool of molten lead serves to stabilize both the thermal and chemical conditions of the reaction. The actual amount of lead retained as a reaction pool will depend upon operating conditions and system design. In small apparatus it has been found preferable to maintain a pool of molten lead equivalent to about ten times the weight of the amount of lead introduced as lead sulfide per hour. However, this ratio may vary considerably and be as low as three to five pounds of molten lead per pound of lead introduced as lead sulfide per hour. The optimum ratio for

any given reactor may readily be determined during operation.

It may not always be possible to continuously maintain the desired balances between lead sulfide and total oxygen fed within the system and therefore it may be desirable to correct such imbalances as may arise periodically before drawing off any molten lead from the system. Thus an excess of oxide in the lead may be reduced by introducing additional lead sulfide or sulfur into the system, while an excess of sulfide may be corrected by introducing additional quantities of an oxidizing gas or agent, or by the introduction of some lead oxide or lead sulfate.

The quality of the ore or concentrate used may determine the necessity or desirability for the introduction of a flux into the system. This may be done in accordance with well-known techniques. The flux is generally required to control the melting point and viscosity of the slag. Any of the fluxes which are known in the art to achieve this result may of course be incorporated into the feed into the system. Typical fluxes include, but are not limited to, calcium oxide, magnesium oxide, silica, sodium hydroxide, limestone, dolomite and calcium fluoride. As will be apparent from FIG. 1, the flux may be introduced at any of several points. It may be introduced into the gas prior to its blowing into the molten pool and thus be entrained along with the lead sulfide feed and oxygen. Alternatively, it may be introduced into the vessel directly onto the top of the slag as also indicated in FIG. 1.

FIGS. 1 and 2 illustrate that it is possible to introduce the lead sulfide feed and oxygen-containing gas either at the bottom of the molten pool of lead or somewhere intermediate between the top and bottom of the lead pool. The depth at which the lead sulfide and the oxygen-containing gas are introduced into the molten pool is an important factor of the process of this invention. It may be defined as at least that depth which is sufficient to permit the completion of the reactions and the consumption of all of the oxygen. Thus it is necessary to introduce the lead sulfide and oxygen at a depth which is sufficient to complete the reactions involved before any unreacted lead sulfide, or intermediate lead oxide, or any substantial quantity of oxygen, reaches the lead-slag surface. This deep blowing and the resulting completion of the reactions minimizes fume and dust loss in the process. Furthermore, the utilization of substantially all of the oxygen produces an effluent gas having a high  $\text{SO}_2$  content, and makes it possible to recover this material economically.

FIG. 2 illustrates the tangential introduction of the gas and lead sulfide fed into the reaction chamber. This has the advantage of causing the solids introduced to impinge on the edge of the bubble walls formed and thus to achieve more rapid and complete dissolution. The apparatus used and the operating conditions employed (e.g., temperature, feed pressure, and ore particle size) will determine the optimum depth. Generally, however, this will be greater than eight inches below the surface of the molten lead pool.

As indicated above, the process of this invention makes it possible to take advantage of the exothermic nature of the reaction between oxygen and molten lead. It may however be necessary to supply a certain quantity of additional heat to be process. This may be done in a number of ways. Where heat losses are such that it is required to supply additional heat beyond what the exothermic reaction supplies, such heat may be supplied by preheating the air or the oxygen-containing gas. In a similar manner, the ore may be preheated, but it is usually more desirable to preheat the gas in which the ore is entrained. It is also possible to burn gaseous, liquid or solid fuels within the reaction vessel either above the reacting pool or in the form of submerged combustion. The system shown in FIG. 1 make possible the use of

one or more of several alternatives. The fuel may be introduced into an inert gas which is used to carry the lead sulfide feed into the system, or it may be introduced into the oxygen-containing gas which also has the lead sulfide feed entrained in it. As shown in FIG. 2, fuel and combustion air may be introduced above the molten reaction mass by any technique known in the combustion art. Finally, it is also of course possible to supply heat electrically by induction heating. A fuel-fired reactor may also be used. The quantity of heat introduced will be that which is required to maintain the reaction mass within the temperature range specified above.

Molten lead may be removed continuously or periodically. It may be preferable to remove the molten metal by use of a siphon tap and lead well, as is well known in the art. The slag will of course be removed at convenient intervals.

Dust-laden gases coming from the vessel will contain  $\text{SO}_2$ , other constituents such as nitrogen, etc., unreacted particulate lead sulfide, lead oxide, some vaporized lead compounds and lead metal. Inasmuch as all of these wastes can be withdrawn at one point, it is possible to collect the solids contained therein in a dust collector, the solid materials being retained on suitable filtering surfaces such as bags.

The gases, including a high-concentration of  $\text{SO}_2$ , are removed and sent to a suitable recovery system such as an acid plant. Periodically, the filters which have collected the solid materials (including lead, lead sulfide and lead oxide) are treated to remove the solid materials and return these into the system as shown in FIG. 1. Thus, it is possible continuously to recover valuable lead, lead sulfide, and lead oxide, and at the same time to use the by-product  $\text{SO}_2$  in an economical manner. In contrast to prior practice, the recovery of the solid materials is relatively less expensive in the process of this invention because of the smaller gas volumes involved.

As shown in FIG. 1 the apparatus of this invention comprises a reaction vessel 10; tuyeres 11 adapted to deliver the gaseous and solid feed to the molten lead pool 12; conduits suitably valve-controlled to introduce the PbS source and oxygen source into the tuyeres, as well as any inert gaseous carrier, fuel, combustion oxygen or air and flux if these are used; suitably valve-controlled conduit means for removing slag 13 and product lead; and a conduit system for removing the fumes to a dust collector 14 and for returning solid matter to the reaction vessel. A modification of the apparatus, shown in FIG. 2, incorporates a conduit system 15 and tuyeres 16 designed to introduce the lead sulfide particles entrained in a suitable gas tangentially into the molten lead pool.

The reaction vessel 10 may be of any well-known type such as a Bessemer-type converter or a Smith-Pierce type converter. The tuyeres may be located at the converter base or on the side. Lance blowing of the feed downward into the molten lead may also be used. The primary consideration in introducing the feed into the molten lead pool is that the depth of introduction or blowing with respect to the surface of the molten pool be sufficient as defined above. The reaction vessel may be stationary or tippable. If it is stationary, suitable means, such as a siphon tap and well, must be provided for withdrawing the molten lead.

It will be seen from the foregoing description that the process of this invention makes it possible to carry out the production of lead in a single reaction vessel in an essentially one-step process. The process takes advantage of the exothermic characteristics of the overall reactions involved to balance the heat input that is required, thus eliminating or materially reducing the need for an external heat source. Moreover, recovery of by-products, both gaseous and solid, is economical and easy; and the process is flexible with respect to operational conditions, to the quality of lead sulfide feed, as well as to the adjustment of temperatures and reaction conditions.

It will be thus seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above process and in the constructions set forth without departing from the scope of the invention as defined in the appended claims, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. A process for the production of lead which comprises introducing beneath the surface of a body of molten lead maintained at a temperature above about  $800^\circ\text{C}$ . a gas-suspended particulate lead sulfide-containing material and an oxygen-containing gas, the oxygen content of the gas being sufficient to effect the substantially complete conversion of the sulfur content of the lead sulfide-containing material introduced concurrently therewith into sulfur dioxide during the passage of the oxygen-containing gas through the body of molten lead.

2. A process for the production of lead which comprises introducing beneath the surface of a body of molten lead maintained at a temperature above about  $800^\circ\text{C}$ . a gas-suspended particulate lead sulfide-containing material and an oxygen-containing gas, the oxygen content of the gas being sufficient in combination with the oxygen content of any oxygen-containing lead compounds introduced into the body of molten lead to effect the substantially complete conversion of the sulfur content of the lead sulfide-containing material introduced concurrently therewith into sulfur dioxide during the passage of the oxygen-containing gas through the molten lead.

3. The method as defined in claim 1 wherein the particulate lead sulfide-containing material and the oxygen-containing gas are introduced tangentially into the body of molten lead below the surface thereof.

4. The method as defined in claim 1 wherein the particulate lead sulfide-containing material is introduced into the body of molten lead in suspension in the oxygen-containing gas.

5. The method as defined in claim 1 wherein the particulate lead sulfide-containing material is introduced into the body of molten lead in suspension in a stream of inert gas.

6. The method as defined in claim 1 wherein lead is removed from said body of molten lead at a rate substantially equal to the rate of production of lead from the lead-compounds introduced into said body.

7. The method as defined in claim 1 wherein the body of molten lead is maintained at a temperature in the range of from about  $1000^\circ\text{C}$ . to about  $1150^\circ\text{C}$ .

8. The method as defined in claim 1 wherein the oxygen-containing gas is air.

9. The method as defined in claim 1 wherein the solid particles contained in the effluent gases from the body of molten lead are separated from said gases and reintroduced into the body of molten lead.

10. The method as defined in claim 1 wherein heat is supplied to said body of molten lead by the combustion of a fuel in said body.

11. The method as defined in claim 1 wherein heat is supplied to said body of molten lead by the combustion of a fuel above said body.

12. The method as defined in claim 1 wherein a fluxing agent is supplied to said body of molten lead.

13. A method as defined in claim 1 wherein the particulate lead sulfide-containing material contains or is introduced together with lead oxide.

14. A method as defined in claim 1 wherein the particulate lead sulfide-containing material contains or is introduced together with lead sulfate.

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