No. 816,764. PATENTED APR. 3, 1906.

W. VALENTINE & A. G. BETTS.

PROCESS OF SMELTING LEAD ORES.

APPLICATION FILED JUNE 15, 1904.

2 SHEETS—SHEET 1.

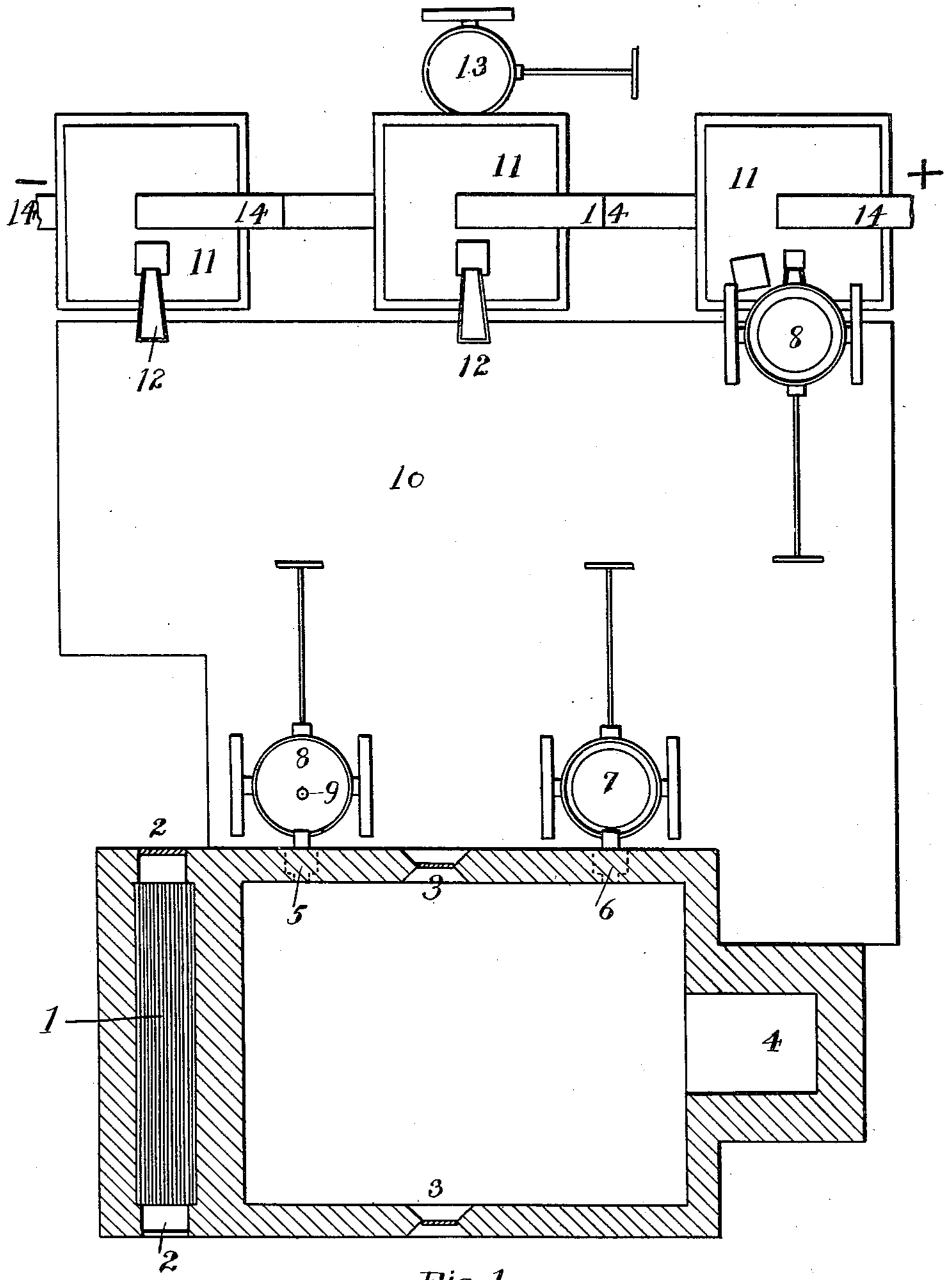

Fig. 1

Witnesses

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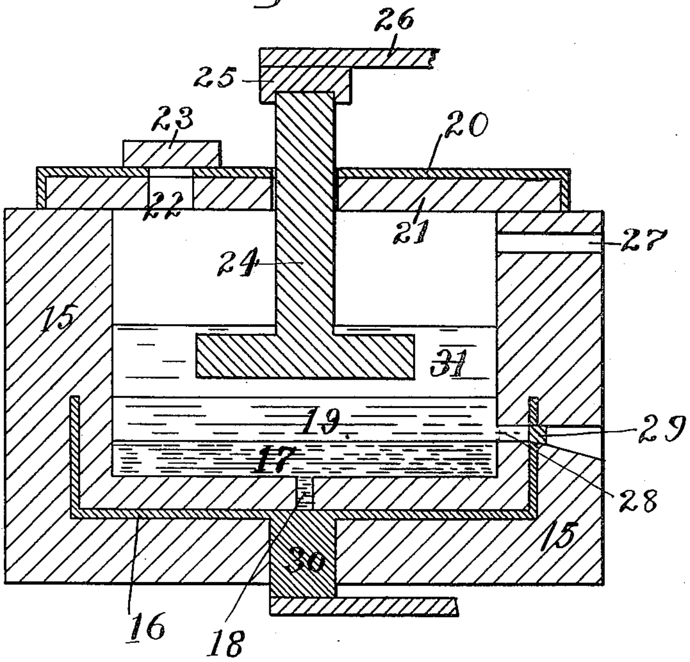
Fig. 2



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# UNITED STATES PATENT OFFICE.

WILLIAM VALENTINE AND ANSON GARDNER BETTS, OF TROY, NEW YORK.

## PROCESS OF SMELTING LEAD ORES.

**No. 816,764.** **Specification of Letters Patent.** **Patented April 3, 1906.**

Application filed June 15, 1904. Serial No. 212,745.

*To all whom it may concern:*

Be it known that we, William Valentine, a subject of the King of Great Britain, and Anson Gardner Betts, a citizen of the United States, and residents of Troy, New York, have invented certain new and useful Improvements in Processes of Smelting Lead Ores, of which the following is a specification, accompanied by drawings.

Figure 1 of the drawings is a plan of the apparatus in which our processes are carried out, and Fig. 2 shows in vertical section the details of our electrolyzing-furnace.

The principal objects of our invention are to recover lead and sulfur from ores containing galena without appreciable loss of lead. Other objects will appear in connection with the following description of our process.

Our invention consists in freeing the metallic sulfids of the ore from the earthy gangue by fusion and in reducing lead from the lead sulfid by bringing the sulfid into contact with a cathode in a bath of a fused salt in which lead sulfid is practically insoluble, as hereinafter more fully described.

We melt the ore, with the addition of fluxes, if necessary, in a smelting-furnace for the purpose of converting the earthy materials in the ore into a slag and for fusing the galena, which usually carries with it from the ore iron and zinc sulfids. The slag produced usually contains from three to twelve per cent. of lead, the greater part of which can be recovered by smelting the slag in a lead blast-furnace.

Analyses of matte and slag produced give:

| | Pb | Fe | FeO | Zn | CaO | Insol ($SiO_2$,$Al_2O_3$) | S |
|---|---|---|---|---|---|---|---|
| | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | |
| Matte | 67.73 | 10.6 | | 1.0 | trace | trace | 19.83 |
| Slag | 11.77 | | 20.37 | 1.6 | 18.5 | 30.5 | 2.1 |
| Matte | 75.44 | 6.6 | | 1.0 | trace | trace | 14.28 |
| Slag | 12.84 | | 27.22 | 1.2 | 18.60 | 32. | 1.94 |

The elimination of gangue by a preliminary fusion is a desirable step in the preparation of lead ore for treatment by other processes—for instance, electrolysis of lead sulfid dissolved in fused lead chlorid—and for the reduction of lead from the sulfid by smelting with carbon and sodium carbonate with or without the use of iron oxid. (See, respectively, applications for Letters Patent of Anson G. Betts, Serial No. 208,947, filed May 20, 1904, and No. 208,946, filed May 20, 1904.)

We prefer to further treat the fused matte directly, without allowing it to cool to the solidifying point.

Our electrolyzing apparatus consists of a furnace on the bottom of which is a suitable cathode, usually molten lead; but other electrodes may be used—for instance, carbon. Above the cathode we keep a layer of matte containing lead sulfid, usually though not necessarily liquid, and above the matte a fused electrolyte in which lead sulfid is substantially insoluble, preferably sodium chlorid containing sodium sulfid. A carbon anode dips into the fused electrolyte. On passing a current of electricity chlorin is liberated at the anode unless sufficient sulfid is dissolved in the electrolyte, when sulfur is liberated instead of chlorin, and the sodium ion or other cathion appearing at the cathode reacts with lead sulfid, giving metallic lead and sodium sulfid or other sulfid. The sodium sulfid formed when the electrolyte contains sodium chlorid partly dissolves in the matte and partly in the electrolyte. It thus happens that in case the bath on the start contains only sodium chlorid sodium sulfid accumulates in the electrolyte, so that sulfur chlorid soon appears at the anode, and eventually pure sulfur is given off. The matte from which the contained lead has been largely reduced is taken from the furnace, preferably by tapping, and fresh matte high in lead added. We prefer to make the charging and tapping processes nearly continuous, so that the matte in the furnace does not vary greatly in composition and may have about the following composition: FeS, 47.9 per cent.; ZnS, 7.8 per cent.; PbS, 22.4 per cent.; $Na_2S$, 8.4 per cent.; NaCl, 8.5 per cent.; CaS, 4.3 per cent.

If the matte charged contains FeS 15.7 per cent., ZnS 2.5 per cent., and PbS eighty per cent., the percentage of the lead extracted in the electrolyzing-furnace is about ninety-one per cent.

The matte tapped from the furnace can be easily leached, as it rapidly disintegrates when placed in water. The salt and sodium sulfid which dissolve may be recovered by evaporation and added to the electrolyte in the electrolyzing-furnace. It is desirable to add an amount of sodium sulfid to the electrolyte from time to time sufficient to replace that taken out with the matte tapped, as otherwise chlorin will come off with the sulfur. After extracting salt and sodium sulfid from the tapped matte the residue is so porous that it takes fire on drying and may be permitted to roast before further treatment. The roasted product may be added to the ore-melting process. In melting the ore we prefer to use a reverberatory furnace and to keep the atmosphere in the furnace reducing to prevent loss of lead by volatilization. We can add natural galena direct to the electrolyzing-furnace, particularly when nearly free from earthy gangue.

Our process is particularly applicable to extracting lead from other kinds of matte—for example, that produced in smelting lead ores in a blast-furnace.

Mattes are not true electrolytes, as they permit the passage of an electric current without electrolysis, so that they are not well suited for direct electrolysis. This difficulty is obviated in our process, as is apparent from the foregoing description.

Having reference to the accompanying drawings, in Fig. 1 we have shown in horizontal section a reverberatory furnace of the usual construction, in which 1 is the fire-place; 2, firing-doors; 3, working doors; 4, the stack; 5, the tap-hole for matte, and 6 the slag-tap. The slag is tapped into the pot 7 and removed and the matte into pots 8, with a tap-hole 9 near the bottom. The matte is wheeled on the main floor 10 to a position above the electrolyzing-furnaces 11 and the spouts 12 and tapped from the pot 8, while still liquid, into the furnaces 11. The metallic lead and matte largely freed from lead are tapped at a lower level into a pot 13. 14 represents bus-bars connecting the furnaces 11 in electrical series with a direct-current dynamo.

In Fig. 2 we have shown in vertical section the details of our electrolyzing-furnace. The furnace is constructed of refractory material 15, with an iron pan 16 built in to prevent escape of lead. The iron pan is electrically connected to the bath of lead 17 in the furnace by lead in a space 18 left in the refractory material. A layer of matte 19 floats on the lead, and above this is a layer of fused salt 31. It is not necessary, though it is usual, for the matte to be melted, as the process succeeds with solid pieces of matte. The furnace has an iron cover 20, lined with fire-brick 21, with two openings left, one, 22, for the introduction of matte when the cover 23 is removed and the other allowing the passage of a carbon anode 24. At the end of the carbon anode is connected a copper terminal 25, to which is connected the positive conductor 26 of a dynamo. A hole 27 is left through the side of the furnace for the escape of sulfur, which may be condensed or burned. A tap-hole 28, closed by a plug of fire-clay 29, allows for tapping the furnace and removing matte and lead. An iron block 30 in contact with the pan 16 extends to the outside of the furnace and is connected to the negative pole of the source of the electric current.

It is understood that when the material containing lead sulfid is brought into contact with a cathode in a fused electrolyte the material being a conductor of the first class may be considered to itself become the cathode.

What we claim as new, and desire to secure by Letters Patent, is—

1. The process of recovering lead from lead-sulfid ores which consists in fusing the ore and accompanying gangue into a matte and a slag, and electrolytically separating lead from the matte by bringing the matte into contact with a cathode in a fused electrolyte in which lead sulfid is substantially insoluble.

2. The process of recovering lead from lead-sulfid ores which consists in fusing the ore and accompanying gangue into a matte and a slag, and electrolytically separating lead from the matte by bringing the matte into contact with a cathode in a fused electrolyte containing a dissolved sulfid, and in which lead sulfid is substantially insoluble.

3. The process of recovering lead from lead-sulfid ores which consists in fusing the ore and accompanying gangue into a matte and a slag, and electrolytically separating lead from the matte by bringing the matte into contact with a cathode in an electrolyte of fused sodium chlorid, containing sodium sulfid.

4. In the electrolytic process of reducing lead from lead sulfid by reduction at a cathode in a fused electrolyte which does not dissolve lead sulfid to a substantial degree, the step of adding a sulfid soluble in the electrolyte.

5. In the electrolytic process of reducing lead from lead sulfid by reduction at a cathode in an electrolyte of fused sodium chlorid, the step of adding sodium sulfid to the electrolyte.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

WILLIAM VALENTINE.
ANSON GARDNER BETTS.

Witnesses:
Ethel K. Betts,
Edward F. Keni.