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METALLURGY OF METAL SULFIDS.

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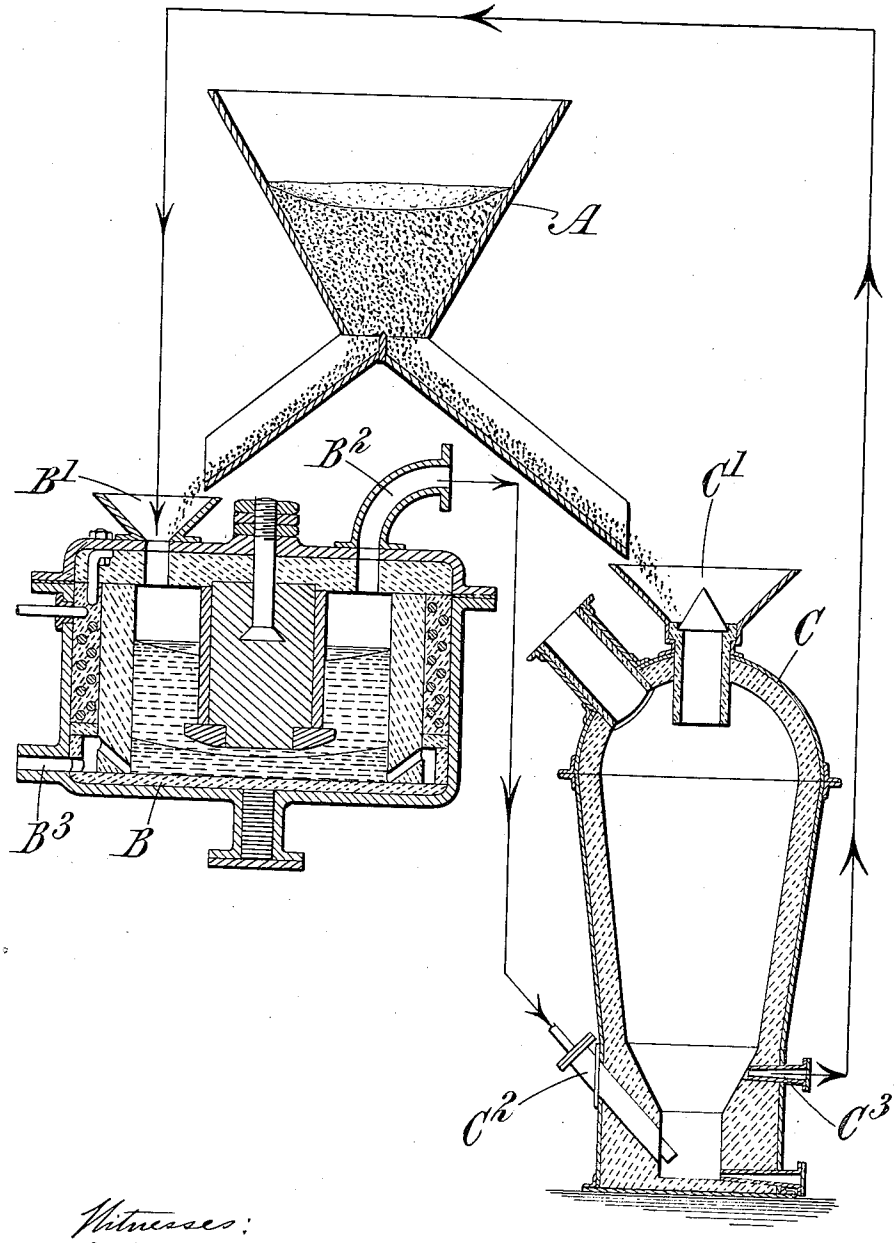
1,011,900.

Patented Dec. 19, 1911.



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UNITED STATES PATENT OFFICE.

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METALLURGY OF METAL SULFIDS.

1,011,900. Specification of Letters Patent. Patented Dec. 19, 1911.

Application filed April 9, 1910. Serial No. 554,511.

To all whom it may concern:

Be it known that I, EDGAR ARTHUR ASHCROFT, subject of the King of England, residing at Sogn, Norway, have invented certain new and useful Improvements in the Metallurgy of Metal Sulfids, of which the following is a specification.

This invention relates to improvements in the metallurgy of metal sulfids.

Sulfids of metals nearly free from gangue are produced in large quantities from the mechanical concentration of the well known Broken Hill refractory ores which are taken here as sufficiently illustrative of similar ores which occur with slight modifications all over the world and are likewise amenable to the treatment herein described.

Two leading products from the concentrating mills are recognized in the arts today, viz: (A) zinc concentrates containing upward of 40% zinc and under 12% lead and some silver, and (B) lead concentrates containing upward of 50% of lead and under 12% of zinc and some silver. Also in smaller quantities. (C) intermediate products such as slimes and middlings of varying composition. In treating (A) the process of zinc smelting in retort furnaces is the one generally employed and the lead and silver and sulfur are either lost or very imperfectly recovered from the residue at great expense. (B) the process of lead smelting is now almost universally employed and the zinc and sulfur are lost. The intermediate products (C) are at present only capable of economical treatment by mixing with other ores in smelting furnaces in trifling quantities or by being first converted by mechanical separation into products resembling either (A) or (B) in composition.

The present invention has for its principal object the more economical treatment of the zinc sulfid residues left after the treatment of the products A. and B. according to the method described in my U. S. applications Serial No. 554,508, filed April 9th, 1910, and Serial No. 554,509, filed April 9th, 1910. But either of the products A. B. or C. or any other metal sulfid may also be treated without departing from this invention, it being self evident that if separate metals are desired the sulfids must be separated. According to British Patent No. 10829[a]/ 1897 J. Swinburne has suggested the treatment of such products or the original ore from whence they are derived by electrolyzing sulfids in a bath of fused chlorids and getting off sulfur and metals. This reaction however requires a high temperature (about 600°–700° C.) and very violent agitation of the melt to prevent settling and has never been carried out in practice.

I have discovered that a more practical and convenient process for the above purpose is to so electrolyze the melt as to get off one or other of the chlorids of sulfur and metals according to one of the following reactions which will take place if the electrolysis is conducted at or about the respectively stated temperatures.

(1) $MS+2MCl_2=3M+SCl_4$ Temp. 350°C.
(2) $MS+MCl_2=2M+SCl_2$ " 450°C.
(3) $2MS+MCl_2=3M+S_2Cl_2$ " 550°C.

The sulfur chlorid given off may be readily condensed, (assisted in the case of the less stable products of reactions 1 and 2 by artificial cooling) and afterward reacted with metal sulfids as described in Swinburne and Ashcroft's U. S. Patent No. 691,822, dated January 28th, 1902 producing sulfur and metal chlorids the latter being added to the electrolysis bath to compensate for the chlorids decomposed by the above reactions. According to this invention, therefore, a process of recovering metals from a mixture containing other sulfids consists in treating the mixture with a fused metallic chlorid and electrolyzing the melt at the low temperatures referred to so as to produce the metals and chlorids of sulfur.

The above process is very economical of electric energy and of apparatus.

When zinc is the metal under recovery it is desirable to first remove any iron present from the fused chlorids to prevent contamination of the deposited metal and this may be carried out by known methods of purification. The preferred method of eliminating the iron is however to fractionally electrolyze the melt receiving the iron first into an alloy with molten lead from which it can be very economically recovered by known furnace processes. A cathode of pure molten zinc is afterward substituted from the iron lead alloy and pure zinc thereby obtained. When however lead is the metal being deposited from a mixed chlorid and sulfid bath it is not necessary to first remove the iron as the latter is always maintained in the ferrous state by the reducing

action of the sulfids present and so does not interfere with the precipitation of lead as it does when no sulfid is present in the bath.

At the end of the reaction it may be desirable to separate the zinc or lead from the chlorid and I find that for this purpose a sulfid of any other metal may be employed instead of sulfid of zinc or sulfid of lead, for instance sulfid of sodium may be added to a bath of chlorid of zinc or chlorid of lead, producing chlorid of sodium, metallic zinc or lead, and chlorid of sulfur according to the following equation. For example

$$2ZnCl_2+Na_2S=2Zn+SCl_2+2NaCl.$$

The accompanying drawing is a diagram illustrating one method of carrying this invention into effect as applied for example to a zinc sulfid residue.

The ore from a bin A is fed both to an electrolytic vat B and to a converter C. The ore enters the electrolytic vat at the inlet B′ through which is also supplied the fused zinc chlorid. Chlorid of sulfur is evolved and passes out through the outlet B^2 and the metallic zinc is removed from the outlet B^3 at the bottom of the electrolytic vat. The zinc sulfid residue passes from the ore bin A through the inlet C′ to the converter, the chlorid of sulfur from the electrolytic vat is introduced through the twyer or other inlet C^2 to the converter. The sulfur chlorid reacts with the zinc sulfid in the converter, the chlorin combining with the zinc to form zinc chlorid and the sulfur being given off. The reaction takes place according to the following equation:—

$$ZnS+CCl_2=ZnCl_2+S_2.$$

and the resulting zinc chlorid is removed by the outlet C^3 from the converter and returned to the electrolytic vat.

The form of the apparatus can be varied to suit the conditions under which it is used.

What I claim as my invention and desire to secure by Letters Patent is:—

1. A process of recovering metals from a mixture containing their sulfids which comprises treating the mixture with a fused metallic chlorid and electrolyzing the melt at low temperature so as to produce the metals and chlorids of sulfur.

2. A process of recovering metals from a mixture containing their sulfids which comprises treating the mixture with a fused metallic chlorid and electrolyzing the melt at low temperature to produce the metals and chlorids of sulfur, condensing the chlorids of sulfur and reacting them with metal sulfids to produce sulfur and metal chlorids, and adding the latter to the electrolytic bath.

3. A process of recovering zinc from a mixture containing zinc sulfid which comprises treating the mixture with fused zinc chlorid and electrolyzing the melt at low temperature to produce zinc and chlorid of sulfur.

4. A process of recovering zinc from a mixture containing zinc sulfid which comprises treating the mixture with fused zinc chlorid and electrolyzing the melt at low temperature to produce zinc and chlorid of sulfur, and reacting the chlorid of sulfur with a mixture containing the zinc sulfid to form zinc chlorid and sulfur, the zinc chlorid being added to the electrolytic bath.

5. A process of recovering zinc from a mixture containing zinc sulfid which comprises treating the mixture with fused zinc chlorid, electrolyzing the melt over a bath of molten lead so as to remove the iron as an alloy, subsequently electrolyzing the melt at low temperature to produce zinc and chlorid of sulfur, and reacting the chlorid of sulfur with a mixture containing the zinc sulfid to form zinc chlorid and sulfur, the zinc chlorid being added to the electrolytic bath.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

EDGAR ARTHUR ASHCROFT.

Witnesses:
HARRY B. BRIDGE,
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