

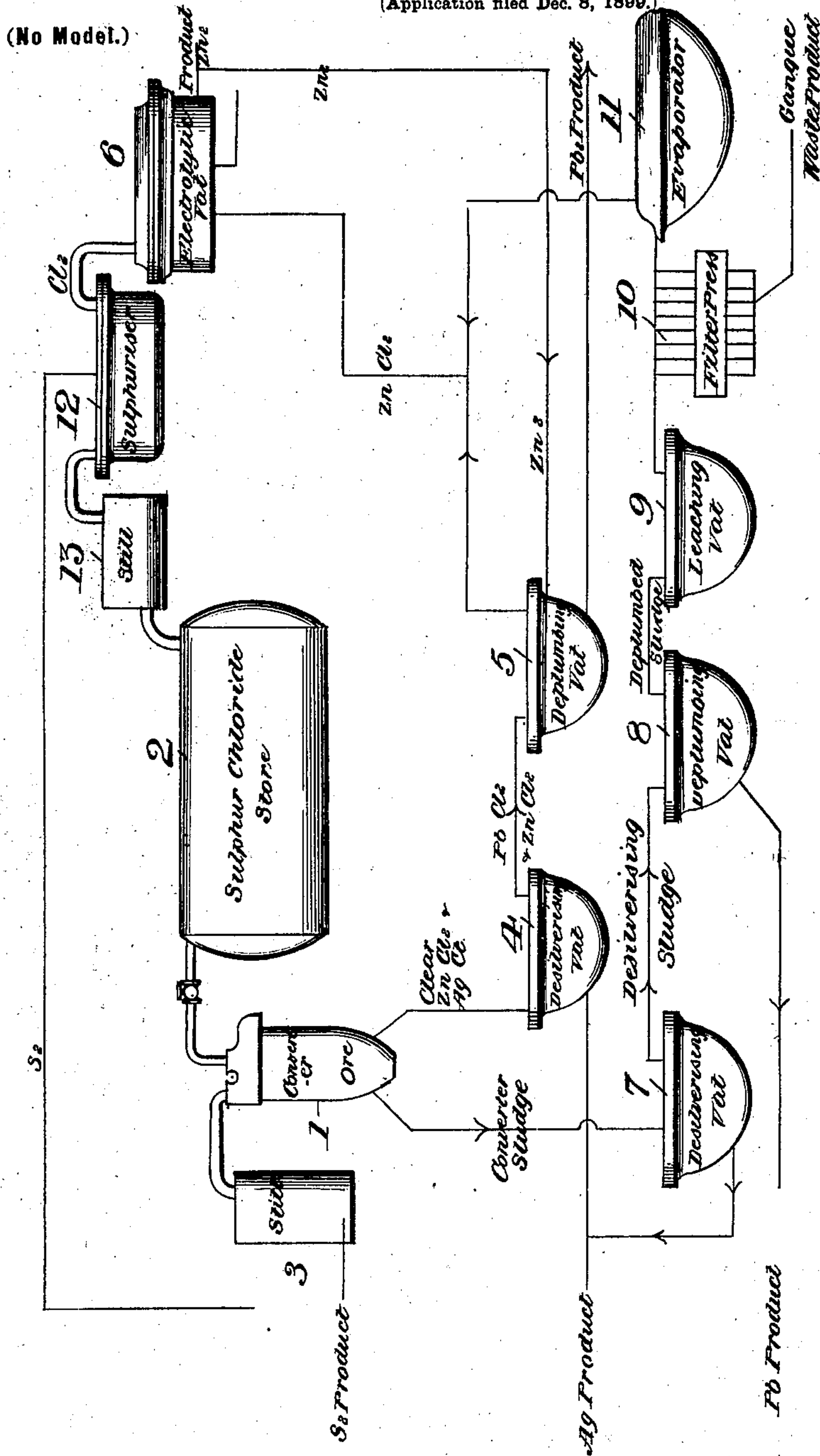
No. 691,822.

Patented Jan. 28, 1902.

J. SWINBURNE & E. A. ASHCROFT.

EXTRACTION OF METALS FROM SULFID ORES BY TREATMENT WITH CHLORID OR SULFUR AND ELECTROLYSIS.

(Application filed Dec. 8, 1899.)



INVENTORS.

WITNESSES:

L. C. Mills
Walter Allen

James Swinburne
Edgar Arthur Ashcroft.

BY

Knight & Potts Attorneys

UNITED STATES PATENT OFFICE.

JAMES SWINBURNE AND EDGAR ARTHUR ASHCROFT, OF LONDON,
ENGLAND.

EXTRACTION OF METALS FROM SULFID ORES BY TREATMENT WITH CHLORID OR SULFUR AND ELECTROLYSIS.

SPECIFICATION forming part of Letters Patent No. 691,822, dated January 28, 1902.

Application filed December 8, 1899. Serial No. 739,684. (No specimens.)

To all whom it may concern:

Be it known that we, JAMES SWINBURNE and EDGAR ARTHUR ASHCROFT, subjects of the King of England, residing at Westminster, London, England, have invented a certain new and useful Improvement in the Extraction of Metals from Sulfid Ores by Treatment with Chlorid of Sulfur and Electrolysis, of which the following is a specification.

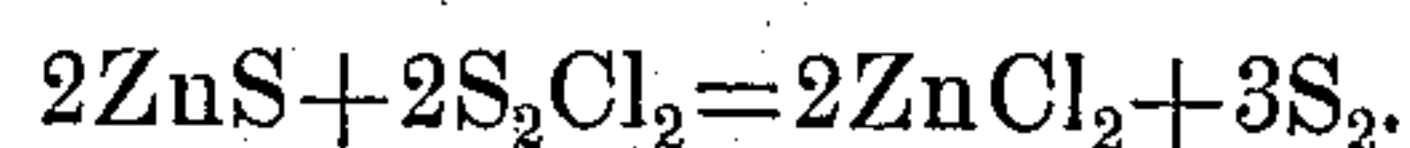
10 Our invention has reference to the treatment of sulfid ores in the dry way at high temperatures with chlorid of sulfur in connection with electrolysis.

15 In carrying this invention into effect the ore is in most cases run into a fused salt, such as chlorid of zinc, contained in a converter or chlorinator. Liquid or gaseous chlorid of sulfur is then introduced into the bottom of the converter. The chlorid of sulfur is normally S_2Cl_2 ; but it may contain either sulfur in solution or higher chlorids of sulfur, according to the circumstances of formation. The chlorin contained in the chlorid of sulfur is absorbed by the metal contained in the ore, 25 and the sulfur contained in the ore and in the chlorid of sulfur is liberated and distils off. The metallic chlorids so formed may be then electrolyzed. In most cases this electrolysis is conducted with the electrolyte in the fused state. The chlorin produced in the electrolysis is caused to come into contact with sulfur, and the chlorid of sulfur produced is condensed into liquid form. The sulfur contents of the chlorid employed is liberated at the 35 same time as the sulfur contents of the ore and may be employed for the regeneration of the chlorid of sulfur. The process is thus cyclic or regenerative as to the chlorid of sulfur, the ore being decomposed into free sulfur and metal and the chlorid of sulfur being regenerated.

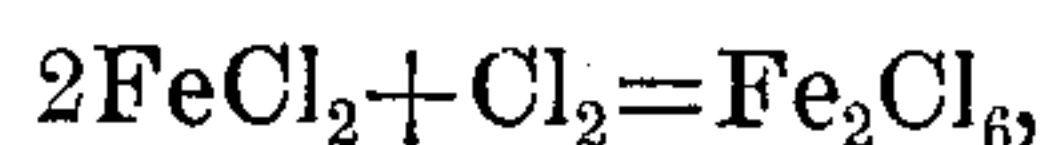
40 In some cases the formation of chlorid of sulfur may be simply effected by putting the sulfur into the zinc-chlorid-electrolyzing vats, where it melts and floats, and providing the surface temperature of the chlorid is not above the vaporizing-point of sulfur the chlorid of sulfur distils over, more or less free from dissolved sulfur, ($S_2 + Cl_2 = S_2Cl_2$.) 45 When it is desired to form the higher chlorids of sulfur or where the above temperature con-

dition is not obtainable, the chlorin is led into separate vessels containing, respectively, sulfur or sulfur monochlorid.

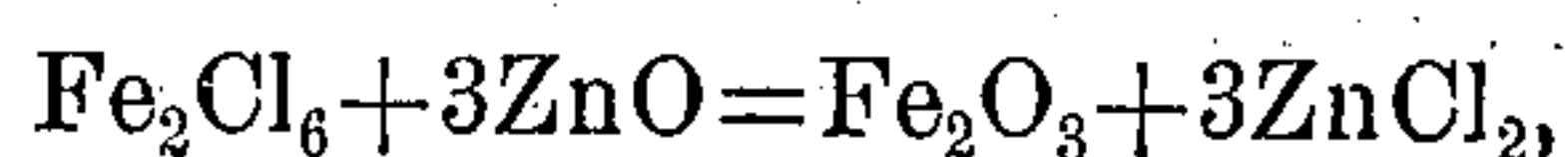
The process is applicable to the numerous 55 sulfid ores in which various metals are contained singly or together; but we describe it particularly in connection with mixed lead, zinc, and silver sulfid ores, which are difficult to treat by existing metallurgical methods. 60 As an example of our process, treatment of lead-zinc-sulfid ore may be taken. It is crushed, but not roasted, and it is run into fused chlorid of zinc contained in a chlorinator. The temperature of the mixture may 65 be between 500° and $1,000^\circ$ centigrade and may be controlled by regulating the blast of sulfur chlorid. The sulfur chlorid is run in at the bottom through an earthenware pipe and, becoming vaporized, bubbles through 70 the mixture of fused chlorid and sulfid. The sulfur of the chlorid and the sulfur of the ore come off together and are condensed.



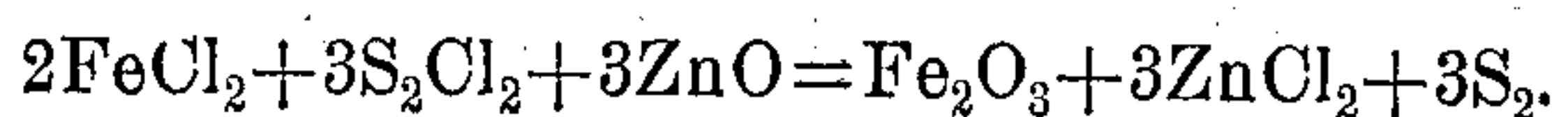
75 If the passage of the chlorid of sulfur is rapid, and especially if the temperature is low, the vapor generally contains some unaltered chlorid of sulfur, which may be removed from the sulfur by fractional distillation and condensed in any suitable vessel. The metallic sulfid in the ores is thus converted into chlorid. This chlorid is then preferably purified from iron and manganese, as iron would contaminate the zinc and manganese would accumulate when the process is worked cyclically. We may remove iron by converting it into ferric chlorid, 85



and treating the ferric chlorid with zinc oxid, 90

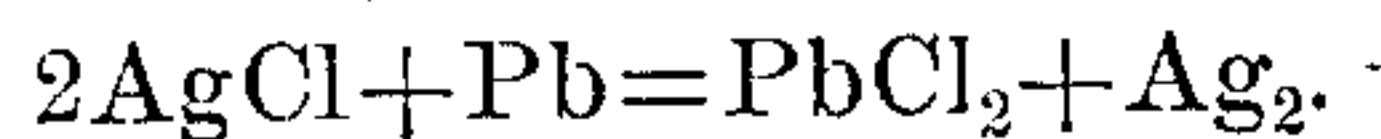


in the wet way. We may remove the manganese by passing chlorin gas or sulfur chlorid into the fused mass in the presence of 95 zinc oxid. Both manganese and iron are precipitated then as oxids,

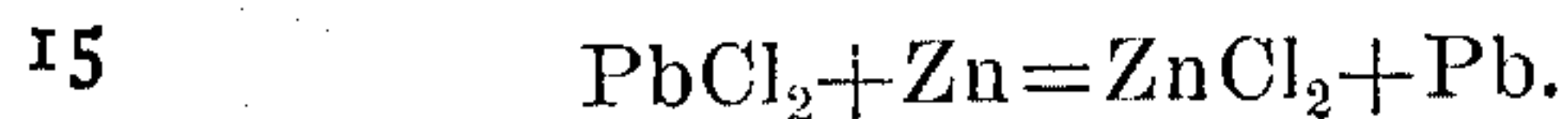


100 The zinc and lead and other metallic chlorids thus produced may be removed from the un-

changed gangue by raising the temperature, in which case they mostly distil over. The various metals may be separated from the fused chlorids or their solutions by substitution. For instance, the precious metals and antimony may be removed by lead, forming lead chlorid,



If excess of lead is used for extracting the precious metals from lead chlorids, a rich alloy is produced. The lead may be removed from the mixed chlorids by zinc, forming zinc chlorid,

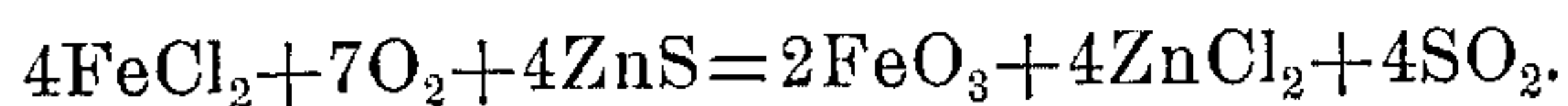


Copper may be similarly removed by zinc, and if excess of zinc is used to extract copper from fused salts the copper comes out in alloy with zinc as brass. The metals may also be separated by fractional electrolysis of the fused chlorids or their solutions.

The zinc chlorid to be electrolyzed is while still fused passed into the electrolytic vat, which contains also in admixture potassium or sodium chlorid. Metallic zinc and chlorin result from the electrolysis. The chlorin is passed to some of the sulfur from the chlorinator, thus reforming the chlorid of sulfur, and the metallic zinc is removed by periodically tapping off. The chlorid of sulfur is preferably formed or condensed or stored at a high level, so that it can be run into the chlorinator by gravity.

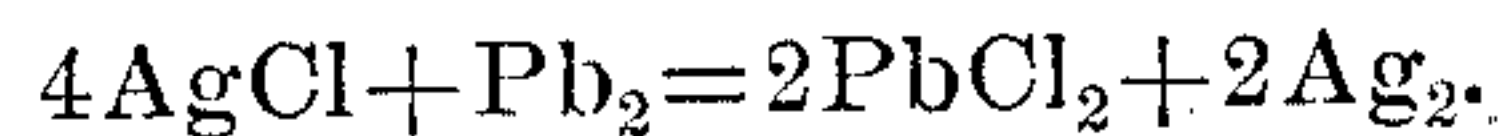
In order that our invention may be fully understood, we will proceed to describe it with reference to the accompanying drawings, which show a specimen scheme of our process applied to lead-zinc-sulfid ore.

Tracing the progress of the ore, it is led into the chlorinator 1, where it is run into fused zinc chlorid, so as to form a semifluid mixture. The chlorinator is of fire-clay, preferably glazed inside. A little zinc chlorid is melted separately in a ladle and run into the chlorinator, and a little ground sulfid ore is run into it. Chlorid of sulfur is run in from tank 2. The sulfur formed is condensed in the still 3. The sulfur is subsequently fused to separate the chlorids that have been carried over with it, which settle out of the fused mass, and is then a final product. At the final stage of the conversion air is also blown into the chlorinator to precipitate iron and manganese as oxids.

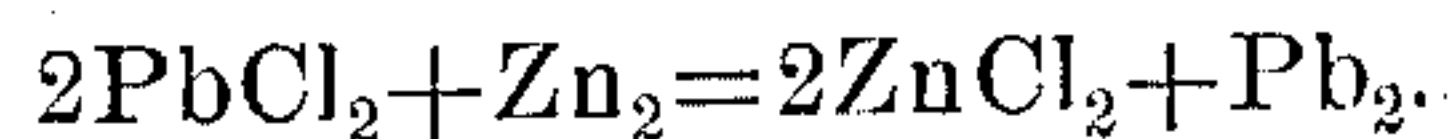


The air is blown into the converter by an ordinary air-blower and is supplied through the sulfur-chlorid pipe. When the conversion of the sulfids into chlorids is complete, the charge in the chlorinator is allowed to settle, and the clear chlorids of silver, lead, and zinc—that is, chlorids free from gangue—with any chlorids of antimony or arsenic, are run into the desilverizing-vat 4, where the silver, an-

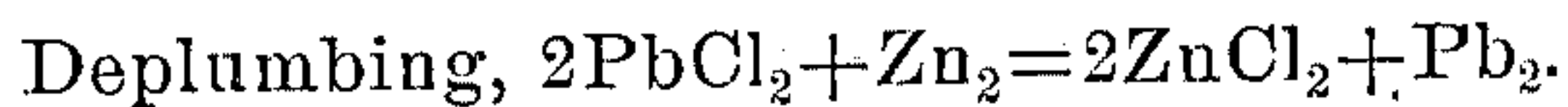
timony, and arsenic are taken out by substitution of lead.



The rich silver bullion from this vat is a final product. The desilverized lead and zinc chlorids are led to the deplumbing-vat 5, when the lead is removed by zinc,



The lead is a final product, and the zinc chlorid goes to the electrolytic vat 6. The other portion of the chlorinator charge or sludge consists of gangue and iron and manganese oxids reduced to the consistence of mud by fused chlorids. This chlorinator sludge is led to the desilverizing-vat 7 and then to the deplumbing-vat 6. The materials are maintained in a fused condition in the desilverizing, deplumbing, and electrolysis vats. The desilverizing and deplumbing processes are quick enough to be carried out before the mass cools, and the electrolysis-vat is kept hot by the electric current, as in the case of aluminium; but in the case of zinc chlorid a much smaller surplus electrical pressure is needed.



After that it is cooled and led to the leaching-vat 9, where the chlorid of zinc is dissolved in water. It is separated from the gangue by the filter-press 10 and by further leaching, and the solution is mixed with potassium chlorid. The potassium chlorid is to form a double salt with the chlorid of zinc. This double salt dehydrates on heating without forming oxychlorid to any serious extent. The mixture is evaporated down in the evaporator 11 until the salt is anhydrous and fused in it and then led to the electrolytic vat 6. In this vat it is electrolyzed, yielding zinc chlorin. The chlorin is led to the sulfurizer 12, where it is converted into chlorid of sulfur.

The sulfurizer is a vessel containing sulfur heated externally nearly to the boiling-point of sulfur. The chlorin is led so as to blow onto the surface of the sulfur, and combination takes place easily and quietly. The chlorid of sulfur is condensed in the still 13 and stored in the closed vat 2 on a higher level than the chlorinator.

Chlorid of sulfur has an advantage over chlorin as an agent for splitting up the sulfid ores in that it is easily stored and handled. It is easily formed and can be kept in bulk. It would thus not be outside our present invention to convert chlorin into chlorid of sulfur to get the advantages of easy handling and storage and to decompose the chlorid of sulfur more or less by heat before passing it into the sulfid ore.

In most cases the ore is treated suspended in a bath of fused haloid salt; but this is not

essential. Ores with volatile chlorids—such as antimony or arsenic, or even zinc sulfid—may be treated with chlorid of sulfur without any bath of fused salt. The ore is then heated 5 above the boiling-point of its chlorid and is then treated with sulfur chlorid. The reaction is as before, sulfur and chlorid of the metal distilling over.

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

1. The herein-described process consisting in treating sulfid ores in the dry way at a high temperature with chlorid of sulfur S_2Cl_2 to form chlorid of the metal or metals and free 15 sulfur substantially as described.

2. The herein-described process consisting in treating metallic sulfids in a bath of fused haloid salt with chlorid of sulfur S_2Cl_2 substantially as described.

20 3. The herein-described process consisting in treating sulfid ores in a fused haloid salt with chlorid of sulfur and producing sulfur

and chlorid, electrolyzing the chlorid thereby producing chlorin and metal and combining the chlorin with some of the sulfur from the 25 treatment of the sulfid ore and using the so-regenerated sulfur chlorid for treating more ore and so on.

4. The process herein described consisting in electrolyzing a metallic chlorid, thereby 30 producing chlorin, combining sulfur with said chlorin and producing chlorid of sulfur, and then treating heated sulfid ore with said chlorid of sulfur, and producing therefrom chlorid of metal in the ore, and free sulfur. 35

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

JAMES SWINBURNE.

EDGAR ARTHUR ASHCROFT.

Witnesses:

E. E. SKINNER,

V. HIPWELL.