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METALLURGY OF METAL SULFIDS.

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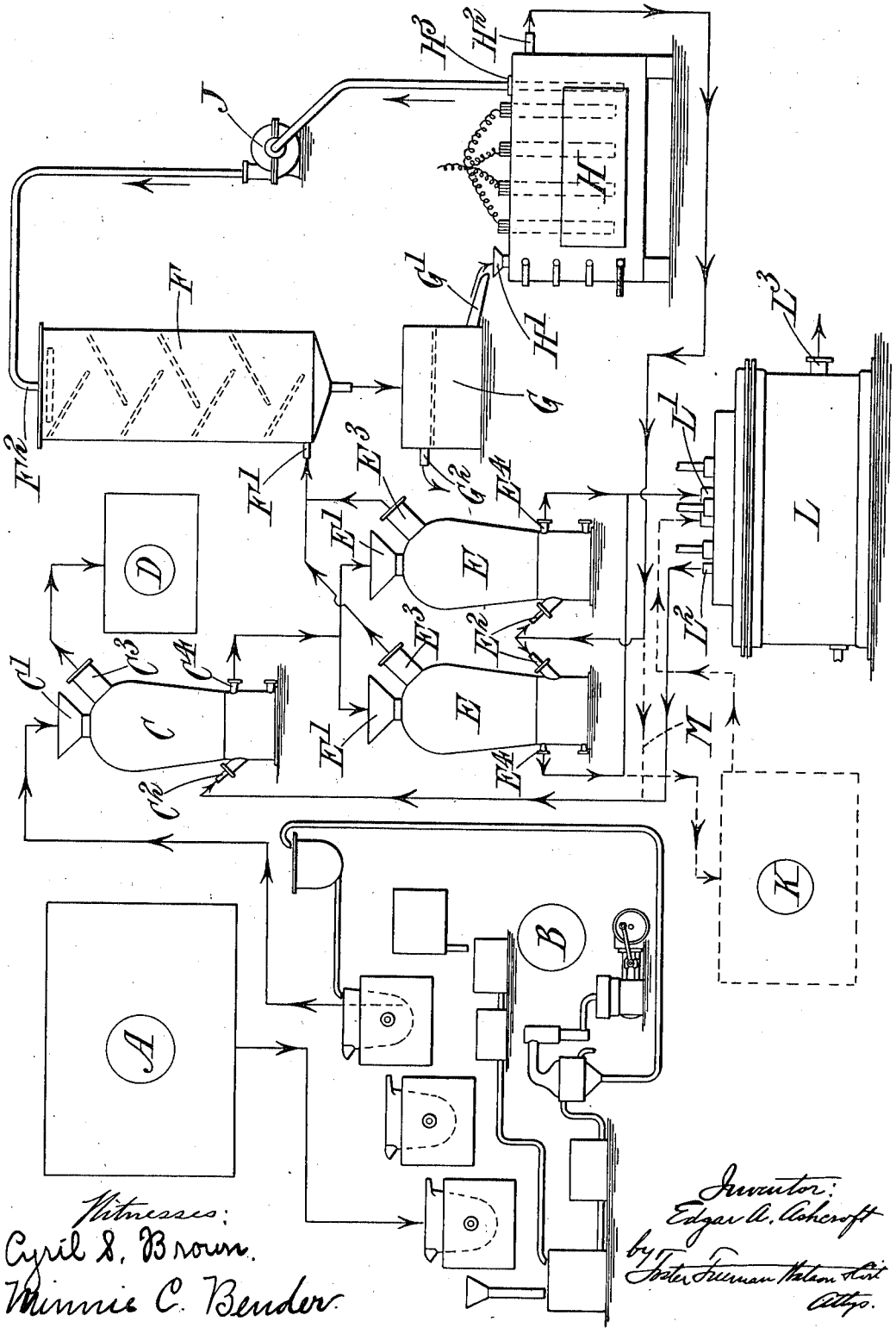
1,011,899.

Patented Dec. 19, 1911.



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UNITED STATES PATENT OFFICE.

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METALLURGY OF METAL SULFIDS.

1,011,899. Specification of Letters Patent. Patented Dec. 19, 1911.

Application filed April 9, 1910. Serial No. 554,510.

To all whom it may concern:

Be it known that I, EDGAR ARTHUR ASHCROFT, a 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.

Sulfids of metals nearly free from gangue are produced in large quantities from 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 residues at great expense. In treating (*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 in 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 specifications U. S. applications Serial No. 554,508 and Serial No. 554,509. But either of the products (*a*) (*b*) or (*c*) or any other metal sulfid may also be treated without departing from this invention.

According to Swinburne and Ashcroft's U. S. Patent No. 691,822, the original ore from which such products are derived is treated by the process known as "dry chlorin (or sulfur chlorid) smelting with electrolysis". In this process great difficulties were experienced in eliminating the gangue matter and the iron and manganese chlorids from the fused melts and in recovering the chlorin which is combined with such impurities. In consequence of which difficulties this process which otherwise presents great advantages over other forms of treatment has found a very limited application.

I have discovered that a more practical and economical process for the above purpose is as described below:—The special features characterizing this process are:—(1) Gangue matter is first eliminated as completely as possible from the mixed sulfids. (2) Lead and silver sulfids are decomposed and lead and silver separated and recovered in any usual manner, or preferably according to the methods described in my co-pending applications Serial Nos. 554,508 and 554,509 filed April 9, 1910. (3) The remaining zinc sulfid residues are treated by chlorin (or chlorid of sulfur) smelting followed by electrolysis according to the reaction described in U. S. Patent No. 691,822 with modifications as described below for the elimination of iron and manganese and recovery of the chlorin which enters into combination with these metals.

Although the above is the preferred method of working step 2 may be omitted and the lead and silver recovered at subsequent stages of the process when economically desirable.

The chlorin smelting process may be briefly described as follows:—The ore (from which the gangue has been removed and from which preferably the lead and silver have been substantially removed as above referred to) is made into a cream with fused chlorid of zinc. The cream is treated in a converter or suitable vessel with a chlorinating agent viz., chlorin or sulfur chlorid, the gas or liquid being forced in at the bottom. At a suitable temperature (for instance a low red heat) the chlorin is rapidly absorbed by the metals and sulfur is given off in its place. The reaction is most vigorous at a temperature of 600° C. and upward which is well above the fusing point and well below the vaporizing point of zinc chlorid, and being exothermic, the temperature may be maintained and regulated by increasing or decreasing the blast of chlorin and regulating the supply of ore. To start the operation it is convenient to fuse the chlorids etc. in a separate vessel or large

ladle, the converter being previously heated by internal fire or other means. The treatment is carried on until all the sulfids are converted into chlorids and fresh supplies of sulfids are added to the converter at regular intervals throughout the treatment and the operation is carried on until the resulting mixture of metal chlorids has accumulated so as to fill or nearly fill the converter. During the whole of the process the chlorin is completely absorbed, sulfur being liberated. This is collected and condensed. Toward the end a little excess of chlorin may be passed and will merely result in raising some of the iron chlorid to the ferric state. The point at which reaction in the converter is complete (all the sulfur present being then eliminated) is clearly and usefully indicated by the disengagement of copious brown fumes of ferric and manganic chlorids which can be instantly detected by opening a small test hole. At the end of the treatment the converter contains varying quantities of fused chlorids of zinc, (lead and silver if present in the ore) and iron and manganese. The iron and manganese are present mainly as ferrous and manganous chlorids.

The modifications in the subsequent treatment referred to under (3) above are as follows according to the present invention:—The converter operation, is now carefully regulated and stopped as nearly as possible at the moment that all the sulfur is eliminated from the melt and while the iron and manganese chlorids are still in the ferrous and manganous states and care is taken to prevent much excess of chlorin being introduced beyond this point so as to avoid volatile chlorids such as

$$Fe_2Cl_6,\ MnCl_3$$

passing into the sulfur as these destroy its marketable value and are somewhat troublesome to recover or remove. The melt is tapped while still hot into other converters, a sufficient quantity of the hot charge being left in the main converter to restart the process with fresh quantities of ore. Escape pipes from the second converters are carried to an absorption apparatus as described below. Into the second converters a slow stream of chlorin is passed from below for a considerable time, and results in the volatilization of the iron and manganese from the melt in the form of the higher chlorids of these metals which are very volatile and tend to leave the melt as soon as formed; if no sulfid is present to react with them re-forming the lower chlorids. A small quantity of zinc chlorid may be carried over mechanically if the temperature is too high. This will, however, be caught in the absorption apparatus in solution with sodium chlorid and readily recovered either by crystallization as double chlorid of sodium and zinc, which may be electrolyzed in the principal electrolysis apparatus or as zinc hydrate by precipitation with a small excess of soda solution.

A supplementary electrolytic apparatus is provided wherein sodium chlorid is decomposed in aqueous solution, resulting in pure strong chlorin gas (which is passed back to the converters) and a solution of NaOH (with some NaCl which, however, does not interfere) which may be made of any desired strength (preferably about 10% to 15% NaOH). This is used in any convenient absorption apparatus for the precipitation of iron and manganese hydrates with the re-formation of the sodium chlorid solution. The hydrated oxids are filtered hot from the solution of NaCl thus recovering all chlorin and a by-product of iron and manganese hydrates free from all other impurities. The occluded salt solution may be readily washed out. The iron and manganese hydrates so produced are a valuable by-product, and may be sold as paint or smelted for the production of ferro manganese. These reactions are as follows:—

$$Fe_2Cl_6(+H_2O+6NaOH = Fe_2O_3(+H_2O)+6NaCl+3H_2O$$

$$2MnCl_2(+H_2O)+6NaOH = \left\{\begin{matrix}MnO_2\\MnO\end{matrix}\right\}(+H_2O)+6NaCl+3H_2O.$$

The resulting "iron free" fused chlorids if more metals than zinc are present may be treated for their metallic contents in any well-known manner, as for example by fractional precipitation or fractional electrolysis. In either case the proportion between the size of the electrolysis vats for treating the fused chlorids and those for manufacture of soda solution for treating the ferric and manganic chlorids, depends upon the composition of the ore and should be correctly balanced.

The accompanying drawing is a diagram representing one arrangement of apparatus suitable for carrying this invention into effect.

A represents a concentration plant of any type suitable for the removal of gangue from sulfids.

The small diagram B represents an apparatus of the type described in my previous U. S. application Serial No. 554,508, to indicate that at this stage the lead and silver sulfids may be eliminated. The ore, with or without this preliminary treatment, is made into a cream with fused chlorid of zinc and introduced into a converter C through the inlet C^1. Chlorin or chlorid of sulfur is forced in through the twyer or inlet C^2. Sulfur is given off through the outlet C^3 and passes into a condenser D where it is collected.

The mixed chlorids are removed from the outlet C^4 of the converter and introduced through the inlets E^1 into two secondary converters E. Into the secondary converters chlorin is passed through the twyers or inlets E^2. The iron and manganese chlorids escaping through the outlet E^3 are passed through an inlet F^1 into an absorption apparatus F into which is also introduced caustic soda solution through the inlet F^2. The contents of the absorption apparatus are passed into a filter G from which the sodium chlorid solution produced by the reactions in the tower is withdrawn through one outlet G^1 and the iron and manganese hydrates are withdrawn through the outlet G^2. The sodium chlorid solution is passed through an inlet H^1 into an electrolytic vat H from which the chlorin is removed through outlet H^2 to the twyers E^2 of the converters E. The resulting caustic soda solution is removed through an outlet H^3 and conducted through a pump J to the inlet F^2 of the absorption apparatus F. The fused chlorids in the converters E having been freed from iron and manganese are removed through the outlet E^4 and may be treated for the removal of lead and silver in an apparatus K if this has not already been done; and in any case the fused zinc chlorid is introduced through the inlet L^1 to an electrolytic vat L from which the chlorin is removed through the outlet L^2 to the twyer C^2 of the converter C and the metallic zinc (final product) is removed from the outlet L^3. As indicated by the dotted line M the chlorin supplies from the two electrolytic vats H and L are interchangeable.

This process is applicable to the treatment of all kinds of sulfid ores and of products such as metals containing other metal-sulfids such as nickel, antimony, cobalt, copper and the like and the treatment will of course be modified to suit the particular contents of the ore or product under treatment.

When an ore or product contains antimony or arsenic these elements are converted into highly volatile, and easily fusible chlorids and will leave the melt immediately, thus constituting a valuable means of separation. The typical reaction in such cases is as follows:—

$$Sb_2S_3+3ZnCl_2=2SbCl_3+3ZnS.$$

The antimony chlorid is volatile at 200° C. and fusible at 70° C. and completely separates from the other chlorids such as zinc, lead etc. It may be afterward converted to antimony oxid with regeneration of zinc chlorid by treatment with zinc oxid according to the reaction

$$3ZnO+2SbCl_3=Sb_2O3+3ZnCl_2.$$

The antimony oxid is a valuable product and the zinc chlorid is used again in the process.

The gangue (if any) may be allowed to settle, preferably in a separate vessel and the chlorids poured off during any convenient subsequent stage of the process for instance in the second converters after finishing the charge or in any of the storage pots.

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

1. A process of treating sulfid ores or products which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with a fused metal chlorid, subjecting the melt to the action of a chlorinating agent, removing the melt to other converters, and treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids.

2. A process of treating sulfid ores or products which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with a fused metal chlorid, subjecting the melt to the action of a chlorinating agent, removing the melt to other converters, treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, and thereafter recovering the other metals present by extracting them by fractional precipitation and electrolysis.

3. A process of treating sulfid ores or products which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with a fused metal chlorid, subjecting the melt to the action of a chlorinating agent, removing the melt to other converters, treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, and thereafter recovering the other metals present by extracting them by fractional precipitation and electrolysis.

4. A process of treating sulfid ores or products which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with a fused metal chlorid, subjecting the melt to the action of a chlorinating agent, removing the melt to other converters, treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, separating and electrolyzing the sodium chlorid for the production of chlorin and sodium hydrate, utilizing the chlorin for reacting

with the mixed sulfids and chlorid in the first converter and the mixed chlorids in the second converters, passing the sodium hydrate to the absorption apparatus to react with the iron and manganese chlorids, and thereafter recovering the other metals present by extracting them by fractional precipitation and electrolysis.

5. A process of treating sulfid ores or products which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with fused metal chlorid and separating the antimony present as a volatile chlorid, subjecting the melt to the action of a chlorinating agent, removing the melt to other converters, treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, separating and electrolyzing the sodium chlorid for the production of chlorin and sodium hydrate, utilizing the chlorin for reacting with the mixed sulfids and chlorid in the first converter, and the mixed chlorids in the second converters, passing the sodium hydrate to the absorption apparatus to react with the iron and manganese chlorids, and thereafter recovering the other metals present by extracting them by fractional preciptation and electrolysis.

6. A process of treating sulfid ores or products which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with fused metal chlorid and separating the arsenic present as a volatile chlorid, subjecting the melt to the action of a chlorinating agent, removing the melt to other converters, treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, separating and electrolyzing the sodium chlorid for the production of chlorin and sodium hydrate, utilizing the chlorin for reacting with the mixed sulfids and chlorid in the first converter, and the mixed chlorids in the second converters, passing the sodium hydrate to the absorption apparatus to re-act with the iron and manganese chlorids, and thereafter recovering the other metals present by extracting them by fractional precipitation and electrolysis.

7. A process of treating sulfid ores or products which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with fused metal chlorid and separating the antimony present as a volatile chlorid, treating the antimony chlorid with zinc oxid for the production of antimony oxid and zinc chlorid which is re-acted with a further quantity of ore, subjecting the melt to the action of a chlorinating agent, removing the melt to other converters, treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, separating and electrolyzing the sodium chlorid for the production of chlorin and sodium hydrate, utilizing the chlorin for reacting with the mixed sulfids and chlorid in the first converter, and the mixed chlorids in the second converters, passing the sodium hydrate to the absorption apparatus to react with the iron and manganese chlorids, and thereafter recovering the other metals present by extracting them by fractional precipitation and electrolysis.

8. A process of treating sulfid ores or products, which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with fused metal chlorid and separating the arsenic present as a volatile chlorid, treating the arsenic chlorid with zinc oxid for the production of arsenic oxid and zinc chlorid which is re-acted with a further quantity of ore, subjecting the melt to the action of a chlorinating agent, removing the melt to other converters, treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, separating and electrolyzing the sodium chlorid for the production of chlorin and sodium hydrate, utilizing the chlorin for re-acting with the mixed sulfids and chlorid in the first converter, and the mixed chlorids in the second converters, passing the sodium hydrate to the absorption apparatus to re-act with the iron and manganese chlorids, and thereafter recovering the other metals present by extracting them by fractional precipitation and electrolysis.

9. A process of treating zinc sulfid containing lead and other metal sulfids which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with fused zinc chlorid and subjecting the melt to the action of chlorin gas, removing the melt to other converters, and treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids.

10. A process of treating zinc sulfid containing lead and other metal sulfids which consists in eliminating the gangue matter, separating the lead and silver present, mix-

ing the remaining product with fused zinc chlorid and subjecting the melt to the action of chlorin gas, removing the melt to other converters and treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, and thereafter recovering the zinc by electrolyzing the melt.

11. A process of treating zinc sulfid containing lead and other metal sulfids which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with fused zinc chlorid and subjecting the melt to the action of chlorin gas, removing the melt to other converters and treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, and thereafter recovering the zinc by electrolyzing the melt.

12. A process of treating zinc sulfid containing lead and other metal sulfids which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with fused zinc chlorid and subjecting the melt to the action of chlorin gas, removing the melt to other converters and treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, separating and electrolyzing the sodium chlorid for the production of chlorin and sodium hydrate, utilizing the chlorin for reacting with the mixed sulfids and chlorid in the first converter, and the mixed chlorids in the second converters passing the sodium hydrate to the absorption apparatus to react with the iron and manganese chlorids, and thereafter recovering the zinc by electrolyzing the melt.

13. A process of treating zinc sulfid containing lead and other metal sulfids which consists in eliminating the gangue matter, separating the lead and silver present, mixing the ore with fused zinc chlorid, and separating the antimony and arsenic present as volatile chlorids, subjecting the melt to the action of chlorin gas, removing the melt to other converters and treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, separating and electrolyzing the sodium chlorid for the production of chlorin and sodium hydrate, utilizing the chlorin for reacting with the mixed sulfids and chlorid in the first converter, and the mixed chlorids in the second converters passing the sodium hydrate to the absorption apparatus to react with the iron and manganese chlorids, and thereafter recovering the zinc by electrolyzing the melt.

14. A process of treating zinc sulfid containing lead and other metal sulfids which consists in eliminating the gangue matter, separating the lead and silver present, mixing the remaining product with fused zinc chlorid and separating the antimony and arsenic present as volatile chlorids, treating the antimony and arsenic chlorids with zinc oxid for the production of antimony oxid and arsenic oxid and zinc chlorid which is reacted with a further quantity of ore subjecting the melt to the action of chlorin gas, removing the melt to other converters and treating the mixture with chlorin to volatilize the iron and manganese as higher chlorids, passing the chlorids to absorption apparatus wherein they are treated with a solution of sodium hydrate to form sodium chlorid and iron and manganese hydrates, separating and electrolyzing the sodium chlorid for the production of chlorin and sodium hydrate, utilizing the chlorin for reacting with the mixed sulfids and chlorid in the first converter, and the mixed chlorids in the second converters, passing the sodium hydrate to the absorption apparatus to react with the iron and manganese chlorids, and thereafter recovering the zinc by electrolyzing the melt.

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,
PERCY HEWITT.