G. MOJANA.

PROCESS FOR TREATING ZINKIPHEROUS SUBSTANCES.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

WITNESSES:

INVENTOR
Guido Mojana

ATTORNEYS
To all whom it may concern:

Be it known that I, Guido Mojana, a civil engineer, residing at Milan, Italy, have invented and perfected a process for treating zinciferous substances, of which the following is a specification.

My present invention relates to a process for treating calamine smithsonite, blende, concentrates and tailings, zinc ashes, namely the residues of the zinc plating industry and all other industries where zinc is treated, with the object of forming a soluble compound with the zinc contained in such materials; such compound is then extracted from the remainder of the mass by lixiviation, depressurized and eventually electrolyzed in order to obtain metallic zinc.

It is well known that when calamine, for instance, is treated with chlorin in various conditions of temperature and pressure only a part of the zinc it contains is transformed into chlorid. The same happens with all the other ores and materials containing zinc not in the state of sulfid, if the zinc is contained in the form of sulfid, as in the blende, by operating under certain conditions upon the ore, the chlorin is rapidly absorbed, sulfur is set free and a chlorid of zinc is formed. The Ashcroft and Swinburne process is based upon this reaction and cannot be applied to other ores beside blende nor to roasted blende, nor to ashes.

I have discovered that by acting in the presence of porous carbon and under certain determined conditions the zinc contained in the calamine can also be almost totally transformed into a soluble compound (chlorid) and the same result is obtained with the other zinciferous substances. The process based upon said discovery may thus be applied to calcined and uncalcined calamine, blende smithsonite, zinc ashes, concentrates and tailings. For this purpose I may use charcoal, or other material obtained from the distillation of coal, peat, lignite, and wood, and which is broken into small particles. It must be intimately mixed with the zinciferous substances and preferably wetted a little before mixing the temperature must generally be above 150° centigrade; chlorin is at first absorbed in considerable quantity the absorption then grows less rapid and becomes very slow. During the operation carbonic acid, oxid of carbon and naturally the chlorin not absorbed are given off from the mass. For this reason the apparatus for working the process has been so designed as to compel the gases given off from the mass which has been almost completely treated to pass through another mass only slightly treated. Chlorin is thus all absorbed and the gases are set free in the atmosphere.

According to circumstances it is well to inject together with the chlorin (but not at intervals) a jet of steam.

The reaction between gaseous chlorin and the zinc ore is likely to take place in consequence of the presence of steam, developing either from the humidity, natural or artificial, of the ore under treatment, or from the humidity the chlorin carries.

The quantity of water required for the reaction is small in comparison with the amount, which would correspond with the quantity of chlorin, as reckoned on the base of the chemical equation, this depending upon the circumstance that water is being produced in the same quantity as required by the reaction which is going on.

The reaction may be considered as consisting of two phases, respectively represented by the equations:

\[(1) \quad 2H_2O + 2Cl_2 + C = CO_2 + 4HCl\]

\[(2) \quad 4HCl + 2ZnO = 2ZnCl_2 + 2H_2O\]

As the chlorid of zinc thus formed is a strongly hygroscopic substance which absorbs water even at temperature of about 200° C., it may happen that, while the chlorinization is going on and the amount of chlorid of zinc is increasing, the steam, necessary for the completion of the reaction may not be present in the parts of the apparatus situated at a distance from the point of entrance of chlorin. In this case the introduction of a special jet of steam may prove advantageous.

Other elements by which the reaction is influenced are, besides the presence of steam, the temperature, the quantity of carbon and its intimate mixture with the ore.

By the use of the comminuted carbon the reactions, by which the chlorid of zinc is formed from the charge, are obtained at a comparatively low temperature, the reactions taking place at about 100° C., though the best results are obtained at about 200° C. In the annexed drawing I have illustrated two different forms of construction of the apparatus which may be used for carrying out my process.
Figure 1 is a vertical section of a continuous action apparatus. Fig. 2 is a plan view of a modified form, Fig. 3 is an elevation, Fig. 4 a section on line A—B of Fig. 3, and Fig. 5 a section on line p—q of Figs. 3 and 4, of an alternating action apparatus.

The continuous apparatus shown in Fig. 1 consists of a cylinder S made in one piece or formed of special bricks and mortar that resist the action of chlorin, the cylinder being as thin as possible. The pipe t in the lower part serves for introducing chlorin. The heating of the cylindrical retort is attained by circulating around and inside the same the products of combustion of a common furnace properly diluted with air. The hot gases enter the earthenware pipe L, with thin walls located inside the retort S, and rise through it, then they come down into the annular chamber C along the retort and again rise along C₂, whence they pass into an iron pipe which discharges them into the atmosphere. In the bottom of the retort there is a door for the discharge, the charging being effected from the top.

The alternating action apparatus (Figs. 2 to 5) consists of two retorts 1, 2 (Fig. 3), arranged in series. These retorts are each surrounded by two annular chambers C₁, C₂ communicating with each other at their lower portion and forming two jackets around the retort. A pipe M connects with the upper part of the annular chamber C₁ and a outlet pipe leads from the upper part of the chamber C₂. The retorts are heated by the combustion gas from the furnace which enters through the inlet pipe M and passes downward through the annular chamber C₁ and then upward through the chamber C₂ to the outlet pipe. Chlorin is introduced so that after it has gone through the retort 1 from bottom to top it passes into the retort 2 through pipe w also from bottom to top. When the retort 1 is saturated with chlorin this is sent direct into retort 2 and the former is then discharged from the bottom by removing the lower cover E (kept against the bottom by a screw). When the retort 1 is recharged chlorin from retort 2 is sent through it until retort 2 is saturated and so on. These operation are effected by using in addition to pipes u and w, cocks r' and R, this latter being a three way cock. The pipe a which supplies the chlorin can be connected by the cock R with the pipe b leading to retort 1, or with the pipe c leading to retort 2. When the pipe a is connected with pipe b the chlorin will enter the retort 1, and as the retort 1 is closed at the top, the chlorin, not absorbed in retort 1, will pass with the other gases into the pipe w. The cock r' in the pipe w being open, the chlorin will pass through pipe c into the retort 2 where it will be absorbed. At this time the retort 2 is open at the top so that the gases will be discharged into the atmosphere. During this period the cock r' remains closed. When the charge in retort 1 is saturated, the retort is discharged and is then recharged after the cock R has been turned so as to cause the pipe a to communicate with the pipe c, and the cock r' has been closed and the cock r' opened. Then retort 2 is closed at the top, retort 1 being left open at the top after the recharging. This is continued until retort 2 is saturated and then the operation is repeated.

In the continuous apparatus a partial discharge is effected at regular intervals of time and it is then at once refilled from the top until the retort is full.

The two apparatuses described show one of the ways of carrying out my process, but they can be modified in many ways: the retorts for instance may not be of circular section, the inside earthenware pipe L in the first apparatus may be dispensed with or changed as also the circulation of the gases and so on. Where convenient the draft of the heating gas may be increased by a section at the discharge of the heating chamber. The heating may also be obtained by circulating around the retort, in an annular chamber or jacket, steam at a suitable temperature and pressure or by introducing steam inside the retort together with the chlorin. An important simplification can be obtained by heating the retort electrically, that is by passing a current of suitable voltage through an iron coil around the retort or through a mass of granular coke around the retort, or by passing the current through the mass of coke and zinkiferous substance contained in the retort and upon which the chlorin must act. The mass which has been thus treated is first sieved for the purpose of separating the charcoal from the remainder. This is taken into lixiviation tanks and treated with the washing water of said charcoal. The mixture obtained by lixiviation is made hot by the introduction of a jet of steam. It is then passed through a filter press. The solid part which remains in the filter press may eventually be treated in any suitable manner to obtain silver or lead, but this forms no part of the present invention. The liquid containing the chlorids of Zn, Pb, Fe and Mn. are cooled at 0° centigrade and filtered, thus separating Cl₂ Pb₂; the liquid is then successively treated with oxidants (such as chlorin, calcium hypochlorite and with substances containing oxid of zinc (calamin, roasted blende, calcined calamin or others) and it is then filtered. I thus get a solution of Cl₂Zn which may at once be subjected to electrolysis. Or the said solution may be dried, and in such case the chlorid of zinc thus obtained may be placed on the market or it may be melted and in that con-
dition subjected to electrolysis. When treating the solution or the molten salt by electrolysis the metallic zinc will gather on the cathode and the chlorin on the anode. This chlorin is sent into the chlorinating tub after it has been dehydrated if necessary, and is then heated by passing through an earthenware coil arranged within the furnace. Cl₂Zn may also be separated from the mass discharged from the charcoal, by sublimation in an earthenware retort above the boiling point of Cl₂Zn, concentrating the vapors in a suitable tank, depurating the Cl₂Zn sublimated and electrolyzing when necessary.

The process, when electrolysis is used, constitutes a closed cycle. In order to make up for the inevitable losses it will be necessary to furnish the cycle with a certain quantity of chlorin from one of the apparatuses in use for the electrolytic production of soda.

Having now fully described my said invention and how the same is to be performed, what I claim is:

1. In a process for the treatment of zinciferous substances, subjecting the said substances to the action of chlorin in the presence of porous carbonaceous matter and moisture.

2. In a process for the treatment of zinciferous substances, at a comparatively low temperature, subjecting the same to the action of chlorin in the presence of porous carbon and steam.

3. In a process for the treatment of zinciferous substances, at a comparatively low temperature, subjecting the same to the action of chlorin in the presence of porous carbon and steam, removing the carbon from the mass thus obtained, and lixiviating, filtering, and treating the liquid residuum with oxidizing agents and oxid of zinc.

4. A process for the treatment of zinciferous substances, at a comparatively low temperature, consisting in subjecting the same to the action of chlorin in the presence of porous carbon and steam, removing the carbon from the mass thus obtained, lixiviating, filtering, and treating the liquid residuum with oxidizing agents and substances containing oxid of zinc, to obtain zinc chlorid, and electrolyzing the zinc chlorid to obtain metallic zinc.

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

GUIDO MOJANA.

Witnesses:
B. CARLO SALVOLI,
M. SIEBSMORFER.