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H. WOLF ET AL
PROCESS FOR THE MANUFACTURE OF ZINC
Filed June 21, 1938

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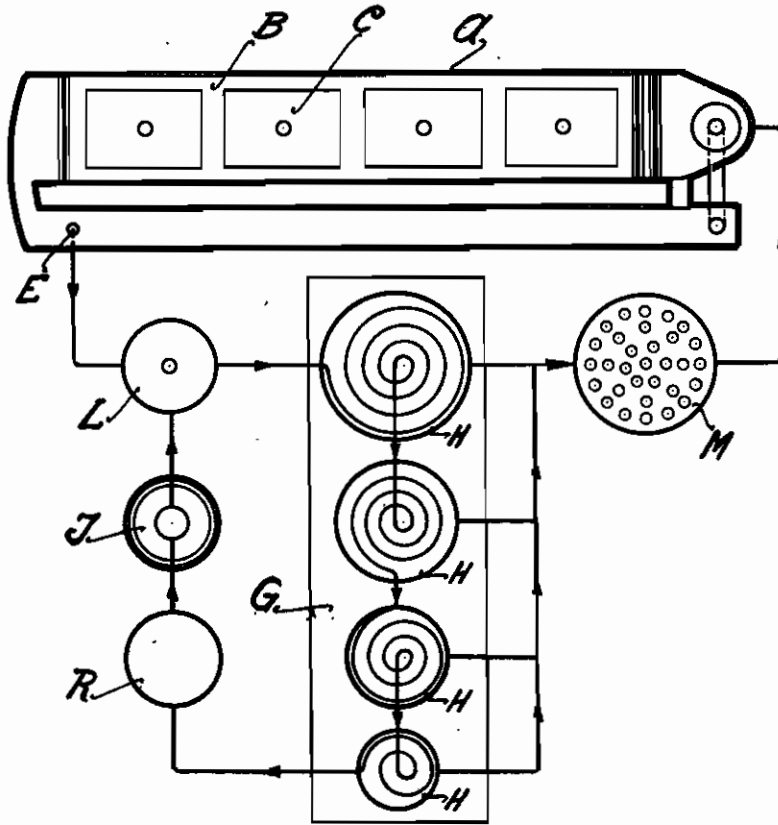


Fig. I

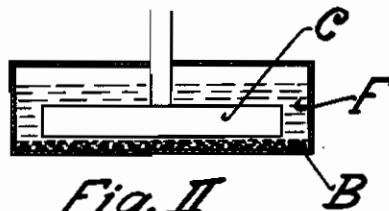


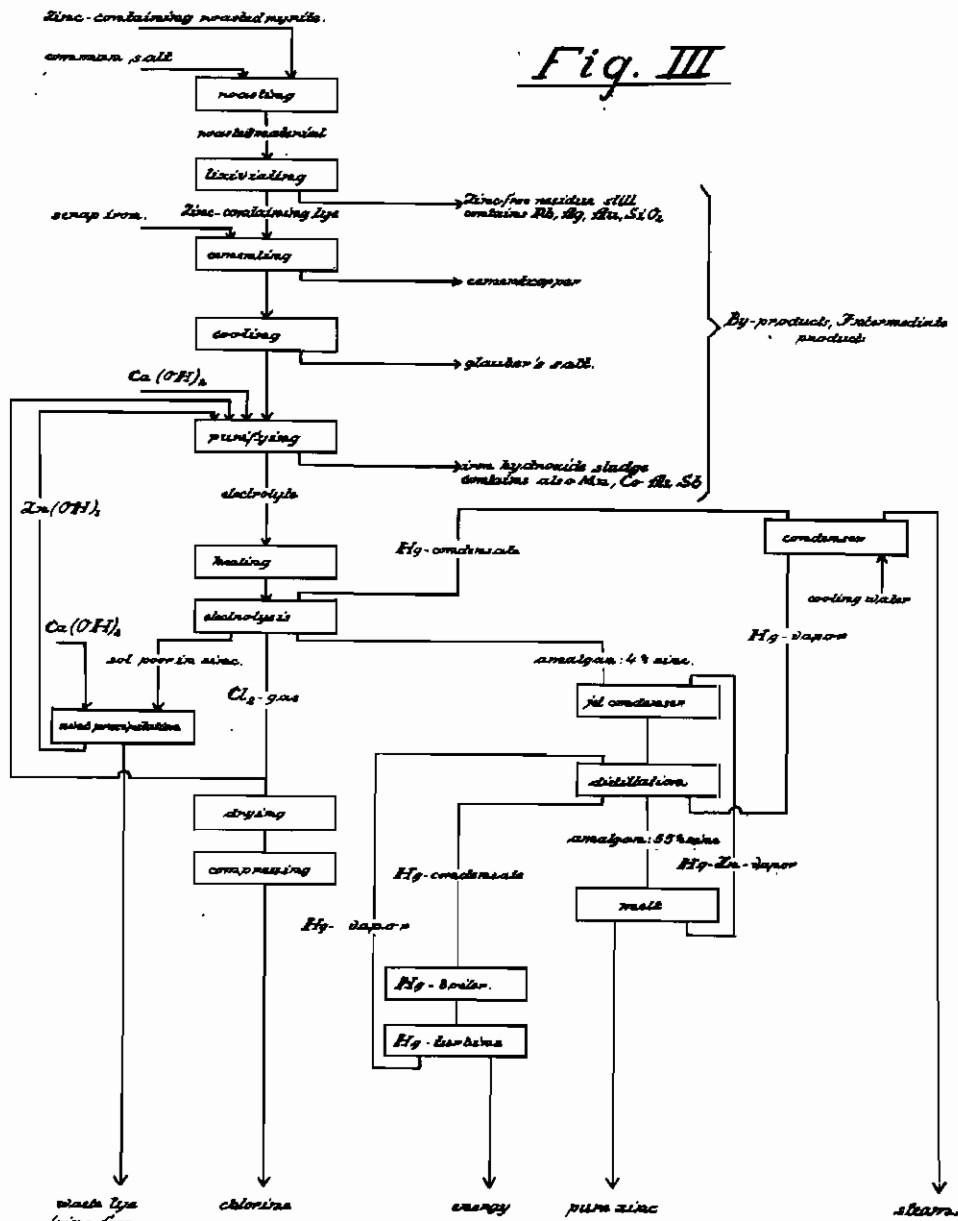
Fig. II

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ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF ZINC

Hermann Wolf, Ernst Kuss, Hans Hohn and Fritz Stletzel, Duisburg, Germany; vested in the Alien Property Custodian

Application filed June 21, 1938

The present invention relates to the electrolytic production of zinc by use of a mercury cathode.

It is known that many difficulties are encountered in the electrolytic production of zinc according to the usual processes due to the strongly electro-negative character of the metal, the tendency for hydrogen to simultaneously deposit, corrosion of the deposited metal by local elements produced by impurities in the electrolyte, the formation of zinc sponge, and the like. By reason of the strongly electro-negative character of zinc, the zinc has a marked tendency to redissolve in the electrolyte. This tendency is greatly augmented when the zinc deposits irregularly to form warts and buds on the cathode since there occurs at these irregularities a lowering of the hydrogen overvoltage with a resultant corrosion of the cathode. It is, therefore, necessary to interrupt the electrolysis when the cathode, by reason of the formation of such irregularities, reaches a certain size.

It is quite universally the practice to deposit the zinc from sulfate solutions from which any chlorine ions should be excluded. While the electrolysis of zinc chloride solutions is theoretically superior to the electrolysis of sulfate solutions because of the possibility of simultaneously obtaining chlorine, this theoretical superiority is difficult of realization in practice due to the yield diminishing corrosion to which the cathode is exposed by virtue of the presence of dissolved chlorine in the electrolyte. It has been considered necessary in order to avoid this corrosion as far as possible, to employ a diaphragm to separate the anode from the cathode. This of itself adds to the expense of the process as does the time which must be spent in attending to the diaphragm. Furthermore an appreciable amount of voltage is absorbed by the diaphragm, making its use further objectionable for this reason. When all these factors are added to the further factor which requires the use of extremely pure electrolytes in order to obtain reasonable current efficiencies, it will be appreciated that the electrolytic recovery of zinc presents very serious obstacles to its practical adoption.

It has now been found that most of the disadvantages which have heretofore manifested themselves in the electrolytic recovery of zinc may be overcome by the utilization of a mercury cathode for the electrolysis while operating at elevated temperatures and while observing certain precautions in separating the zinc from the mercury cathode for reuse of the mercury in the

process. There have been some proposals in the past to employ mercury as a cathode for the electrolytic production of zinc. In most of these proposals it was suggested that the zinc amalgam obtained be immediately subjected to distillation. In certain cases, however, it was suggested that the zinc amalgam produced in the original electrolytic step be used as an anode in a subsequent step, the zinc being dissolved from the anode and being re-deposited on a solid cathode. The employment of mercury as a cathode has certain disadvantages which were not overcome in the prior processes. Thus mercury cathodes, when subjected to the action of an electric current, have a tendency to pulsate whereby furrows and elevations are formed in the surface of the mercury which either lead to short circuits with the anode or at least make it impossible to space the anode and cathode a short distance apart to insure a working at relatively low bath voltages. Furthermore amalgamation between the mercury and the deposit metal often does not take place properly, the zinc frequently forming as a very reactive gray mud or slime on the surface of the mercury whereby the cell becomes covered with this mud or slime and the current efficiency decreases. The mud operates also to develop hydrogen and in addition cannot be worked up into pure zinc. The mud also effects a clogging of pipes and pumps necessary in a continuous process, thereby preventing a continuous and automatic operation.

On the other hand there are particular advantages which are offered by the use of a mercury cathode on which attention has not been particularly focused up to the present time and which recommend the use of a mercury cathode providing of course that the disadvantages previously mentioned can be overcome. For instance the amalgams have for the same current efficiency an essentially smaller surface area than solid cathodes and for this reason alone the tendency for the deposited metal to re-dissolve is lessened. The amalgams moreover behave quite generally against corroding electrolyte constituents in a nobler manner than metallic zinc and therefore permit electrolysis of zinc chloride solutions without the utilization of a diaphragm. There is, moreover, no tendency for couples to be formed in the amalgams so that a far-reaching purification of the electrolyte which is necessary with solid anodes in order to prevent formation of such couples with resultant corrosion is not required. There is in addition no necessity to add special preparations such as colloids and the

like to the electrolyte. Finally inasmuch as the amalgams are liquid, their preparation and working up can be effected in a completely continuous and automatic manner. In spite of these advantages all processes suggested up to the present time for obtaining zinc by use of mercury anodes have been technically unsuccessful probably because steps were not taken to overcome the disadvantages mentioned above as well as certain difficulties which make their presence felt in the working up of the amalgam.

It is an object of the present invention to provide a process for the deposition of zinc from zinc containing lyes which is free from the difficulties which previously were encountered in the electrolytic recovery of zinc from zinc-containing solutions.

It is a further object of the present invention to electrolytically deposit zinc from zinc-containing solutions while employing a mercury cathode and while insuring that the cathode may be spaced a short distance from the anode without the danger of the formation of short circuits arising.

It is a further object of the invention to electrolytically recover zinc from zinc-containing solutions by means of a cell having a mercury cathode while operating at elevated temperatures.

A further object of the invention comprises the electrolytic deposition of zinc with a mercury cathode while circulating the cathode and the electrolyte.

A further object of the invention involves the provision of steps to preclude contact of atmospheric oxygen with the amalgam formed in the electrolysis during the working up of the amalgam.

It is a further object of the invention to facilitate separation of the zinc from the amalgam by mechanically concentrating the amalgam prior to the isolation of the zinc from the mercury.

It is a further object of the invention to insure purification of the electrolyte from arsenic and antimony compounds.

A further object of the invention involves the separation of the zinc from the mercury in the amalgam obtained by electrolysis by an efficient distillation procedure.

A further object of the invention comprises a two-stage distillation of the amalgam, the first stage being conducted under reduced pressure.

It is a further object of the invention to provide a process for recovering zinc from chlorine-containing solutions without the use of a diaphragm.

It is a further object of the invention to provide a process for electrolytically recovering substantially pure zinc from zinc-containing solutions while realizing a high current efficiency.

A further object of the invention involves the apparatus for carrying out the electrolytic process.

Other objects will be apparent from the following detailed description.

As previously stated, we have now found that it is technically possible to take advantage of the possibilities of a mercury cathode in producing zinc from zinc-containing lyes by taking certain precautions during the electrolytic process and during the decomposition of the amalgam into zinc and mercury. These precautions involve, first, the use of elevated temperatures, preferably from 55° C to the b. p. for the elec-

trollysis of the zinc-containing solutions. By working at these higher temperatures, the tendency of the mercury to pulsate is avoided and the formation of the zinc in the form of a mud is precluded even at high current densities. This permits circulation of the cathode without disturbance to the mechanical equipment. Furthermore the anode and cathode can be spaced within a few millimeters of each other without dangers of short circuiting, a considerable saving in current thereby being realized.

Generally elevated temperatures are avoided in the electrolysis of zinc solutions for the reason that they lead to a decrease in current efficiency by lowering the hydrogen overvoltage and by increasing the rate of chemical corrosion (see heading (f), page 314 of "Applied Electro-Chemistry" by Allmand and Ellingham, 2nd Edition). It is, therefore, surprising that in the process developed by us the utilization of high temperatures contrary to leading to the objections noted in the above treatise, operate to facilitate the carrying out of the electrolytic process.

The second precaution involves the production of an amalgam having a "good flowability." By an amalgam with a good flowability is understood an amalgam which resembles pure mercury in its flowability, does not contain any solid amalgam particles and does not show any tendency to separate into more or less thick amalgam pulps. The good flowability of the zinc amalgam is a function of the temperature and the amalgam concentration so that these 2 factors must be most carefully supervised. The following examples serve to further illustrate what is meant by an amalgam with a good flowability:

Amalgams with 2% Zn at 25°
Amalgams with 4% Zn at 70°
Amalgams with 5% Zn at 80°

If these limits be surpassed the amalgams, it is true, are still liquid. They will not, however, flow well in the sense of the present process as they are no longer quite homogeneous and tend to eliminate crusts and pulpy products.

The consistency of the amalgams at a specified zinc content and a constant temperature may fluctuate a good deal. Dry, well flowable amalgams, especially when in movement, are slowly permeated by thick, spongy deposits or dross, which destroy their flowability and clog the pipes and apparatus in time. This can be avoided by carefully excluding oxygen of the air from contact with the amalgam, for instance by employing closed apparatus and conduits or by causing an inert gas to flow over the surface of the amalgam. It is also possible to operate with great advantage by covering the amalgam in the troughs or channels provided for its conduction and also in other apparatus parts with a weak acid, for instance very dilute hydrochloric acid. In this case the channels may be subdivided by means of plates or riffles partially immersed in the amalgam, that is to say the plates or riffles do not extend to the bottom or floor of the troughs or channels. It is expedient, too, in this case to exclude the oxygen of the air from contact with the amalgam.

A further precaution concerns correlation of current density with speed of movement of the mercury cathode. It has been discovered that with the mercury cathodes lower current efficiencies are obtained when the cathodes are in motion than when the cathodes are at rest, the decrease in efficiency being the greater, the

greater the movement of the mercury. In order to obtain good current efficiencies, the current densities must not be too low. On the contrary, they must be the higher the greater the speed of flow of the mercury. The movement of the amalgam must in any case be slow and as even as possible, turbulence in movement being avoided at all costs, else the current efficiency decreases strongly and less pure, especially nickel- and cobalt-containing amalgams are obtained. Advantageously the movement is restricted to such an extent that it just suffices to guarantee a uniform concentration of the amalgam in continuous operation and to avoid the occurrence of isolated deposits of higher zinc concentration. This movement may be effected by forming the mercury cathode in horizontal streams or rows which have a uniform fall or gradient of 1 to 2 millimeters per meter.

We have found that especially satisfactory current efficiencies can be obtained if the enrichment of the zinc in the amalgam be effected in steps in various cells operating in series rather than in a single cell. For instance the process may be operated in such a manner that the amalgam formed in each cell is led in a cycle, a certain part of the amalgam being branched off from each cell and led to the next succeeding cell. The quantity of amalgam branched off from each cell should as a rule be high enough to correspond to the quantity of zinc simultaneously precipitated by the electric current. The amalgam concentration prevailing in each cell can be regulated by a temporary throttling of the amalgam supply or by adding fresh mercury. It is preferable to operate so that in each succeeding cell the amalgam concentration increases by about 1%. For the conduction of the amalgam and for effecting the necessary current interruption it is advantageous to arrange the related cells one over the other so that the amalgam flows without the aid of pumps or other conveying devices and merely under the influence of gravity from one cell to the other.

It is advisable to carry out the electrolysis with lyes rich in zinc, for instance with 100 grams of zinc per liter. It is a characteristic of the process, however, that it is also suitable for electrolysis of lyes poor in zinc. The process offers for example the possibility of working up lyes obtained by a chlorinating roasting of pyrites in a simple manner to zinc and chlorine. As is known, the main elements in such lyes are copper and zinc combined with lead, nickel, cobalt, cadmium, gold, silver and other impurities. The individual elements are eliminated in known manner one after the other by suitable operations until there remain only zinc dissolved as zinc chloride in comparatively slight concentration together with alkaline earth chlorides and large quantities of sodium chloride and different heavy metal impurities. In former practice lyes of this type were treated by precipitating the zinc as oxide, dissolving the oxide in sulphuric acid and after a high purification, electrolyzing the resultant sulfate. This conversion of very impure chloride solutions into highly purified sulfate solutions is cumbersome and difficult and the economic success is problematical.

By our process the treatment of such zinc lyes requires merely a simple cementation by means of zinc dust to precipitate the major part of the other metals present. It is not necessary

to completely purify the lyes since purification need only go so far as is commensurate with the desired degree of purity of the deposited zinc. Of the impurities present the copper, lead and cadmium go quantitatively into the zinc amalgam upon electrolysis, nickel only partly and cobalt hardly at all. As no couples are formed, the current efficiencies are not influenced to any particular extent. The presence of magnesium and alkaline earths in the electrolytes is of no importance. The presence of large amounts of sodium chloride is, however, quite desirable. Contrary to the electrolysis of the sulfate solutions in which traces of chlorine in the electrolyte cause a strong corrosion of the anodes, the electrolysis of zinc chloride solutions with mercury cathodes and anodes stable to chlorine is not affected at all by large amounts of sulfate. The chlorine developed at the anode has the usual purity and can be collected dried and densified in the usual manner.

The current efficiencies obtainable with mercury cathodes decrease after the removal of zinc from the lyes has advanced to a certain stage. Accordingly, therefore, the electrolysis is discontinued when the zinc content of the electrolyte reaches about 15 to 20 grams per liter. The lye is then treated with lime to precipitate zinc hydroxide which is recovered and used for the removal of iron from the initial lyes.

It is believed pertinent to note that the amalgam cathodes are not insensitive to the impurities of the electrolytes in all cases. We have found that at high temperatures and with other conditions adjusted so as to otherwise obtain a suitable deposition of zinc, a spongy deposition of zinc may occur if there be present in the electrolyte arsenic or antimony compounds. These disturbances can be avoided if these two impurities are removed quantitatively from the electrolyte. This can be accomplished in a known manner by precipitating the ferric iron present in the electrolyte as ferric hydroxide. If necessary, in order to accomplish this purpose, iron may be separately added to the electrolyte. Similarly the effect of very small quantities of arsenic or antimony compounds can be minimized or avoided by adding small quantities of mineral acids. If this method be resorted to, it is preferable not to exceed a certain acidity such as about $\text{pH}=1$.

A further precaution which must be observed deals with the distillation of the amalgam by which the zinc is recovered in pure form and the mercury regenerated for further use. It is of decisive importance that this distillation be effected with the best possible utilization of heat, with cheap heat sources, without loss of mercury and as continuously as is possible. The furnace material must be resistant to attack by fused high percentage amalgam and pure zinc respectively. The mercury must be practically completely removed from the zinc. This requirement can be satisfied only by the employment of temperatures at which difficulties are to be expected with the materials for the distillation apparatus. Either the materials that come into question are resistant to hot zinc and zinc amalgam and are not impermeable to gas and do not permit the employment of economical heating methods, i. e. ceramic materials, or they permit the employment of economical heating methods but are quickly destroyed by high percentage hot amalgams, i. e. metallic materials. The zinc is thereby contaminated to a non-desirable extent.

The distillation apparatus utilized up to the present time are such that a pure zinc and especially a zinc practically free from mercury cannot be obtained in a technically satisfactory manner.

We have now ascertained that the main quantity of mercury can be eliminated by heating the amalgam to comparatively very low temperatures, and the remainder by heating the zinc for a short time up to or almost up to its boiling point. The distillation can, therefore, be effected with special advantage in two main steps, in the first of which the amalgam from the electrolytic cells is enriched to a concentration of, say, about 50 to 60% zinc in one or more distillation apparatus connected with each other and in the second of which the mercury still present is completely eliminated in a further distillation apparatus operated at essentially higher temperatures. The distillation apparatus for the first step preferably has metallic heat conducting parts which are provided with a suitable protective coating. It is advisable in operating these apparatus to supply heat externally and to distill under strongly reduced pressure. As the protective coating there may be used enamel since the distillation temperatures under reduced pressure lie below the temperature destructive of enamel. While the amalgam is still comparatively liquid, that is while it contains only up to about 10% of zinc, said protective layer may be omitted and there may be employed as the furnace material either cast iron, weldable iron or thermosilide (an alloy of iron and silicon). The external heating of the distillation apparatus may be advantageously effected by mercury vapor which either comes directly from a mercury boiler and is reintroduced into the boiler without a pump, or by the exhaust steam of mercury turbines, high pressure mercury vapor, gas or any other suitable and cheap source of heat. In this distillation step there may be employed continuous working thin layer evaporators or circulation evaporators of suitable construction which are arranged in series and which operate at different working temperatures. These temperatures increase from chamber to chamber with increasing amalgam content and may be lower the better the vacuum and the wider the pipes from the distillation chamber to the condensation plant. The temperature of each individual unit must not exceed the melting point of the amalgam treated therein. This result can be secured by suitable reduction of pressure and by a properly selected speed of throughput. The size of the individual units decreases considerably with increasing amalgam concentration. The quantity of mercury distilled from each chamber should be continuously maintained under control. The condensation of the mercury vapors can be effected in coolers or heat exchangers which are located at the highest point of the plant. By this method, a decrease in the quantity of circulating mercury and a simple return of the mercury to the cells may be achieved. The heat of condensation may expeditiously be employed for the production of steam. In this first distillation step there may be distilled off more than 75% of the total mercury. As a consequence the greatest part of the total heat required is utilized in this step and, therefore, the efficiency of the process depends to a large extent upon the possibility of relying upon a cheap source of heat for this step.

The distillation apparatus for the second distillation step is preferably a melting furnace con-

structed of ceramic material or pressed graphite and is operated without a reduction in pressure or with only a slight reduction in pressure. The amalgam may be continuously introduced into the furnace by a barometric overflow pipe, the pure zinc being taken off also continuously by means of an overflow syphon filled with nitrogen. It is possible to construct the melting furnace in the form of a column. However any other apparatus which may be operated at the necessary high temperatures is capable of utilization.

It is advantageous to conduct so much heat to the distillation unit that a quiet or even slightly violent distillation of the zinc is effected. Furthermore it is advisable to provide the melt with large surface areas, to effect movement of the melt and to lead a rapid current of gas over the surface of the melt. For best results the heating in this unit should be similar to that of the so-called high frequency furnaces. Moreover, to avoid zinc deposits it is preferable to construct the condenser attached to the distillation chamber according to the principle of the injection condenser and to operate it with the initial amalgam. We have also discovered that a considerable decrease in the size of the distillation plant can be achieved if the warm and well flowable zinc amalgam leaving the electrolytic cells is not subjected to distillation without further ado but is first cooled by allowing it to flow into cold, weakly acid water and by separating the amalgam into a concentrate rich in zinc, destined for distillation, and into a fraction poor in zinc which, diluted with the mercury obtained by distillation, is led back into the cells. This fractionation of the mercury may be effected by decanting, sieving, centrifuging or the like. The amalgam concentrate obtained in this way is advantageously further concentrated by mild pressing to a sandy, butter-like or loamy consistency. In this way there is obtained an amalgam having a zinc content of about 12%. The exhausted fraction which is returned to the cells is the poorer in zinc the lower it is cooled before fractionation.

The accompanying drawing illustrates diagrammatically an apparatus suitable for carrying out the present invention.

The invention will be further explained by reference to the following examples. It is to be understood, however, that these examples are illustrative only.

Example 1

A zinc sulfate lye containing about 100-105 gms. of zinc per liter of solution, prepared from an oxidic starting material and sulphuric acid and purified according to usual methods, is electrolyzed at 70° C. with a current density of 1000 amperes per square meter and a voltage of about 3.2 volts while using a mercury cathode and a "Tainton" anode until there is obtained an amalgam containing 3.65% of zinc. A part of the electrolyte is branched off and recirculated continuously for the dissolution of further parent material while simultaneously neutralizing the sulfuric acid electrolytically formed. The readily flowable amalgam is drained off and dried under a vacuum. It is separated in a distillation apparatus operated under vacuum and a temperature slowly increasing to about 640° C. into a mercury distillate having a zinc content of 0.23% and into a zinc melt which is drawn off into casting molds. The mercury is recycled to the electrolytic cells. The zinc obtained has a purity of 99.98%.

Example 2

Roasted pyrites of 55.10% Fe, 1.99% Cu, 2.39% Zn, 240 gms/ton Co, 300 gms/ton Mn, 0.04% Sb, 3.45% S, 0.11% As, 1.40% Pb, 4.05% SiO₂, 62.0 gms/ton Ag, 1.02 gms/ton Au are, after addition of 10% sodium chloride, chlorinatingly roasted and lixivated to produce a lye. The lye is de-coppered with iron clippings and cooled to 0° to effect the removal of the bulk of the sodium sulfate. The remainder of the sulphur together with Fe, As, Sb, Mn and Co are precipitated by lime with simultaneous introduction of chlorine to a pH of 5.5. After filtration there is obtained a zinc chloride lye rich in sodium chloride, which contains magnesium- and calcium-chloride in small amounts. The zinc content amounts to 60 gms/liter. In the lye there are still present per liter, 12 mg Fe., 13 mg Co, 5 mg Ni and some Pb as well as Cd. This lye is electrolyzed in cells designated on the drawing as A which are similar to the cells used in alkali-chlorine electrolysis. The mercury cathode B is cycled inside the individual cells and flows in the form of a horizontal stream for a distance of 8 millimeters under the graphite anode C with a speed of 9 cm/sec. The working temperature is 70° C., the current density 1200 amperes per square meter and the voltage of ab.3.2.v Mercury is continuously introduced in each cell and amalgam with 4-4.5% zinc is continuously drawn off from each cell by an overflow E. The electrolyte F circulates through the cells in a continuous stream and leaves the cells with a content of about 20 grams of zinc per liter. The zinc is precipitated with lime and the zinc hydroxide obtained is utilized in lieu of the calcium compound for the purification of the initial lye. The amalgam is continuously led to a concentration plant G comprising four chambers H, wherein it is brought to a content of 55% zinc by employment of reduced pressure. Thereby are distilled off from the total mercury to be separated:

- 80% at a temperature around 220°
- 8% at a temperature around 280°
- 5% at a temperature around 300°
- 3% at a temperature around 350°

The necessary heat is supplied to the distillation units by mercury vapor. The heat passes through the iron wall of the units which are protected by an enamel layer against the action of the hot amalgam. The concentrate obtained in this distillation step flows into an equalizing vessel R and from there into a distillation furnace I constructed of ceramic material. This furnace contains a zinc sludge maintained at a boiling temperature by high frequency heating. In this furnace the last residues of the mercury are evaporated and are precipitated together with the simultaneously developed zinc vapors in an injection condenser L which is loaded with the initial amalgam. The mercury vapors from the first distillation are precipitated in heat exchangers M arranged at a highly elevated position in the system in which superheated steam is produced. The mercury condensate flows under the influence of gravity to the electrolytic cells. Zinc is obtained in a purity of 99.95%. The chlorine gas obtained is dried in the usual manner and condensed. In contradistinction to the chlorine gas obtained in the electrolysis of potassium chloride, it is free from hydrogen.

Example 3

A concentrate of zinc-lead-ore, which has been obtained by the flotation process, is mixed with a 24 fold quantity of roasted pyrites. The mixture then contains 57.90% Fe, 0.84% Cu, 3.57% Zn, 200 gms/ton Co, 15 gms/ton Ni, 20 gms/ton Cd, 300 gms/ton Mn, 0.04% Sb, 0.09% As, 2.18% Pb, 4.95% SiO₂, 3.20% S, 49.0 gms/ton Ag, 1.26 gms/ton Au. It is mixed with 12% of sodium chloride and converted to a zinc lye in the manner described in Example 2. The lye is then subjected to cementation with zinc dust to precipitate the metals more electro-positive than zinc. The lye now has a zinc content of 65 gms per liter. The zinc is removed therefrom by a treatment in 4 electrolytic cells, lying one above the other so that the amalgam passes successively through the cells under the influence of gravity. The amalgam is moved in a cycle in each cell. The quantity of amalgam branched off is so controlled that in the first cell there is maintained an amalgam with a concentration of 1% of zinc; in the second 1.8% of zinc; in the third 2.6% of zinc and in the fourth 3.4% of zinc. The temperature of electrolysis is about 75° C., the current density about 1000 amperes per square meter and the voltage of about 3.2 volts. The current efficiency is 95-97%. By working up the amalgam according to the method of Example 2, zinc having a purity of 99.995% is obtained.

Example 4

Roasted Meggener pyrites is mixed with copper containing roasted pyrites in a proportion of 1:1. The mixture contains 53.00% Fe, 0.55% Cu, 5.20% Zn, 240 gms/ton Co, 750 gms/ton Mn, 0.04% Sb, 0.14% As, 0.53% Pb, 8.30% SiO₂, 3.95% S, 25.00 gms/ton Ag, 0.82 gms/ton Au. Sodium chloride in an amount of 12% is added to the mixture and converted into a zinc lye containing 65 grams of zinc per liter according to the method of Example 2. The lye obtained is electrolyzed at a temperature of about 75° C with a current density of 800 amperes per square meter and a voltage of about 3.1 volts in four electrolytic cells while operating as described in Example 3. An amalgam containing 4.35% of zinc is produced in the electrolysis. The amalgam is cooled to 5° C by allowing it to flow into air-free cold water containing 0.5 grams of HCl per liter, and is separated by means of a helical sieve into 56 parts of a readily flowable fraction containing 1.65% of zinc and into 44 parts of a doughy concentrate containing 7.80% zinc. The concentrate is continuously forced by means of a conveyor press into the distillation apparatus. By distillation 40.6 parts of mercury are obtained whereas, had the amalgam been distilled without mechanical concentration, it would have been necessary to have distilled off 75.4 parts of mercury. The distillate is combined with the aforementioned readily flowable fraction to produce an amalgam containing 1% of zinc which is then returned to the electrolytic cells. The last traces of mercury are removed from the zinc by heating in a graphite furnace brought to 900° C by "Kryptol" heating (a form of resistance heating wherein the resistance element is made from a mixture of graphite, carborundum and the like). A zinc having a purity of 99.96% is obtained.

Example 5

A zinc amalgam obtained by electrolysis according to Example 4 is cooled to 18° C by allowing it to flow into 0.01 n hydrochloric acid. By

leading the amalgam over a shaking screen and mildly pressing it, there are obtained 21.5 parts of concentrate containing 12.2% of zinc and 78.5 parts of a fraction containing 2.2% of zinc. The subsequent distillation of the concentrate results in the production of 18.9 parts of mercury whereas, had the amalgam been directly distilled without previous concentration, the distillation would have led to the production of 57.6 parts of mercury. The concentration prior to distillation, therefore, results in a 66% saving in the distillation.

Example 6

The shaking screen apparatus employed for the separation of the amalgam according to Example 5 is completely closed and a gas stream consisting of 97% of nitrogen and 3% of hydrogen, which has previously passed a hot furnace maintained at about 500° C and loaded with copper screen or net, is slowly introduced. It is possible by this means to insure that there will be no formation of slag in the amalgam during the working up of the amalgam.

Example 7

The trough or channel serving for the circulation of the amalgam in a cell is provided with an air-tight closure and is sealed at its ends by means of plates immersed in the amalgam to such an extent that, while the amalgam may still flow in the trough, the plates operate to close

off the whole transverse section of the trough which is not occupied by amalgam. In other words, said end plates, while immersed in the amalgam, do not extend to the bottom or floor of the channel or trough. Water at a temperature of about 70° C and containing 3.5 gms per liter of HCl trickles over the surface of the amalgam inside of the trough. This provides an alternative method for insuring that oxygen will not be permitted to contact the amalgam, thereby preventing the formation of slag in the amalgam.

Example 8

A zinc-chloride lye containing sodium chloride, .03 grams per liter of arsenic and .04 grams per liter of antimony, has added thereto an excess of ferric chloride. The iron is then precipitated by the addition of lime. The lye thus obtained is filtered and the filtrate brought to pH=1.5 by the addition of hydrochloric acid. The solution is then electrolyzed at 80° C with a mercury cathode at a current density of 1500 amperes per square meter and a voltage of about 3.4 volt. while operating according to Example 3. The zinc amalgam thus obtained is then worked up into zinc and mercury in the manner previously described.

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