PROCESS FOR THE PRODUCTION OF ELECTROLYTIC ZINC POWDER

Filed Aug. 21, 1963

25% NaOH 5-20 g Zn/l

ZINC METAL DUST

10 ZINC SULFIDE ORE (ZnS)

11 OXIDIZING ROAST

12 SULFUR OXIDE SO2

13 LEACHING OPERATION

14 200°F - 4 HRS.

15 SLURRY

16 FILTERING OPERATION

17 INSOLUBLE RESIDUE

18 IMPURE SODIUM ZINCAT SOLUTION

19 CEMENTATION

20 > 122°F - 1 HR.

21 INSOLUBLE RESIDUE

22 PURIFIED SODIUM ZINCAT SOLUTION 25% NaOH 71 g Zn/l

23 WATER WASH

24 ELECTROLYSIS STAGE

25 METALLIC ZINC SPONGE, DUST, FLAKE OR POWDER

26 DRYING OPERATION

27 METALLIC ZINC SPONGE, DUST, FLAKE OR POWDER

INVENTOR

ERNEST A. WINTER

ATTORNEYS
PROCESS FOR THE PRODUCTION OF ELECTROLYTIC ZINC POWDER
Ernest A. Winter, College Park, Ga., assignor to Tennesse Corporation, New York, N.Y., a corporation of Delaware
Filed Aug. 21, 1963, Ser. No. 303,510
5 Claims. (Cl. 264—10)

This invention relates generally to a process for producing metallic zinc and more particularly to a process for producing metallic zinc in the form of zinc dust, powder, flake or sponge by electrolysis of a sodium zinicate solution.

There are three ways by which zinc is generally extracted from its ore: the hydrometallurgical or electrolytic process, the pyrometallurgical or retort process, and the electrotechnic or continuous electric furnace process. Many types of ore, generally referred to as oxidized or mixed oxide-sulfide base-metal ores, are of such low tenor or so situated that the treatment of the ore by the pyrometallurgical method or the electrotechnic method is prohibitively costly. Frequently, the ores are a complex association of the minerals of several metals intermingled so intimately with gangue minerals that the physical separation of the metallic minerals from each other and the gangue is almost impossible. Thus, many types of ore are not being commercially exploited because of the lack of an economically feasible process for their treatment. Very often, resort must be made to the electrolytic process.

Most electrolytic zinc is made by the electrolysis of a zinc sulfate solution. For example, in the process for the production of solid zinc plate, a sulfate ore containing zinc is ground and then by a process of flotation, a fraction rich in zinc sulfate is produced. This fraction is known as a zinc concentrate and will usually assay better than 50 percent zinc. The zinc sulfate, which still contains impurities such as iron sulfur, copper sulfate, lead sulfate and silica, is roasted to produce an impure zinc oxide calcine and sulfur dioxide gas. The calcine is leached with sulfuric acid to dissolve the zinc oxide. The slurry is then filtered to remove the acid insoluble impurities. The resulting solution of zinc sulfate is purified by treatment with zinc dust. This is called cementation. The metallic zinc dust goes into solution and precipitates other metals such as copper, cadmium, lead and iron which are lower than zinc in the electromotive series. These metallic impurities are filtered off and the purified solution is electrolyzed through the lead anodes and aluminum cathodes of an electrolytic cell. Solid plate zinc metal or sheets are deposited on the aluminum cathodes and the cathodes are removed periodically so that the zinc metal sheets may be stripped therefrom. The cathodes may then be returned to the electrolytic cell. In such processes for the production of solid plate zinc, cooling of the electrolytes during electrolysis is essential.

In the production of non-solid plates of metallic zinc, i.e., zinc dust, powder, flake or sponge, the roasted zinc sulfate or concentrate containing zinc oxide (ZnO) can be leached with a strong alkali solution such as caustic soda (NaOH). In caustic solution, zinc is soluble as sodium zinicate and the resulting sodium zinicate solution (Na₂O-ZnO) can be purified by cementation with zinc dust and deposited electrolytically on magnesium cathodes to produce cathodic zinc. In this case, the zinc can be deposited in a form of a loosely adherent powder, dust, sponge, or flake. Unlike the case wherein solid zinc plates are produced, the nonsolid plate material is loosely adherent and can be jarred, pushed or flushed off the cathode and removed from the bottom of the cell by a screw conveyor or by a pump. Consequently, there is no need to remove the cathode as is necessary in the acid process where solid zinc plate is produced.

In known processes for the production of cathodic zinc in the form of zinc dust, powder, flake or sponge that collects as a loosely adherent deposit on the cathodes, it has generally been theorized that the upper temperature limit during cementation or purification, and the upper temperature limit of the electrolyte during electrolysis for the successful production of the metallic zinc dust, powder, flake or sponge is 122° F. The reason for this has been theorized to be due to the fact that zinc dust, powder, flake or sponge will redisolve readily because of its high surface area, when in contact with electrolyte solutions having a temperature above 122° F.

For example, in Canadian Chemistry and Process Industries, March 1949, p. 216, it is stated "With rising temperature this electrolyte increases sharply in conductance, but the rate of re-solution of the zinc sponge in it also rises, and hence yields decrease. The optimum operation temperature is 30° C. (86° F.), and the electrolyte must be cooled to maintain this temperature.

The same quotation is found in Information Circular 7466, by B. C. Ralston of the United States Bureau of Mines in connection with the I. G. Farben's operation in Germany. Also, in the Journal of Electrochemical Society, April 1953, p. 170, Baroch, Hilliard and Lang of the U.S. Bureau of Mines states: "While the cell voltage lessens with increasing electrolyte temperature, it is impractical to operate a cell above 50° C. (122° F.), because re-solution of the zinc powder accelerates very rapidly at temperatures above this."

Contrary to the published technical references, I have found that not only is purification with zinc dust and electrolysis at elevated temperatures above 122° F. entirely possible and practical, but operation at such elevated temperature produces results which are entirely unexpected and actually superior to the purification and/or electrolysis at lower temperatures used in heretofore known processes.

In accordance with my invention, the purification with zinc dust and electrolysis is performed at temperatures above 122° F. and may be as high as 192° F. Experimental results indicate that the temperature range may even exceed 192° F. I have found that the zinc dust, powder, flake or sponge produced at these elevated temperatures do not redisolve at an appreciable rate and that the current efficiencies of the process are close to 100 percent. The power consumption, due to the lower voltage, is actually lower at high temperatures than at low temperatures. Thus, contrary to the teachings of the prior art, operation at these elevated temperatures is commercially practicable and introduces a considerable cost saving since the need for cooling of the electrolyte, and subsequent reheating when recycled for leaching, is obviated.

Accordingly, it is an object of the present invention to provide an improved process for purifying sodium zinicate.

Another object of this invention is to provide an improved process for producing metallic zinc in the form of zinc dust, powder, flake or sponge which is extremely efficient and economical in operation.

A further object of this invention is to provide an improved process for producing metallic zinc in the form of zinc dust, powder, flake or sponge which obviates the
need for cooling and subsequent reheating of the electrolyte when recycled for leaching.

Yet another object of this invention is to provide an improved process for the electrolysis of a sodium zincate solution which obviates the need for cooling of the electrolyte.

An additional object of this invention is to provide an improved process for producing zinc metal by electrolysis of a sodium zincate solution at an elevated temperature.

In carrying out this invention, in one form thereof, a zinc sulfide or concentrate is roasted and subsequently leached with an alkaline solution. The slurry is filtered and the sodium zincate filtrate purified by treatment with zinc dust at an elevated temperature above 122° F. The purified sodium zincate solution is passed through an electrolysis stage maintained at an elevated temperature above 122° F. to deposit metallic zinc in the form of zinc dust, powder, flake or sponge that is loosely adherent to the cathodes.

Accordingly, two main features of this invention are (a) purification of sodium zincate solutions with zinc dust at above 122° F. and (b) electrolysis of a purified sodium zincate solution at above 122° F.

While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter regarding this invention, it is believed that the invention will be better understood from the following description taken in connection with the accompanying drawings, wherein the single figure is a diagrammatic illustration of a system for carrying out the treatment according to the present invention.

Referring to the drawing, a sulfide ore 10, such as zinc sulfide (ZnS) is subjected to an oxidizing roast 11 conducted by various well known means to drive off the sulfur as gaseous sulfur oxides (SO₂). Sulfide minerals themselves are not soluble in the leaching solution, with a few exceptions, such as arsenic, mercury and antimony sulfides, and to obtain satisfactory concentrations, the sulfide ore is pre-treated by oxidizing roast 11. The prepared ore from the oxidizing roast 11 is translated by suitable means to a leach tank where it is subject to a leaching operation 13. The solids of the ore are brought intimately into contact with an alkaline solution 14. Various methods of leaching may be utilized such as agitation methods, percolation, heat leaching, etc., the individual method chosen depending on the one that is most suitable or most economical for a specific ore or product. With the exception of heat leaching, most leaching operations are conducted in tanks, which may be made of concrete, wood lined with alkali-resistant paint or compounds, or steel and other metals which are resistant to the alkaline solution. Leaching is most effective when the solids and solution are intimately in contact with each other and when the solid particles in the solution are mixed or moved with relation to each other. In agitators, the solids in solution form a slurry kept in motion more or less violently by propellers, paddles or other mechanical devices. In percolation and heat leaching, the solution is moved by pumps and allowed to flow through or percolate to a bed of stationary solids. The leaching may be conducted in batches or in a continuous operation.

The alkaline solution 14 may be made up of a large variety of readily soluble alkaline compounds, together with other accessory salts or compounds, dissolved in water. The strong caustic alkalis such as caustic soda, NaOH, caustic potash, KOH, appear to be the most universally satisfactory solvents for the dissolution of the largest number of metallic minerals, although solution containing mild alkalis or a mixture of a strong caustic alkali and a mild alkali are sometimes effective. The chemical reactions involved in the dissolution of minerals are not known with scientific exactness; however, they are apparently closely related to the reactions of many amphoteric elements with basic compounds.

Zinc forming compounds known as zincates are a typical example of the reaction involved, and the solubility of zinc oxide as sodium zincate in a hot caustic alkali is demonstrated according to the following equation:

\[ \text{ZnO} + 2\text{NaOH} = \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O} \]

Accordingly, the leaching process may be maintained at a temperature of 200° F. with the prepared ore being subject to the leaching solution for a period of about four hours.

After the leaching operation, the slurry produced proceeds by a suitable mechanical arrangement to a filtering operation 16 where the insoluble residue 17 of the slurry is filtered or separated from the metal bearing, impure solution of sodium zincate. This operation may be further performed by any of a large number of hydrometallurgical techniques, such as, for example, settling, decantation, centrifuging, etc. The insoluble residue 17 may be washed and recovered by means of another process if desired.

The metal bearing impure solution of sodium zincate proceeds to the cementation tank where the impure sodium zincate solution is purified by cementation 18, i.e., treatment with zinc metal dust 19. Before zinc can be recovered in a commercially pure condition from the solution by electrolysis, all the metals lower than zinc in the electromotive series must be eliminated from the solution. Otherwise, such metals will tend to co-deposit with the zinc on the cathodes and contaminate the result of the zinc metal, making it less desirable commercially. The most valuable commercial metals found associated with zinc ores, and which are readily soluble in the alkaline solution, are copper, cadmium, lead and iron. The removal of these metals from the alkaline solution is accomplished with zinc dust 19.

The purification occurs by chemical displacement or substitution whereby zinc replaces the other metals which are thereby precipitated in a spongy, finely divided precipitate. While the chemical reaction is simple, completely a complete removal of these metals is incomplete except when a very large excess of zinc dust is used. I have found no difficulty in removing the copper, cadmium and lead to concentrations lower than the most stringent specification. In addition, the iron, which has heretofore caused serious difficulties in previous attempts to produce a sufficiently high-purity zinc, was readily removed except at room temperature. However, when operating at a temperature above 120° F., and particularly in the neighborhood of 192° F., the cementation or purification was most effective.

The temperature at which precipitation of other metals by zinc dust takes place is important. The proper temperature range has been theorized to be influenced by two factors: one, the replacement reaction between zinc and the other metals, which replacement reaction has been stated to be accelerated by elevated temperatures, and two, the solubility of metals which is said to increase rapidly with elevated temperature. If the temperature is too low, then not only will the treatment time be excessive, but it becomes increasingly difficult to remove the unwanted metals to the degree desirable or necessary. It has been postulated that a temperature too high will consume an excessive amount of zinc dust, causing little replacement to occur and any of the metals precipitated would also re-dissolve rapidly. In accordance with these theories, the optimum temperature of operation has been theorized to be in the range of 98° F. to 122° F.

Contrary to this postulation, I have discovered that purification with zinc dust at temperatures above 122° F. particularly above 150° F. and indeed as high as 192° F., are entirely practical. In addition, I have found that the zinc sponge that is deposited, during electrolysis, does not redissolve at an appreciable rate and, consequently, the current efficiencies are 96% to 100%. In addition, the power consumption, due to the low voltage
at high temperature, is reduced to a greater extent than when operating at low temperatures. Operation at these elevated temperatures reduces the voltage and power requirements as well as the electrical power consumed as heat in itself.

The following specific example illustrates the results of my findings: A zinc sulfate or concentrate containing approximately 54% Zn, 11% Fe and 33% S was roasted to ZnO, Fe₂O₃ and SO₂ gas. This roast was leached with a 25% caustic soda (NaOH) solution for four hours at 200° F. The slurry was then filtered. The filtrate contained 71 grams of zinc per liter. The impurities were 0.015 g. Fe/l., 0.29 g. Cu/L, <0.008 g. Cd/L and 0.05 g. Pb/l.

Various portions of this solution were purified by treatment with minus 325 mesh zinc dust at temperatures in excess of 122° F. for one hour. There was no difficulty in removing the Cu, Cd, or Pb impurities to concentrations lower than the most stringent specifications. The iron, which exhibits some difficulty in removal at room temperatures, was readily removed at elevated temperatures. The following table illustrates the effects of temperature on iron removal:

<table>
<thead>
<tr>
<th>Temp., °F.</th>
<th>Zn used, g/l.</th>
<th>Fe remaining, g/l.</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>80</td>
<td>4</td>
</tr>
<tr>
<td>60</td>
<td>120</td>
<td>1</td>
</tr>
<tr>
<td>60</td>
<td>180</td>
<td>1</td>
</tr>
</tbody>
</table>

It should be noted that while purification was effective at room temperature, it was even more effective at elevated temperatures above 120° F., and most effective at extremely elevated temperatures in the neighborhood of 184° F. Minus 325 mesh zinc dust was used in the specific example for purifying the sodium zincate solution at different temperatures. This fine zinc dust was used in the example to demonstrate that even fine particle zinc dust can be used at elevated temperatures without undue re-solution of the zinc. If desired, a coarser zinc dust, e.g., minus 60 mesh, plus 200 mesh can be used with good re-

Electrolysis may be conducted in cells of any convenient design, the main essential of a cell being a group of plane surfaced electrodes supported or suspended in a body of electrolyte so that a direct electric current may pass between one or a group of these electrodes, called cathodes, to one or more of other electrodes called anodes. Conveniently, a plurality of electrodes is usually placed in a box-like tank, alternating anodes with cathodes, which are spaced more or less evenly and parallel. The electrolyte may be agitated or maintained quiescent. Generally, a continuous flow of electrolyte enters one end of the cell, while the used electrolyte overflows at the other end. The electrolyte may pass successively to a group of cells or each cell may have individual electrolyte inflow and outflow, as desired. Usually, several cells are arranged electrically in series to conform with good engineering practice to provide a good balance between voltage and amperes in a direct current-electric supply.

The tanks for the cells may be constructed of a corrosion-resistant material which will withstand the alkaline electrolyte. Iron, steel and nickel are good materials for this purpose, however, if the highest purity of zinc is desired, in accordance with known procedures, a non-metallic surface is best to prevent contamination of the zinc such as, for example, glass, rubber or synthetic plastic linings.

The cathodes may be practically of any metal which will not dissolve readily in the outflowing electrolyte. Iron, all varieties of steel and ferro-alloys, nickel, zinc, magnesium and magnesium alloys are most desirable; however, others such as copper, bronze and rare metals are also suitable. The anodes are subject to strong oxidation during electrolysis, therefore, choice of anode material is limited to those elements which are very difficult to oxidize or whose oxides are insoluble in the alkaline electrolyte. These include iron, nickel, steel, carbon and precious metals.

In accordance with my invention, various portions of purified solutions may be electrolyzed using nickel anodes and magnesium cathodes spaced one inch apart. The following table illustrates the results of several runs conducted in accordance with the teachings of my invention:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70-105</td>
<td>71-146</td>
<td>99</td>
<td>2.60</td>
<td>59.9</td>
<td>1.06</td>
</tr>
<tr>
<td>2</td>
<td>100-130</td>
<td>71-12</td>
<td>158</td>
<td>2.77</td>
<td>96.7</td>
<td>1.03</td>
</tr>
<tr>
<td>3</td>
<td>117-140</td>
<td>71-13</td>
<td>158</td>
<td>2.63</td>
<td>97.9</td>
<td>1.01</td>
</tr>
<tr>
<td>4</td>
<td>120-160</td>
<td>71-13</td>
<td>158</td>
<td>2.55</td>
<td>97.9</td>
<td>0.99</td>
</tr>
<tr>
<td>5</td>
<td>180-192</td>
<td>71-15</td>
<td>158</td>
<td>2.90</td>
<td>95.8</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Contrary to prior teachings, it was found that the current efficiencies were maintained high at all temperatures, that is, appreciable re-solution of zinc sponge did not take place at the elevated temperature above 122° F. It was found that the power consumption was reduced with the increased temperature, and in no case was cooling required. This results in a considerable savings in capital cost for cooling, the savings resulting from the elimination of the equipment and cooling medium necessary for cooling during the process. In addition, the spent electrolyte, when recycled back to the leaching stage, need not be heated. The only cooling that takes place is that which occurs naturally, e.g., heat losses to the atmosphere through the walls of the cell and evaporated water going out with the oxygen gas leaving the cell. These heat losses to the atmosphere are relatively minor and permit operations at temperatures above 122° F.

The metallic zinc deposits on the magnesium cathodes
of the electrolytic cells in the form of a loosely adherent sponge or flake which can be easily removed by shaking of the cathodes. The metallic zinc sponge drops to the bottom of the electrolytic cells and is pumped out as a slurry. Other means for removing the zinc can be employed without removing the cathodes from the cell. For example, the zinc can be pushed off with a plastic scraper or it can be removed by agitation of the electrolyte. After removal from the electrolytic cells, the zinc particles are subject to a water-wash 23 in the filtering operation 24 to free them of the electrolyte, and are then passed to the dryer 25. Drying is accomplished, preferably, under vacuum, and if desired, the dried metal particles 26 can be melted and poured into slabs. In the example, the iron content was reduced to 0.0005 g./l. or less. With a net transfer of 50 g. Zn/l. in the electrolysis this would result in 0.001% Fe or less in the product. Normally this degree of purity is not needed for commercial grades of zinc. Thus, prime western zinc calls for a maximum of 0.08% Fe. Special high grade zinc calls for a maximum of 0.005% Fe. Certain special grades call for as low as 0.0035% Fe.

While the invention has been described with the recovery of metallic zinc from a sulfide ore, any source of zinc oxide can be used. For example, a carbonate ore could first be ignited to zinc oxide and then leached with caustic soda (NaOH). Accordingly, it is meant to include as a source of zinc oxide all materials classified mineralogically as belonging to oxidized ores as differentiated from sulfide ores, and includes true oxides, hydrate oxides, hydrous sulphates, carbonates, sulphates, chlorides, hydrous silicates, and similar compounds. In the example the source of zinc was an impure material. If desired, one can start with pure or purified zinc oxide. In this case the zinc oxide is dissolved in recycled electrolyte and passed to the electrolytic cell for electrolysis at above 122° F. The advantages of electrolysis at above 122° F. are retained, no cooling required, lower power consumption, etc. This would not depart from the spirit of the invention.

While a 25% NaOH solution was used in the example, lower or higher concentrations can be used without departing from the invention. In general, the preferred range is 15-35% NaOH, but the invention is not limited to these concentrations.

In addition, I have found that the conditions of electrolysis can be varied considerably. The current density may be varied from 14 amps. to 1,000 amps./sq. ft., while the zinc content of the electrolyte may be varied from 120 g./l. down to 3 g./l. The important factor is that the process is conducted at elevated temperatures above 122° F., thereby obviating the need for electrolyte cooling and subsequent reheating for leaching as well as reducing the power consumed as heat in the cell.

Although a single embodiment of the subject invention has been described, many modifications may be made, and it is intended by the attendant claims to cover all such modifications which fall within the true spirit and scope of the invention.

What is claimed is:

1. A process for producing metallic zinc in a form of zinc dust, powder, flake or sponge by electrolysis of a sodium zincate solution comprising steps of: purifying the sodium zincate solution by treatment with zinc dust while maintaining said solution at a temperature between 150° F. and 192° F., separating the precipitated products resulting from the purification, and electrolyzing the purified sodium zincate solution at a temperature between 150° F. and 192° F. to deposit metallic zinc in the form of zinc dust, powder, flake or sponge.

2. A process for the recovery of zinc from oxidized zinc ore comprising steps of: leaching the oxidized ore with a strong hot alkaline solution, displacing the metals other than zinc from the alkaline solution at a temperature of approximately 180° F. by contacting the solution with zinc dust, separating the precipitated products resulting from the displacement, and electrolyzing the purified sodium zincate solution at a temperature above approximately 180° F. to deposit metallic zinc in the form of zinc dust, powder, flake or sponge.

3. The method of recovery of zinc from oxidized zinc ore comprising the steps of: leaching the oxidized ore with a strong hot alkaline solution at a temperature of approximately 200° F., displacing the metals other than zinc from the alkaline solution at a temperature above 150° F. and below 192° F. by contacting the solution with the zinc dust, separating the precipitated products resulting from the displacement, and electrolyzing the purified sodium zincate solution at a temperature above 150° F. and below 192° F. to deposit metallic zinc in the form of zinc dust, powder, flake or sponge, and recycling the spent electrolyte to the leaching operation.

4. The method of recovery of zinc from oxidized zinc ore comprising the steps of: leaching the oxidized ore with a strong hot alkaline solution containing about 25% of caustic alkali, separating the insoluble residues resulting from the leaching operation, purifying the resultant impure sodium zincate solution by treatment with zinc dust for a sufficient time to reduce the iron impurities in said impure sodium zincate solution to an iron content below 0.0005 g. Fe/l. while maintaining the impure sodium zincate solution at a temperature above 150° F. and below 192° F., and electrolyzing the purified sodium zincate solution to deposit metallic zinc in a form of zinc dust, powder, flake or sponge, and recycling the spent electrolyte to the leaching operation.

5. The method of recovery of zinc from oxidized zinc ore as set forth in claim 4, wherein said sodium zincate solution is maintained at a temperature of approximately 180° F. and electrolyzing is carried out at a temperature of approximately 180° F.

References Cited

UNITED STATES PATENTS

1,795,079 3/1931 Davis et al. .......... 204—55
2,655,472 10/1953 Hilliard et al. .......... 204—116

FOREIGN PATENTS

24,121 1897 Great Britain.

JOHN H. MACK, Primary Examiner.
W. VANSISE, Assistant Examiner.