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PREPARATION OF ZINC ELECTROLYTES

Max L. Hollander, Plainfield, and Yurii E. Lebedeff, Metuchen, N. J., assignors to American Smelting and Refining Company, New York, N. Y., a corporation of New Jersey

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This invention relates to the preparation of zinc-bearing solutions from zinciferous material. More particularly, it relates to the preparation of zinc electrolytes from oxidic zinciferous material, from which electrolytes zinc is recovered by electrolysis; it especially relates to the treatment of such electrolytes for the removal of iron therefrom.

In the commercial recovery of zinc by electrolysis, a cyclic process is used. In accordance with this process an acid zinc sulfate solution is electrolyzed, using an insoluble anode and a suitable cathode such as, for example, an aluminum cathode. As the electrolysis proceeds, zinc is removed from the electrolyte and a corresponding amount of sulfuric acid is formed. In order to conduct the electrolysis with the highest efficiency and with greatest economy, it is important to maintain the zinc and acid concentrations and the purity of the electrolyte as nearly constant as possible during the electrolysis. To accomplish this, a stream of electrolyte is continuously withdrawn from the electrolysis tank and is used to leach zinc-bearing material, thereby restoring the zinc depleted from the electrolyte and at the same time consuming the acid released during the electrolysis. The refortified solution is then purified and is continuously returned to the electrolysis tank.

During the leaching, iron which is unavoidably present in the material to be leached, or iron otherwise unavoidably introduced into the refortified solution, is removed as ferric hydroxide or basic ferric sulfate, or mixtures thereof, by precipitation under oxidizing conditions. The precipitated iron is then removed by filtration.

Long experience has shown that removal of the iron causes considerable difficulty in the electrolytic process. The precipitated iron is of a gelatinous nature and is filtered with great difficulty, requiring long and varying filtration periods. As a consequence, it is extremely difficult to maintain uniform flow of the solution through the various steps in the cyclic process. In order to overcome this difficulty, enlarged storage and filtration capacity has been used. Even with such enlarged capacity, the process as heretofore practiced is subject to the hazard that the filtration period may suddenly and unaccountably increase to such an extent that a decrease in the rate of return of the refortified electrolyte to the electrolytic tank may be required. Additionally, difficulty in filtration may result in an undue loss of the electrolyte itself. Thus, the nature of the iron precipitate may be such as to occlude relatively large amounts of electrolyte which cannot, as a practical matter, be separated from the iron precipitate by filtration.

The principal object and advantage of the invention is to overcome these difficulties in the recovery of zinc by the electrodeposition process. Other objects and advantages will become apparent from the following more detailed description of the invention.

The invention comprehends recovering zinc from zinciferous material involving steps of leading the zinciferous material with an acid solution to form an acid zinc-containing solution which is subsequently subjected to electrolysis for the electrodeposition of zinc therefrom. Prior to the electrodeposition, the residual acid in the leach solution is at least partially neutralized in the presence of an oxidizing agent until the dissolved iron in the leach solution is precipitated. The precipitated iron is then removed from the solution by filtration. At any time in the process prior to the filtration step, a compound selected from the group consisting of soluble phosphate and arsenate compounds is added.

In the preferred mode of practicing the invention, the zinc is recovered by electrodeposition from a zinc sulfate electrolyte, from which a cyclic stream of the acid electrolyte is continuously withdrawn, refortified by leaching a zinciferous material, purified and returned to the electrolysis tank. Oxidic, zinciferous materials are preferred as the material to be leached during the refortification step. Satisfactory results are obtained with zinc carbonate materials and with zinc calcines such as, for example, calcined or roasted zinc concentrates in which the zinc values are largely or entirely in or are converted to zinc oxide. Best results are obtained with zinc oxide fumes, especially deleaded zinc oxide fumes. Such fumes are obtained from zincy lead blast furnace slags by treating the molten slag with a reducing agent to vaporize metallic zinc therefrom. The vaporized zinc is oxidized with an excess of air to form zinc oxide fumes in a region above the molten bath, and thereafter the zinc oxide fume is cooled and recovered. The fume may then be deleaded by heating it with a relatively small amount of reducing agent such as coal, coke or coke breeze so as to reduce the lead and vaporize it from the fume.

Any alkaline material may be used as a neutralizing agent during the neutralization step to precipitate the iron. For example, oxides, hydroxides and carbonates of calcium, magnesium and the like, and of other alkali metals and alkaline earth metals may be used. However, the use of oxidic zinciferous materials such as zinc calcines and zinc oxide fumes are preferred in the neutralization step as the use of these materials results in a further refortification of the recycled electrolyte. Zinc oxide fume, especially deleaded zinc oxide fume, is the most preferred neutralizing agent.

The neutralization of the residual acid in the leach liquor may be carried to completion although this is not desirable as it involves undue precipitation of the zinc. For best results, the residual acid in the leach solution is only partially neutralized until the dissolved iron present in the solution is precipitated without at the same time causing substantial or undue precipitation of the zinc. In terms of pH value in this latter instance, the residual acid is partially neutralized until the pH value of the refortified solution is in the range of about 4.3–4.6, with a pH value of about 4.6 preferred. Except as otherwise noted herein, all pH values are determined at 90° C. with a standard glass electrode standardized at room temperature with a sodium acetate-acetic acid buffer solution.

For best results, the neutralization and filtration are conducted at elevated temperatures, preferably in the range of about 50–95° C.; with a temperature of about 85–90° C. most preferred. The neutralization is conducted in the presence in the solution of a suitable oxidizing agent capable of converting any ferrous iron to the ferric state. Thus, for example, air potassium permanganate, manganese dioxide and the like may be used as the oxidizing agent. Manganese dioxide has been found to be most convenient and is, therefore, most preferred.

It has been discovered that soluble phosphate and

arsenate compounds radically affect the rate of filtration in the separation by filtration of the precipitated iron from the refortified electrolyte. The addition of such compounds at any stage of the refortification prior to the filtration step greatly increases the filtration rate of the refortified solution and drastically reduces the time of filtration. Their use eliminates or greatly reduces variations in the flow of the recycled stream of electrolyte through the refortification and purification steps and the return of the rejuvenated electrolyte to the electrolysis step. This, in turn, results in a regularizing of the entire electrolysis procedure and at the same time permits reduction of equipment size without affecting capacity.

Good results are obtained when the addition of such a compound is made just prior to the filtration step. In the case of the preferred neutralization procedure in which the refortified solution is partially neutralized to precipitate the iron without undue precipitation of zinc, the addition may be delayed until after or just before the pH of the fortified solution has been increased to a value of about pH 4.3–4.6 to obtain good results. Enhanced results are obtained when a compound of this type is added before visual precipitation of iron takes place during neutralization. Visual precipitation of iron usually commences when the pH value of the fortified solution is in the range of about 3.2–3.8. Best results are obtained by adding such a compound before the neutralization step. In this latter case, the addition may be made before, during or after the leaching step.

In practice, the leaching is conducted until most of the acid in the solution to be refortified is consumed. This latter state is considered to be reached when the pH value of the solution is at or below about pH 2.8–3.1, and preferably below about pH 2.8. As a consequence, the pH value of the solution during most of the leaching step is well below this range. In this connection it should be noted that the initial liquor passing to the leaching step contains free acid on the order of magnitude of about 180–210 grams per liter calculated as H_2SO_4 and in the case of recycled electrolyte may also contain 50–65 grams per liter of dissolved zinc. The pH of the initial leach liquor is below 1. The leach solution at the end of the leaching step contains zinc on the order of magnitude of about 165–185 grams per liter and about 5 grams per liter of free acid calculated as H_2SO_4.

Any soluble phosphate or arsenate compound or compounds (i. e., soluble pentavalent phosphorus or arsenic compounds containing combined oxygen) may be used to obtain an enhancement of the filtration rate. Such a compound or compounds may be added, as such, or they may be present or formed in situ in the solution. In the latter instance, bone ash and calcium phosphate have been found to give good results when added to the leach solution before the leaching step. The use of these latter and similar materials which supply phosphate ions without supplying an equivalent amount of iron ions are included within the scope of the invention. The preferred compounds for use in the invention are phosphoric acid, and arsenic acid (H_3AsO_4) which may be formed by dissolving As_2O_5 in an acid solution. Of these preferred compounds, phosphoric acid is the most preferred.

The optimum effective amount of the added compound or compounds depends somewhat upon the amount of soluble iron in the solution from the leaching step. In practice it has been found that the dissolved iron introduced into the refortified solution either or both through the material that is leached or the neutralizing agent, ranges in amounts of about ½–5 grams per liter calculated as Fe. It may on occasion be above or below this range. In most instances it is present in amounts of about 1 gram per liter calculated as Fe, especially when deleaded zinc fume is used both in the leaching and neutralizing steps. Amounts of phosphoric acid or As_2O_5 or their equivalents in the range of about ½–5 grams per liter have been found to be effective in most instances although larger and smaller amounts may also be used. Within this range it is preferred that, in terms of chemical equivalents, the phosphate or arsensate compound be present in the solution in amounts not in excess of about 0.7 of the chemical equivalent of the dissolved iron calculated as Fe, with the exception that where the soluble iron content is about 1 gram per liter or less (calculated as Fe), it is preferred to use not less than about ¼ gram per liter of phosphoric acid or H_3AsO_4 or their equivalent. In the more usual case where the soluble iron content of the solution is about 1 gram per liter calculated as Fe, about .65 gram per liter of phosphoric acid or its equivalent has been found to be most effective.

The invention is further illustrated in the following examples. It should be understood, however, that the examples are given for purposes of illustration and that the invention in its broader aspects is not limited thereto.

Example I

An amount of ferric sulfate equivalent to 1.5 grams per liter of iron was dissolved in an aqueous solution containing 6 grams per liter of sulfuric acid. To 250 cc. of this solution, adjusted to a temperature of 90° C., were added 2 grams of zinc oxide in the form of a slurry which was also at 90° C. The suspension was stirred for twenty minutes, at the end of which time its pH was 4.6. Also at the end of this period the iron was precipitated. The solution was then filtered and it was found to pass through the filter in less than one minute and that the filtrate was clear.

Example II

A chemically pure zinc sulfate electrolyte was prepared which contained 65 grams per liter of zinc sulfate calculated as zinc, and 200 grams per liter of sulfuric acid. Distilled water, U. S. P. zinc oxide and chemically pure sulfuric acid were used to prepare the electrolyte which was free of iron. 39 grams of the pure zinc oxide were leached with 250 cc. of the thus prepared electrolyte by adding the zinc oxide to the solution and stirring until the oxide was dissolved. The residual acid in the solution was then neutralized with the pure zinc oxide to a pH value of 4.6 at 90° C. by the addition of 1.75 grams of zinc oxide in the form of a slurry. After stirring for twenty minutes the suspension was completely filtered in 1.25 minutes. The leaching, neutralization and filtering were conducted while the solution was maintained at a temperature of about 90° C.

Example III

The procedure of Example II was repeated with the exception that ferric sulfate in an amount equivalent to 1.5 grams per liter of Fe was dissolved in the 250 cc. of electrolyte before the leaching step. In this example, as well as in the other examples, all filtrations were carried out in a Buchner filter having funnel of 300 cc. capacity and a liter flask. Nine-centimeter "Whatman Number Four" filter paper was used. Suction was applied by means of an aspirator. In the instant example, after the 39 grams of chemically pure zinc oxide were leached and dissolved, 2.125 grams of chemically pure zinc oxide were added in one step to neutralize a sufficient amount of the residual acid in the leach solution to precipitate the iron. The pH of the leach solution before neutralization was 2.7. The pH of the solution before filtration was 4.5 and after filtration was 4.91 (this latter value was determined at 24° C.). 30 minutes were required to filter the solution and to obtain incipient dryness in the cake; that is, the point at which no liquid remains on top of the cake. Just prior to the end of the filtration, the pressure in the flask was measured and was found to be equivalent to a column of mercury 2.6 cc. in height. Comparing these results with those

of Examples I and II, it will be seen that the presence of appreciable zinc sulfate interferes with the formation of an easily filtrable iron precipitate .

Example IV

The procedure of Example III was repeated in a series of tests with the exception that the various compounds in the amount indicated in the following table were added and dissolved in the chemically pure electrolyte before the leaching step. Also, where indicated, 0.5 gram of MnO_2 were added prior to the neutralization. The results obtained are shown in the table.

Compound added, grams	MnO_2	pH Readings		Filtration time, minutes	Minimum pressure, centimeters of mercury	cc. of liquid left in funnel
		Before filtration	Filtrate			
0.34 $KSbC_4H_4O_7 \cdot \frac{1}{2} H_2$	None	4.5	5.07 (17°C.)	>30	2.2	40
0.15 Sb_2O_3	do	4.5	4.75 (18°C.)	>30	2.2	35
0.17 Sb_2O_5	do	4.4	4.80 (17°C.)	>30	2.3	60
0.14 As_2O_5	do	4.5	5.01 (17°C.)	14	3.0	None
0.16 As_2O_3	do	4.5	5.00 (17°C.)	>30	2.2	60
0.18 GeO_2	Added	4.6	4.81 (18°C.)	>30		80
0.24 $SnCl_2 \cdot 2H_2O$	do	4.5	4.90 (25°C.)	>30	2.7	75

Example V

The procedure of Example IV was repeated with the addition of the compounds in the following table, except that these compounds were added after the leaching step. In the present example also, 0.25 gram of manganese dioxide was added to the 250 cc. solution during the leaching step and pure zinc oxide was used as the neutralizing agent. The following results were obtained:

Compound added	pH before filtration	Complete filtration time, minutes
.17 grs. H_3PO_4	4.4	4½
.38 grs. As_2O_5	4.5	5½
.19 grs. As_2O_5	4.4	9¾
5.59 grs. $BaCl_2 \cdot 2H_2O$	4.4	48

Example VI

A synthetic zinc electrolyte, comparable to that which in the commercial process is continuously withdrawn from the electrolyte tankhouse for refortification, was made up to contain 65 grams of zinc sulfate per liter calculated as zinc, and 200 grams of sulfuric acid per liter. The electrolyte was prepared with distilled water, chemically pure H_2SO_4 and U. S. P. zinc oxide. 250 cc. portions of the thus prepared electrolyte were heated to 56° C. and amounts of commercial deleaded zinc oxide fume indicated in the following table were added to each portion at a rate designed to bring the solution to incipient boiling. 0.25 gram of manganese dioxide was added at about the midpoint of this fume addition. The solution was then stirred for about 30 minutes and during the stirring the solution was maintained at a temperature of 90° C.±3° C. This procedure closely approximates the leaching procedure in the commercial process. The iron was precipitated from the leach solution by the addition of deleaded zinc oxide fume until a pH of 4.3–4.6 was obtained. The suspension was then stirred for an additional 10 to 20 minutes and was then filtered as described in Example III. During the neutralization, stirring and filtering the solution was maintained at 90° C.±3° C. During this experiment the various compounds indicated in the following table were added to the series of test solutions at the point in the procedure indicated in the table. The following results were obtained:

Grs. of fume added	pH at start of neutralization	Compounds added, grams	Point at which compounds added	Grams fume added during neutralization	pH before filtration	Filtration time, minutes
42.00	2.6	None		2.68	4.3	26
41.00	2.4+	0.08 H_3PO_4	After leach	3.00	4.3+	7
41.00		0.15 H_3PO_4	do	2.95	4.3	4+
42.00	2.8	0.15 H_3PO_4	During leach	2.00	4.2+	5+
42.00	2.8−	0.15 H_3PO_4	Before leach	2.00		5−
41.50	2.7	0.25 $Ca_3(PO_4)_2$	After leach	2.32	4.4	4½
41.50	2.7	0.25 $Ca_3(PO_4)_2$	Before leach	2.32	4.3+	5
41.50	2.7	0.50 $Ca_3(PO_4)_2$	After leach	2.25	4.3+	3−
41.50	2.8	0.50 $Ca_3(PO_4)_2$	Before leach	2.25	4.5	5
41.50	2.7−	0.50 phos. rock	do	2.50	4.4−	6
41.50	2.7+	0.50 phos. rock	During leach	2.25	4.3−	9
41.50	2.7	0.50 phos. rock	Before leach	2.42	4.4	7
41.50	2.6+	0.50 phos. rock	During leach	2.68	4.3	6
41.0	2.9	0.380 As_2O_5	Before leach	2.20	4.35	5¼
40.50	3.0	0.33 As_2O_3	do	2.15	4.4	>30
41.0	3.1	0.184 $NaH_2PO_2 \cdot 2H_2O$	do	1.90	4.6	19
42.00	2.8	0.12 P_2O_5	After leach	2.60	4.3+	5½
42.00	2.8	0.75 bone ash	Before leach	2.65	4.4+	4½
42.00	2.7	0.30 bone ash	After leach	2.85	4.4	18

The above tests of the example were repeated using a series of different deleaded zinc oxide fume products. Comparable results were obtained except that in the first test of each series, in which no compounds were added, the filtration time varied from about 26–60 minutes. This range of filtration time is representative of that which is normally encountered when the present additives are not used. Occasionally, and unpredictably, even higher filtration rates may be encountered.

Example VII

The procedure described in Example VI was repeated in a series of tests. In each test, 41 grams of deleaded zinc oxide fume were leached in each case, and 0.25 gram of MnO_2 were added to the solution at the mid-point of the leach. Where indicated in the following table, 0.17 gram of phosphoric acid was added to the electrolyte before the leaching step. Various neutralizing agents in the amounts indicated were used to neutralize the residual

acid in the leach solution. The results shown in the table were obtained.

pH at start of neutralization	Neutralizing agent, gas	Phosphoric acid added	pH before filtration	Filtration time, minutes
2.8	2 grs. NaOH	Yes	4.6	12½
2.8	2 grs. NaOH	No	4.6	26
2.8	2.1 grs. $CaCo_3$	Yes	4.6	5¾
2.8	2.1 grs. $CaCo_3$	No	4.6	8¼

From the foregoing examples it will be seen that the use of soluble phosphate and arsenate compounds drastically reduce the filtration time required to separate the precipitated iron from a zinc electrolyte. Such reduction in the filtration period results in greater uniformity in the entire electrolysis system. Additionally, from the foregoing it will be apparent that the present invention may be practiced for the separation of iron from zinc in solution regardless of whether or not the resulting solution is used as an electrolyte from which zinc is recovered by electrodeposition. Any such procedure is also within the scope of the invention.

What is claimed is:

1. In a method of electrowinning zinc involving electrolyzing a zinc sulfate electrolyte with an insoluble anode, and cyclically refortifying the spent electrolyte from the electrolysis and removing dissolved iron from the refortified electrolyte under non-reducing conditions by a procedure involving leaching an oxidic zinciferous material with said spent electrolyte to refortify the latter, partially neutralizing the refortified solution while oxidizing ferrous iron therein to the ferric state to precipitate the iron contained in the solution without substantial precipitation of dissolved zinc, and filtering the refortified solution to separate therefrom the thus precipitated iron, said partially neutralized solution being characterized by variations in its filtering rate, the improvement comprising introducing a soluble pentavalent arsenate compound at a point in said procedure after said electrolysis step and prior to said filtration step thereby reducing variations in the filtering rate of the partially neutralized solution and the net filtering time thereof.

2. A method according to claim 1 in which said refortified electrolyte at the end of said leaching step contains 165 to 185 grams per liter of dissolved zinc and ½ to 5 grams per liter of dissolved iron, and said selected compound is introduced into the solution after the leaching step in amounts not in excess of about $\frac{7}{10}$ of the chemical equivalent of the dissolved iron content of the solution but not less than the equivalent of ¼ gram of arsenic acid per liter of solution when the latter contains less than 1 gram per liter of dissolved iron.

3. A method according to claim 2 in which said compound is arsenic acid.

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