GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.


PROVISIONAL SPECIFICATION.

ELECTROWINNING OF ZINC AND RECOVERY OF ELEMENTAL SULPHUR FROM ZINC SULPHIDE ORES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTRED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification describes the nature of this invention.

This is an invention by VEERABAGAVA ARAMUTTAN and RANGACHAR SRIKVASAN, both of the Central Electrochemical Research Institute, Karaikudi, India, both Indian citizens.

A zinc sulphide ore is double decomposed with commercial ferric chloride solution of about 20 to 30 per cent. concentration by boiling with 1-2 times the theoretical amount of ferric chloride necessary for the reaction. Particles sizes finer than 250 mesh react very favourably and the reaction is completed half to one hour. After the reaction is over, the solution is filtered off and the filtrate is used as anolyte feed. The residue is worked for sulphur recovery either by taking advantage of the difference in solubilities of sulphur in hot and cold solvent (petroleum distillate fractions) concentration by heating the distillate off contact with air to volatilise free sulphur. Catholyte for the electrolisis is pure zinc chloride to which a small amount of sodium fluoride is added to improve the nature of the deposit and anolyte. Graphite anodes and stainless steel or aluminium cathode are employed. The anode compartment is separated from the cathode compartment by a porous diaphragm.

Novelty in the Process:

Although it is known that zinc chloride solutions can be electrolysed either in admixture with sodium chloride, sodium acetate etc., no commercial method has been reported to connect the same with sulphur recovery as elemental sulphur from the raw material zinc sulphide ore, employing ferric chloride as leaching agent. On the otherhand, it has been published in literature from time to time that the ferric chloride leaching is employed to dissolve out the sulphides of copper, silver, gold, lead, iron etc., leaving zinc sulphide untouched from a complex sulphide ore. We have found that ferric chloride can act as a leaching agent even in the case of zinc sulphide concentrates and the speed of the reaction is mostly governed by the particle size of the ore, other conditions such as the concentration of ferric chloride, time of boiling, etc., remaining constant. As stated earlier, zinc sulphide ores in mesh 250 mesh are best suited for ferric chloride leaching and not less than 70 per cent. leaching of zinc is possible in one stage.

The process described here is a cyclic one involving the conversion of the ferrous chloride by the chlorine liberated in the anode compartment during the electrolisis to ferric chloride to be used in subsequent leaching operations. Besides eliminating the need for wet chlorine handling which is very commonly associated in the aqueous chloride electrolysis of many metals inclusive of zinc, this also serves to lower the cell voltage and also to increase the life of the anode. This process also serves to utilise the dross obtained in melting and casting operations of zinc metal. The zinc oxide present in the dross can convert the mixture of ferric chloride and zinc chloride coming out from the anolyte compartment to iron hydroxide as a soluble precipitate leaving behind zinc chloride in solution. After repeating the leaching operations once or twice with the same amount of ferric chloride, the treatment with dross will help in the production of pure zinc chloride for use as catholyte feed. The utilisation of dross does not present any difficulty in this process whereas it cannot be used in the conventional zinc sulphate electrolysis to get zinc metal, the objection to its use in sulphate electrolysis being the present of chlorides along with the zinc oxide in the dross.

We are also working on the methods of separating pure zinc chloride or iron chloride from a mixture of zinc and iron chloride obtained in the double decomposition of zinc sulphide ore with ferric chloride.

By the said arrangement, we have been able to maintain conditions for depositing pure zinc in a continuous sheet form for some hours at 7 to 8 volts lower in comparison with the sulphate electrolytic method for zinc production, all the conditions remaining the same in both processes such as current density about 30 ampere ft., temperatures of 25 to 30°C etc. The addition of sodium fluoride in very small concentrations of about 1 to 1.5 grams per litre of zinc chloride solution containing 100 to 120 grams of zinc per litre kept at a pH of 1 to 3 enables bright, uniform sheet deposits to be obtained from a chloride bath which has not also so far been reported in literature.

The following is the typical data obtained on a laboratory scale for the leaching and electrowinning of zinc:

**Composition of the zinc concentrate:**

<table>
<thead>
<tr>
<th>Material</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>51.1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>31.9</td>
</tr>
<tr>
<td>Iron</td>
<td>6.02</td>
</tr>
<tr>
<td>Silica</td>
<td>1.87</td>
</tr>
<tr>
<td>Lead</td>
<td>0.73</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.2</td>
</tr>
<tr>
<td>Amount of ore taken</td>
<td>100 gms</td>
</tr>
<tr>
<td>Amount of ferric chloride as FeCl₃</td>
<td>240 gms</td>
</tr>
<tr>
<td>Volume of solution</td>
<td>800 cc</td>
</tr>
<tr>
<td>Time of boiling</td>
<td>1 hour</td>
</tr>
<tr>
<td>Sulphur extracted</td>
<td>22.2 gms</td>
</tr>
</tbody>
</table>

**Electrolisis:**

- **Volume of catholyte:** 750 cc of pure zinc chloride solution containing 180 gms of zinc chloride and 0.8 gms of sodium chloride.
- **Electrolytic vessel made of perspex:** 7"x2"x4".
- **Anolyte:** 250 ccs of a mixture of ferrous and zinc chlorides in a continuous flow inside two porous diaphragms of 2" internal diameter and 4" height, each.
- **Anode:** 2 graphite electrodes each one dipping in the anolyte to the extent of 2"x2"x1" (thick).
- **Cathode:** One aluminium plate immersed to the following dimensions 2"x2"x1/4" (thick) kept in a perspex frame and in between the porous diaphragms.

**Temperature of electrolysis:** 30°C.

**Voltage across the solution:** 2.7.

**Current density:** 20 amperes / sq. ft. (2.2 amperes) of the cathode.

**Duration of electrolysis:** 3 hours.

**Amount of zinc recovered:** As sheet metal | 7-1 grams.

R. BHASKAR PAI
Patents Officer, Council of Scientific and Industrial Research.

Dated this 13th day of November, 1957.

Price: TWO RUPEES.
COMPLETE SPECIFICATION.

ELECTROWINNING OF ZINC AND RECOVERY OF ELEMENTAL SULPHUR FROM ZINC SULPHIDE ORES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN RESEARCHED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This is an invention by VEERARAGAVA ARAYA MUTHAN and RANGACHARI KRISHNAMCL, both of the Central Electrochemical Research Institute, Karaikudi, India, both Indian citizens.

This invention relates to a process for the electrowinning of zinc and recovery of elemental sulphur from zinc sulphide ores.

The production of zinc chloride solutions by reacting ferric chloride solution with oxidised zinc ores was employed by Ashcroft who concentrated his attention only on the electrowinning of zinc without caring for the recovery of sulphur in the elemental form. Moreover, he employed iron anodes in the electrolytic production of zinc and there is every reason to believe that he did not produce pure zinc under these conditions. A process developed by A. Schmacher and George W. Hesse in 1940 relates to the use of ferrous chloride solutions for extracting zinc as chloride from the sulphide ores. The resulting ferrous chloride-zinc chloride solutions are electrolysed employing porous carbon anodes. Zinc containing iron in small amounts is obtained.

The invention for the production of zinc consists in leaching zinc sulphide concentrates substantially —200 mesh size with ferric chloride solutions to obtain a zinc chloride solution (and a residue from which elemental sulphur can be obtained as a useful by-product), and electrolyzing the zinc chloride solution thus obtained.

Our process produces pure zinc free from iron, and elemental sulphur from the zinc sulphide concentrates. Thus, it is different from either Ashcroft process or the Schmacher-Hesse process. We do not employ soluble iron anodes as in Ashcroft process or porous carbon anodes as in Schmacher process. We employ a two compartment cell with a porous partition. The electrolyte in both compartments is pure zinc chloride unlike in Schmacher-Hesse process where a mixture of zinc and ferrous chloride is used as electrolyte. By a successive leaching procedure, we are able to utilize not only the anodic chloride effectively but also recover greater quantities of zinc from the ore for a given amount of ferric chloride solution. Consequently, the use of zinc oxide for precipitation of ferric iron ultimately (as hydroxide) is kept at a minimum. We employ fluoride as an addition agent for getting smooth metal deposits.

Outline of the Process:

Zinc sulphide concentrates are reacted with 10-25 per cent solution of commercial ferric chloride. The amount of ferric chloride is 1.2 times the theoretical amount of ferric chloride necessary for the reaction represented by the equation:

\[ \text{ZnS} + 2 \text{FeCl}_3 + \text{2FeCl}_2 + \text{ZnCl}_2 + \text{S} \]

Particle sizes finer than 200 mesh react very favourably and the reaction is complete in 1 to 4 hours. After the reaction is over, the solution is filtered off and the filtrate is reacted with the anodic chloride evolved in the electrolytic process. Mixture of ferric and zinc chloride solutions obtained in the above reaction is used for leaching fresh amounts of the ore. This process is repeated until a zinc iron ratio of 4 : 1 is obtained. Then the iron present in the ferric state is eliminated as ferric hydroxide by the addition of zinc oxide. In a modification of the process, a portion of pure zinc chloride solution is treated with lime or other alkali to alkaline earth hydroxides to get zinc hydroxide which is then used for the elimination of iron. Thus, a cell feed containing about 100-120 grams of pure zinc in the form of zinc chloride solution is obtained.

The residue resulting in the decomposition of zinc sulphide concentrate with ferric chloride or mixtures of ferric chloride and zinc chloride is treated by any one of the following ways for the recovery of sulphur. (1) Sulphur is volatilised by heating out of contact with air and (2) sulphur is recovered by taking advantage of the difference in solubility of sulphur in kerosene or other petroleum distillates in hot and cold.

Electrolyte:

0.5 to 1.5 grams of sodium fluoride are added per litre of zinc chloride solution containing 100-120 grams of zinc. The same solution is employed as anolyte and catholyte in a two compartment cell. The anode area is the same as the cathode area. The volume ratio of catholyte to anolyte can be 1 : 1 to 2 : 1. This volume ratio is not very critical especially when continuous flow of catholyte is maintained. The pH of the solution is kept between 1.5 to 3.5. Electrolysis is conducted at temperatures ranging from 25-35°C. The chlorine formed in the anode chamber is siphoned off. A current density of 30 amperes per ft. is employed. The voltage across the cell is 2.5. The current efficiency is not less than 90 per cent.

The following is the typical data obtained on a laboratory scale for the leaching and electrowinning of zinc:

**Composition of the zinc concentrate:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>61.9</td>
</tr>
<tr>
<td>Iron</td>
<td>4.02</td>
</tr>
<tr>
<td>Silica</td>
<td>1.27</td>
</tr>
<tr>
<td>Lead</td>
<td>0.73</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Leaching:**

- Amount of ore taken: 100 gms. (~250 mesh).
- Amount of ferric chloride in solution: 310 gms.
- Volume of solution: 2.5 to 2.5 litres.
- Time of boiling: 1 hour.
- Sulphur extracted: 22.2 gms.
- Zinc obtained in solution: 36.0 gms.

**Data for successive leaching:**

In successive leaching experiments, the same amount of iron of the same volume of solution is alternately utilized and reduced in the cyclic process but contains increasing amounts of zinc chloride.

**Zinc iron ratio in the leaching solution:**

<table>
<thead>
<tr>
<th>Zn/Fe</th>
<th>Percentage of zinc extracted from the ore.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>71%</td>
</tr>
<tr>
<td>1.04</td>
<td>72%</td>
</tr>
<tr>
<td>1.12</td>
<td>71%</td>
</tr>
<tr>
<td>1.24</td>
<td>72%</td>
</tr>
<tr>
<td>1.36</td>
<td>71%</td>
</tr>
</tbody>
</table>

**Electrolytic vessel made of porcelain.**

- **Diaphragm:** Two porcelain or microporous rubber diaphragms each of 2 1/2" diameter and 4" height.
- **Anodes:** Two graphite plugs dipping to the extent 2-3" in solution.
- **Cathode:** Aluminium or stainless steel 2" x 3" dipping in solution and kept between two porous plugs.
- **pH:** 1.5 to 3.5.
- **Temperature of electrolysis:** 30°C.
- **Current density:** 30 amperes per ft. (2.5 ampere current passed).
Duration of electrolysis 4 hours
Amount of zinc deposited 10.9 grams

Advantages of this Process:

In comparison with the zinc sulphate electrolysis for the electrowinning of zinc, there is a considerable reduction in cell voltage. The cell voltage for a current density of 39 amps per square foot at temperatures ranging from 25-35°C with a zinc concentration of 100-120 grams per litre is 2.9 for the chloride bath whereas under the same conditions the voltage across the cell in the sulphate bath is 3.4. In the sulphate process for the electrowinning of zinc, the sulphur content of the ore is released as sulphur dioxide which in many instances cannot be economically utilised for want of required concentration and purity. In our chloride process most of the sulphur (about 70 per cent) is obtained in the elemental form. Hence, there is a possibility of realising the value of the sulphur content of the ore better in this process than in the zinc sulphate process.

Zinc dust available from melting and casting operations of zinc metal can be converted to electrolytic zinc metal by this process. On the other hand, it cannot be recycled in electrowinning of zinc from zinc sulphate bath owing to the presence of chlorides in the bath, which are classified as harmful impurities for sulphate bath. This process is also valuable for utilising iron-zinc alloy containing entrapped zinc usually termed as "dross" available from galvanising operations. It is stated that for every 100 tons of zinc used in galvanising operations, 25 tons of dross are formed. To utilise this dross by this process, pure zinc chloride solution is electrolysed and the anodic chlorine is utilised to produce mixed chlorides of iron and zinc from the dross. By the addition of zinc oxide in required amounts to the mixed chloride solutions, iron is eliminated as hydroxide.

We claim:

1. A process for the production of zinc which consists in leaching zinc sulphide concentrates of substantially 20 mesh size with ferric chloride solutions to obtain a zinc chloride solution (and a residue from which elemental sulphur can be obtained as a useful by-product), and electrolysing the zinc chloride solution thus obtained.
2. A process as claimed in Claim 1 wherein the ferric chloride solution used is about 10-25 per cent in strength (W/w).
3. A process as claimed in Claim 2 wherein the zinc sulphide concentrates are boiled with 1-2 times the theoretical amount of ferric chloride required, for a duration of 1-1.5 hours to leach out zinc.
4. A process as claimed in Claims 1 or 2 wherein ferric chloride solution is got from the leaching operation and the said ferric chloride solution is oxidised by anodic chlorine from electrolysis of zinc chloride solutions and again the mixture of zinc chloride-ferric chloride solution is recycled for further leaching and this process is repeated until a zinc iron ratio of 4:1 or higher is obtained in the zinc chloride ferric chloride solution.
5. A process as claimed in any of the preceding claims wherein the zinc chloride ferric chloride solution with a zinc iron ratio of 4:1 or higher is mixed with the effluent from the cells for electrowinning of zinc by electrolysis of zinc chloride and treated with zinc oxide of zinc hydroxide to remove iron.
6. A process as claimed in Claim 5 wherein this zinc oxide or zinc hydroxide is got by roasting of zinc sulphide or by treating a required portion of zinc chloride solution with alkali or alkaline earth metal hydroxides respectively.
7. A process as claimed in any of the preceding claims wherein the pure zinc chloride solution prepared as mentioned in Claim 5 and containing 100-120 grams per litre of zinc is electrolysed in a two compartment cell using porcelain, microporous rubber or PVC as diaphragm, the cathode being stainless steel or aluminium and the anode being graphite; the current density employed is 39 amps per square foot at a temperature of 25-35°C; the voltage is 2.9.
8. A process as claimed in Claim 7 wherein the chlorine from the anode compartment is sucked off and used to oxidise ferrous chloride resulting from leaching operation to ferric chloride in the presence or absence of zinc chloride.
9. A process as claimed in any of the preceding claims wherein a zinc chloride solution containing 0.5 to 1.5 gram of sodium fluoride per litre is electrolysed to give a smooth deposit of zinc which can be peeled off easily (the cathode being protected by a suitable paint like chlorinated rubber at the solution level).
10. A process as claimed in any of the preceding claims wherein the zinc dross obtained from melting and casting operation or from galvanising plants, is recycled in the electrowinning operations.

B. BHASKAR PAI,
Patents Officer,
Council of Scientific and Industrial Research.

Dated this 30th day of August, 1958.