

Specification No. 62292. Application No. 62292, dated 10th November 1957. Complete specification left on 8th September 1958. (Application accepted 3rd April 1959.)

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 REGISTERED 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 VEERARAGAVA ARAVAMUTHAN and RANGACHARI SRINIVASAN, 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. Particle sizes finer than 250 mesh react very favourably and reaction is complete in 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) kerosene or by heating the residue out of contact with air to volatilise free sulphur. Catholyte for the electrolysis is pure zinc chloride to which a small amount of sodium fluoride is added to improve the nature of the deposit and the depositing conditions. Graphite anode 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 minus 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 electrolysis 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 presence 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 amp/sq. 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 3.5 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 :

Zinc	51.1 per cent.
Sulphur	31.9 "
Iron	6.02 "
Silica	1.87 "
Lead	0.73 "
Cadmium	0.2 "
Amount of ore taken	100 gms
Amount of ferric chloride as FeCl ₃ in 30 per cent. solution	240 gms
Volume of solution	800 ccs
Time of boiling	1 hour
Sulphur extracted	22.2 gms

Electrolysis :

Volume of catholyte 750 ccs of pure zinc chloride solution containing 180 gms of zinc chloride and 0.8 gms of sodium chloride.

Electrolytic vessel made

of perspex	7" × 3½" × 4".
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" × 2" × ¼" (thick).
Cathode	One aluminium plate immersed to the following dimensions 2" × 2½" × ⅛" (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	30 amps/sq. ft. (2.2 amps) of the cathode.
Duration of electrolysis	3 hours.
Amount of zinc recovered as sheet metal	7.1 grams.

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Dated this 13th day of November, 1957.

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
REGISTERED 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 ARAVA MUTHAN and RANGACHARI SRINIVASAN, 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.

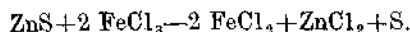
The production of zinc chloride solutions by reacting ferric chloride solution with oxidised zinc ores was employed by Ashcroft who concentrated his attention only on the electrowinning of zinc without caring for the recovery of sulphur in the elemental form. Moreover, he employed iron anodes in the 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. Schumacher and George W. Heise in 1940 relates to the use of ferric chloride solutions for extracting zinc as chloride from the sulphide ores. The resulting ferrous chloride-zinc chloride solutions are electrolysed employing porous carbon anode. Zinc containing iron in small amounts is obtained.

The invented process for the production of zinc consists in leaching zinc sulphide concentrates of substantially —250 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.

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 Schumacher-Heise process. We do not employ soluble iron anodes as in Ashcroft process or porous carbon anodes as in Schumacher process. We employ a two compartment cell with a porous partition. The electrolyte in both compartments is pure zinc chloride unlike in Schumacher-Heise process where a mixture of zinc and ferrous chloride is used as electrolyte. By a successive leaching procedure, we are able to utilise not only the anodic chlorine 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 :



Particle sizes finer than 200 mesh react very favourably and the reaction is complete in 1 to 1½ hours. After the reaction is over, the solution is filtered off and the filtrate is reacted with the anodic chlorine 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 or 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.

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 sucked off. A current density of 30 amps/sq. ft. is employed. The voltage across the cell is 2.9. 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 :

Zinc	51.1 per cent.
Sulphur	31.9 "
Iron	6.02 "
Silica	1.87 "
Lead	0.73 "
Cadmium	0.2 "

Leaching :

Amount of ore taken	100 gms. (—250 mesh).
Amount of ferric chloride in solution	310 gms
Volume of solution	2.2 to 2.5 litres
Time of boiling	1 hour
Sulphur extracted	22.2 gms
Zinc obtained in solution	36.0 "

Data for successive leaching.

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

Zinc iron ratio in the leaching solution.	Percentage of zinc extracted from the ore.
1:0	71%
1:0.4	72%
1:1.2	71%
1:2.4	72%
1:3.6	71%

Electrolysis.

Volume and composition of anolyte or catholyte.	500 cc containing 120 grams of zinc as chloride and 0.5 to 0.675 grams of sodium fluoride per litre.
Electrolytic vessel made of perspex.	7" × 3½" × 4".
Diaphragm	Two porcelain or microporous rubber diaphragms each of 2 1/2" diameter and 4" height.
Anodes.	Two graphite plates dipping to the extent 2" × 3" in solutions.
Cathode	Aluminium or stainless steel 2" × 3" dipping in solution and kept between two porous pots.
pH	1.5 to 3.5.
Temperature of electrolysis	30°C.
Voltage across the cell	2.9 volts.
Current density	30 amps/sq. ft. (2.5 amps 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 30 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 3.6. 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 dross 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 dross, 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 —250 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/v).

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 1-1½ hours to leach out zinc.

4. A process as claimed in Claims 1 or 2 wherein ferrous chloride solution is got from the leaching operation and the said ferrous 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 or 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 30 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.

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Dated this 28th day of August, 1958.