

## RECOVERY OF ZINC FROM INDUSTRIAL BYPRODUCT ZINC COMPOUNDS

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Techniques of suspension electrolysis has been developed for the recovery of zinc from its industrial byproducts such as zinc ash, zinc oxide/hydroxide etc. The process was initially standardised on a 500 amp. cell capable of producing 0.5 kg/hr, which was then scaled up to 1000 amp. cell to produce 1 kg/hour. The process has been licensed for commercialisation and the data collected during the laboratory trials as well as those from the actual production plants are presented and discussed. The merits and problems of the process are also discussed.

**Key Words:** Electrolytic zinc, suspension electrolysis, byproduct zinc compounds

## INTRODUCTION

Zinc is one of the important strategic metals which finds extensive application in a variety of uses. The production of this metal has been reported to be around 55,000 tonnes in 1984-85 whereas the demand is nearly 2-3 times as much. Galvanising industry alone needs nearly 50-60% of the total zinc, considerable quantity of which is generated as waste byproducts such as skimmings, ash and dross. A process for recovery of the metal from such secondary sources has been developed based on the suspension electrolysis [1].

## EXPERIMENTAL

The process involves electrolysis of a suspension of finely divided zinc ash in 2-3 N sulphuric acid using aluminium cathodes and lead silver alloy anodes. The average current density is in the range of 2.5 to 5.0 A/dm<sup>2</sup>. The cathodes are removed at definite intervals and the zinc deposit stripped off from the cathode. The process is made continuous by frequent additions of raw material at predetermined intervals. The reactions underlying the process are simultaneous dissolution and deposition of zinc. Details of the process are described elsewhere [2-4]. Different raw materials have been successfully tried in the process. A comparison of the compositions of different raw materials used is given in Table-I.

**Table I: Analysis data for the different raw materials used in the process**

Material	Zinc ash	Zinc ash	Zinc oxide/hydroxide
Source	Galvanising industry (%)	Zinc remelting plants (%)	Chemical industry (Sodium hydrosulphite) (%)
Zinc content	55-88	70-80	68-75.33
Iron	0.2-1.6	Nil	0.0-0.015
Chloride as Cl	1.08-6.91	0.0-1.11	0.0-0.1
Sulphate as SO <sub>4</sub>	0.00-0.29	Negligible	1.5-9.0
Insolubles	0.15-6.2	0.0-0.14	Negligible-0.075
Volatile	0.0-6.6	Negligible	Negligible-16.03

In the laboratory, the process was standardised on 500 amp. scale and scaling up to 1000 amp. was done in the industry based on our design. The maximum scaled up cell is of 2000 A.

The cell is of the usual rectangular HDPE container of suitable capacity with anodes and cathodes at 5.0 cm. interelectrode distance. Agitation of the electrolyte to keep the material in uniform suspension was carried out by passing compressed air through specially designed air distributor system. The slurry ratio was initially kept at 1:10 (wt/vol.). With progressive electrolysis the zinc concentration is maintained by frequent addition of calculated amount of raw material.

## RESULTS

The following factors affect the efficiency:

*Raw material quality*

The zinc content of the raw material should be not less than 60% even though materials of 50-55% zinc can also be processed. Contamination by copper is detrimental to the process. Zinc in the form of dross contributes to the non-reactive material hence cannot be used in the process. Chlorides in the sparingly soluble form create serious problems during electrolysis. High chloride (>1.0%) results in heavy corrosion of anode and affects the cathode deposit as well.

*Agitation*

Proper agitation of the electrolyte is a must in order to keep the material in good suspension. Hence design of the air distributor system is crucial in the process.

*Temperature*

The cell operates normally at ambient temperature. An increase of temperature occurs due to exothermic dissolution of zinc compounds and when temperature exceeds 60°C the efficiency falls by about 10%. This is overcome by proper addition of raw material as slurry to the electrolytic cell and agitation.

*Concentration of zinc*

Concentration of zinc in the electrolyte should be maintained at 55-80 g/l for good efficiencies. This is achieved by additions of calculated quantities of powdered raw material in the form of slurry.

*Insoluble contents*

Accumulated mud formed from the non-reactive portions of the ash and Fe (OH)<sub>3</sub> results in inducing the dissolution of zinc deposited on the cathode. Depending on the insoluble content

of the raw material the frequency of cleaning is scheduled and accumulation of mud is avoided.

The results of the laboratory trials have been presented in our earlier papers [2-5]. The process has been licensed to eight parties out of which five have gone into production. The plants vary in capacity from 0.5 TPD to 1.0 TPD and the cells are of 500, 1000 and 2000 amperes capacity. The data collected from the plants of licencees are presented and discussed in the paper.

In Fig. 1 are given the variation of cell voltage, temperature, zinc concentration in the electrolyte and current at a fixed applied voltage of 31 V. The data was collected during operation of 500 amp. cells (8 in a bank) on continuous production in a plant of capacity 0.25 TPD. Curve 5 shows the variation of

cell voltage with time in a 1000 amp. cell started afresh in another plant of one tonne capacity. The average cell voltage is around 3.6 V and this value is reached after about 6 to 8 hours during which period the cells get stabilised. The maximum zinc concentration in the electrolyte has been 60-65 g/l and the maximum temperature has been 50° (ambient temp. 35-37°C). Under these conditions an average current efficiency of 80-85% is obtained.

For an evaluation of the process on an industrial scale, data were collected during a period of 18 months from one of the plants of the licencees with a capacity of 0.5 TPD which are summarised in Tables II to V. During the period under study at least three different materials from three different sources were used. Table II gives a summary of data.

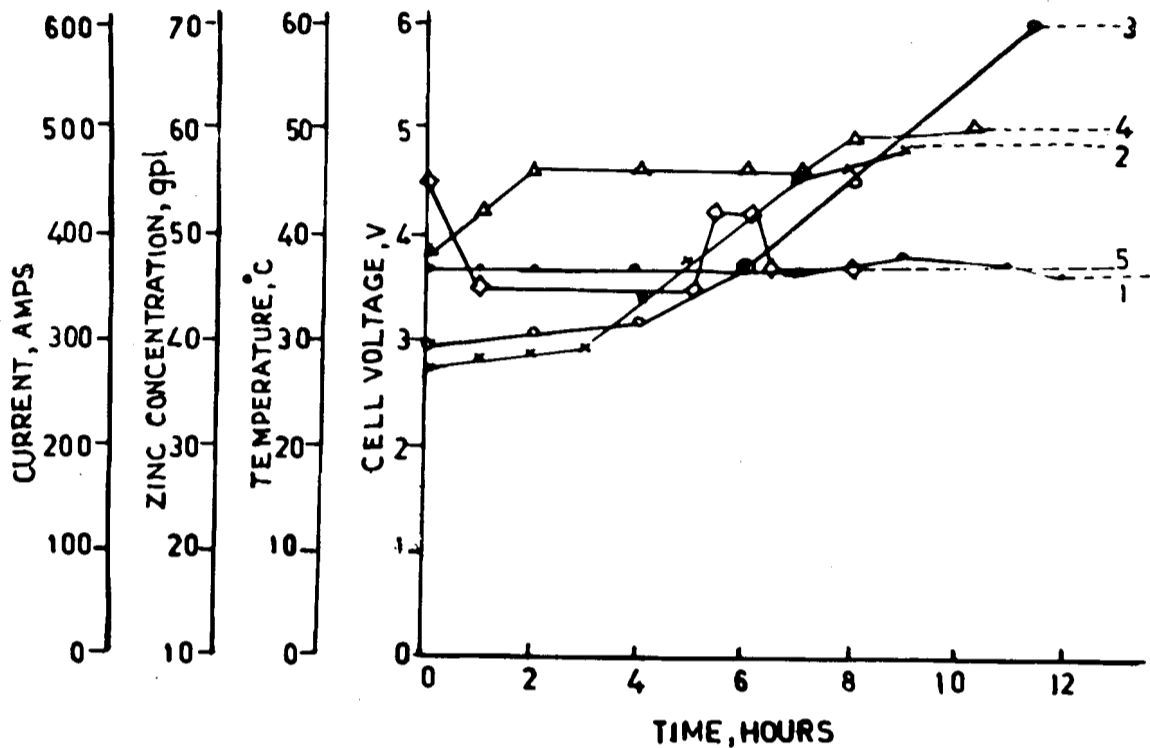


Fig. 1: Variation of cell voltage, temperature, zinc concentration in the electrolyte and current at a fixed applied voltage of 31V. 1. ●—● Cell voltage; 2. X—X Temperature; 3. O—O Zinc concentration; 4. Δ—Δ Current; 5. ◇—◇ C.V. in a 1000 amp. cell

**Table II: Data on zinc recovery from a 0.5 TPD plant collected over a period of 18 months**

Number of cells	: 24 arranged in 4 banks
Capacity	: 1000 amps
Volume capacity	: 1000 l
No. of cathodes per cell	: 10
No. of anodes per cell	: 11
Average zinc concentration	: 50 - 80 gpl
Average cell voltage	: 3.6 - 4.0 V
Energy per kg of zinc	: 4.5 - 8.0 K Wh*
Temperature	: 35 - 50°C
Average current efficiency	: 85 - 90%
Average recovery efficiency	: 88 - 90%
Loss of anodes	: ≈ 500 kg for 30-40T Zn ≈ 12.5 kg/T Zn

\* High value due to larger power requirement for powdering certain raw materials.

In Table III are given data on cells run with zinc hydroxide from a chemical industry. The data obtained in the plant agrees well with those obtained in the laboratory for a similar material.

**Table III: Data on cells collected from 0.5 TPD zinc plant (Average data on 12 cells run at 12.5 A/dm<sup>2</sup> for 18 hr shifts)**

Day	Cell voltage (V)	Temperature (°C)	Zinc conc. (g/l)	C.E. (%)	kWh/t
1	3.9-4.2	42-66	64-70	95.4	4740
2	3.7-4.0	42-46	65-75	96.3	4848
3	3.7-4.1	41-44	68	98.4	4812
28	3.9-4.0	34-42	60-65	92	5740

Table IV gives material balance worked out for the process. The loss in the process had been mainly reported to be due to material handling at various stages which can be minimised by proper care.

**Table IV: Material balance**

Total raw material	: 1200 + 326 = 1526 kg
Zinc content	: 75%
Total zinc content	: 1144.5 kg
Zinc recovered as deposit	: 247.3 kg
Zinc concentration in electrolyte	: 64 - 70 g/l
Total number of cells	: 12
Total volume of solution	: 12000 l
Total zinc in the electrolyte	: 804 kg (assuming average 67 g/l)
Zinc present in the suspension	: 93.2 kg
Raw material remaining in suspension	: 125 (approx. 10 kg/cell)

Table V presents data on melting of zinc sheet deposits. An oil fired crucible furnace was used for melting the deposit and

the metal was ladled out into the moulds. It is observed that the loss of metal during melting ranges from 3.5% to 6%. Long storage of the zinc sheets under corrosive atmosphere results in lowering of melting efficiency due to part of the metal lost as oxide in the scum.

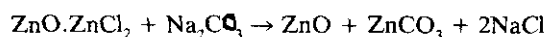
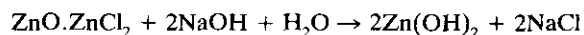
**Table V: Data on melting of zinc sheet deposit**

Sl. No.	Wt. of zinc sheets melted (kg)	Loss (%)
1.	180	4.3
2.	300-400	4.0-6.0
3.	500-550	3.5-5.5
4.	600-700	3.9-4.75
5.	900	4.85-5.0
6.	2130	6.2

Fuel oil for melting - 100 litres/ton

The following problems are generally encountered during the operation. Suitable solutions have been worked out based on the feed back from the operating plants.

(1) *Chlorides* – The ash from galvanising units contains widely varying quantities of chloride which comes from the flux used in the galvanising. This may be present both in soluble and insoluble forms. The soluble chlorides are removed by repeated washing with water. The insoluble chloride which is an oxychloride of zinc is removed best by thermal decomposition or by chemical treatment with NaOH and Na<sub>2</sub>CO<sub>3</sub> resulting in decomposition according to the following equations:



Both these processes have been successfully worked out in the laboratory [5]. It has generally been found that the dry processing is more convenient than leaching process and the licencees have been advised accordingly to adopt roasting at 900°C with excess of air for removal of the chloride. It has been observed that if the temperature is not properly controlled, zinc losses are more than the acceptable limits.

Another source of chloride was found to be from melting and casting sections of the same unit from where the fumes of flux (mainly NH<sub>4</sub>Cl) settle in the cell house. This could be avoided by proper partitioning of the melting as well as roasting operations from the cell house. While drying the sheet deposits, care is taken to avoid the same coming in contact with the fumes from any of the above operations which will otherwise lead to attack on the metal and lowering of the melting efficiency.

(2) *Corrosion of the anodes* – Since the system uses sulphuric acid, lead-silver (0.5 - 1.0%) alloy anodes are used for the process. It has been observed that rolled anodes show better corrosion resistance than the cast anodes. It is very well known that during anodic polarisation lead gets converted to lead dioxide which is formed in layers. During continuous electrolysis after some time the oxide layers get detached from the anode and collect as muck

in the cell. Necessary arrangement is made to collect this and recover lead from the same to minimise anode losses. Such anode loss has been estimated in a 500 kg/day plant as 12.5 - 17 kg/tonne zinc produced. Recovery of lead by thermal reduction at 800-850°C using active charcoal and  $\text{Na}_2\text{CO}_3$  has been worked out for the purpose. Recovery was also carried out in the industry with 85-95.0% efficiency. This operation does not require any additional equipment since there is already a melting furnace for zinc melting.

(3) *Agitation by compressed air* – Design of the air distributor is an important factor in the process since uniform agitation of the slurry is essential for getting good efficiencies. Since the reaction is one of simultaneous dissolution and deposition, effective agitation plays a vital role in establishing a good mass transport and also the required zinc concentration in the electrolyte. The recommended design for the air distribution system (air sprayer) made of PVC and fitted at the bottom of the cell has been found to work satisfactorily.

(4) *Rise in cell temperature* has been often observed. In the process, a temperature upto 55°C is tolerated. Higher temperatures lead to enhanced anode corrosion, dissolution of deposits; loss due to evaporation and lowering of cathode efficiency. The main reasons for temperature rise has been found to be due to exothermic reaction of zinc dust/granules present in the ash with the acid, heat transferred from the headers due to loose contact, low zinc concentration, non-uniform agitation and also dissolution of the cathode due to reasons discussed earlier. When there is considerable metallic zinc granules present in the raw material, suspension is made outside the cell and allowed to cool before the thick slurry is fed to the cell. By proper maintenance the other sources generating heat can also be minimised.

(5) *Quality of raw material*, namely zinc compound plays a vital role in the successful operation of the process. High percentage of insoluble material results in the building up of unreactive material in the cell. As stated before, the cell is operated continuously with frequent addition of zinc compound at definite intervals. Once in a while, depending upon the type of raw material used, the cells are to be cleaned and mud is to be removed from the cell as part of maintenance work. Accumulation of this mud causes blocking of the pores in the air distributor, pitting and dissolution of the cathode deposit as well.

(6) Minor problems arising out of *poor maintenance or improper handling* by the labourers have been encountered. One such problem is occasional shorting due to bending of the headers, loose contact at the points of suspension resulting in the vibration of the electrodes. These could be overcome by taking proper care while starting the cells as well as changing the electrodes during electrolysis.

(7) *Proper cleaning of the cathodes* prior to electrolysis has been found to be a necessity for getting good non-sticky deposit.

(8) Often during melting, *overheating of the charge* has been found to result in increased loss of metal which can be avoided.

The two major problems that face this industry are shortage of continuous power as well as nonavailability of suitable raw material at reasonable prices. On an analysis of the various plants of the licencees, as can be seen from the data presented so far, though the technology is successful, the lack of adequate power and nonavailability of good raw material have led to serious problems in the economic operation of these plants. This being a continuous running, power intensive industry, supply of continuous power is an essential requirement. As regards raw material, the zinc ash being a byproduct of another industry the recovery plant has to depend on the scrap market. This means, the price as well as quality is not stable. Problems due to mechanical contamination by various impurities occur. This can be conveniently avoided, provided the recovery industry is capable of getting its raw material straight from the point of generation. Alternately the zinc recovery plants can even function as an auxiliary unit of a largest zinc consumer, say galvanising industry, wherein the recovered zinc can find a direct use which will serve for better economics even for the galvaniser. The cost of processing works out to be approx. Rs. 8760/-

### CONCLUSIONS

1. It has been demonstrated both on laboratory and on plant scale that the slurry electrolysis process can be successfully adopted for the recovery of zinc from its secondary sources.

2. The main problems facing the industry are: (a) non-availability of continuous and cheap source of power (b) non-availability of raw materials directly from the source such as zinc smelters and galvanising industries, continuously.

The advantages of the process are:

1. The zinc compounds need not be taken into homogeneous aqueous solution for electrolysis.
2. Impurities like iron do not interfere in the electrolysis.
3. The process can be made continuous by addition of powdered raw material in the form of slurry.
4. The electrolyte is used continuously without any detrimental effect either on the purity of the deposit or on the efficiency. Only loss due to handling is made up.
5. The purity of the recovered metal is fairly high (99.9% +)
6. The process is applicable to a wide range of secondary sources and even wastes or zinc content of 50-55% can be processed.
7. The most important advantage is that the process can be operated even on small scale without extensive purification steps prior to electrolysis and no special cooling is needed.

### REFERENCES

1. R Alagusundaram, AL Alagappan, R Vijayavalli, P V Vasudeva Rao and H V K Udupa, Ind. Pat. 142706 (1974)
2. R Alagusundaram, A Narayanan, AL Alagappan, P C Wariar, R Vijayavalli, P V Vasudeva Rao and H V K Udupa, *Trans SAEST*, **10** (1975) 225
3. C A Basha, P C Wariar, AL Alagappan, K V Venkateswaran, R Vijayavalli, P V Vasudeva Rao and H V K Udupa, *J Elec Anal Chem*, **118** (1981) 365
4. C A Basha, P C Wariar, AL Alagappan, K V Venkateswaran, R Vijayavalli, P V Vasudeva Rao and H V K Udupa, *Proc. Seminar on zinc wastes and their utilisation*, ILZIC, (1980) p 2.11
5. P C Wariar, R Vijayavalli, P V Vasudeva Rao and H V K Udupa, *ibid.* p 2.42