Electrolytic recovery of zinc from zinc ash using a catalytic anode

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Abstract: The process of galvanisation of steel generates zinc ash as the waste product, thus creating pollution problems. The recovery of zinc metal from zinc ash, with a zinc content of about 76% by leaching and electrowinning has been studied. The presence of chloride has been identified as the major problem area. A catalytic anode based on iridium dioxide (IrO$_2$) was used as the anode material to overcome this problem. Catalyst loading was kept at an economically acceptable level. The catalyst's stability, energy consumption and efficiency of zinc recovery are discussed. The service life of the IrO$_2$ active coating has been established by an accelerated polarisation test. The zinc deposit recovered from the zinc ash has been examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM).
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1 INTRODUCTION

Zinc ash is generated as a waste material in the process of galvanisation of steel, causing environmental concern. The ash is usually processed to obtain zinc oxide for the paint industry and zinc sulfate for the fertiliser industry. Electrolytic extraction of zinc metal from the ash is an attractive proposition as it would partly meet the demand for the metal in the countries like India. The high chloride content of the ash restricts the viability of the process due to severe corrosion of the traditional lead anode.

Both pyrometallurgical as well as hydrometallurgical processes are practised worldwide to treat zinc wastes. The Waelz kiln process is the most extensively applied in the pyrometallurgical treatment of residues.

A number of studies have been reported for the recovery of zinc from the ash, using different techniques for the removal of chloride. Alkali leaching followed by electrowinning is one of the options reported for the recovery of zinc powder from the galvaniser's ash.[1] Solvent extraction using an organic amine has been employed for the removal of chloride as an amine–ZnCl$_4$ complex.[2] Pyrometallurgical operation is commonly employed for the recovery of zinc from zinc ash, where the crude zinc oxide cake obtained after soda ash treatment is smelted in a rotary kiln and melting furnaces.[3] A route based on roast–leach–electrolysis has been attempted for the recovery of zinc metal from the zinc ash where the total removal of chloride remains as a problem area.[4] Washing of chloride by simple methods is not effective as only 30% of these salts could be removed.[5,6] The chloride can also be removed from the zinc ash as cuprous chloride precipitate by the addition of either copper sulfate and zinc powder[7] or double sulfites of copper such as cupric sulfite and cuprous sulfite.[8] Roasting at high temperature followed by alkali/soda leaching is one of the common hydrometallurgical techniques employed for the removal of chloride.[9] A process based on electrolytic oxidation and air purging has been reported for the removal of chloride from the aqueous acidic zinc sulfate solutions obtained from electric arc furnace dust.[10]

Electrode materials containing IrO$_2$ as the active components have found extensive applications in industrial electrochemistry. This is because they can be successfully employed as oxygen-evolving electrodes in neutral or acid solutions due to their high catalytic activity and stability against anodic corrosion.

This paper describes a laboratory treatment of zinc ash to recover zinc metal by leaching and electrowinning. A catalytic anode based on an IrO$_2$ catalyst has been investigated in the electrowinning of zinc to resist chlorine attack. The efficiency of zinc recovery and the performance of the catalytic anode have been examined. Anodic stability and the service life of IrO$_2$ electrodes have been evaluated by the accelerated polarisation test.

2 EXPERIMENTAL
2.1 Leaching

Leaching of zinc ash was carried out in a glass reactor of capacity 2 dm^3 where 100 g of the ash was leached

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with H_2SO_4 of concentrations ranging from 70 to $200\,g\,dm^{-3}$ for a period of 10–60 min. Agitation was provided with a variable speed mechanical stirrer and temperature was maintained at 50–$90\,^{\circ}C$. The solid to liquid ratio was maintained at 1:6 during leaching. After leaching, the resulting impure zinc sulfate solution was treated with manganese dioxide to oxidise the ferrous ions to ferric ions and the pH was raised by adding zinc ash to remove iron as ferric hydroxide. Zinc dust was added to cement out copper present in the leach liquor. The purified leach liquor was analysed for its impurity levels by AAS.

2.2 Preparation of Ti/IrO₂ anode
The IrO_2 anode was prepared by etching a titanium sheet of dimension 10 cm by 5 cm in 50% HCl at $60\,^{\circ}C$ for 15 min and applying $IrCl_3$ dissolved in isopropyl alcohol to the pretreated substrate. After each coating the solvent was dried at about 80–$90\,^{\circ}C$ and the dried layer was fired for 5 min under the free supply of air at $400\,^{\circ}C$ in a preheated oven. The operation was repeated until the desired level of catalyst was loaded. The anode was finally annealed at the same temperature for 1 h.

2.3 Electrowinning of zinc
The purified zinc sulfate electrolyte containing $55\,g\,dm^{-3}$ zinc and $150\,g\,dm^{-3}\,H_2SO_4$ was electrolysed at $38\,^{\circ}C$ in a rectangular PVC cell of capacity of $1.5\,dm^3$ using an aluminium cathode and an IrO_2-coated titanium anode with the catalyst loading of $0.1\,mg\,cm^{-2}$ for a period of 500 hs. The cathode area exposed to electrolysis was $50\,cm^2$. The current passed varied between 1A and 5A depending upon the current density of 200–$1000\,A\,m^{-2}$ employed and the cell voltage was measured continuously. The electrolyte was circulated to maintain the zinc and acid concentrations. The zinc deposit was stripped every 24 hs and analysed for its impurity levels by AAS. The energy consumption and current efficiency for zinc deposition were determined.

2.4 Anodic polarisation
Anodic polarisation in $1M\,H_2SO_4$ was carried out with the Ti/IrO_2 and traditional $Pb-1\%\,Ag$ anodes at $400\,A\,m^{-2}$ and anode potentials were measured for a period of 30 days.

2.5 Accelerated service life test
Accelerated service life tests were carried out with IrO_2-coated titanium sheets of area $5\,cm^2$ in $1M$ H_2SO_4 at a current density of 0.2–$2.0\,A\,cm^{-2}$ with catalyst loading level of 0.1–$1.0\,mg\,cm^{-2}$ to determine the dissolution rate of catalyst coating. The end of the service life of the anode was indicated by a sudden rise in anode potential.

2.6 XRD and SEM studies
The starting material zinc ash and the product zinc metal were analysed by XRD. The surface morphology was examined by scanning electron microscopy.

3 RESULTS AND DISCUSSION
3.1 Zinc ash composition
Table 1 shows the composition of zinc ash. It was found to be contaminated with metallic impurities like Fe, Cu, Cd and Pb. The high chloride content of 3.55% would result in heavy contamination of the zinc sulfate solution with chloride ions which would affect the traditional lead anodes during electrowinning. The zinc ash was found to be rich in zinc content (76.5%). This level is more than that of most of the zinc concentrates employed for the primary production of zinc. Figure 1 shows the X-ray diffraction pattern of the zinc ash which indicates that it is in the form of zinc oxide.

3.2 Sulfuric acid leaching
The effect of sulfuric acid concentration on the extraction of zinc is shown in Fig 2. Increase in acid concentration is found to improve the leaching of zinc up to $150\,g\,dm^{-3}$. When the sulfuric acid concentration is low the leaching efficiency of zinc ash is found to decrease due to formation of its hydroxides with increasing pH. Hence the optimum acid concentration is fixed at $150\,g\,dm^{-3}$ which is also in line with the studies reported for the recovery of zinc from the electric arc furnace dust.[11]

The effect of temperature on the recovery of zinc is shown in Fig 3. The extraction of zinc is found to increase with rise in temperature and it is only marginal beyond $70\,^{\circ}C$.

3.3 Zinc electrowinning using IrO₂ anode
The composition of the purified leach liquor is given in Table 2. The only objectionable impurity is

Table 1. Composition of zinc ash

Component	Wt (%)
Zinc	76.50
Iron	0.15
Lead	2.45
Copper	0.01
Cadmium	0.31
Chloride	3.55
Insolubles	10–12

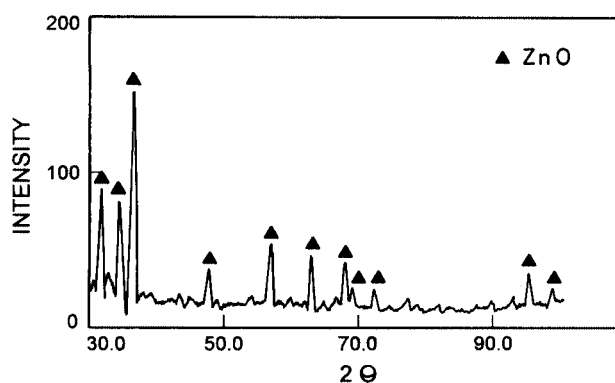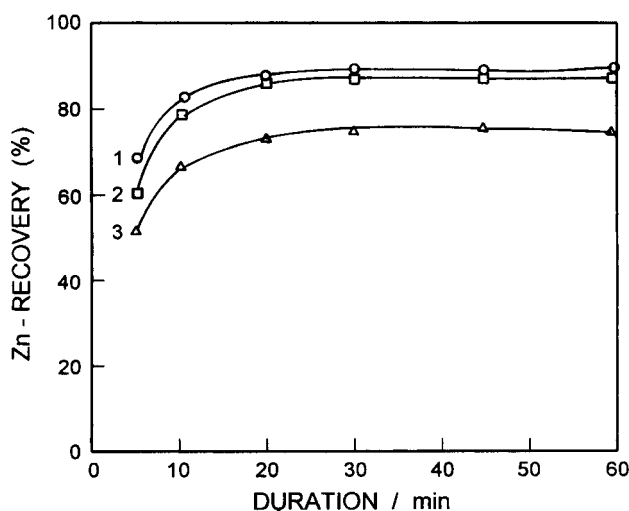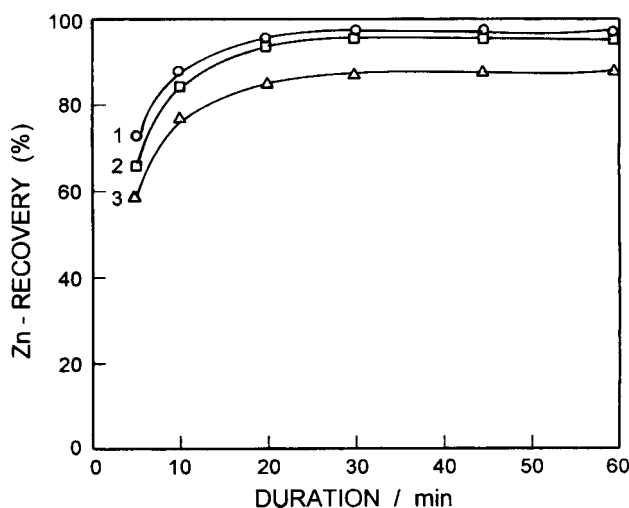**Figure 1.** XRD pattern of zinc ash.

Figure 2. Effect of H_2SO_4 concentration on zinc recovery: (1) $200\,g\,dm^{-3}$, (2) $150\,g\,dm^{-3}$, (3) $70\,g\,dm^{-3}$.

Figure 3. Effect of temperature on recovery of zinc: (1) $90\,°C$, (2) $70\,°C$, (3) $50\,°C$.

Table 2. Analysis of purified leach liquor used for electrowinning of zinc

Component	Concentration ($g\,dm^{-3}$)
Zinc	55.0
Sulfuric acid	150.0
Copper	0.0001
Cadmium	0.0002
Lead	0.0002
Chloride	3.0

chloride which is present to the extent of $3.0\,g\,dm^{-3}$. Zinc electrolytes with a chloride level exceeding $50–100\,mg\,dm^{-3}$ will not permit the use of traditional lead anodes in the electrowinning of zinc. A catalytic anode based on an IrO_2 electrocatalyst is found to resist the attack of chlorine evolved as a part of the anodic reaction. IrO_2 is a good catalyst for both oxygen and chlorine evolution.[12] Figure 4, compares the performance of the Ti/IrO_2 anode with
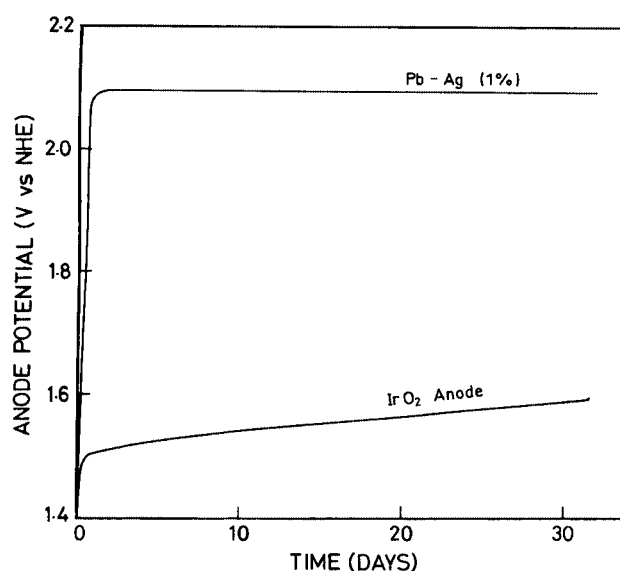
Figure 4. Anode potential–time curves for Pb-1% Ag and Ti/IrO_2 anodes in 1M H_2SO_4 at $400\,A\,m^{-2}$.

the traditional Pb–1% Ag electrode under oxygen evolution conditions. The lead anode is found to be associated with a higher oxygen overpotential, leading to higher anode potential. A solving in anode potential to the extent of 0.5V is seen for the anode coated with IrO_2 catalyst. Anode potential is a major component of the cell voltage and the extent of its saving observed for the IrO_2 anode would bring down the energy consumed in the zinc electrowinning by about 15%. A small initial increase of anode potential is observed for the IrO_2 electrode. This is because some erosion of the porous outer layer of the active coating is possible under intense oxygen evolution. The initial dissolution rate for the IrO_2 coating is reported to be about several orders higher than the steady state dissolution rate.[13]

When the zinc sulfate leach liquor containing chloride is subjected to electrolysis employing the IrO_2-coated anode with a minimum Ir loading level of $0.1\,mg\,cm^{-2}$, the catalytic coating is found to be stable on long term usage at current densities $200–400\,A\,m^{-2}$ and there is no significant rise in the cell voltage. The anodic stability of the catalyst employed has also been established by an accelerated life test in the present work.

The function of the IrO_2-coated anode under acid sulfate electrodeposition conditions is primarily to remain inert and enable oxygen to be evolved at the lowest possible overpotential. IrO_2 has a higher potential for oxygen evolution than RuO_2, a cheaper and well established electrocatalyst. However, IrO_2 has become the most favoured material as an insoluble anode for the electrodeposition of metals from acid electrolytes because of its enhanced life time under acidic oxygen evolution conditions.

Table 3 shows the data on cell voltage and energy consumption for the electrowinning of zinc from the zinc ash leach liquor. Zinc electrowinning at current densities exceeding $600\,A\,m^{-2}$ results in a decrease

Table 3. Effect of current density on energy consumption

Current density ($A\,m^{-2}$)	Cell voltage (V)	Cathode current efficiency (%)	Energy consumption ($kWh\,kg^{-1}$)
200	3.26	92.5	3.51
400	3.92	91.0	3.78
600	4.70	89.1	3.99
800	5.40	86.1	4.21
1000	6.00	85.1	4.49

in current efficiency, leading to an increase in energy consumption.

3.4 Quality of zinc deposit

The zinc deposit stripped every 24 h is dense, compact and dendrite-free with vertical striations. The scanning electron micrographs given in Fig 5 show the general morphology of the zinc deposit. The vertical striations on the surface of the zinc deposit (Figure 5(a)) are due to the upward movement of hydrogen liberated as a side reaction along with zinc deposition. Deep cavities at some sections of the zinc deposit (Fig 5(b)) show the points of hydrogen evolution. The deep cavities surrounding the zinc grains show the points of hydrogen evolution. The change of crystal orientation is generally reported when chloride ion is added to the acid zinc sulfate electrolyte.[14]

The XRD pattern of the zinc deposit (Fig 6) is in good agreement with the diffraction lines of the standard zinc metal.

The purity level of zinc recovered from the zinc ash is shown in Table 4. The lead contamination of the zinc deposit is only 20 ppm. This low level of lead is due to the use of an IrO_2 anode as a substitute for the traditional lead anode. The corrosion of the lead anode is mainly responsible for the lead content of the zinc deposit in the electrolytic zinc process.

3.5 Accelerated service life test and anodic stability

For technological applications the service life of any electrode material is always one of the main concerns. Normally the service life of an electrode is determined under conditions of accelerated corrosion imposing a high current to the system and measuring the potential against the time response.
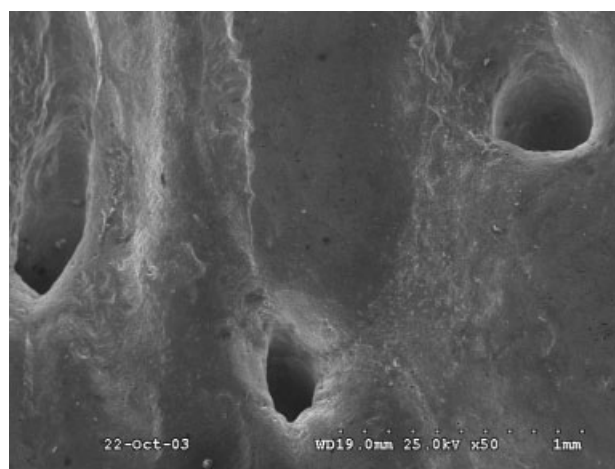
An accelerated life test will shorten the service life, making it possible to estimate the stability of the active IrO_2 coatings under real conditions. Table 5 shows the dependence of service life on iridium loading

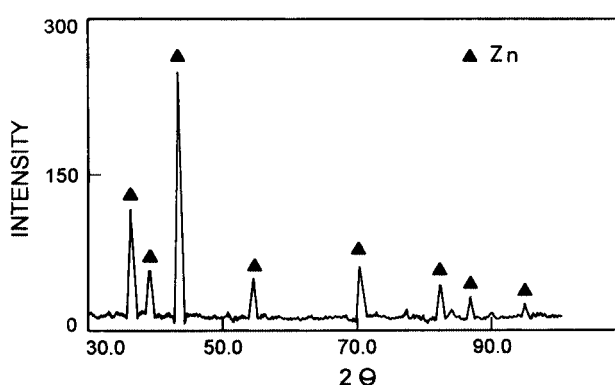**Table 4.** Assay of zinc deposit

Element	Wt (%)
Zinc	99.890
Lead	0.002
Cadmium	0.033
Iron	0.051
Copper	0.024
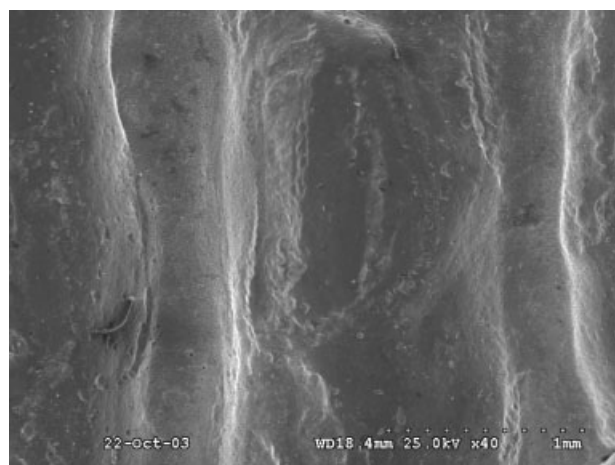
(a)

(b)

Figure 5. SEM micrographs of zinc deposits: (a) and (b) at different locations.

Figure 6. XRD pattern of zinc deposit.

level under accelerated polarisation conditions at a current density of $0.2\,A\,cm^{-2}$. Service life is almost proportional to iridium content in the active layer. This suggests that the active surface layer is uniformly dissolved during the accelerated life test until sufficient iridium content is present. The dissolution rate increases slightly from 1.04 to $1.32\,\mu g\,cm^{-2}\,h^{-1}$ when iridium loading changes from 0.1 to $1.0\,mg\,cm^{-2}$. The service life also depends on current density employed,

Table 5. Dependence of Ir loading on service life of anode at $0.2\,A\,cm^{-2}$ under accelerated polarisation conditions

Iridium loading $(mg\,cm^{-2})$	Service life (h)	Dissolution rate $(\mu g\,cm^{-2}\,h^{-1})$
0.1	142	1.04
0.2	212	1.26
0.5	600	1.14
1.0	1120	1.32

as shown in Table 6. It is interesting to note a drastic increase in the dissolution rate of Ir at higher current densities with a maximum value of $3.12\,\mu g\,cm^{-2}\,h^{-1}$ at a current density of $2\,A\,cm^{-2}$.

Different service life values have been cited in the literature for systems containing IrO_2 as the electrocatalytic component for the oxygen evolution reaction. A direct comparison of these values should be made with extreme caution because differences in the parameters such as the applied current density, oxide layer composition, its thickness, thermal treatment temperature, nature of solvent and nature of metallic support are all considered of great importance for the stability of the oxide. The service life values under accelerated polarisation conditions for the pure IrO_2 anodes employed in the present study vary between 46 and 1120 h depending upon the catalytic loading and the current density employed.

Service life values much larger than those observed in this work have been reported for mixed oxide coatings such as IrO_2-TiO_2[15] and $IrO_2-Ta_2O_5$.[16] The formation of a solid solution of IrO_2 and stabilisers like TiO_2 is responsible for the enhanced anodic stability of the mixed oxide coatings.[17] Although the Ti/IrO_2 anode has high catalytic activity it does not show high mechanical stability under vigorous oxygen evolution, requiring a stabilising agent to improve its anchoring property with titanium substrate. It is known that the addition of a non-conducting oxide into the active coating can improve the anodic stability. Excellent anodic stability has been reported for the IrO_2 coating when it is mixed with Ta_2O_5.[18]

Determination of real service life of the anodes from the accelerated polarisation tests is very complex. However for an anode system such as Ti/IrO_2 (65 mol %)–Ta_2O_5 (35 mol %) it was estimated to be from 5 to 10 years.[13]

As IrO_2 is an expensive electrocatalyst, the industrial application of these anodes will be decided by the cost effective catalyst loadings with service life acceptable to the long term usage. More detailed studies designed to optimise the active coatings with suitable inert metal oxide stabiliser for maximum anodic stability under oxygen evolution conditions are in progress.

4 CONCLUSION

The zinc ash with its zinc content of about 76% has been utilised for the recovery of zinc metal by leaching and electrowinning. The sulfuric acid leaching is found to be effective in extracting more than 90% of zinc values from the ash. The zinc sulfate solution obtained is heavily contaminated with chloride to the level of $3.0\,g\,dm^{-3}$, unacceptable to electrowinning operations. The catalytic anode based on an IrO_2 electrocatalyst having a minimum iridium loading of $0.1\,mg\,cm^{-2}$ was found to withstand this chloride level with high activity and anodic stability on long term usage. These anodes also exhibit a reduction in anode potential to the extent of 0.5V over the traditional lead anodes, leading to considerable energy saving in zinc electrowinning. The accelerated polarisation tests carried out with catalyst loading of $0.1-1.0\,mg\,cm^{-2}$ Ir under oxygen evolution conditions throw much light on the service life of these anodes with the Ir dissolution rate varying between 1.04 and $3.12\,\mu g\,cm^{-2}\,h^{-1}$ depending upon the current density employed.

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Table 6. Dependence of current density on service life of anode with $0.1\,mg\,cm^{-2}$ Ir under accelerated polarisation conditions

Current density $(A\,cm^{-2})$	Service life (h)	Dissolution rate $(\mu g\,cm^{-2}\,h^{-1})$
0.2	142	1.04
0.6	82	1.82
1.2	64	2.74
2.0	46	3.12

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