

RECYCLING OF ZINC WASTE FOR ELECTROGALVANIZING

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Abstract — An objective of Bureau of Mines recycling research is to devise technology that enables the recovery of metals, minerals, and other values from waste products and thus promote the wise and efficient use of our nation's resources. In line with this objective, Bureau researchers are investigating the use of waste products containing zinc as a source of zinc for electrogalvanizing. Industrial wastes used in this work were lead smelter flue dust, wastewater treatment sludge, copper smelter flue dust, and brass smelter flue dust. After zinc extraction with sulfuric acid, the resultant solutions were partially purified and used to electrogalvanize 0.234-cm (0.092-in.) diameter 1070 alloy steel wire, a common electrogalvanized product.

The corrosion resistance of the electrogalvanized wire from waste electrolyte was compared with electrogalvanized wire from relatively pure electrolyte prepared in the laboratory, and electrogalvanized wire from an industrial electrogalvanizing plant.

Corrosion rate measurements indicated that electrogalvanized wire obtained from waste electrolyte prepared from brass smelter flue dusts compared favorably with industrial electrogalvanized wire and electrogalvanized wire from the relatively pure electrolyte. The brass smelter flue dusts were chosen for more detailed studies.

Impurities in the waste electrolyte caused some problems. Copper was undesirable because it passivated the soluble zinc anode. Other impurities such as cobalt and nickel were more tolerable but also slowly coated the anode. Owing to the ease of removal of copper by cementation, it posed no processing problem for electrogalvanizing. Successful completion of bench-scale work with brass smelter flue dusts led to large-scale trials at an industrial electrogalvanizing plant.

INTRODUCTION

There are large amounts of wastes generated in the United States each year that contain zinc. Sixty percent of the zinc used in the United States comes from foreign sources. Conservative estimates place the amount of recoverable zinc from domestic stack dusts alone at about 235 000 tons annually^[1]. Owing to the problem of disposal of these materials and the presence of other recoverable metals such as copper, cobalt, and nickel, it is becoming increasingly important that these secondary resources be utilized.

Most uses of zinc require high-purity materials. Electrowinning of zinc as a means of recovery from waste can be quite complex and costly^[2,3]. Normally zinc is present as zinc oxide in the waste which is leached with sulfuric acid. It also may be roasted with sulfuric acid and finally water leached. During leaching, other metal compounds are also soluble. Metal impurities cause difficulty in electrowinning. Iron, cobalt, and nickel cause reduced cathode efficiencies, while cadmium and lead contaminate the cathode deposit.

During purification iron is removed first by oxidation to the ferric state and precipitated as the hydroxide by raising the pH. Other metal cations more noble than zinc are removed by cementation with zinc dust. In all cases it is desirable to lower the concentration of these metal cations to below 1mg/l^[4,5]. Other impurities such as chloride ion cause mechanical problems such as sticking of the zinc deposit to the aluminum cathodes.

The possibility that some of these impurities could be beneficial in electrogalvanizing has been shown previously^[6]. Cobalt and chromium at low concentrations in electrogalvanizing baths have yielded more corrosion resistant coatings, and indications are that wire drawability may be enhanced by the presence of cadmium^[7].

Previous studies by the Bureau of Mines have involved recovery of zinc from lead smelter flue dust^[2], industrial wastewater treatment sludge^[3], steel furnace dust^[8], and a variety of other process wastes. Owing to the economics involved, no general industrial uses have developed.

This paper describes research in which four wastes were used: lead smelter flue dust, industrial wastewater treatment sludge, secondary copper smelter flue dust, and brass smelter flue dust. After leaching with H_2SO_4 to extract the zinc, the resultant solutions were partially purified prior to being used for electrogalvanizing. The primary purpose of this investigation was to evaluate zinc wastes for possible use in pilot plant scale electrogalvanizing tests to determine the feasibility of using waste as a source of zinc for industrial electrogalvanizing. Zinc deposits on steel wires electrogalvanized in waste solutions were evaluated by comparing them with those electrogalvanized in relatively pure (RP) electrolyte, prepared in the laboratory by dissolving French process ZnO in reagent grade H_2SO_4 , and electrogalvanized wire obtained from an industrial plant.

MATERIALS, EQUIPMENT AND PROCEDURES

Wastes

The average partial compositions of the wastes used in this investigation are given in Table 1. Waste 1 is a blast furnace flue dust from a primary lead smelter. Waste 2 is a lime sludge residue from an automobile radiator producer's wastewater treatment plant after roasting at 600°C. Wastes 3 and 4 are from a secondary copper smelter and a brass smelter, respectively. The wastes are typical for each particular operation.

Table 1. Waste composition, wt %

Waste	Zn	Cd	Cl	Co	Cu	Ni
1	10.8	8.53	2.7	0.016	0.29	0.002
2	31.1	—	0.3	—	1.10	0.40
3	37.6	—	0.3	—	6.68	0.12
4	64.6	—	5.8	—	1.10	—

Extraction and purification

Treatment of the wastes was carried out in a manner specific to their composition. Alkalinity and impurities determined the procedures used. Certain elements such as cobalt and nickel require more stringent conditions for removal.

Extraction was carried out in a 10-l. glass vessel by mixing a quantity of waste, reagent grade sulfuric acid, and distilled water to give a solution with the desired concentration of about 100 g/l Zn^{2+} . The waste material was added to the acid solution at the temperatures given below. Temperatures were maintained at 90–95° C for the times specified. After the prescribed retention time; the insoluble matter was removed by filtration.

The leach solutions obtained were next treated as determined by their composition. For instance, if iron was present in the electrolyte it was removed as ferric hydroxide by oxidation and pH control. Other noble cations were selectively removed or controlled by cementation with zinc dust (50% <70 mesh). Additions of As_2O_3 and $CuSO_4$ were made to selectively control or remove cobalt and nickel. Detailed procedures for preparation of each of the waste electrolytes are given in the following paragraphs and the composition and pH of the zinc solutions after extraction and subsequent controlled purification are given in Table 2.

Table 2. Waste zinc electrolyte composition

Electrolyte	g/l		mg/l					pH
	Zn	Cl	Cd	Co	Cu	Fe	Ni	
1A	132	—	945	82	<1	<1	92	5.42
1B	128	—	500	36	<1	<1	8	2.87
1C	92	—	6	75	<1	<1	48	5.30
2A	75	—	<1	—	2130	7	529	4.62
2B	75	—	—	—	<1	7	154	4.22
2C	75	—	—	—	122	7	497	3.23
3A	105	—	600	—	2860	3230	99	1.58
3B	123	—	540	—	<1	<1	<0.1	5.20
3C	112	—	5	—	<1	<1	<0.1	5.16
4A	120	2.1	64	—	996	9	8	4.80
4B	120	2.0	28	—	<1	3	2	5.10

Electrolyte 1A. Lead smelter flue dust, waste 1 in Table 1, was roasted with sulfuric acid at 450–500° C for 2 h, followed by water leaching^[2]. The solution obtained was then treated to remove iron by oxidation with KMnO_4 and raising the pH to precipitate ferric hydroxide.

Electrolyte 1B. One liter of electrolyte 1A was treated with 0.1 g As_2O_3 , 0.12 g CuSO_4 , and 4 g of zinc dust at 90–95° C for 1 h to lower the cobalt, nickel, and cadmium concentrations.

Electrolyte 1C. One liter of electrolyte 1A was treated with 6.6 g of zinc dust at 50° C for 2.5 h.

Electrolyte 2A. Roasted wastewater treatment sludge was also obtained from prior efforts^[3]. Fourteen-hundred gram batches were leached with 5 l. of 200 g/l H_2SO_4 for 2 h at 90–95° C.

Electrolyte 2B. One liter of electrolyte 2A was reacted with 0.1 g As_2O_3 and 5 g of zinc dust at 90–95° C.

Electrolyte 2C. One liter of electrolyte 2A was treated with 3.8 g of zinc dust at 20° C for 1 h.

Electrolyte 3A. This electrolyte was obtained by leaching 1842 g of secondary copper smelter flue dusts, waste 3 in Table 1, with 8 l. of 148 g/l H_2SO_4 at 90–95° C for 2.5 h.

Electrolyte 3B. Three liters of electrolyte 3A was treated to remove iron by oxidation with KMnO_4 and raising the pH to precipitate ferric hydroxide. After solid/liquid separation the solution was treated with 2 g of As_2O_3 and 20 g of zinc dust at 90–95° C for 2 h.

Electrolyte 3C. One liter of electrolyte 3B was reacted at 50° C for 2 h with 5 g of zinc dust.

Electrolyte 4A. This electrolyte resulted when 1484 g of brass smelter flue dust, waste 4 in Table 1, was leached with 8 l. of 180 g/l H_2SO_4 beginning at 47° C and increasing to 95° C in 15 min; total time was 1h. Iron, precipitated as ferric hydroxide, and some copper were removed.

Electrolyte 4B. One liter of 4A was reacted with 2 g of zinc dust at 90° C for 1 h.

RP electrolytes were prepared by dissolving French Process zinc oxide in reagent-grade sulfuric acid (150 g/l) to give a zinc concentration of 100 to 130 g/l.

Additions of NH_4Cl (18 g/l) for conductivity and H_3BO_3 (12 g/l) for buffering were made to the solutions obtained from purification. Solid licorice was also added to RP electrolytes at a level of 0.3 g/l in certain cases. Licorice is a common additive used in acid zinc plating.

Electrolyte pH was measured with a digital pH meter. Any pH adjustments were carried out by additions of H_2SO_4 or NH_4OH .

Electrocleaning and electrogalvanizing

Electrocleaning and electrogalvanizing were carried out in 250- to 400-ml glass cells at ambient temperature. In both cases the 0.234-cm diameter 1070 alloy steel wire was rotated by a servocontrolled motor-generator with torque limiter. Rotation rates were 35, 70, and 105 rev/min for current densities of 200, 400, and 600 mA/cm², respectively.

Wires were first degreased in trichloroethylene, then electrocleaned in 60 g/l H_2SO_4 to remove rust and scale. The counter electrode was lead-silver (0.75% Ag), as is used in electrowinning. The current density for electrocleaning was 400 mA/cm². The wire was first made cathodic for 1 min, then anodic for 1 min, and this was repeated for four cycles. A bipolar switch was used to reverse the direction of current flow. The wire was rinsed with distilled water after electrocleaning.

A 99.999% pure zinc anode was masked with electroplater's tape, to give an area 1.4 times the area (5–7cm²) of the 1070 alloy steel wire cathode, and used for electrogalvanizing. The rotation rate was set, and the current was applied for the predetermined deposition time. The plated wire was removed from the electrolyte, rinsed with distilled water and then ethanol, and blown dry. A 50-ampere, 40-volt power supply was used to apply the controlled current to the cell. All plating was carried out in stirred electrolytes. Figure 1 shows the schematic of the plating cell and associated equipment.

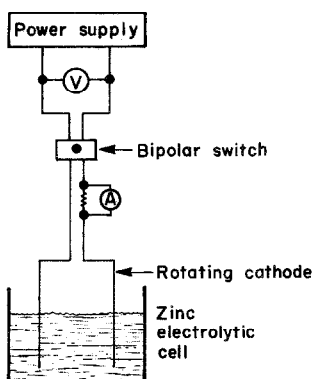


Fig. 1. Schematic of plating arrangement.

Corrosion testing

Preliminary corrosion rate evaluation was carried out in a salt spray cabinet according to ASTM Standard B117–73. Selected electrogalvanized steel samples were evaluated by means of electrochemical measurements. The procedure used for electrochemical corrosion rate measurements was similar to that given by Baugh^[9] for pure zinc.

The corrosion cell was a commercially available 1-l. glass vessel. $M(NH_4)_2SO_4$ prepared from the analytical reagent grade salt was the medium employed. All measurements were performed in deaerated solutions at $25 \pm 2^\circ C$, pH 6 ± 0.1 . The counter electrode was platinum mesh, and the reference was a saturated calomel electrode (SCE). The reference electrode was placed in a bridge tube fitted with a Vycor frit for a minimum resistance drop and low leak rate.

Sample preparation consisted of first degreasing specimens in boiling trichloroethylene, followed by rinsing with absolute ethanol and finally blow drying. The surface area used was 1cm². A scanning potentiostat was connected to the cell, and polarization curves were obtained by scanning at 0.25 mV/s from the corrosion potential, first in the cathodic and then in the anodic direction. Extrapolation of the Tafel region of the anodic portion yielded the dissolution current i_{corr} at the corrosion potential E_{corr} . Potential and current were measured with digital electrometers. All measurements were made in quiescent electrolytes.

Cyclic voltammetry

Cathodic polarization curves were obtained in electrogalvanizing electrolytes on polished 1070 AISI steel wire. Polishing consisted of 240 grit SiC abrasion to remove rust, followed by 600-grit SiC abrasion to yield a reproducible surface. The specimen was then degreased in trichloroethylene and wiped dry. The anode was a 99.999% zinc rod with one face machined to yield a flat surface. Both the cathode and the anode were masked to give 1-cm² surface area. The reference electrode and cell were of the same type as in the corrosion section.

The measurements were performed at 60° C. Scanning was begun at -0.95 V vs SCE and continued in the cathodic direction at a rate of 0.5 mV-s until a current density of 50 mA/cm² was reached. At this point the scan direction was reversed and the scan was allowed to continue until the reversible cell potential was reached. All measurements were made in stirred electrolytes.

RESULTS AND DISCUSSION

Zinc extraction

Extraction efficiency of zinc for the lead smelter flue dust, waste 1, was 95%^[2]. The wastewater treatment sludge, waste 2, had zinc extraction efficiencies of <80% owing to its high alkalinity. The final electrolyte also had low zinc concentrations (see Table 2). The secondary copper smelter flue dust (waste 3) and the brass smelter flue dust (waste 4) gave extraction efficiencies of 95%.

Electrogalvanizing

In industrial electrogalvanizing, current densities are normally as high as feasible^[10]. Deposition times are varied by the speed of the wire through the plating bath. The current densities used in this study were 200 – 600 mA/cm², and the plating times were comparable to the conditions used in one of the largest U.S. industrial electrogalvanizing plants. Zinc coatings were 1 – 2 wt%.

Preparative electrocleaning was required to remove rust and scale so that good adherence of zinc coating to the steel substrate would be possible. Soluble, high-purity zinc anodes maintained the zinc concentrations in the plating electrolytes.

Deposition tests were performed on the electrolytes shown in Table 2 at 25 – 30° C on a 1 cm² cathode for preliminary evaluation. Electrolytes containing copper were undesirable due to rapid zinc anode passivation, resulting from cementation^[11,12]:



Thus, electrolytes 2A, 2C, 3A, and 4A were undesirable. When plating in these electrolytes, dendritic dark cathode deposits were obtained. This observation of “burnt” deposits also eliminated the use of electrolytes containing copper.

Electrolytes containing cobalt and nickel did not show this rapid anode passivation. Continued plating in these electrolytes, however, showed some anode darkening due to cemented cobalt or nickel on the zinc surface. The order of passivation rate from observation is consistent with rate of removal of these impurities from zinc electrowinning electrolytes^[4,5]. This was observed when plating in electrolytes 1C and 2B: The order is as follows:



Electrolytes of the type shown in Table 2 would not be suitable for electrowinning. Electrogalvanizing, however, resulted in suitable or excellent zinc coatings over a wide variety

of compositions. The fact that the brass smelter dust (waste 4) contains a high chloride concentration would be a disadvantage in electrowinning. Chloride causes sticking of the zinc to the aluminum cathode.

Corrosion tests

Deposits from the electrolytes 1A, 1C, 3B, 3C, and 4B were evaluated in the salt spray environment. Waste 2 was eliminated because of low extraction efficiency. Deposits obtained in RP electrolytes were also evaluated for comparison with the waste derived deposits.

Using the criteria for failure as per ASTM standard electrolyte 4B yielded the longest lasting deposits. Therefore it was selected for further testing.

Table 3. Corrosion rates of electrogalvanized steel wire

Plating electrolyte	E_{corr} (V)*	i_{corr} ($\mu\text{A}/\text{cm}^2$)	Plating conditions [†]		
			pH	T	CD
RP	-1.164	10.8	5	65	600
	-1.150	10.8	5	40	600
	-1.161	17.7	3.5	60	600
	-1.152	17.7	3.5	60	600
	-1.150	15	3.5	40	600
	-1.155	9.6	2.3	60	600
	-1.152	7.5	2.3	40	600
Waste 4B	-1.164	8.2	3.5	40	600
	-1.160	10.3	3.5	40	600
	-1.153	5.2	4.7	60	600
	-1.153	8.0	4.7	60	600
	-1.161	7.8	4.7	40	600
	-1.154	6.2	2.0	60	600
Industrial wire	-1.144	9.3	3.5	60	500
	-1.140	9.7	4.8	60	500

*V = volts vs SCE.

[†]T = °C, CD = current density in mA/cm².

Table 3 shows the corrosion rates obtained by electrochemical measurements for wire plated in electrolyte 4B and in RP electrolyte. Both electrolytes contained NH_4Cl and H_3BO_3 , and the RP electrolyte contained licorice. Comparison is also made with an industrial electrogalvanized wire product.

The data show that plating temperature, in the range given, has little if any effect on the corrosion current. Electrolyte pH had a more striking effect in the RP electrolyte than in the waste electrolyte. However, the corrosion rates of wire electrogalvanized in the waste electrolyte were lower than for wire plated in the RP electrolyte. Comparison of these values for wire plated in this laboratory with that produced in an industrial plant is excellent.

Electrogalvanizing of wire causes resistance heating of the electrodes and the bath. The temperature of 60° C is normally used by one of the country's largest electrogalvanized wire producers, and it must be maintained by cooling^[12]. A temperature of 40° C was evaluated for comparison but is not practical in many plant operations when plating at high current densities.

Since this preliminary investigation was designed for possible scale-up to a pilot scale operation, the electrolytes obtained from the brass smelter flue dust (waste 4) appeared to be very promising. The corrosion rate measurements given attest to that fact.

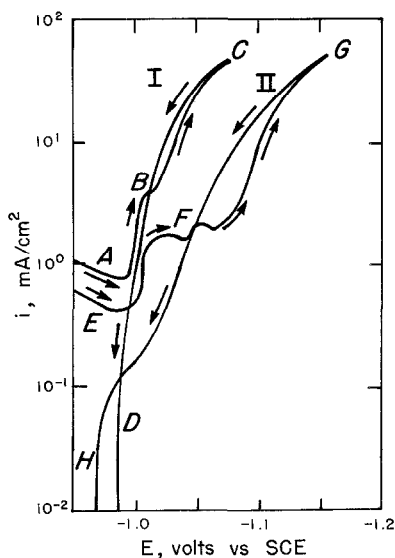


Fig. 2. Cyclic voltammogram; RP electrolyte. I — no licorice; II — 0.3 g/l licorice.

Cyclic voltammetry

The deposition characteristics of zinc electrolytes used for electrogalvanizing are of fundamental concern. This study is by no means all inclusive but aids understanding of the basic process. The method used is a modified version of that used by Wang^[13] in evaluating zinc electrowinning electrolytes.

Figure 2 (curve I) shows the current-potential relationship observed on a steel cathode in a ZnSO_4 electrolyte containing 130 g/l Zn^{2+} , 12 g/l H_3BO_3 , and 18 g/l NH_4Cl at 60° C and pH = 3.6. The scan is initiated in region A, showing the initial current due to proton reduction.

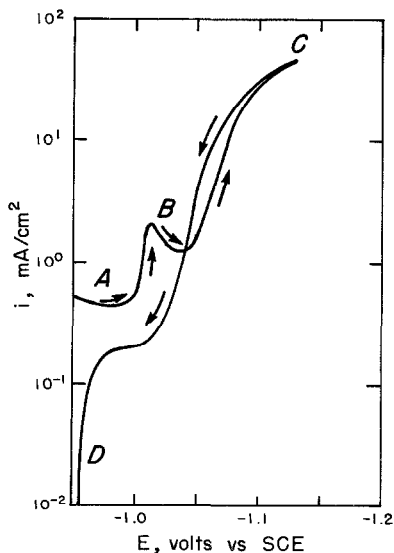


Fig. 3. Cyclic voltammogram waste electrolyte 4B.

At -0.995 V the current begins to increase owing to cathodic zinc ion reduction. At point C (50 mA/cm²) the scan direction is reversed and the current decreases to the reversible potential for zinc in this medium, which is -0.986 V.

Curve II is obtained when 0.3 g/l of solid licorice is dissolved in the ZnSO₄ electrolyte. Once again at point E only hydrogen current is observed. This current is much lower than that observed in the absence of licorice. The total current begins to rise at -1.000 V but rapidly reaches a limiting plateau at about -1.015 V in region F. This region is more pronounced than the shoulder seen at point B in curve I. This limiting effect that licorice has on the zinc ion reduction reaction causes the potential at point G to be more negative than at point C in curve I. The polarization effect by the licorice additive is considered to be beneficial since deposits are "leveled" by its presence^[10-12].

After reversing the scan direction at point G on curve II, the current decreases to point H, the reversible potential, which is -0.967 V. This value is 19 mV more anodic than that observed in curve I at point D. Thus, licorice also causes a displacement of the reversible potential for zinc.

Figure 3 shows the current-potential relationship for waste electrolyte 4B with NH₄Cl and H₃BO₃ added. Note the similarity of this polarization curve to that obtained with licorice present in the RP electrolyte (Fig. 2, curve II). There are certain differences, however, such as the current peak in region B. The overall effect is a polarization at 50 mA/cm² vs curve I in Fig. 2. The potential at point C is -1.130 V. The reversible potential at point D in Fig. 3 is -0.955 V, which is more anodic than the values obtained in RP electrolyte.

Table 4 summarizes the values given above. The zinc reduction potential is $E_{\text{redZn}^{2+}}$, and the reversible potential is E_{rev} . The potential at the point of scanning direction reversal is $E(50$ mA/cm²). It should also be noted that the general shape of this curve implies a diffusion-controlled or current-limiting process.

Table 4. Zinc deposition data

Curve	$E_{\text{redZn}^{2+}}$	$E(50$ mA/cm ²)	E_{rev}
I (Fig. 2)	-0.995 V	-1.077 V	-0.986 V
II (Fig. 2)	-1.000 V	-1.153 V	-0.967 V
Fig. 3	-1.000 V	-1.130 V	-0.955 V

The shape of the polarization curve and the shift by the waste zinc electrolyte suggest that it contains a polarization or leveling agent. The electrolyte is very similar in color to the RP electrolyte containing licorice; both are amber. The regions of the polarization curves after the onset of zinc ion reduction (point F, Fig. 2; point B, Fig. 3) display a somewhat different process. Isolation and identification of the polarizing agent from the brass dust would be of benefit to electroplating technology since it affects crystal growth.

The effects of the organic polarization agents on crystal structure can be seen in Figs 4 and 5. Figure 4 comprises scanning electron micrographs of a zinc deposit from RP electrolyte without licorice addition. Figure 4A shows that at $100\times$ magnification the surface shows "pits" in the deposit; at $1000\times$ magnification (Fig. 4B) rather large crystals are observed. With addition of licorice or other polarization agents, the "pits" are not observed. In Fig. 5A the effect of licorice addition, at a level of 0.3 g/l, is to refine the grain size of the deposit. However, as shown in Fig. 5B, coatings obtained from the waste electrolyte have a much finer grain size. This observation of a finer grained coating obtained from the waste electrolyte correlates with the lower corrosion currents shown in Table 3.

The cathodic polarization curves suggest a method for electrolyte evaluation. The concentration of polarization agents can be analyzed by this criterion. However, there is no information on the grain refining ability of the polarization agent. Deposit grain size must be determined by observation.

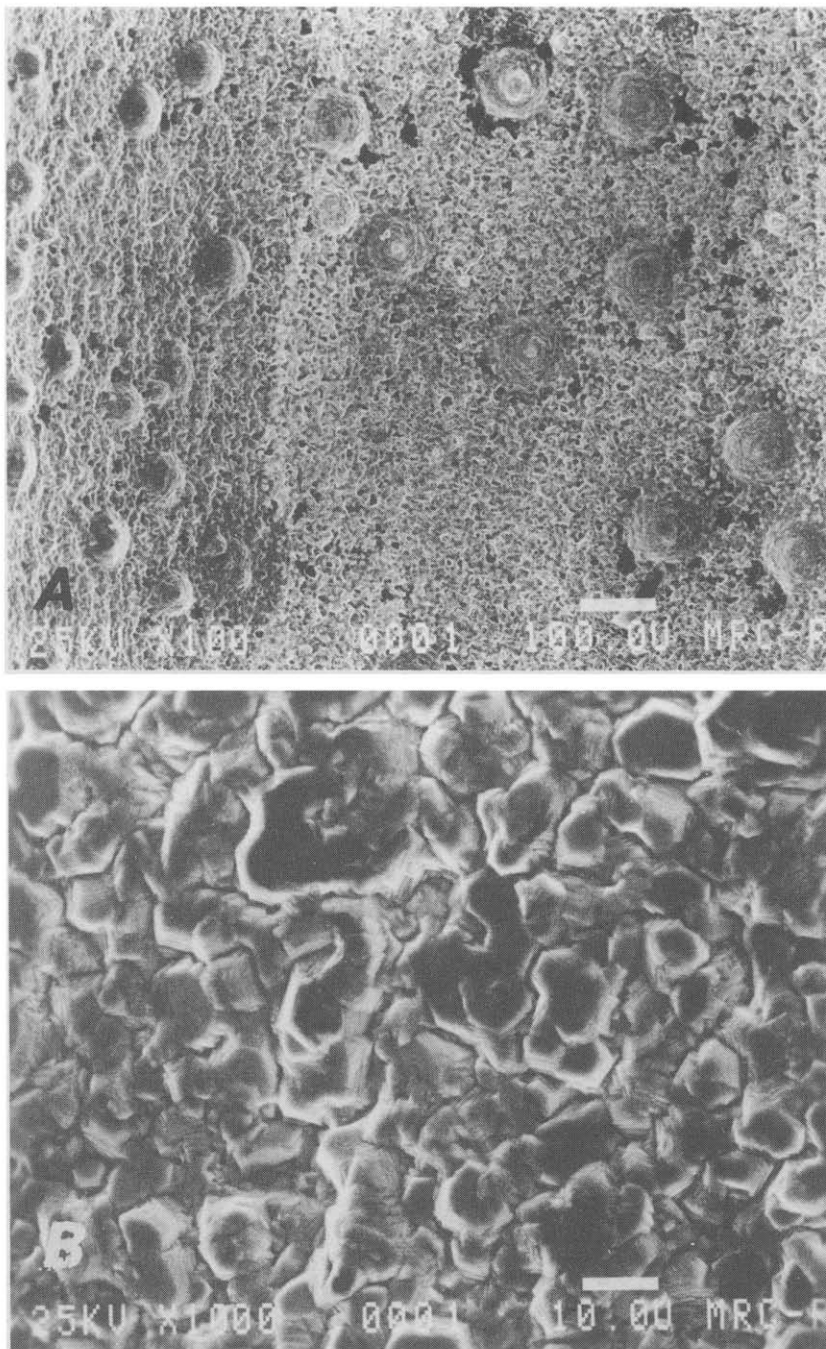


Fig. 4. SEM photographs of deposit obtained from RP electrolyte without organic addition agent. Plated at pH 3.5, 600 mA/cm², 40° C. (A) × 100; (B) × 1000.

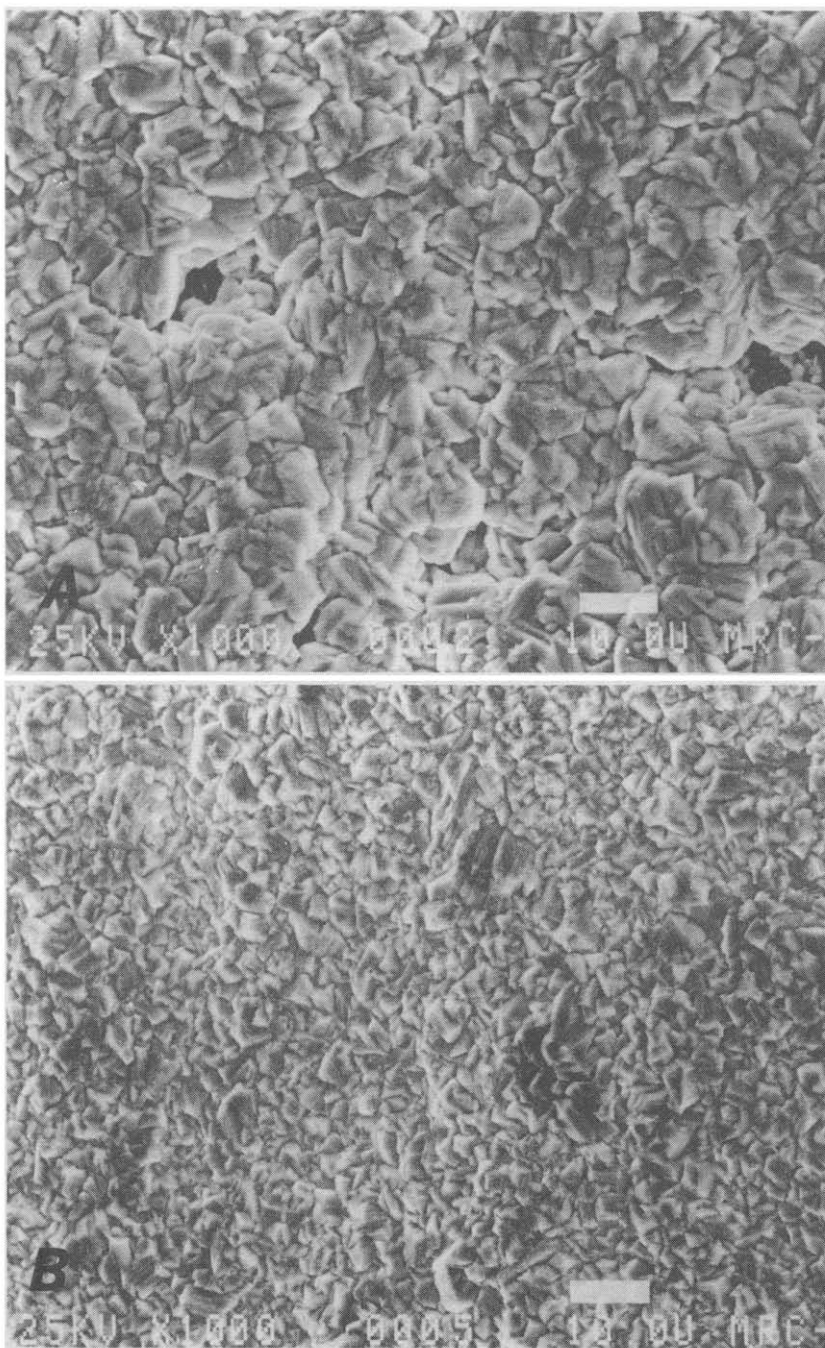


Fig. 5. SEM photographs of deposits obtained from (A) RP electrolyte with 0.3 g/l licorice, 40°C, 600 mA/cm², pH 3.5. (B) Waste electrolyte 4B at the same conditions. Both $\times 1000$.

CONCLUSIONS

Wastes containing zinc provide a potentially viable source of inexpensive zinc for electrogalvanizing. Results of testing electrolytes from extraction of zinc from brass smelter flue dust suggest that it falls in this category. Corrosion rates as measured electrochemically of electrogalvanized steel wire plated in these waste electrolytes are lower than or at least comparable to those of wire plated in RP electrolytes. Also, by this method the corrosion rates of wire plated in an industrial plant compare with those of wire plated in the laboratory. Plating electrolyte pH had a slight effect on the corrosion of wire plated in RP electrolyte, but overall the pH variation and temperature range studied had little effect on the corrosion of the coatings.

The use of cyclic voltammetry to measure the level of cathodic polarization agents offers a means of process control. Factors affecting the zinc deposition reaction also may be studied by this technique. However, empirical observation of the surface characteristics is a valuable method of evaluation since polarizing strength does not correlate with grain size.

Copper is the most undesirable impurity in electrogalvanizing. The ease of removal by cementation allows wastes containing copper to be readily treated for electrogalvanizing. Other impurities such as cobalt and nickel are more tolerable but also slowly coat the soluble zinc anodes. At higher concentrations of these impurities process parameters would have to be adjusted.

Less purification is necessary than in the electrowinning process, a strong economic factor in the utilization of these resources.

Because of its high zinc content and the presence of chloride at a rather high concentration, brass smelter flue dust provides a good electrolyte for electrogalvanizing. Chloride is desirable in zinc sulfate electrolytes used for electrogalvanizing to increase conductivity but is undesirable in zinc sulfate electrolytes used for electrowinning because it causes sticking of the zinc to the aluminum cathodes.

Therefore, wastes that are unsuitable for production of pure zinc may be used as feed for an electrogalvanizing operation. This would provide a more efficient use of waste zinc in the industrial environment. Future efforts will be directed at scaling up the use of brass smelter flue dust in a pilot industrial electrogalvanizing operation.

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REFERENCES

1. F. V. Carrillo, M. H. Hibpshman and R.D. Rosenkranz. Recovery of Secondary Copper and Zinc in the United States. BuMines IC 8622 58 pp. (1974)
2. V. R. Miller and D. L. Paulson. *Resources and Conservation* 9, 95 – 104 (1982).
3. J. B. Stephenson, E. R. Cole and D.L. Paulson. *Resources and Conservation* 6, 203 – 210 (1981).
4. G. C. Bratt. A view of zinc electrowinning theory. *Proc. Tasmania Conf.*, pp 277 – 290 (1977).
5. G. C. Bratt and A. R. Gordon. The Australasian Institute of Mining and Metallurgy. *Research in Chemical and Extraction Metallurgy* 197 – 210, (1967).
6. Characterization, Recovery, and Recycling of Electric Art Furnace Dusts. U.S. Dept. of Commerce Project #99 – 26 – 09886 – 10, pp. IVA1 – IVA26 (February, 1982).
7. T. Adaniya, M. Omura, K. Matsudo and H. Naemura. *Plating and Surface Finishing* 68 (6), 96 – 99 (1979).
8. C. Tsao, Thesis, University of Missouri — Rolla (1982).
9. L. M. Baugh, *Electrochimica Acta* 24, 669 (1979).
10. F. A. Lowenheim. *Modern Electroplating*, 3rd ed., pp. 442 – 460. Wiley Interscience, New York (1974).
11. E. H. Lyons, *Trans. Electrochem. Soc.* 78, 317 (1940).
12. E. H. Lyons, *Trans. Electrochem. Soc.* 80, 387 (1941).
13. Y. M. Wang, T. J. O'Keefe and W. J. James, *J. Electrochem. Soc.* 127, 2589 – 2593 (1980).