

Recovery of certain non-ferrous metals from industrial by-products

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THE resources of the important non-ferrous metals—namely, lead, zinc and copper—are very lean in our country and large quantities of the same are imported. An idea of the extent of the import during 67-68 is given in Table I. Some zinc, lead and copper are being produced in the country but the total production meets only less than 40% of the total requirement. So, recovery of these metals from industrial by-products and wastes in a form which is useful again in the same or similar industry is a necessity. This will substantially reduce the quantity of imports and at the same time improve the economic feasibility of the processes. It is true that the metal thus recovered is only secondary in nature and would yield less favourable results than the primary metal. Still, whenever it is not disadvantageous, attempts should be made to adopt recovery processes and use the recovered metal.

The economics of the process of recovery of these metals is mainly dependent on (1) the resources of the raw material and its availability in bulk at a place where a recovery plant can be set up, (2) the operating costs and the efficiency of the process and (3) the re-usability of the recovered metal and its market value.

Copper

The by-product is mainly copper oxides obtained from rolling and drawing mills. A rough estimate shows an availability of 200 to 300 tons of the oxide per year and not less than 10 to 20 tons at a place. Besides this, there is oxide of copper mixed with lot of other material which can also be processed for recovery of copper—say for example—from mills producing brass sheets. The present method seems to be to dissolve this by-product in acids to make copper salts which have a market.

Lead

The main source of the by-product is (a) spent lead acid batteries, (b) wastes from battery manufacturing plants and paint manufacturing units. The current production figure of approximately 8 00 000 batteries per

SYNOPSIS

The primary resources of certain non-ferrous metals that are of great industrial value, such as copper, zinc and lead, are lean in our country and the entire demand for the same cannot be met fully but for the import. Quite a good percentage of the total consumption is available as by-product oxides and hydroxides. Any attempt to recover the metals from such by-products will be of great value especially with respect to saving foreign exchange. In this communication, the methods for the recovery of copper, zinc and lead from by-products are reviewed. Well known thermal and electrolytic processes are briefly discussed and two processes that have been developed for the recovery by the authors are discussed in detail. The first method involves direct electrolytic reduction of the by-product oxide or hydroxide to the respective metal powder when the same is kept as a sediment on a metal cathode immersed in an alkaline medium. The characteristics of the metal powder obtained depends on those of the starting material. In the other method, known as suspension electrolysis, the finely powdered by-product is suspended in a suitable medium and the suspension is then electrolysed. The metal can be recovered either in the form of powder or sheet by varying the condition of electrolysis. The above mentioned methods as applied to the recovery of copper, zinc, lead and silver are discussed.

TABLE I Imports of copper, lead and zinc*

Metal	1966-67 Rs	1967-68 Rs
1. Copper	39,11,36,234 39.11 Crores	35,45,99,489 35.46 Crores
2. Lead	10,42,60,971 10.43 Crores	6,20,89,957 6.21 Crores
3. Zinc	10,86,06,550 10.86 Crores	14,29,50,673 14.30 Crores

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*Monthly Statistics of the Foreign Trade of India II—Imports, March 1968.



1 Schematic representation of the cell set up used for direct reduction of by-product compounds
 1. Wire gauze anode
 2. Electrolyte-alkali solution
 3. Cell container cathode
 4. Solid by-product compound

year, capable of giving, on an average, active material and scrap weighing about 15 kg each, gives roughly the availability of the raw material. Scrap metal from other industries such as cable sheaths and pipes has not been taken into account here. The collection of raw material no doubt presents a problem in the case of old lead acid batteries. Still, the arrangement that new batteries will be sold only to parties who surrender the old ones makes the availability of raw material easier. The thermal process of recovery seems to be best adopted for the recovery of this metal. But this method though claimed to be very efficient and economical, is not advantageous for processing small quantities of the waste. Since the lead and lead oxides used in batteries are of high purity, scrap from the same are also of required purity and can be used for making grids. It has also been found by Russian workers that lead obtained by reclamation of battery waste material does not present any difficulties for use in grids.

Zinc

Zinc is available in the form of a number of com-

pounds such as oxide, hydroxide, carbonate and sulphite. The chief sources of these by-products are chemical industry using zinc reduction processes and the pigment industry. By-products obtained from hydrosulphite plants contain mainly hydroxide, carbonate and oxide with small amounts of sulphite and sulphide whereas the zinc waste from organic chemical producing plant are generally contaminated with only the organic compounds produced. Coarse fraction zinc oxide obtained from pigment industry is of high purity and is uncontaminated. Zinc compounds obtained from galvanising industry are normally contaminated with iron and chloride flux and are obtained in three different forms, viz (a) zinc dross—an alloy of Fe and Zn having an approximate composition of Fe-Zn₁₃, (b) galvaniser's ash—analysing to zinc 60-85%, Fe 0.2-1.5%, Pb 0.3-2.5% and chlorine 2-12%, (c) flux skimmings containing Zn 35-60%, Fe 0.2-1.5%, Pb 0.3-1.0% and chlorine 15-35%. In addition to these zinc skimmings are also obtained during steam blowing of galvanised tubes. Nearly half of the total zinc consumed in the country is used for galvanising. The demand of zinc is estimated to be 90 000 tonnes and is likely to rise to above 1 30 000 tonnes per year by 1970-71, whereas the production is expected to be only 38 000 tonnes. The percentage of zinc lost during galvanising varies widely i.e., 20% to 60% of the total zinc used in the process depending on various factors such as the process, shape of the galvanised article, etc.

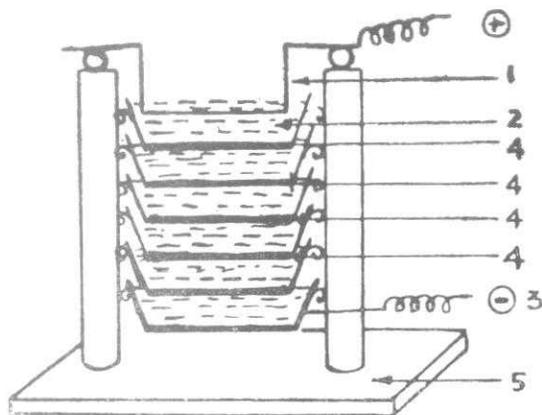
Recovery processes

The various methods of recovery of these metals can be grouped under two major classes.

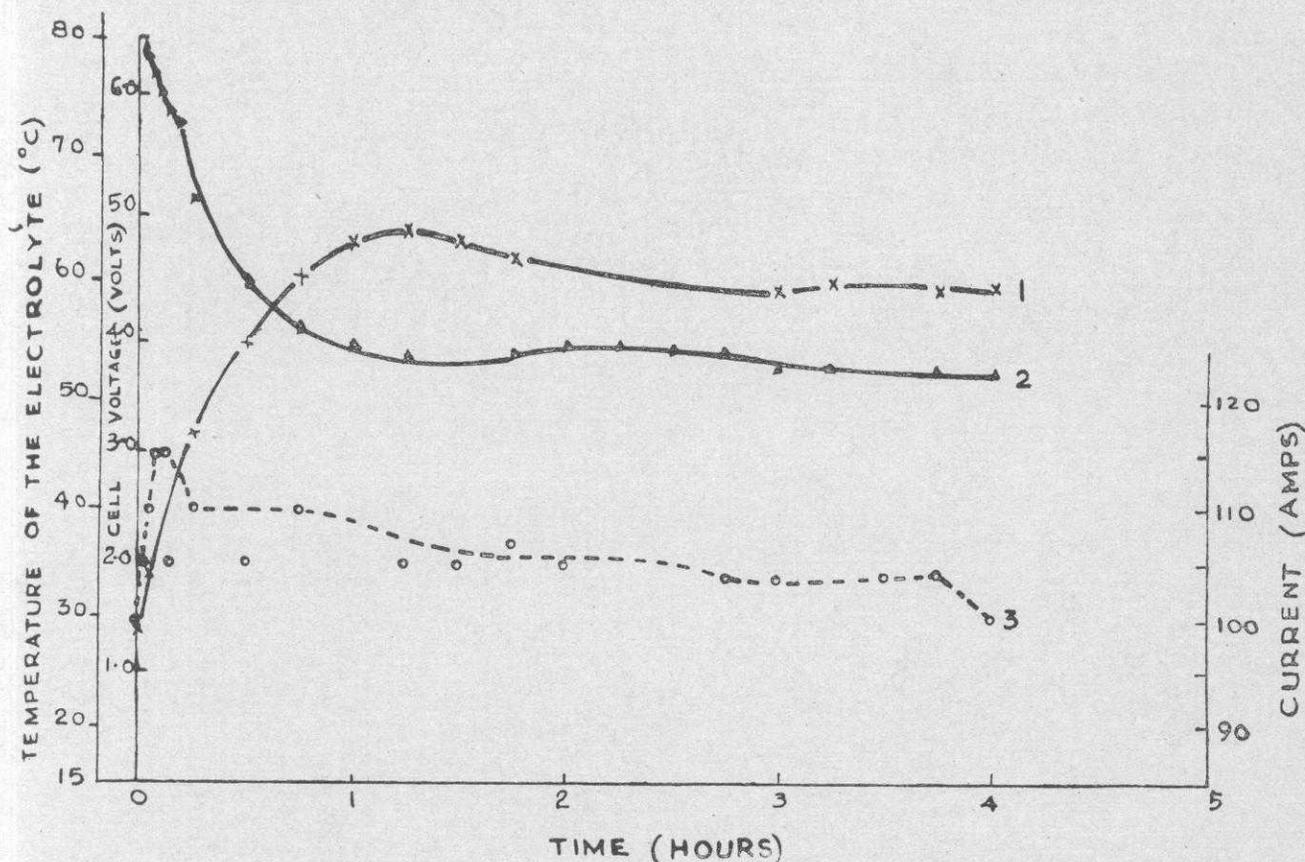
Thermal methods

These are very widely used for the recovery of metals from their scraps.

(a) Smelting in high temperature furnaces: This is generally adopted for recovery of lead from battery wastes and zinc from wastes obtained in galvanising industry. This suffers from a number of drawbacks such as heavy loss of metal in the form of slag if proper precautions are not taken while operating the



2 Bipolar arrangement containing six cells for direct reduction of by-product compounds
 1. Wire gauze anode
 2. Electrolyte-alkali solution
 3. Cathode-bottom cell container
 4. By-product compound solids
 5. Wooden frame for mounting the cells



3 Variation of cell voltage and temperature of electrolyte while operating a 100 amp. cell
1. temperature ; 2. cell voltage ; 3. current

process. This is more important for small smelting units.

(b) Reduction by carbon monoxide or hydrogen or carbon itself in high temperature furnaces. This is normally adopted for recovery of copper from copper oxide. Though the metal obtained is of good purity, careful controlling of the process variable makes it rather difficult.

(c) Partial recovery of processes employed for the recovery of zinc from zinc dross includes the liquidation³ process, sweating process,⁴ filtration process and pressure filtration. The recovery in the first two processes do not exceed 15-25% whereas 75% of the recoverable metal is recovered at 600°C by the third method.

(d) Techniques making use of the greater affinity of a third element to the impurity metal present in the by-product have also been developed and similar methods have been used for separating zinc from zinc dross using aluminium. This method is known as the aluminium process⁵ and makes use of the fact that aluminium has more affinity to iron than for zinc and the alloy formed is much lighter than molten zinc and can be skimmed off. This method gives a low yield and the zinc obtained contains good amount of

aluminium. A modification of this method by adding Pb increases the yield as well as the purity of the metal recovered.^{6,3}

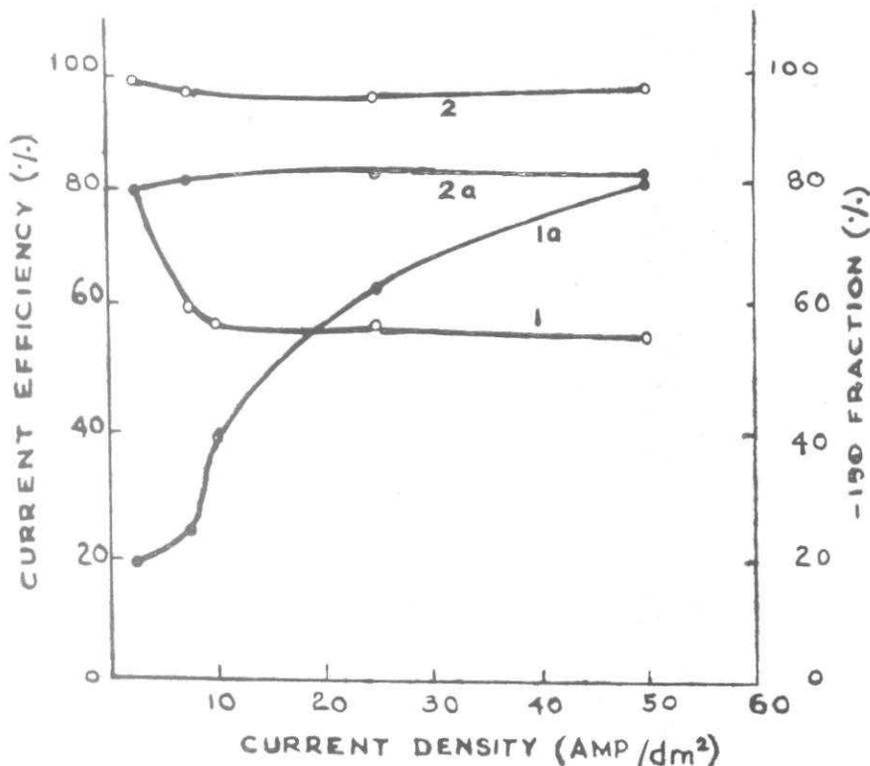
(e) Distillation process⁷: This offers the best technique for good recovery of pure zinc from scraps and dross. The process may be carried out either under atmospheric pressure or at reduced pressure. Fractional distillation is also employed for the recovery of zinc from dross. Improved equipments and techniques have made the vacuum distillation process a very important one.

Electrolytic processes

These are widely used for the recovery of metals from their by-product wastes.

(a) Conventional electrolytic process: The wastes are first taken into solution by leaching the same with proper leachants and the impurities present are removed by precipitating the same. The solution after the purification step serves as the electrolyte and the metals are recovered by electro-deposition on a suitable cathode.

Copper is recovered from copper sulphate solutions obtained by dissolving the scraps in sulphuric acid. The metal obtained is of high purity.



4 Variation of current efficiency and percentage-150 fraction in the reduced powder with change in current density during direct reduction of lead compounds to lead powder; 1 and 2: variation of current efficiency for the reduction of PbO and PbO_2 respectively; 1a and 2a: percentage-150 fraction in the lead powder obtained from PbO and PbO_2 respectively

Lead wastes are converted into either fluoroborate⁸ or plumbate⁹ from which solution it is recovered. While converting the lead wastes obtained from battery plates into plumbate an intermediate step of bringing the waste active material into solution as nitrate is also needed.

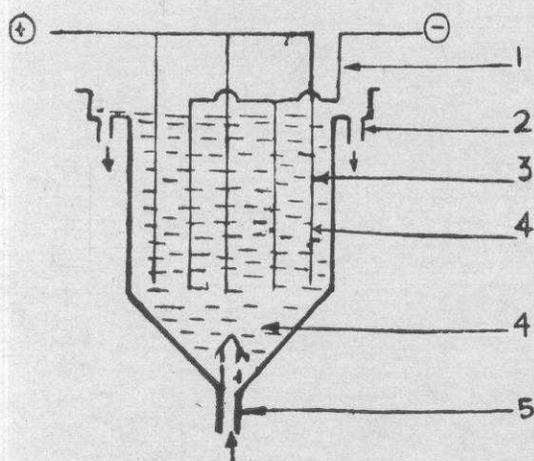
Zinc wastes can be leached with HCl ¹⁰ or H_2SO_4 ¹¹ or alkali¹² and the resulting chloride or sulphate or zincate solution is used as the electrolyte. Due to the fact that the composition and nature of the zinc wastes vary very widely depending on the industry from where the by-product is obtained, the preliminary steps of purification also are different for different by-products. Sulphur and organic compound containing wastes are usually roasted before taking the same for leaching operation¹¹—whereas iron-contaminated wastes are first dissolved and from the solution the iron is removed as hydroxide by precipitation and filtration.¹³

This process offers a few disadvantages along with certain advantages. The high purity of the recovered metal is the major advantage of this process. Strict control of process variables such as metal concentration in the electrolyte, pH of the solution and temperature. Handling of large volumes of solution and difficulties experienced in running the cell to complete depletion are also among the major disadvantages. Further, in the case of chloride and sulphate electrolyses the high corrosive nature of the electrolyte limits the easy operation of the cell. Even though the metal can be recovered either in the form of powder or sheet by suitable modification of the conditions of electrolysis, it is not possible to make the

powder of very fine particle size by electro-deposition. For making the sintered compacts very fine powder of the order of -200 to -300 mesh size are needed and this fine fraction obtainable from an electro-deposit is very low.

(b) Direct electro-chemical techniques: As the name implies the principle underlying this process is the direct electrochemical reduction of the by-product compound by keeping the same as a sediment on a cathode metal substrate immersed in an alkaline electrolyte. The efficiency of the process depends on the nature of the by-product, i. e., whether soluble or insoluble, conductor or semi-conductor or non-conductor. If the by-product is an insoluble non-conductor then the reduction is not possible whereas the reduction proceeds with 100% efficiency in the case of semi-conductors such as PbO_2 , etc. The cell set up for such a reduction is shown in Fig. 1. When current is passed through the cell the by-product gets reduced to the metal powder. The characteristics and purity of the end product can be controlled by controlling the properties of the starting material viz., by-product. Since the process is one of direct reduction of the by-product compound any metallic impurities present in the starting material will also be present in the powder obtained. The desired fineness, of the metal powder obtained, could be achieved by this method by proper selection of the size fraction of the powdered raw material. Bipolar arrangement of the cells as shown in Fig. 2 makes the process more advantageous.

Very fine copper powder suitable for making sintered compacts and the ball bearings has been prepared by



5 Continuous cell for electrolysis of suspension of the by-product in alkali

1. Cathode
2. Outlet for the overflow of the slurry
3. Anode
4. Slurry or suspension of by-product compound in alkali
5. Inlet for pumping the slurry into the cell

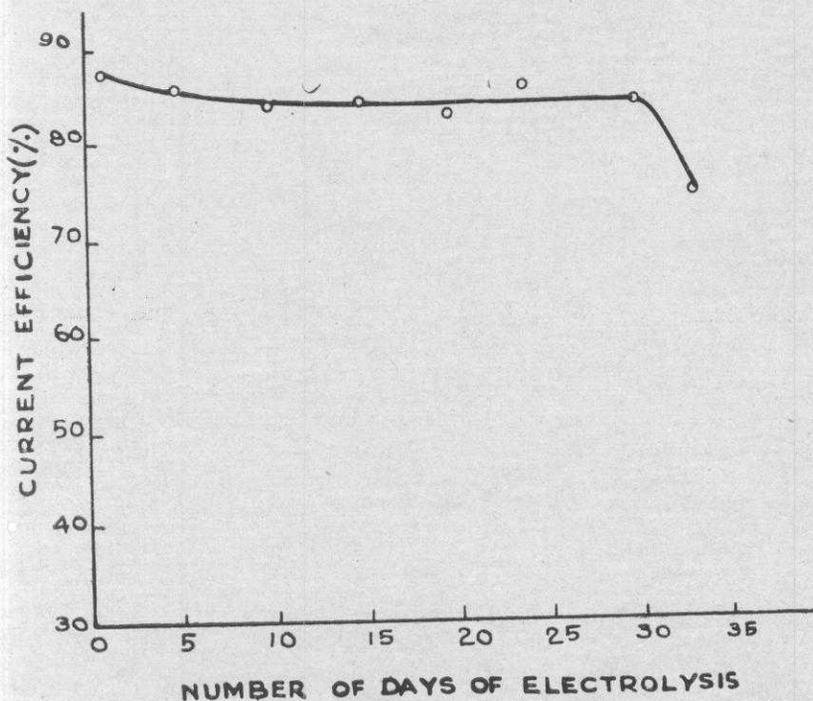
this method.¹⁴ The reduction carried out with a copper scrap obtained from a sheet rolling industry which analyses roughly to the formula CuO , was found to proceed with 85–90% current efficiency.

Lead powder was prepared from lead monoxide and dioxide by this technique.¹⁵ Very fine powder having the apparent density values 4 to 5.5 and 2.5g/cc was obtained from PbO and PbO_2 respectively under opti-

mum conditions. Recovery of lead as powder has also been made from battery waste active material.¹⁶ The surface area and apparent density of the powder obtained were 4 to 5.5g/cc and 1200 cm^2/g respectively.

Recovery of zinc from by-product zinc compound¹⁷ found to proceed with an average current efficiency of 85% and the percentage free metal content of the dried powder was 85% whereas the wet powder analyses to 92 to 95% free metal content. The data obtained in a 100 amp cell for the reduction of zinc compound from hydrosulphite plant are shown in Fig. 3. The apparent density of the powder obtained from by-product obtained from a hydro-sulphite plant was 0.76 gm/cc and the surface area was 400 sq cm/gm .

A careful examination of the mode of reduction revealed that streaks of metal are first formed projecting from the cathode to the surface and these act as centres for further reduction.¹⁸ The reduction can take place either by dissolution and deposition or by reduction in the solid phase. If the reaction proceeds by the former variation in the concentration of electrolyte and current density affect the properties of the powder as in the case of lead from lead monoxide. Whereas if the reaction takes place by the second mechanism then the powder properties are unaffected by the conditions of the reduction as in the case of PbO_2 . In Fig. 4 the effect of current efficiency and percentage—150 fraction of the powder are shown for the preparation of lead powder from lead monoxide and lead dioxide which indicates that the mechanism I is applicable to PbO which is soluble in alkali whereas mechanism II takes place in the case of PbO_2 which is insoluble and semi-conducting in nature.



6 Variation of current efficiency with number of days of electrolysis of a continuously operated cell

The system and the reaction taking place can be written as follows:

System

By product compound solid	Cathode on metal substrate	Alkali electrolyte	Anode
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This method has been extended for the preparation of fine silver powder from silver compounds and the powder prepared was found to be suitable for making conducting inks.¹⁹ Since the reduction proceeds with 100% efficiency in the case of reduction of PbO₂ and silver compounds, this can be adopted as an analytical method for the determination of the composition of the same.²⁰⁻²¹

The process offers the following advantages:

1. Simple and straightforward; easy to operate and maintenance is minimum.
2. Very high current densities of the order of 25 amp/dm² can be employed.
3. Can be operated as a batch process.
4. In the case of zinc this process is more advantageous since the wet powder from the reduction cell can be directly taken for the chemical producing plant which makes the overall process cyclic and economic.
5. Bipolar arrangement of cells enables savings in space and energy.
6. The powder characteristics can be easily controlled by controlling the properties of the starting material and very fine powder can be obtained by this process.
7. Large capacity cells can be operated for producing powders.

(c) Suspension electrolysis: This is applicable to by-products that are low in metal content. This method involves the electrolysis of a suspension of finely powdered material in a suitable medium. The medium of suspension should be so chosen that the respective metal should be soluble in the same and also that the solution should be conducting. The mechanism underlying the electrolysis is the simultaneous dissolution and deposition. It is very important that the material in suspension should be homogeneous and hence effective stirring of the suspension is necessary. This can be achieved either by stirring the suspension with separate stirrers fitted in two diagonally opposite corners of a rectangular cell or by having a continuously flowing cell as shown in Fig. 5. In the latter case the slurry from a reservoir is pumped into the cell through the inlet and the level of electrolyte is maintained by the overflow arrangement.

Lead has been recovered from battery waste active material using this technique.¹⁶ Purity of the metal obtained was high and the current efficiency was found to be 85-90%.

Zinc was produced from galvanizer's waste²², zinc oxide by-product obtained from pigment and chemical industries. The metal recovered analyses to 99.6% purity

and the reaction proceeds with 15-90% efficiency. Zinc metal recovered from galvanizer's ash contained about 0.4% iron which was reduced to 0.1-0.15% by remelting the deposit to be cast as ingots. A cell was operated continuously for 40 days with frequent additions of the powdered ash at predetermined intervals and the deposit was removed at definite intervals. Fig. 6 indicates the variation of current efficiency with number of days of electrolysis. It can be seen from the figure that the current efficiency remains at 85-90% even after 30 days of electrolysis. When the cell was run to complete depletion the efficiency was 75%. This indicates clearly the possibility of operating a cell continuously with frequent additions of the powdered raw materials. Build up of a carbonate in the electrolyte was found to be only to an extent of about 10% during this experiment.

The advantages of this process are (a) certain steps such as dissolution, purification, filtration, etc. are eliminated, (b) the process can be operated continuously without any lowering of current efficiency or purity, (c) the process can be adopted even for low metal content by-product, (d) impurities like iron, etc., do not interfere with the electrolysis and (e) the metal can be obtained either in the form of fine powder or plate-like deposits by varying the conditions of electrolysis.

References

1. Monthly statistics of the foreign trade of India, IInd, imports, March 1968.
2. Parthasarathi, M. N. : Proc. of the Seminar on Zinc wastes and their utilisation, p. 9 (1965).
3. Chakravarthy, P. K. et al. : *Tisco*, 8 (3) pp. 1-8 (1961).
4. Hughes, M. C. and Humphreys, R. : *Sheet metal industries*, 30 (5) p. 955-66 (1953).
5. Kapoor, A. N. et al. : *J. Sci. Indus, Res.* 15 A., p. 179-82 (1956).
6. Thomson, A. G. : *Metallurgia* 50 (300) p. 159-60 (1954).
7. Subramanian, M. et al. : Proc. of the seminar on 'Zinc wastes and their utilisation', p. 26 (1965).
8. Dey, B. B., Aravamuthan M. and Rajagopalan, P. R. : *Indian Mining Journal*, Spl. issue, (1957).
9. do
10. Aravamuthan, V. and Srinivasan, R. : *Journal Ind. Chem. Engr.* 2, Nos. 3 (1960).
11. Aravamuthan, V., Srinivasan, R. and Meenakshisundaram, N. : 'Proc. Symposium on Zinc wastes and their utilisation', p. 71-73 (1965).
12. Viswanathan, R., Sampath, S. and Udupa, H. V. K. : *J. Mines, Metals and Fuels*, IX 15, (1961).
13. Aravamuthan, V., Srinivasan, R. and Meenakshisundaram, N. : 'Proc. Symposium on Zinc wastes and their utilisation' p. 49-51, (1965).
14. Rao, P. V. V. and Udupa, H. V. K. : Under publication.
15. Rao, P. V. V. and Udupa, H. V. K. : *Transaction of the Indian Inst., of Metals*, June 1966.
16. Waheed, A. K. A., Rao, P. V. V., Ghosh, S. and Udupa, H. V. K. : *J. Indian Chemical Engineers*, 3, 4 (1961).
17. Rao, P. V. V. and Udupa, H. V. K. : *Chem. Industry News (India)*, Vol. VII, June 1962.
18. Rao, P. V. V., Ghosh, S. and Udupa, H. V. K. : *Electroplating (India)*, October 1959.
19. Rao, P. V. V. and Udupa, H. V. K. : Under publication.
20. Rao, P. V. V. and Udupa, H. V. K. : *Electrochem. Acta* 10, 651 (1965).
21. Vijayavalli, R., Rao, P. V. V. and Udupa, H. V. K. : Presented at Symposium on Photographic Science and Technology, April 1968, under publication.
22. Vijayavalli, R., Rao, P. V. V., and Udupa, H. V. K. : Proc. of the Seminar on Zinc wastes and their utilisation, p. 65, (1965).