Recovery of non-ferrous metallic values from metallurgical wastes

G. BASAK, V. S. SAMPATH and P. P. BHATNAGAR

SYNOPSIS

Recovery of non-ferrous metallic values from metallurgical wastes would greatly help in conservation of metals in which the country is deficient. The paper briefly outlines the various methods developed at the National Metallurgical Laboratory for recovery of metallic values from wastes such as aluminium dross, brass dross, zinc die casting scrap, zinc dross, ashes, blowings, etc. apart from a reconditioning method developed for oxidised magnesium powder.

WITH the increased tempo of industrial expansion and ever-increasing consumption of common non-ferrous metals like Al, Cu, Pb, Zn, Sn in India, conservation, substitution and reclamation from waste products and substandard raw materials are of paramount importance for the country, not only to tide over the present crisis but also in the larger interests of economic growth and self-sufficiency. Self-sufficiency can be attained by developing processes for the utilization of low grade and complex ores, recovery of metals from waste products, like slags, ashes, drosses, apart from conservation of the non-ferrous metals not available in the country, by their judicious use and also by substitution wherever possible.

Further, reclamation of metal from wastes becomes a matter of survival during the time of war and other emergencies, when the sources of supplies are generally cut off.

The National Metallurgical Laboratory has been actively engaged on studies pertaining to the recovery of metallic values from low grade ores, reclamation of valuable elements from waste materials and substitution of strategic non-ferrous metals.

This paper briefly outlines the work done and also the work in progress at the National Metallurgical Laboratory on the reclamation of metallic values from the metallic wastes such as drosses, ashes and residues.

Recovery of aluminium from aluminium dross

(a) Samples of aluminium dross containing between 8% to 14% aluminium in the form of fines, as inclusions in the flux, were economically treated for the reclamation of metallic values. About 60% of metallic aluminium was recovered by simple grinding followed by melting of the coarser fraction.

(b) A sample received from a local firm contained 49·9% metallic aluminium associated with considerable gangue material. The sample was upgraded to 79% metallic aluminium by wet grinding in a rod mill followed by desliming. The deslimed product after drying analysed 79% metallic aluminium, from which ingot aluminium was obtained after suitably melting with a flux. The overall recovery was 75% metallic aluminium. Direct melting of the dross was not feasible because of the presence of high proportions of gangue material and heavy coating of oxide on the metallic particles.

Recovery of metallic values from brass dross

A sample of brass dross received analysed 34·93% total copper, 34·46% total zinc. The impurities were chiefly oxides of copper and zinc. Coke particles and silica were also found associated with the sample.

The sample was in the form of fines and completely passed through 10 mesh (B.S.S. sieve). The metallics could be recovered by grinding the sample in a rod mill to liberate the metallic particles and the liberated metallic particles could be easily separated from the gangue material by tabling.

The metallics so recovered could be used for the manufacture of brass or subjected to remelting along with brass scrap.

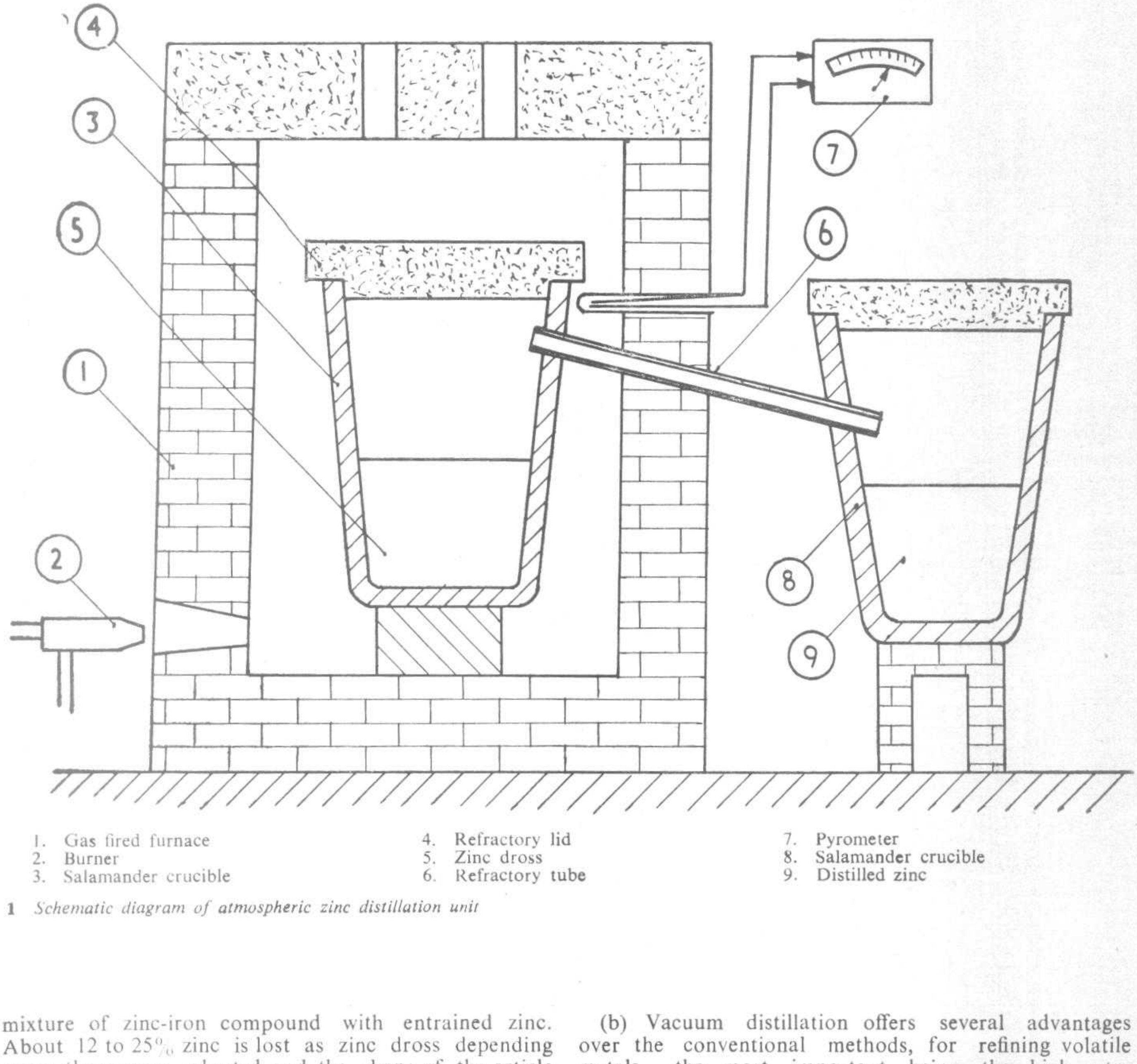
The tailing collected from tabling could be processed for obtaining zinc sulphate.

An overall recovery of 95·4% of total zinc and 94·1% of total copper content of the original brass dross was obtained.[1]

Recovery of zinc from zinc dross

Zinc dross formed during galvanizing is essentially a

Messrs G. Basak, V. S. Sampath and P. P. Bhatnagar, National Metallurgical Laboratory, Jamshedpur.



1. Gas fired furnace
2. Burner
3. Salamander crucible
4. Refractory lid
5. Zinc dross
6. Refractory tube
7. Pyrometer
8. Salamander crucible
9. Distilled zinc

1 *Schematic diagram of atmospheric zinc distillation unit*

mixture of zinc-iron compound with entrained zinc. About 12 to 25% zinc is lost as zinc dross depending upon the process adopted and the shape of the article galvanized.

Distillation process offers the best technique amongst the complete recovery processes. A good recovery of high purity zinc can be obtained by subjecting the dross to distillation at high temperature at atmospheric pressure or at lower temperature, under reduced pressures.

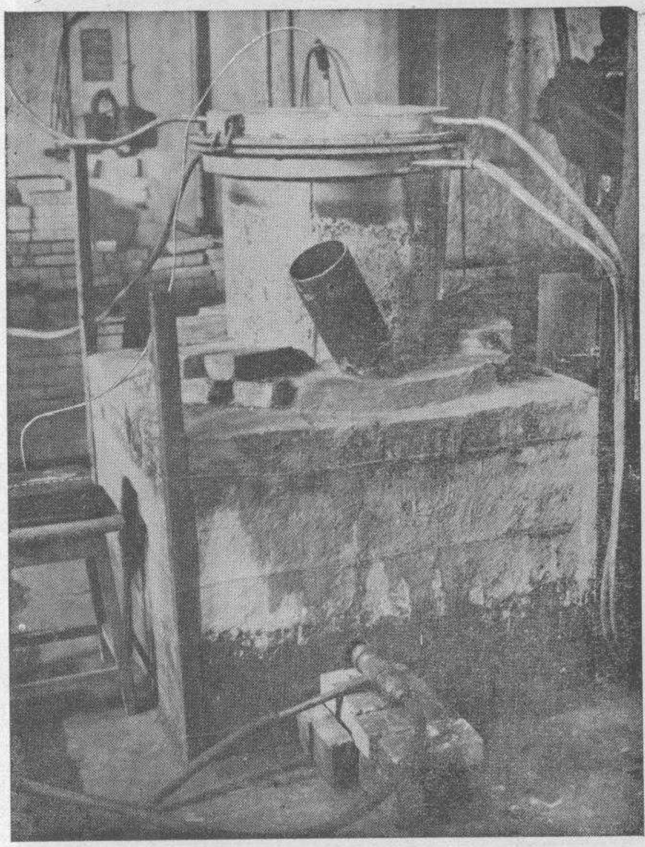
(a) Systematic studies were carried out on the distillation of zinc dross at atmospheric pressure as well as at reduced pressure. Experiments carried out at atmospheric pressures at 1200°C with zinc dross sample containing 3·6% Fe gave a recovery of 92% zinc with an average distillation rate of about 8 kg/hr. These experiments were carried out in ordinary salamander crucibles and the distillation unit is schematically shown in Fig. 1.

(b) Vacuum distillation offers several advantages over the conventional methods, for refining volatile metals, the most important being the high rates of evaporation at relatively low temperatures, better separation and elimination of oxidation possibilities.

A mild steel pot for distilling 100-150 kg zinc dross per batch under vacuum was designed and fabricated at the National Metallurgical Laboratory. A photograph of the unit is shown in Fig. 2 and the condenser with the condensate is shown separately in Fig. 2a.

A distillation rate of about 7·3 kg/hr was obtained at a charge temperature of 540–560°C. The recovery was over 90% Zn. The distilled zinc obtained by distillation under vacuum was purer than the zinc obtained by atmospheric distillation.

Work is still under progress and a few modifications are being made in the pot design for attaining better performance.



2 *Photograph of the vacuum zinc distillation unit in operation*

Treatment of zinc wastes obtained in the form of fine powder

(a) Distillation trials

Vacuum distillation of zinc fines was also attempted. It was found possible to recover zinc, only after the fines were briquetted with a suitable binder and charged into the vacuum distillation unit. The product obtained was purer than the one obtained by direct melting with the addition of flux. The process was found to be rather expensive in view of the various steps involved in briquetting, charging, distilling and stripping of the condensate and discharging of the residues.

(b) Melting trials

Coarse size particles of oxidised zinc can be easily melted without fluxes and without much melting losses. The melting of fine particles is extremely difficult under normal practice.

A sample of oxidised zinc powder passing through −170 mesh (B.S.S. sieve) and containing 71% metallic zinc, could not be melted in the absence of fluxes. However, on the addition of flux, with the application of patented process,[2] a recovery of 88% metallic zinc was achieved.

Samples of −170 mesh zinc containing different amount of oxides were also treated similarly with flux additions and the recoveries are shown in Fig. 3.

It is seen from the Fig. 3 that with the increase of the oxide content the recovery falls. But good recoveries can be obtained with oxide content of less than 30%.

A typical sample of 'zinc blowing' containing about 81·2% zinc was melted with fluxes and a recovery of about 94% was obtained, whereas melting without fluxes gave a recovery of 45% only.

Treatment of zinc ash

A sample of zinc ash received from a galvanizing plant analysed 52·8% metallic zinc and 84·9% total zinc. Generally zinc ash from galvanizing plants contain, on an average, 85% total zinc most of which is present in metallic form and is around 78%. The low zinc content (52·8%) in the particular sample is attributed to aging.[3]

The sample was crushed and the metallic zinc of bigger size (+3 mesh) was hand-picked. The −3 mesh was subjected to jigging. The total zinc recovery from hand-picking as well as that recovered by jigging accounted for a recovery of 97·5% metallic zinc.[4]

The zinc so collected can easily be melted. It is emphasized that ashes should be treated by the 'cylinder method' wherever possible. This method is simple and does not require a separate furnace installation. Further, the same labour available in the galvanizing plant can be employed. The heat already present in the ash when cleared from the bath is also available.

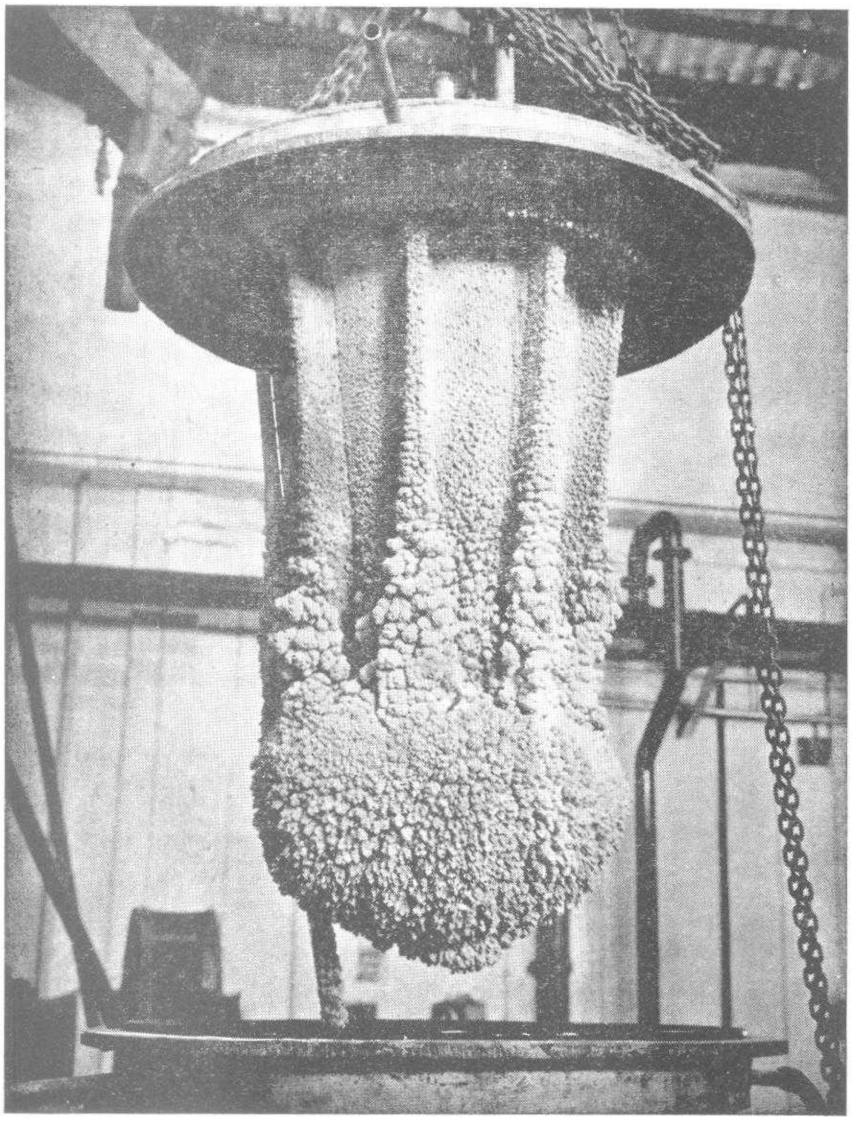
The recovery of metallic zinc ranged from 76–90% from six tests carried out by the cylinder method[3] and an average recovery of 82% metallic zinc has been reported.

Treatment of waste magnesium metallic fines

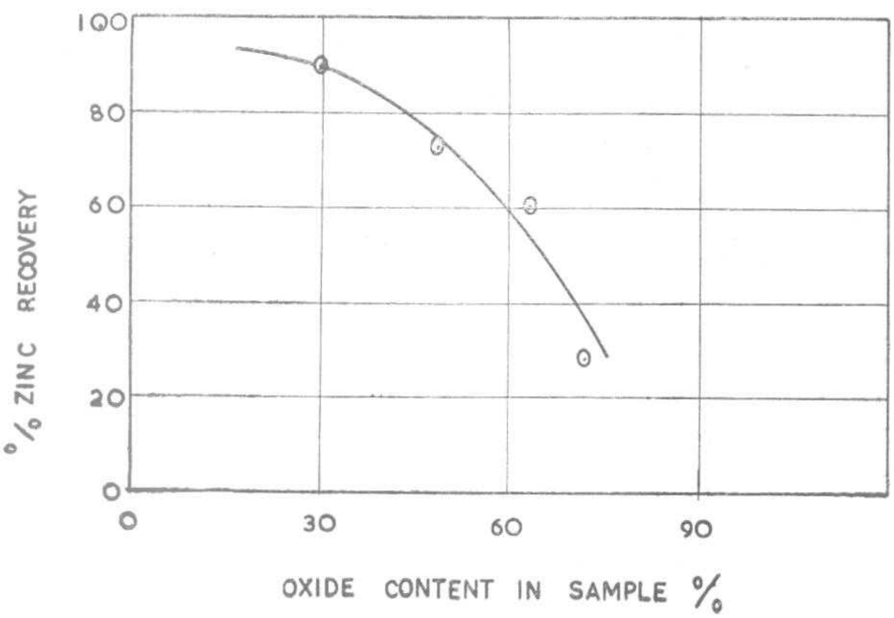
Magnesium powder is prone to oxidation on long storage and the deterioration of the powder depends on the mode of packing, storage and particle size of the powder, the atmospheric conditions and the period of storage.

Studies were undertaken on the removal of oxide coating from the magnesium powder which had deteriorated during storage resulting in the metallic content varying from 68 to 93%. This deteriorated powder is not suitable for pyrotechnic purposes unless upgraded to contain over 98% metallic magnesium.

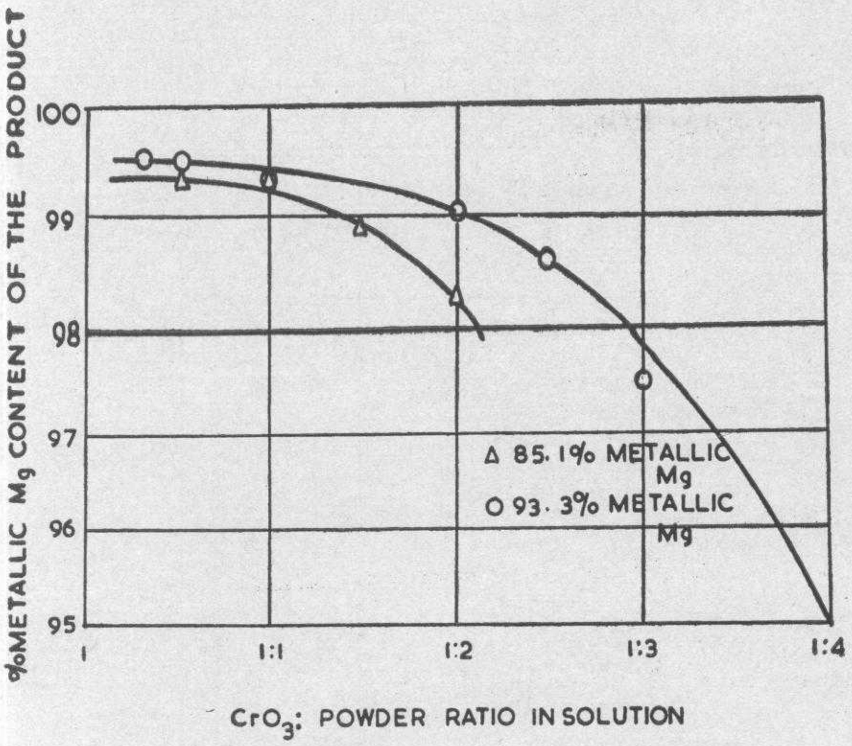
Melting of the oxidised magnesium powder was not found practicable because of its fineness and the reactive nature. Vacuum distillation was also attempted and it was found possible to recover magnesium in a massive form as condensate, after briquetting the powder with



2a *Photograph of the zinc condenser showing the deposit of pure zinc*



3 *Effect of oxide content on the recovery of —170 mesh zinc blowing*



4 *Effect of varying CrO_3 : oxidised magnesium powder ratio (93·3% Mg and 85·1% Mg) on the purity of the product*

a suitable binder and charging into the vacuum pot. Distillation under vacuum was not economical since the material could be obtained only in a massive form and would have to be further processed for rendering it into a powder form.

Both mechanical and chemical methods were tried and it was found finally that chromic acid[5] alone could remove the oxide coating without unduly attacking the metallic portion and affecting the apparent bulk density.

Detailed studies were thereafter undertaken to arrive at optimum conditions for reconditioning oxidised magnesium powder and the effects of chromic acid concentration, pickling temperature, period of contact with pickling liquor, presence of impurities in the wash liquor and drying temperature of the treated powder were investigated.

It was observed that the solution containing 10–20% chromic acid was enough to remove the oxide coating without further attacking the freshly exposed metallic surface. Spectrographic analysis of the treated product indicated the presence of small amounts of chromium. The presence of chromium however, did not interfere with the pyrotechnic properties of the powder. In fact, it was found to give better shell-life to the powder so treated. The quantity of the acid required for upgrading the powder depended on the oxide content of the powder. The effect of CrO_3 : Mg powder ratio of the two grades of powders, on the metallic content of the treated powder is shown in Fig. 4.

It was also found that the spent acid could be regenerated by subjecting it to electrolysis using lead electrodes separated by a porous diaphragm. Analysis of the different powders upgraded by treatment with CrO_3 is shown in Table I.

This problem was referred to the National Metallurgical Laboratory by the defence establishment of the country during the India-China war in 1962 and about 10 tonnes of various grades of powders were treated successfully.

TABLE I Analysis of different powders upgraded by treatment with CrO_3

Sl. No.	Apparent bulk density	Metallic Mg. content of the sample	CrO_3 : Mg. powder ratio w/w	% Recovery of metallic Mg. content	Products upgraded to% metallic Mg.
1	1·10	92·15	1 : 1·69	93	99·05
2	0·80	91·60	1 : 1·59	92	99·04
3	0·55	90·20	1 : 1·37	92	99·10
4	0·78	85·60	1 : 0·93	93	99·14
5	1·15	76·15	1 : 0·56	94	99·24
6	0·75	80·50	1 : 0·68	90	98·80
7	1·20	82·60	1 : 0·77	91	99·00

Treatment of die casting scrap alloys

Zinc-base die-casting alloys of zamak group contain extremely low amounts of impurities like Fe, Pb, Cu and Sn. Die-casting scrap alloys which were slightly out of specification were treated for obtaining a refined product.

The samples contained tin and lead more than the specified limits and were easily separated by distillation under vacuum. Pure zinc was obtained as a condensate containing some aluminium and magnesium. Major portion of impurities remained in the residue.

The work is already under progress to treat 100-150 kg per batch of the zamak scrap alloy in the semi-pilot scale unit that has been designed and fabricated at the National Metallurgical Laboratory.

Conclusion

In conclusion it may be mentioned that samples of similar origin may not be amenable to recovery treatment by the same process, but may need a slight alteration in the treatment in view of the variation in the nature of the product. The most suitable process for a particular sample will have to be worked out keeping in view the overall economics of the process.

Acknowledgement

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References

1. Recovery of metallic values from industrial brass dross, N.M.L., I. R. No. 256/62.
2. Indian Patent No. 102483, Jan. 1966.
3. Second international conference on hot-dip galvanising held at Dusseldorf, 1952.
4. Recovery of metallic zinc from zinc ash I. R. No. 312/66 January 1965.
5. Indian Patent No. 83968, September 1962.

Discussions

Mr **K. C. Choudhuri** (Research, Designs and Standards Organization, Lucknow) : The National Metallurgical Laboratory has done good work on recovery of zinc from (i) zinc dross and (ii) zinc ash. Experiments show that the methods developed give efficient recovery of zinc. Would the author indicate whether any party has come forward to put up a plant on commercial scale?

Author : The National Metallurgical Laboratory has submitted a detailed investigation report in early 1968 to the General Manager, Workshop, Post and Telegraphs, Calcutta, on the recovery of zinc from the zinc dross obtained at their workshop. He has evinced considerable interest in putting up a distillation unit based on our findings. We hope that a commercial unit would be put up by them soon.